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FOREWORD

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STRATEGIC AND CRITICAL MATERIALS
PROGRAM ANNUAL REPORT

By R. E. Chaney¹ and others

ABSTRACT

This report summarizes the research on the Strategic and Critical Materials Program tasks conducted at the Idaho National Engineering Laboratory (INEL) between May 1984 and April 1985.

The work is divided into two areas:

1. Production Technologies - Tasks directed at developing advanced extraction technologies
 - o Biologically-Assisted Minerals Processing
 - o Metal/Gas Reactions and Thermal Plasmas
 - o Dehydration of Aluminum Chloride Hexahydrate (completed).
2. Conservation/Substitution Technologies - Tasks directed toward establishing the technical processing base which will permit the use of advanced materials
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 - o Joining of Silicon Nitride-Based Ceramics
 - o Nondestructive Evaluation of Ceramic and RSA Joints and Materials
 - o Substitute Catalytic Materials for Platinum.

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INTRODUCTION

By R. E. Chaney 1/

In May of 1983, the Idaho National Engineering Laboratory (INEL), through the support of the U.S. Department of the Interior's Bureau of Mines, began a research program to address some of the basic problems facing this nation with respect to strategic and critical materials. This report summarizes the work completed during the second year of the program (May 1984 through April 1985) (1).

The U.S. lacks domestic resources from which to provide, in necessary quantities, many materials which are critical to our economy. Furthermore, because of competition from foreign producers, economic conditions, reduction in the quality of available ores, and many associated reasons, the ability of industry to meet domestic needs for many materials has declined in recent years. Consequently, importation of critical and strategic materials has steadily increased and has caused the concern of many individuals, organizations, and agencies. This issue and the justification for concentrated research efforts in several technology areas have been widely discussed in recent years (2-16).

As a result of the situation, Congress enacted The National Materials and Mineral Policy, Research and Development Act of 1980, PL 96-479, October 21, 1980. The objective of the act is: "To provide for a national policy for materials and to strengthen the materials research, development, production capability, and performance of the United States, and for other purposes." In the act, Congress declared, ". . . that it is the continuing policy of the United States to promote an adequate and stable supply of materials necessary to maintain national security, economic well-being and industrial production." To accomplish this, several requirements were put forward including: identification of materials needs; coordination of Federal materials programs; vigorous, comprehensive, and coordinated research and development; international cooperative research; and promotion of private enterprise. To achieve the intended results, several assignments to federal agencies were made including support for basic and applied research.

The Administration on April 5, 1982, issued its "National Materials and Mineral Program Plan and Report to Congress," which summarizes the activities to be undertaken to reduce America's materials vulnerability. A component of that plan is research and development. The role of government-financed R&D will be to focus on long-term, high-risk technology with wide generic application to materials problems and increased productivity.

In May 1983, a research program was initiated at the Idaho National Engineering Laboratory, which was funded through PL 97-377, and administered through the Bureau.

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The overall goal of this program is to provide fundamental knowledge to the scientific community so that superior mineral production processes can be developed and substitutes can be perfected.

In this work there are two primary areas of focus: (a) to develop advanced technologies for extraction of metals from low grade resources and wastes, and (b) to develop efficient processes to facilitate use of substitute materials. The activities undertaken in these areas represent only a small portion of the research required to resolve the problems facing the U.S.

The tasks described here were selected to complement the ongoing work being conducted by the Bureau in areas not being extensively pursued by other agencies and to bring to bear the expertise available at the INEL. It is an excellent example of interagency cooperation to resolve pressing national problems.

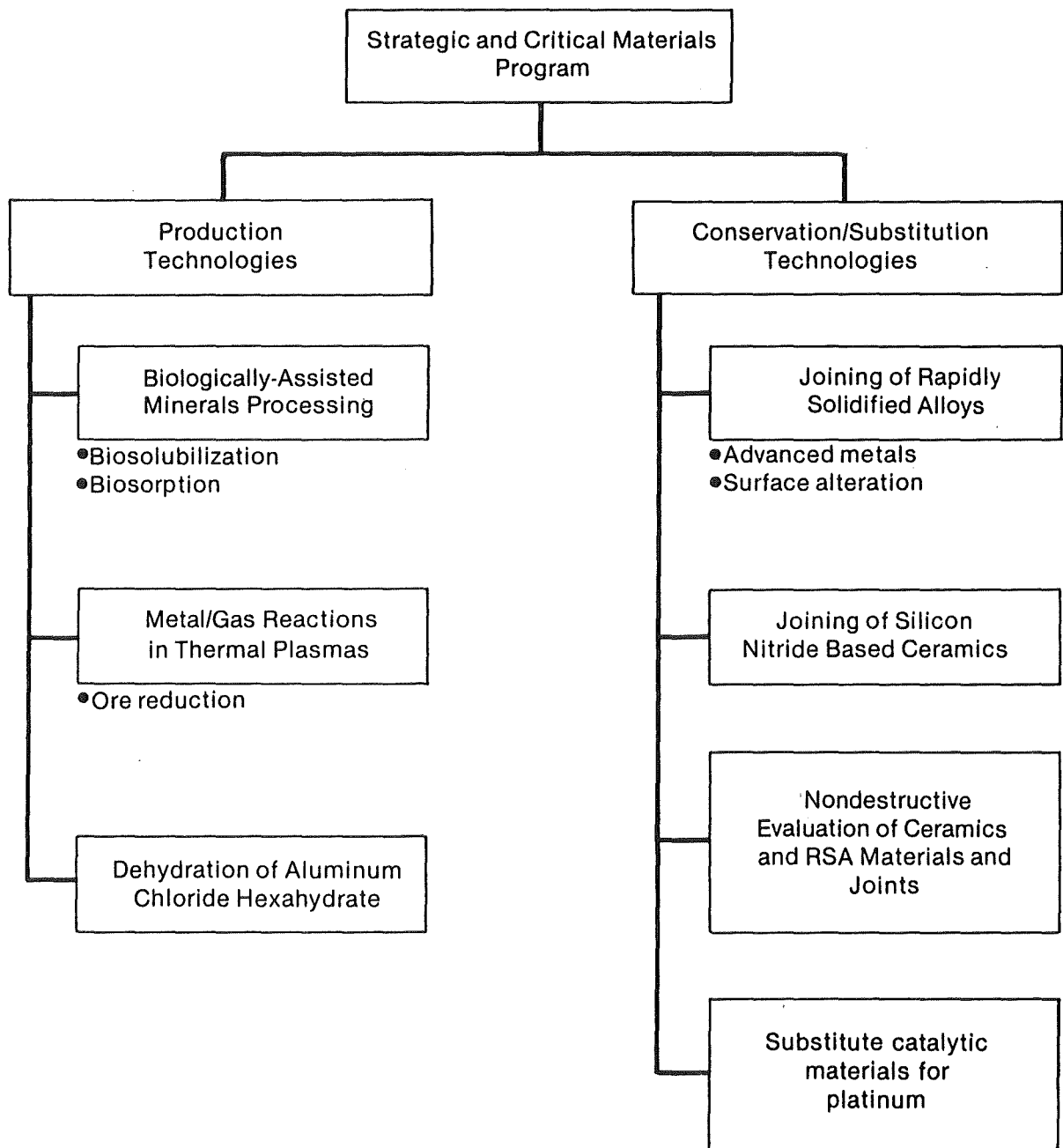
The Work Breakdown Structure for the program is shown in figure 1-1. There are two major categories, Production Technologies and Conservation/Substitution Technologies, which contain a total of six ongoing tasks.

The work on Production Technologies is directed toward obtaining the scientific understanding to permit subsequent technological development of new methods for producing critical materials from domestic resources which are not currently economical to exploit. The three projects are:

1. Biologically-Assisted Minerals Processing - a mechanistic investigation of the role which microorganisms play in leaching and accumulation of metals
2. Metal/Gas Reactions and Thermal Plasmas - a fundamental study of the processes occurring in high temperature thermal plasmas which may be applicable to the reduction of metals from ores
3. Dehydration of Aluminum Chloride Hexahydrate - an investigation of chemical and physical means for the extraction of water from this intermediate in the production of aluminum from domestic resources. This task was completed during the second year of the program.

Conservation/Substitution activities are of a similar scientific nature and are directed toward technologies necessary for more efficient use of materials whether they are currently in use or are potential replacements in the future. These tasks include:

1. Joining of Rapidly Solidified Alloys (RSA) - obtaining the fundamental understanding of the methods necessary to consolidate RSA powders and pieces into complex structures without degrading their unique properties



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Figure 1-1. Work breakdown structure (WBS) for the current Strategic and Critical Materials Program.

2. Joining of Silicon Nitride-Based Ceramics - these materials have excellent high temperature properties, but developing the complex structures required in practice is extremely difficult
3. Nondestructive Evaluation (NDE) of Ceramic and RSA Joints and Materials - a project complementary to the previous two which is aimed at extending the current state-of-the-art in NDE to these new material systems
4. Substitute Catalytic Materials for Platinum - A comprehensive examination of the physical, structural, and surface chemical properties which control the catalytic activity and product selectivity of platinum-based catalysts and, in turn, preparation of new intermetallic catalysts based on non-strategic metals.

Detailed descriptions of the accomplishments of each task are contained in the following chapters.

REFERENCES

1. U.S. Bureau of Mines. Strategic and Critical Materials Program Annual Report, May 1984.
2. U.S. Bureau of Mines. The Domestic Supply of Critical Minerals. Department of the Interior, 1983.
3. U.S. Army. U.S. Army Overview, FY-84, 1983.
4. Strategic and Critical Nonfuel Minerals: Problems and Policy Alternatives. Congressional Budget Office, August 1983.
5. U.S. Department of Commerce. Critical Materials Requirements of the U.S. Aerospace Industry, October 1981.
6. U.S. Department of Commerce. Critical Materials Requirements of the U.S. Steel Industry, 1983.
7. The National Policy Agenda for Strategic Minerals and Materials Colloquium Proceedings. Federation of Materials Societies and the National Society of Professional Engineers, February 2, 1983.
8. Seventh Biennial Conference on National Materials Policy Report, 16-6270, U.S. Government Printing Office, 1983.
9. U.S. Senate. National Materials Policy Hearings, No. 96-122. Committee on Commerce, Science, and Transportation, July 1980.
10. U.S. Department of Energy. Critical and Strategic Materials: Proceedings of the Laboratory Study Group Meeting. CONF-830474, June 1983.

11. Executive Office of the President. Inventory of Federal Materials Research and Technology, Fiscal Year 1982. Federal Coordinating Council for Science, Engineering and Technology, Committee on Materials, Office of Science and Technology Policy, June 1983.
12. U.S. Congress. An Assessment of Alternative Economic Stockpiling Policies. OTA-M-36, Office of Technology Assessment, August 1976.
13. American Society for Metals. Quality Assessment of National Defense Stockpile Cobalt Inventory, August 30, 1983.
14. Rapid Solidification Processing: Status and Facilities. NMAB-401, National Academy Press, 1982.
15. U.S. Department of Energy. Contractors Meeting on Problems and Opportunities in Structural Ceramics. Conf-8209111, Energy Materials Coordinating Committee, April 1983.
16. U.S. Department of Energy. Implementation Plan for a National Materials and Minerals Policy Program. Developed by Grand Junction DOE Area Office, Idaho National Engineering Laboratory, and Los Alamos National Laboratory, August 4, 1982.

BIOLOGICALLY-ASSISTED MINERALS PROCESSING

By J. H. Wolfram, P. L. Wichlacz 1/

INTRODUCTION

This investigation of biologically-assisted beneficiation of metals from ores or effluents includes research in two broad areas, (a) biological mineral solubilization and (b) the removal of metals from leachates and effluent streams using microbial accumulation. The work emphasizes discerning the mechanisms by which the microorganisms act in order to establish the base for using microorganisms to process complex low grade ores containing strategic and critical minerals.

Naturally occurring bacterial/mineral interactions form the basis of a complex ecological system, which results in the continued dissolution of mineral sulfides (i.e., leaching) in the presence of air and water. This naturally occurring process has been exploited as a commercial method for the recovery of certain metals. Most notable has been biological leaching to more fully recover value from low grade copper ores. Iron and sulfur oxidizing bacteria, e.g. Thiobacillus ferrooxidans, have been considered the primary contributors to the processes leading to mineral solubilization. Relatively little is known about the diversity of microbes contributing to mineral leaching. Furthermore, the biochemical and ecological mechanisms underlying these processes are poorly, if at all, understood.

Improvement of processing rates and yields are all possible if bacterial oxidation rates or efficiencies are increased. The biological catalysis involved in mineral solubilization is likely enzyme mediated. Cell-free enzymatic mineral processing may be viable. Understanding the basic mechanisms underlying both the biochemical and other microbial activities associated with leaching is the key to improving existing processes, developing new ones, and applying biological leaching to other mineral types.

Biological interactions with metals are not limited to those involving mineral solubilization. A wide variety of enzymatic reactions are due to metal ion valence changes. Natural systems of protection from toxic heavy metals are found in all manner of living things, including yeasts and bacteria. Biological accumulation and sequestering of heavy metals is readily observed in nature. Heavy metal toxicity is most often due to the bonding of the metals to proteins. The potential exists for using biological molecules for the selective concentration of metals from processing or waste streams. The development of methods to economically glean currently wasted metals, or improve the efficiency of concentrating solubilized metals, would allow the exploitation of large quantities of waste or other low grade ores present in the United States.

Highlights of the accomplishments over the past year are discussed in the following sections.

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BIOSOLUBILIZATION

Research on biosolubilization has been concentrated in two areas: the microbiology/ecology and biochemistry/physiology of bacteria important in leaching.

Microbiology/Ecology

Microbial leaching has been practiced as an economical means of recovering metal from low grade mineral sulfide ores. The bacterium Thiobacillus ferrooxidans has been ascribed the primary role in the dissolution of sulfide minerals. Although biological leaching is practiced on industrial scale, little information exists with regard to the cellular and molecular mechanisms underlying the process.

There have been discoveries of bacteria (i.e., heterotrophs, thermophiles) which were not previously associated with mineral sulfide environments. Furthermore, there exists several genetically different types of T. ferrooxidans. The contribution to leaching of the respective bacterial groups is unknown. In order to improve or broaden the applicability of bacterial leaching, an understanding of the basic microbiology is necessary. The research being conducted on the microbiology and ecology of bacteria associated with leaching is directed toward building a basic understanding of the mechanisms important to biocatalysis of mineral sulfide dissolution.

Isolation/Characterization

Non-thiobacilli

A diverse microbial population exists in environments typically associated with mineral sulfide leaching (1). This population is responsible for the continued production of mineral laden waters. Selective pressure, whether artificial or natural, is likely responsible for the proliferation of a specific population at a given site. Similarly, ambient environmental conditions will extend a selective pressure favoring the population most suited to grow under the prescribed conditions. Certain environments (e.g., hot springs), not associated with biohydrometallurgical processes, are rich in dissolved minerals and sulfides. Bacteria inhabiting such atypical environments may possess unique, previously unidentified, properties. Metal tolerance, substrate utilization rate, and temperature tolerance of these organisms are likely to coincide with the ambient conditions of the environment in which they reside.

Chemolithotrophic bacteria represent one physiological group present in mineral sulfide environments. Heterotrophic bacteria, apparently adapted to acidic, mineral rich conditions, have been found in close association with the acidophilic thiobacilli (2,3). The role of these organisms in mineral solubilization has yet to be established. However, it is speculated that they serve a vital role in removing organic substances inhibitory to thiobacilli. These bacteria may also

serve in the production of the slime which chemolithotrophs inhabit, in the initial colonization, and in the genesis of acidity from mineral sulfide substrata.

The highly acid, mineral rich, oxygen depleted nature of certain geothermal springs was considered representative of the conditions under which potentially useful bacteria could exist. The purpose of this research was to determine if such bacteria inhabit hot spring environments. The search for the following physiologically distinct groups of bacteria was successful:

1. Acidophilic, thermophilic iron-oxidizers
2. Acidophilic, thermophilic heterotrophs
3. Thermophilic heterotrophs
4. Thermophilic, hydrogen oxidizing sulfur reducers.

The search for thermophilic bacteria able to reduce sulfate was apparently unsuccessful.

Thiobacilli

It is likely that iron-oxidizing bacteria similar to Thiobacillus ferrooxidans are capable of attacking and solubilizing cobalt from cobalt-bearing ore. Furthermore, bacteria capable of attacking cobaltite are likely to occur in association with weathered mineral sulfide cobalt deposits. The purpose of this study was to isolate bacteria indigenous to a cobalt-rich environment potentially influencing cobalt solubilization. Several strains of iron-oxidizing and heterotrophic bacteria have been isolated from samples of yellow boy, mine, and overburden drainage collected from Noranda, Inc. property at Cobalt, Idaho. These isolates are presently being screened for their ability to solubilize cobalt from CoS_2 .

Chemostat Culture

Bacterial growth under natural conditions is most closely mimicked in the laboratory using continuous culture (chemostat) conditions. The iron-oxidizing bacteria Thiobacillus ferrooxidans 13598 P and WVa are being tested for maximum growth rate and substrate requirements using continuous culture. Identical 2-L bench top chemostats equipped with ports for inoculation, chemical additions, aeration, baffling, media addition, and sampling are employed in this study. They are equipped for control of pH, media flow rate, temperature, and aeration.

Data was collected for the following detention times (hours): 20, 18.5, 15.1, 14.4, 12.7, 10, 9.2, 8.2, 5.8, 3.5, 3.0, 2.5, 2.0, 1.75, 1.5, and 1. The preliminary results indicated that neither culture had reached μ_{max} (maximum growth rate); both strains tested exhibited wall growth. Attachment to the vessel wall by bacteria allows tolerance of very short detention times without washing out. The

$\mu_{\max}$ (maximum growth rate) values cannot be accurately obtained when wall growth is present. To alleviate this problem the vessel and all internal parts were coated with an organosilicane surface treating agent and tests were begun again. Data have been thus far been collected for the following detention times (hours): 14.7, 11.8, 9.2, 6.7, 4.7, 3.7, 3.0, 2.5, 2.1, 1.8. The various strains of thiobacilli in our possession will be tested to determine if differences exist in growth kinetics.

Model of Fixed-Film Growth

A mathematical model of growth and ferrous iron oxidation for attached bacteria was applied to rotating biological contactor (RBC) units treating mineral sulfide waters (4). The model describes attached bacterial growth as a saturation function, where the rate of iron oxidation is determined by a maximum oxidation rate constant, a half saturation constant, and the concentration of substrate within the RBC. The maximum oxidation rate constant was proportional to flow rate and the iron concentration in the reactor varied with influent concentration. The model was tested at three separate sites and with three different size RBC units. The ability of the model to predict the rate of iron oxidation under all test conditions was significant. The accuracy of the model was found to be affected by unit size and vary with specific test site. The present model defines the effectors of bacterial growth on ferrous iron. Future work will entail combining the effects of oxidation of Fe(II) and mineral sulfide substrates.

Leaching

The relative leaching capabilities of the various iron-oxidizing bacteria have not been characterized. Furthermore, the contribution of acidophilic heterotrophic bacteria to mineral leaching has not been addressed. A series of experiments is under way wherein mixed and monocultures of iron-oxidizing and heterotrophic bacteria are incubated in media containing various ores (e.g., MoS_2 , CoS_2) and substrates (e.g., glucose and iron). The results of these experiments are expected to be valuable in assessing the capabilities of the individual bacterial strains as well as any synergisms which may exist. Iron and/or glucose are monitored along with solubilized metal and respective cell concentrations. Cell number is determined using most probable number procedures. Ferrous iron is measured using a dichromate titration procedure. Total iron and metal are measured by atomic absorption spectrometry. Glucose is measured using high performance liquid chromatography. Six of the 14 strains tested thus far grew in the presence of MoS_2 . After one week of incubation a maximum of 75 mg/L soluble molybdenum was detected, compared to a control value of 10 mg/L.

All of 18 bacterial strains tested grew in the presence of CoS_2 . The maximum amount of cobalt solubilized (7 days leaching) was found to be 226 mg/L in the presence of, and 156 mg/L in the absence of, ferrous iron with respective abiotic control concentrations of 68 and 44 mg/L.

Inhibition of iron oxidation caused by the presence of glucose was apparently relieved by the addition of a heterotrophic bacterium to the

iron oxidizer culture. The results to date indicate that the inhibitory effect of molybdenum on iron-oxidizing bacteria may not be limiting to microbial leaching of the metal. Furthermore, cobalt sulfide appears to be amenable to bacterial leaching.

Biochemistry/Physiology

The physiology of bacterial iron and sulfur oxidation is fundamental to both the generation of ferric iron and the direct dissolution of mineral sulfides. The biochemical mechanism and enzymological diversity of iron-sulfur oxidation is poorly understood. Improvement in the rates and applicability of whole cell and cell free mineral dissolution depends on understanding the basic biochemistry of action. The research we have undertaken in biochemistry molecular biology and physiology is intended to further the understanding of microbe/metal interactions and biochemical limitations to metal dissolution. Development and application of genetic engineering technology to leaching requires a primary characterization of the genetic material of the contributing bacteria.

Heavy Metal Resistance

Thiobacilli

Chemolithotrophic iron-oxidizing bacteria occur ubiquitously in nature, but are most abundant in environments where leaching of sulfide minerals occurs. Typical leach waters contain high concentrations of sulfates, hydrogen ion, and metals. Iron-oxidizing bacteria are generally able to tolerate high concentrations of cationic metals (5). However, thiobacilli are susceptible to, and leaching of certain mineral sulfide bearing ores may be limited by, the toxicity of heavy metals (e.g., arsenic, silver, mercury). Relatively few strains of iron-oxidizing bacteria have been tested for metal tolerance. The purpose of this study was to determine if variability exists amongst a wide variety of iron-oxidizing bacteria. Thiobacillus ferrooxidans strains Decp, D-26, DSM583, A4, FD-1, LP, C-52, and F221 have been utilized in this study.

Test metal solutions were filter sterilized and added to cooled sterilized basal salts-ferrous iron media. The metal cations tested, and their concentrations, are given in table 2-1. All media were inoculated in duplicate (10% v/v) and incubated at 23°C. Assessment of growth was accomplished by visual and microscopic inspection.

Precipitation problems were encountered with $K_2Cr_2O_7$, $AgNO_3$, $NaAsO_2$, $NaMoO_4 \cdot 2H_2O$, and $UO_2SO_4 \cdot 3H_2O$. Future experiments are planned with various salt combinations designed to eliminate any precipitation problems.

The highest concentration (table 2-1) of cobalt, copper, manganese, and zinc tested (10,000 mg/L) was tolerated by all of the strains tested [Decp, D-26, DSM583, C-52, F221, A4 (not test with Co), FD-1 (not tested with Zn), and LP (Zn only tested)]. These values are

TABLE 2-1. - Inhibitory concentration (mg/L) of metal ions for thiobacilli

Salt	Metal	Decp	D-26	DSM583	C-52	F221	A4	FD-1	LP
CoSO ₄ •7H ₂ O.....	Co ¹	>1,000	>1,000	>1,000	>1,000	>1,000	² NT	>1,000	NT
Cr ₂ (SO ₄) ₃ •15H ₂ O.....	Cr	NT	NT	NT	NT	NT	10,000	NT	10,000
CuSO ₄ •5H ₂ O.....	Cu ¹	>10,000	>10,000	>10,000	>10,000	>10,000	>10,000	>10,000	NT
HgCl.....	Hg	1.0	1.0	NT	0.1	0.1	NT	NT	NT
MnSO ₄ •H ₂ O.....	Mn ¹	>10,000	>10,000	>10,000	>10,000	>10,000	>10,000	>10,000	NT
ZnSO ₄ •7H ₂ O.....	Zn ¹	>10,000	>10,000	>10,000	>10,000	>10,000	>10,000	NT	>10,000

¹Highest concentration tested; growth was present.

²NT = Not tested.

higher than those previously reported (5) for I. ferrooxidans. All strains tested were inhibited by 1.0 mg/L Hg except F221 which was inhibited by 0.1 mg/L Hg. A4 and LP were inhibited by 10,000 mg/L Cr^{3+} .

Non-thiobacilli

The microbial consortium populating mineral sulfide environments consists of several distinct physiological types. The combined activities of the major bacterial groups are responsible for the continued leaching of mineral ores. Acidophilic heterotrophic bacteria have been found in acidic coal mine drainage, metal leaching dumps, and as contaminants of Thiobacillus ferrooxidans cultures (1-3). The direct contribution of these bacteria to metal leaching is unknown. These bacteria must possess characteristics similar to the acidophilic thiobacilli in order to exist in mineral sulfide environments (1,3,6). The ability of these bacteria to exist under highly acid conditions is known; however, their relative abilities to tolerate metals is unknown.

The application of biohydrometallurgy to strategic and critical materials will require bacteria resistant to these metals. Growth requirements and characteristics of the thiobacilli limit the application of genetic engineering techniques to increasing metal tolerance or growth. Genetic manipulation of the thiobacilli is hampered by low cell yield and growth rate (in batch culture) and substrate specificity (iron and sulfur). Acidophilic heterotrophic bacteria offer certain desirable characteristics for genetic manipulation, e.g., high cell yields and growth rates, and substrate diversity. Development of a genetic engineering system for the acidophilic heterotrophs would be a first step in achieving such abilities for other mineral sulfide microbiota. The first step in developing a genetic manipulation system is the identification of characteristics of interest that hold the possibility of being transformed.

This research dealt with the tolerance of acidophilic heterotrophs to various metal ions and the possible capacity of these bacteria to increase their tolerance to metal ions.

Acidiphilium cryptum (L-Het); A. violaceum (OP); A. angustum (KLB); A. facilis (PW2); and Acidiphilium sp. (QBP) have been utilized in this study. Metal solutions were filter sterilized and added to cooled sterilized media. The ten metal cations tested, and their concentrations, are given in table 2-2. All the media were inoculated in duplicate (1% v/v) and incubated at 23°C. Assessment of growth was accomplished by visual and microscopic inspection.

The type and concentration of metal inhibitory to the heterotrophs varied with strain (table 2-2). All five strains of Acidiphilium exhibited the same response to copper (i.e., growth at 100 mg/L and inhibition at 1000 mg/L) and chromium (i.e., growth at 0.1 mg/L and growth inhibition at 1 mg/L). The inhibitory level for copper was the same as reported for Thiobacillus ferrooxidans (5). Equal or higher

TABLE 2-2. - Inhibitory metal concentration for acidophilic heterotrophic bacteria

Salt Added	Metal	QBP	KLB	OP	PW2	L-Het	T. ferrooxidans
AgNO ₃	Ag	0.1	100	0.1	1.0	1.0	50
NaAsO ₂	As	10,000	1,000	1,000	1,000	1,000	200
CoSO ₄ •7H ₂ O.....	Co	1,000	1,000	1,000	10,000	1,000	10,000
K ₂ Cr ₂ O ₇	Cr	1.0	1.0	1.0	1.0	1.0	Not Done
CuSO ₄ •5H ₂ O.....	Cu	1,000	1,000	1,000	1,000	1,000	1,000
HgCl.....	Hg	0.1	1.0	0.1	1.0	1.0	Not Done
MnSO ₄ •H ₂ O.....	Mn	¹ >10,000	¹ >10,000	¹ >10,000	¹ >10,000	10,000	10,000
NaMoO ₄ •2H ₂ O.....	Mo	¹ 100	¹ 100	¹ 100	¹ 100	100	5
UO ₂ SO ₄ •3H ₂ O.....	U	1,000	1,000	1,000	1,000	1,000	700
ZnSO ₄ •7H ₂ O.....	Zn	¹ >10,000	¹ >10,000	¹ >10,000	¹ >10,000	¹ >10,000	10,000

¹Highest concentration tested; growth was present.

tolerances than that reported for T. ferrooxidans were found for zinc (QBP, KLB, and OP), manganese (QBP, KLB, OP, PW2), and molybdenum for all five Acidiphilium strains tested.

All bacteria tested except for PW2 showed lower inhibitory level for cobalt than T. ferrooxidans. Inhibition by silver also occurred at lower concentrations for all Acidiphilium strains. Strain QBP demonstrated very high tolerance to arsenic (1000 mg/L) and molybdenum (100 mg/L).

Precipitation problems were encountered with silver, molybdenum, and arsenic. Silver precipitated when 1000 mg/L was added to the media. Due to this precipitation, the dilutions may not represent desired concentrations. Variations noted between duplicates in silver testing were likely due to precipitation.

All five heterotrophs will be retested with silver using a media with no chloride to prevent precipitation problems. Poor quality water used in the original test apparently caused molybdenum and arsenic to precipitate and these two metals will also be retested.

Similar tolerances to heavy metal were found for the heterotrophs and T. ferrooxidans. Some of the metals (e.g. Cr, Cu) show the same tolerance among all the heterotrophs tested. Other metals (Ag, As, Co, Zn, Hg, Mn, Mo, U) show ten or hundred-fold differences between the bacteria tested. These differences may prove useful in research involving genetics of the various bacteria.

Selective pressure induced by exposure may increase heavy metal resistance. The ability of the heterotrophs to increase their tolerance to metal ions varied with the strain and metal ion (table 2-3). Strain QBP showed no increased tolerance to higher metal concentrations. Strains PW2 and LHet showed increased tolerance to four metals.

TABLE 2-3. - Induced increases in inhibitory metal concentration for acidophilic heterotrophic bacteria

Metal	QBP		PW2		L-Het	
	Original	Induced	Original	Induced	Original	Induced
Co	1,000	10,000	10,000	¹ 10,000	1,000	10,000
Cr			1.0	10	1.0	10
Cu			1,000	10,000	1,000	10,000
Zn			10,000	¹ 10,000	10,000	¹ 10,000

¹Highest concentration tested; growth was present.

Plasmid Isolation

Plasmids are genetic material found within the cellular matrix and are not chromosomal DNA (extrachromosomal). Plasmids are double-stranded,

closed circular DNA molecules that contain genes coding for enzymes that may be advantageous to the bacterial host. Commonly expressed phenotypes expressed by different plasmids are (7,8):

- o resistance to toxic metals
- o resistance to antibiotics
- o production of antibiotics
- o degradation of complex organic molecules
- o production of colicins (bacteriocins, i.e. substances which are lethal to bacteria not carrying a resistance gene).

It has been proposed that heavy metal tolerance in Thiobacillus may be encoded by plasmid DNA (9). The identification of heavy metal tolerance in association with a plasmid would be of importance to recombinant DNA technology for biohydrometallurgical applications (10-12). Our initial efforts have been directed at determining if plasmids exist in acidophilic, heterotrophic bacteria common to mineral sulfide environments.

Five strains of acidophilic heterotrophic bacteria (11) have been examined using two methods of plasmid preparation and purification. Plasmid DNA has been recovered from three of these strains. The inability to obtain plasmid DNA from the other two does not necessarily mean that plasmids are absent in these strains. Instead it could mean that the test techniques were not effective in resolving the presence of the plasmids or it may be that the plasmids were in such few numbers that they were not detectable by the separation and purification methods. There are several plasmid purification schemes available, and their use depends on the final purification level and quantity needed as well as the length of time available to perform the plasmid purification procedures (7,8,13,14). Bednarska et al. (15) indicated that the pH of the solution at the time of plasmid purification introduced variability in plasmid DNA recovery. Replication of plasmid DNA is catalyzed by many of the same enzymes used to duplicate chromosomal DNA (8). Therefore, replication of the plasmids may be under "stringent control" of the host so that only one or a few copies of the plasmid are produced.

Further investigation will include identification of the presence of plasmids in other bacteria and amplification of plasmid concentration in strains thus far revealing no plasmids. Through the use of specific chemicals (e.g. chloramphenicol) host protein synthesis may be stopped and the copy number of plasmids could be increased to several thousand per cell (6). Determination of the plasmid-borne properties will be attempted.

Iron-Sulfur Enzymology

The growth of I. ferrooxidans is highly resistant to certain divalent heavy metals, and is very sensitive to other metal ions. During the last year the research of Dr. David Oliver at the University of Idaho has concerned (a) the effect of silver and uranium ions on sulfur and iron oxidation by Thiobacillus ferrooxidans and (b) the identification of the

enzyme sulfite oxidase (sulfite - cytochrome C oxidoreductase) from this organism. Silver and uranyl ions are potent inhibitors of bacterial growth. In general, both of these metals are stronger inhibitors of iron than of sulfur oxidation by the bacteria and silver is the more potent of the two inhibitors.

Uranium

It has been shown (5) that the inclusion of low concentrations of uranyl sulfate (UO_2SO_4) acutely inhibited cell growth by T. ferrooxidans. The effect of uranyl sulfate concentration on the respiration rates was determined for both iron-grown and sulfur-grown cells (figure 2-1). The oxidation of iron by iron-grown cells was very sensitive to the addition of uranyl sulfate. In the presence of 0.57 mM UO_2SO_4 , oxygen uptake was inhibited 35%. Fifty percent inhibition required about 1 mM and full inhibition required 2.3 mM. The oxidation of sulfur by sulfur-grown cells was much less sensitive to inhibition by uranyl sulfate. Under conditions where iron oxidation was inhibited over 90% (2.3 mM), sulfur oxidation was inhibited by about 15%.

The limited inhibition of the rate of sulfur oxidation indicates that the enzymes of sulfur oxidation and the general enzymes of intermediary metabolism are fairly resistant to attack by uranium ions. The increased sensitivity of iron oxidation to uranium inhibition suggest that the uranyl ions are specifically inhibiting the enzyme(s) responsible for iron oxidation.

The inhibition caused by uranium is both rapid and not reversed by washing the cells after exposure to uranium (1.7 mM UO_2SO_4) for 15, 30, or 60 min (fig. 2-2). The inhibition of iron oxidation apparently results from the irreversible modification of the iron oxidizing enzyme by reaction with the uranyl ion.

The inhibition was lessened by increasing iron concentrations (fig. 2-3). This indicates that uranium inhibits a specific protein which is responsible for binding iron and the effect of the reaction with uranyl ions is to alter this enzyme in such a manner that it has a decreased affinity for binding ferrous ions (increased K_m).

Silver

Earlier experiments (5) suggested that silver ions inhibit the reaction with sulfur more strongly than the oxidation of iron. Further investigations, however, have shown that this was an artifact resulting from the very rapid reaction between silver and ferrous ions. As a result the effective concentration of silver in the iron oxidation experiments was much lower than in the sulfur oxidation experiments. These experiments have been repeated using cells that have been carefully washed with the potassium sulfate buffer. Silver inhibition is very similar to that noted for uranium although the inhibition occurs at much lower concentrations.

Very low concentrations of silver ions inhibited the oxidation of iron (fig. 2-4) but had very little effect on the oxidation of sulfur.

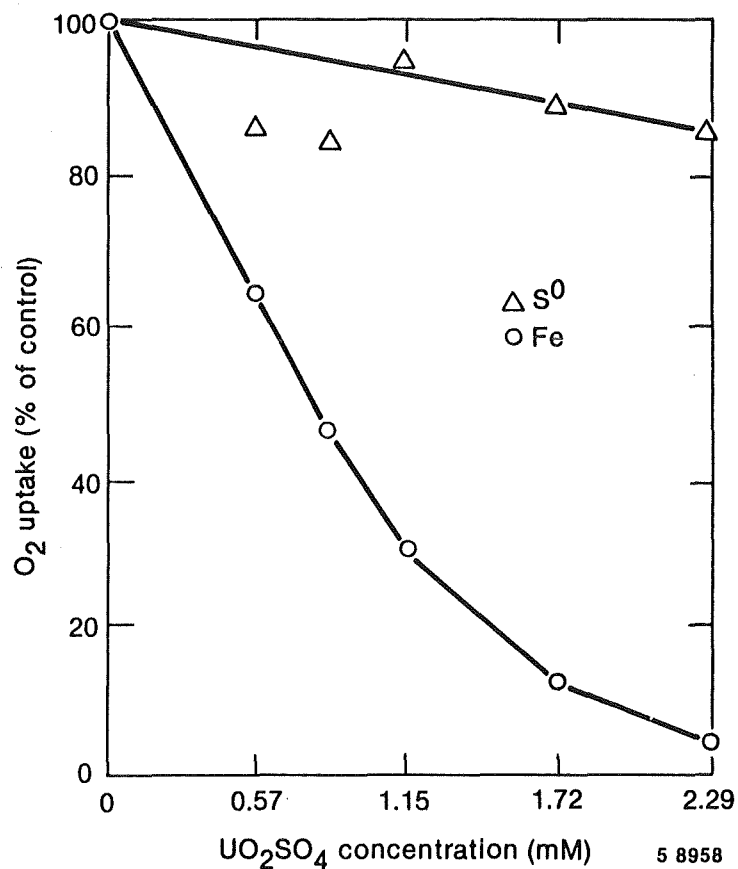


Figure 2-1. The effect of increasing uranyl sulfate concentrations on sulfur and iron oxidation by Thiobacillus ferrooxidans.

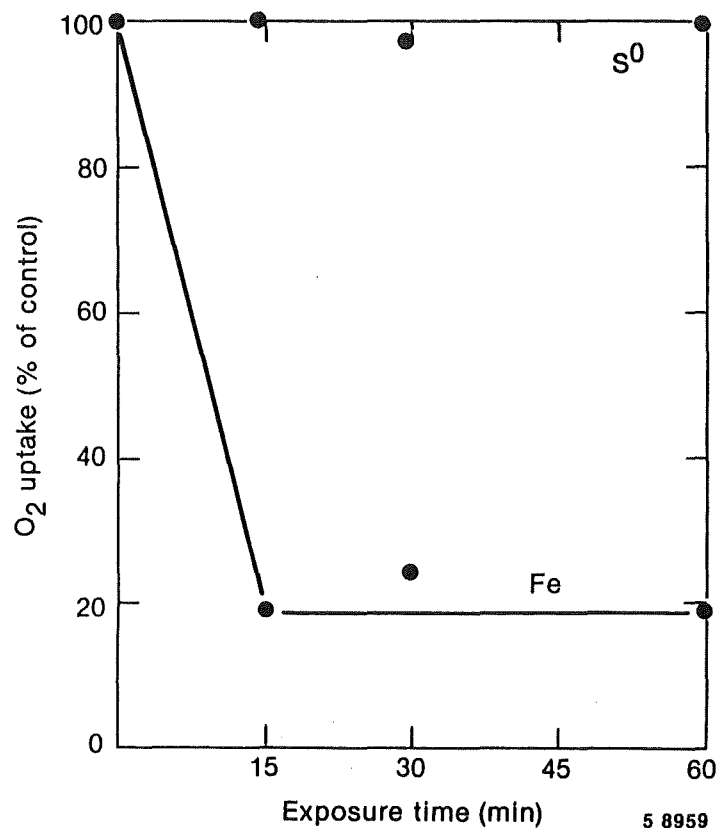


Figure 2-2. The effect of increasing the time of exposure to uranyl sulfate on the oxidation of iron and sulfur by Thiobacillus ferrooxidans.

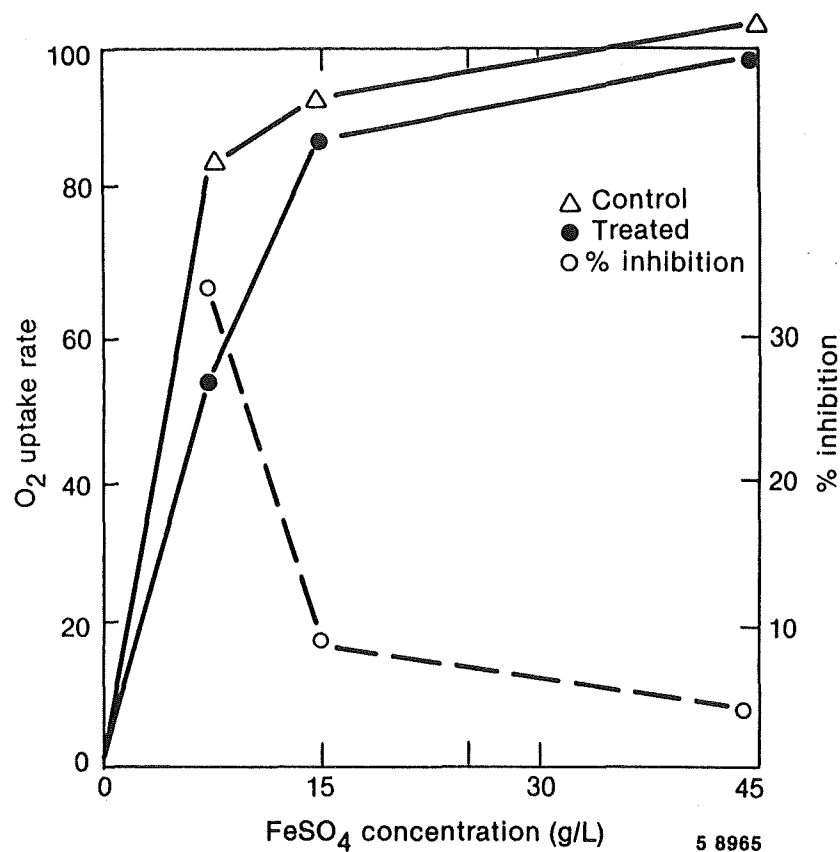


Figure 2-3. The effects of increasing ferrous sulfate concentrations on the inhibition of iron oxidation caused by treatment with 1.7 mM uranyl sulfate.

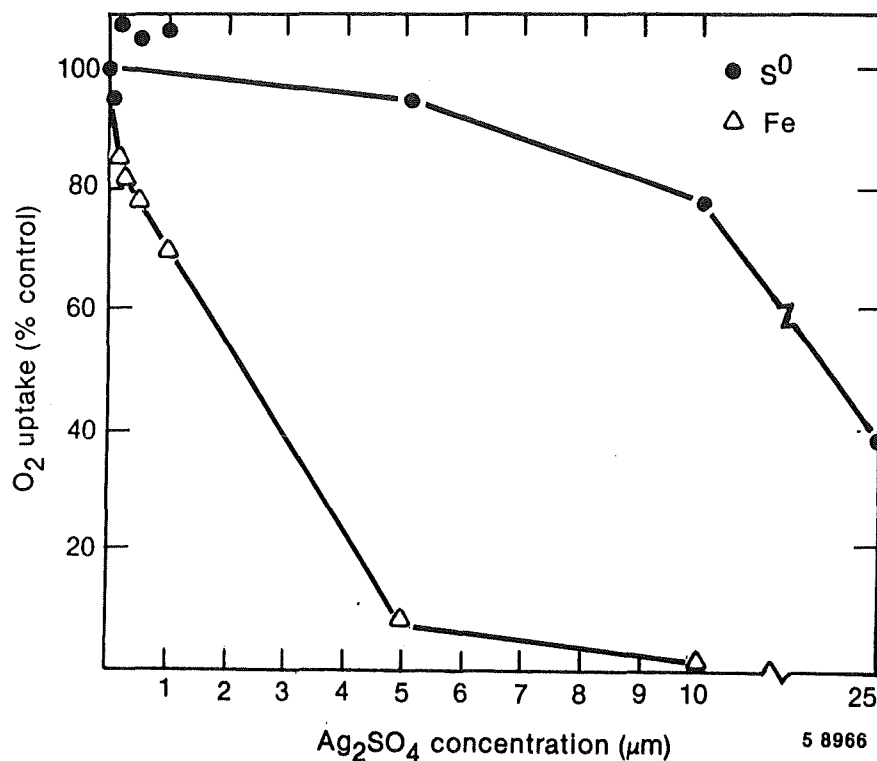


Figure 2-4. The effect of increasing silver sulfate concentrations on the oxidation of iron and sulfur by Thiobacillus ferrooxidans.

Half maximal inhibition of iron oxidation occurred at about $4 \mu\text{M}$ Ag_2SO_4 ($8 \mu\text{M}$ silver ions) and a Ag_2SO_4 concentration of $15 \mu\text{M}$ ($30 \mu\text{M}$ silver ions) inhibited iron-dependent oxygen uptake by over 90%. This indicates that silver ions are about 100-times more inhibitory than are uranyl ions.

The mechanism of inhibition by both silver and uranium appears to be similar in that the inhibition is specific for the iron oxidation pathway and is not reversed by washing the cells free of either cation. Work is continuing on the specific details of the inhibition by silver. In addition we are checking the silver sensitivity of a Thiobacillus ferrooxidans culture collected from the effluent from an old silver mine in Wallace, Idaho to see if these cells exhibit any resistance to silver.

Enzymes of sulfur oxidation in Thiobacillus ferrooxidans

Thirty preparations of T. ferrooxidans cells (5 to 10 g fresh weight of sulfur-grown cells per preparation) have been assayed for enzyme-dependent sulfite oxidation coupled to the reduction of either cytochrome C or ferricyanide. Only two preparations showed enzyme activities; these were about 1% and 3% of the specific enzyme activity reported by Lu and Kelly for Thiobacillus versutus (A2).

It is not known just why the enzyme has been so recalcitrant to isolation and assay. The only known difference is that these bacteria were grown on amorphous sulfur while in the other studies the bacteria were grown on thiosulfate. In table 2-4 the rates of sulfur, thiosulfate, and sulfite oxidation are compared for one of our cultures grown on amorphous sulfur (pH 5.0). The rate of oxygen uptake was measured in an oxygen electrode using washed cells at pH 5.0.

TABLE 2-4. - Oxygen uptake by Thiobacillus ferrooxidans using different sulfur sources

Substrate	O_2 Uptake (nmoles/min)
Amorphous sulfur	17.25
Sulfite	3.75
Thiosulfate	2.25
Sulfur and sulfite	19.88
Sulfur and thiosulfate	18.75

These cells can use sulfur at about five times the rate that they can use sulfite and eight times the thiosulfate rate. The low rates measured with sulfite and thiosulfate are not the result of inhibition by these compounds because adding them to cells oxidizing sulfur resulted in approximately additive rates. The conclusion is that these cells are not oxidizing sulfite and thiosulfate effectively.

It has been found in the past that these cells will grow on thiosulfate if the pH of the culture medium is maintained at about

pH 5. When cells are transferred from the sulfur media (pH 2) to the thiosulfate media, a long lag of about 3 to 4 weeks was noted before cell growth continued. This was even longer than the lag that occurred when cells were transferred from iron media to sulfur media (about 2 weeks). Although there are several possible explanations for this lag when cells are switched from sulfur to thiosulfate, one currently being considered is that different pathways are needed for sulfur and thiosulfate oxidation. Thus what is being measured would be the adaptation period for this new pathway. It is possible that the enzyme being measured (sulfite oxidase) is not present in sulfur grown cells. Cells are currently being adapted to thiosulfate in an attempt to test this possibility by comparing their abilities to oxidize sulfur, thiosulfate, and sulfite and attempting to isolate sulfite oxidase from them.

BIOSORPTION

Biological concentration of metals is a readily observed natural phenomenon. Mammalian cells as well as algae, bacteria, and yeast are known to be able to concentrate heavy metals (16,17). However, little research has been directed toward process application, enhancement, or understanding the mechanisms of biosorption. Exploitation of this ability for the concentration of strategic and critical materials from low grade ores and waste streams may be possible. The research on biosorption of metals has been divided into two separate sections: metallothionein genetic engineering and metallothionein enzymology.

Most invertebrate and vertebrate animals produce a small protein which binds a variety of heavy metals including cadmium, mercury, copper, zinc, cobalt, bismuth, silver, and nickel (18). The protein, metallothionein, may prove useful in the selective concentration of strategic and critical metals. The protein may also be of use in the recovery of heavy metals owing to its stability and high affinity for metals. In order for metallothionein to be practically employed at an industrial level, large quantities must be available. Although metallothionein can be isolated from kidneys and livers of mammals, industrial-scale isolation of protein from such sources is not practical. With the introduction of recombinant deoxyribonucleic acid (DNA) technology, it has become possible to produce mammalian proteins in microorganisms such as bacteria (19,20). If metallothionein could be produced at high levels in a microorganism, a relatively cheap source of a uniform metallothionein product would be available for research and development. Thus, the purpose of the metallothionein research, conducted by Dr. L. K. Miller of the University of Idaho, is to achieve expression of a mammalian metallothionein gene in a microorganism using genetic engineering.

Understanding the basis of enzymological metal binding is the objective of research on metallothionein produced by microorganisms being conducted at the INEL. Screening and characterization of microorganism-produced metallothionein-like protein is being performed to assess the potential use of metallothionein and other metal-binding proteins in metal recovery processing.

Genetic Engineering

Recombinant Expression Plasmid Construction

Two recombinant plasmid DNAs have been constructed that carry a monkey metallothionein gene under the control of the outer membrane protein F (ompF) promoter or a promoter known as TAC (a fusion of the promoters of two E. coli operons, the tryptophan (trp) and lactose (lac) operons). The general features of the plasmid constructs are shown in figure 2-5.

The plasmids, referred to as pOMPF-MT and pTAC-MT1 respectively, have the following common properties:

1. The plasmids contain an origin for replication in E. coli (ori) that is responsive to chloramphenicol amplification so that the plasmid copy number can be enhanced.
2. The plasmids contain an ampicillin resistance (AMP) which can act as a selective marker for bacteria carrying the plasmid.
3. The plasmids contain a high-level promoter, ompF or TAC, which is inducible in appropriate E. coli strains either by a temperature shift (as in ompF) or by a metabolic inducer (lactose or IPTG in the case of TAC) so that levels of metallothionein can be controlled. This latter aspect is necessary to allow the organism to survive but also achieve high-level metallothionein production at will.

Each plasmid has certain distinctive features which should allow high level metallothionein production. In pOMPF MT, the metallothionein II gene of monkeys is attached to the signal sequence of the E. coli outer membrane protein to allow export of metallothionein from the E. coli cell. (Signal sequences are required for transport of most proteins across cell membranes and are proteolytically cleaved from the remainder of the protein during or following export.)

The TAC promoter is a much more fully characterized promoter and is reliably controlled by a metabolic inducer. In the pTAC-MT1 plasmid, there is also a strong transcriptional termination signal downstream from the metallothionein gene so that high-level transcription from the plasmid is limited to the metallothionein gene itself.

The plasmids were constructed using recombinant DNA technology in vitro. The plasmids were cloned in E. coli by first selecting for ampicillin resistant clones and then screening the plasmid DNAs of several clones for the presence of the metallothionein gene. The correct orientations and overall constructions were confirmed by restriction endonuclease analyses.

Testing the E. Coli clones for expression of metallothionein

To determine if the E. coli clones containing the appropriate pOMPF-MT or pTAC-MT1 plasmid constructs were actually synthesizing

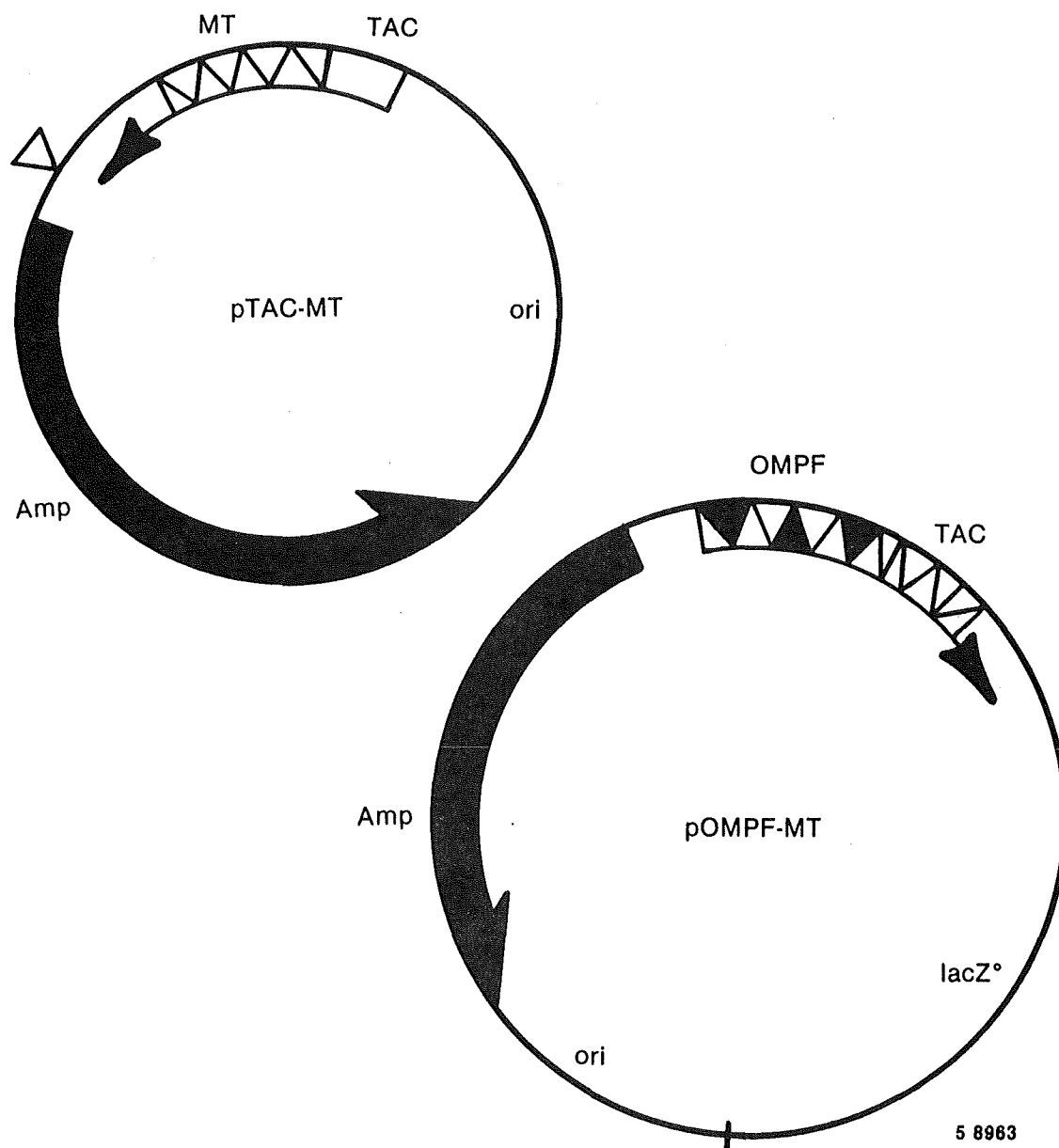


Figure 2-5. Schematic representation of plasmid constructs used to carry monkey metallothionein.

metallothionein protein upon induction, the cellular proteins were analyzed by polyacrylamide gel electrophoresis in the presence of sodium dodecylsulfate (SDS-PAGE). The metallothionein protein is approximately 9,000 daltons, so electrophoresis was carried out at very high acrylamide concentrations (20%) to separate small molecular weight proteins. In the case of pOMPF-MT, where the metallothionein was attached, 15 amino acids residues downstream from the ompF signal sequence of 21 amino acid residues, a protein of either 10,500 or 12,600 daltons was expected depending on whether or not the signal was cleaved on export from the cell.

Before loading the proteins onto the gels, their sulfhydryl groups were blocked by iodoacetate treatment to prevent aggregation of metallothionein via the multiple cysteine residues. Since metallothionein does not stain well by coomassie blue staining, the protein profiles of the SDS-PAGE gels were revealed by a silver staining technique.

Using this detection system, which should be sensitive enough to detect medium levels of metallothionein production, no trace of metallothionein has been observed.

Thus, there appears to be no substantial synthesis of metallothionein in these recombinant clones. The reasons are not known. In the case of pOMPF-MT we have conducted experiments to determine if the metallothionein is rapidly degraded upon synthesis in E. coli. Pulse-labeling of E. coli with ³⁵S-cysteine did not reveal evidence of a rapid turnover of metallothionein. Functional analysis of metallothionein protein, based on increased resistance of E. coli clones to metal ion toxicity, also failed to reveal the presence of active metallothionein protein. Recent studies, in other laboratories, have indicated that there is a very complex control on the ompF-promoter. Thus, high-level transcription from this poorly understood promoter may not be occurring in our metallothionein construct.

In the case of pTAC-MT1, the translational initiation signal of the metallothionein gene is placed approximately 50 nucleotides from the ribosome recognition signal known as the Shine-Dalgarno sequence. The distance can be critical for obtaining high level gene expression from a given mRNA. Ideally, this distance should be 10 to 20 nucleotides. Thus, before concluding that high metallothionein synthesis cannot be achieved in E. coli, it will be necessary to remove approximately 40 nucleotides between the Shine-Dalgarno sequence and the metallothionein initiation codon in pTAC-MT1 and test expression of metallothionein. This work is currently in progress. Other possible systems for expressing the metallothionein gene are also under consideration.

Metallothionein Enzymology

A procedure for metallothionein recovery/detection from cell extracts of microorganisms has been developed and three microorganisms, copper-adapted Saccharomyces cerevisiae (a baker's yeast), Neurospora

crassa (a mold), and Bacillus subtilis (a bacterium), have been screened for the presence of copper-induced metallothionein. Copper-metallothionein is apparently synthesized by all three microorganisms. The results obtained with S. cerevisiae and N. crassa were similar to previously reported research. The copper-metallothionein yield (based upon copper recovered) from S. cerevisiae was much higher than previously reported. With N. crassa, the copper-binding proteins that were isolated were similar to proteins found in previous studies, but the relative distribution of the proteins differed from previous results. B. subtilis has not been previously examined for the presence of metallothionein and the isolation of a metallothionein-like protein from B. subtilis is a new finding.

Screening studies are continuing with additional metal-resistant microorganisms and additional metals. At the completion of the screening studies, one or more microorganisms will be selected for metallothionein production and the metal-binding properties of metallothionein will be characterized. Based upon these data, conceptual metal recovery processes will be designed and process research and development studies with metallothionein will be performed.

REFERENCES

1. Harrison, A. P. Jr. The Acidophilic Thiobacilli and Other Acidophilic Bacteria That Share Their Habitat. Ann. Rev. Microbiol. v. 38, 1984, pp. 265-292.
2. Wichlacz, P. L., and R. F. Unz. Acidophilic, Heterotrophic Bacteria of Acidic Mine Water. Appl. Environ. Microbiol. v. 41, 1981, pp. 1254-1261.
3. Wichlacz, P. L., R. F. Unz, and T. A. Langworthy. Acidophilic Heterotrophs. J. Systematic Bacteriology, 1985. In Press.
4. Wichlacz, P. L., and H. Olem. Kinetics of Bacterial Ferrous Iron Oxidation. Microbiological Effects on Metallurgical Processes. AIME Publication, 1985. In Press.
5. Tuovinen, O. H., S. I. Niemela, and H. G. Gyllenberg. Tolerance of Thiobacillus ferrooxidans to Some Metals. v. 37, 1971, pp. 489-496.
6. Silverman, M. P., and H. L. Ehrlich. Microbial Formation and Degradation of Minerals. Advan. Appl. Microbiol. v. 6, 1964, pp. 153-206.
7. Broda, P. Plasmids. San Francisco, California, W. H. Freeman and Company Limited, 1979, 197 pages.
8. Maniatis, T., E. F. Fritsch, and J. Sambrook. Molecular Cloning: A Laboratory Manual. Cold Spring Harbor, New York, Cold Spring Harbor Laboratory, 1982, 545 pages.

9. Mao, W. H., Michael, P. R. Dugan, P.A.W. Martin, and O. H. Tuovinen. "Plasmid DNA in Chemoorganotrophic Thiobacillus ferrooxidans and T. acidophilus. FEMS Microbiology Letters, 8, 1980, pp. 121-125.
10. Holmes, D. S., J. H. Lobos, L. H. Bopp, and G. C. Welch. Setting Up a Genetic System de Novo for Studying the Acidophilic Thiobacillus T. ferrooxidans. Ch. in Recent Progress in Biohydrometallurgy, ed. by G. Rossi and A. E. Torma. 1983, pp. 541-554.
11. Olson, G. J., F. D. Porter, J. Rubinstein, and S. Silver. Mercury Reductase Enzyme from a Mercury-Volatilizing Strain of Thiobacillus ferrooxidans. Journal of Bacteriology, v. 151, No. 3, 1982, pp. 1230-1236.
12. Rawlings, D. E., C. Gawith, A. Petersen, and D. R. Woods. Characteristics of Plasmids and Potential Genetic Markers in Thiobacillus ferrooxidans. Ch. in Progress in Biohydrometallurgy, ed. by G. Rossi and A. E. Torma. 1983, pp. 555-570.
13. Brandsch, R., and K. Decker. Isolation and Partial Characterization of Plasmid DNA from Arthrobacter oxidans. Archives of Microbiology, 138. 1983, pp. 15-17.
14. Rodriguez, R. L., and R. C. Tait. Recombinant DNA Techniques: An Introduction. Addison-Wesley Publishing Company, 1983, 236 pages.
15. Bednarska, M., E. K. Jagusztyn-Krynicka, J. Popowski, and M. Wlodarczyk. Extrachromosomal DNA in Thiobacillus A2. FEMS Microbiology Letters, 16, 1983, pp. 183-185.
16. Norris, P. R., and D. P. Kelley. Accumulation of Cadmium and Cobalt by Saccharomyces cerevisiae. J. Gen. Microbiol., v. 99, 1977, pp. 317-324.
17. Strandberg, G. W., et al. Microbial Cells as Biosorbents for Heavy Metals: Accumulation of Uranium by Saccharomyces cerevisiae and Pseudomonas aeruginosa. Appl. Environ. Microbiol., v. 41, 1981, pp. 237-245.
18. Kagi, J. H. R., and M. Nordberg (eds.). Metallothionein. Birkhäuser Verlag. Boston, 1979.
19. Goeddel, D. V., et al. Nature, v. 281, 1979, p. 544.
20. Goeddel, D. V., et al. Proc. Natl. Acad. Sci., v. 76, 1979.

METAL/GAS REACTIONS IN THERMAL PLASMAS

INTRODUCTION

L.S. Richardson ¹/ and others

The direct reduction of ores to metals using a thermal plasma to dissociate them has been proposed and experimentally evaluated for many years. Industrial use of these processes has been hampered by a lack of understanding of what actually occurs within the plasma; most industrial users have assumed that the plasma is simply a source of hot gas and have designed their processes for equilibrium conditions. Processes utilizing the non-equilibrium conditions within a plasma have been developed by strictly empirical means (e.g. the production of ethylene from coal and hydrogen and the production of pigment-grade TiO_2). A more fruitful approach, generically applicable to any process, would be to find methods to actually understand the internal workings of thermal plasmas.

Models predicting the interior conditions of plasmas have been developed over the last fifteen years to allow evaluation of processes as diverse as supersonic wind tunnels, ablation testing, and rocket exhaust chemistry. A second set of models has been developed for use in predicting behavior in arc welding. These models have generally assumed continuum behavior and local thermodynamic equilibrium (LTE). Recently, Pfender, Boulos, Fauchais, and their students have begun developing more realistic models, specifically for use in metallurgical processes. Szekely has attempted to use a model developed for arc welding to predict behavior in electric arc furnaces, but his results have not been universally accepted. One problem with most of the model development work has been the lack of experimental data to verify the predictions. Attempts to measure temperatures and velocities within the plasma have been reported by Fauchais and Boulos, with limited agreement with predictions. No efforts have been made to measure compositions within a plasma to allow comparisons with computer predictions. The purpose of the current work is to provide an integrated study on prediction and verification of temperature, velocity, and composition within a plasma.

An important variable in thermal plasma processing is the scale of the process. Measurements on small plasmas have not been successfully scaled up to larger processes. An important part of the present study is to make measurements under a wide variety of experimental conditions, specifically utilizing higher power plasmas than those previously measured.

Measurement of temperatures within a plasma is far from a trivial task. Spectroscopic measurements are used to determine population densities for certain excited states, and population ratios can then be used to estimate temperatures. Several different approaches can be

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taken to these measurements. The electron density can be measured and temperatures determined by use of the Saha equation. Boltzmann distributions can be assumed and temperatures determined by using two or more spectral lines. A third approach is to measure the ratio of a single line to the radiation continuum. The results of these different measurements are not always in agreement. A second problem has to do with the geometry of measurement. Each measurement consists of the integrated intensity along the line of sight from the viewing point, while what is desired is the emittance from each individual point. The standard method of obtaining point data from line data is to use the Abel integral inversion technique. However, this method requires a known amount of symmetry, and also suffers from the problem that the standard computational approach utilizes successive digital differentiation and integration steps in the calculation, which magnifies the errors of observation. Another approach is to use a tomographic approach, which requires more measurements and somewhat greater precision in the optical positioning of the detector and source.

Measurements of the velocity of the particles have also been done optically, utilizing laser doppler anemometry (LDA). Particles are introduced into a plasma and are then assumed to "track" the flow contours of the hot gas. By using a split beam from a laser and measuring the beat frequency from the combined reflection, it is possible to measure the particulate velocity. This measurement rests on two assumptions, both of them poor. Small particles move (nearly) with the velocity of the gas and are accelerated rapidly by the gas to that velocity. Unfortunately, small particles exposed to plasma conditions do not survive long enough for useful measurements to be made. Larger particles, which will survive, lag velocity changes and are not accelerated rapidly enough to give true values. Additional problems have to do with the greater incidence of momentum transfer on the hot side of the particles compared with the cold side, which provides a force moving the particles away from the hot region (thermophoresis). Direct measurements of the gas velocity can be made utilizing laser holographic interferometry (LHI). In this technique, reference holograms are constructed from a carefully controlled setup, which can be either hot or cold. A trace gas of different optical properties is then introduced by a pulse technique into the plasma and high speed photography is used to record the movement of interference fringes created between the reference hologram and the moving gas. Turbulence can be determined directly and non-axial velocities can also be determined. The technique requires extreme precision in optical techniques.

Spectroscopic determination of composition as a function of position can be accomplished using laser induced fluorescence (LIF). A particular energy state of an excited species is saturated by using a tuned laser source to pump from a lower energy state. The decay of this state, usually (but not necessarily) back to the ground state, releases photons of a precisely defined frequency. If the amount of this fluorescent emission is well above the background radiation of the plasma, a direct measurement of the quantity of that species can be

made. The technique requires optical precision and good knowledge of the spectral lines (energy levels) and lifetimes of the desired species. Reasonably high power is needed for the exciting laser.

Computational models include those used for rockets, arcs, and supersonic wind tunnels. In general, these models do not allow for such local effects as Knudsen flow, thermophoresis, Soret effect, and the like. In principle, these models can provide a global view that can then be modified with local conditions. This approach has the advantage that it can be achieved in a step-wise fashion, allowing verification of each individual change. The assumption of LTE is more difficult to replace. Pfender and others have been using a two temperature model, wherein the electron and ion temperatures are separately modeled. The extension of this model to three or more temperatures is possible, if not straightforward. Experimental confirmation of multiple species temperatures is now being produced, primarily in the analytical chemistry literature.

During the second year of this program, previously procured and installed equipment was used to produce experimental maps of temperature and velocity. Considerable difficulty was encountered in producing valid maps of temperature. The Abel inversion was not successful in producing reasonable maps from the ICP torch, due to the lack of symmetry, the instability of the plasma column, and the appearance of off-center maximum temperatures. Tomographic techniques to reduce emittance to temperature were developed and fitted to "phantom" data, produced by reversing the Abel inversion with assumed temperature curves. After demonstrating that the reconstruction produced adequate reproductions of the original curves, a small arc torch was set up so that line scans could be taken at 20° intervals over one half the circumference. Initial attempts were unsuccessful because of the small size of the arc, which made it impossible to maintain optical alignment. Larger scale experiments will be performed.

Velocity maps were easier to obtain. Maps of the ICP were taken at several different elevations and a contour map for one set of conditions was obtained for comparison with computer predictions. An expected problem arose from these measurements--the lack of survival for small particles. Both Al_2O_3 and SiC particles were used. Particles below 5 μm did not make it from the injection point to the measurement volume, while coarser particles (50 μm) survived but were relatively sluggish, not following rapid variations in velocity. Intermediate sizes of particles are now being used to demonstrate where the changeover occurs.

A parallel program investigating welding arcs presented the opportunity to utilize the dye laser built in the first year to investigate the composition of a plasma. Measurements of the concentration of manganese over a weld pool were made, demonstrating the deficiencies of the system. A second, more powerful dye laser was obtained, and measurements were taken during the remaining months of the second contract year.

Mathematical models were established, describing the plasma column and plasma plume for both the TAFA and the ICP torches. Thermochemical calculations were made for the carbothermic reduction of aluminum in argon plasmas for those two systems. Temperature and velocity fields were predicted from arc initiation to free plume expansion. Assuming instantaneous achievement of equilibrium, the composition could then be calculated by combining the two codes. Two papers discussing this work were presented at the Materials Research Society meeting in Boston.

Work on aluminum chloride dehydration was completed, with a uniform lack of success in all approaches. A final report was written, documenting all efforts made on this part of the project.

Work at the University of Idaho was concentrated on theoretical studies. A method for quantifying particle shape was developed for use in evaluating changes occurring during transit through a plasma. Models for evaluating mass transfer under steep temperature gradients were developed, and two papers written describing the work. Methods for calculating the thermodynamics of gaseous species at very high temperatures were reduced to computer programs; model predictions compared favorably with experimental data at lower temperatures. A "black box" economic/energy balance program is under development to allow comparison between plasma processing and more conventional methods.

EQUIPMENT

A. D. Donaldson 1/ and K. A. Prisbrey 2/

Two major plasma generating systems exist in the plasma laboratory, along with an additional smaller welding arc. The 60 kW ICP system has been in operation for more than a year; almost all of the diagnostic work is performed in it. The 180 kW TAFA system was received early in the year, but has only been used to check out operation of the system. An environmental chamber for the system was designed, constructed, and installed. Additional pollution control equipment was necessary to remove particulate matter from the exhaust gas. In addition, arsenic and sulfur oxides in the gas must be removed. A three-stage cleanup unit has been designed, and is now being constructed. The stages are a cyclone, a wet scrubber, and a high efficiency particulate (HEPA) filter, with the ability to bypass the scrubber when it is not needed. The size of this equipment required the acquisition of additional laboratory space, located in the area immediately adjacent to the previous space. The doubling of space from 75 m² (800 ft²) to 150 m² allowed rearrangement of space to much less crowded condition. An advantage to the new arrangement is the availability of the dye laser system [on a 1.5 by 3.6 m (5 by 12 ft) table], without major moving of optical equipment. The delays due to the need for optical realignment are thus minimized.

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The hollow carbon electrode furnace has been conceptually designed with final design planned for May. Construction of that torch and chamber will be performed expeditiously. The power supply for the torch is the same for the TAFA torch. It will be possible to switch from one torch to the other in a day so that diagnostic studies can be made for both configurations.

A 60 kW dc arc torch was procured from Plasma Energy, and installed at the University of Idaho. The containment chamber, a double shelled, water-cooled tank, has inadequate cooling, making runs longer than 7 min impossible. Improved water cooling methods are being sought. Initial use of the chamber was to examine the spectroscopic lines of argon, with the future goal of examining the spectroscopic transitions of aluminum and other materials of interest to the plasma program.

PLASMA DIAGNOSTICS

J. A. Batdorf 1/

Due to the high temperature of the plasma, emission spectra, both molecular and atomic, are easily obtained. These are extremely useful for qualitative analysis, such as species identification. However, in order to characterize the reaction environment, it is necessary to obtain quantitative information--specifically, species concentrations and a measure of the energy level. Classically, the energy level of a system is identified by measurement of temperature and pressure. For thermal plasmas, the straightforward identification of temperature with energy level is complicated by the fact that various species are not in complete thermodynamic equilibrium (CTE). Most current plasma researchers assume LTE, and identify the energy level by a single value of temperature. Species concentration measurements also require the assumption of LTE conditions and are based on this value of temperature.

The present experimental work has been conducted on the ICP torch. This torch was operated with argon as the primary plasma species and low concentrations of aluminum and oxygen from evaporation of particulate aluminum oxide (-200, +325 mesh). Particles were introduced into the top of the ICP with an argon carrier gas. Emission spectroscopy measurements concentrated on neutral argon species, measuring the relative intensities of five emission lines to provide an estimate of the plasma temperature. The temperature is estimated from the inverse slope of a plot of $\ln(\text{intensity})$ against energy level. This procedure is sensitive to the amount of separation between energy levels. The five lines (shown in table 3-1) were chosen based on the following criteria:

1. maximum separation between energy levels
2. similar intensities, so that signal-to-noise ratios would be smaller for equal integration times

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3. spectrally close so that a minimum number of scans could be used to obtain the data
4. sufficient isolation that the lines could be completely resolved from their neighbors.

TABLE 3-1. - Wavelength and energy level of argon emission lines studied

Identification	Wavelength, nm	Upper Energy Level, 1/cm
A	518.775	123,400
B	516.229	123,400
C	427.217	117,200
D	426.629	117,200
E	425.936	118,900

The first two lines could be observed with one monochromator setting, while the other three were observed at a second setting. Although other energy levels from 110,000 to 126,000 cm^{-1} were available, the above lines met all of the four criteria.

Experimental data was taken with the ICP torch operating at atmospheric pressure, a total argon flow of 1.42 m^3/h (50 scfh), and a plate power of 50 kW. Spectroscopic measurements were made between 0.18 and 0.25 m below the torch exit. The plasma plume was optically imaged onto the entrance slit of a 0.3 m monochromator. A vidicon detector was used to determine the spectral emissions from a horizontal line of spatial locations across the plume. Since the plasma is viewed from the side, the observed intensity for each location on this line is the sum of emissions along the line of sight through the plasma. The first set of data obtained was deconvoluted using Abel's integral inversion with results indicating a centerline temperature of 9500 K, decreasing parabolically to 5000 K at a distance of 20 mm. More accurate emission measurements were then made to provide a complete map of the tail plume. Unfortunately, these measurements demonstrated that the Abel inversion analysis method was not usable in all cases. The primary problem is due to the exaggeration of experimental variances by the digital differentiation step within the computerized Abel inversion.

Several other methods of analyzing the raw data have been tried with varying degrees of success. Presmoothing of the raw data reduced the problems caused by the Abel transform and indicated a centerline temperature of 10,000 K. A tomographic technique has also been developed and tested. While this technique requires data from several views, adding to measurement complexity, it is capable of reconstructing an asymmetric emission source. Data for an initial test of the tomographic technique were obtained by physically rotating a small welding torch about its axis and recording emission data from 20 points for each of 21 views. The data collected did not produce useful results due to arc instabilities. A nonlinear least squares method has

also been used. This method assumes a temperature profile, predicts the intensity profiles that would be observed, and compares these to the measured profiles. The difference is then used to readjust the temperature profile and the procedure is repeated.

A second complete map of the ICP was obtained with an improved optical system. This raw data appeared to be smoother than previous data, but produced similar results with the Abel transform method of data reduction. The least squares method was used to predict temperatures from this data. The results are shown in figures 3-1 and 3-2. The first figure compares the predicted values of observed intensity with those measured experimentally for one of the five emission lines. These figures are for the intensities observed at axial position 8.0. Figure 3-3 shows the temperature profiles obtained by this method for several axial positions. The flat profiles obtained in the lower regions are due to the combined effects of plasma fluctuations and time averaging of the data collection method. Visual observation of the plasma plume indicates a flickering of the lower portion of the plume in a pendulum fashion. Time averaging of the emissions from this region results in a reduction of the observed centerline emissions and an increase in observed emissions at the edges.

The theoretical work developing the least squares analysis method has produced some interesting results, not previously discussed in the literature. Figure 3-4 shows a plot of three temperature profiles for three hypothetical plasma conditions. The temperature profiles all have a centerline temperature of 10,000 K and decrease with radial position to 8800, 7500, and 5000 K. Figure 3-5 shows the prediction for observed intensity for each of these cases. In order to observe these profiles the detection equipment must be capable of monitoring 1, 2.5, and 8 orders of magnitude of light intensity, respectively. A photomultiplier tube can handle 6 orders of magnitude, but only with careful adjustments of gain and special output amplification. While the vidicon detector used in these experiments is sensitive over several orders of magnitude, the signal to noise ratio for the linear response region is only slightly over 1 order of magnitude. Therefore, complete analysis of a plasma environment will require careful blocking of high intensity regions to allow examination of lower intensity regions and prevent saturation of the detector.

PARTICLE MEASUREMENTS

J. R. Fincke ^{1/}

Particles injected into a plasma are accelerated by the rapidly moving gas and can achieve velocities in excess of 1000 m/s. Predicting the behavior of such particles requires a knowledge of the velocity of both particles and plasma as a function of spatial location and injection conditions. Measurement of these velocities is an important part of this investigation. If sufficiently small particles are injected into a plasma, they will rapidly reach the same velocity

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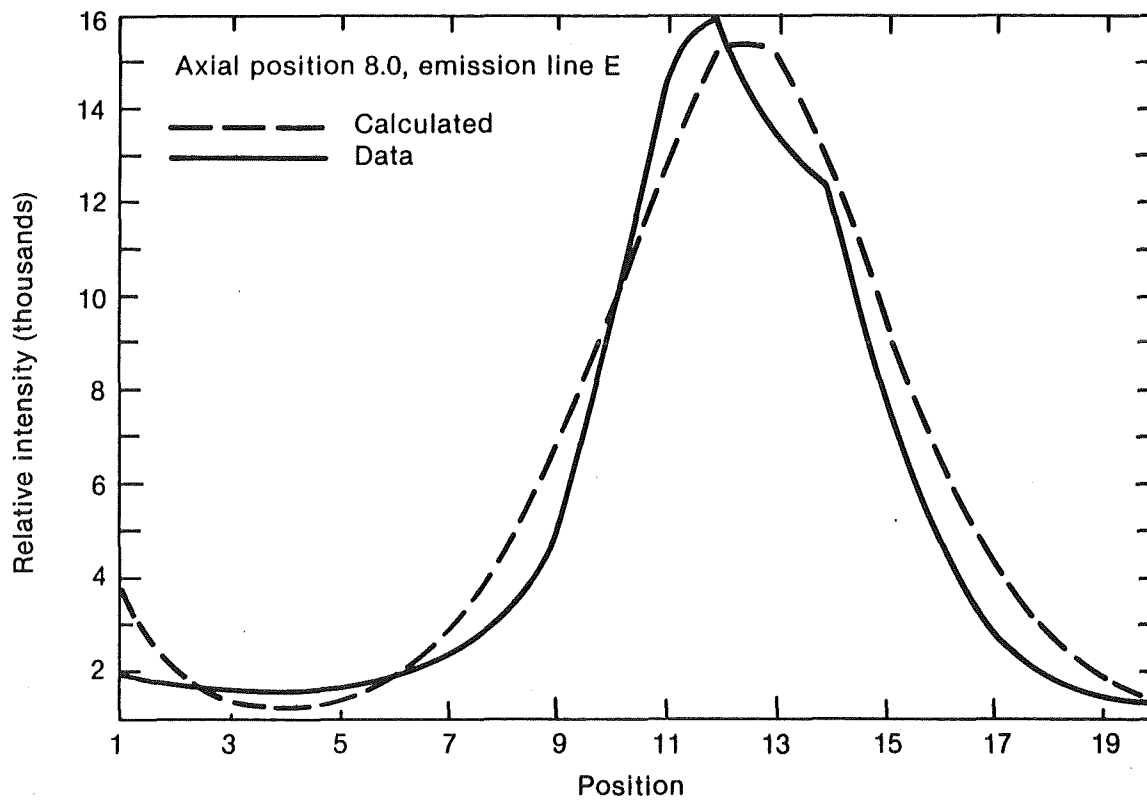


Figure 3-1. Calculated vs. observed intensity profiles in the ICP.

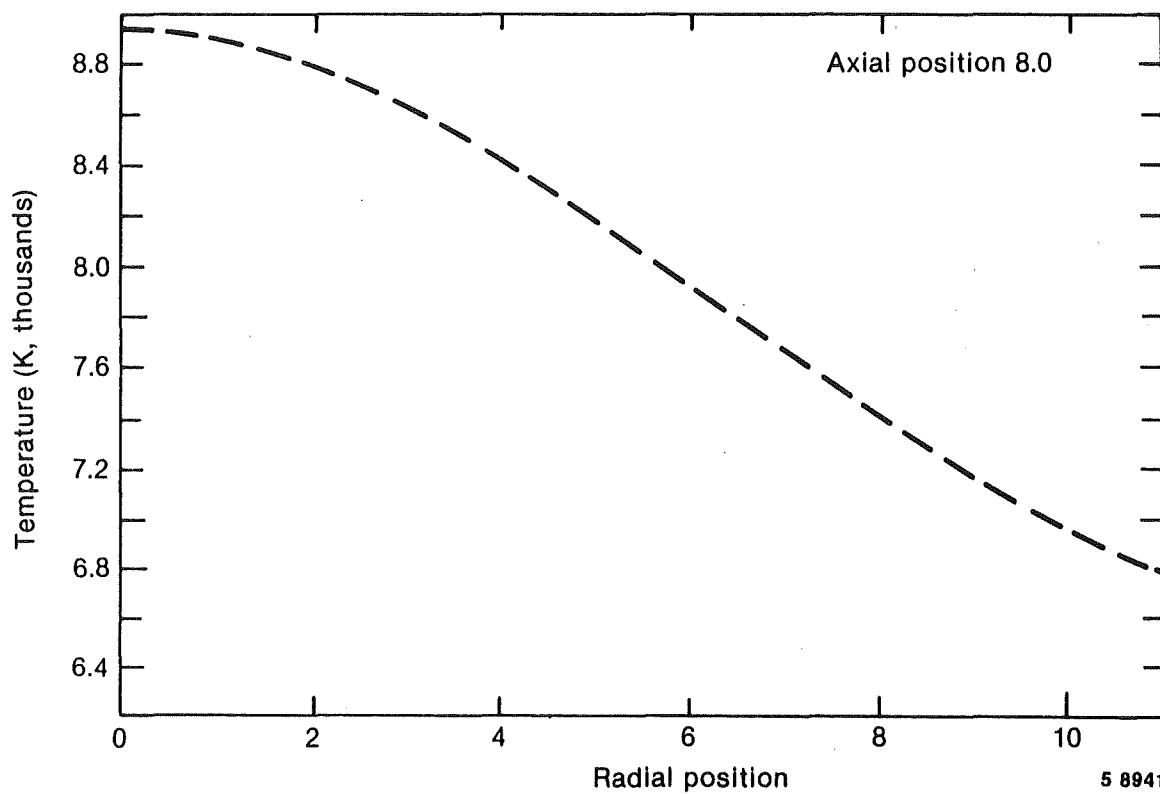


Figure 3-2. Temperature profile in the ICP.

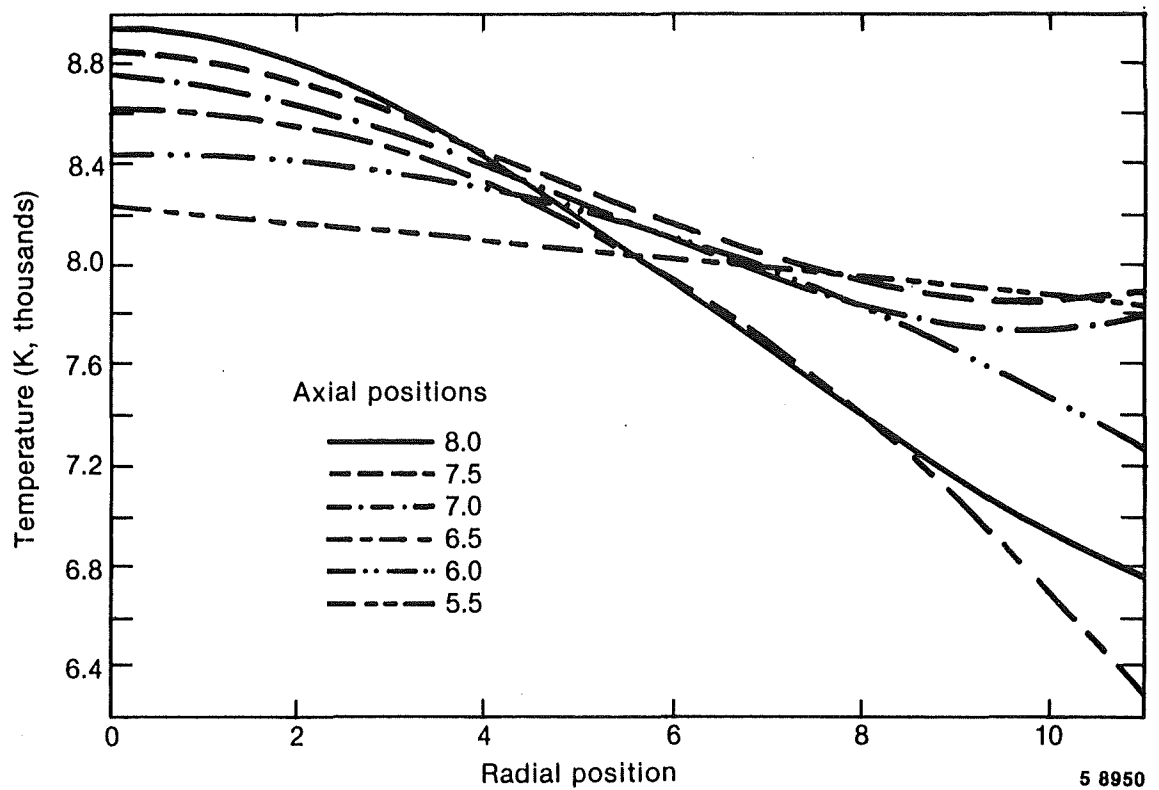


Figure 3-3. Temperature profiles at various axial positions in the ICP.

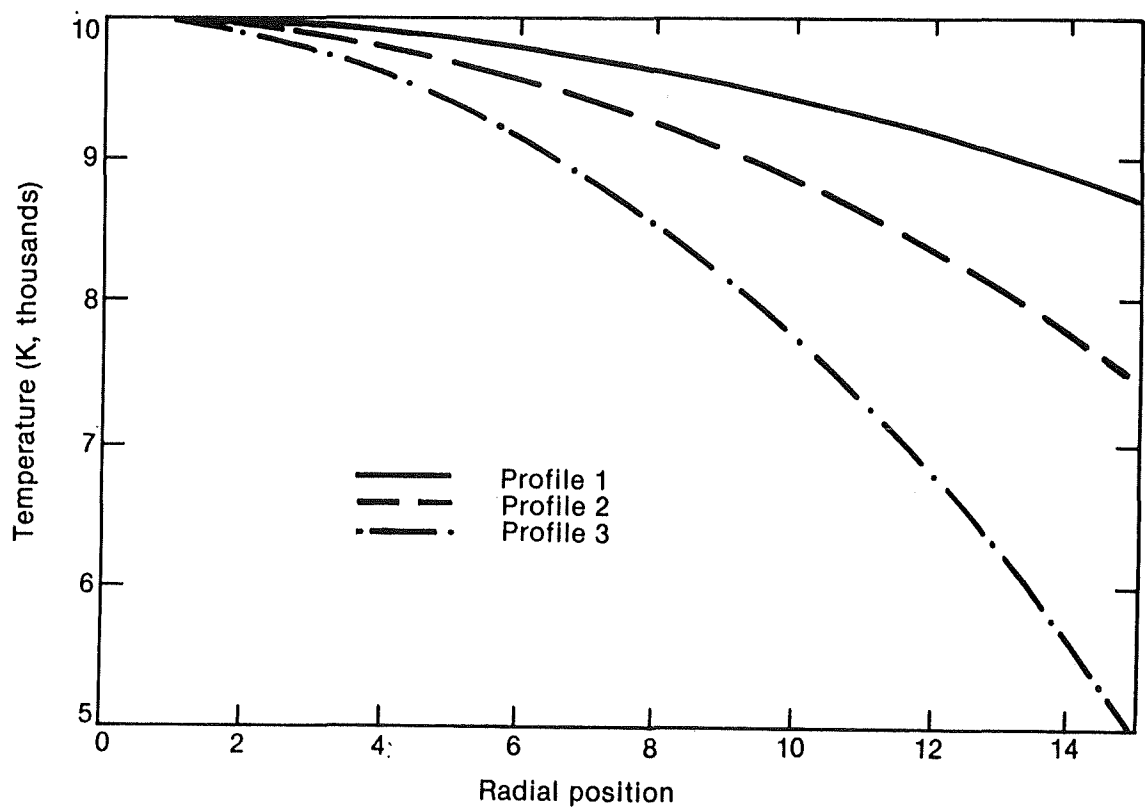


Figure 3-4. Hypothetical temperature profiles.

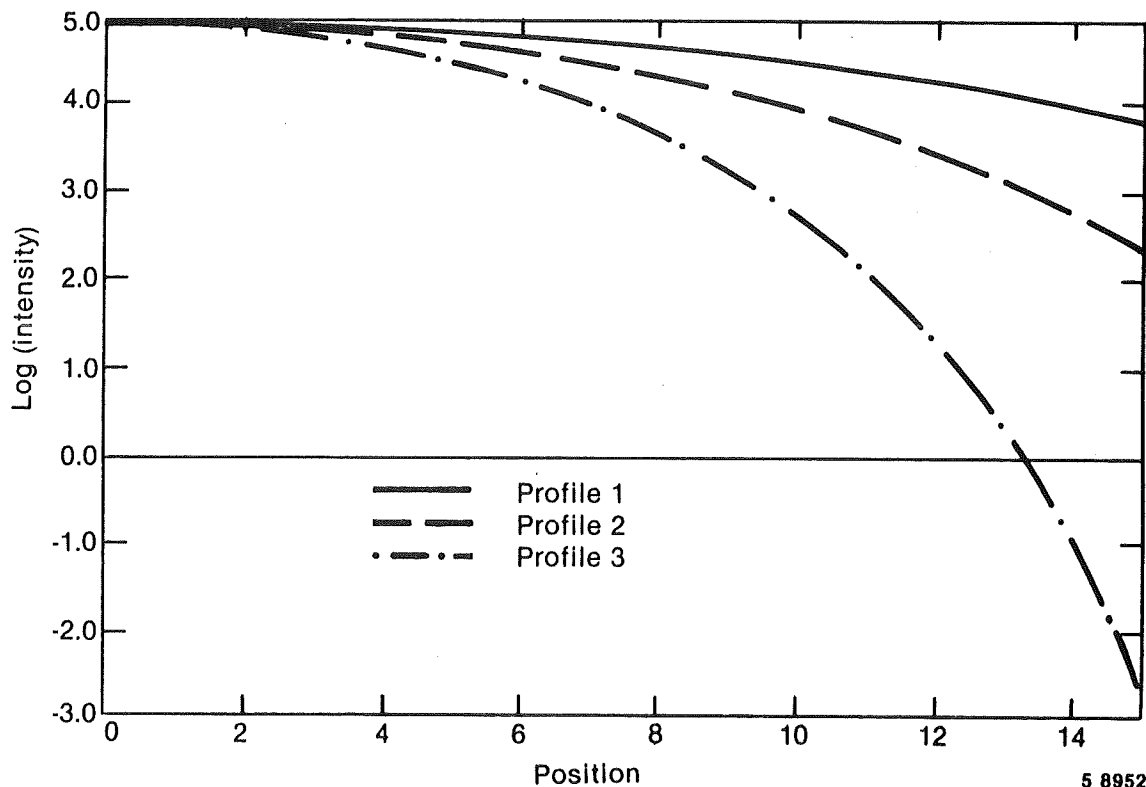


Figure 3-5. Observed intensity calculated for hypothetical temperature profiles.

as the gas. Unfortunately, response times for 50 μm particles are on the order of several milliseconds, which is longer than the estimated residence times in the plasma; smaller particles will not survive the plasma conditions long enough to be observed. Thus the present techniques can only measure particle velocity and not plasma velocity.

Particle velocity measurements were made with a laser doppler anemometer (LDA) system, shown schematically in figure 3-6. The entire optical assembly is mounted on a movable rail controlled by a stepping motor with a lead screw drive mechanism, which allows the measurement volume, defined by the intersection of two laser beams, to be traversed across the flow field. The light flux scattered from a particle at the intersection of the two focused laser beams is optically collected and focused onto a photo detector. Due to the laser beam geometry, light scattered from one beam is upshifted in frequency while light from the other is downshifted. When mixed on the photo detector surface, the resulting beat frequency is proportional to the particle velocity. This system is based on a Thermo Systems Incorporated LDA used in the forward scatter mode. A beam expander is included to reduce the measurement volume size to an ellipsoid of ~ 500 by $75 \mu\text{m}$. The laser is a Level 4 W argon ion laser operating at 514 nm (green). To protect the photomultiplier tube from the plasma radiation, a 1 nm full-width, half-maximum (FWHM) narrow band interference filter was placed behind the collection optics.

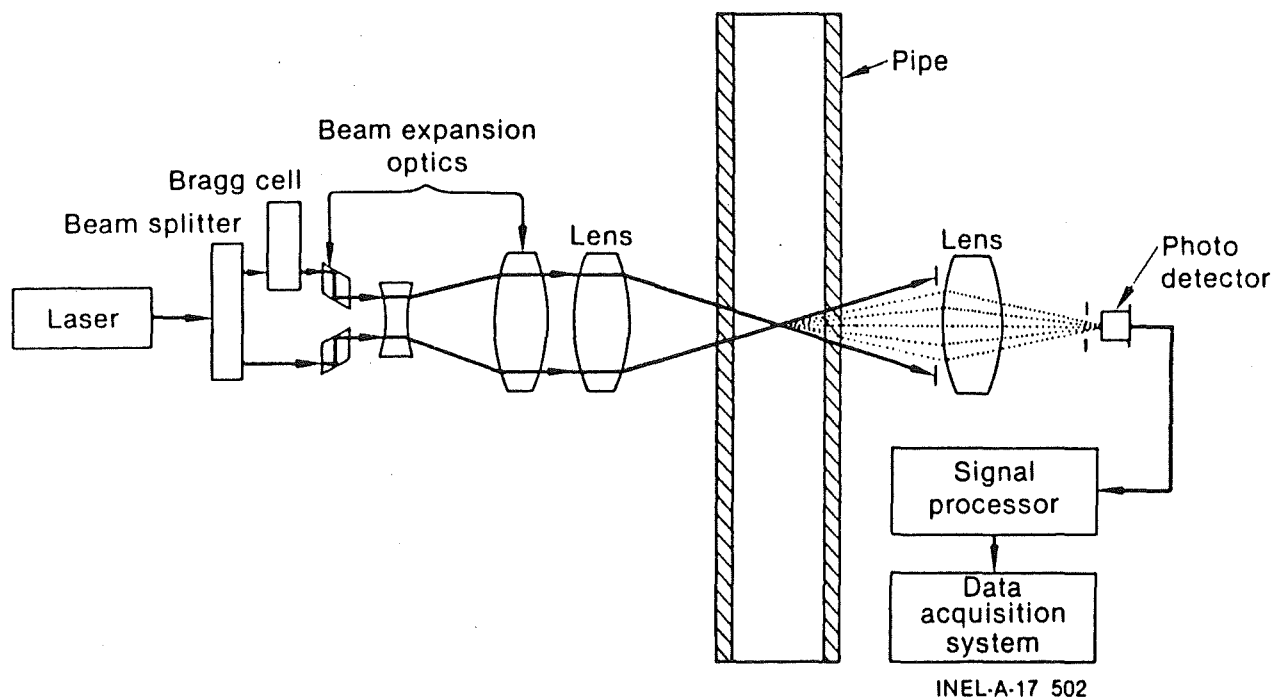
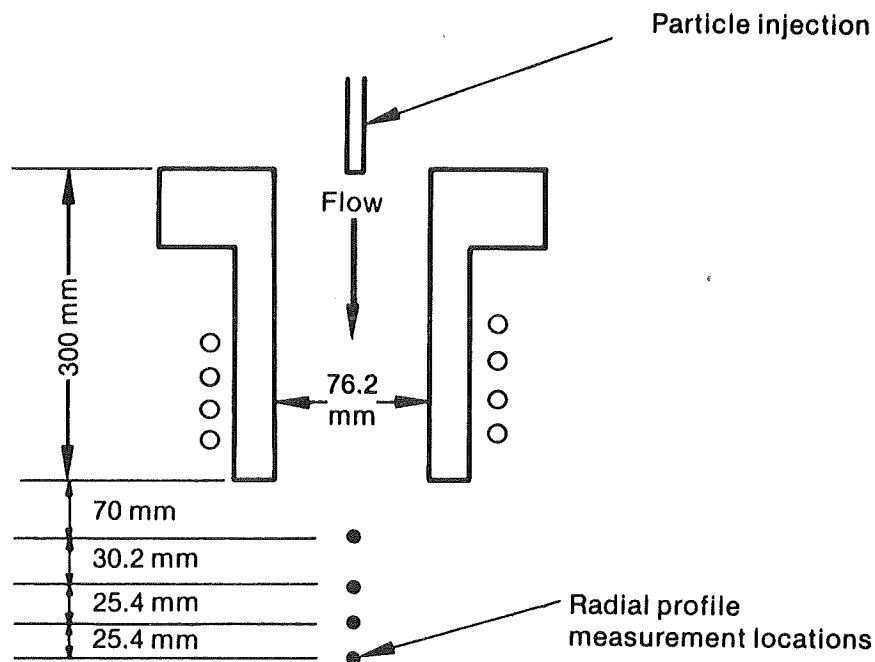


Figure 3-6. Schematic of laser Doppler anemometer system.

The LDA system optics have been modified to accommodate the size of the ICP experimental chamber. The noise caused by the rf-driven ICP (~ 0.4 MHz) on the LDA detector system and electronics is significant though not overpowering. Measurements can be made without additional shielding or precautions, providing the signal of interest does not fall close to the ICP frequency. If signal-to-noise ratios become unacceptable, two techniques of dealing with the problem have been evaluated: (a) proper grounding and mu-metal shielding, and (b) a fiber optic link between the receiving optics and the detector system. A simple optical fiber link has been constructed and found to work satisfactorily. To date, neither of the two possible solutions has been needed, although as wider range of test conditions is evaluated further work may be required.

Particles were injected into the ICP through a 6.4 mm (0.25 in.) tube centered above the fireball, figure 3-7. A uniform dispersion of the particles in the injection gas was achieved by passing the gas through a fluidized bed of mixed particles. The major constituent of the bed was a relatively coarse (~ 200 μm) iron grit, with the particles to be injected mixed in. This mixed bed also breaks up any agglomerated particles. Two different powders were injected: 50 μm Al_2O_3 and 1.5 μm SiC . The data acquisition rate for the fine powder was unacceptably low, providing no useful results. The coarser powder achieved data rates of 10 to 100 points per second.

A plot of axial velocity versus radial coordinate appears in figure 3-8 for four different elevations in the ICP tail flame. Each point is the average of about 2500 individual data points, averaging not only turbulent fluctuations and plasma instabilities, but also different particle sizes. While the nominal size range of the injected particles was from 43 to 63 μm , random fluctuations in the plasma



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Figure 3-7. Particle injection point and radial velocity profile measurement locations.

provided a much larger range of sizes due to the different thermal conditions seen by individual particles. The measurements indicate a jet of particles which gradually spreads as it moves away from the fireball. Relatively few particles are found outside the limits indicated on the plots. The relatively slow loss of velocity as the edge of the plume is reached is due to the coarseness of the particles, whose momentum is sufficient to carry their velocity well into the periphery of the tail flame.

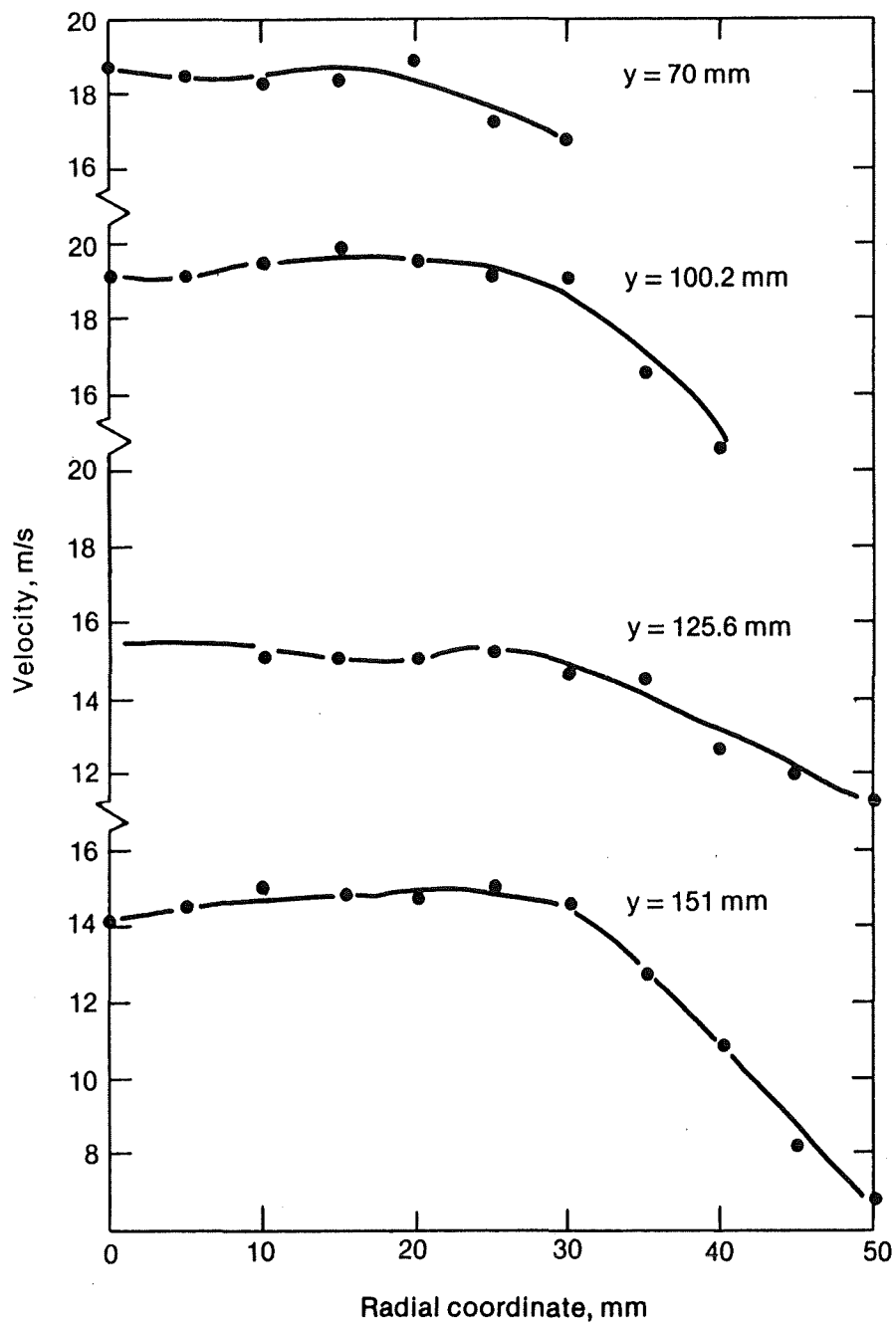
COMPUTER MODEL DEVELOPMENT

D. J. Varacalle, Jr. 1/ and J. Y. Park 2/

Modeling energy transport in current-carrying thermal plasmas requires solving the full set of conservation equations, including current continuity. Because of the complexity of this task and considering the time constraints, the decision was made to obtain several available computer programs as a starting point. These codes can then be modified to allow more nearly accurate procedures. The codes are sufficiently comprehensive to provide a process model fully describing the interacting electrical, magnetic, fluid, and thermal effects of a plasma in conjunction with the thermochemistry of an

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Figure 3-8. Particle axial velocities.

injected species. The flow field can be described from arc initiation through the free plume expansion. The thermochemistry of the process (e.g. carbothermic reduction of alumina) can also be studied.

Prof. Emil Pfender, University of Minnesota, has supplied working versions of his plasma codes, which are now implemented on the CYBER system. These codes have been used to replace ARCFL02 and SPF1. Predictions similar to those described above were obtained.

A parametric method of analysis was used, with the JANAF code providing the thermodynamic data for equilibrium calculations by ACE. The output of this code (thermodynamic and transport properties) was input to either ARCFL0 or a code developed by Pfender (PCOL), which then calculated temperature/velocity/enthalpy distributions in the plasma column. Final free expansion calculations were made using SPF1 or PPLUME, allowing for the interaction of the plasma with a surrounding atmosphere. This calculation could be considered a first order approximation. The data derived from this set of calculations were used to prepare maps of velocity, temperature, and chemistry as a function of radial and axial position. The assumptions made in this calculation are: uniform dispersion of injected species, instantaneous heat transfer from plasma to particle, and instantaneous achievement of LTE. While the assumptions need to be improved, they allow a first approximation to be made, leading to a comparison with experimental measurements and providing a base for second order calculations.

First order thermodynamic calculations for the Al/O/C system were made for both ICP and TAFA torches during the second contract year. Some 35 species were considered as possible constituents of the plasma. Figure 3-9 shows the dominant species as a function of temperature for the TAFA torch.

A parametric study using ARCFL02 was made of the behavior of the TAFA torch. To allow for the slightly flared design of the nozzle, a diverging nozzle subroutine (DIVNOZZ) was written to modify the straight pipe assumptions of ARCFL02. The output from the modified ARCFL02 was then used as input for SPF1. For 37 kW and 1000 A, figures 3-10 and 3-11 show the predicted velocity and temperature fields through the entire plasma regime. Combining the results of figures 3-10 and 3-11, resulted in maps of the total gaseous aluminum concentration as a function of location in the plasma (fig. 3-12).

Prof. Maher Boulos, Universite de Sherbrooke, made calculations for the ICP, predicting the temperature and flow fields for conditions of 15 kW power, 330 kHz frequency, and 0.4 L/s (50 scfh) gas flow. This code simultaneously solved the two-dimensional momentum and energy equations and the one dimensional electromagnetic field equations. Figure 3-13 shows the temperature contours and velocity patterns from this calculation. This was then used as input to SPF1, and calculations were carried out as described earlier. Figures 3-14 and 3-15 show the resulting velocity and temperature predictions. Composition was predicted as previously described for the TAFA torch.

One of the two major factors that complicate the plasma/particle mass transfer is the large temperature gradients existing in the vicinity of

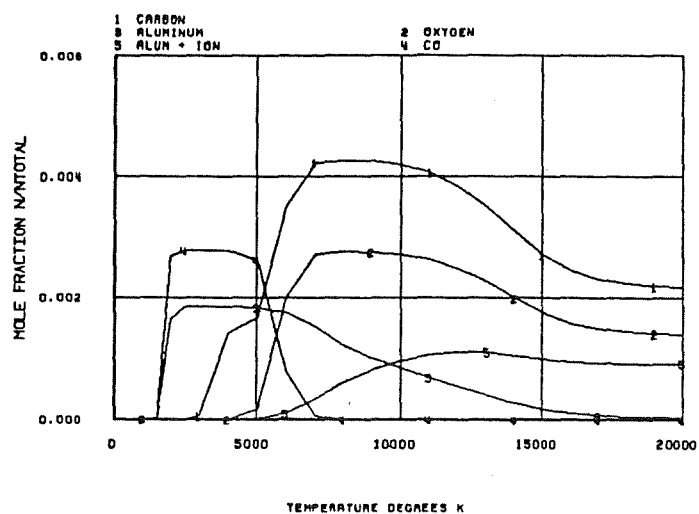


Figure 3-9. Predominant predicted species of the carbothermic reduction of alumina.

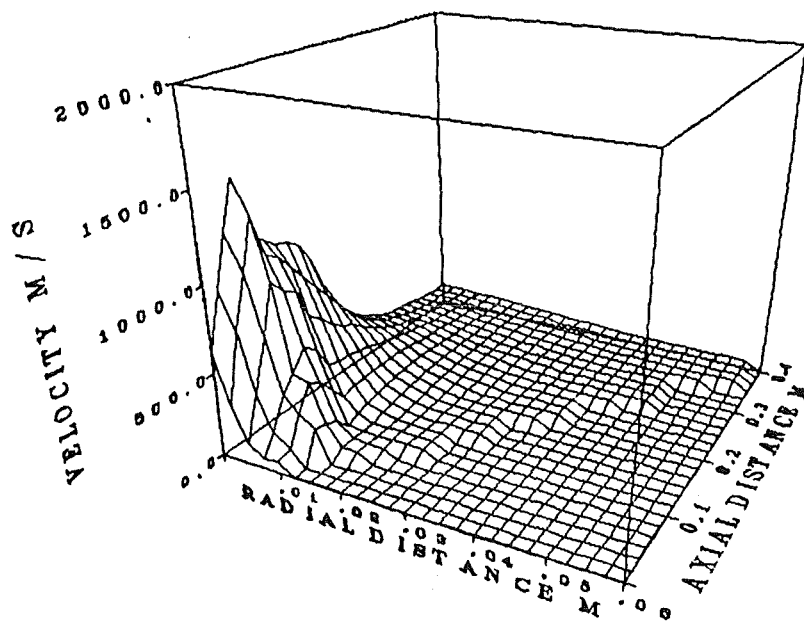


Figure 3-10. Prediction of velocity vs. location (cathode through free plume).

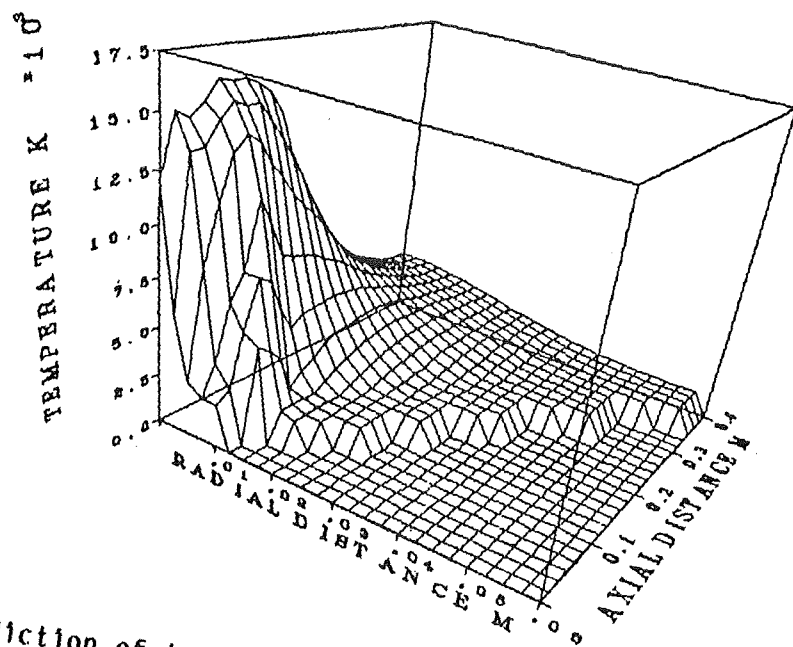


Figure 3-11. Prediction of temperature vs. location (cathode through free plume).

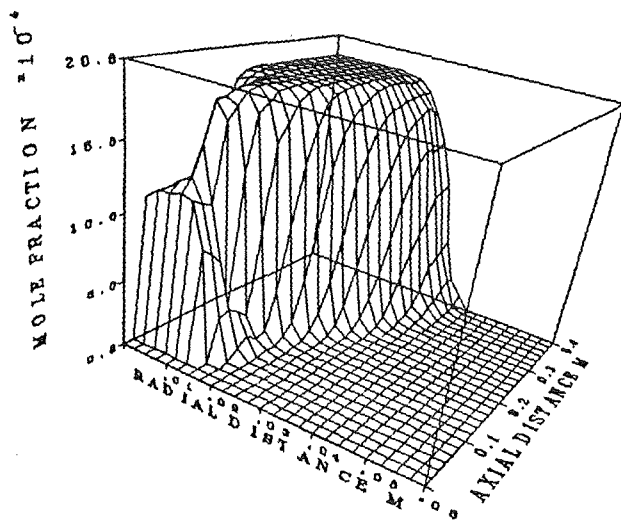


Figure 3-12. Predicted concentration of aluminum species in free plume.

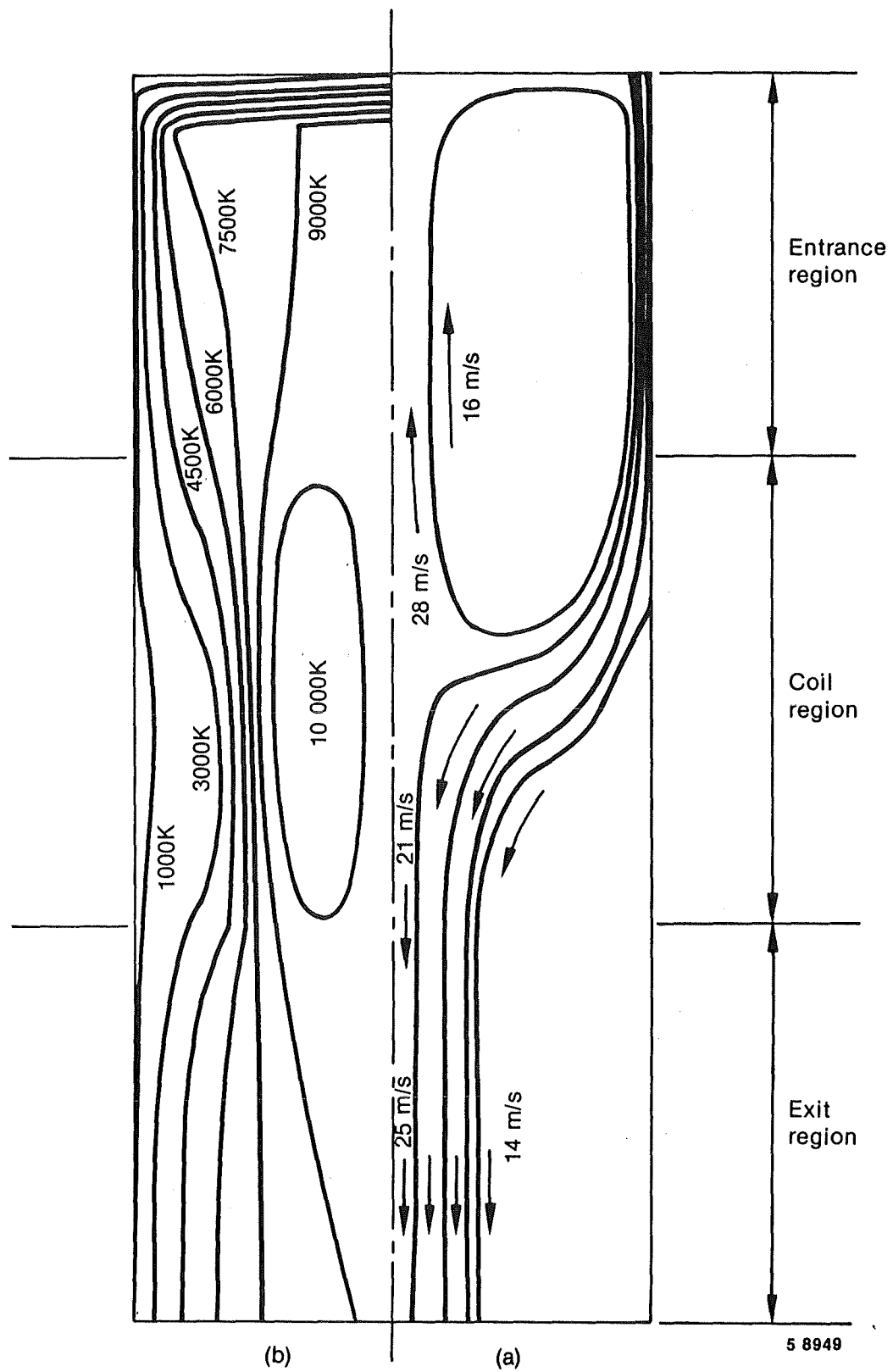


Figure 3-13. Stream lines (a) and temperature isocontours (b).

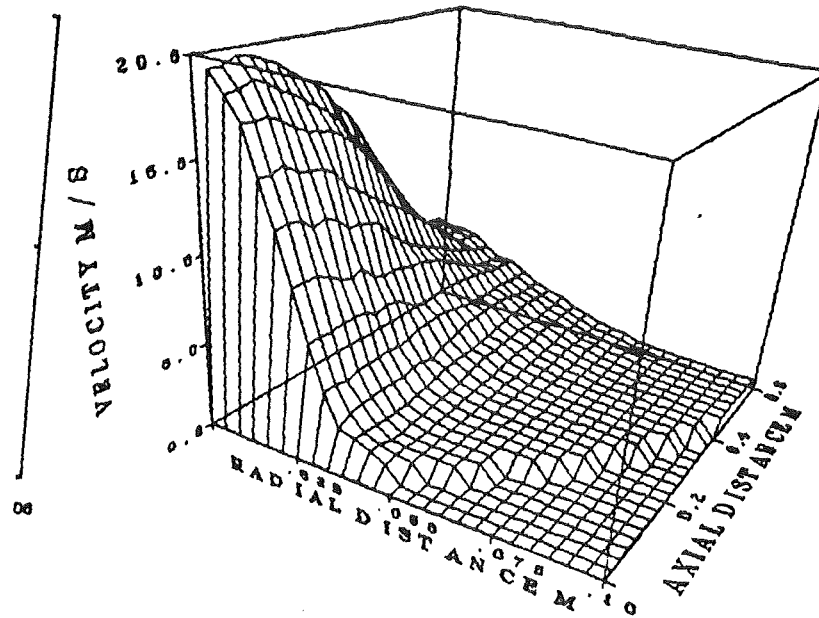


Figure 3-14. Three-dimensional plot of calculated velocity vs. location.

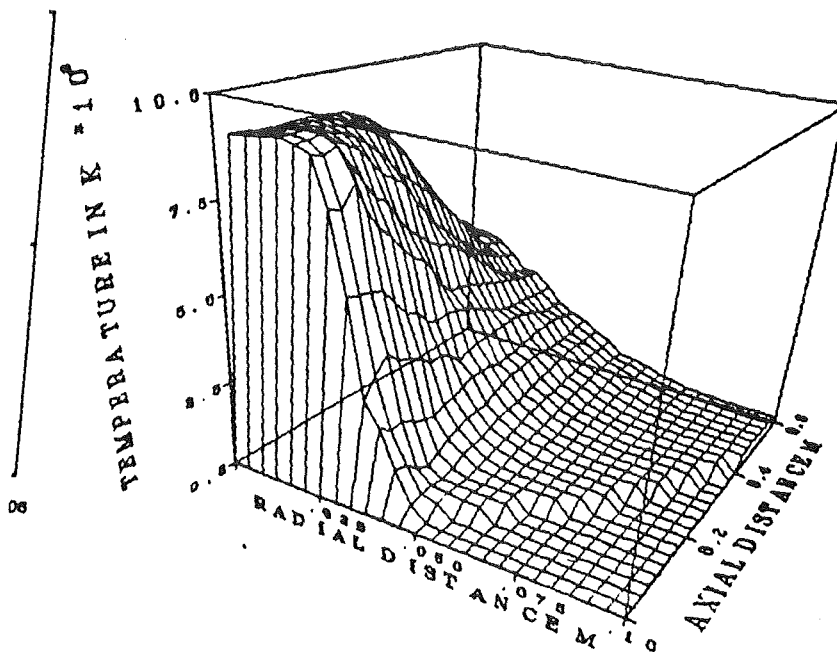


Figure 3-15. Three-dimensional plot of calculated temperature.

the particle immersed in the plasma, and the resulting variation in the transport properties of the plasma gas. For heat transfer calculations, the heat conduction potential method has been used to account for the variation in thermal conductivity of the plasma gas. Theoretical work at the University of Idaho has developed a similar method for mass transfer. The method is applicable to a wide variety of binary systems encountered in practice. The results were summarized in a paper accepted for publication.

Theoretical effort on the effect of Knudsen (non-continuum) flow on mass transfer has also been made. Similar to the work of Pfender and his students on heat transfer, quantitative calculations can be made showing the magnitude of the effect. A paper summarizing this work will also be submitted for publication.

ECONOMIC/ENERGY MODELS

P. R. Taylor 1/

A means to determine the economic feasibility of a proposed metallurgical process using plasma is under development. The study, based on energy and material balances, is intended to give economic and engineering insight to such processes.

The following goals have been defined:

1. Development of a mathematical model based upon energy and material balance considerations.
2. Comparison of the process on an equivalent basis to a conventional process.
3. Experimental confirmation of the model's validity.

The results will be used to derive a better understanding of the potential applications of plasma processing, to screen new and promising methods for extracting metals from ores and concentrates, and to develop preliminary economic data for untried processes.

THERMODYNAMIC DATA BANK FOR PLASMA SPECIES

S. Gyorkey Hutchinson and C. M. Wai 1/

Thermodynamic data for gaseous species above 2000 K is largely unavailable. Some species are represented in the JANAF tables, but many species of importance to plasma research are not. Using statistical thermodynamics, it is possible to make "first principle" calculations for many of these materials. Monatomic and diatomic species are relatively straightforward to handle. A computer program calculating free energy and enthalpy for gaseous oxides has been

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written using this approach. The calculations are made from 298 to 6000 K. Data for the following oxides have been calculated and are now stored in the data bank: AgO, AsO, CoO, GaO, GeO, MnO, NiO, PtO, ScO, ThO, and YO.

The computer program is relatively small, and can be run on a small personal computer. The present version uses the BASIC language (for the IBM PC), but can easily be modified for other computers. The listing is available as an appendix of an interim report. The program can be combined with free energy minimization programs, so that predictions of relative concentrations for complex systems can be made (similar to the ACE81 code described previously).

The methods require knowledge of a number of different spectroscopic parameters, many of which are not known for some species. Determination of these constants is an area of future work.

PARTICLE SHAPE ANALYSIS

K. A. Prisbrey 1/

A general population balance model has been developed for a distribution of particles flowing through a plasma fireball. The change in particle shape of a group of particles should supply information as to the mechanisms of melting, ablation and/or evaporation. A particularly interesting parameter to observe is the "shape change velocity," measured as the rate of change of other shape parameters. The most efficient shape parameters are the principal axes of a set of ellipses, which can be combined to give a highly accurate outline of the particle. The set of ellipses can be derived from the Fourier transform of the silhouette of the particle, which in turn is measured using digitization with the Opticram (a new instrument developed by Micron Technology).

Different harmonic components of the Fourier transform measure various features of particle shape. The low harmonic components measure the gross features of a particle--whether it is round, elliptical, or needle shaped. Higher harmonics measure increasingly fine details, serrations or other irregularities. Since these finer details will change dramatically during plasma treatment, the rates of change of these parameters can supply useful measures of the degree of plasma/particle interaction.

Melting and ablation can be defined as two extremes of possible plasma interactions. During melting, the heat transfer is slow and the surface becomes smoother, flowing because of surface tension. During ablation, material is removed so rapidly that heat transfer to lower layers does not occur, preserving or increasing the surface irregularities.

A population balance model was derived for particles undergoing shape change in a plasma (the details will be published in an interim report

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within the next few months). The model was translated to a computer program and variations in the shape change velocity were simulated. Results to date are inconclusive.

ALUMINUM CHLORIDE HEXAHYDRATE DEHYDRATION

R. L. Miller 1/

The objective of this research was to make anhydrous aluminum chloride (ACA) directly from aluminum chloride hexahydrate (ACH) without producing alumina as an intermediate step. The necessity of competing successfully with the commercial Hall-Heroult process was an accepted part of the project. In summary, the objective was not realized.

Five approaches were taken to the possible dehydration step: solvent extraction, ligand exchange, azeotropic distillation, chemical dehydration, and energy specific direct heating. Studies on the first four all produced negative results, as reported in last year's annual report. This report discusses only the energy specific direct heating approach. The final project report will document all work performed in this area.

Heating of ACH results in the decomposition of the compound over a long temperature range to produce Al_2O_3 , H_2O , and HCl . The reaction starts at about 80°C and is more or less complete by 500°C . The possibility of exciting the aluminum-oxygen bonds in ACH directly to remove the water was examined. Initial experiments were conducted using a microwave oven operating at 2450 MHz and a glow discharge plasma furnace operating at 13.56 MHz.

Microwave Studies

The necessity of utilizing a water ballast in the microwave studies was quickly learned. Other investigators have found that self destruction of the magnetron could thus be prevented. Three different ballasts (flat, cylindrical, and helical) were constructed and calibrated for energy absorption. Using these ballasts, water evaporation rate, chloride loss and water loss (from the ACH) were determined.

The rate of evaporation from a small sample was slightly less than linear, decreasing as the amount of water remaining decreased. This is due to the lower efficiency of absorption with smaller amounts of water. The rate of evaporation could be fitted to a second degree polynomial.

Heating samples of ACH in the microwave oven for ten to twenty minutes produced little or no loss of chlorine. Similar experiments were run to determine water loss. Karl Fischer titration (after

1/EG&G Idaho, Inc., Idaho Falls, Idaho.

dissolution of the samples in methanol) yielded slight loss of water in two of three experiments, indicating that some selective water loss was occurring.

Although partial success was achieved in selectively evaporating water from ACH, the improvement was small and no further experiments were performed.

Plasma Studies

The atomic spectra of the glow discharge furnace were determined when ACH was present in an argon atmosphere, using a recording spectrometer. Only the argon spectrum was observed, with no indication of aluminum present. A second experiment was performed using a 3.5 m Jarrell-Ash spectrograph. No aluminum was detected in this experiment, indicating that no ACH had been dissociated to active species. Further experiments were carried out in air or ammonia atmospheres.

Tables 3-2 and 3-3 summarize the results of these experiments. It is apparent that both water and chlorine were removed by the plasma exposure, with greater amounts of water. However, the simultaneous loss of both indicates that the ACH structure is being destroyed by the exposure to plasma, producing alumina rather than ACA. Physical examination of the samples confirms that conclusion.

It was concluded that plasma heating, even under an ammonia atmosphere, does not selectively remove water but proceeds by destroying ACH just as ordinary heating does.

TABLE 3-2. - Results of chloride removal during plasma dehydration of ACH

Atmosphere	Pressure, mm	Time, min	Power		Chloride remaining, percent	Available chloride removed, percent
			Forward watt	Reflected watt		
Air.....	1.5	20	200	10	30.23	30.24
Ammonia.....	2	30	200	10	6.37	85.51
	2	10	200	10	42.75	1.35
Untreated ACH..	--	--	--	--	43.33	--

TABLE 3-3. - Results of water removal during plasma dehydration of ACH

Atmosphere	Pressure, mm	Time, min	Power		Chloride remaining, percent	Available chloride removed, percent
			Forward watt	Reflected watt		
Air.....	2	10	200	10	24.60	45.68
Ammonia.....	2	10	200	10	11.83	74.82
Untreated ACH..	--	--	--	--	50.87	--

JOINING AND CONSOLIDATION OF RAPIDLY SOLIDIFIED ALLOYS

J. E. Flinn 1/ and others

Most of the rapidly solidified materials were acquired at the end of the first year of this task. The second year activities involved numerous experimental efforts for characterization of the baseline rapidly solidified Type 304 stainless steel (SS) powders and the extrusion consolidated powders, joining investigations on the extruded material, and dynamic consolidation studies on the powder. The results obtained from the various activities on the rapidly solidified Type 304 SS materials indicate that these materials are significantly different than conventional-wrought Type 304 SS. More testing, examinations, and analyses are required to explain the differences between the rapidly solidified and the conventional-wrought Type 304 SS materials. This is the main goal for the third year of this task.

JOINING OF RAPIDLY SOLIDIFIED ALLOYS

By D. E. Clark, C. J. Einerson, and R. B. Loop 1/

The second program year for the Joining of Rapidly Solidified Alloys Task saw the continuation and expansion of the experimental joining work that had just begun at the end of the first program year, and the initiation of microstructural analysis and model verification activities. Subcontracted cooperative work with the Colorado School of Mines, The Ohio State University, and the Oregon Graduate Center was completed very satisfactorily, owing to the excellent cooperation and initiative of personnel at those institutions. Work done in the second program year has resulted in two papers selected for presentation at the annual meeting of the American Welding Society in Las Vegas in April 1985; subsequent journal publications based on these presentations are anticipated. The scanning transmission electron microscope (STEM) was installed in the latter part of the second year and, based on the results obtained so far with optical and scanning electron microscopy (SEM) instruments, will be essential for the further analysis of the base material and weld fusion and heat-affected zones, both for existing specimens and those expected from future work.

Welding Metallurgy of the Baseline Type 304 Rapid Solidification Processed (RSP) Material

Work this year resulted in an initial metallurgical characterization of the baseline RSP material, Type 304 centrifugally atomized powder consolidated by hot extrusion. This is covered in more detail in the section on consolidation and characterization; some of the more relevant welding characteristics of this material are discussed here.

1/EG&G Idaho, Inc., Idaho Falls, Idaho.

Despite the careful handling of the powder during production and consolidation, a great deal of porosity occurs for any welding process that melts this base material. There are also stringers, parallel to the extrusion direction, that have been identified as manganese sulfides; these are apparently at least partially dissolved in weld heat-affected zones (HAZs). The as-received material appeared to be partially recrystallized, yet it was extremely fine grained and resistant to grain growth. This resistance to grain growth is due to more than oxides on prior particle boundaries since the grain size is much smaller than the prior particle size. Finally, the solidification of welds in the RSP 304 material appears to differ from that of conventional 304 in that an equiaxed zone forms near the fusion line.

The grain growth and solidification characteristics are graphically illustrated in figures 4-1 and 4-2. This gas tungsten arc (GTA) spot weld includes a portion of the conventional 304 can in which the powder was consolidated. It can be seen in figure 4-1 that the heat-affected zone grain size of the can material is an order of magnitude larger than that of the RSP material, which has shown no growth. Figure 4-2 shows, at a higher magnification, that the weld metal above the can material grows epitaxially into a dendritic structure, while that above the RSP material exhibits a rather featureless band (revealed by solute-sensitive etchants to be an equiaxed part of the fusion zone) before dendritic solidification occurs.

Other welding processes, covered in more detail below, show microstructures analogous to those seen with the GTA process. The fact that grains do not seem to grow in this material under welding conditions is significant, since one of the criteria in selecting welding processes for RSP alloys was a minimization of this undesirable side effect. This does not address the question of welding heat effects on any metastable phases that might be present; more detailed analysis with the STEM may provide such answers.

Welding Process Investigation

Many processes were explored on paper during the first program year. Initial experimental results and the practicality of the process were used to narrow this number. The processes selected for further investigation cover a wide variety of time/temperature regimes and therefore permit a fairly complete assessment of the weldability of RSP materials. Processes in which experimental work was done or is still under active consideration include: gas tungsten arc, capacitor discharge, laser, inertia, and explosion welding; resistance welding with powder interlayer; and Gleeble weld simulation. A brief description of the experimental activities and results for each of these processes follows.

Gas Tungsten Arc Welding

Although it is anticipated that this process will be unsuitable for RSP material joining, owing to its slow cooling rates and segregated

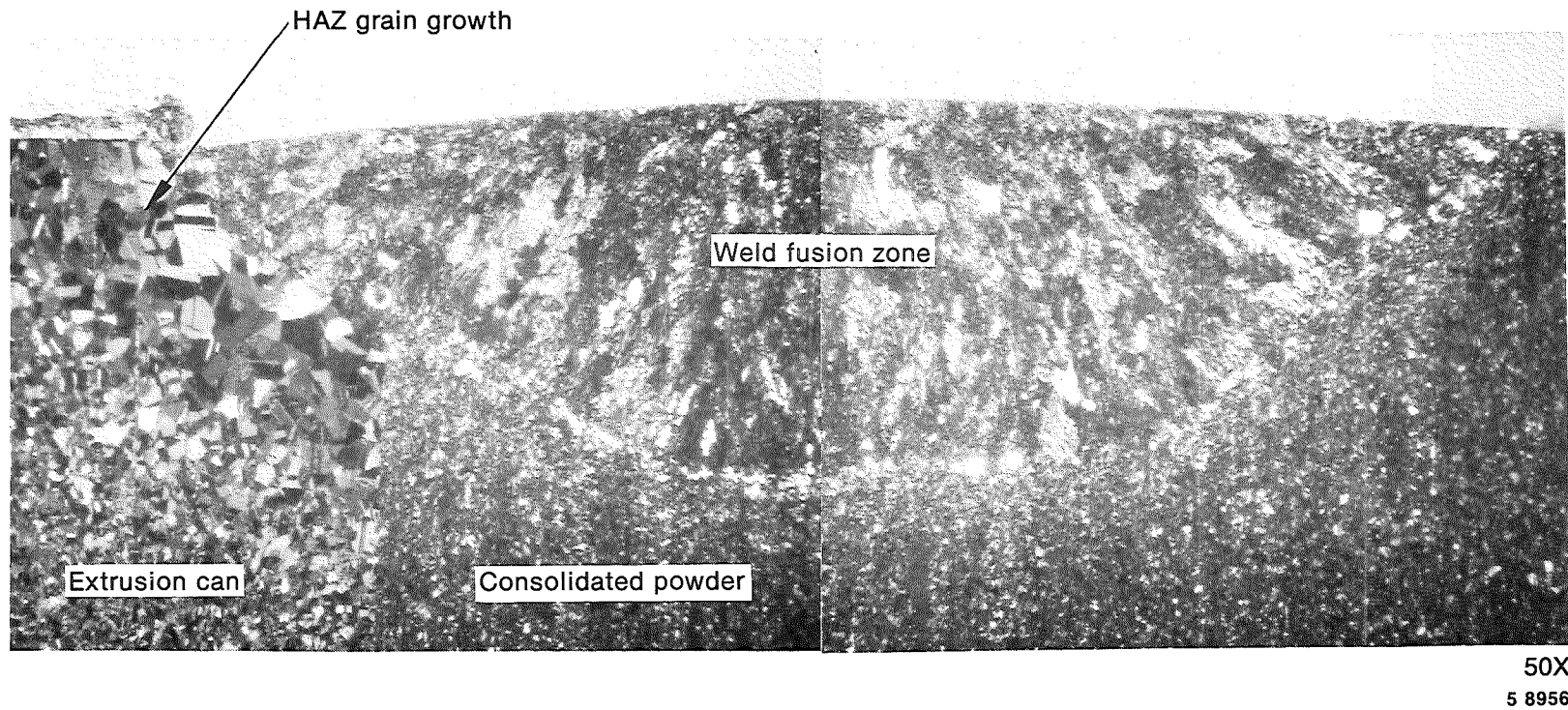


Figure 4-1. Cross section of GTA spot weld in 304 RSP material compacted by hot extrusion. Large-grained base material to the left is the conventional 304 of the extrusion can. 80X, oxalic weld etch.

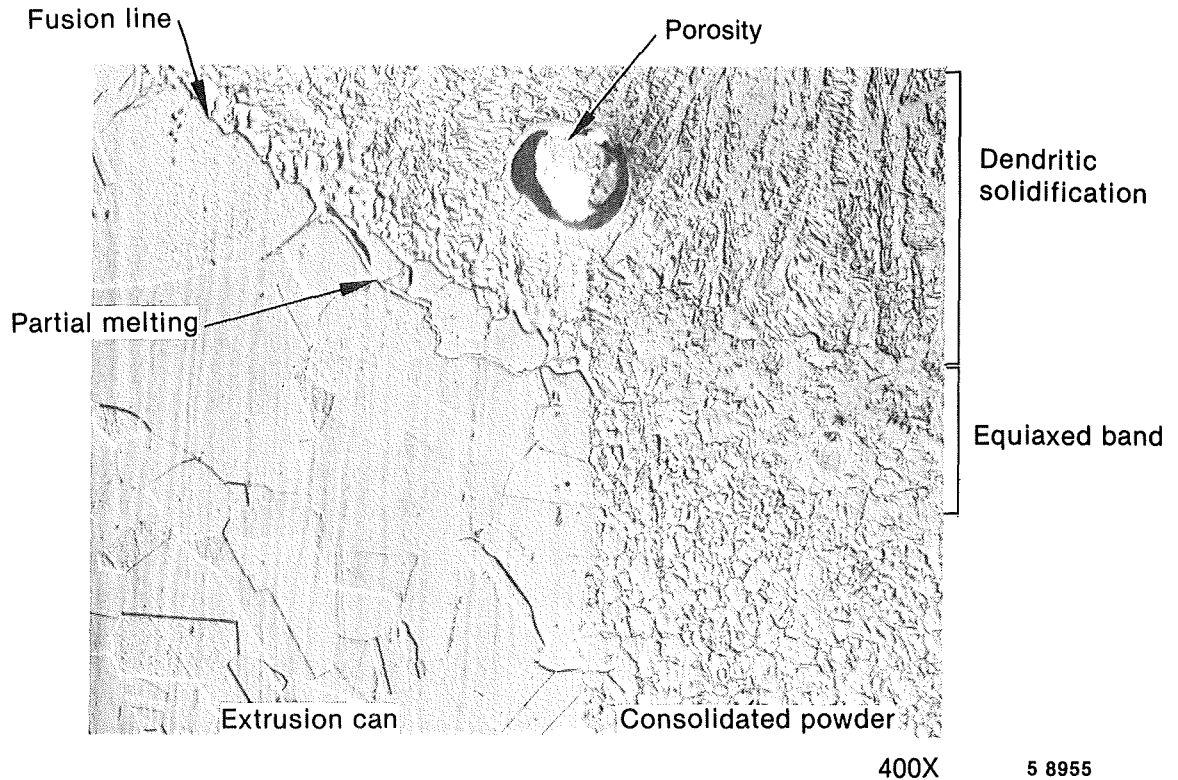


Figure 4-2. Cross section of the same weld as in figure 4-1 at higher magnification. Note the large grain size in the can material (lower left), the small grain size and grain refinement near the fusion line in the powder material (lower right), and the difference in solidification modes from the fusion line: the conventional can material begins columnar dendritic growth directly, while there is a relatively featureless layer above the RSP material, above which columnar dendritic solidification commences. 400X, oxalic acid etch.

microstructure, it is a standard, well-characterized process that should reveal much about the general welding metallurgy of the 304 RSP material. Metallurgical results to date for this process were summarized above in the discussion of the general metallurgy of the 304 RSP material. STEM analysis of the samples obtained thus far will be crucial to complete understanding of its overall the welding metallurgy.

Capacitor Discharge (CD) Welding

Work in this process was suggested and carried out under subcontract by Profs. W. E. Wood and J. E. Devletian of the Oregon Graduate Center (OGC). It was known that the CD welding time period was very short, 3 to 5 ms, but analysis of the results provided some interesting insight into both the process and the RSP material. These welds have a very fine solidification structure and exhibit little or no mixing between molten zones. Figure 4-3 shows some of the implications of the fine microstructure. Solidification rates for rapidly solidifying

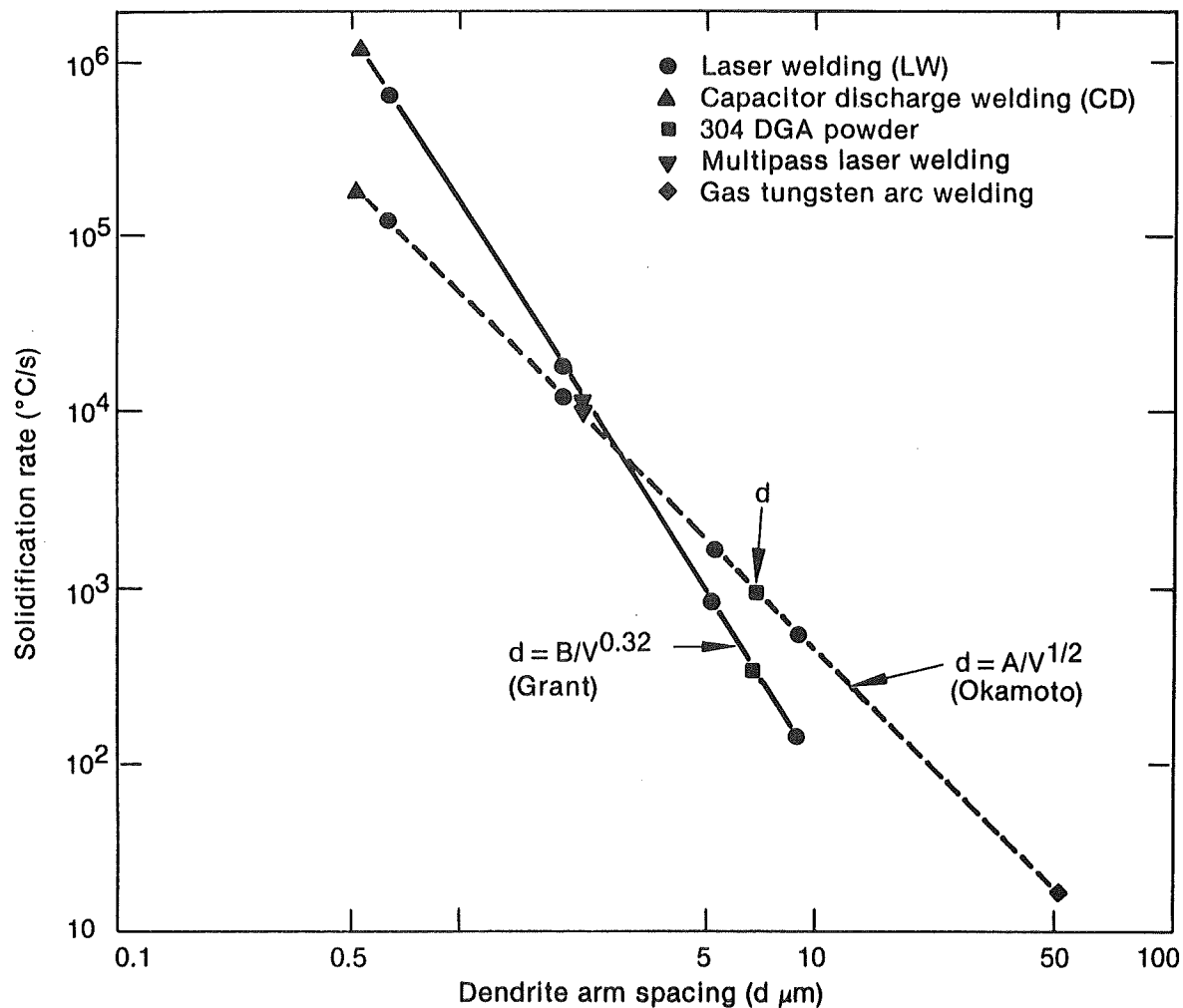


Figure 4-3. Cooling rate as predicted by two different dendrite arm spacing extrapolations from Grant (1) and Okamoto (2). Dendrite arm spacings are measured from welds or powder samples. Note that the CD welding process and some of the laser welds produce cooling rates higher than that of the DGA powder.

materials, like most welds and RSP products, are commonly estimated by measuring the dendrite arm spacing and extrapolating from the generally linear relationship between the two, which is established experimentally at lower cooling rates. According to figure 4-3, then, the CD welding process, and laser welding at a number of possible parameters, produce a finer dendrite arm spacing than that found in the original dissolved gas atomization (DGA) RSP powders. For this process, as for others, anticipated STEM examination of the weld samples is expected to provide crucial analytical information.

Laser Welding

The laser welding process is interesting because it can provide very high cooling rates in the linear joint geometries required by many

practical RSP material applications. Variants of this process were pursued at the Oregon Graduate Center and at the INEL. The OGC work, performed with their 1200 W CO₂ laser, concentrated on melting powder material with the idea of filling a weld joint with RSP material, while the INEL effort, using a 400 W YAG laser, concentrated on conventional autogenous (no filler material added) laser welding.

The solidification characteristics of the welds made at OGC were incorporated along with the CD weld data into their solidification rate analysis (fig. 4-3); some of these welds were found to exceed RSP powder cooling rates, others did not. The INEL welds were observed optically; in-depth studies await STEM examination and the preliminary results of STEM analysis of the GTA welds.

Inertia (friction) Welding

A small series of inertia welds were made using the RSP 304 SS which had been hot extruded from centrifugally atomized (CA) 304 SS powder. This series was prepared as a scoping study; the work was performed using welding engineering department facilities at the Ohio State University.

A sufficiently high energy input to the weld resulted in sound bonds. Lower energy inputs left cracks at the edges of the weld due to insufficient weld upset material. Little grain growth occurred in the weld area, as expected, due to the solid state bonding and heavy deformation characteristics of the process.

The base material, HAZ, and fusion zone contain, to varying extents, what appear to be a fine second phase or phases. This phase appears uniformly oriented along the extrusion axis in the base material and follows the material flow pattern as the weld line is approached. The phase appears to be randomly oriented around the fusion line. There is a region in the HAZ where the phase disappears altogether, apparently returning to solution. Two characteristic precipitates have been tentatively identified, one appearing to be very fine, stringer-like, and high in manganese and sulfur (MnS), and the other discrete precipitates high in silicon. Precipitate size ranges from approximately 0.3 to 3 μm . The presence of the high MnS precipitate agrees with the finding of what appear to be MnS stringers in extruded CA powder in the powder consolidation task, though on a much finer level. Additional effort in this area will involve a STEM analysis of selected samples from these weldments.

A series of microhardness traverses were made on a representative weld sample. The resulting data presented a more complicated pattern than published results for conventional wrought 303 stainless steel (3). Analysis of these results awaits the more detailed phase analysis work identified above.

Explosion Welding

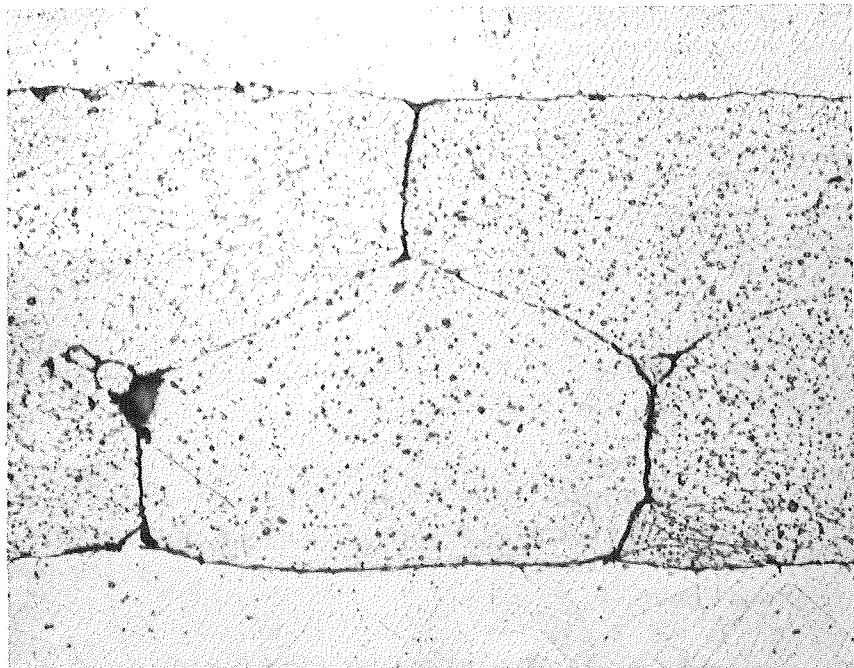
Two variants of this process, one conventional and the other with a powder interlayer, were described in the previous annual report for

this task. Neither was pursued this program year, owing to lack of manpower, scheduling problems with anticipated cooperative work with Los Alamos National Laboratory, and the difficulty of scheduling explosive tests. The process is still under active consideration, however, and INEL scheduling problems have been eased with the establishment of a permanent explosive consolidation facility.

Resistance Welding with a Powder Interlayer

This process was invented and developed at INEL for the special demands of joining RSP materials. The intention is to provide a layer of powder at the resistance welding interface which will localize the energy dissipation, allow solid-state bonding, and assure that any material that is melted will resolidify in the RSP regime.

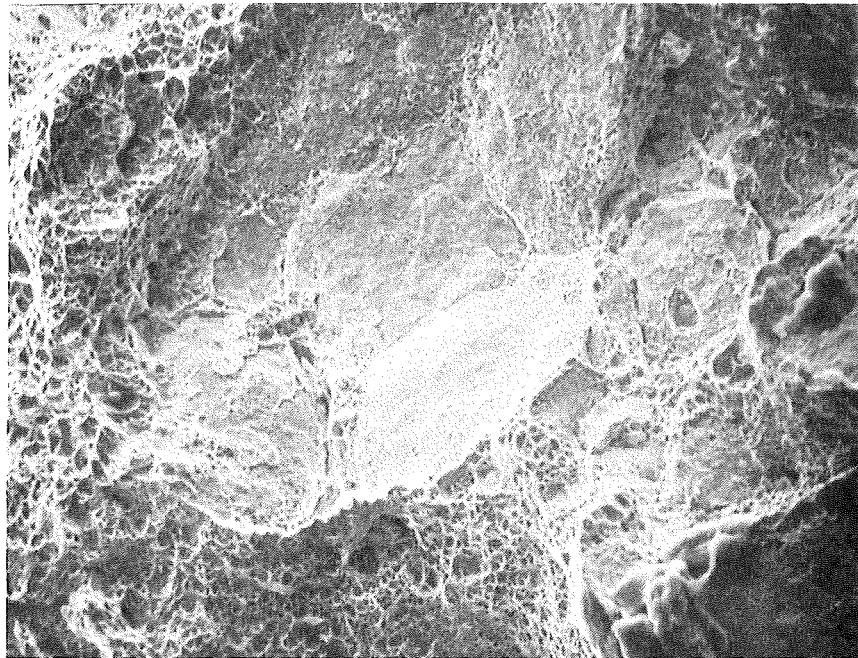
The development proceeded through several stages, involving procedures for the alignment of the base material pieces and the placement of the powder layer and critical parameters that had to be observed for repeatable results. Late in the program year specimens capable of providing useful mechanical data were produced. Substantial modifications to the resistance welding machine, a standard production unit, were also made to assure better alignment and repeatability. Both DGA and CA powders were used in the interlayer. Figure 4-4 shows a cross section of a weld made with this process; the original particles can be seen, deformed to fill the available space. Figure 4-5 shows a similar sample at two magnifications after being



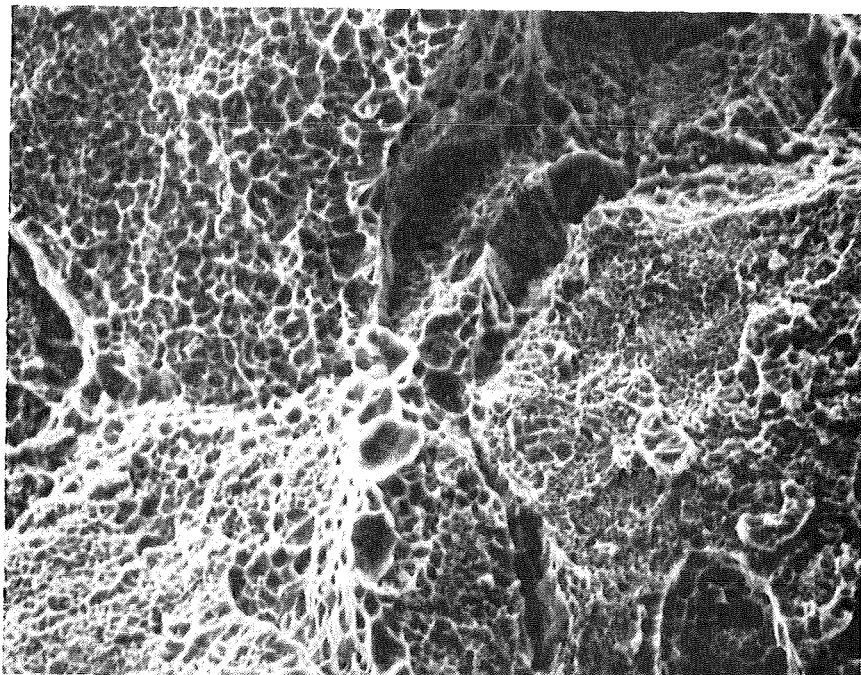
400X

5 8957

Figure 4-4. Weld cross section of a resistance weld with a DGA powder interlayer. Note that the outlines of the plastically deformed powder particles can still be seen. 400X, oxalic acid etch.



~500X



~2000X

5 8954

Figure 4-5. The broken surface of a weld similar to that shown in figure 4-4, pulled in tension; note that prior particle boundaries can be seen, (a) 500X. (b) The same surface at 200X. Note the dimpled rupture surface, indicating good metallurgical bonding.

pulled apart. Note that some of the original particles can still be seen, but that the fracture surface is finely dimpled, characteristic of the void nucleation and growth of ductile rupture. This indicates that sound solid-state bonding is occurring. Tensile samples indicate joint efficiencies (ratio of weld strength to base material strength) as high as 90%.

Further work in this process will include instrumentation to achieve in-process monitoring and eventually process control based on electrical characteristics of the weld.

Gleeble Weld Simulation

Some Gleeble work on the hot-extruded RSP material was done under subcontract by Prof. Elliot Brown of the Colorado School of Mines; STEM and further transmission electron microscope (TEM) evaluation will be undertaken at the INEL. The INEL Gleeble, obtained through another program, is scheduled for delivery in late May. This will allow further Gleeble work, particularly model verification but also including available shock-compacted or alternate alloy RSP materials, to be conveniently evaluated.

Modeling

Since thermal cycling of RSP materials during secondary fabrication is considered crucial to maintaining their unique properties in service, a heavy emphasis has been placed on obtaining adequate mathematical models of any joining processes considered. Such models are essential for predetermining the process effects, for example, for correlating observed microstructures in actual welds with Gleeble-simulated microstructures. Models of some of the processes, including laser and gas tungsten arc welding, have been of general interest in the welding research community for some time; these have been used when available. Other processes, such as inertia welding and explosion welding, have been modeled in the literature, but not with the precision required for RSP work. Still others, including capacitor discharge welding and resistance welding with a powder interlayer, have not to our knowledge been so explored, but are amenable to modeling with recently developed techniques.

An example of the use of modeling in RSP materials during this program year was the application of COUPLE, an INEL finite-element code, to the GTA spot welds in extrusion-consolidated RSP powder mentioned above. The goal was to understand the thermal cycles in or near the fusion line that might have produced the unusual equiaxed, featureless microstructure. COUPLE allows two-dimensional solutions that include convection and radiation from free surfaces, internal heat generation (as by Joule heating), the variation of thermal properties with temperature, latent heat of fusion, and the solution of the transient case. Figures 4-6 and 4-7 show the isotherms and thermal cycles for this case; there are unexpected deviations in the thermal cycles at the fusion line that will have to be taken into account in interpreting the metallographic evidence.

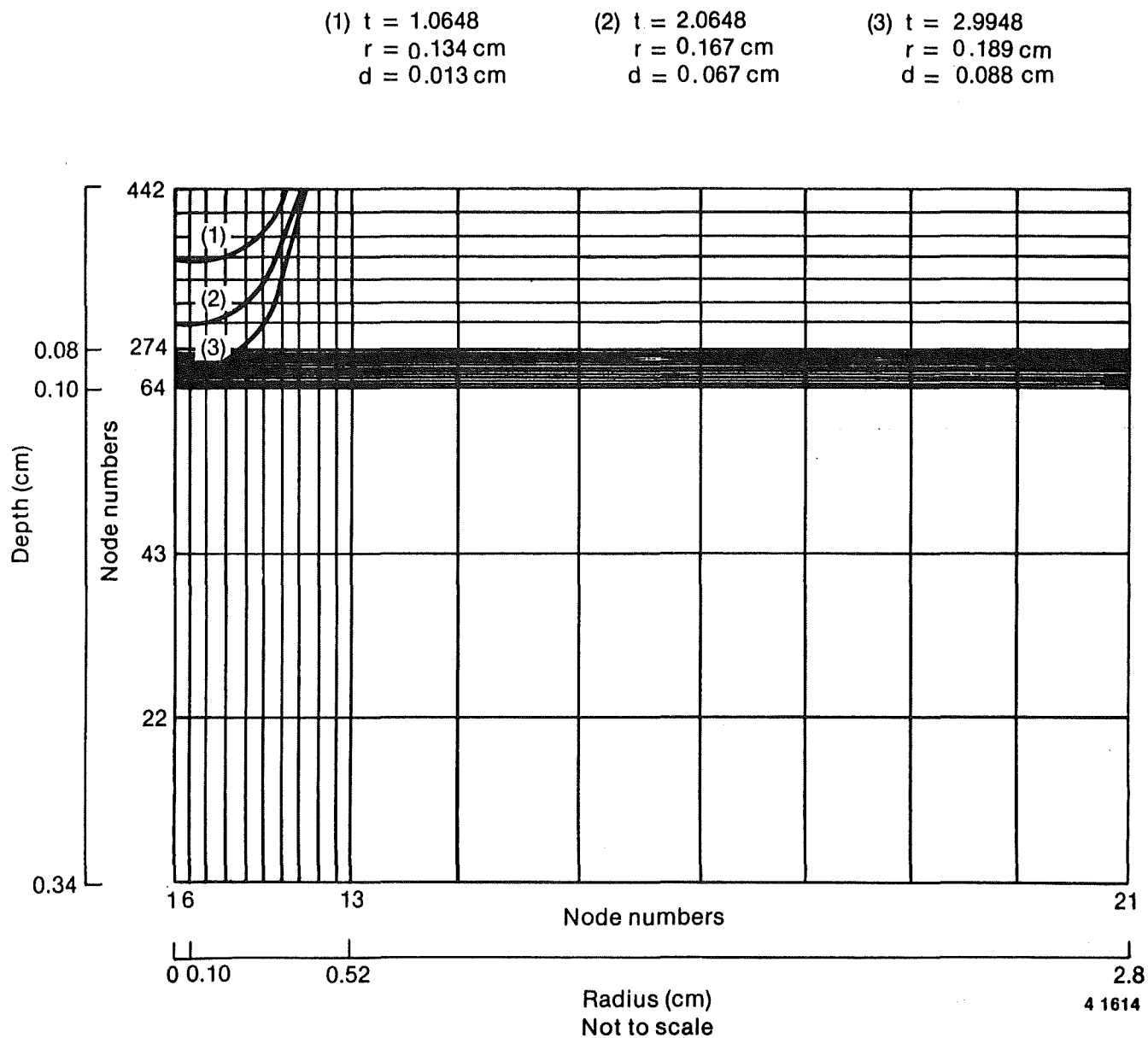
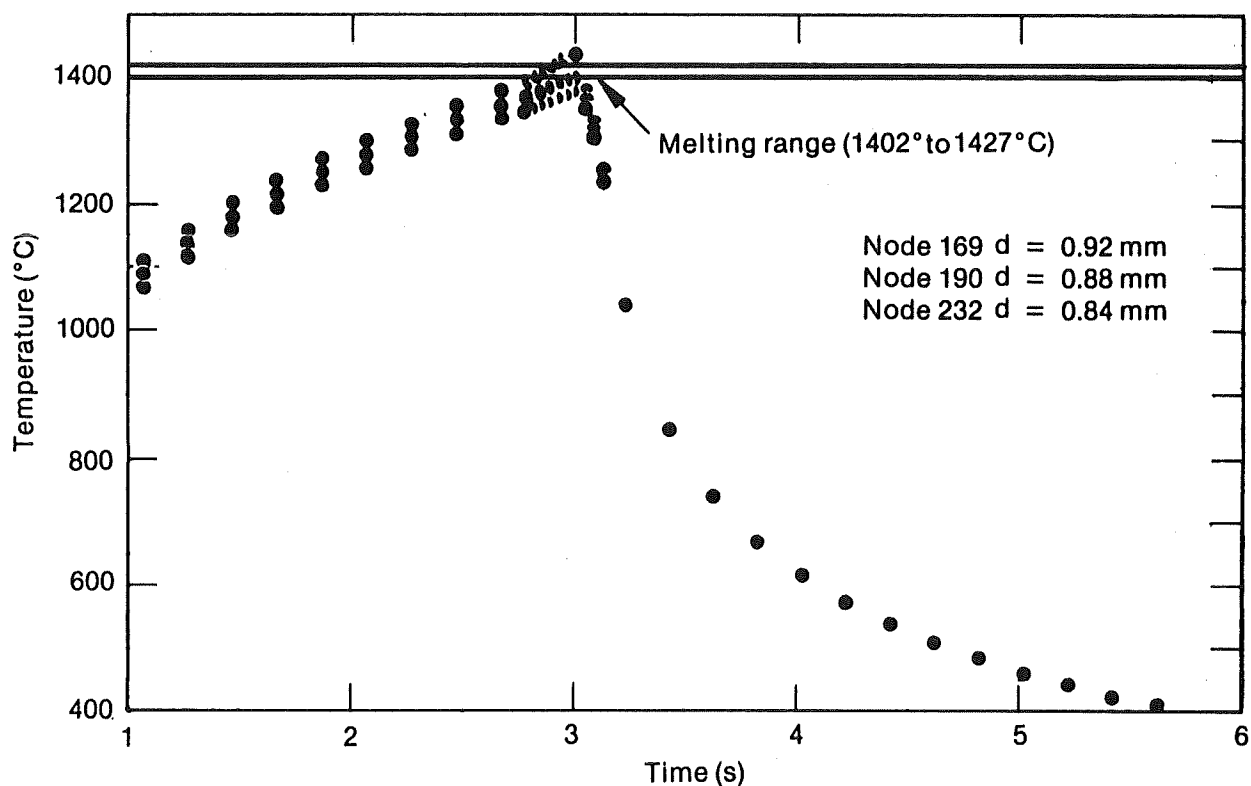


Figure 4-6. Thermal cycles for nodes for the fusion line of a GTA spot weld, calculated by the COUPLE thermal analysis code.



4 1613

Figure 4-7. Isotherms for the fusion line at different time steps during a GTA spot weld, as calculated by the COUPLE thermal analysis code. Note the fine grid near the bottom of the weld, useful for resolving fusion line thermal phenomena.

COUPLE is also currently being applied to the laser welding process, and it is expected that it will be used for the capacitor discharge process as well, though some modifications will be necessary to account for the material expelled during this process. COUPLE will also be useful in modeling the special Gleeble specimens required for rapid cooling rate simulation. For modeling the resistance welding with powder process, where a substantial amount of deformation occurs, the possibility of applying Sandia Livermore's TACO code is being explored.

CONSOLIDATION AND CHARACTERIZATION OF RSP POWDER ALLOYS

By J. E. Flinn, G. E. Korth, L. H. Schoenlein, and R. C. Green 1/

Centrifugally atomized Type 304 SS powder and extrusion consolidated CA Type 304 SS powder were received at the end of the first year of the

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project. The major effort of second year was devoted to characterization of the CA Type 304 SS powder, the DGA Type 304 SS powder, and the extrusion consolidated CA Type 304 SS material. The results from these studies provide baseline information for joining, consolidation, and NDE correlations. Also, a significant amount of effort was given to the dynamic consolidation of the DGA and CA Type 304 SS powders. The dynamic consolidation studies involved explosive and gas gun techniques. The results obtained from the above investigations, as well as other related activities during the second year are summarized below.

Characterization of DGA and CA Type 304 SS Powders

Chemical Analysis

A chemical analysis was obtained on "grab" samples for the DGA and CA Type 304 SS powders. The results are shown in table 4-1. There is a significant difference between the two alloys in the composition levels for the minor elements such as silicon, manganese, carbon, molybdenum, and copper. The reason for the differences is not known, but could be that different sources of 304 SS and different melting practices and systems were used by the two manufacturers.

TABLE 4-1. - Type 304 SS powder compositions in weight percent

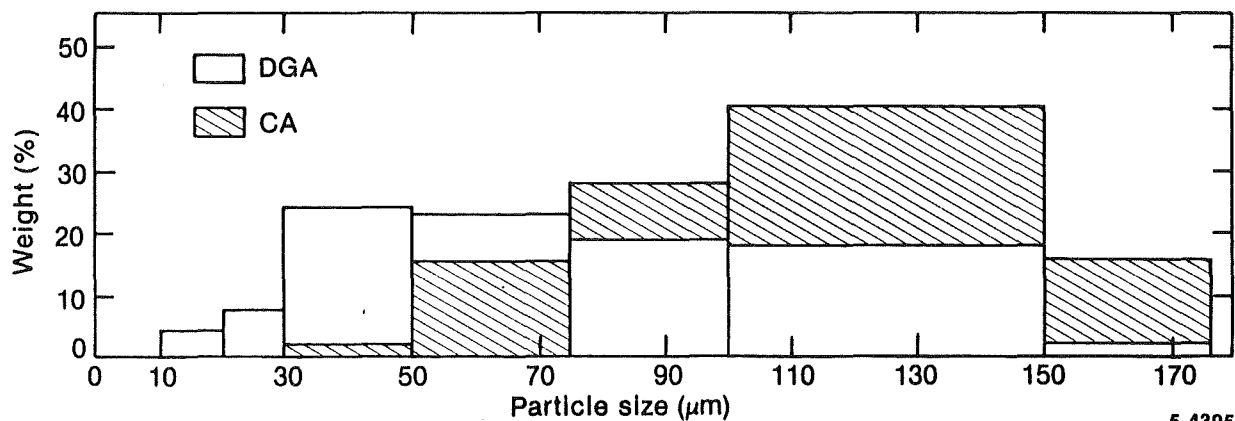
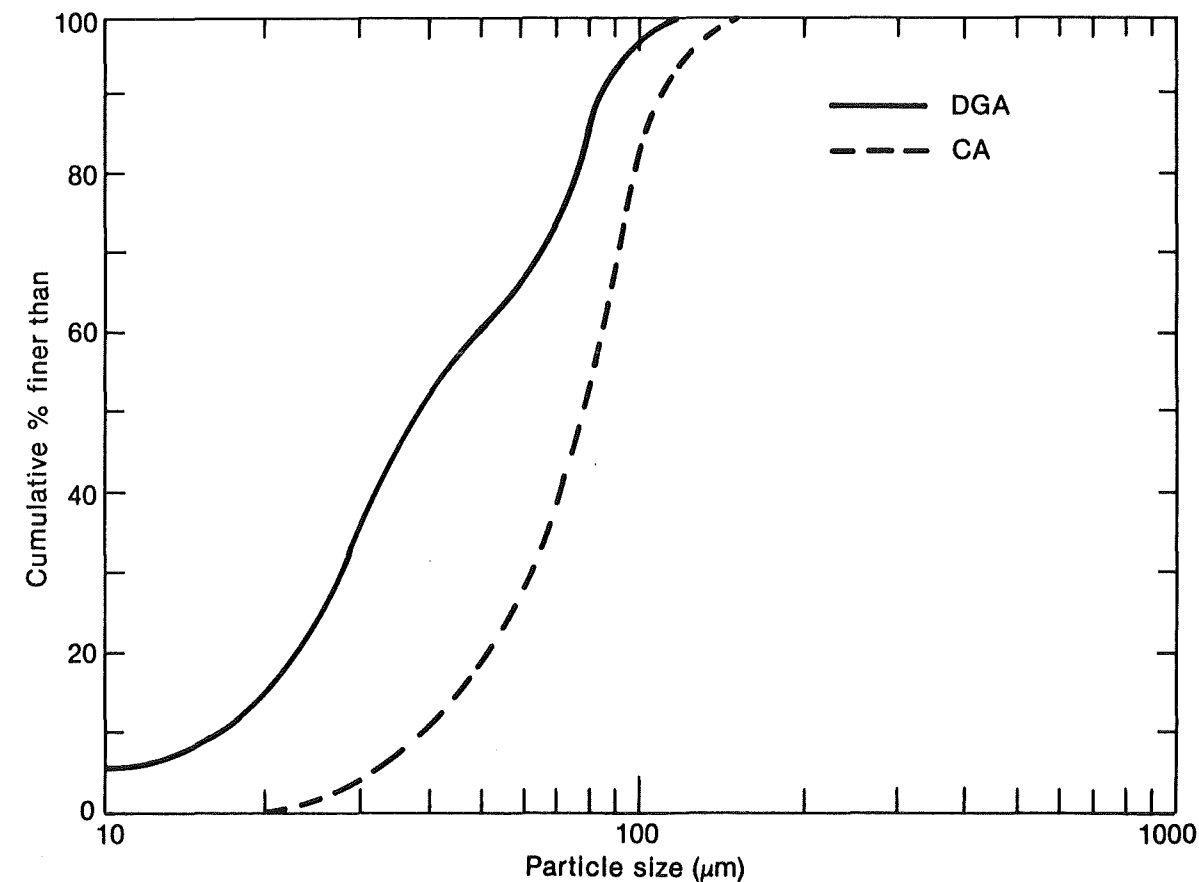
Alloy	Fe	Ni	Cr	Si	Mn	C	Mo	Cu	S	P
DGA	71	9.9	19.0	0.04	0.03	0.015	0.015	0.005	0.005	0.005
CA	70.5	9.1	18.4	0.65	0.80	0.052	0.60	0.50	0.002	0.023

Particle Sizes and Shapes

Approximately 1 kg quantities of the DGA and CA Type 304 SS powders were sieved to determine their respective particle size distributions. The distributions for the two powder materials are shown in figure 4-8. These distributions are markedly different; particle sizes in the 100 to 150 μm range dominate the weight distribution for the CA powder, whereas the DGA appears to be spread equally over the range of 30 to 150 μm . Based on a cumulative % finer than correlation, the average particle sizes are about 40 and 80 μm , for the DGA and CA powder, respectively.

Tap density measurements for the two powders were performed. The tap densities observed on "grab" samples are 65.4% and 66.5% of theoretical for the DGA and CA powders, respectively.

The shapes of the particles for both the DGA and CA powders are primarily spherical. The DGA powder exhibits a large number of satellites, particularly in association with larger particles. The particle shapes observed for the two powder materials after sieving to various particle size ranges are shown in figure 4-9.



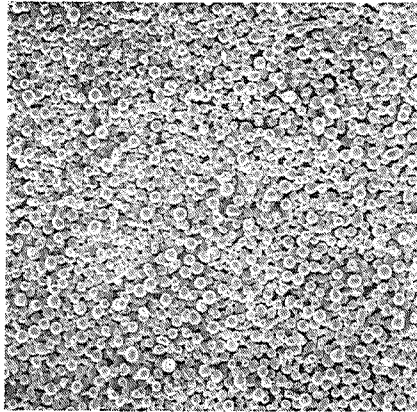
5 4395

Figure 4-8. Particle size distributions for DGA and CA RSP Type 304 SS powders.

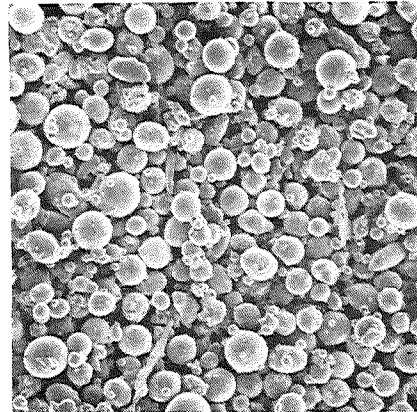
Structure Characteristics

X-ray diffraction assessments were performed on sieved (i.e., various particle size ranges) powder lots for both the DGA and CA Type 304 SS materials. The diffractometer scans for the DGA powders show a predominant fcc phase, however, there was evidence that a strong bcc phase was also present. The apparent amount of bcc phase did not significantly vary with particle size, as might be expected to occur if

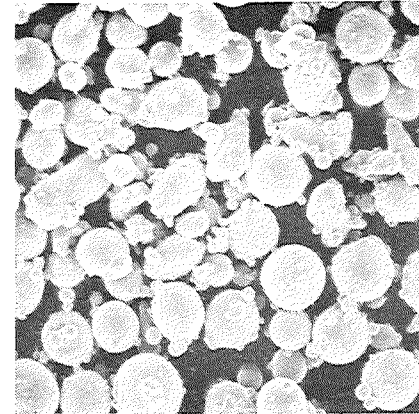
(a) DGA particles, ~70X



>20<30 μm

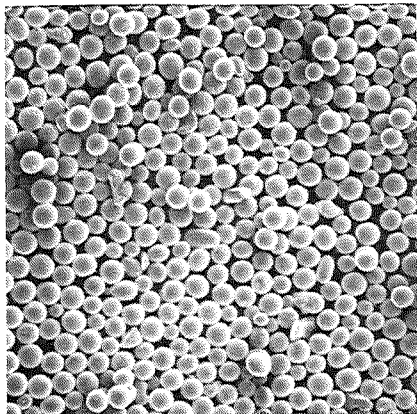


>50<75 μm

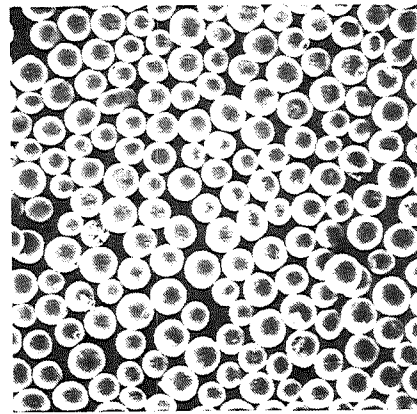


>100<150 μm

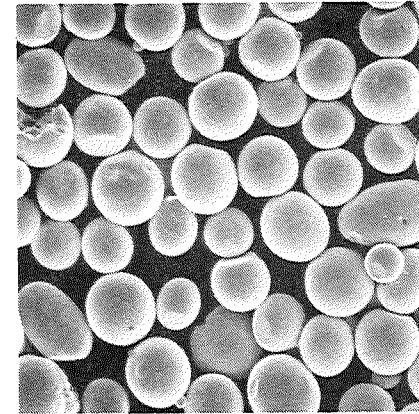
(b) CA particles ~70X



>30<50 μm



>50<75 μm



>100<150 μm

5 8940

Figure 4-9. Particle shapes corresponding to various particle size ranges for DGA and CA RSP Type 304 SS.

it was metastable and primarily associated with the smaller particle sizes. It is conceivable that the presence of the small satellites on the larger particles could account for the presence of the bcc phase. The x-ray diffraction measurements performed on the CA powders showed that the larger particles were virtually all fcc with only a trace of a bcc phase being present. However, particles in the 30 to 50 μm range were predominantly bcc; this obviously reflects a strong dependency on particle size. Efforts are underway to characterize the predominantly bcc particles (obtained by magnetic separation).

Optical microscopy examinations were performed on polished and etched cross sections of sieved DGA and CA powders. Both powder materials were very difficult to etch and numerous etching solutions were evaluated before success was realized. For the CA powder, a solution of sodium thiosulfate in water with 10% HCl produced satisfactory microstructural features. However, this etchant had virtually no effect on the DGA powder; a solution of ammonium bifluoride and potassium metabisulfate in water with 10% HCl did produce adequate microstructural features. Representative microstructural features for the DGA and CA powders are shown in figure 4-10 for two 100 μm particles. The CA powders appear to be mostly microdendritic, however the smaller particles, 30 to 50 μm , show evidence of cellular patterns. The DGA particles appear to have a more of a cellular microstructure throughout the range of particle sizes.

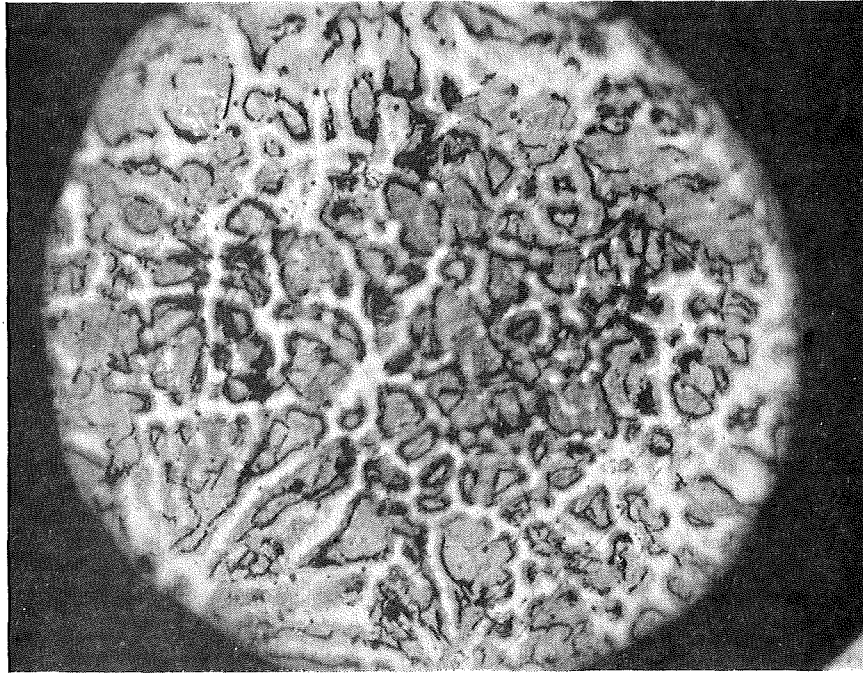
Foils of both powder materials are being prepared for STEM examination and analysis. Several particles sizes for each powder material will be examined. A high temperature-stable epoxy is being used as a matrix to contain the particulate.

Surface Films

Auger analysis has been performed on the CA Type 304 SS powders to determine surface films, i.e., oxide layers and other contaminants. The powders have been under an inert/very low oxygen environment during processing, shipping, and subsequent handling. Three environmental exposure conditions were examined: non-atmospheric-glovebox, dry air-desiccator, and air at 100% relative humidity. In addition, a conventionally processed coupon of Type 304 SS sheet was also examined for comparison with the exposed powder samples. All four samples, including the conventionally processed coupon, displayed an iron-oxide coating which was 20 to 25 angstroms thick. These observations indicate that subsequent handling of the CA Type 304 SS powders in very clean inert environments may not be crucial. Auger examinations are planned for the DGA Type 304 SS powders.

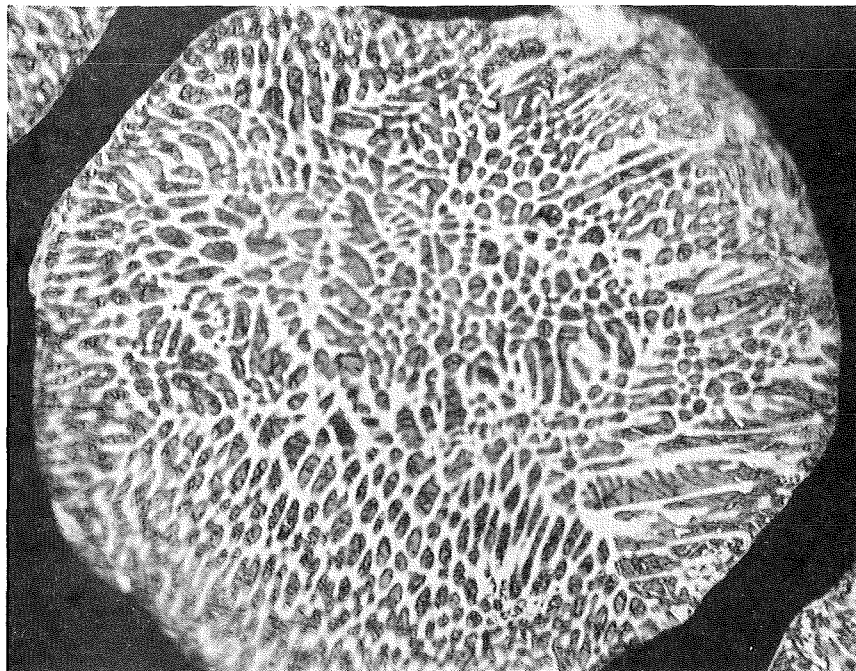
Characterization of Extrusion Consolidated CA Type 304 SS Powders

The CA Type 304 SS powder consolidated by hot extrusion (i.e., $\sim 900^\circ\text{C}$ and an extrusion ratio of 8:1) has been designated as the baseline consolidated form and serves as a baseline for comparing powder consolidation behavior using dynamic and HIPping techniques. The focus of the joining research has been on the extruded material.



(a) DGA particle

1000X



(b) CA particle

1000X

5 8947

Figure 4-10. Microstructural patterns for ~100 μm DGA and CA Type 304 SS particles.

Considerable progress has been made on the characterization of the extruded rod material. The assessments include heat treatment response, mainly in association with grain growth behavior; and mechanical properties including tensile/flow curve behavior, creep-creep rupture, and fatigue. The heat treatment studies utilized the attendant canning material, conventional wrought Type 304 SS, and results reported by Oak Ridge National Laboratory on conventional wrought Type 304 SS for comparisons (4-6).

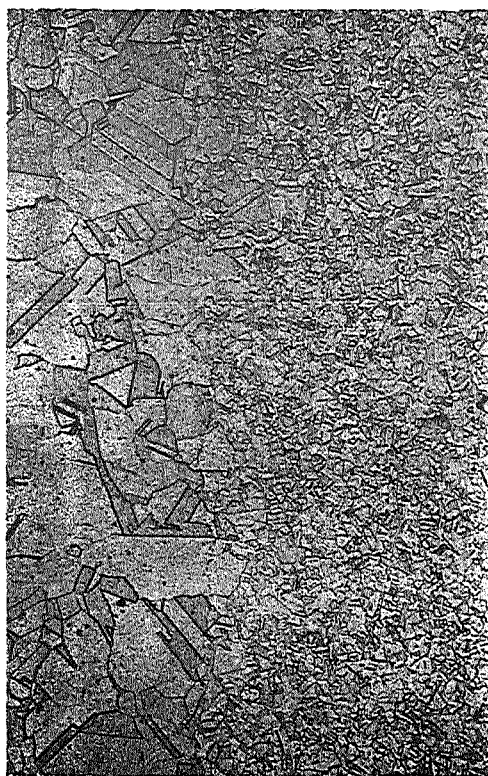
Microstructure and Heat Treatment

The grain morphology of the as-received extrusion consolidated CA Type 304 SS powder was reported in the previous annual report (7). X-ray diffraction (XRD) assessments were performed on the hot extruded materials: the conventional Type 304 SS end cap material and the consolidated CA powder. The results of the XRD measurements, shown in table 4-2, reflect a qualitative representation of the texture of the two materials. The obvious conclusion is that the texture is markedly different for the transverse sections of the two materials, even though they were extruded together.

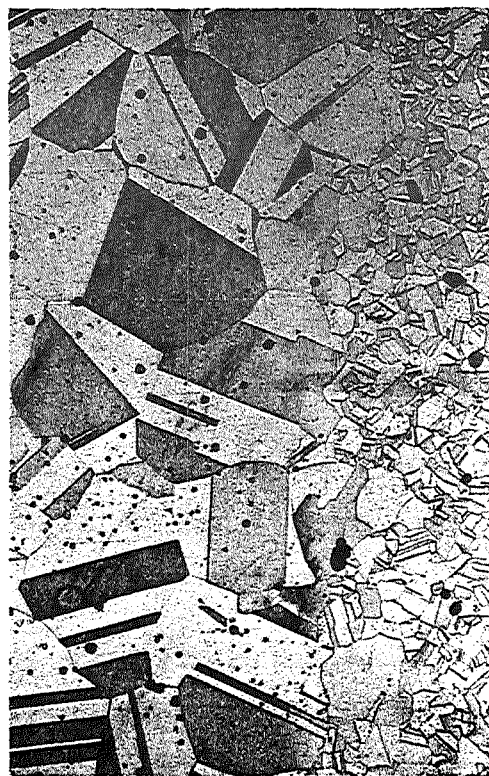
TABLE 4-2. - XRD assessments on Type 304 SS extrusions

Specimen Description	Relative Peak Heights		
	{111}	{200}	{220}
End cap conventional 304:			
Transverse view.....	6520	690	--
Longitudinal view.....	224	66	153
Consolidated CA powder:			
Transverse view.....	563	1525	10
Longitudinal view.....	228	180	169

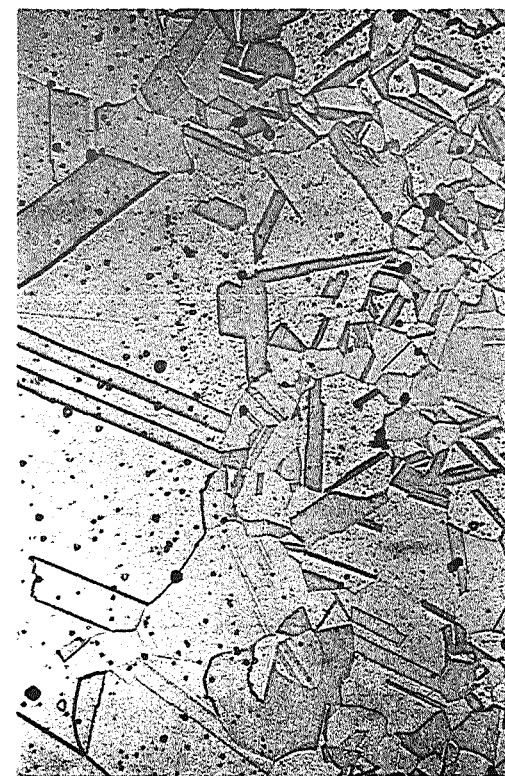
Heat treatment studies were performed on the extrusion consolidated CA powder material with attendant, conventional Type 304 SS cladding for comparisons. The parameters for the study were heat treatments in sealed quartz capsules under argon at 800, 900, 1000, 1100, and 1200°C, each for 1, 10, and 100 h. Some representative micrographs obtained on transverse sections at the consolidated powder/cladding interface are shown in figure 4-11. It is obvious from the micrographs that the grain growth of the consolidated powder is markedly less than for the cladding. This observation is more quantitatively reflected in figure 4-12 in terms of the average grain diameter after 1 h heat treatments at various temperatures. It should be noted that similar patterns between the cladding and the consolidated powder are observed after the 10 and 100 h heat treatments.



(a) 900°C 270x



(b) 1100°C 270x



(c) 1200°C 270x

Figure 4-11. Microstructures at clad/consolidated CA powder interface for CA Type 304 SS after 1 h heat treatments.

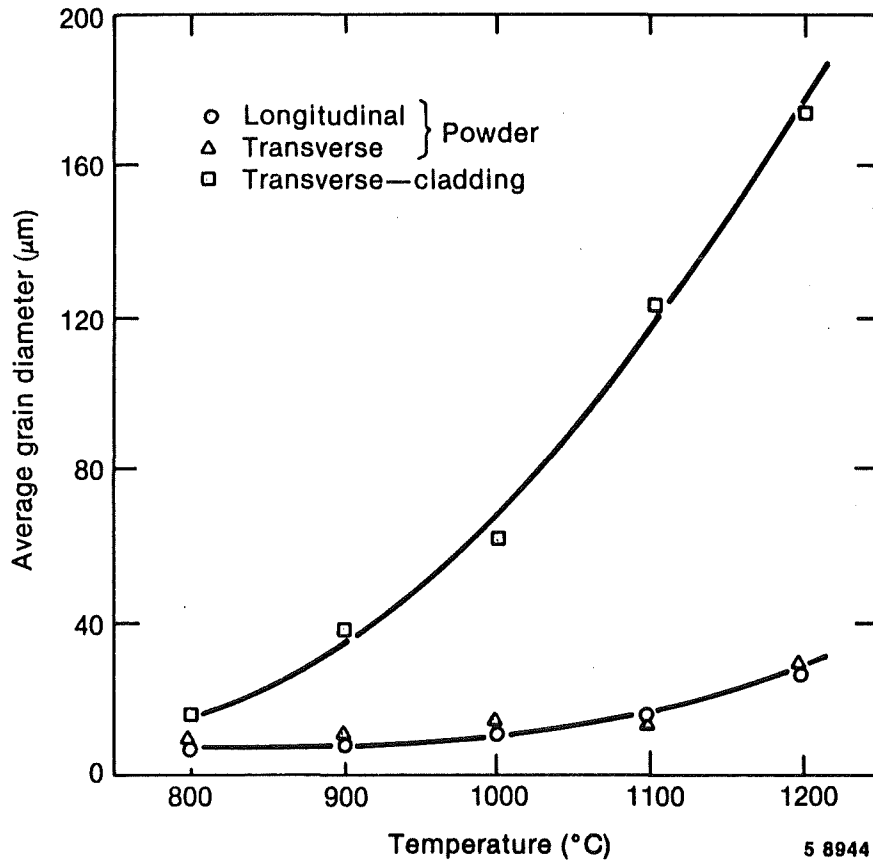


Figure 4-12. Grain growth behavior for Type 304 SS extrusion cladding and consolidated CA powder after 1 h anneals.

The mechanisms for grain stability observed for the extrusion consolidated CA powder are not resolved. Optical microscopy does not show significant evidence of carbide precipitation at the grain boundaries. Hopefully, STEM examinations and analyses will explain the retention of the fine grains at high temperatures for the consolidated powder.

Mechanical Behavior

The mechanical behavior of the extrusion consolidated CA Type 304 SS was evaluated from tensile, creep, and fatigue tests. Prior to testing, the specimens were given a precondition heat treatment, primarily 1 h anneals at 900 and 1200°C. The results from the tests were compared with wrought ingot metallurgy results reported by other investigators (4-6).

Tensile Behavior

Tensile tests were performed on specimens given preconditioning heat treatments of 900 and 1200°C, each for 1 h. The tests were performed at room temperature, 200, 400, 500, 600, and 800°C. Engineering

tensile properties for the specimen series preconditioned for 1 h at 900°C are shown in figure 4-13 along with results obtained for conventional wrought Type 304 SS (4-6).

The engineering tensile strengths for extrusion consolidated CA material are significantly higher compared to conventional wrought Type 304 SS. The reduction in areas are comparable, and the total elongation is slightly lower for the rapidly solidified material. The uniform elongation for CA material is about half of that for wrought Type 304 SS, except at the highest test temperature where it is significantly higher. The tensile properties observed for the specimens preconditioned for 1 h at 1200°C show similar behavior to those shown in figure 4-13. One notable exception was that the yield values, proportional limit, and 0.2% offset, were significantly lower than observed for the 900°C pretreated material. However, the ultimate tensile stresses for the two preconditioned materials were equivalent.

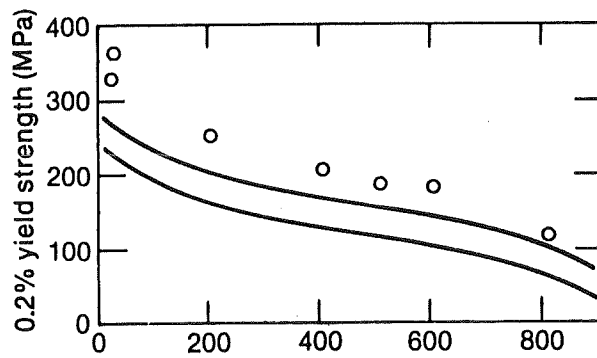
Flow curve behavior associated with the tensile results on the 900 and 1200°C preconditioned specimens is being analyzed. Two stages of strain hardening are observed: a low rate of strain hardening is associated with a low plastic strain region and a high strain hardening rate is associated with the high plastic strain region. For the 900°C preconditioned specimens, the two strain hardening values appear to be insensitive to test temperature, except for the higher plastic strain region associated with the 800°C test. This region exhibits a markedly reduced strain hardening exponent which suggests that dynamic recovery processes are occurring. Similar patterns are observed for the series of specimens preconditioned at 1200°C and tensile tested at various temperatures. The analysis of the flow curve behavior for the extrusion consolidated CA Type 304 SS material is continuing. Interrupted tensile tests at particular strain levels are planned in order to provide specimens for STEM examinations, and hence structure/property correlations for the flow curve behavior.

Creep Behavior

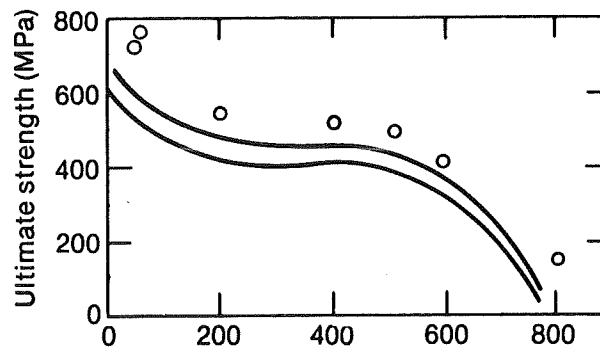
Creep tests have been performed on the extrusion consolidated CA Type 304 SS powder material. The test series uses specimens which have been preconditioned with 1 h heat treatments at 900 and 1200°C. Most of the tests were run at 500 and 600°C under constant load conditions. The stress versus time to rupture behavior for the alloy is shown in figure 4-14 with the upper and lower bounds which have been determined for conventional wrought Type 304 SS (5). It is apparent that the rapidly solidified Type 304 SS material exhibits creep-rupture behavior that is at least equivalent, if not slightly superior, to the best heats of the conventional wrought material.

Fatigue Behavior

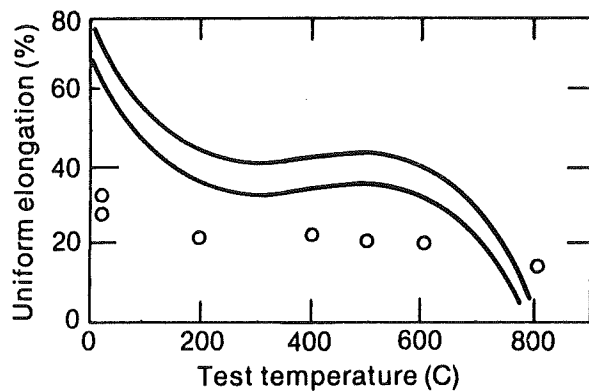
Strain-controlled low-cycle fatigue tests were performed at 24°C on the extrusion consolidated CA Type 304 SS powder. The results from these tests are shown in figure 4-15 with comparisons of conventionally processed (wrought) austenitic stainless steels (8). Only one of the



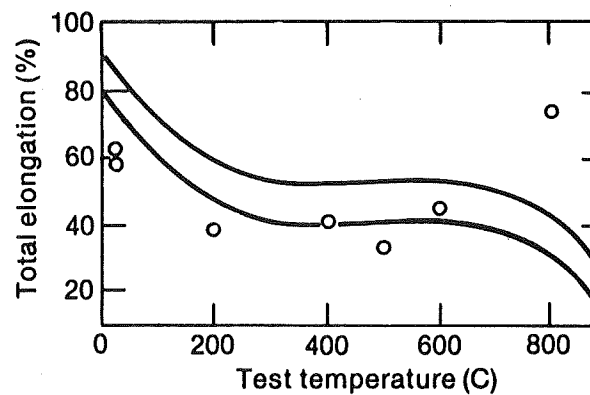
(a) Yield strength



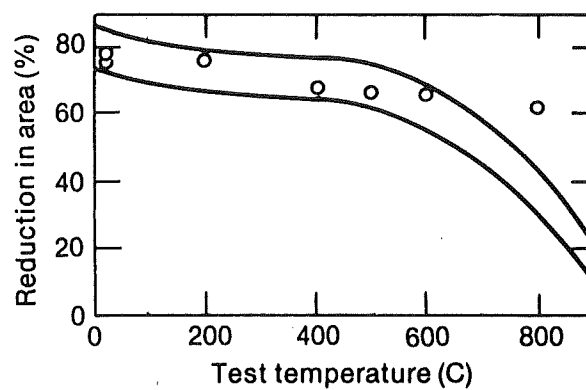
(b) Ultimate strength



(c) Uniform elongation



(d) Total elongation



(e) Reduction in area

4 1729

Figure 4-13. Tensile properties comparisons of extrusion consolidated CA powder (preconditioned at 900°C) and conventional wrought 304 SS. Lines represent upper and lower bounds of conventional wrought Type 304 SS.

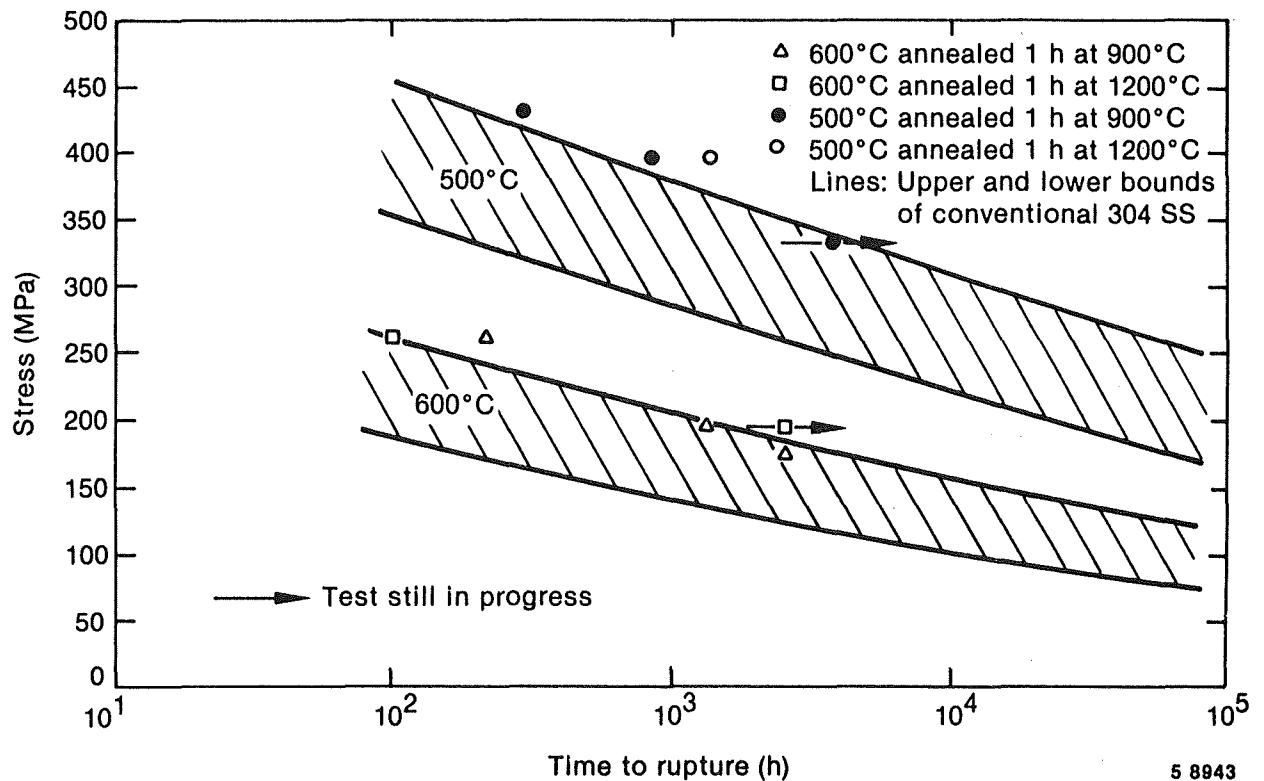
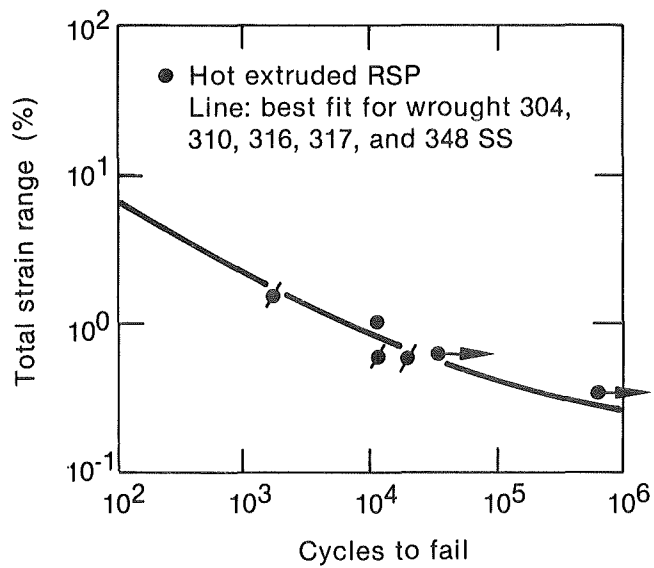


Figure 4-14. Stress rupture of extrusion consolidated CA Type 304 SS.

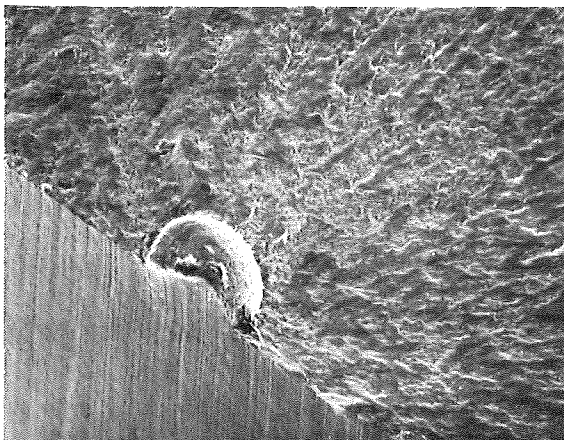
data points shown in figure 4-15a is considered to be a valid test. Two of the tests failed prematurely due to machine malfunctions, and the three other tests are associated with premature failures due to influences from foreign particles. Evidence of the foreign particles are shown in figure 4-15b and c; they probably came from a prior run of powder from the centrifugal atomization system. Microchemical analysis, using energy dispersive spectrometry techniques, of the impurity particles showed them to be nominally comprised (wt.%) of the following elements:

<u>Fe</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>Al</u>	<u>W</u>
2.1	67.5	9.4	1.2	8.2	11.5

The microchemical analysis did not resolve carbon levels. The microhardness of these particles was ~460 DPH compared to 190 DPH for the rapidly solidified Type 304 SS matrix. The fatigue results shown in figure 4-15a, in spite of the premature failures, indicate that the RSP material is at least equivalent and possibly superior to conventionally processed austenitic stainless steels. A portion of the results obtained on the mechanical properties of the extrusion consolidated CA Type 304 SS powder was presented at a symposium on "Mechanical Behavior of Rapidly Solidified Materials." Publication of these results is anticipated in a forthcoming proceedings.

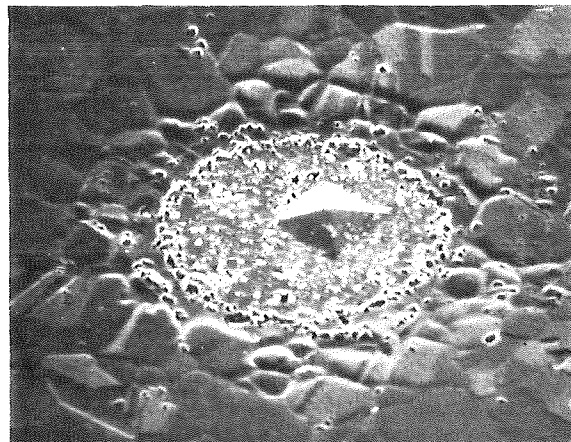


- (a) Crack initiated at impurity defect
 Machine malfunction caused buckling at this point



100 μm

(b) Fracture surface of fatigue specimen CA3-38 showing crack initiation from impurity particle.



10 μm

(c) Impurity particle in cross-section (indent from hardness measurement).

5 8948

Figure 4-15. Low cycle fatigue observations for extrusion consolidated CA Type 304 SS powder.

Consolidation of Rapidly Solidified Type 304 SS Powders

The consolidation methodology for rapidly solidified powders requires careful development in order to preserve the unique microstructural features obtained during powder processing. The methodologies selected are reflected in table 4-3, where potential processes can be separated into three ranges associated with densification rate.

TABLE 4-3. - Process correlations with principal parameters for powder consolidation

Densification Rate, s^{-1}	Consolidation Methodology	Stress	Bulk Temperature	Time, s
10^{-3} to 10^{-4} (Low)	Inert gas hot pressing Vacuum hot pressing Hot isostatic pressing	Low-Med Low-Med Low-Med	High High High	10^3 to 10^4 10^3 to 10^4 10^3 to 10^4
10 (Medium)	Forging Rolling Extrusion	Med-High Med-High High	Med-High Med-High Med-High	10 to 100 10 to 100 10
10^5 (High)	Dynamic	Very High	Low-Med	10^{-5}

The medium densification rate consolidation process selected for evaluation is extrusion; the results pertaining to the characterization of this material were presented in the previous sections. There is no attempt to perform a parametric study for extrusion consolidation of the rapidly solidified powder. The extruded CA Type 304 SS material received is fully densified and bonded and deemed suitable for baseline comparisons with other consolidation processes being pursued at the INEL.

Two consolidation processes have been selected for systematic study in association with rapidly solidified powders: hot isostatic pressing (HIPping) and dynamic consolidation. These represent low and high densification rate methods, respectively. As noted in table 4-3, the densification rates are markedly different, however in both methods particle interactions are with the same near-neighbors during densification.

HIPping Studies

A research HIP was purchased and installed during the second year of the project. HIPping assessments on both the DGA and CA Type 304 SS powders will begin during the third year of the project. The initial emphasis will be on developing appropriate canning procedures for the powders. The characterization results obtained from the extrusion consolidated CA Type 304 SS powder material should aid in establishing

some parametric guidelines for HIPping the RSP powders. In particular, the results obtained on the heat treatment/grain growth behavior as well as the flow curve and creep behavior will be utilized.

Dynamic Studies

Significant advancements were made on the dynamic consolidation of RSP powders during the second year of the project. Tests were performed using explosives and a gas gun for dynamic consolidation. In addition, a dedicated site for explosive work was obtained, and plans have been initiated for acquiring a bunker to perform instrumented tests at the site.

Explosive Efforts

The explosive consolidation research on RSP Type 304 SS powders involves consolidation tests and characterization of the consolidated products. A major achievement was the development of a die/target design which provides fully dense, crack free, and nearly completely metallurgically bonded monoliths. This design also proved to be very effective for the gas gun tests.

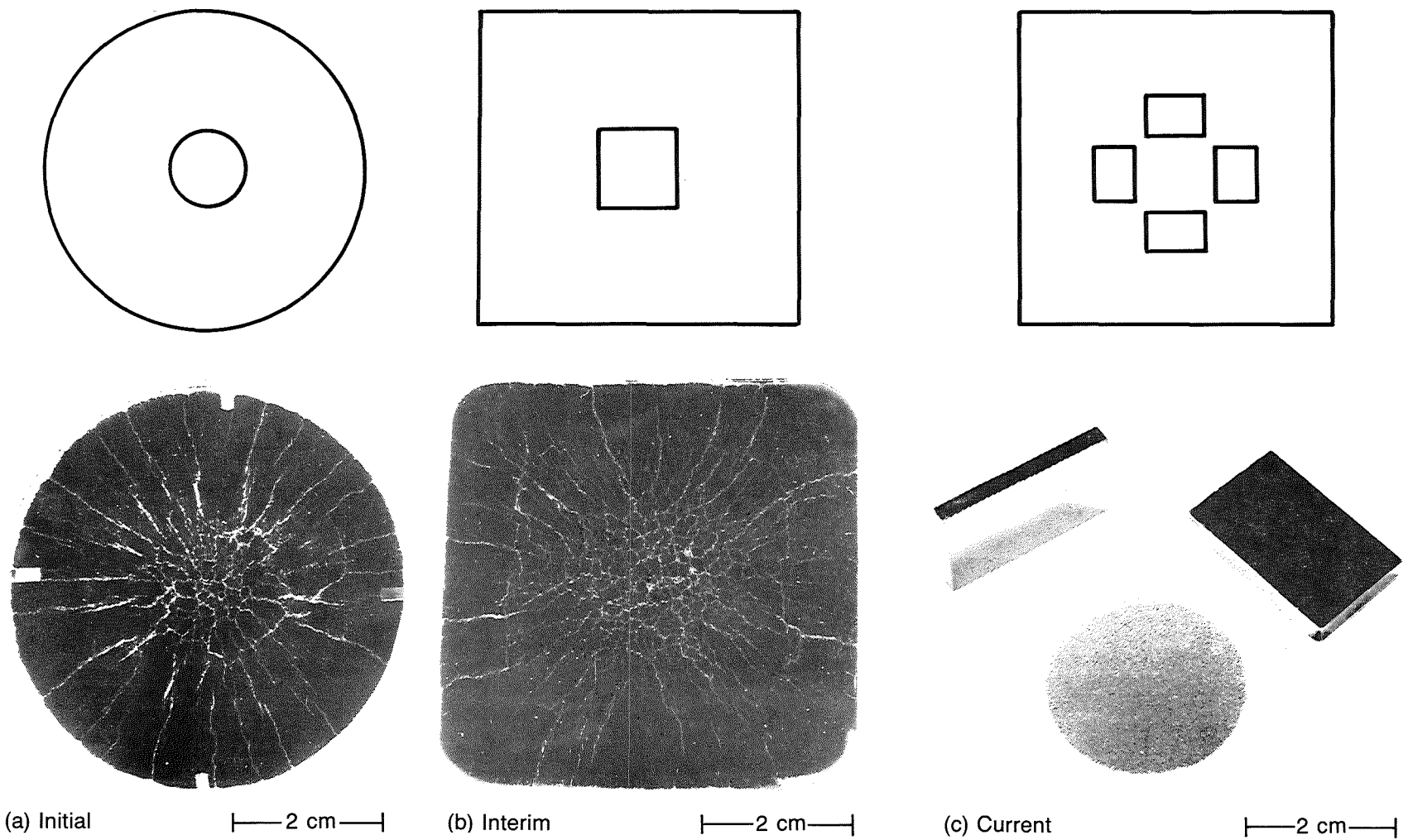
The die-target evolution, which occurred during the second year of the project, is shown in figure 4-16. The current design, indicated in figure 4-16c and shown in more detail in figure 4-17, involves four rectangular powder cavities off-set from the center of the die-target, but in a four-fold symmetry arrangement. This configuration appears to reduce the influence from tensile waves which promote cracking, and also provides four monoliths per shot.

One test performed during this reporting period requires particular mention. The test involved explosive consolidation of a two-layered bed of powder. The bottom half of the cavity was filled with copper powder ¹/₂ and the top half-filled with CA Type 304 SS powder. The purpose of this test was to determine particle mixing and movement during the passage of the dynamic stress wave. The shock impedance of the two materials is very similar and they are readily distinguished with optical microscopy. Cross sections from this test, shown in figure 4-18, demonstrate that a rather distinct interface is retained between the copper and Type 304 SS materials. This suggests that during shock wave compaction the interaction of the particles is one of nearest neighbor behavior. This observation should be most beneficial for future modeling efforts.

The results from the explosive consolidation efforts on RSP Type 304 SS powders obtained to date were presented at the AIME/TMS Fall meeting in Detroit, MI.

One hour anneals have been performed on specimens ~1 x 1 x 0.4 cm which were sectioned from both DGA and CA Type 304 SS explosively

¹/The copper powder was kindly supplied by W. H. Gourdin of Lawrence Livermore Laboratories.



5 8939

Figure 4-16. Explosive die/target evolution and corresponding consolidated RSP Type 304 SS monoliths.

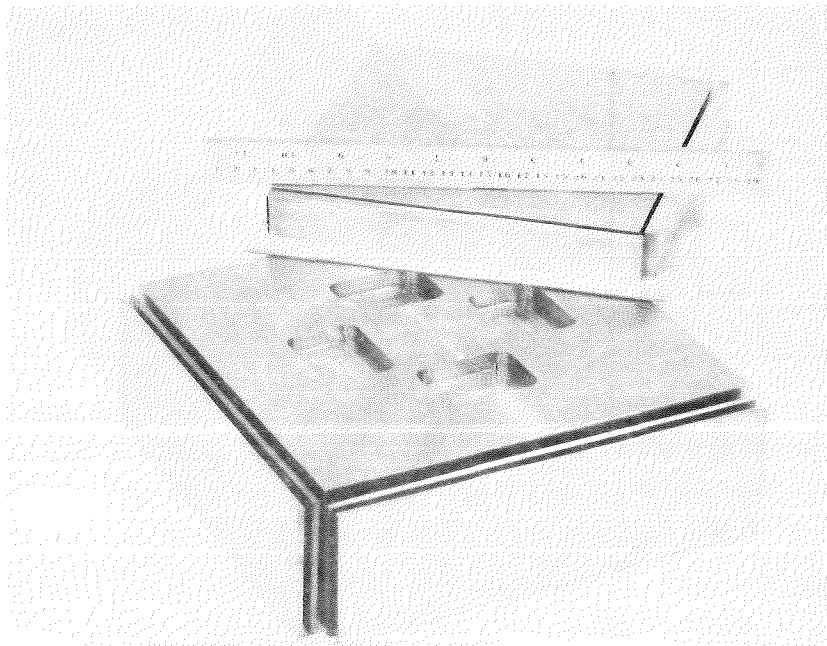


Figure 4-17. Current die/target for explosive consolidation of RSP powders.

consolidated monoliths. The intent of the assessment is to evaluate the recovery, recrystallization, and grain growth patterns of the explosively consolidated RSP materials. The heat treatments were for 1 h at temperatures of 200, 400, 500, 600, 800, 900, 1000, 1100, and 1200°C. A specimen of each material in the "as-consolidated" condition was included for comparison. Specimens for the higher temperatures were sealed under argon in quartz capsules. The techniques used in the evaluation include low resolution microscopy, XRD for line broadening measurements, positron annihilation, and microhardness; high resolution STEM is planned. In addition, NDE evaluations using ultrasound on these specimens have been performed.

The observations and measurements obtained to date are summarized below. The XRD measurements for line broadening assessments are difficult to resolve due to "double-peaking" behavior. The usefulness of these measurements is currently being evaluated, however relative peak heights appear to be informative with respect to influences of the various annealing temperatures.

Optical microscopy examinations on the annealed specimens for both DGA and CA Type 304 SS did not reveal marked changes in microstructure until 800°C. At this temperature, recrystallization has been initiated and also there is considerable evidence that the residual particle boundaries are disappearing. This observation is interpreted as being associated with sintering. Micrographs of the CA Type 304 SS specimens after heat treatments of 900 through 1200°C are shown in figure 4-19. After the 900°C anneal, only occasional traces of particle boundaries are observed and recrystallization is occurring, though it appears to

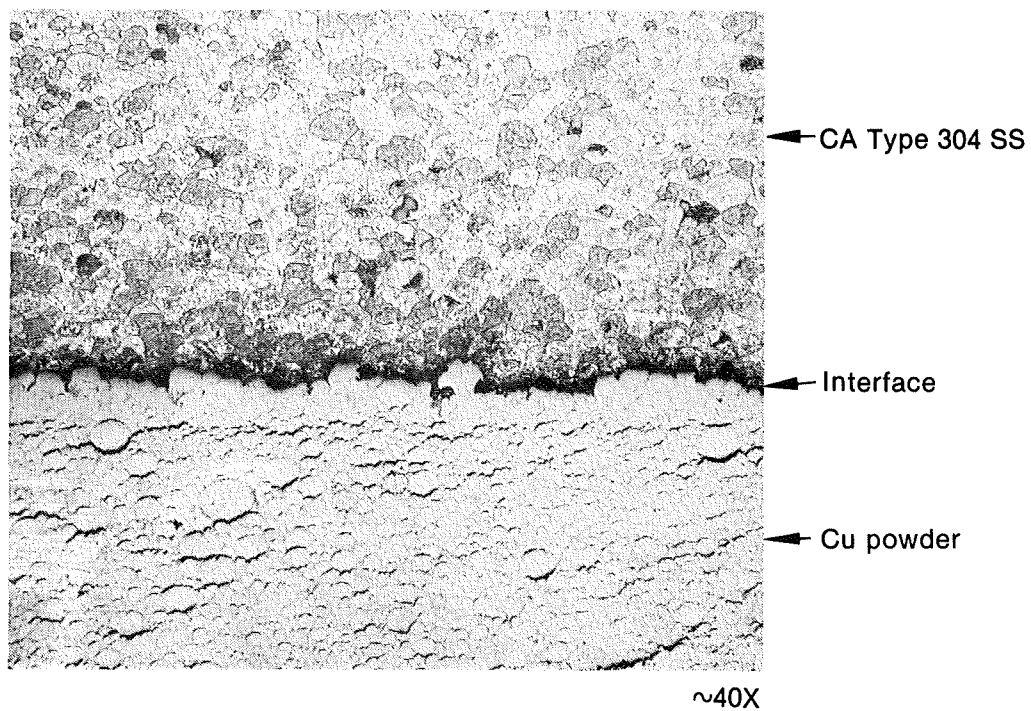
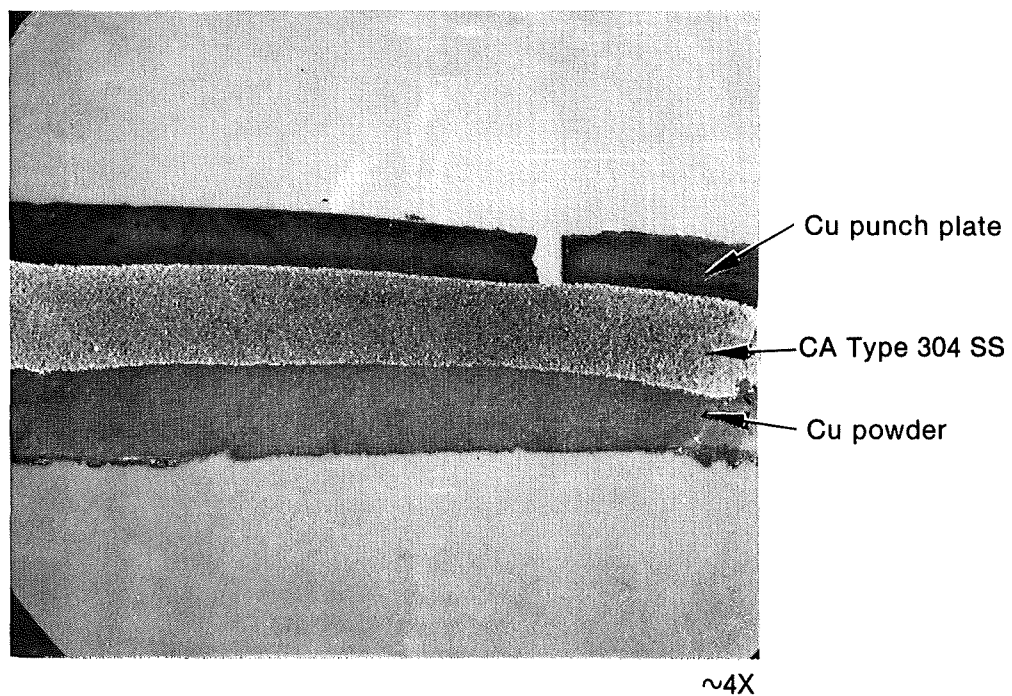
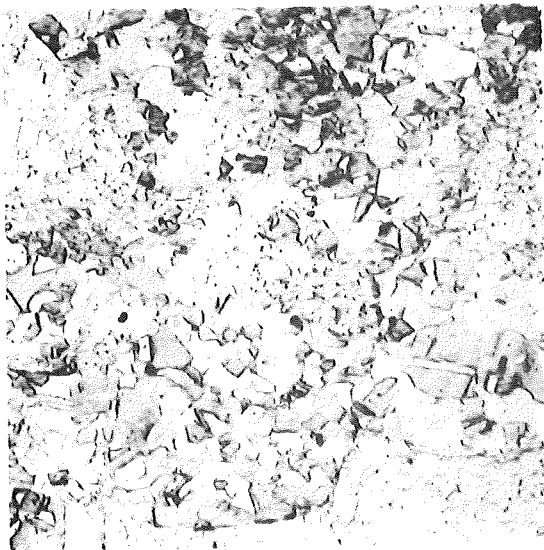


Figure 4-18. Cross section of CA Type 304 SS and copper powder explosive consolidated compact.



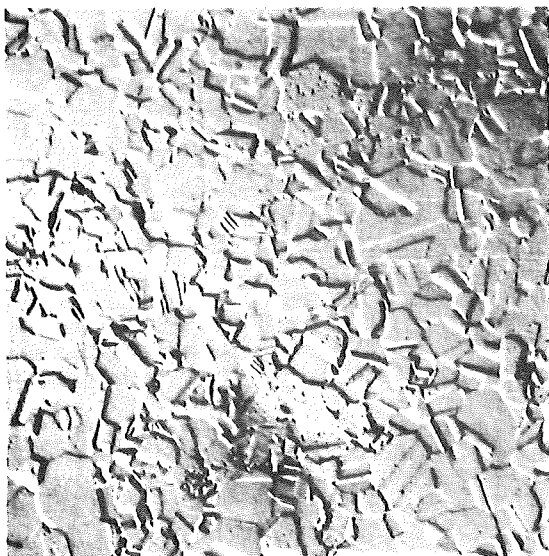
(a) 900°C

400x



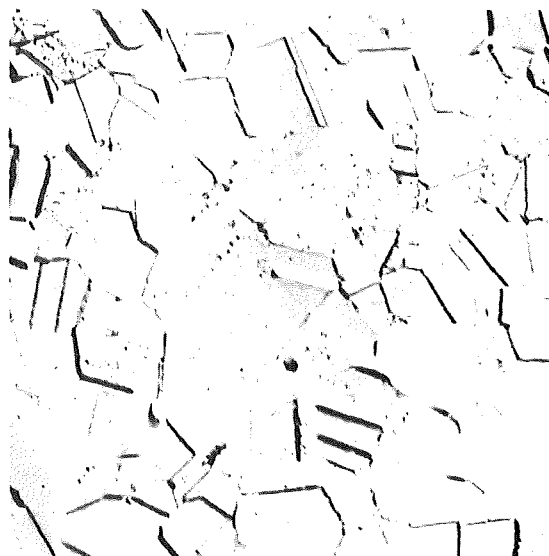
(b) 1000°C

400x



(c) 1100°C

400x



(d) 1200°C

400x

Figure 4-19. Microstructure of explosively consolidated CA Type 304 SS powder after 1 h heat treatments.

be associated with individual powder particles. After annealing at 1000°C, the grains exhibit a duplex grain size. The grain configurations, including size as well as twinning, for the 1100°C and 1200°C anneals are comparable to the extrusion consolidated CA Type 304 SS powder shown in figure 4-11.

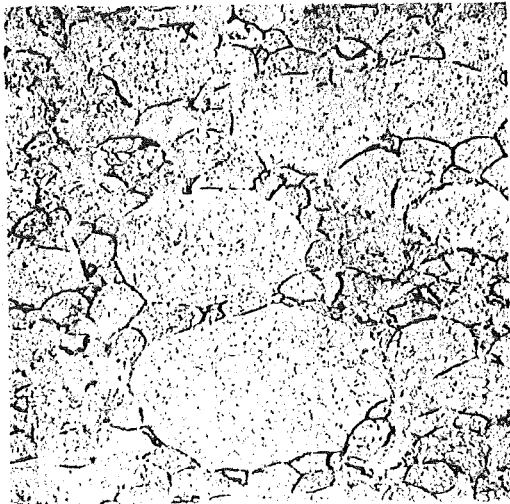
The high temperature heat treatment response for the explosively consolidated DGA Type 304 SS powder is shown in figure 4-20. Also shown (fig. 4-20a) is the "as consolidated" microstructure. It should be noted for the DGA specimen series that a heat treatment at 1200°C was not performed due to unavailability of material. The sintering behavior for the DGA material is evident in figure 4-20 with the particle boundaries disappearing with increasing temperature. The DGA material appears to be markedly different from the CA material (see fig. 4-19) in terms of its recrystallization and grain growth response. The microstructural features of the material remain very fine even after annealing at 1100°C. Also, the microstructure does not evolve to where distinct grain and twin boundaries form, at least in comparison with the CA material.

Positron annihilation (PA) measurements ^{1/} have been determined on specimens which have been annealed at temperatures up to and including 800°C for 1 h. Additional measurements are planned for the specimens which have been annealed at 1000°C. Microhardness measurements have been completed for the DGA series of specimens. These results, along with the positron annihilation measurements, are shown in figure 4-21. The original specimen used for the 200°C anneal may not be representative of the DGA explosively consolidated series. An additional specimen has been evaluated in terms of hardness (asterisked data point), but remains to be measured for positron annihilation response. The recovery results shown in figure 4-21 exhibit an interesting response at 500°C. It appears that the PA measurements do not significantly decrease compared to 400°C, and furthermore, the hardness reflects an apparent slight increase.

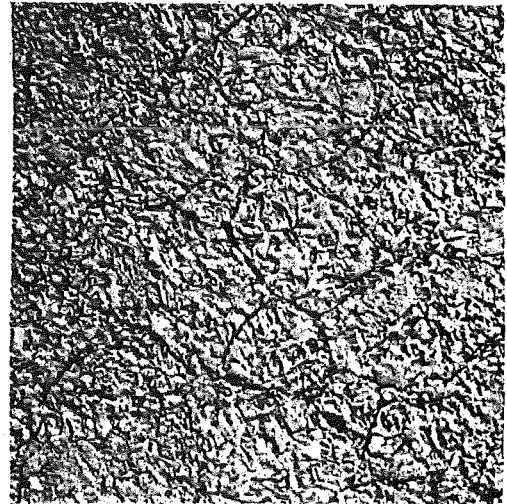
The recovery results obtained to date for the explosively consolidated CA Type 304 SS powder specimens are shown in figure 4-22. Both the PA and microhardness measurements show that something is occurring during annealing from 400 to 600°C. To understand the annealing response for both the DGA and CA materials, high resolution STEM examinations are required. Such examinations are planned in the near future.

The explosive tests planned for the near future will address improvements in explosive configurations and detonation. The production of suitable monoliths from both DGA and CA type powders is planned for additional characterization and joining assessments.

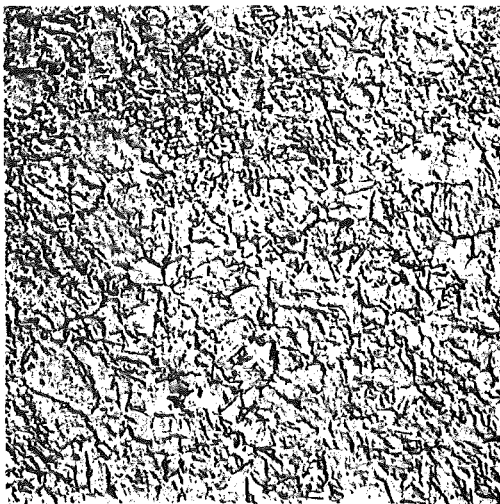
^{1/}The measurements basically determine the residence time of positrons in defects.



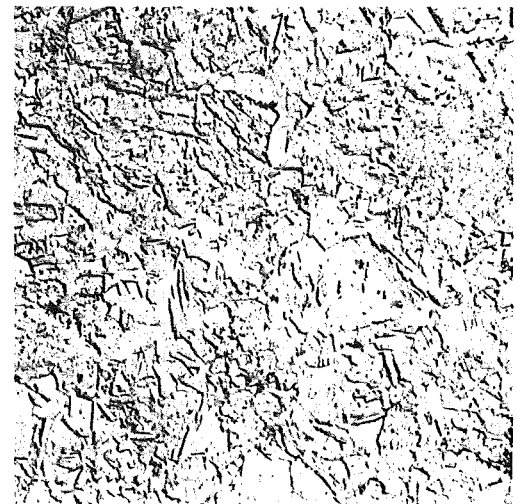
(a) As consolidated



(b) 900°C



(c) 1000°C



(d) 1100°C

4 1583

Figure 4-20. Microstructure of explosively consolidated DGA Type 304 SS powder after various 1 h heat treatments
a) 225x, b) 360x, c) 360x, d) 360x.

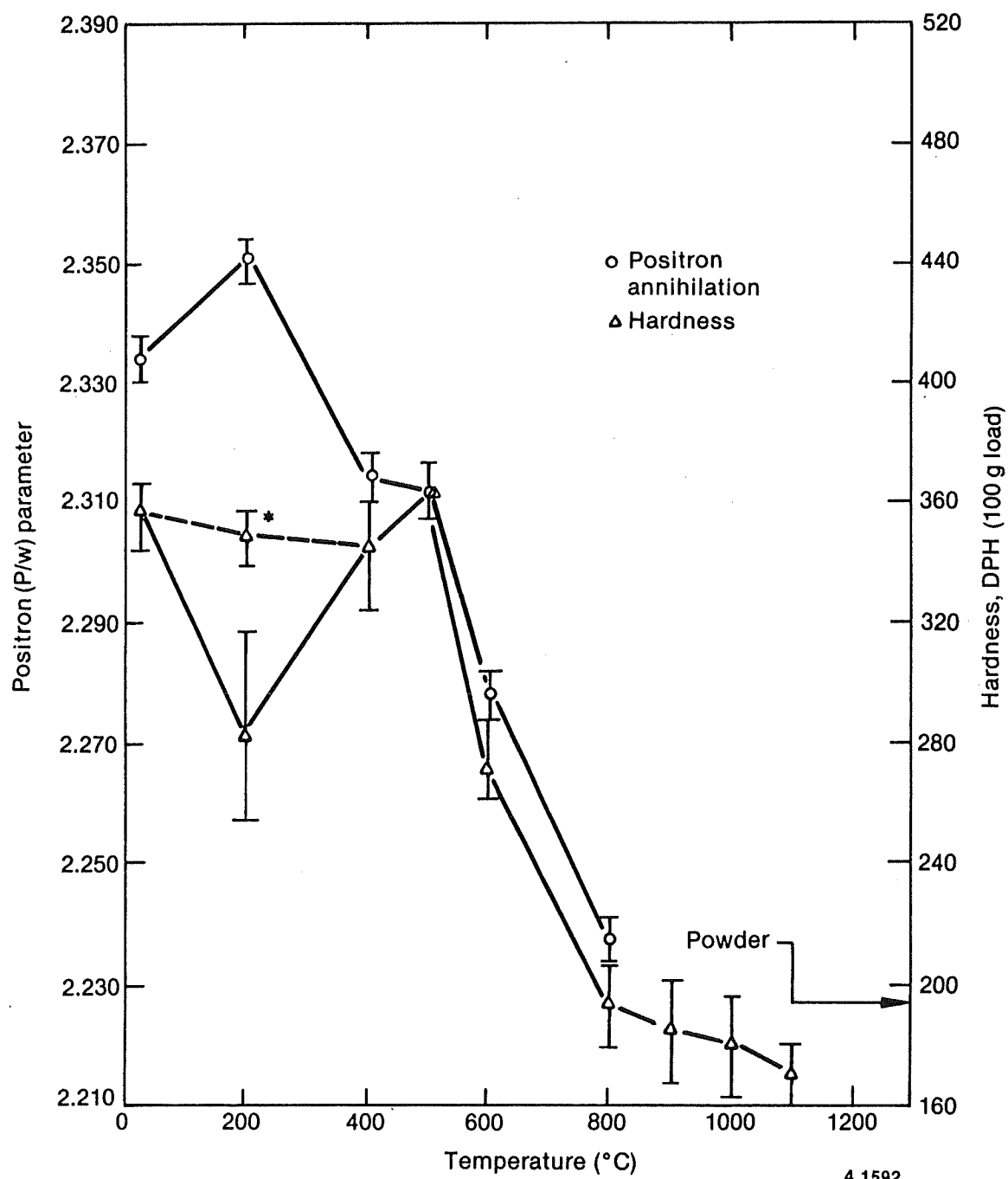
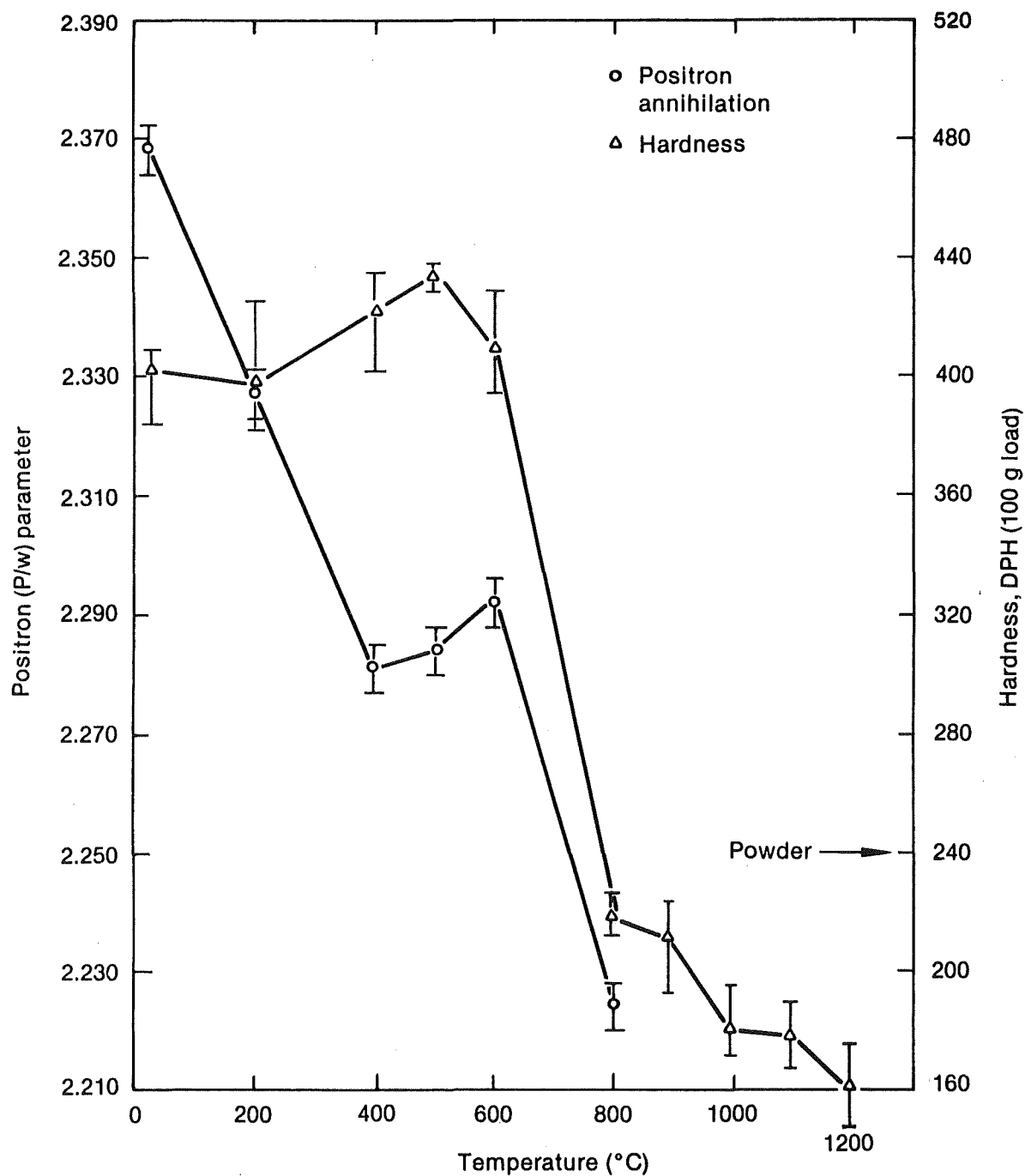


Figure 4-21. Recovery measurements after 1 h anneals on explosively consolidated DGA Type 304 SS.



4 1608

Figure 4-22. Recovery measurements after 1 h anneals on explosively consolidated CA Type 304 SS.

Gas Gun Efforts

The Shock Dynamics Laboratory at Washington State University, under the direction of Professor Y. Gupta, performed (under subcontract) three gas gun consolidation tests on DGA and CA Type 304 SS powders. The test parameters associated with the three shots are given in table 4-4. The die/target configuration was similar to that being used for the explosive efforts, but scaled down to accommodate a 10.2 cm diameter projectile. Each target contained four die cavities offset in a symmetrical manner from the center of the target. The size of the cavities was 1.91 x 1.27 x 0.60 cm deep, except for the third shot where the depth was a test variable. Bonded to the target were duplicate lateral as well as longitudinal momentum traps or spall plates. All target components were machined from copper. The impactor was a modified square copper plate bonded to the face of the aluminum projectile.

TABLE 4-4. - Gas gun test parameters

Test No.	Cavity Depth, mm	RSP Powder	Projectile Velocity, mm/ μ s	¹ Peak Pressure, GPa	² Duration, μ s
1	5.59	Alt. DGA & CA	0.598	11.65	2.21
2	5.59	Alt. DGA & CA	1.01	21.1	2.05
3	4.57 5.59 8.34 9.14	DGA DGA DGA DGA	0.741	14.79	2.15

¹Calculated from "LASL Shock Hugoniot Data".

²Based on a 4.83 mm copper flyer plate.

After each shot was fired the consolidated specimens as well as target and projectile debris were recovered from the catcher system. The recovery system consisted of a large volume of cloth rags placed in a heavy duty wire cage attached to a monorail inside the catcher tank. For the three shots, twelve consolidated powder monoliths were recovered intact, most of which were metallurgically bonded and crack free. For those specimens where cracks were observed, the cracking was attributed to collisions which occurred during recovery and not to shock wave conditions arising during powder consolidation. The remarkable aspect of the recovered materials was that the monoliths were intact but the die-target and impactor were virtually destroyed. Only the components associated with the low projectile velocity shot, hence low peak pressure (shot 1 in table 4-4), could be identified. For the two higher velocity shots, the recovered components were not distinguishable, and appeared only as copper metal fragments. The significance of the recovery aspects of the tests is two fold: (a) the

gas gun can provide an effective research tool for powder consolidation; and (b) the die-target design which evolved from the explosive efforts is indeed effective for producing appropriate consolidated powder monoliths. Examination of the recovered monoliths is currently ongoing. Some of the preliminary observations are summarized below.

Dimensional measurements were performed on each specimen, and both lateral as well as longitudinal contractions were observed. These results are shown in table 4-5, where the "zero" subscripts represent the initial cavity dimensions. The fact that the lateral dimensions also reflect contraction after consolidation is surprising, since the lateral dimensions of monoliths from the explosive shots are nearly the same as the original cavity dimensions. As a result, the densification for the explosive specimens is totally reflected in the thickness. The importance of these observations on the dimensional changes associated with the gas gun consolidated specimens relates to the contractional stresses and the time frame associated with the consolidation event of the powders. These results are currently being analyzed in more detail.

TABLE 4-5. - Dimensional changes for gas gun consolidated RSP Type 304 SS monoliths

¹ Spec. No.	Peak Pressure, GPa	² Specimen dimension ratio			
		b_f/b_o	a_f/a_o	t_f/t_o	V_f/V_o
H1A	11.65	0.91	0.87	0.80	0.64
H1B	11.65	0.91	0.88	0.80	0.64
P1A	11.65	0.92	0.91	0.81	0.68
P1B	11.65	0.92	0.91	0.81	0.68
H3A	14.8	0.92	0.90	0.73	0.61
H3B	14.8	0.91	0.87	0.79	0.63
H3C	14.8	0.89	0.87	0.67	0.52
H4C	14.8	0.89	0.86	0.77	0.59
H2A	21.1	0.91	0.89	0.80	0.64
H2B	21.1	0.88	0.90	0.80	0.63
P2A	21.1	0.92	0.91	0.80	0.67
P2B	21.1	0.91	0.93	0.80	0.68

¹H DGA; P-CA.

²a - narrow lateral dimension.

b - long lateral dimension.

t - thickness.

v - volume.

Subscripts f and o indicate final specimen dimensions and original cavity dimensions, respectively.

Low resolution microscopy assessments and microhardness measurements have been initiated on the gas gun consolidated specimens. In terms of pressure influences, the degree of particle bonding and particle extrusion increases with increasing pressure. It was observed that the population of gas bubbles increased with increasing pressure. The source of the gas bubbles has not been conclusively resolved. Residual gas entrainment during RSP of the powders, and the fact that the void regions of the powder-filled cavities were not evacuated but contain argon, are the likely sources. Also observed are thin regions on the bottom (i.e., back surface with respect to dynamic loading) of the specimens which have undergone melting during dynamic consolidation.

Microhardness measurements have been performed on five of the specimens (three DGA and two CA). The results of these measurements are shown in figure 4-23 as a function of peak pressure. The apparent lower hardness observed at the highest peak pressure, particularly for the DGA material, is a rather surprising result and probably associated with the mode and degree of particle interactions during densification. This behavior requires more analysis and interpretation.

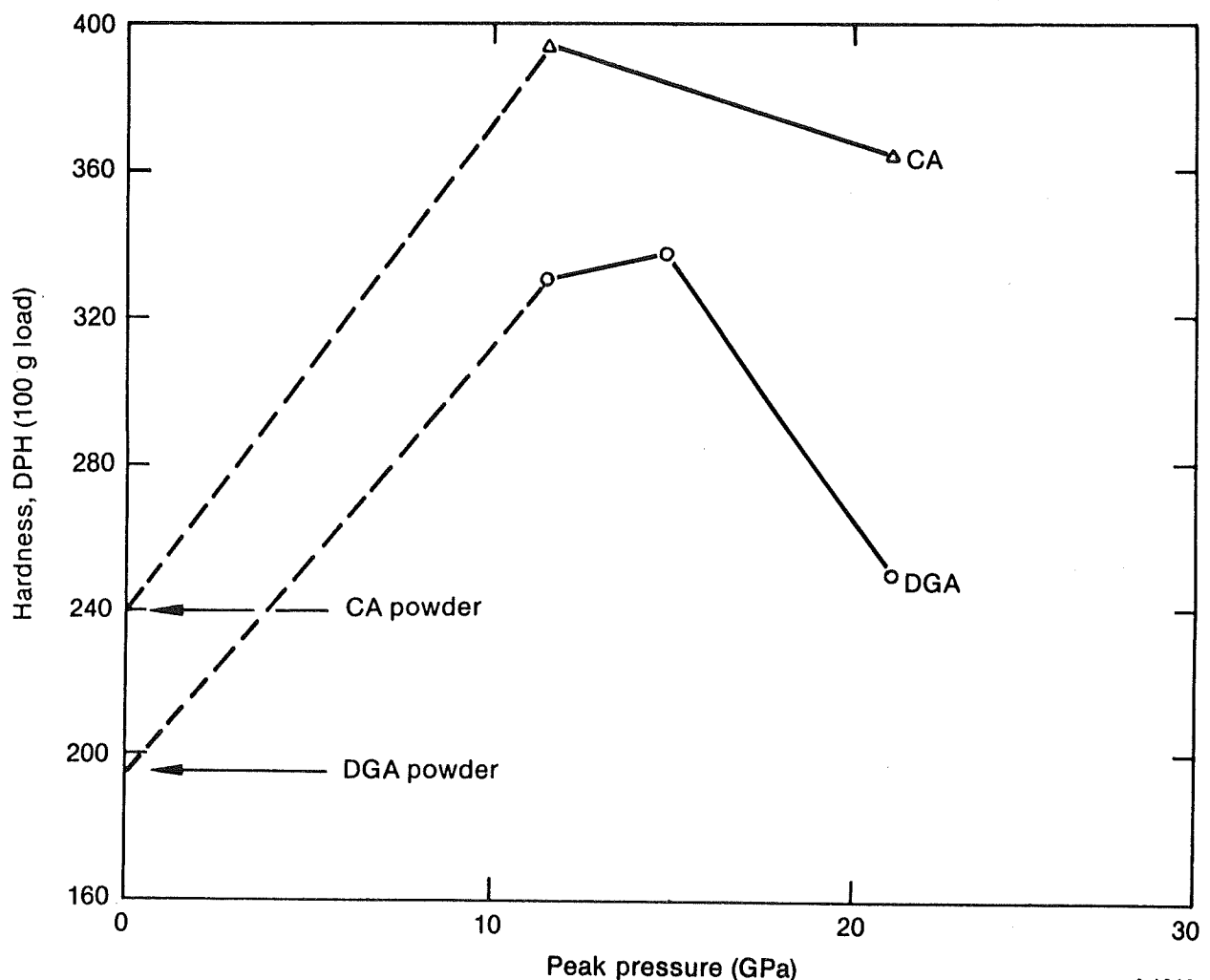


Figure 4-23. Average hardness for dynamically consolidated (gas gun) DGA and CA Type 304 SS powders.

A considerable effort will be devoted in the near future to the characterization of the monoliths from the gas gun tests. In addition, the dynamic stress wave behavior will be analyzed and correlated with the morphological features observed for the specimens.

The initial results obtained from the gas gun tests were reported at the fall AIME/TMS meeting in Detroit, MI.

REFERENCES

1. Grant, N. J. J. Met., v. 35, No. 1, 1983, pp. 20-27.
2. Okamoto et. al. Trans. Iron and Steel Institute of Japan, v. 21, 1981, pp. 641-648.
3. Lippold, J. C., and B. C. Odegard. Technical Note: Microstructural Evolution During Inertial Welding of Austenitic Stainless Steels. Welding J. v. 63, No. 1, 1984, pp. 35s-38s.
4. Sikka, V. K., et al. Tensile Properties of Type 304 Stainless Steel. Oak Ridge National Laboratory Report No. ORNL-5325, Oak Ridge, TN 37831, February 1978.
5. Personal communication, C. R. Brinkman and V. K. Sikka, Oak Ridge National Laboratory, Oak Ridge, TN 37831, October 1984.
6. Swindeman, R. W., V. K. Sikka, and R. L. Klueh. Residual and Trace Element Effects on the High-Temperature Creep Strength of Austenitic Stainless Steels. Met. Trans. A, v. 14A, April 1983, pp. 581-583.
7. Idaho National Engineering Laboratory. Strategic and Critical Materials Program Annual Report, Ongoing BuMines Minerals and Materials Research Contract J0134035 (May 1984).
8. Jaske C. E., and W. J. O'Donnell. Fatigue Design Criteria for Pressure Vessel Alloys. J. Pressure Vessel Technology, v. 99, November 1977, pp. 584-592.

JOINING OF SILICON NITRIDE-BASED CERAMICS

R. L. Tallman, J. C. Mittl, J. G. Jolley, and R. M. Neilson, Jr. 1/

INTRODUCTION

Structural ceramics are potential substitutes for strategic and/or critical materials. These ceramics would provide economic benefits from increased thermodynamic efficiency and other advantages of higher temperature operations. Other performance improvements would result from decreased weight and improved resistance to wear and corrosion. Furthermore, these ceramics are composed of relatively low cost materials which are in abundant domestic supply. However, while promising decreased reliance on strategic and/or critical materials and significant performance improvements, the technology is not sufficiently developed to permit widespread use of structural ceramics.

Many of the potential applications of structural ceramics require components that are too intricate or too large to be fabricated by existing techniques. The use of structural ceramics in such applications can be achieved by joining simpler and smaller ceramic bodies to fabricate intricate parts and/or large subsystems. In addition to ceramic-ceramic joints, various applications require ceramic to metal joining (e.g., ceramic wear surfaces on metal structures). Methods producing ceramic-ceramic and ceramic-metal joints are crucial to widespread application of structural ceramics and hence to substitution for strategic and/or critical materials.

This program is developing information leading to a fundamental understanding of ceramic joining with an emphasis on joining silicon nitride-based ceramics. Silicon nitride-based ceramics are particularly interesting because of their outstanding properties, especially thermal shock resistance. An assessment of ceramic joining work provided by this program (1) revealed significant limitations in ceramic joining information. Especially apparent is the desirability of obtaining fundamental information basic to the required development of joining techniques and structurally sound joints. This program will satisfy these information needs.

This program has focused upon oxynitride glass joining materials producing joints strengthened by the precipitation of silicon nitride crystals and other toughening and strengthening precipitates. Experimental efforts to date have concentrated on developing and characterizing oxynitride glasses and glass-ceramics in which large concentrations of silicon nitride were dissolved by melting at high temperatures (up to 1900°C) and high nitrogen pressures (up to 207 MPa) in a hot isostatic press (HIP).

1/EG&G Idaho, Inc., Idaho Falls, Idaho.

OXYNITRIDE JOINING MATERIAL PREPARATION

The two HIP runs conducted this year (Run 3 and Run 4) produced sixteen oxynitride glass and glass-ceramic melts. The compositions of these melts are listed in table 5-1. HIP Run 3 produced 90-g batches of four oxidation-resistant compositions [3(1)-3(4)] and 60-g batches of four low aluminum compositions [3(5)-3(8)]. HIP Run 4 consisted of eight lanthanum-containing compositions which were produced in individual 90-g melts. These HIP runs were conducted at Gorham International, Inc.

The procedure developed for HIP Run 3 and Run 4 melts was as follows (actual times and temperatures varied slightly for both runs). Powders were mixed and compressed into slugs in a cold isostatic press. These slugs were placed into specially designed, high purity, boron nitride crucibles which were loaded into the HIP furnace. The temperature was raised to 1200°C and held for one hour in vacuum to remove volatile materials. The temperature was then increased to 1750°C using the HIP convection (base) heater while nitrogen was introduced, raising the nitrogen overpressure to approximately 3 MPa (450 psi), over a period of one hour. The radiation heater was then energized and the melts maintained at a temperature of 1750°C with a 6.9 MPa (1000 psi) nitrogen overpressure for fifteen minutes. Both convection and radiation heaters were used to increase the melt temperature to 1900°C while nitrogen was added to the pressure vessel to increase the pressure to 207 MPa (30,000 psi) over 2.5 h. The temperature and nitrogen pressure were maintained at 1900°C and 207 MPa (30,000 psi), respectively, for 1.5 h. The heaters were then turned off to cool the melts. When the melt temperature decreased to 1000°C, nitrogen was bled off to decrease the overpressure. A small nitrogen overpressure was maintained during further cooling [e.g., 2 MPa (290 psi) at 240°C] to room temperature.

The crucibles and HIP operating parameters were specifically designed to minimize or eliminate bubbles in the glass melts. These HIP Run 3 and Run 4 melts were essentially devoid of bubbles, in contrast to HIP Run 1 melts where porosity as high as 40 volume percent was noted. In HIP Run 2 the molybdenum crucibles were attacked and destroyed by the melts; the 1900°C melt temperature, together with the high nitrogen activity, resulted in much greater attack than had been expected. Both the crucible design and the selection of HIP operating parameters were major achievements of this work in permitting the routine production of large (90 g) void-free melts. The vacuum bakeout step also significantly extends graphite furnace life.

OXYNITRIDE JOINING MATERIAL CHARACTERIZATION

The batch compositions of the melts produced in HIP Runs 1, 3, and 4 are listed in table 5-1. This table also includes the volume percentages of precipitates (usually a silicon nitride phase) present in the melts.

Chemical Analysis

The nitrogen and oxygen contents of the eight Y-Si-Al-O-N melts from HIP Run 3 and the eight La-Y-Si-Al-O-N melts from HIP Run 4 were measured by

TABLE 5-1. - Batch compositions and precipitate concentrations in oxynitride HIP melts

Melt Number	Equivalent Percent Element					Precipitate Volume % ²
	La	Y	Si	Al	N ¹	
	<u>HIP Run 1: High N Extension of Known Glass</u>					
1(1)	--	28	56	16	18	0
1(2)	--	28	56	16	29	8
1(3)	--	28	56	16	40	15
1(4)	--	28	56	16	51	13
1(5)	--	28	56	16	62	³ 100
	<u>HIP Run 3: Oxidation Resistant Compositions</u>					
3(1)	--	26	54	20	20	0
3(2)	--	19	51	30	30	13
3(3)	--	22.5	53.5	24	30	11
3(4)	--	15.3	52.4	32.3	40	29
	<u>Low Aluminum Compositions</u>					
3(5)	--	36	56	8	18	0
3(6)	--	36	56	8	29	6
3(7)	--	36	56	8	40	11
3(8)	--	44	56	0	40	³ 100
	<u>HIP Run 4: Lanthanum-Containing Compositions</u>					
4(1)	16.7	--	52.5	30.9	30.9	12.7±0.7
4(2)	12.9	4.3	52.1	30.7	30.7	14.4±1.4
4(3)	19.8	--	55.3	24.8	31.0	11.6±2.0
4(4)	15.4	5.1	54.9	24.6	30.8	10.3±2.2
4(5)	10.5	3.5	50.4	35.6	35.6	25.5±1.6
4(6)	10.4	3.4	53.3	32.9	40.7	26.3±1.4
4(7)	39.1	--	60.9	--	45.9	³ 100
4(8)	30.1	10.0	60.0	--	50.5	⁴ 17.3±30

¹Equivalent percent oxygen is (100 minus equivalent percent nitrogen).

² β' -sialon (silicon nitride) phase predominately. One determination, except where estimate of standard deviation is given (three determinations).

³No β' -sialon phase recognized, melts are essentially all crystalline.

⁴No β' -sialon phase recognized.

Leco fusion analysis. This method was also used to determine the carbon content in HIP Run 4 melts. Boron, yttrium, and aluminum in both HIP Run 3 and HIP Run 4 melts were measured by emission spectroscopy (DCP); the silicon content of these melts was determined gravimetrically.

These data indicated that nitrogen (from the HIP atmosphere) was exchanged for oxygen in the melts. Total nitrogen increases measured for HIP Run 3 ranged from two to six equivalent percent and showed no dependence on melt composition. These increases are only small fractions of the high nitrogen concentrations in the melts, which ranged from 24 to 43 eq.%. A fraction of any measured increase in nitrogen should be ascribed to the dissolution of boron nitride from the crucibles, which contained only negligible concentrations of boric oxide.

Boron content may adversely affect joint performance. In devitrification of oxynitride glasses in joints, boron is likely to concentrate in the glassy phase, lowering its softening point. Boron contents of HIP Run 3 melts with ≥ 30 eq.% nitrogen ranged from 0.01 to 0.12 wt.% in central regions of the melts. In melts 3(1) and 3(5), which contained ~ 20 eq.% nitrogen, the boron contents averaged ~ 0.3 wt.% in central, top, and wall regions. Boron concentrations in HIP Run 4 melts ranged from 0.01 to 0.17 wt.%. Melt 4(4), which was prepared in a pyrolytic boron nitride crucible in an attempt to minimize boron dissolution, had an average boron content of 0.042 ± 0.002 wt.% in the central region. This boron content is within the range of the boron contents of melts prepared in high purity hot-pressed boron nitride crucibles. A sample of the 4(4) melt taken 0.5 to 3 mm from the crucible wall contained 0.139 ± 0.005 wt.% boron. This is evidence of an appreciable boron content gradient. The boron gradient in this melt is ascribed to its higher viscosity; this melt contained about 11 vol.% precipitate and initially 30.8 eq.% nitrogen, compared to lower viscosities in melts 3(1) and 3(5) which were completely glassy and showed no significant boron gradient.

The carbon contents of HIP Run 4 melts were determined. During this run, a hot spot at a loose furnace connection caused a shutdown at 1250°C during initial pressurization. Visual observation of the HIP furnace indicated that carbon particles were blown about, although none was observed in any of the crucibles at that time. However, subsequent optical microscopy of melts 4(6) and 4(7) indicated the presence of fine fibrous and granular black particles. Leco fusion analysis determined a carbon content of ~ 0.1 wt.% in melts 4(7) and 4(8). Melts 4(1) through 4(6) contained 0.02 to 0.04 wt.% carbon. Repressurization of the HIP, after the furnace connection repair, apparently blew carbon into the melts. This was possible due to the loose-fitting crucible lids.

Thermodynamic calculations performed indicate that carbon can react with silicate glass to produce high carbon monoxide pressures which increase with increasing nitrogen pressure. Total gas pressures in pores, including this carbon monoxide, could thus exceed HIP pressures and result in voids in melts (or joints). Furthermore, as little as 0.01 wt.% carbon significantly accelerates high temperature oxidation of silicon nitride (3). The absence of hot connections in the INEL HIP graphite furnace should reduce the potential for carbon contamination of melts and joints.

Analytical data for batch cations (yttrium, aluminum, and silicon) suggested no significant deviations from the batch concentrations.

In general, the oxynitride glass melting techniques developed in this work have been shown to provide relatively uniform and controlled compositions. This contrasts to much previously reported work in which significant fractions of the nitrogen were lost by decomposition. Losses by evaporation of such species as SiO or AlO, which are characteristic of glass-making in general, were not observed.

Microchemistry

Energy dispersive spectrometry (EDS) data were collected from HIP Run 3 and Run 4 melts to determine compositions for large areas (up to 1 mm x 1 mm), glassy regions between precipitates, and individual precipitate crystals.

EDS data from large areas of HIP Run 3 melts were analyzed by several computational techniques; analysis of EDS data from HIP Run 4 precipitates is continuing. "Standardless" analysis provided acceptable results for HIP Run 3 melts, although this analysis technique indicated low lanthanum contents in HIP Run 4 melts. Mass attenuation calculations suggested that substitution of nitrogen for oxygen should not provide significant matrix effects for the cations of interest. Consequently, analysis of Al/Si ratios in β' -sialon crystals performed on HIP Run 3 melts appear to be satisfactory.

EDS data indicated that cation ratios are uniform throughout the glassy phases of HIP Run 3 melts. EDS analysis of precipitates (expected to be β' -sialon) from these melts indicated uniform silicon/aluminum ratios within individual crystals, but variations among crystals. Some correspondence was found between these cation ratios and the loss of aluminum and silicon from glassy phases.

Microstructure

The microstructures of melts from HIP Runs 3 and 4 were examined by optical microscopy, scanning electron microscopy (SEM), and x-ray diffractometry (XRD).

Optical microscopy of the glassy melts from HIP Runs 3 and 4 indicated only limited precipitate contents, ranging from 5 to 38 vol.%. Precipitate contents are listed for individual melts in table 5-1. Only melts containing ≥ 35 eq.% nitrogen contain > 25 vol.% precipitate. Melt 4(7) was essentially crystalline with no glassy phase.

Precipitate crystals in melt 4(8), which contained no aluminum, are ~ 20 μm in diameter. This is an order of magnitude larger than the crystals in other melts. The large crystals in melt 4(8) have a hexagonal tube morphology.

XRD indicated that the precipitates in the glassy melts of HIP Run 3 are β' -sialon. The fully crystalline melt, 3(8), contains no β -Si₃N₄.

phase, but instead N-melilite ($Y_2O_3 \cdot Si_3N_4$) and YN-apatite ($10Y_2O_3 \cdot 9SiO_2 \cdot Si_3N_4$). Lattice dimension changes measured by shifts in peak angle were found for β' -sialon. Peak angle shifts and peak breadths correspond with the variations in aluminum content in β' -sialon crystals found by EDS. HIP Run 4 melts have not been examined by XRD, but chemical analysis provided by EDS suggests that β' -sialon precipitates are present in these melts 4(1)-4(6). Melts 4(7) and 4(8) contained no aluminum and have lanthanum present in crystalline phases, precluding the presence of β' -sialon.

The glassy phases present in HIP Run 3 and 4 melts appeared unstructured under optical and scanning electron microscopy.

Microhardness

Vickers microhardness measurements were obtained for all of the HIP Run 3 and Run 4 melts. Glassy melts exhibited microhardness values of 9 to 11 GPa. These values were largely unaffected by precipitate crystals since few crystals were close to indentations and no correlation with hardness was observed. (Crystals of β' -sialon have hardnesses of >20 GPa.) Only small variations of microhardness within each of the glassy melts from HIP Run 4 were observed, suggesting limited inhomogeneity. Some locally low microhardness values were obtained in HIP Run 3 melts. These may be associated with inhomogeneities resulting from a short time at high temperature. Microhardness is expected to increase with increasing nitrogen content, however the literature suggests that the largest increases in hardness occur at low nitrogen contents (4,5).

The two crystalline phases in melt 4(7) had an average microhardness of 16.4 GPa (38 vol.% precipitate phase) and 8.6 GPa (62 vol.% precipitate phase) respectively. The large precipitate crystals in melt 4(8) exhibited microhardnesses of approximately 21 GPa.

Fracture Toughness

A microindentation technique was used to determine the fracture toughness of melts from HIP Run 1. These values apply to the glassy phase of the melts (except 1(5) which is essentially crystalline) since cracks did not interact sufficiently with the small volume of precipitate particles. Microindentation K_{IC} values measured for melts 1(1) to 1(5) were 1.17, 1.45, 1.33, 1.57, and 1.92 $MPa \cdot m^{1/2}$ respectively. The standard deviation associated with these measurements was low. Fracture toughness generally increased with increasing nitrogen content. This behavior was expected since nitrogen provides additional network bonding in the glass.

Glass Transition Temperature, Devitrification, and Oxidation

Differential thermal analysis (DTA) was performed to determine glass transition temperatures and to investigate oxidation and crystallization phenomena in HIP Run 1 melts. Glass transition temperatures were determined for the glassy melts 1(1) to 1(4). The glass transition temperatures measured were 960, 970, 1010, and 1020°C respectively, increasing with increasing nitrogen content in the melt.

Based upon the DTA studies, quench temperatures were selected to investigate oxidation and crystallization phenomena in HIP Run 1 melts. Three quench temperatures, ranging from 1000 to 1350°C, were selected. X-ray diffraction of the quenched melts revealed oxide, oxynitride, and nitride crystalline species. In general, low nitrogen content glasses crystallized only to oxides, whereas the high nitrogen content glasses formed oxide, oxynitride, and nitride crystalline phases. β -Si₃N₄ was the only all nitride crystalline phase which appeared upon quenching. The higher temperature quench experiments resulted in a large number of crystalline phases in all glasses.

PRELIMINARY JOINING EXPERIMENT

Two preliminary joining experiments were added to HIP Run 4 using melts 3(1) and 3(5) as joining materials. This HIP run was designed for oxynitride glass melting, consequently the joining experiments were exposed for 1.5 h to 1900°C at 207 MPa nitrogen pressure after being held at 1750°C for 2.5 h as the nitrogen pressure in the HIP was increased from 3.1 MPa to 207 MPa. Although the HIP operating parameters were not selected to optimize conditions for joining, the joints that were produced did provide significant information.

Both joints had appreciable strengths and appeared to be too strong to be separated for examination of interfacial regions. Cross sections of the joints were examined. Joint thicknesses of 0 to 7 μ m were observed. (Boron nitride shims were used between the silicon nitride pieces joined in order to provide a range of joint thicknesses.) At the 0 μ m joint thickness, no joining material was apparent and the joint was indistinguishable from the silicon nitride except for scattered carbon particles (from the furnace burnout). For increased joint thicknesses, joining material was observed by optical microscopy. EDS analysis indicated that the joining materials lost much of their initial yttria and alumina contents. Small voids were also observed in the thicker joint cross sections. Scanning electron microscopy indicated the same contrast (secondary electron emission) for the joint material and the silicon nitride. Microhardness measurements of 18 to 20 GPa were obtained in the joints. These data suggest that the joint material is largely silicon nitride, possibly β' -sialon.

JOINING TECHNIQUE DEVELOPMENT

INEL Hot Isostatic Press

A HIP has been procured from Autoclave Engineers, Inc. (Erie, PA) and installed in the Idaho Laboratory Facility (ILF). It will support both the Ceramic Joining and RSA Joining tasks of the Strategic and Critical Materials Program. This HIP (Model 30-L 5-11 GU 200 YOKE) has a maximum operating pressure of 30,000 psi; the pressure vessel can be evacuated to 10 μ m Hg. It was obtained with both a molybdenum and a graphite furnace which can operate at temperatures of up to 1500°C and 2000°C respectively. Either furnace can be operated in an argon or nitrogen atmosphere. The furnaces will accommodate eight workpiece thermocouples for improved temperature monitoring.

A Safety Analysis document was written and approved to support installation of the HIP in the ILF. This installation includes a 0.5 in. thick missile barrier around the HIP and a 2 in. diameter vent line to exhaust the working gas to the atmosphere.

INEL Joining Experiments

Installation of the HIP in the ILF brings this program to a new phase in which the emphasis is upon the fabrication and characterization of joints.

Initial joining experiments have been designed, and an apparatus assembled, to fabricate joints between silicon nitride pieces using a compressive-filling technique. Fabrication rig designs for an alternate joining technique, capillary filling, have also been investigated.

SUMMARY

Oxynitride melts of various compositions have been prepared by HIPping and characterized. HIP operating parameters and crucible materials were developed which permit the preparation of large (90 g), homogeneous, void-free oxynitride melts. Characterization of the oxynitride melts provided valuable chemical and physical property information that can be applied to joining. The devitrification of oxynitride glasses to produce β' -silicon precipitates was demonstrated. Initial joining experiments were performed using oxynitride glasses and joining materials. Joints with appreciable strength were produced and examined. These joints confirmed the approach of utilizing oxynitride glass joining materials to produce joints strengthened by the precipitation of silicon nitride and other toughening and strengthening precipitates.

REFERENCES

1. Tallman, R. L., R. M. Neilson, Jr., J. C. Mittl, S. P. Henslee, and P. V. Kelsey. Joining of Silicon Nitride Based Ceramics: A Technical Assessment. EGG-SCM-6572, March 1984.
2. U.S. Bureau of Mines, Strategic and Critical Materials Program Annual Report, May 1984, pp. 209-232.
3. Ezis, A., (Ford Motor Company) unpublished data, presented at the Seventh Annual Conference on Composites and Advanced Ceramic Materials, Cocoa Beach, FL, January 16-19, 1983.
4. Makishima, A., et al., Microhardness and Transparency of an La-Si-O-N Oxynitride Glass. Journal of the American Ceramic Society, v. 66, No. 3, 1983, pp. C-55-56.
5. Loehman, R. E., Oxynitride Glasses, Journal of Non-Crystalline Solids, v. 42, 1980, pp. 433-446.

NONDESTRUCTIVE EVALUATION OF CERAMIC AND RSA JOINTS AND MATERIALS

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and T. A. Place 2/

INTRODUCTION

The properties of substitutes for strategic materials depend on particular microstructural features unique to each material. Rapid solidification of alloy powders produces materials with very small grain size and improved corrosion resistance. Ceramics exhibit superior resistance to wear and corrosion at high temperatures but are prone to failure from very small microcracks and porous features. The role of nondestructive evaluation is to develop methods for measuring these critical microstructural features with field adaptable techniques so that the fitness for purpose of these advanced materials can be determined.

The primary effort of the NDE research task is in ultrasonic material characterization, coupled with a subcontract to the University of Idaho for internal friction measurements. The goal of these tasks is to correlate microstructural features with specific measurements. Ultrasonic measurements include velocity, attenuation, and backscattered radiation. The internal friction measurements investigate vibration loss factor, thermoelastic and hysteresis loop effects, and their correlation with mechanical properties. The ultrasonic techniques can be local and microscopic whereas the internal friction measurements reflect macroscopic averaged parameters of the material which are often useful for structural engineering.

The first part of this report summarizes the work done during the past year in the area of ultrasonic characterization in general and as it is applied to rapidly solidified processed (RSP) Type 304 stainless steel in particular. The three sections correspond to the three principal objectives for this year: determination of statistical grain size distribution parameters, characterization of microvoids and inclusions, and applications to RSP material properties and phase ratios. Improvements made in measurement techniques, limitations found in the utilization of the techniques, and results along with conclusions of the measurements are described in each section. The second part of the report presents the results of the internal friction subcontract.

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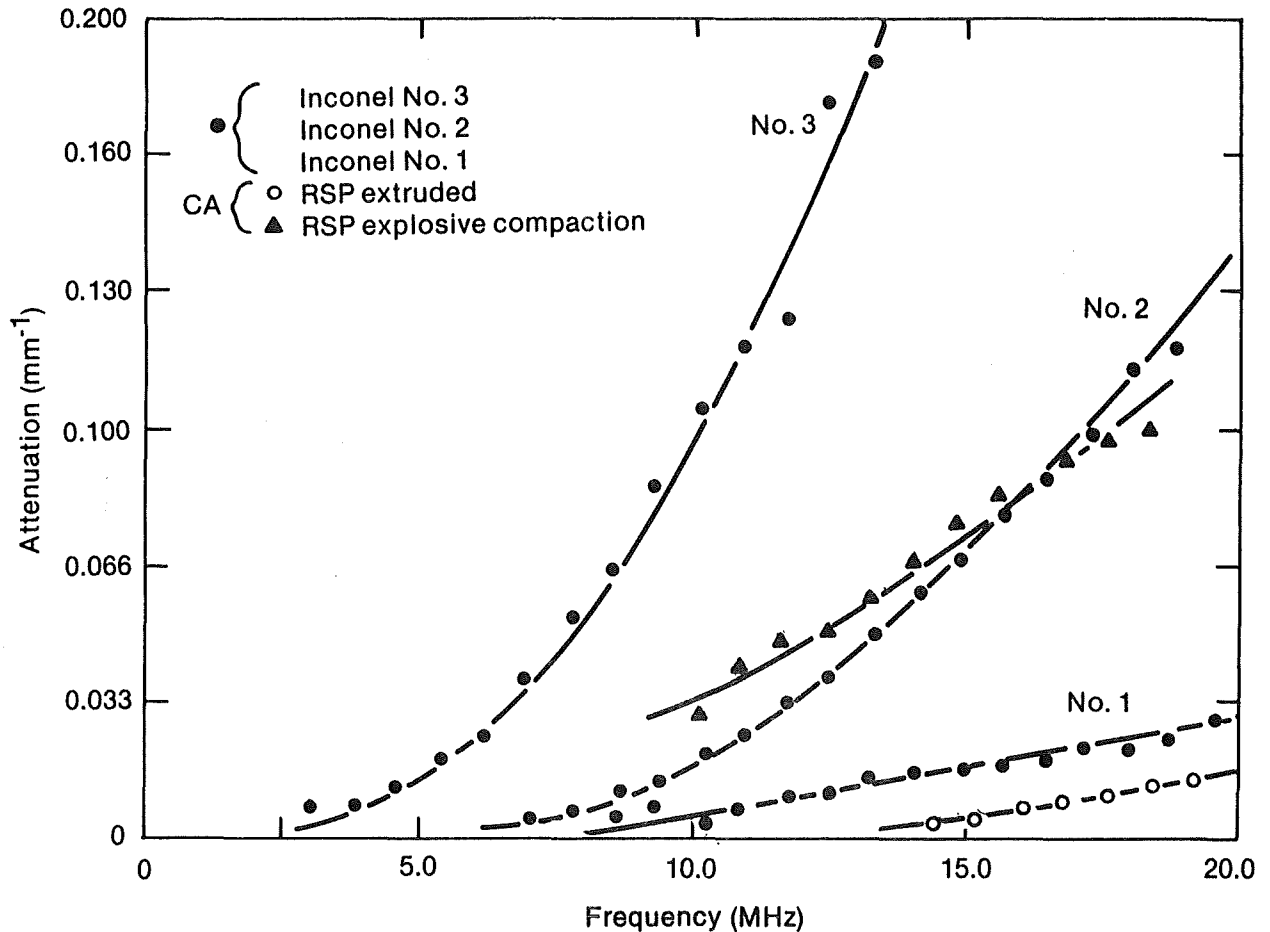
STATISTICAL GRAIN SIZE DISTRIBUTION

Many important physical properties of metal alloys depend strongly on the microstructure and particularly on the grain size, shape, and distribution. The goal of ultrasonic characterization is to determine as many parameters of the grain structure as possible nondestructively. Scattering of ultrasonic waves from grain boundaries and anisotropies is the primary source of information for these types of measurements. Experimentally, scattering leads to attenuation and backscattered radiation which are characteristic of the grains and readily measured.

Attenuation measurements were improved over the past year by the implementation of new equipment and software. New delay-line transducers and a 200 MHz digitizer allow routine measurements at frequencies up to near 100 MHz. Software, developed locally, accounts for the diffraction effects of the transducers and provides for quick and reproducible measurements. Several limitations were found in this technique. The inherent signal-to-noise ratio and the 8-bit digitization of the experimental equipment limit the measurement to samples with total attenuation within a specific range. Thus samples with a high attenuation coefficient or which are relatively thick must be measured at low frequencies. Some of the RSP samples exhibited such small attenuations that the highest frequencies had to be used. This restriction, coupled with uncertainty in extrapolating results beyond the range of measurement, can make comparisons between different samples difficult. Other limitations of this technique are that opposite faces of the sample must be parallel planes and that no depth information can be obtained.

A correlation of grain size with attenuation has been well established in the literature and in this work (1). Attenuation is used in this program as a standard technique for material properties determination. A set of Inconel alloy 718 samples form standards with varying grain sizes and evidence of twinning and precipitate formation--all characteristics which affect ultrasonic waves. Figure 6-1 shows the measured ultrasonic attenuation for the Inconels, which is directly correlated with the grain size. Results for Type 304 stainless steel powders consolidated by two different techniques--explosion and extrusion--are also shown. The large difference in attenuation between the two RSP samples is attributed to unconsolidated powder boundaries in the explosively consolidated sample resulting in increased scattering. Microscopic examination of the samples confirms this and shows that the extrusion sample exhibits complete consolidation and a very small grain size, typically less than 10 μm (2). As can be seen, attenuation measurements reflect important microstructural features and therefore form a very useful laboratory technique. Results concerning consolidation in RSP materials with annealing are presented in a subsequent section.

A potentially more useful technique is to record the radiation backscattered to the transducer as the ultrasonic wave passes through the material the first time. This signal is solely due to scattering



4 1588

Figure 6-1. Measured attenuations for centrifugally atomized (CA) RSP Type 304 SS materials prepared by extrusion and explosive consolidation along with Inconel alloy 718 samples with average grain sizes of No. 1 (22 μm), No. 2 (76 μm) and No. 3 (107 μm).

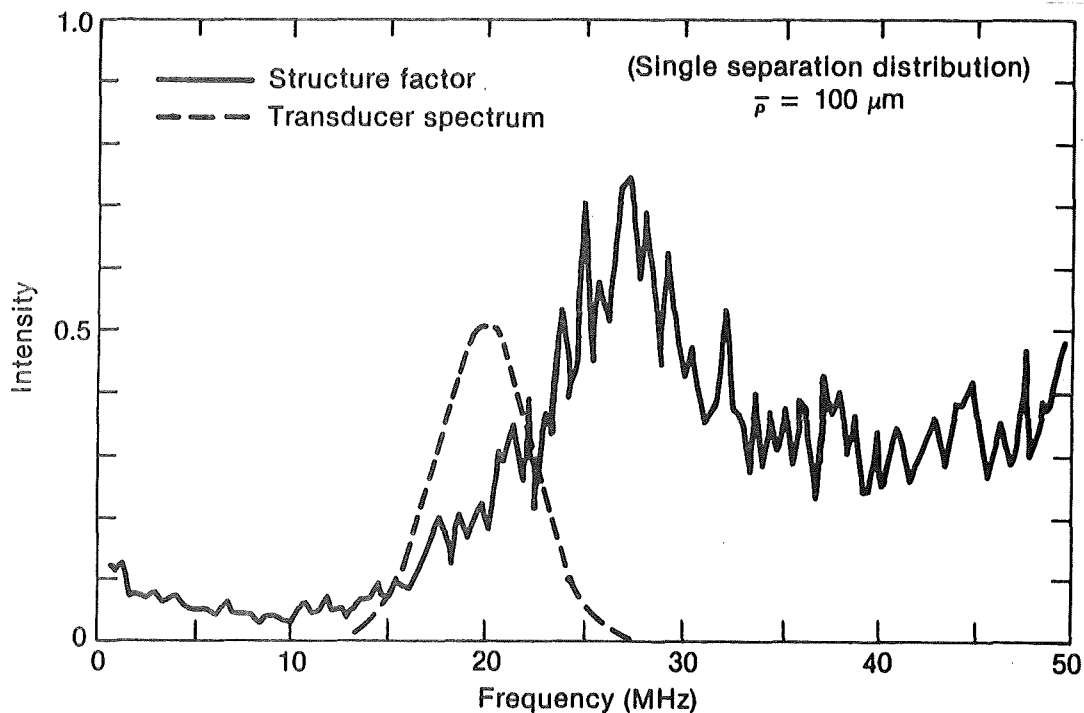
from the microstructure and its detection does not require access to the back face of the sample. Field use of this backscatter technique is relatively easy for these reasons; however, more stringent requirements are placed on the transducer and associated electronics. This program has set the development of the backscatter technique as one of its primary goals. To this end, the scattering process has been modeled on the computer to aid interpretation of experimental tests, test measurements have been made on standard and RSP samples, and the experimental requirements and limitations of the method have been characterized.

The computer model treats the scattering centers in the material as collections of individual particles. Each particle scatters the incident wave in a known way based on simple approximations of its shape and physical parameters, usually taken to be a sphere much smaller than an ultrasonic wavelength. The total backscattered signal is formed from summing contributions from all these particles while taking into account their locations in the incident beam. With suitable parameters, a variety of backscatter experiments can be

simulated and various types of data processing routines can be compared with theoretical expectations. A limitation of the model is that it does not take into account multiple scattering of waves within the bulk of the material, which occurs to some extent. This model does, however, provide results of primary importance in the scattering process and may help delineate regions where multiple scattering must be taken into account.

In RSP and ceramic materials the grain or flaw size is typically much smaller than the ultrasonic wavelength. The spatial distribution of the scattering centers then becomes more important than their size. The model is especially helpful in this case as the effects of particle position are readily apparent in the backscatter power spectrum. In particular, the distribution of particle positions gives rise to a structure factor which multiplies the backscatter spectrum and tends to shift the backscatter spectrum peak to higher frequencies than that of the incident pulse.

Figure 6-2 shows this simulated structure factor along with a typical incident pulse power spectrum. The backscatter spectrum is essentially the product of these two terms. An average of several measurements at different locations on the sample was required to bring out the average weighting effect seen in the structure factor. The peak in the structure factor occurs at a frequency corresponding to the mean interparticle separation distance for the sample. The more closely packed the particles are, the higher in frequency this peak occurs.



5 4397

Figure 6-2. Incident pulse power spectrum and calculated average structure factor for a collection of spherical inclusions with a gaussian separation distribution.

Figure 6-2 also shows that the effect of the structure factor is to weight more heavily the higher frequency components of the incident pulse. This appears to be observed in the measurements. However, if the particle position distribution is complex and cannot be described by a single mean interparticle distance, then the structure factor emphasizes a different and usually lower region of the power spectrum.

Several sample sets have been studied experimentally. These include the Inconel standards, a ceramic-metal composite known as a cermet, a synthesized glass with second phase inclusions, and explosively compacted RSP materials. The experiments consisted of recording the "grain noise" signal which is observed between the front and back surface reflections of the ultrasonic wave passing through the sample. This backscattered signal is windowed to separate contributions from different regions within the sample and subjected to one of several data processing routines. One such routine computes the cross-correlation between the signal observed at some reference point and neighboring points. The model predicts that the results should represent a mean correlation length similar to the interparticle separation. Unfortunately, the beam width of the transducer also enters and can mask the microstructure parameter. The measurement results show only a small change with grain size, so the beam width is believed to be the limiting factor. Improvements in narrowing the effective beam width such as may be obtained using the synthetic aperture approach might make this type of measurement very useful.

Another data processing routine tried was that of averaging the absolute value of the backscattered signal and determining its decay with time, which represents distance into the material. (The further the wave travels in the sample the more scattering it encounters which diminishes the wave amplitude.) This technique yielded results which correlated well with the mean grain size. The resulting decay constant was not comparable in magnitude to the attenuation coefficient measured earlier, although the same dependence on grain size was seen. This technique could be useful for comparative measurements, but it requires relatively thick samples to obtain a good determination of the decay constant.

A third routine calculates the power spectrum of the backscattered signal along with its first two moments. This calculation can be done for any windowed region of the backscatter signal and holds the potential for yielding depth information. The energy of the power spectrum was seen to scale very closely with attenuation, especially in the RSP materials where scattering is predominant. In addition, depending on the complexity of the microstructure, an upward shift of the average frequency of the backscatter was observed for the smaller grain size materials. A general pattern is evident from this comparative backscatter measurement of the set of materials described earlier.

In general, materials with grain size (or other scattering centers) much smaller than the ultrasonic wavelength produce little backscatter and hence attenuation. This is true even for very dense packings of small particles. Scattering does occur but it all adds constructively

in the forward direction. If the particles are arranged in clusters, then, as the model indicates, a great deal more scattering can occur as the cluster appears to the wave as a larger scattering particle.

Both the power spectrum area and the average frequency are descriptive of the size and distribution of the grains or scattering centers. Figure 6-3 shows the backscatter spectrum observed from the Inconel samples with a mean grain size of $22\text{ }\mu\text{m}$ along with the incident spectrum. The upward shift in frequency is apparent here but absent in similar data taken on a sample with a larger grain size of $107\text{ }\mu\text{m}$. These results and their interpretation formed the content of a presentation made at the IEEE 1984 Ultrasonics Symposium (3). These results of the past year's study show that several techniques can provide measurement of material grain structure and distribution through correlation of features of the backscatter signal. This work completes our planned initial study of the application of backscatter analysis to the determination of microstructure features; however, the positive correlations found provide encouragement that further research into signal processing and measurement methods will allow more quantitative characterization to be obtained nondestructively. In particular, work is planned for the next year to develop the positional cross-correlation and depth analysis techniques.

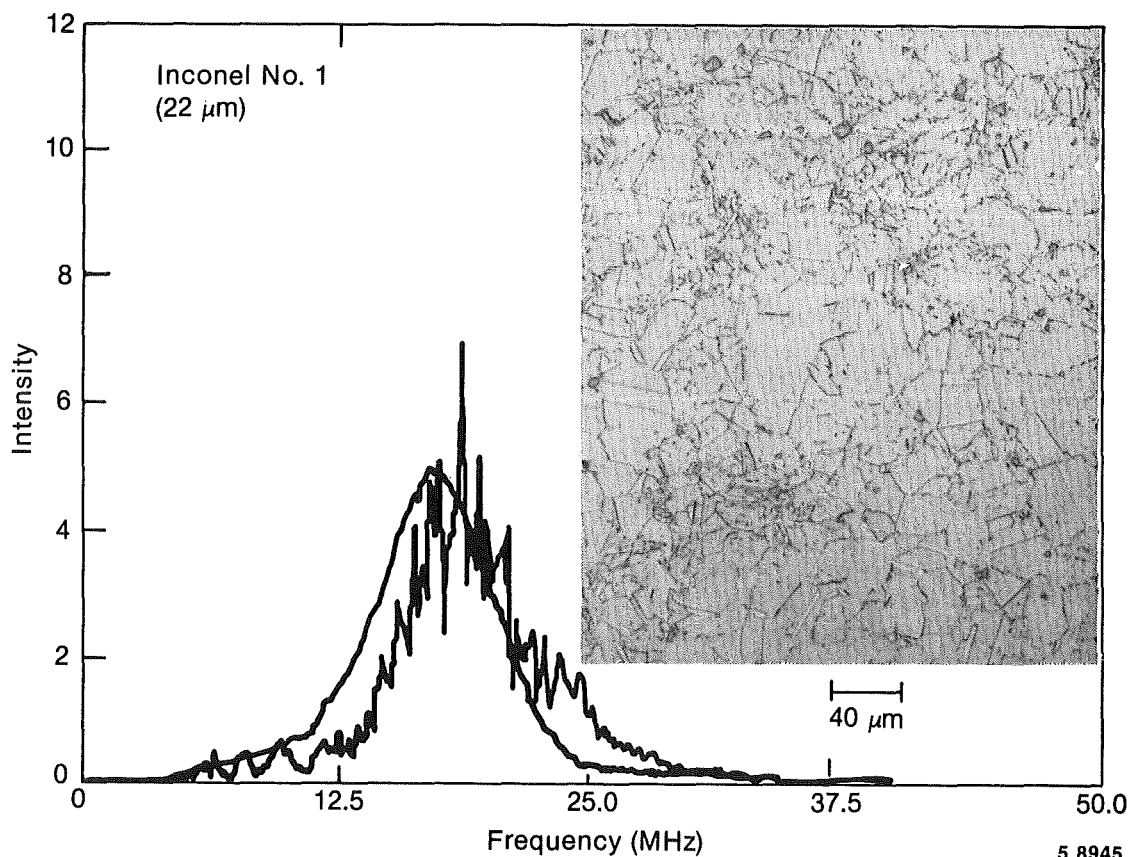


Figure 6-3. Incident pulse (smoother curve) and backscatter power spectra from the Inconel sample with grain size of $22\text{ }\mu\text{m}$.

Figure 6-2 illustrates some inherent limitations to the backscatter technique of measurement. The structure factor should be measured over the entire frequency range in order to have all the information possible; however, the measurement is limited to the bandwidth of the transducer. At low frequencies, where transducers are readily available, little scattering occurs due to the long wavelength. In the high frequency region the wide bandwidth of the transducer limits its sensitivity so that signal-to-noise ratio problems become a dominant factor. Narrow band transducers can increase sensitivity but sacrifice time and hence depth resolution. Therefore, the utility of the backscatter measurement depends on how these conflicting restrictions can be traded off. At present, measurements can be performed readily up to frequencies of 20-30 MHz, which is sufficient to observe scattering from particles smaller than 10 μm , depending on their number and spatial distribution. Even with this limitation, detailed tests of the consolidation of RSP powders were possible as described later. There is still room for considerable improvement with the acquisition of lower noise electronics and transducer optimization.

CHARACTERIZATION OF VOIDS AND INCLUSIONS

Small voids and/or inclusions of impurities and secondary phases can be detrimental to the performance of an advanced material. The problem of detecting their presence and concentration is much the same as that of measuring grain size and distribution. Ultrasonic measurements are again probably the most sensitive to imperfections such as voids and inclusions. Ultrasonic waves scatter significantly from these features since they present a large local change in acoustical impedance. The impedance of a void is essentially zero whereas that for an inclusion may be larger or smaller than the host material. This program has studied voids in cermet materials; a large increase in attenuation and backscatter was observed in comparison to the same material without voids. At present samples with known void distribution parameters have not been found.

A major emphasis has been placed on inclusions, as they are the more difficult to characterize. During the first year of this program, work was begun to develop a suitable solid material with controllable inclusions. A particular glassy material was chosen which could be synthesized with second phase spherical inclusions of controlled size and number (4). This material was made by the Ceramics group of the Materials Research Branch (INEL). This past year they were successful in synthesizing five samples of this glass with a variety of inclusion distribution parameters. The inclusions range from a high density ($1.1 \times 10^6/\text{mm}^3$), mean size of 2.5 μm , and uniform distribution to a small density ($8.0 \times 10^3/\text{mm}^3$), mean size of 5.0 μm , and nonuniform distribution. The very small inclusion sizes were chosen to simulate possible inclusions or grain sizes actually found in RSP materials.

The glass samples exhibit very little attenuation, making this type of comparison difficult. However, a wide range in the backscatter was recorded. Since the ultrasonic wavelength is about 300 μm in these samples at the test frequency, the model would predict little

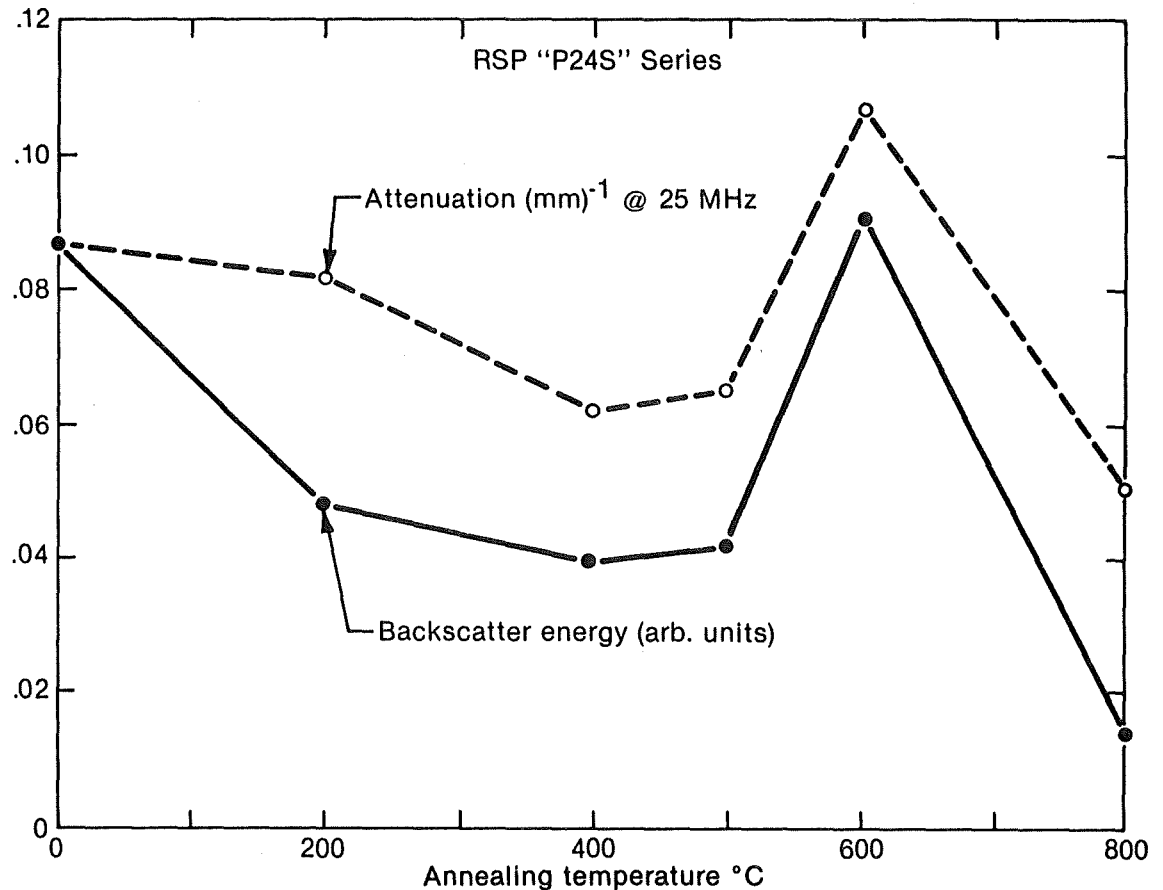
backscatter for inclusions of these sizes if they were uniformly distributed. The backscatter should scale as Na^6 , where "N" is the number of particles in the ultrasonic beam and "a" is the particle radius, assuming all the particles to be identical. The measurement results basically confirm this scaling. Of course, a distribution of particle sizes is present, as was measured microscopically. One sample, consisting of a high density of uniformly distributed 2.5 μm inclusions, showed a correspondingly very small backscatter barely above the electronic noise. Another sample with a similar high density of 2.5 μm inclusions exhibited backscatter about an order of magnitude larger. This second sample showed definite evidence of clustering and aggregation of the inclusions in some regions under microscopic examination. In other respects, the backscatter spectra were similar to those seen with the small grained Inconel test samples. The sample producing the most backscatter had the fewest inclusions but of the largest size, 5 μm , and exhibited substantial clustering.

This work completes the initial tests planned on synthesized glasses and was intended to highlight the most important parameters describing a collection of inclusions. These parameters are the size and number of inclusions and, equally significant, the manner in which they are distributed. Clustering was found to greatly increase the backscatter, probably since it introduces characteristic lengths into the distribution of inclusions on the order of the ultrasonic wavelength. This accounts for the fact that backscatter from these very small inclusions was observable at all.

RSP MATERIAL PROPERTIES AND PHASE RATIOS

Samples of both extruded and explosively consolidated RSP 304 stainless steel powders were obtained from the Metals Branch (INEL). Attenuation measurements on these samples were shown in figure 6-1. The extruded sample exhibited very small attenuation and essentially no measurable backscatter due to the extremely small grain size of less than 10 μm , which indicates that complete consolidation of the powder was obtained. From the discussion on inclusions above, this fact suggests that the grain structure is also uniform.

The explosively consolidated samples show considerable attenuation and backscatter, which is believed due to unconsolidated powder boundaries. With the present sensitivity and noise levels in the measurement technique, different structural phases in the grains of the material are not observable due to the small size of the grains. Two sets of annealed, explosively consolidated RSP samples are being tested ultrasonically. The sets include both centrifugally atomized (P24S series) and dissolved gas atomized (H24E series) powders. Figure 6-4 shows initial results of these tests for the P24S series. Both attenuation and backscatter energy (normalized for the unheated sample) are displayed and agree quite well with each other. Microscopic examination has thus far revealed that changes in the unconsolidated powder boundaries are occurring with annealing temperature. The exact nature of these changes is under study. At 600°C a large increase in scattering occurs which drops abruptly at 800°C. This signals the



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Figure 6-4. Measured attenuation and backscatter energy for the RSP "P24S" series samples explosively consolidated and annealed for 1 h at various temperatures. The backscatter is arbitrarily normalized to the attenuation for comparison.

onset of sintering of the boundaries with complete loss of the boundaries being observed for temperatures above 800°C. Initial results for the H24E series show similar changes with annealing temperature, though less pronounced. Both the attenuation and backscatter for this material are considerably smaller than for the P24S series, indicating smaller, more uniformly distributed unconsolidated boundaries are present. This work is still in progress and has been submitted for presentation at the upcoming review conference on nondestructive evaluation of materials (5).

INTERNAL FRICTION

The purpose of this work is to develop a nondestructive means of estimating mechanical properties. The basis for this approach is the knowledge that the microstructure affects mechanical properties and internal friction measurements; however it is not known if the same microstructures affect both in the same relative manner. Engineering judgement is being used in this research in attempting a correlation between internal friction and mechanical property measurements.

A710 steel was used in these tests because mechanical properties have already been determined by EG&G and rapidly solidified alloys (RSA) were not yet available. The measurements of internal friction investigated initially are loss factor and load-strain hysteresis.

This report is four parts. The first part presents the effect of cold rolling and test temperature on the loss factor (damping) of A710 steel longitudinal specimens. The next part reports on results from specimens employed to maximize the thermoelastic damping effect as hypothesized by Zener (6). The third section gives an overview of the work in progress on testing specimens with different microstructures at high strain amplitudes in an MTS 810 Structural Test System for comparison of damping capacity using the hysteresis loop technique. The final part describes work which will be performed at the INEL using a piezoelectric crystal technique.

Effect of Cold Rolling and Temperature on Loss Factor

A710 steel longitudinal specimens with different microstructures were tested using the impulse-excitation technique to detect changes in loss factor (damping capacity). The specimens were originally designed to be tested as free-free beams with dimensions of 12 in. (length) x 0.75 in. (width) x 0.2 in. (thickness). This specimen geometry was arrived at for obtaining damping data covering the medium frequency range (100-25,000 Hz) since this was the limitation of the available frequency spectrum analyzer. Figure 6-5 shows the influence of cold rolling (0, 25, 40, and 50%) on the loss factor at room

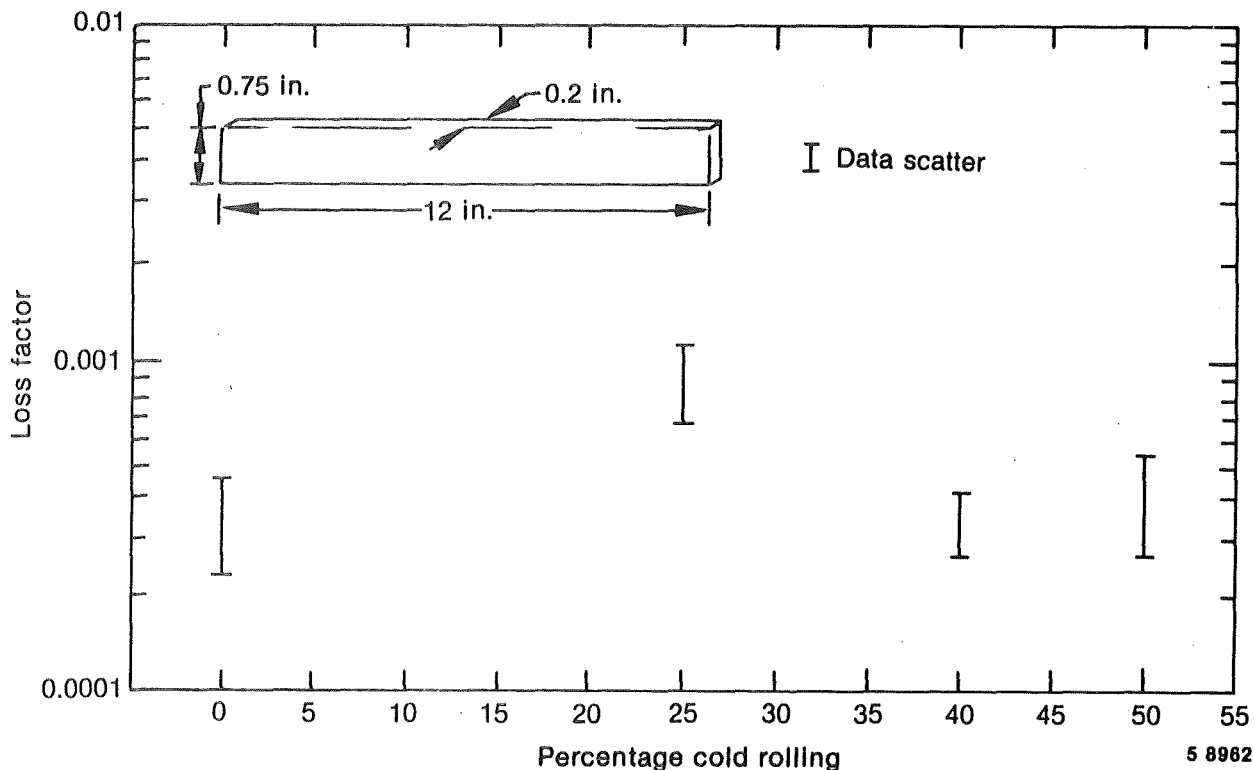


Figure 6-5. Influence of cold rolling on the loss factor of A710 steel (at room temperature).

temperature. The graph shows the scatter with three specimens tested in each state of plastic deformation. As can be observed, the loss factor shows an increase of approximately a factor of three from 0% cold rolling (CR) to 25% CR but surprisingly drops and remains constant for the 40% CR and 50% CR specimens. The increase in loss factor with increase in cold rolling to 25% is correlated to the increase in yield strength (450 MPa at 0% CR and 750 MPa at 25% CR). The decrease in loss factor for increased cold rolling (>25%) is a reversal, since the yield strength continues to increase but at a much lower rate. The fracture toughness decreases with increasing cold rolling which suggests no correlation with the loss factor although sufficient data are not available to make a more definite observation. This reversal of loss factor illustrates that a change in the fundamental parameters affecting internal friction has occurred.

Since A710 is a ferritic steel, it undergoes a ductile-to-brittle transition at around -18°C . Therefore the damping capacity measurements for the cold rolled material (0 and 25%) were obtained over the temperature range -60°C to 150°C for evaluating the response of this technique to changes in mechanical behavior without changes in microstructure. The loss factors are constant and overlapping for -60 , -20 , 100 , and 150°C , but are distinctly different at room temperature. The room temperature results cannot be explained at this time.

Thermoelastic Damping

All previous specimens had been designed to avoid the thermoelastic peak. The present specimens were deliberately designed to maximize thermoelastic damping at 20 Hz. According to Zener's damping theory, thermoelastic damping is a function of Young's modulus, the coefficient of linear expansion, and specific heat. His theory was used to design a specimen that would have a fundamental resonant frequency of 20 Hz. This was verified experimentally. The variation of damping with frequency, as per Zener's thermoelastic theory, is shown by the solid line in figure 6-6. The experimental results for 0, 25, and 40% CR are also shown in figure 6-6. Distinct differences were observed between the 40% CR specimens and the 0 and 25% CR specimens. The 0 and 25% data are very close to the theoretically predicted value. The loss factor is continuing to increase for cold rolling ranging from 0 to 50% as compared to the results given in figure 6-5. The former results are consistent with the constant changes in yield strength and fracture toughness. At the present time, it is not possible to reconcile these different observations. Work is still in progress on evaluating the effect of temperature on specimens with this geometry. Air damping has been evaluated and was not found to be a serious problem for these damping capacity measurements.

High Strain Methods

The results discussed in the first two sections are based on internal friction measurements made at low strains. It was deemed necessary to make internal friction measurements at high strains since the

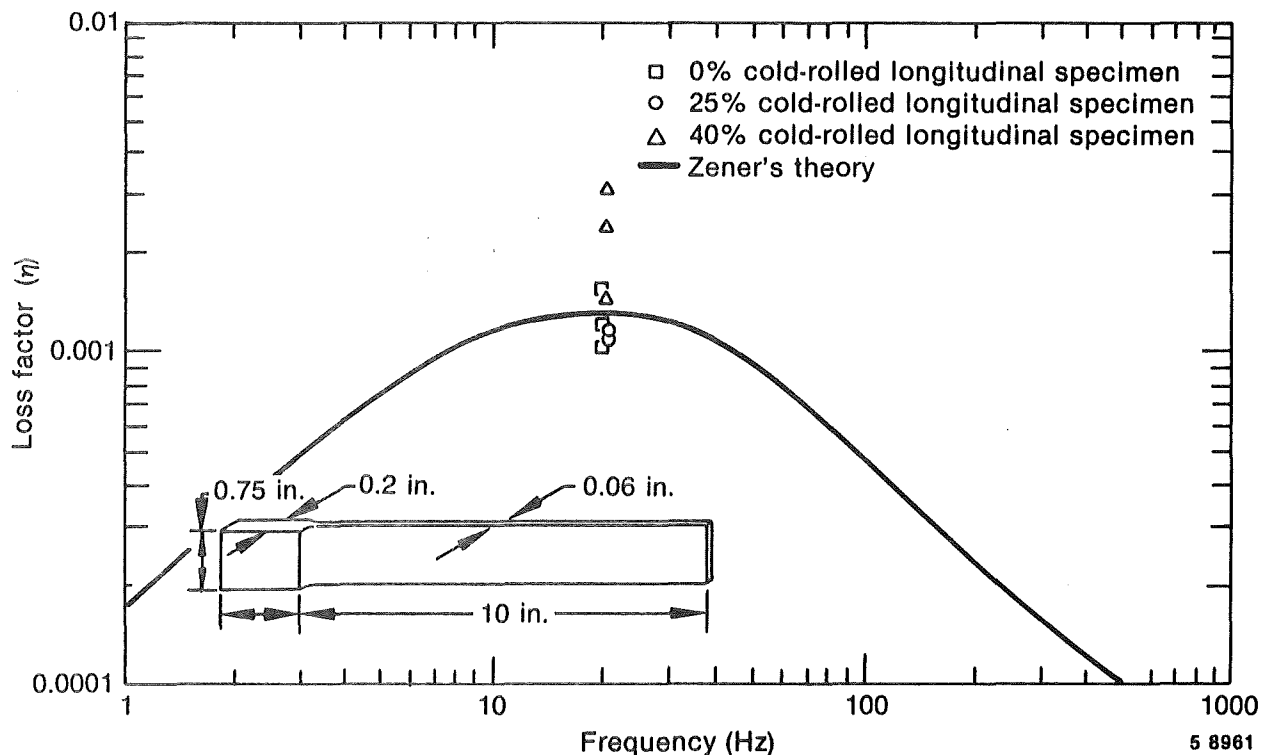


Figure 6-6. Influence of cold rolling and frequency on loss factor (for A710 steel thermoelastic damping specimens).

microstructure-mechanical property relation occurs at higher strains, e.g., break away of dislocations resulting in yield. Therefore, the following work is conducted at higher values of strain.

A servo-hydraulic test machine is being used to obtain internal friction measurements. Damping data for small strain gaged specimens (0, 25, and 40% CR) were obtained from the resulting load-strain (or stress-strain) hysteresis loop on an X-Y plotter. Loading was applied through 3/8 in. diameter steel clevis pin fixtures. A tensile prestress was applied so that the specimen was always in tension and possible nonlinearities associated with load reversal were avoided. The amplitude of the alternating load was about 80% of the yield stress. Data from the measured hysteresis loops were converted to damping in terms of the loss factor. The loss factor here is as defined in Reference 7.

The X-Y plotter introduced its own phase lag at frequencies above approximately 0.1 Hz. Thus, with the equipment used, the frequency for the damping measurements was limited to 0.1 Hz. The hysteresis loops for these specimens showed large variations between specimens with the same microstructure, so the specimen geometry and the grips have been redesigned to allow the specimen to be subjected (without phase lag) to a tension-compression cyclic loading at 0.1 Hz. With such a configuration, it is expected that the resulting hysteresis loop would be wider and would stabilize after a number of cycles permitting proper comparison of the damping data for the various microstructures.

Internal Friction Measurements Using Piezoelectric Crystals

The tests performed at INEL will investigate the effect of changes in microstructure and the effect of temperature through the brittle-ductile transition (no microstructural change) on internal friction (mechanical damping) measurements. A710 specimens will be mechanically vibrated by a piezoelectric quartz crystal in the 40 kHz range. The mechanical damping parameter is obtained from the driver and gauge voltages as described by Marx (8), and Robinson and Edgar (9). The 40 kHz range is dictated by the quartz crystal drivers. Strains will extend up to 10^{-3} to completely characterize damping response. These test results at 40 kHz will be compared with those obtained at 0.1 Hz at the University of Idaho. These comparisons will provide similar results at substantially different frequencies. Preparation for these experiments is currently underway.

REFERENCES

1. Seydel, J. A., et al. Nondestructive Evaluation of Ceramic and RSA Joints and Materials. Ch. in Strategic and Critical Materials Program Annual Report, May 1984. Ongoing BuMines contract J0134035, p. 234.
2. Flinn, J. E. and G. E. Korth. RSP Powder Consolidation and Characterization. SCM Program Status Report, August through November 1984, p. 95.
3. Telschow, K. L. and G. D. Lassahn. Effects of Scatterer Spacing Statistics on Ultrasonics Backscatter Signal Spectra. Proceedings of the IEEE 1984 Ultrasonic Symposium, ed. by B. R. McAvoy. IEEE Publishing Services, New York, v. 2, 1984, p. 852.
4. IBID., Seydel, J. A., et al., p. 257.
5. Telschow, K. L. and J. E. Flinn. Ultrasonic Backscatter and Attenuation in Consolidated RSP Powder. Review of Progress in Quantitative NDE Conference 1985, Williamsburg, VA, June 1985.
6. Place, T. A., Third Progress Report, 13 March 1984.
7. Gibson, R. F. Vibration Damping Characteristics of Graphite/Epoxy - Composites for Large Space Structures. Proceedings of NASA Large Space System Technology. Third Annual Review, November 16-19, 1981.
8. Marx, J. Use of Piezoelectric Gauge for Internal Friction Measurements. Rev. Sci. Ins. v. 22, 503 (1951).
9. Robinson, W. H., and A. Edgar. The Piezoelectric Method of Determining Mechanical Damping. Physics and Eng. Lab., D.S.I.R., New Zealand, TN, 204, November 1970.

SUBSTITUTE CATALYTIC MATERIALS FOR PLATINUM

By R. B. Wright 1/

A significant portion of all of the platinum used in this country is utilized in catalytic materials for the petroleum, chemical, and environmental control industries. Given the industrial economic pressures to reduce costs and increase productivity, and the potential vulnerability of platinum from foreign suppliers, the need to develop new substitute materials with the catalytic performance characteristics of platinum is obvious. Platinum-based catalysts are used in a number of different catalytic reactions; this project has primarily addressed the catalytic reforming process which is used to convert saturated hydrocarbons to aromatic hydrocarbons necessary for high octane gasoline (1).

For reforming-type catalytic processes, the platinum or platinum containing bimetallic cluster is dispersed on a high surface area oxide support which itself participates in the overall catalytic process. There appears to exist a definite synergism between the metal and the oxide support, but a complete understanding of this interaction is still lacking. Other aspects of the catalytic process which are not sufficiently understood are the roles played in the various catalytic reactions by the metal electrons, their occupancy and spatial extent, and the structural arrangement of the metal atoms. Since platinum appears to possess rather unique electronic and structural properties, this project was undertaken to investigate the catalytic potential of a number of intermetallic alloy systems in the hope that they may duplicate or exceed the catalytic performance of platinum and thus serve as alternatives for platinum-based reforming catalysts.

Intermetallic compounds are alloys of two or more metals which have characteristic crystal structures and definite stoichiometries. As a group, these intermetallic compounds exhibit remarkable chemical and thermal stability (both desirable in a catalyst) as well as possessing unique electronic arrangements. By altering the intermetallic composition of these materials it may be possible to duplicate, or even improve upon, the electronic and physical structure of platinum. The work of Engel and Brewer (2-4) has demonstrated that intermetallic alloys formed from "early" transition metals (Groups IIIB, IVB, VB, and VIB) in combination with the "late" transition metals (Groups VIII and IB) maximize the utilization of all electrons and atomic orbitals resulting in very stable compounds possessing properties of potential catalytic significance (5).

During the first year of this program unsupported intermetallic compounds containing Group IVB (Ti and Zr) and Group VIII (Fe, Ni, and Pt) and Group IB (Cu) transition metals were prepared by direct arc melting, and aqueous precipitation and freeze-drying methods followed by thermal decomposition and reduction. Various bulk and surface sensitive compositional and structural techniques were used to

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characterize the samples with regard to their surface chemical composition, physical structure, and morphology. A versatile system using catalytic microreactors was designed and assembled to test the catalytic reactivity and product selectivity of the prepared intermetallic alloys by using model reactions of relevance to catalytic reforming. Pure platinum samples served as a basis for comparison for these studies. The second year of this program will expand these efforts to include new intermetallic compounds, the preparation of supported catalysts (i.e., intermetallic alloys dispersed on high surface area oxides and other inorganic supports), and additional model catalytic test reactions to monitor their catalytic performance.

In order to fully understand the properties of a catalyst system, three principal areas of catalyst design are addressed in this study:

1. Catalyst preparation
2. Catalyst characterization (before and after testing)
3. Catalyst testing

Research into each of these three interrelated areas has been undertaken and the results thus far in each area are summarized below.

CATALYST PREPARATION

Techniques for preparing pure, single phase, low surface area samples of selected intermetallic alloys consisting of combinations of Group IVB (Ti and Zr) with Group VIII (Fe, Ni, and Pt) and Group IB (Cu) metals have been investigated. A direct arc melting method employing a tungsten stinger in a Ti-gettered, argon backfilled, arc melter equipped with a water-cooled copper sample hearth was used to prepare the following intermetallics: ZrNi_3 (2 samples), ZrCu_3 (2 samples), ZrPt_3 (3 samples), TiNi_3 (2 samples), TiNi (1 sample), TiCu_3 (2 samples), and TiPt_3 (2 samples). Each sample button weighed between 1 to 10 g; the buttons were arc melted five times to help assure homogeneity. Starting metal purity was at least 99.99% and either powder or metal foil pieces were used. (These samples were prepared by Dr. David Cocke and M. Owens at the Chemistry Department, Texas A&M University, College Station, Texas.) The metal buttons were sawed in half using a diamond impregnated saw; one half was mounted in epoxy resin and polished for SEM/EDX analysis. The other half of the button was powdered using a liquid nitrogen cooled hammer mill and sieved to -200 (74 μm) +320 (44 μm) mesh. The sieved samples will be used for the characterization and testing aspects of the program. It should be noted that no iron was picked up during the hammer milling as indicated by EDS and Auger analysis of the powders.

Vacuum freeze-drying has been used to prepare a number of intermetallic precursor compounds. This technique offers the opportunity to prepare fine, homogeneous intermetallic powders with excellent control over impurity levels and composition. Nominal ZrCu_3 , ZrNi_3 , ZrFe_2 , TiCu_3 , TiNi_3 , and TiFe_2 mixtures have been prepared using stoichiometric amounts of the respective chlorides dissolved in water. This solution is then sprayed into a container of

liquid nitrogen which rapidly freezes the mixture, retarding the ionic mobility and thus maintaining the homogeneity that was present in the original aqueous solution. The frozen sample is then rapidly transferred to a vacuum vessel which is in turn evacuated with a liquid-N₂ trapped mechanical vacuum pump to 10⁻³ Torr. The vacuum causes the water to sublime, leaving a fine powder consisting of an intimate mixture of the metal chlorides. This powder will in turn be decomposed at elevated temperature and reduced with hydrogen to the desired intermetallic. It is hoped that this method will permit the preparation of samples having higher surface areas than those achievable by grinding the buttons prepared by arc melting.

Precursor intermetallic compounds are also being prepared using a technique wherein an insoluble stoichiometric mixture of the precursor intermetallic is precipitated from an aqueous solution using a suitable precipitating anion. The precursor compound ZrNi₃ has been prepared using potassium oxalate (K₂C₂O₄), sodium hydroxide (NaOH), or ammonium hydroxide (NH₄OH) as the precipitating reagent. Of the hydroxides, NaOH appears to be the best since it avoids the possible formation of soluble amine complexes which is possible with NH₄OH. The starting compounds ZrCl₄ and NiCl₂·2H₂O were dissolved in distilled water in the stoichiometric amounts required to form ZrNi₃ after decomposition and reduction of the precipitate. The precipitate was formed by addition of the chosen precipitating agent. Due to the gelatinous nature of the precipitates, conventional filtration techniques proved unacceptable so the solutions were centrifuged. The centrifuged material was washed five times with water, centrifuging between each washing, and finally air dried overnight at 105°C in an oven. The next step will be to attempt to decompose/reduce the precipitates to the intermetallic and still maintain the high surface area of the powder. The development of this technique will also be of importance during the second year of the project when the preparation and properties of intermetallic alloy clusters supported on carbon and inorganic oxides will be studied.

Preparation of intermetallic alloys was also attempted by melting stoichiometric quantities of the powdered alloying metals in alumina and graphite crucibles placed in a resistively-heated tungsten wire basket under a vacuum of ~10⁻⁷ Torr. The temperature was slowly raised until melting occurred as observed through an optical window on the vacuum chamber. Due to obvious vaporization of copper and nickel from the melts when ZrCu₃, ZrNi₃, and TiNi₃ were made, this method was discontinued due to nonstoichiometric compound formation.

Initial attempts to grow single crystals of the intermetallics were not successful. ZrPt₃ (m.p. = 2152°C) was the first material selected for single crystal growth. A modified horizontal Bridgeman technique using a graphite Brew furnace was used. A specially machined MgO capsule to contain the intermetallic during growth was first tried but was not successful due to flow distortion. Vitreous carbon capsules of linen-based phenolic resins that had been machined to twice the desired size and then heat treated in vacuum to 1000°C were next tried. The ZrPt₃ wet the surface of the vitreous carbon capsule, but

no carbide formation was observed. One requirement for the successful growth of single crystals by this method is that the temperature of the furnace be stable for at least 3 to 4 h. Arcing problems developed in the furnace which caused the temperature controller to shut off. This problem persisted and the attempt was discontinued.

CATALYST CHARACTERIZATION

The sliced, mounted, and polished arc melted samples were studied using SEM/EDX methods to determine their phase homogeneity and bulk composition. Most of the samples were found to be single phase with the expected composition. The exceptions were those containing copper where it was determined that in addition to the expected phase (ZrCu_3 and TiCu_3), MCu and M_2Cu_5 ($\text{M} = \text{Zr}$ or Ti) were also found, indicating that some copper was lost due to vaporization during sample preparation.

Studies of the surface chemistry, composition, and structure are being conducted using ultra-high vacuum surface analytical techniques: Auger spectroscopy (scanning and static Auger microprobe equipment, INEL), X-ray photoelectron spectroscopy, XPS (INEL and Texas A&M University), and secondary ion mass spectrometry, SIMS, and ion surface scattering spectrometry, ISS (both at Texas A&M University). Initial results using Auger spectroscopy indicate that the samples are enriched in zirconium or titanium at their surface due to surface segregation induced by formation of the very stable oxides (ZrO_2 and TiO_2) of these metals. These measurements were made by depth profiling the surface composition using a 2 keV Ar^+ beam to slowly erode away the sample's surface while simultaneously monitoring the composition with the Auger technique. The sample surfaces were all highly oxidized and it was found that it was extremely difficult to achieve, let alone maintain, an oxide-free surface even under the ultra-high vacuum conditions ($\sim 5 \times 10^{-10}$ Torr) present in our equipment.

In support of these observations a theoretical model has been developed based on the thermodynamics of a regular solution approximation of a binary alloy. Included in this model are approximations to account for the inducement of surface segregation by the adsorption of reactive gases and the subsequent formation of surface chemical compounds on the binary alloy. This model indeed predicts the segregation of zirconium and titanium in their respective copper and nickel alloys upon exposure to oxygen as was experimentally observed.

CATALYTIC TESTING

In order to satisfactorily complete a comprehensive examination of the catalytic utility of the selected intermetallic compounds, their catalytic performance must be evaluated. Since the project is concentrating on the catalytic performance of platinum in reforming-type catalytic processes, various test reactions have been chosen, to be performed in laboratory microreactors, to evaluate the reactivity

and selectivity of the intermetallic compounds. Reactions of importance to catalytic reforming are hydrogenolysis, hydrogenation, dehydrogenation, and isomerization.

A catalytic microreactor test system was designed and assembled during the past year for use in the determination of the catalytic potential of the prepared intermetallic alloys. Essentially this system consists of a glass catalytic test cell with provisions for controlled heating of the cell, introduction of various gaseous reactant streams, and analysis of the catalyzed reactant products. The microreactor test cell, shown schematically in figure 7-1, uses glass-to-metal seals, copper gasketed Conflat-flanges, and 316 SS Swagelok fittings. The vacuum system uses a 300 L/s turbomolecular pumping system connected to an all Conflat-flanged vacuum chamber. The gas manifold is constructed out of 316 SS Swagelok fittings with provision for purifying the gases used for the catalytic testing. There are three independent manifolds, each of which can be pre-evacuated using the vacuum pumping system. Each manifold also contains a variable mass flow rate controller to mix the different reactants in various proportions. The reactant manifolds are connected together at a common junction for delivery to the test cell. A schematic diagram of one of these manifolds is shown in figure 7-2. Extra care was taken to assure a leak-free system (a He leak detector was used during assembly) and means to remove O_2 and H_2O impurities from the gas streams in order to control, and later study, the effects of these gases on the catalytic performance of the intermetallic compounds.

The initial test reaction which will be used is the hydrogenation of ethylene. Values for the reaction rates of various unsupported metals (including Pt) are available in the literature. Pure platinum will initially be tested in the system to, in a sense, calibrate it and thereby obtain a standard of reference for comparing the activity of the above described intermetallics as determined in our test system. The reaction test conditions are given in figure 7-3.

The test system will be slightly modified to permit additional test reactions to be run. A standard reaction to test the hydrogenolysis (C-C bond rupture with subsequent C-H bond formation) activity of a catalyst is to study ethane hydrogenolysis to form methane. Another test reaction to determine the activity, as well as selectivity of the prepared materials, is the hydrogenolysis of n-heptane. Products of the hydrogenolysis of n-heptane are C_1 - C_6 alkanes, in relative amounts dependent on the catalyst.

Isomerization reactions of alkanes and cycloalkanes are another class of reactions which are very important for the catalysts used in commercial reforming. These reactions occur readily on bifunctional catalysts which contain both metal and acidic sites (due to the oxide support). In these bifunctional catalysts the metal and acidic sites catalyze different steps in the isomerization reaction sequence. Test reactions for isomerization activity of supported intermetallic catalysts will be heavily utilized in the second year of the program.

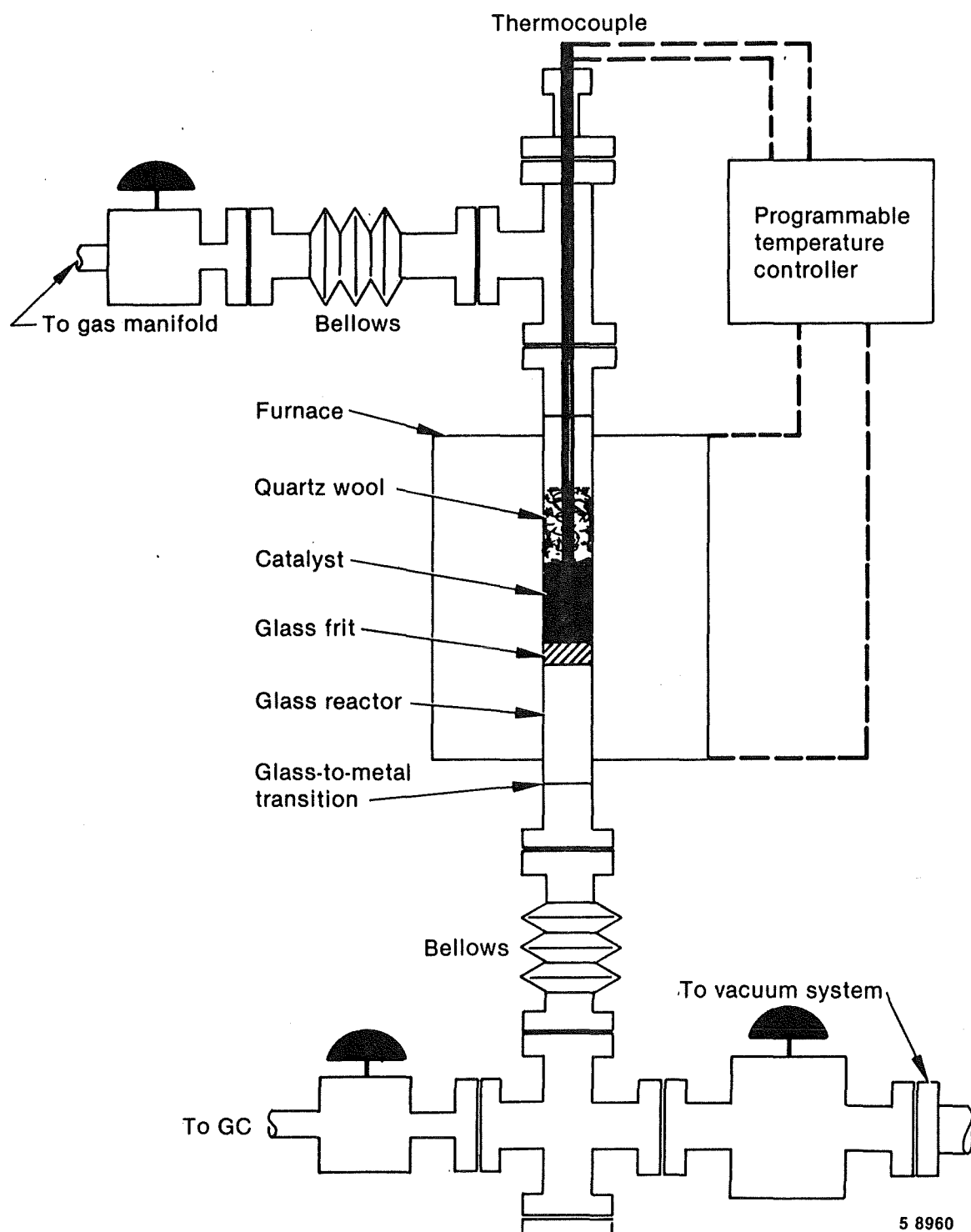
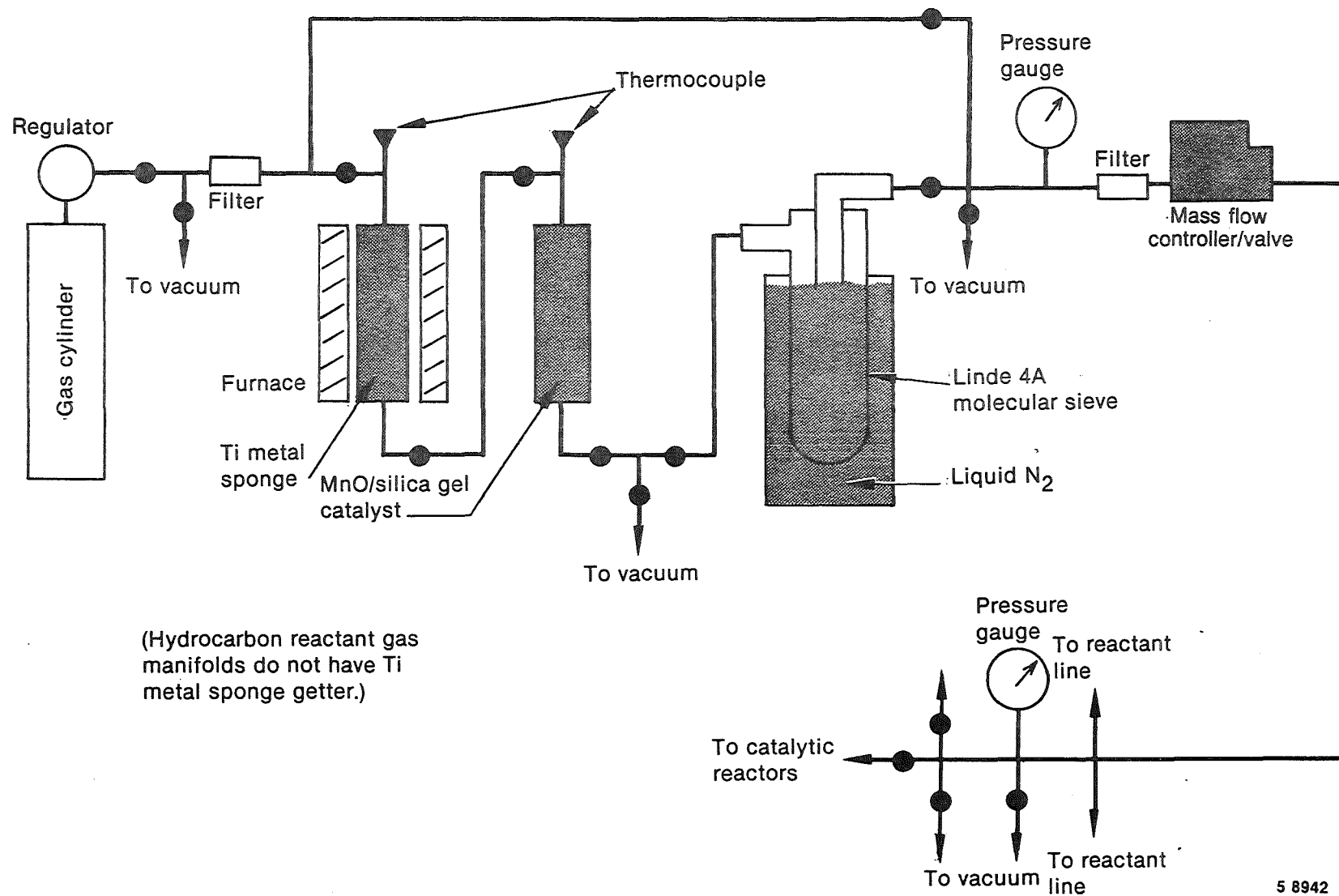


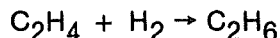
Figure 7-1. Diagram of the catalytic microreactor test cell.



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Figure 7-2. Reactant gas manifold.

Ethylene hydrogenation to ethane



Reaction conditions:

- 10-15 mg powdered intermetallic [44-74 microns (-200 + 320 mesh)]
- 1 atm total pressure
500 std. cm³/min flow rate
0.02 to 0.35 atm C₂H₄
0.05 to 0.8 atm H₂
Balance He (or Ar)
- 25-160°C temperature range

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Figure 7-3. Catalyst test reaction.

However, it is also well established that isomerization reactions of alkanes and cycloalkanes can occur on metal catalysts which do not contain separate acidic sites. One test reaction involves the conversion of n-hexane to 2-methylpentane and 3-methylpentane.

Correlations amongst the preparation, characterization, and testing aspects of the program will be formulated and used to successively understand the relevant catalytic interactions and processes. These correlations will in turn be used to determine the selection of the intermetallic composition and to refine and control the steps required to produce a desired property in the finished catalyst.

REFERENCES

1. Gates, B. C., J. R. Katzer, and G. C. A. Shuit. Chemistry of Catalytic Processes. McGraw-Hill, New York, 1979, p. 184.
2. Engel, N. Acta Metall. v. 15, 1967, p. 557.
3. Brewer, L. Acta Metall. v. 15, 1967, p. 553.
4. Brewer, L. Ch. in High Strength Materials, ed. by V. F. Zackay, Wiley, New York, 1965, p. 12.
5. Cusumano, J. A., R. A. Dalla Betta, and R. B. Levy. Catalysis in Coal Conversion. Academic Press, New York, 1978, p. 124.