PRODUCTION OF MOLYBDENUM METAL BY MAGNESIUM REDUCTION OF MOLYBDENUM OXIDES

By T. T. Campbell, F. E. Block, and E. R. Andersen

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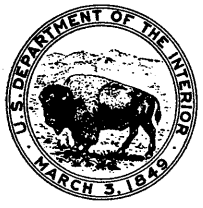

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CONTENTS

	Page
Summary	1
Introduction	2
Experimental procedures and results	2
Reduction of molybdenum trioxide	6
Reduction of molybdenum dioxide and mixtures of dioxide and trioxide	10
Properties of bomb-reduced molybdenum	13
Chemical and spectrographic analyses of bomb-reduced molybdenum	15
Evaluation of bomb-reduced, arc-melted molybdenum	17
Fabrication of arc-cast molybdenum	19
Conclusions	20
Bibliography	22

ILLUSTRATIONS

Fig.		
1.	Free-energy change for magnesium and calcium reductions of molybdenum oxides	3
2.	Loaded reactor before firing	4
3.	Pressure diaphragm assembly	5
4.	Molybdenum regulus produced in 4-inch diameter bomb. Half section shows typical porosity of regulus metal	10
5.	Thirty-seven pound cast molybdenum regulus	13

ILLUSTRATIONS (Con.)

Fig.		Page
6.	Consumable electrode formed by welding molybdenum reguli together	14
7.	Arc-melted molybdenum ingot weighing 124 pounds	15
8.	Macro-etched molybdenum ingot showing typical large columnar grain structure	17
9.	Microstructure of magnesium-reduced molybdenum from run MoA 34 (X 500)	18
10.	Microstructure of calcium-reduced molybdenum from run MoA 55 (X 500)	18
11.	Microstructure of magnesium-reduced molybdenum from run MoA 36 (X 500)	18
12.	Microstructure for magnesium-reduced molybdenum from run MoA 38 (X 500)	18
13.	Molybdenum ingot sections after press forging	19

TABLES

1.	Analyses of impurities in components of the charges	6
2.	Effect of charge composition and bomb size on pressures and yields during magnesium reductions of MoO_3	8
3.	Effect of carbon additions on oxygen and carbon contamination in bomb-reduced, arc-melted molybdenum	9
4.	Effect of charge composition on pressures and yields during magnesium bomb reductions of mixtures of MoO_2 and MoO_3	11
5.	Chemical and spectrographic analyses of bomb-reduced molybdenum metal	16
6.	Analyses and hardness data for bomb-reduced molybdenum	17
7.	Results of forging tests on molybdenum ingots	20

PRODUCTION OF MOLYBDENUM METAL BY MAGNESIUM REDUCTION OF MOLYBDENUM OXIDES[1]

by

T. T. Campbell,[2] F. E. Block,[2] and E. R. Andersen[3]

SUMMARY

This investigation was undertaken by the Bureau of Mines to determine if high-purity ductile molybdenum of uniform quality can be prepared by bomb reduction techniques.

Molybdenum trioxide (MoO_3) and mixtures of molybdenum dioxide (MoO_2) and trioxide were reduced by magnesium in closed steel bomb reactors. Very high pressures in excess of 5,000 p.s.i. developed during magnesium reductions of MoO_3. The addition of calcium oxide to the bomb charges caused a significant reduction in pressure. Reaction efficiencies higher than 95 percent were obtained during magnesium reductions of either MoO_3 or mixtures of MoO_2 and MoO_3, but high pressures were encountered when the charges contained from 30 to 60 percent MoO_2. Reaction efficiencies were usually low (less than 80 percent) when the bomb charges contained more than 40 percent MoO_2. The charges with the best composition considering operating pressure, yield, and purity contained from 10 to 30 percent MoO_2. The addition of small amounts of carbon to the reaction charges was helpful because some deoxidation occurred during the reduction and also during subsequent arc-melting of the regulus metal. The purity of the bomb-reduced, arc-cast molybdenum metal ranged from 99.2 to 99.8 percent and in some instances the metal contained as little as 5 parts per million oxygen.

The regulus metal can be collected as a cast ingot in the bomb. These rough ingots were joined into consumable electrodes that were subsequently arc-melted into sound arc-cast ingots. The ductility of the arc-cast, bomb-reduced metal was determined by fabrication tests. Ingot sections were impact forged through reductions of over 50 percent. Workability of the metal could not be correlated with chemical analyses or hardness data; however, large amounts of carbon and oxygen did harden and embrittle the metal.

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INTRODUCTION

The first known reduction of metal oxides by active metals was the aluminothermic process described by Goldschmidt in 1898 (3).[4] The application of bomb reduction techniques for the preparation of vanadium metal was first described by Marden and Rich in 1926 (5). Their process involved the reduction of vanadium pentoxide by calcium in a closed steel bomb. McKechnie and Seybolt (6) refined the process, principally by the addition of iodine to the reaction charge as a thermal booster. Vanadium is presently being produced commercially by bomb reduction techniques as a result of these developments. The production of high-purity uranium, zirconium, and hafnium metals by bomb reduction of their fluoride salts was developed and described by researchers at the Ames, Iowa, laboratory of the Atomic Energy Commission (1, 7).

The production of molybdenum metal by calcium reduction of molybdenum trioxide was reported by Gilbert and Block in 1955 (2). The metal was recovered in massive regulus form rather than as powder. As such, it was easily formed into consumable electrodes for subsequent arc-melting into ingot form.

Magnesium was preferred as a reductant because calcium obtainable from commercial sources was much costlier and contained undesirable quantities of carbon and nitrogen that embrittle molybdenum. High-purity magnesium containing only a few parts per million of these impurities was readily available from commercial sources. The atomic weight of magnesium was another factor that favored its use because 1 pound of magnesium will reduce almost as much molybdenum oxide as 2 pounds of calcium. This permits the reduction of a greater quantity of oxide in a given size reactor.

The Bureau hoped to prepare ultra high-purity molybdenum by magnesium reduction of molybdenum oxides and convert the metal into usable forms at less cost than by the powder-metallurgy techniques employed in current commercial practice.

When magnesium was used to reduce molybdenum trioxide, higher melting points for the slags and much higher pressures were encountered than when calcium was used. Magnesium would be a better reductant than calcium if a way could be found to reduce the high pressures developed during magnesium reductions and if suitable slag-fluidizing agents could be found.

EXPERIMENTAL PROCEDURES AND RESULTS

Previous work performed at the Albany Metallurgy Research Center of the Bureau showed that high-purity molybdenum metal can be prepared by the calcium reduction of molybdenum trioxide (2).

As shown by thermodynamic calculation, calcium metal is a better reductant than magnesium (fig. 1), but the free energy curves for magnesium reactions with molybdenum oxides indicate that these reactions are feasible.

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[4] Underlined numbers in parentheses refer to items in the bibliography at the end of this report.

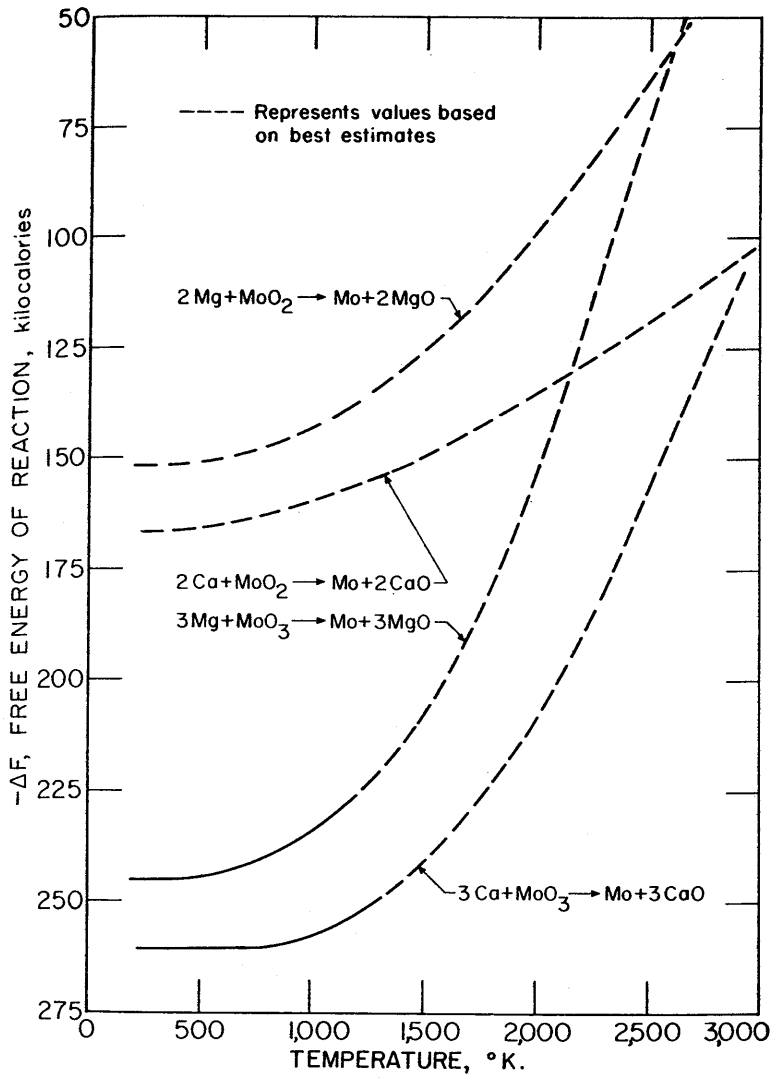


FIGURE 1. - Free-Energy Change for Magnesium and Calcium Reductions of Molybdenum Oxides.

Early studies in which magnesium was used as the reductant were somewhat discouraging because of bomb-liner failures, high pressures (in excess of 5,000 p.s.i.), and low yields.

Most of the reductions were performed in mild steel bombs that had a 4-inch i.d. and were 20 to 26 inches high; however, larger bomb-reactors 8-1/2 and 11-1/2 inches in diameter were used during the course of the work. The 4-inch bombs were provided with 1-inch-thick welded flanges at both ends and with blind 1-inch-thick pressure plates that were supported on 1/8-inch annular rings machined in the ends of the bombs. Copper O-rings used as gaskets sealed the bombs to prevent leakage. Mating flanges held in place by high-tensile-strength alloy bolts or cap screws completed the end closures. The larger diameter bombs, (8-1/2- and 11-1/2-inch) were constructed from 1/2- and 3/4-inch-thick seamless steel tubing and were designed to withstand pressures up to 2,000 p.s.i. with safety factors from 3 to 5.

The copper O-rings used to seal the bombs against leakage at high pressure were very effective because high internal pressures compressed the O-rings between the blind plate and the top flange. Because the O-ring seat in the blind plate was machined to a 60° angle, the pressure on the bomb flanges was reduced by a factor of 0.5.

Several techniques were used to provide the bombs with refractory liners, necessary to protect the bomb walls from the molten metal and hot gases formed during the reaction. Temperatures estimated to be as high as 3,000° C. are developed inside the bombs during metallic reduction of molybdenum oxides. Satisfactory liners were formed by two different methods. One involved

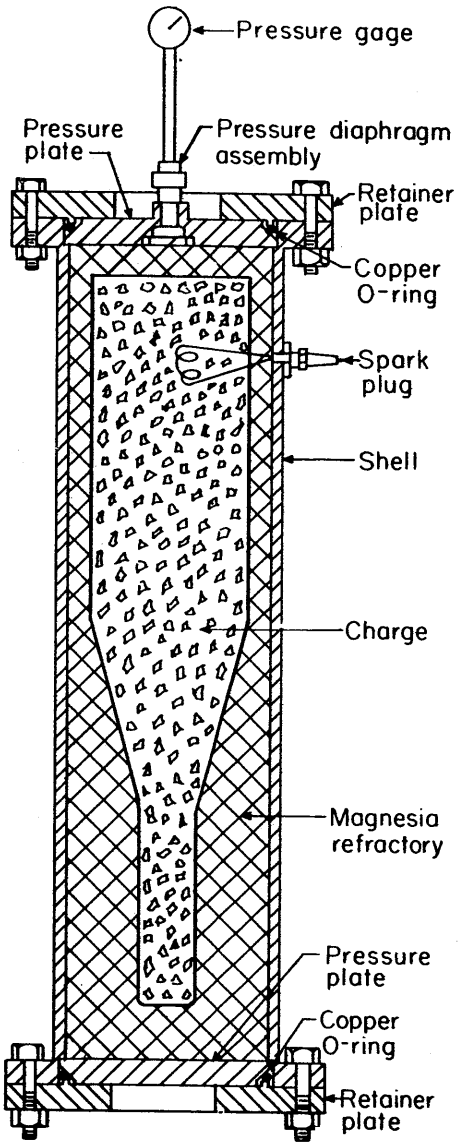


FIGURE 2. - Loaded Reactor Before Firing.

forming a massive rammed liner around a tapered wood or metal mandrel, and the other involved spraying a water slurry of magnesium oxide and waterglass on the heated bomb wall.

The dry method was used when the regulus metal was cast into a rough ingot shape during the reduction. In this case, 99.7 percent pure minus 100-mesh electrofused magnesia was tamped into the space between the bomb wall and the mandrel. An air-operated vibrator was attached to the bomb wall during this procedure to facilitate the formation of firm monolithin liners. These liners varied in thickness from approximately 1/2 inch at the top of the bomb to 1 inch or more at the bottom depending on the height of the bomb and whether the metal was to be cast into a mold or collected as a flat regulus.

When the regulus metal was collected as a round, flat mass in the bottom of the bomb, sprayed liners were found adequate. The most satisfactory spraying mixture was a slurry consisting of 85 percent water, 5 percent waterglass ($Na_2O(SiO_2)x$), and 10 percent magnesia. The slurry was sprayed on the heated bomb walls with a paint spray gun to a thickness of from one-sixteenth to one-eighth inch. Bomb walls were heated to from 350° to 400° C. with a gas burner before spraying. This temperature range was found to be quite critical in obtaining firmly adherent liners. Both the top and bottom plates of the bombs were protected by a 1- to 2-inch-thick layer of magnesia.

Graphite molds were inserted in the bombs in many of the runs when the object was to recover the regulus metal in a cast-ingot form. The use of graphite molds was also studied on the assumption that some deoxidation of the molybdenum metal would result from their use. In practice, these molds were somewhat unsatisfactory because they usually cracked during reduction and the molten metal penetrated the molds. Also, little deoxidation occurred presumably because of restricted surface contact and the short period of time during which the molten metal was in contact with the mold.

After the bombs were lined, reaction charges were introduced to within 4 or 5 inches of the top of the bomb. A molybdenum resistance wire connected to an automotive spark plug was embedded in a calcium-iodine ignition charge, and additional reaction charge was then introduced to within 1 inch of the top of the bomb. The charge was covered with a 1-inch-thick layer of magnesia;

the top plate, O-ring, and top flange were attached, and the bomb was ready for firing. Current was supplied to the molybdenum ignition wire by a variable transformer. This started the reaction of the ignition charge and triggered the main reaction. A schematic drawing of a loaded bomb ready for firing is shown in figure 2.

Before firing, the loaded bombs were placed in a reinforced concrete revetment located outside of the laboratory to protect personnel in the event of an explosion or in case the bomb wall was penetrated because of a liner failure. The bomb walls were cooled either by immersing the bomb in a tank of flowing water before firing or by a water spray located in the revetment. During the reaction, the regulus metal flowed to the bottom of the bomb or into the ingot mold, and the molten slag solidified immediately above the regulus metal. This left a void space in the area previously occupied by the charge. The excess reductant vaporized and condensed as a solid deposit on the walls of the reaction vessel. Despite the fact that very high pressures in excess of 5,000 p.s.i. were sometimes encountered, none of the bombs failed due to excessive pressure. Over a 3-year period, bomb wall penetrations occurred only two or three times. In one case, over 40 reactions were performed in a 4-inch-diameter bomb before it had to be discarded because of warpage or fatigue. In general, larger bombs (11-1/2-inch-diameter with 1/2-inch walls) could only be used for 10 to 20 runs because of warpage that eventually precluded forming tight closures.

Although strain gauges were utilized in earlier work to determine the pressures developed during bomb reductions, this method was somewhat tedious. In most instances, pressures were determined by means of a bourdon tube pressure gauge connected to the bomb by an oil-filled pipe. The pipe was in turn attached to a pressure diaphragm assembly (shown in figure 3 that was welded to the top plate of the bomb.

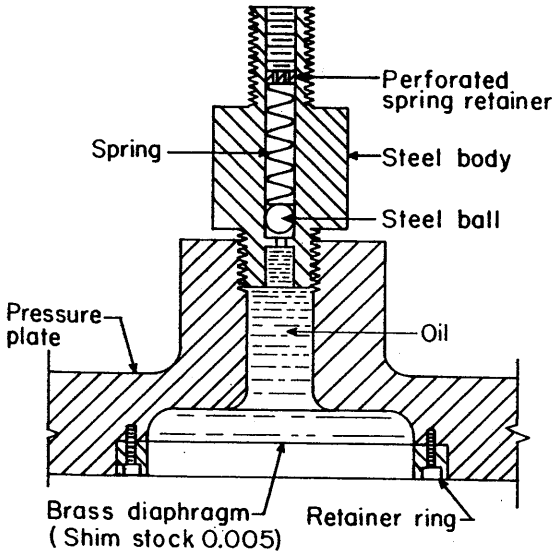


FIGURE 3. - Pressure Diaphragm Assembly.

The bourdon gauge and the pipe leading to the diaphragm were evacuated and then backfilled with oil before attachment to the diaphragm. Although the use of a bourdon gauge did not give precise pressure readings because of override, the readings were considered accurate to within 200 p.s.i. of the indicated pressure.

In almost all reactions, the charges contained approximately 20 percent more reductant than the stoichiometrical requirement. This optimum percent excess figure was based on previous work with calcium reductions of MoO_3. Because any impurities present in the components of bomb charge will introduce impurities into the molybdenum metal, every effort was made to obtain and use only high-purity reagents. Typical chemical and spectrographic analyses of the charge components

are shown in table 1. Iodine, which was used in the ignition charge, and anhydrous calcium oxide were purchased as CP grade chemicals of higher than 99-percent purity from commercial suppliers.

TABLE 1. - Analyses of impurities in components of the charges,[1] p.p.m.

Impurity element	Molybdenum trioxide	Magnesium	Redistilled calcium, -4- + 10-mesh
Al	10-100	50	10-100
Ca	<1,000	-	-
Co	-	<5	-
Cr	-	<30	-
Cu	<10	<10	<10
Fe	-	10	10-100
K	-	-	-
Mg	10-100	-	100-1,000
Mn	-	20	10-100
Mo	-	<10	-
Ni	-	6	-
Pb	-	<10	-
Si	10-100	125	100-1,0000
Sn	-	-	10-100
Ti	-	20	-
V	-	<20	-
Zn	-	60	-
Zr	-	-	-
S	110	-	-
O_2	-	7-25	-
H	-	-	-
N_2	<10-40	10-30	10-40
C	60-80	30-150	40-150

[1]Molybdenum trioxide and calcium impurities obtained by semiquantitative analysis. Magnesium impurities obtained by quantitative spectrographic analysis based on high-purity standards.

Reduction of Molybdenum Trioxide

Initial experiments involving magnesium reductions of MoO_3 were performed in 4-inch i.d. by 20- to 30-inch-high bombs provided with rammed magnesia liners and ingot molds. The reaction charge was made by preparing separate standard charges containing 2 moles of MoO_3 (288 grams) approximately and 20-percent more magnesium (173 grams) than the stoichiometric requirement for the reaction:

$$MoO_3 + 3\ Mg \longrightarrow Mo + 3\ MgO.$$

The magnesium was in the form of 0.003- to 0.007-inch turnings, and the MoO_3 was minus 200-mesh powder. Slag fluidizers and other reagents that were added to this standard charge (CaO, C, NaCl, and others were minus 100 mesh finely divided crystalline or amorphous materials. The standard reaction charges including slag-fluidizing and deoxidizing reagents were intimately

mixed by tumbling them in 2-quart glass jars. These charges were added in increments, and an ignition charge was added after the bomb reactor was filled to the level of the spark plug hole. The ignition charge usually consisted of the following:

Component	Weight, grams
MoO_3	144
Ca	184
I_2	254

In some instances (see runs 14 and 15, table 2) larger quantities of calcium and iodine were used to obtain more fluid slags.

Very high pressures ranging from 2,000 to 3,400 p.s.i. resulted when these reaction charges were fired. The maximum pressures recorded during a reduction usually occurred when the charge was ignited. In almost all cases the pressure dropped to 0 to 100 p.s.i. within 10 to 20 seconds after ignition. Because 30 to 60 seconds usually were required for the heat generated in the bombs to transfer through the refractory liners, the bomb walls were close to room temperature (at maximum strength) when the pressure was at a maximum.

Because reportedly CaO reduces the vapor pressure of MoO_3 (4), the addition of this compound to the bomb charges was studied. The addition of CaO to the bomb charges not only reduced pressures in the bombs but also produced a lower melting slag that increased yields by permitting better metal-slag separation. The lower pressures presumably resulted either because of the reaction of CaO with MoO_3 to form $CaMoO_4$, which reduced the vapor pressure contributed by the MoO_3 in the charge, or by serving as a diluent in the reaction charge, which retarded the reaction rate.

Pressures during reductions of charges containing CaO ranged from 400 to 1,000 p.s.i. This work indicated that the optimum amount of CaO required in the bomb charges was approximately 0.67 mole per mole of MoO_3. When the amount of CaO was increased above 0.9 mole per mole of MoO_3, the yields tended to fall off. When the CaO was reduced to 0.45 mole per mole of MoO_3, the pressure tended to increase above desirable levels. As a result, 75 grams of CaO were always added to the standard reduction charge (2 moles of MoO_3 per charge).

The effect of adding a small amount of finely divided carbon to the bomb charges was studied concurrently with the use of CaO. This work indicated that a significant decrease in oxygen resulted when 0.15 gram of carbon was added to the standard reduction charge. The work just described indicated that the optimum charge for the reduction of MoO_3 was the following:

Component	Weight, grams
MoO_3	288
Mg~(20% excess)	173
CaO	75
C	.15

As was previously found during studies involving calcium reductions of MoO_3 (2), yields significantly increased, when the scale of the reductions was increased from 4-inch-diameter to 8-1/2- or 11-1/2-inch-diameter bombs. Yields of approximately 3 pounds of metal were recovered from 4-inch-diameter by 26-inch-high bombs, 17 pounds from 8-1/2- by 20-inch bombs, and up to 29 pounds from 11-1/2- by 26-inch-high bombs. The effects of charge composition and bomb size on pressures and yields during magnesium reductions of MoO_3 are shown in table 2.

TABLE 2. - Effect of charge composition and bomb size on pressures and yields during magnesium reductions of MoO_3

Run	Standard charge		Total charge		Bomb diameter, inches	pressure, p.s.i.g.	Yield of molybdenum	
	Components	Weight, grams	Components	Weight, grams			Weight-percent	Weight, kilograms
14	MoO_3	288	MoO_3	4,464	4	2,400	79	2,345
	Mg	173	Mg	2,422				
	C	.3	Ca	552				
			I_2	762				
			C	4.65				
15	MoO_3	288	MoO_3	3,168	4	2,500	85.4	1,801
	Mg	173	Mg	1,730				
	C	.6	Ca	368				
			I_2	508				
			C	6.6				
21	MoO_3	288	MoO_3	1,872	4	2,500	87.2	1,087
	Mg	173	Mg	1,038				
	C	.15	Ca	184				
			I_2	254				
			C	1				
25	MoO_3	288	MoO_3	2,160	4	700	81.5	1,174
	Mg	173	Mg	1,211				
	CaO	100	Ca	184				
	C	.15	I_2	254				
			CaO	700				
			C	1.1				
26	MoO_3	288	MoO_3	2,160	4	1,000	84.6	1,218
	Mg	173	Mg	1,211				
	CaO	75	Ca	184				
	C	.15	I_2	254				
			CaO	525				
			C	1				
30	MoO_3	288	MoO_3	2,448	4	1,400	85.9	1,402
	Mg	173	Mg	1,504				
	CaO	50	Ca	184				
	C	.15	I_2	254				
			CaO	400				
			C	1.2				
27	MoO_3	288	MoO_3	9,360	8.5	400	94.8	5,908
	Mg	173	Mg	5,540				
	CaO	75	Ca	184				
	C	.15	I_2	254				
			CaO	2,400				
			C	5				
37	MoO_3	288	MoO_3	19,440	11.5	-	96.5	12,500
	Mg	173	Mg	11,660				
	CaO	75	Ca	184				
	C	.15	I_2	254				
			C	10.2				

A series of reductions was performed in which efforts were made to increase yields by the addition of slag-fluidizing salts. Various quantities and combinations of NaCl, CaF_2, and $MgCl_2$ were added to the bomb charges. Although the addition of these salts resulted in more fluid slags, yields were generally lower than those obtained without their addition. Other adverse factors associated with the use of slag fluidizers were that higher pressures (up to 3,400 p.s.i.) developed in the bombs and that the bomb liners failed, presumably because of the formation of low-melting salt mixtures.

As mentioned earlier, the addition of carbon as a deoxidizing agent was studied. The data on the effects caused by varying the amount of carbon used in the charges on the levels of oxygen and carbon in the reduced metal are given in table 3.

TABLE 3. - Effect of carbon additions on oxygen and carbon contamination in bomb-reduced, arc-melted molybdenum

Run	C per mole of MoO_3, grams	Chemical analysis, parts per million	
		C	O
MoA 10.....	0.00	300	150
MoA 11.....	.15	1,000	106
MoA 12.....	.15	900	23
MoA 13.....	.15	1,300	<5
MoA 15.....	.30	2,200	([1])
MoA 17.....	.075	330	([1])
MoA 25.....	.075	630	40

[1]Indicates no analysis performed.

These results indicate that the addition of up to 0.075 gram of carbon per mole of MoO_3 reduced oxygen levels and did not introduce undue amounts of carbon in the reduced metal. Because carbon in excess of 800 to 900 parts per million embrittles molybdenum, additions in excess of 0.075 gram of carbon per mole of MoO_3 introduced undesirable amounts of this element into the reduced metal.

Molybdenum metal resulting from magnesium bomb reductions was recovered as a massive cast regulus as shown in figure 4. The half section shown is typical of bomb-reduced regulus metal. The density of the regulus metal ranged from a minimum of 58 percent to a maximum of 94 percent of the true density of molybdenum metal; however, the metal averaged around 70 to 75 percent of true density. No correlation of density as a function of the charge composition could be made; however, the denser metal was prepared in large scale reductions (8-1/2- and 11-1/2-inch-diameter bombs). Usually the bulk of the metal was recovered as a single fused regulus, although in a few instances small amounts (5 to 20 percent) of the total metal were recovered as beads and pieces dispersed in the slag.

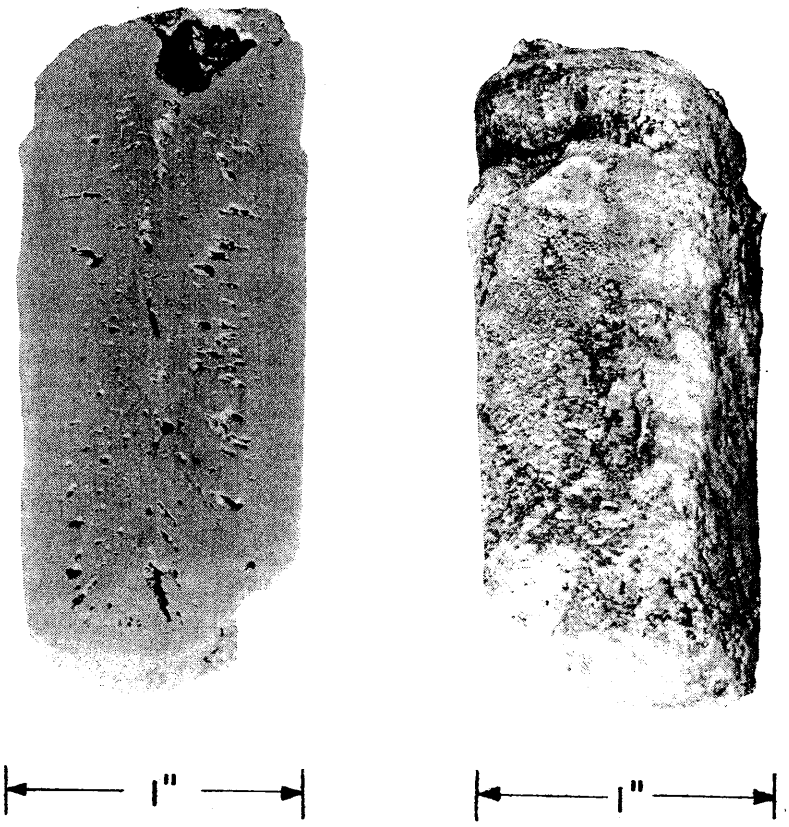


FIGURE 4. - Molybdenum Regulus Produced in 4-Inch-Diameter Bomb. Half Section (left) Shows Typical Porosity of Regulus Metal.

Reduction of Molybdenum Dioxide and Mixtures of Dioxide and Trioxide

Although thermodynamic calculations indicate that free energy relationships are not as favorable for the magnesium reduction of MoO_2 as for the trioxide, the large negative ΔF values (see fig. 1) show that the reaction

$$MoO_2 + 2\ Mg \rightarrow Mo + 2\ MgO$$

is feasible; however, extrapolation of the curve to temperatures above 3,000° K. indicates that this reaction is reversible. Because only 2 moles of reductant are required per mole of molybdenum metal, some saving in reductant cost results when the dioxide is reduced with magnesium; nevertheless, this saving is largely offset by the cost of preparing the dioxide which is generally made by hydrogen reduction of MoO_3. Considering costs, the reduction of the dioxide has a slight advantage over reduction of the trioxide because a greater quantity of metal can be prepared in the same size reactor than can be obtained with the trioxide. The trioxide contains only 66 percent molybdenum as compared with 75 percent for the dioxide. Molybdenum dioxide used in the reduction tests was prepared by hydrogen reduction of MoO_3 at temperatures ranging from 400° to 425° C. The reaction was performed in stainless steel equipment in which approximately 1,500 grams of MoO_2 were prepared per batch.

Reductions of mixtures of MoO_2 and MoO_3 were performed in the same manner previously described for the reduction of MoO_3. Initial studies were conducted with charges in which from 10 to 30 percent of the total molybdenum was present as MoO_2. These reductions did not contain calcium oxide in the reaction charges because the effect of calcium oxide additions on the pressures developed during reductions was not known at that time. As a result, exceedingly high pressures ranging from 2,500 to 5,000 p.s.i. developed when charges containing 10 to 30 percent MoO_2 were reduced. A second series of reductions was subsequently performed; however, CaO was included in these charges. Pertinent data on mixed-oxide reductions are shown in table 4.

TABLE 4. - Effect of charge composition on pressures and yields during magnesium bomb reductions of MoO_2 and MoO_3

Run	Charge composition		$\frac{MoO_2}{(MoO_2+MoO_3)}$, percent	Moles CaO / mole Mo	Bomb diameter, inches	Maximum pressure, p.s.i.	Yield of molybdenum	
	Component	Weight, grams					Kilograms	Percent
MoA 18	MoO_2	187	10	0	4	2,500	1.12	87
	MoO_3	1,702						
	Mg	1,025						
	C	.8						
	Ca	184						
	I_2	254						
MoA 19	MoO_2	337	20	0	4	4,500	1.00	87
	MoO_3	1,350						
	Mg	878						
	C	.6						
	Ca	184						
	I_2	254						
MoA 20	MoO_2	890	30	0	4	5,000+	1.47	70
	MoO_3	2,128						
	Mg	1,578						
	C	1						
	Ca	184						
	I_2	254						
MoA 50	MoO_2	3,019	100	0	4	1,200	1.65	73
	Mg	1,320						
	Ca	108						
	I_2	63.5						
MoA 32	MoO_2	297	10	.59	4	200	1.65	82
	MoO_3	2,680						
	Mg	1,660						
	CaO	660						
	C	1.3						
	Ca	184						
	I_2	254						
MoA 33	MoO_2	468	20	.52	4	300	1.40	87
	MoO_3	1,872						
	Mg	1,252						
	CaO	300						
	C	1.0						
	Ca	184						
	I_2	254						
MoA 41	MoO_2	1,968	20	.52	8.5	1,800	6.39	95
	MoO_3	7,940						
	Mg	5,586						
	CaO	2,028						
	C	4.6						
	Ca	184						
	I_2	254						

TABLE 4. - Effect of charge composition on pressures and yields during magnesium bomb reductions of MoO_2 and MoO_3 (con.)

Run	Charge composition		$\frac{MoO_2}{(MoO_2+MoO_3)}$, percent	Moles CaO / mole Mo	Bomb diameter, inches	Maximum pressure, p.s.i.	Yield of molybdenum	
	Component	Weight, grams					Kilograms	Percent
MoA 34	MoO_2	649	30	0.6	4	600	1.50	97
	MoO_3	1,510						
	Mg	1,112						
	CaO	473						
	C	.9						
	Ca	184						
	I_2	254						
MoA 35	MoO_2	1,117	40	.51	4	2,200	1.69	86
	MoO_3	1,677						
	Mg	1,261						
	CaO	532						
	C	.8						
	Ca	184						
	I_2	254						
MoA 48	MoO_2	2,018	70	.41	4	1,000	1.72	82
	MoO_3	862						
	Mg	1,385						
	CaO	472						
	Ca	90						
	I_2	63.5						
MoA 47	MoO_2	2,288	80	.27	4	500	1.76	84
	MoO_3	572						
	Mg	1,335						
	CaO	333						
	Ca	90						
	I_2	63.5						
MoA 46	MoO_2	2,176	90	.13	4	500	1.27	70
	MoO_3	238						
	Mg	1,080						
	CaO	140						
	Ca	29						
	I_2	63.5						

The data in table 4 shows that the addition of calcium oxide to bomb charges lowered the pressures developed during reductions of charges containing over 70 percent MoO_3 [ratio of $MoO_3/MoO_2 + MoO_3$]. When the ratio of $MoO_3/(MoO_2 + MoO_3)$ in the charges was varied from 30 to 60 percent, pressures become undesirably high, but when charges containing less than 30 percent or from 70 to 100 percent MoO_2 were reduced, pressures did not exceed 1,200 p.s.i. When a larger diameter bomb was used (see run 41), the pressure reached 1,800 p.s.i. despite the fact that the charge contained only 20 percent MoO_2. This increase of pressure with increasing bomb size was verified when a large scale magnesium reduction of a MoO_3 charge containing CaO was reduced in a 22-inch-diameter bomb. This bomb was provided with a rupture disc

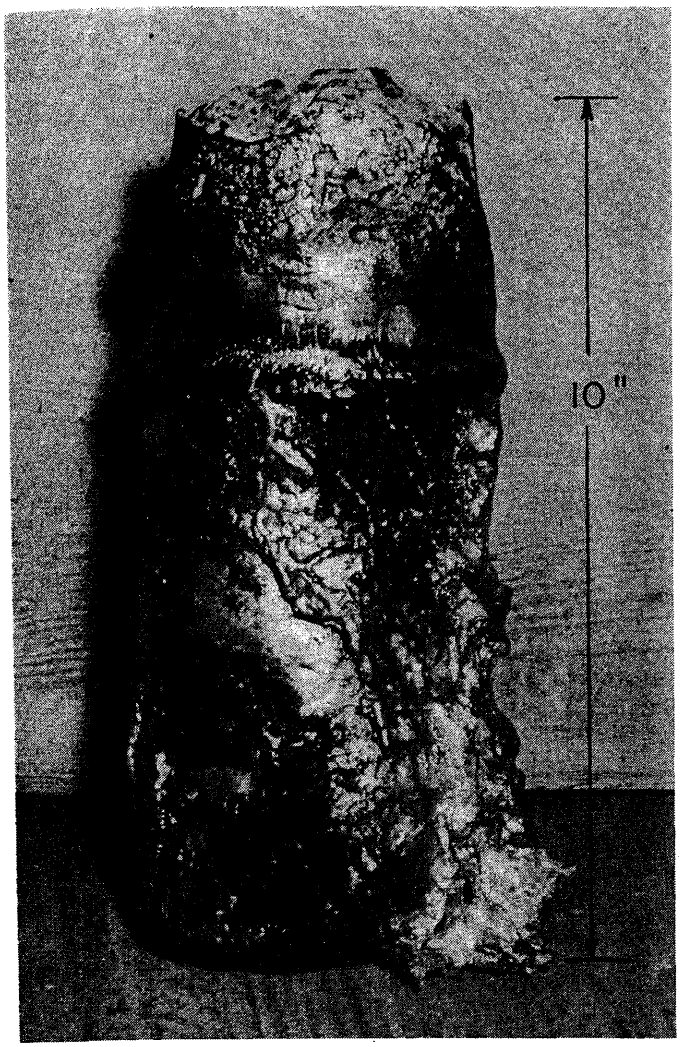


FIGURE 5. - Thirty-Seven-Pound Cast Molybdenum Regulus.

previously calibrated and designed to fail at 1,550 p.s.i. When the charge was ignited the disc was immediately blown from the bomb.

Highest yields were obtained in runs that contained from 10 to 40 percent MoO_2 in the charge, and a distinct drop in yield occurred with charges that contained from 70 to 100 percent MoO_2 and from 0.13 to 0.41 moles of CaO/mole Mo. An exception to this statement was noted in run MoA 20 in which the yield was 70 percent; however, the charge used in this run did not contain CaO. When CaO was added to a similar charge (run MoA 34) the yield of metal was 97 percent.

PROPERTIES OF BOMB-REDUCED MOLYBDENUM

The regulus metal resulting from the bomb reduction tests was consolidated into ingots either by consumable-electrode arc-melting in water-cooled copper molds or by nonconsumable (tungsten electrode) arc-melting of sections of the reguli into buttons. Buttons or ingots were then examined metallographically and tested for hardness. Specimens were prepared for vacuum fusion analyses (O_2, N_2) and for chemical and semiquantitative spectrographic analyses. Both hammer- and press-forging tests were used to evaluate the metal further.

Buttons were arc-melted under partial vacuum with absolute pressures ranging from 1- to 4-inches of mercury of inert gas consisting of 10 to 25 percent argon and the balance helium. The power input during button melting ranged from 150 to 800 amperes at 17 to 25 volts. When large reguli with approximately 3-1/2- inch diameter (fig. 5) were welded together and remelted into an 8-inch-diameter ingot, the power input required was 4,500 amperes at 32 volts. Figure 6 shows a welded consumable electrode, and figure 7 shows a 124-pound arc-melted molybdenum ingot.

FIGURE 6. - Consumable Electrode Formed by Welding Molybdenum Reguli Together.

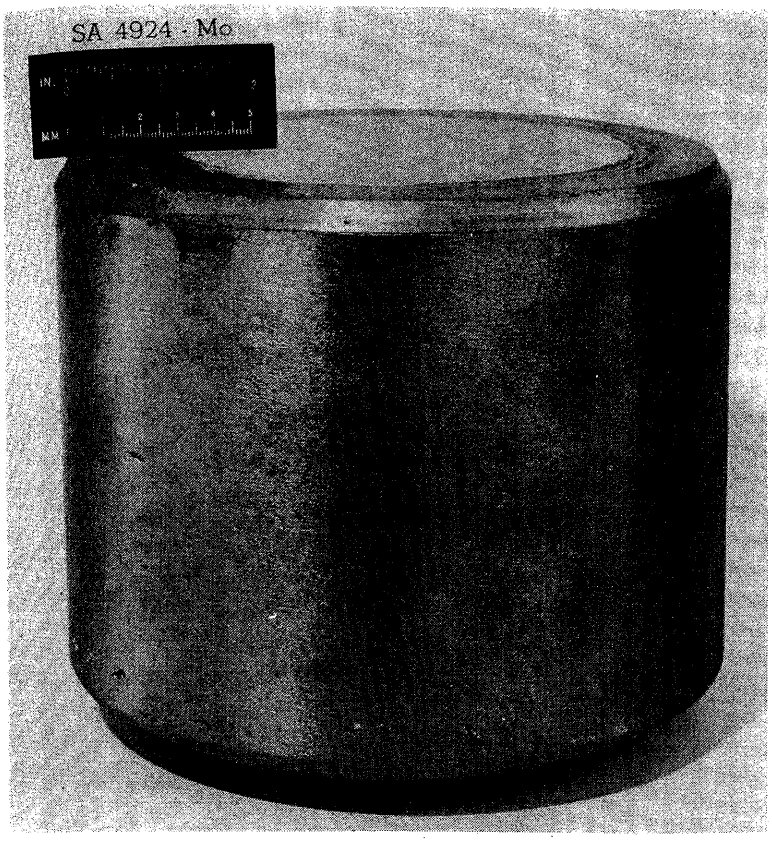


FIGURE 7. - Arc-Melted Molybdenum Ingot Weighing 124 Pounds.

Arc-melted buttons and ingots were sound and showed little porosity as shown by the macroetched ingot section in figure 8. The typical large columnar grain structure of arc-cast molybdenum shows clearly.

Chemical and Spectrographic Analyses of Bomb-Reduced Molybdenum

Analyses were performed on both regulus metal and on samples taken from arc-cast buttons or ingots. Emission spectroscopy was used to obtain semiquantitative data on metallic impurities. Too much reliance cannot be placed on these data because the chemical analyses almost invariably proved that the spectrographic analyses were showing higher impurity levels than were actually present in the metal. This conclusion was substantiated by preparing photomicrographs of the arc-cast metal (fig. 9). The absence of significant amounts of either intergranular or intragranular material, as seen in the photomicrographs, indicate that the metal is quite pure. Standard methods of chemical analysis were used to determine carbon, iron, nitrogen, silica, and other metallic impurities. The oxygen, nitrogen, and hydrogen contents were determined by vacuum-fusion analysis.

Because many runs were performed during this investigation, it is impracticable to include complete analytical data, and accordingly the data considered typical are shown in table 5.

Table 5 shows that some impurities are removed during arc-melting. In all instances, the amount of interstitial impurities in the arc-cast buttons were much lower than in the regulus metal. Volatile impurities such as calcium and magnesium were also removed during arc-melting. The data indicate that some deoxidation occurred during melting because carbon and oxygen impurity levels were much lower in the arc-cast button than in the regulus metal. Comparison of the molybdenum prepared by magnesium reduction (MoA samples) to calcium-reduced metal (MoR 65 sample) indicates that the magnesium-reduced metal is of equal quality. The purity of the magnesium-reduced metal was estimated to range from 99.2 to 99.8 percent molybdenum.

TABLE 5. - Chemical and spectrographic analyses of bomb-reduced molybdenum metal

Sample[1]	Chemical analyses, parts per million								Spectrographic analyses, percent[2]											Remarks
	C	O	N	H	Ca	Mg	Fe	Si	Al	B	Co	Ca	Cu	Fe	Mg	Mn	Ni	Si	V	
MoA 26 R.....	220	310	110	118	-	-	-	-	-	F	-	E	-	E	E	-	E	E	-	Magnesium reduction of MoO_3; see run details table 2.
MoA 26 B.....	200	80	50	<10	-	-	-	-	-	-	-	F	-	E	G	-	E	E	F	
MoA 27 B.....	300	45	90	2	-	-	400	-	-	-	-	F	-	E	G	-	-	E	F	Magnesium reduction of MoO_3; 8-1/2-inch bomb-run; details in table 2.
MoA 29 R.....	1,500	80	295	-	-	<100	-	-	-	F	-	E	G	E	E	-	F	D	F	Magnesium reduction of MoO_3; graphite mold.
MoA 29 B.....	570	10	20	4	-	-	-	-	-	-	-	F	-	E	F	-	-	E	F	
MoA 30 R.....	1,400	210	210	-	-	-	-	-	-	F	-	-	G	E	E	-	E	D	F	Same as above except see run data in table 2.
MoA 30 B.....	110	65	60	<10	<200	-	300	100	-	F	-	-	G	E	E	-	E	D	F	
MoA 31 R.....	460	80	430	-	-	-	-	-	E	F	E	D	-	E	E	F	-	D	F	Magnesium reduction MoO_3; sprayed liner; no mold.
MoA 31 B.....	80	30	100	-	-	-	600	100	E	F	E	E	G	E	F	-	-	E	F	
MoA 32 R.....	1,260	95	200	-	-	-	-	-	E	F	E	D	-	E	F	F	-	D	E	Mixed oxide reduction--10 pct. MoO_2 and 90 pct. MoO_3 sprayed liner; no mold.
RoA 32 B.....	110	5	120	<1	-	-	-	-	E	F	E	E	G	E	G	-	-	E	F	
MoA 34 R.....	660	250	180	-	<200	-	200	100	E	F	-	D	-	E	E	F	E	D	F	Mixed oxide reduction, 30 pct. MoO_2 and 70 pct. MoO_3.
MoA 34 B.....	80	<10	80	-	-	-	-	-	E	-	-	E	-	E	-	-	E	E	F	
MoA 37 R.....	850	155	230	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Large scale magnesium reduction of MoO_3; 11-1/2-inch bomb.
MoA 37 B.....	80	22	50	-	-	-	-	-	F	F	E	E	G	E	G	-	E	E	F	
MoA 35 R.....	660	740	80	108	-	-	-	-	E	F	-	D	-	E	E	F	E	D	F	Mixed oxide reduction, 40 pct. MoO_2 and 60 pct. MoO_3.
MoA 35 B.....	110	85	50	<10	<200	<100	300	<100	E	-	-	E	G	E	F	-	E	E	F	
MoR 65[3] B....	190	70	110	-	-	-	-	-	E	-	-	E	G	E	G	-	-	E	F	Calcium reduction of MoO_3.

[1]R represents analyses of regulus metal, and B represents samples from arc-cast buttons.
[2]Letters indicate estimates from qualitative analysis: D = 0.1 to 1 pct., E = 0.01 to 0.10 pct., F = 0.001 to 0.01 pct., G = <0.001 pct., and - = not detected.
[3]Included for purpose of comparison.

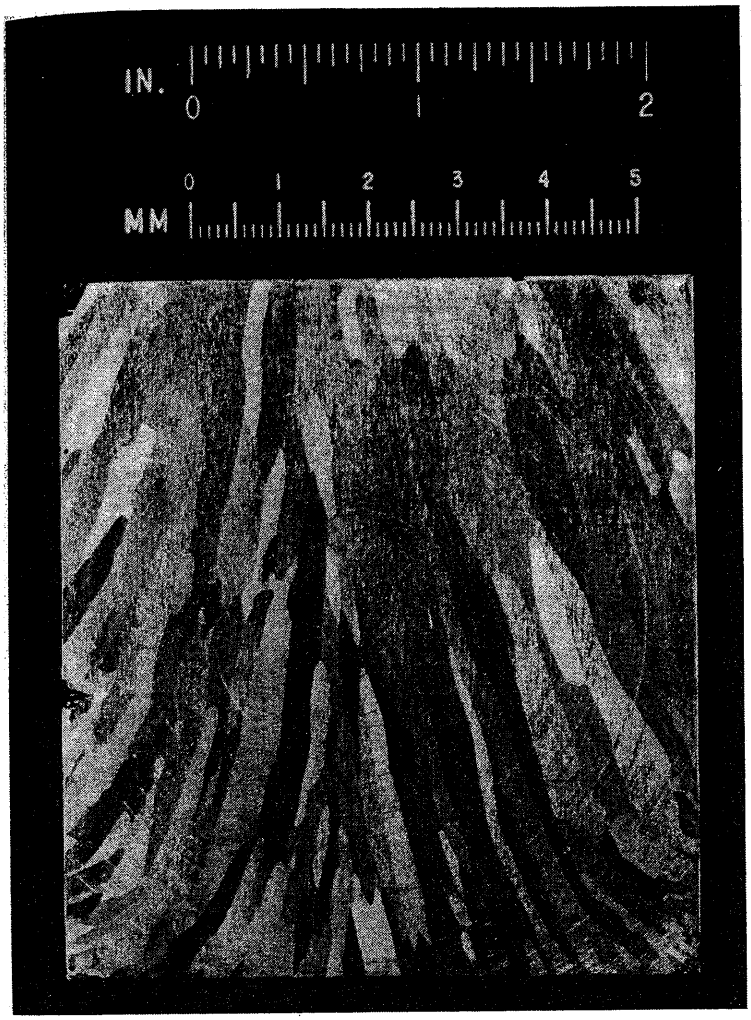


FIGURE 8. - Macroetched Molybdenum Ingot Showing Typical Large Columnar Grain Structure.

Evaluation of Bomb-Reduced, Arc-Melted Molybdenum

The quality of the molybdenum metal was evaluated further during this investigation by metallographic examination, hardness tests, and by forging tests. In general, it was not possible to establish any specific correlation between the hardness of the metal and the amount of metallic or specific interstitial impurities present. However, large amounts of oxygen and carbon hardened the metal, and the lower the level of interstitial impurities, the softer the metal, as shown by the representative analytical and hardness data in table 6.

The hardness data are somewhat anomalous because they indicate that some of the bomb-reduced molybdenum may have a ductile-brittle transition between room temperature and 100° C. whereas in other cases no transition was noted over this temperature range.

TABLE 6. - Analyses and hardness data for bomb-reduced molybdenum

Sample	Chemical analyses, parts per million			Hardness, Rockwell B	
	C	O	N	Room temperature	100° C.
MoA 24.....	630	40	100	80	80
MoA 26.....	220	80	50	75	72
MoA 31.....	80	30	100	71	70
MoA 34.....	80	<10	80	73	66
MoA 36.....	3,600	25	90	87	82
MoA 37.....	80	22	50	72	64
MoA 38.....	80	3,590	60	86	84

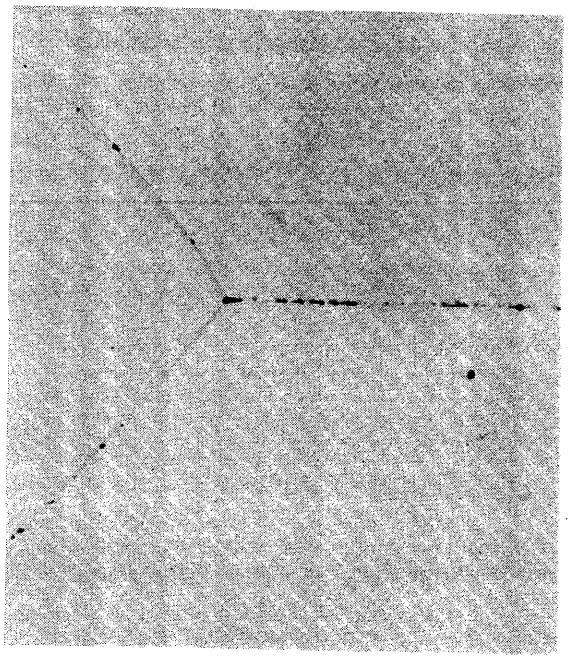


FIGURE 9. - Microstructure of Magnesium-Reduced Molybdenum From Run MoA 34 (500X). Etchant, $K_3Fe(CN)6$-KOH-H_2O.

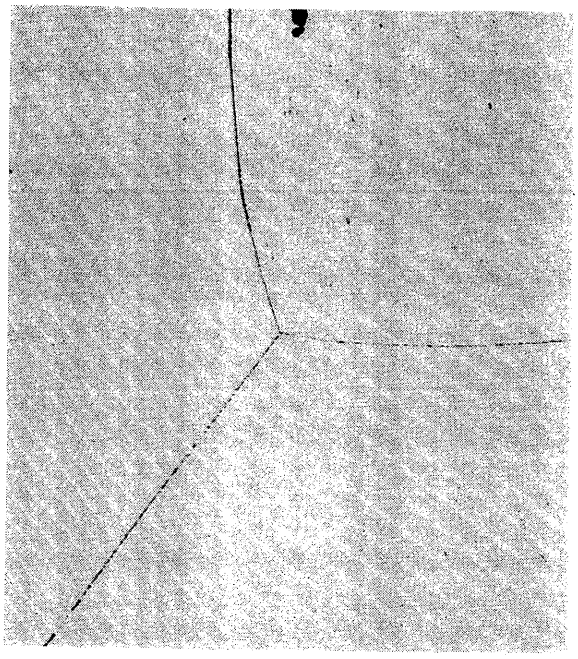


FIGURE 10. - Microstructure of Calcium Reduced Molybdenum From Run MoA 55 (500X). Etchant, $K_3Fe(CN)6$-KOH-H_2O.

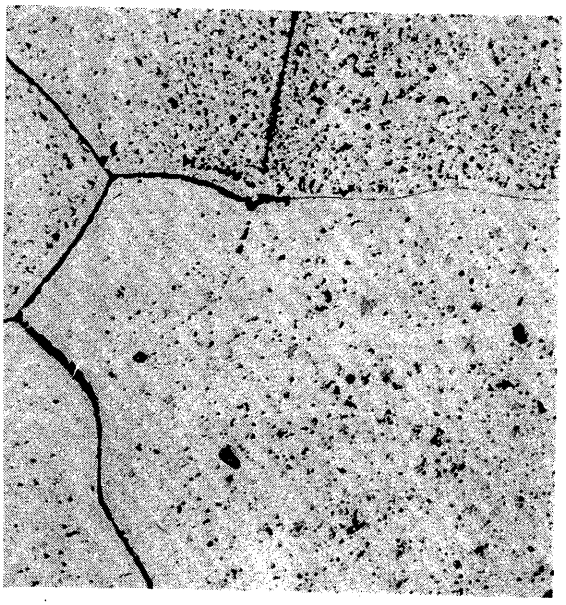


FIGURE 11. - Microstructure of Magnesium-Reduced Molybdenum From Run MoA 36 (500X). Etchant, $K_3Fe(CN)6$-KOH-H_2O. Many carbide inclusions.

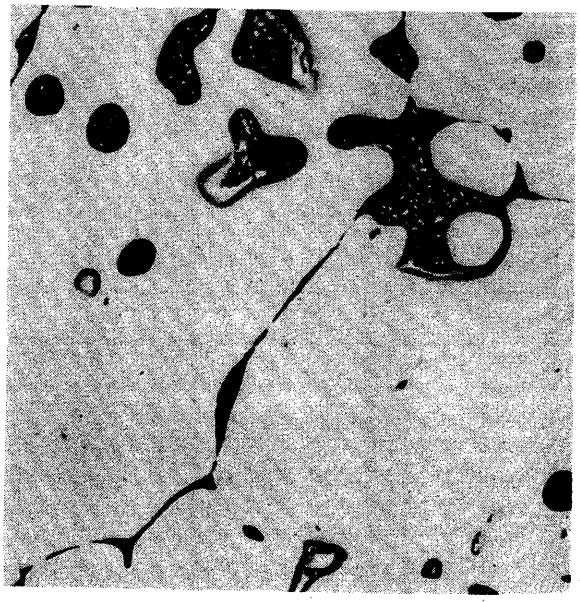


FIGURE 12. - Microstructure for Magnesium-Reduced Molybdenum From Run MoA 38 (500X). Etchant, $K_3Fe(CN)6$-KOH-H_2O. Many oxide inclusions.

Photomicrographs of metal specimens prepared in runs MoA 34, 36, and 38 are shown in figures 9, 11, and 12 with a photomicrograph of calcium-reduced molybdenum (fig. 10), which is included for comparison. The effects of gross contamination of the specimens of metal from runs MoA 36 and 38 (see table 6) are evident. Specimens from runs MoA 34 and MoR 55 show very clear grain boundaries with a minimum amount of included material.

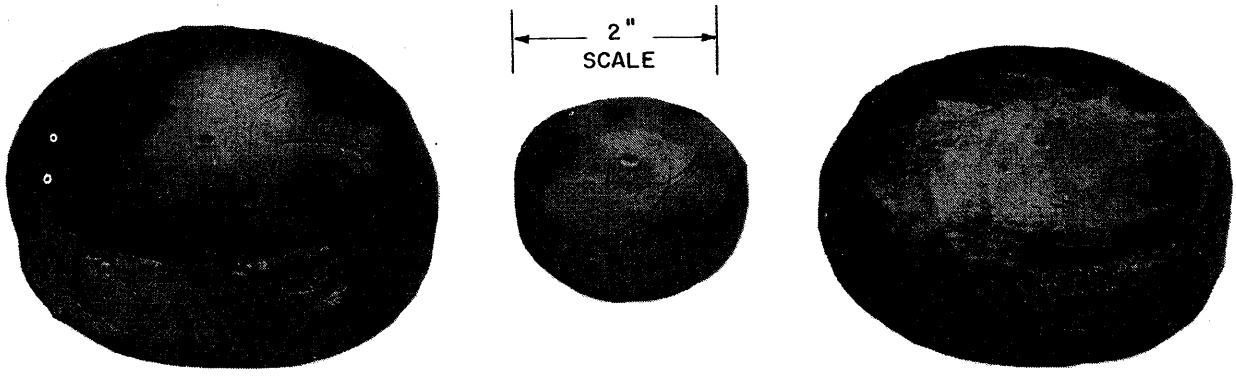
Fabrication of Arc-Cast Molybdenum

Fabrication tests were performed on arc-cast molybdenum buttons or on sections of arc-cast ingots to evaluate the quality of the metal. In general, the procedure was to heat the specimens either under argon or helium atmospheres at temperatures ranging from 2,350° to 2,400° F. The buttons or ingot sections were either press or impact forged by upsetting with the flat faces parallel to the hammer dies.

Because the forges were several feet from the furnace used to heat the specimens and because of the small size of the ingot sections or buttons in relation to the anvils, the actual forging temperatures were probably 100° to 200° F. lower than the furnace temperature when ingots were worked and from 200° to 300° F. when buttons were forged. This led to frequent failures during the tests because the initial breakdown of the arc-cast structure of molybdenum is customarily performed at temperatures ranging from 2,400° to 2,600° F. The edges usually cracked severely when buttons were forged with the result that oxygen penetrated the metal and further working was impossible.

Despite the low working temperatures used necessitated by the equipment available, several ingot sections were successfully forged and reduced more than 50 percent. The data on ingot-forging tests are shown in table 7.

After forging, the ingots were water quenched from approximately 1,800° or 1,900° F. Because adequate furnaces and rolling equipment were not available, no effort was made to reduce the forged ingots further by hot rolling,



Mo - A
28 - 29 - 30

Mo - A
34 - 35

Mo - A
37

FIGURE 13. - Molybdenum Ingot Sections After Press Forging.

but some forged buttons were sheathed in stainless steel and rolled to sheet. Three ingots successfully forged are shown in figure 10.

No correlation between forgeability, chemical analyses, and hardness could be derived from the data obtained in this investigation. The poor forgeability of the ingot (ingot sample MoA 31, table 7) from reduction run MoA 31 is indicative of this situation, because it was one of the softest ingots tested and because chemical analyses showed that it contained lower amounts of impurities than the other ingots that were successfully forged. In almost all cases failures during forging and rolling tests on arc-cast, bomb-reduced molybdenum were of an intergranular nature.

TABLE 7. - Results of forging tests on molybdenum ingots

Ingot sample	Initial dimensions, inches		Final dimensions, inches		Reduction in thickness, percent
	Diameter	Thickness	Diameter	Thickness	
MoA (34-35).....	1-1/4	1-1/4	2	5/8	50
MoA 37.....	2-1/4	2-1/2	3-5/8	1-1/16	57.5
MoA 28, 29, 30.....	2-7/8	2-1/4	3-3/4	1-1/8	50
MoA 52.....	2-3/4	1-5/8	3-1/16	1-3/16	27
MoA 31.....	1-3/4	1-3/4	2-1/2	1-1/4	28.5

Ingot sample	Preheat, minutes	Forge-ability	Hardness, Brinell		
			After forging	After vacuum annealing at 1,500° C.	Prior to forging
MoA (34-35).....	15	Good	212	156	[1]128
MoA 37.....	20	Very good	212	163	[1]120
MoA 28, 29, 30.....	25	Very good	217	156	[1]156
MoA 52.....	30	Fair	217	-	164
MoA 31.....	10	Poor	-	-	[1]118

[1]Converted from Rockwell B scale.

CONCLUSIONS

High-purity ductile molybdenum can be prepared by the magnesium reduction of MoO_3 in closed steel bombs with reaction efficiencies above 95 percent. The purity of the metal ranged from 99.2 to 99.8 percent. The addition of calcium oxide to the bomb charges reduced pressures significantly during magnesium reductions of MoO_3.

Reductions of mixtures of MoO_2 and MoO_3 showed that charges containing up to 20 percent or over 70 percent MoO_2 could be performed without the development of high pressures but the reduction of charges containing from 30 to 60 percent resulted in excessive pressures. Reductions of charges containing from 60 to 100 percent of the dioxide were generally characterized by low reaction efficiencies. Thin liners prepared by spraying a water slurry of

magnesia and waterglass on the bomb walls provide adequate protection for the bomb reactors. The regulus metal can be cast into refractory molds by the use of massive rammed liners.

The cast regulus can be welded into consumable electrodes and consolidated into sound ingots by standard arc-melting techniques. Fabrication studies showed that arc-cast bomb-reduced metal can be forged and thickness can be reduced more than 50 percent, demonstrating its inherent ductility.

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[6]Titles enclosed in parentheses are translations from the language in which the item was published.

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