

IMPURITY EFFECTS IN SECONDARY COPPER ALLOYS

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Abstract—As part of the continuing research program to develop technology for conserving domestic mineral resources, the Bureau of Mines is investigating scrap identification techniques to improve sorted mixed scrap grade. This paper focuses on various classes of wrought and cast copper alloys produced with recycled scrap. Based on a survey of the literature, principal alloys, such as the brasses and bronzes, are examined with respect to impurity elements and their effects on metallurgical behavior. Effects of various elements, including lead, antimony, iron, chromium, and aluminum are discussed. The metallurgical effects described include hot shortness, fire cracking, and undesirable phase transformations.

INTRODUCTION

Old scrap, as a component of the U.S. copper supply in 1981, amounted to 26% of the total 2 278 000 metric tons, and is expected to be approximately 29% by 2000 [3]. Details on secondary copper are available in other publications by the Bureau of Mines and the National Association of Recycling Industries (NARI) [4,23,30,31].

Specifications for the various alloys produced by the industry dictate the quality and the extent of upgrading and refining that may be required. It has been estimated that at one time as many as 500 commercial copper alloys were made in the United States. With such a large number of alloys and the almost infinite varieties of mixtures that can occur when these alloys come back into the recycling process, the task of proper upgrading is indeed monumental. This task is greatly lessened by the use of classifications such as those published by NARI [22]. These classifications provide a standardised system for use by the industry to segregate mixed copper alloy scrap into recyclable categories.

Several routine techniques are traditionally used in the copper recycling industry to identify scrap for effective segregation. These include identification based on object recognition, color, apparent density, magnetic attraction, and chemical spot tests. These techniques, when properly applied by skilled sorters to mixtures of copper alloys, permit effective identification and segregation into specified categories.

Traditional sorting methods are often effective with regard to generic or descriptive specifications; however, there still can be many opportunities for introduction of impurities into alloys made from improperly segregated scrap. More sophisticated techniques have become commercially available and appear to offer improved product grade. These include fluorescent X-ray spectroscopy, portable optical emission devices, and thermoelectric sorters. Previous Bureau of Mines research [18,19,24,26] reported on improved techniques for metal scrap identification.

The purpose of this paper is to examine some of the reported metallurgical effects of impurities in copper alloys. Although the impurities may not have been introduced by improper scrap sorting, the general overview and case studies reported in this paper support concern that

scrap must be carefully and accurately sorted. The metallurgical effects discussed include hot shortness, fire cracking, and unwanted phase transformations. Mention is made also that not all of the metallurgical effects are attributable solely to composition. In some cases, the mechanisms of the problems encountered are still not fully understood, and, in other cases, improper metallurgical processing with respect to foundry control and/or heat treatment may be more to blame than the presence of impurities.

EFFECTS OF IMPURITIES ON COPPER ALLOYS

An overview

A standard designation system for copper and copper alloys has been published by the Copper Development Association, Inc. [6].

Approximately 12 pages of wrought- and cast-copper alloys are listed under various families within the following four general classes: brasses, bronzes, copper–nickels, and nickel–silvers. Within given families of alloys, such as high-copper alloys, silicon bronzes, and manganese bronzes, there are wide compositional ranges for many elements that can cause metallurgical problems, singly or through combined effects. Many elements are intentionally added to impart special properties to alloys. For example, antimony, arsenic, and phosphorus are added in small amounts to wrought alloys to inhibit dezincification; lead to enhance machinability and to promote smooth edges during shearing and blanking operations; tellurium, selenium, and sulfur for improved machinability; aluminum for resistance to impingement corrosion in condenser tubing alloys; and chromium to form a heat-treatable alloy [17]. Some of these elements are added to cast alloys for the same reasons. In addition, lead is added to bearing alloys; iron, silicon and aluminum may be used to enhance mechanical properties; phosphorus and boron (as well as silicon) are used as deoxidisers [17]. In general, cast copper alloys can tolerate higher impurity levels than wrought alloys since they are not subjected to mechanical working. Impurities in wrought alloys affect response to working (e.g. hot and cold shortness) or response to heating (e.g. recrystallisation, fire cracking), while in cast alloys impurities generally affect castability, soundness and physical properties [29].

Wrought alloys

Wrought alloys are generally hot worked above the recrystallisation temperature of the alloy and thus are free from the work hardening effects associated with cold working. Cold working is done at temperatures below recrystallisation. Foulger [11] has discussed impurity effects on hot and cold workability of copper alloys. In cold working, impurities that affect the amount of the relatively hard and brittle beta phase must be carefully controlled. As a general rule, beta and alpha plus beta alloys are more easily hot worked, even in the presence of impurities, while single-phase alpha alloys require a much higher purity level. Hot shortness in wrought alloys is caused by such low-melting elements as lead, antimony and bismuth, and in some cases iron and silicon. Antimony occasionally finds its way into brass from spent cartridge cases. Even extremely low levels of these impurities can be detrimental. Bismuth and antimony, for example, are detrimental in amounts just sufficient to form a single atomic layer along grain boundaries [5,11,16,20]. Limits for lead and bismuth based on commercial hot rolling experience were reported by Jackson [16] for four common copper alloys as listed in Table 1. One method of countering the effect of lead and bismuth is to add an element which forms a high melting intermetallic compound. For example, lithium has been shown to alleviate the effect of bismuth in copper alloys [16].

Cold shortness is a loss in ductility in metals worked at temperatures below the recrystallisation temperature. Glickman [13] has shown that cold shortness is an intergranular

Table 1. Compositional limit for Pb and Bi in α -copper alloys for hot rolling, wt% [16]

Alloy	Pb	Bi
70:30 brass	0.02	0.002
Phosphor bronze (95.5)	0.004	0.0004
Nickel-silver	0.015	0.001
Cupro-nickel	0.015	0.001

phenomenon caused by extremely low amounts of Bi, Te, Sb or B segregated along grain boundaries.

Fire cracking has also been attributed to the low-melting impurities that form brittle intercrystalline films, such as bismuth and lead [5,15]. Copper alloys may undergo heat-affected-zone cracking when Pb, Te, Bi or S are present, even though actual fire cracking does not take place [12].

Recrystallisation and grain growth are also affected by impurities. For example, Fargette [10] has shown, for relatively simple copper alloys, that a few hundred ppm or less of Ag, P, Cd, Mn or Sn can increase the recrystallisation temperatures. Recrystallisation is inhibited because impurities segregate at dislocations and grain boundaries, reducing their mobility [8,10]. Impurities have also been shown to affect grain size and orientation during the recrystallisation process [21,25].

Cast alloys

Cast copper alloys are used for sand castings or permanent mold castings of various components. Typically, alloy additions are made to improve characteristics such as hardness or corrosion resistance. One characteristic is often improved at the expense of another. For example, iron is added to some yellow brasses to increase tensile strength; however, it reduces the ductility of the material. Although the compositions of cast alloys can have greater latitudes than comparable wrought alloys, the effects of impurities can be just as serious. Mechanical properties can be impaired in certain tin bronzes by Mg, Si, Al and even Zn. These elements have similar properties in that they form oxide films on the surface of molten bronzes which break up on pouring and cause rough surfaces on the resulting permanent mold cast products. Film formation interferes with feeding within the mold by causing fissure porosity which greatly reduces mechanical properties [33]. Arsenic and antimony concentrations as low as 0.12 and 0.18 wt% were found to severely reduce the ductility of tin bronzes by decreasing the solubility of tin, thus increasing the brittle delta phase [32]. Impurities such as aluminum, silicon, and iron can cause casting voids or induce the formation of gamma-phase, which serve as sites for stress cracking [1,2,7].

Undesirable effects of impurities on phosphor bronzes, tin bronzes, and their leaded alloys have been reported by Winterton [33] and Stolarczyk [32]. For example, Table 2 [33] illustrates the effect of Al, Si, Fe, Pb and Bi on CP5-phosphor bronze. In general, an increase in impurities decreases tensile strength and elongation, while hardness is variable. Small impurity levels significantly affect the measured physical properties. Additionally, they cause microstructural changes in cast copper alloys. For example, grain shape or size can be changed, as in the case of iron in brasses [9]. In other cases, solid solutions or compounds are formed. It has also been shown [25] that chromium, although below specified maximum concentrations, can lead to fatigue failure in a Mn-Ni-Al bronze alloy (75 Cu, 12 Mn, 8 Al, 2 Ni, 3 Fe).

It is important to note that the literature from which these data are taken also mentions the use of composition controls (e.g. special alloy additions) to enhance hot workability. On the

Table 2. Effect of impurities on CP5-phosphor bronzes [33]

	Composition (wt%)	Tensile strength (tons in ⁻²)	Elongation (%)	Hardness (B.H.N.)
Standard alloy*		27.2	18	138
Aluminum	0.005	25.3	15	123
	0.01	21.8	5	133
	0.47	23.2	6	130
Silicon	0.01	26.3	18	119
	0.07	24.3	9	131
	0.38	24.2	7	137
Iron	0.28	28.5	15	136
	0.80	26.1	11	132
	1.69	22.2	4	139
Lead	0.24	26.3	15	128
	0.70	25.4	15	125
	1.61	23.8	10	126
Bismuth	0.32	25.6	14	127
	1.25	23.8	20	126

*88 Cu, 10.5 Sn, 0.75 P.

other hand, even without harmful levels of impurity elements, improper metallurgical procedures can cause hot shortness.

Factors affecting hot workability include controlling the ingot's crystal structure, soundness, segregation and composition. The quality of the cast ingot prior to working and the response to homogenising treatments are extremely important factors affecting hot working. A fine, uniform cast grain structure, for example, generally results in better hot workability and tolerance for impurities than a coarse, nonuniform grain structure. The severity of hot working also has a bearing on hot workability, so that a given alloy may fail during hot piercing for tube-making but behave satisfactorily during hot rolling or extrusion. Alloys such as brasses, aluminum bronzes, cupro-nickels, and silicon bronzes contain up to 1 or 2 wt% of additional alloying elements to achieve desired mechanical properties. Except for lead and other low-melting elements, the alloying elements enter into solid solution and generally have little or no effect on hot workability. Interaction effects from impurities at relatively low concentrations can have detrimental effects on hot rolling, although little seems to have been published on this subject. Regarding workability of metals in general, Semiatiin [28] gives an excellent description of the action of dislocations and intergranular impurities on the formation of voids at grain boundaries. Tensile stresses develop at the voids during metal working operations, eventually leading to fracture.

Clearly the most prevalent and harmful element affecting hot workability of copper alloys is lead. The maximum amount of lead that can be tolerated depends on such factors as overall composition, structure and processing technique. Toleration to lead can be improved with melt additions of iron [9] and zirconium [14], and rare earths. The formation of a stable, high melting point intermetallic compound such as UPb_3 or Ce_2Pb can improve lead toleration.

In brasses, lead is harmful at levels as low as 0.01 wt%. In phosphor bronzes, Jackson [16] showed that 0.004 wt% lead is considered the maximum tolerable for hot rolling (Table 3). In other alloys, lead may be tolerated up to 0.02 wt%, and even 0.05 wt% or higher. Extreme care is needed if alloys containing lead for machinability are to be hot worked. For Cu-Ni alloys, Bi, Te and Se may be extremely harmful, requiring that they be controlled to levels as low as 0.001, 0.003 and 0.006 wt%, respectively [11]. The harmful effects of lead (and the other low-melting elements) are attributed to the general characteristics of low melting point and limited solid solubility in the parent alloy. The lead and/or its low melting compounds segregate along grain boundaries and are liquid at normal hot working temperatures. Hot shortness may or may

Table 3. Effect of chemical composition on fire cracking [15]

Alloy	Composition (wt %)				Phase(s) present	Sensitive to fire cracking
	Cu	Zn	Ni	Pb		
A	62	19	18	1	α	Yes
B	62	20	18	—	α	No
C	62	24	13	1	α	Yes
D	53	38	8	1	α	Yes
E	47	41	10	2	α/β	No
F	51	42	6	1	α/β	No
G	71	28	—	1	α	No

not occur depending on the interfacial tension between the liquid phase and the solid grains of the parent alloy [5,16,33]. The effect of such impurities may be enhanced or diminished depending on other factors such as grain size control, other elemental additions, initial cast structure, and processing techniques.

Fire cracking is a form of embrittlement that occurs during rapid heating to annealing temperatures. This type of cracking has been the subject of a number of studies, yet the mechanism is not fully understood. Sato [27] investigated fire cracking of aluminum brass, cupro-nickel, and chromium copper. Sato concluded that embrittlement occurred as a result of voids along grain boundaries, similar to the behavior observed with alloys subjected to high-temperature creep and tensile tests. The embrittlement due to void formation was further found to be closely related to several factors, including:

- (1) magnitude of the residual stress from cold working;
- (2) heating rate;
- (3) time at temperature;
- (4) annealing temperature;
- (5) grain size;
- (6) reduction ratio during cold working.

The effects of impurities were not described, implying that they were minor compared with the above-mentioned factors. Actually, impurities may be an overlooked major factor causing embrittlement.

Isler and Form [15] undertook a detailed study to define the mechanism of fire cracking. Table 3 shows results of preliminary tests relating chemical composition to fire cracking. The alpha alloys with lead were clearly prone to fire cracking; the presence of beta-phase reduced the tendency. All cracks were intercrystalline. A large number of tests revealed that alloys could exist in a sensitive (to fire cracking) as well as a nonsensitive state after being cold worked and heat treated in presumably identical fashion. This observation led to the conclusion that in addition to lead concentration and type of crystal structure, there were other factors that governed sensitivity to fire cracking. Further detailed studies were conducted to examine effects of residual stresses from cold work, the rate of heating, grain size, the role of porosity, and the role of lead. Casting porosity was clearly a major factor rendering alloys sensitive to fire cracking. The effect of lead was studied in considerable detail, providing the major subsequent observations on which Isler and Form base their proposed mechanism [15].

Heating tests on alloys containing Pb revealed that cracking began at 318°C, slightly lower than the melting point of lead (327°C). Microprobe analysis showed that lead particles contained the main alloying elements of the matrix (Cu, Zn and Ni). This and the fact that lead is known to form low-melting intermetallic compounds with these elements (e.g. 318°C with 0.5% Zn) supported the conclusion that the fire cracking temperature coincided with the melting point of the lead particles. The fire cracking temperature was found to be independent of the matrix composition. Liquid metal embrittlement was thus suspected of being responsible

for fire cracking, and a series of tensile tests were run to show whether alpha nickel – silver and lead formed an embrittling couple. The results of tensile ductility testing (and supporting Charpy impact tests) showed a marked drop in ductility at about 300°C for all alloys, owing to spontaneous strain aging for the alpha-phase alloys and to intercrystalline cavity formation for the alpha – beta alloy.

Microprobe analysis was also conducted to show that there is a marked concentration of lead along the fissures of the advancing crack front during fire cracking.

Other tests were conducted to study stress relaxation and desensitising phenomena, the latter being related to dislocations piling against grain boundaries. The results were related to the Griffith – Orowan fracture theory, leading to the following general characteristics associated with alloys sensitive to fire cracking:

- (1) A second phase is present that melts during heating up, forming an embrittling couple with the alloy.
- (2) The melting point of the second phase must be low enough so that the residual stresses are relaxed only slightly when melting occurs.
- (3) High yield strength of the matrix alloy permits substantial buildup of the residual stresses.
- (4) The alloy must contain voids along the potential fracture path, thus eliminating the need for crack initiation.

Microstructural effects, such as solute element segregation at grain boundaries and phase relationships, were considered to some extent in the above discussions on hot workability and fire cracking. Other reported studies concentrated on microstructural evaluations to determine the effects of various elements on the microstructure of tin bronze; and to determine the cause of failure of cast Mn – Ni – Al bronze propeller blades.

Couture [8] studied a tin – bronze alloy (88 Cu, 10 Sn, 2 Zn) to determine the effects of Ni, P, Fe, Pb, Sb, S and Si on microstructure. The purpose was to produce microstructures that would serve as an aid to explain the influence of these elements on the properties of tin bronzes investigated by other researchers. The observations made from micrographs are highlighted here.

- (1) Grain structure changed from columnar to equiaxed with some grain refinement attained by adding Ni, Fe or Si. Grain size and shape were not affected by P, Pb, Sb or S.
- (2) The binary Cu – Sn phase diagram predicts alpha plus epsilon as the equilibrium phases at room temperature in tin – bronze alloys. The eutectoid decomposition of delta to alpha plus epsilon (350°C) is sluggish, however, and delta is retained down to room temperature. Although the delta would be expected to contain 32.6% tin, the presence of more than 2% zinc and additional elements will alter the delta composition.
- (3) Metallographic examination revealed that phosphorus and lead segregated in or near the eutectoid as compounds or solid solutions and were present in the matrix between dendrite arms, thus confirming that they segregated in the last-to-freeze liquid.

The results demonstrate some of the effects of various elements on mechanical properties of tin bronzes. For example, antimony, upon going into solid solution, decreases the solubility of tin. This produces a larger amount of brittle delta, decreasing ductility of the tin – bronze alloy. Refining by air oxidation can be used to remove aluminum, iron and silicon as slag, however, the amount of oxidation must be controlled to prevent the removal of desirable constituents.

Raymond [25] performed detailed microstructural analysis to determine the cause of failure of large propellers. Two 6-ton cast propellers failed while in service on a U.S. Coast Guard icebreaker. The alloy was a Mn – Ni – Al bronze alloy, selected for excellent mechanical properties and good erosion and corrosion resistance in high-velocity seawater. Foundry and welding characteristics of the alloy are superior to those of conventional aluminum bronzes.

When properly alloyed, a stable microstructure of approximately 50% alpha and 50% beta is obtained.

Chemical analyses were compared among samples from the failed blades and a good blade, and against the specification MIL-B-21230 A, Alloy 2. The compositions all were similar. However, a slightly higher concentration of chromium was noted in the samples from the failed blades. This small amount of chromium resulted in microsegregation, which led to an unstable microstructure, also causing a degradation of mechanical properties. For example, tensile strength, elongation and Charpy V-notch energy were respectively 25, 50 and 75% lower than typical values.

Raymond's analysis included microstructural analysis, mechanical property evaluation, thermal analysis, and fracture mechanics. The overall objective was to devise a corrective weld repair and heat treatment that would permit salvaging additional propeller blades.

Chromium was isolated as the deleterious contaminant which formed an iron-rich dendritic phase ('Sparkle') during solidification from the melt. A detailed ion microprobe mass analysis on a dendrite showed:

- (1) The dendrite was composed of Fe, Cr, Mn and only a small amount of Ni.
- (2) Surrounding phases were discontinuous alpha, richer in copper than the discontinuous beta, which was richer in manganese and iron.
- (3) Aluminum and nickel were uniformly distributed between the alpha and beta phases.

From these observations, it was concluded that trace amounts of chromium caused the formation of Fe-Cr-Mn dendrites at high temperatures. The surrounding matrix was thus depleted of (1) the manganese necessary to suppress eutectoid decomposition and (2) the iron necessary for fine grain structure. Manganese suppresses eutectoid decomposition because, being soluble in copper, it lowers the melting point of the alloy. The decomposition of eutectoid beta results in a brittle ternary phase, observed as fine lamellar precipitates in the beta phase. After welding repair, two detailed heat treatments were devised for restoration of mechanical properties, both requiring that the eutectoid temperatures of 675°C (1250°F) be exceeded.

SUMMARY

Wrought copper alloys are generally sensitive to even minor amounts of low-melting elements such as Pb, Bi and Sb. Depending on the impurity, harmful effects have been observed for concentrations as low as 0.0004%, although considerably higher concentrations can be tolerated for many of the alloys under appropriate processing conditions. The predominant effects are hot and cold shortness and fire cracking tendency due to grain boundary segregation of such elements. Sensitivity to impurities is related to phase relationships, with single-phase alpha alloys being most sensitive. Certain other elements, including iron and silicon, may produce harmful effects. However, iron can also counteract the harmful effects of low-melting impurities. Increased tolerance for otherwise harmful impurities is achieved also with additions of zirconium, rare earths, or uranium.

Cast alloys are considerably more tolerant of impurities than wrought alloys, although various impurities can have pronounced effects on castability and mechanical properties. Some of the elements known to adversely affect properties if not closely controlled are Mn, Si, Al, Fe, As, Sb, Pb and Bi. Small amounts of chromium (0.015%) caused serious failures in cast aluminum bronzes owing to preferential segregation and subsequent effects on transformation kinetics and brittle behavior.

Although the effects of impurities have been well defined for many alloy systems and adequate information seems to be available to reevaluate alloy specifications, it is important to

note that definitive information is not available for all cases. This is because of the complexity of some alloys and the involved interaction effects. The many processing variables and service conditions further prevent a clear understanding of impurity effects in commercial alloys.

A major objective of Bureau of Mines recycling research has been to improve the efficiency of recycling by introducing new technologies to more accurately identify and sort scrap metals [18,19,26] thereby minimising the chance of introducing tramp elements. The evidence clearly supports the often expressed concern that scrap must be carefully and accurately segregated to avoid harmful impurity effects when recycled. However, all metallurgical problems are not attributable solely to impurities. Care must also be exercised to assure that established metallurgical treatments are followed when processing recycled alloys and when putting them into service. Unfounded claims that processing or service failures are caused solely by impurities from scrap do not effectively serve the recycling industry, the scrap user, or the economy when conservation measures such as recycling are so vitally needed in extending our mineral resources.

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