



Conductivity of Copper-Carbon Covetic Composite

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Abstract

NASA is currently engaged in the development of highly electrically conductive wire for power and propulsion applications in space and aviation. Higher levels of electrical conductivity and lower densities than those of copper and aluminum are needed to improve the efficiency of commercial aviation and space flight. Carbon, in various forms, is being considered as a component in composites to increase conductivity and decrease density in Cu and Al. One form of carbon that is currently receiving much interest is known as covetic. The technology currently known as covetics was first introduced by Shugart and Scherer whose patents claimed, "Carbon can be incorporated into any of these metals by melting the metal, mixing the carbon into the molten metal and, while mixing, applying a current of sufficient amperage to the molten mixture such that the carbon becomes incorporated into the metal, thereby forming a single-phase metal-carbon material." It is reported that in this process a conversion reaction occurs, with the carbon forming covalent bonds with the host metal, and that covetic processing enables higher carbon solubility and improvements in properties. Although there is a growing body of work in support of covetic materials, it is still a very new and somewhat controversial field. Composition, density, and electrical conductivity measurements of a covetically processed alloy ingot of Cu and C, with a nominal composition of Cu-0.4C (wt%), were made. A pure Cu ingot was similarly processed for comparison. Sections of these ingots were worked into wire and tested. Only small amounts of C could be detected in the Cu-0.4C ingot, and only 0.006 to 0.2 wt% were found in the wire. All wires had densities very close to the full density of pure Cu, indicating a high level of Cu purity and low void fraction. Finally, the electrical conductivity of the Cu-0.4C wires were 9 percent lower than the samples similarly processed but without C additions. The wires made without C additions had conductivities approximately equal to pure Cu. The low conductivity of the Cu-0.4C material is believed to be due to (1) a structure of interfaces in the wire created by collapsed voids lined with elemental C, (2) impurities, such as Fe in the Cu, which came from the added C, and (3) a small volume fraction of voids.

Introduction

Higher levels of electrical conductivity and lower densities than those of commercial copper and aluminum alloys are needed to improve the efficiency of commercial aviation and space flight systems (Refs. 1 and 2). Carbon in various forms is being considered as a component in Cu- and Al-based composites to increase conductivity and decrease density. One form of carbon that is currently receiving much interest is known as "covetic." Of materials subjected to covetic processing, NASA is primarily interested in Cu and Al covetics.

One of the first works published on covetics was by Scherer et al. (Ref. 3). Shortly after, process patents were granted to Shugart and Scherer of Third Millennium Metals LLC (now known as GDC Industries LLC) (Ref. 4). The claims of this and related patents state, "Carbon can be incorporated into

any of these metals by melting the metal, mixing the carbon into the molten metal and, while mixing, applying a current of sufficient amperage to the molten mixture such that the carbon becomes incorporated into the metal, thereby forming a single-phase metal-carbon material.” In a review of covetic materials by Bakir and Jasiuk it is reported that a conversion reaction occurs, with the carbon forming covalent bonds with the host metal, and that covetic processing enables higher carbon solubility and improvements in properties (Ref. 5).

Balachandran et al. examined the properties of covetically processed Cu with a nominal concentration of 3 wt% C and found no significant difference in density between the pure Cu control specimen (8.91 g/cc) and the 3 wt% C material (8.89 g/cc) (Ref. 6); the electrical conductivity of the 3 wt% material was about 6.8 percent higher than the pure Cu control. Density measurements by Brown et al. were similarly unable to confirm the presence of C in their covetically processed aluminum samples; the slight departures of their samples from fully dense were likely due to void fraction (Ref. 7). After T6 heat treatment, Brown’s covetic sample had the same electrical conductivity as the sample without C added. The high conductivity of the as-extruded covetic sample needs to be repeated since it is not consistent with the other conductivity measurements or density results; also, the sample length was short and the diameter was large, which results in lower resistance and higher levels of uncertainty (Ref. 7). Forrest et al. examined Cu covetic material and found negligible density changes, a 20 °C increase in melting temperature, and premature failure in tension; the weakness of the material was attributed to porosity in the centrifugally cast specimen (Ref. 8). In work of Isaacs et al., nominal Cu-4 and 5 wt% C covetic material was supplied by GDC Industries and then used as target material in evaporation deposition processes to form thin-film transparent electrodes (Ref. 9). Photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) showed carbon structures in the bulk covetic material, but C could not be detected in the deposited films. Still, impressive improvements in transmittance and sheet resistance were observed in the films deposited from the covetic targets. However, this might be due to the presence of additional trace impurities in the Cu from impure C added in the covetic process, where these trace impurities getter oxygen, or manipulate the production of metal oxides and thus modify properties (Refs. 10 and 11). Because the deposited films were between 20 and 70 at.% O, property differences caused by variations in the form of various oxides seems more plausible than the effects of covetic C, especially because no C could be detected in the films. Balachandran has examined impurity concentrations in C supplies and in resulting covetics and has found rather high concentrations of Fe, an element that lowers Cu conductivity. Salamanca-Riba et al. examined the structure of Cu and Al covetics and found carbon nanoparticles in the diameter range of 5 to 200 nm with EELS (electron energy loss spectroscopy) and corresponding Raman data characteristic of carbon nanotubes (CNT) (Ref. 12). This is inconsistent with the idea of a “single-phase metal-carbon material,” but such a composite would still be expected to have benefits over the pure metals in terms of density and perhaps conductivity, depending on the intrinsic conductivity of the carbon phase. Knych et al. examined the chemistry, density, hardness, and conductivity of three covetically processed Cu ingots (Ref. 13) and found that (1) nominal amounts of C were measured in the processed ingots, and these C additions added about 10 ppm Fe, Ni, and S to the Cu; (2) all densities were greater than 99.3 percent of pure copper’s, which was not consistent with C composition levels; (3) hardness was actually lower in the covetically processed ingots; and (4) the electrical conductivity of the covetic material was the same as the pure Cu standard.

Although there is a growing body of work supporting covetic materials, much of it is based on XPS, and this method is prone to inaccurate C determination because of background C in the chamber and the use of SiC polishing papers. Also, if elemental C is located in pores, it will be detected, but that does not mean it is an effective component in the matrix. This memorandum reports the examination of a covetically processed alloy ingot of Cu and C with a nominal composition of Cu-0.4C (wt%). A similarly processed pure Cu ingot is also reported for comparison.

Experimental Procedures

Covetic Material Processing

To make the covetic material examined in this study, 99.9 percent pure Cu and –200 mesh graphite powders were milled in isopropyl alcohol with zirconia media and later loaded into a grounded graphite crucible that was placed into the hearth of an electron beam chamber and evacuated to $<10^{-3}$ torr. The mixture was degassed by preheating at a pressure of $<10^{-4}$ torr using a beam current of 200 mA; then melted by increasing the current; and mixed by moving, or rastering, the electron beam. After the melt was stirred by the convection caused by the rastering of the beam, the electron beam was turned off, the melt allowed to solidify and cool, the chamber vented, and the ingot removed. Figure 1 shows the pure Cu and Cu-0.4C (wt%) (or Cu.4C) ingots examined in this study, which were made at Argonne National Laboratory. The pure Cu ingot was clean, bright, and Cu colored. The Cu.4C ingot was dusty and gray. The gray color of the covetic sample appeared to be primarily due to a black powdery residue on the ingot surface. Much of this residue washed off (as can be seen in Fig. 1) and was assumed to be C-rich, although the surface residue was never actually analyzed. The masses of the ingots were 18.3, 14.7700, and 14.768 g for the pure Cu, unwashed Cu.4C, and washed Cu.4C ingots, respectively. The mass of material removed from the Cu.4C ingot upon washing was 0.002 g. Even assuming that this was all C, this small loss would not represent a significant portion of the 0.6 g expected in the ingot. Both ingots were sectioned into samples that could be readily made into wire. Three samples were cut from each ingot using a low-speed metallographic saw equipped with a thin diamond-coated blade. The approximate dimensions of the sectioned samples were 2.5 by 0.4 by 0.4 cm. One section from each ingot was either

1. Worked into wire from its as-received condition
2. Hot isostatically pressed (HIPed) and then worked into wire
3. Placed in a pure Cu tube, sealed under vacuum, HIPed, and then worked into wire

Wire Processing

The as-received ingot sections were worked directly into wire through cold work, which included as needed: hammering with the use of an anvil, rolling in a Pepetools 188.20A rolling mill (shown in Fig. 2), and drawing through a draw plate with WC inserts. The rolling mill produces a nonround, six-sided cross section. The wire is made longer and round by passing it through the draw plate. The evolving wire was stress relieved in air at 310 °C as needed throughout the process. Landstrom (Ref. 14) has shown CNT to be stable at air temperatures less than 400 °C; thus the annealing is not expected to damage the C in the covetic composites. After each anneal, the wire was cleaned through pickling in a solution of 50 ml water, 15 ml sulfuric acid, and 40 ml hydrogen peroxide.

Even though concentrated solutions of nitric and sulfuric acid are used to purify, functionalize, and disperse CNT (Ref. 15), there is concern that the pickling acid might damage C structures through the creation of covalent σ -bonds and disruption of the sp^2 structure (Ref. 16). Such disruption of the sp^2 hybridization is believed to decrease the conductance of CNT, as was shown by Bergeret et al., by a loss in the metallic character of CNT due to nitric acid purification treatments (Ref. 17). However, the pickling process used to clean the wire samples after annealing is not expected to damage the C in the covetic composites because the solution is dilute and briefly applied to the wire exterior only.

The primary reason for processing wires was to produce samples for electrical conductivity measurements. To determine the conductivity of such wires, the following are measured:

- A Wire cross-sectional area
- L Wire length between the leads measuring the resistance of the wire
- R Wire resistance



Figure 1.—As-received, ~1-in.-diameter ingots of pure Cu (left) and Cu-0.4C (wt%) before washing (center). Both ingots were covetically processed. The Cu-0.4C ingot after washing and cutting is shown (right).



Figure 2.—Rolling mill used to cold work samples into wire; rollers are 55 mm in diameter.

These are used to calculate electrical conductivity, ρ : $\rho = A/(R*L)$ thus in an effort to make measurements as accurately as possible, A , R , and L should all be as large as possible. The problem is that as you increase A , R decreases. To minimize total error and uncertainty, sample size is optimized by considering the uncertainties of each measurement. Wire in this study was drawn to diameters in the 0.7 to 1.0 mm range, resulting in total length of about 1 m. Wire diameters were measured using calibrated calipers at four locations along the length to be tested, and at each location along the length, the wire diameter was measured at four different azimuthal locations around its circumference for a total of 16 diameter measurements. Prior to diameter measurements the calipers were calibrated against a set of NIST traceable pin gauges of the same diameter as the wire. These pin gauges are accurate to within ± 0.0001 in. This process resulted in an estimated diameter measurement accuracy of ± 0.0003 in. Wire diameter variation azimuthally and along the lengths tested were negligible (< 0.0003 in.). This results in an uncertainty of about ± 1 percent for a 0.8-mm-diameter wire, and since diameter is squared in the area calculation, the uncertainty of A is about ± 2 percent.

Hot Isostatic Pressing (HIPing)

A section of each ingot was HIPed, and an additional section from each ingot was placed in an evacuated pure Cu tube and HIPed; for these later samples, the Cu tube was left on and became part of the wire. HIPing conditions were 954 °C and 105 MPa, for 3 h. Figure 3 shows an example of samples sealed in Cu tubes prior to HIPing. To seal samples in the tubes, about a 5-in. length of tube is cut, pickled, rinsed, and dried, and then the end is sealed by crushing a 1-cm length of it. Afterward, the crushed end is cold-welded closed using a POD-375 Cold Weld Pinch-Off Tool from CHA Industries. The sample is placed in the tube, and the tube is connected to a vacuum system. A high-temperature heating strap is wrapped around the tube so it can be heated to about 250 °C to achieve better vacuum levels. Other parts of the system are heated to 150 °C, which is the limit for the valves and gauge. Once vacuum levels were near 10^{-7} torr, the tube above the sample was crushed and sealed. This crushed section is needed to create a large section of pure Cu that becomes completely solid and malleable after HIPing. Otherwise, the weld joint has a tendency to break open.

Chemistry and Electron Microscopy

The chemical compositions of the ingots and wire were measured using inductively coupled plasma atomic emission spectroscopy (ICP–AES) for trace metallic elements and a combustion infrared detection technique using a LECO C/S analyzer (Laboratory Equipment Corporation) for carbon (C/S refers to carbon/sulfur), which has an estimated accuracy of the greater of ± 0.0015 wt% or ± 5 percent of the reported value. ICP trace element measurements are expected to have an uncertainty of ± 10 percent of the reported value. The compositions of the following samples were measured: the pure Cu as-received ingot, wire made from as-received pure Cu ingot, wire from pure Cu HIPed in a Cu tube, as-received Cu.4C ingot, wire from as-received Cu.4C ingot, wire from Cu.4C HIPed in a Cu tube, and wire made from an empty HIPed Cu tube.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were done on the exterior and interior surfaces of Cu.4C wire, which failed during rolling, and on longitudinal and transverse cross sections of both pure Cu and Cu.4C wire. Maps of Cu and C distribution were made.

Density Measurements

Good-quality samples were cut from the center of each wire for density measurements. The length of the specimen used for density depended on the quantity of available wire, which varied between 2 and 20 in. Specimen mass was measured on a scale with an uncertainty of ± 0.00015 g, and volume was calculated based on wire length and diameter. These combined to yield an estimated uncertainty of ± 0.1 g/cc, or about ± 1 percent, for the density.



Figure 3.—Samples sealed in evacuated, pure Cu tubes.

Resistance Measurements

A calibrated, four-wire Keithley 580 micro-ohmmeter was used to measure the resistance, R , of the wire length, L . The accuracy of the meter was checked using a NIST traceable 0.3333 m Ω shunt accurate to within ± 0.0003 m Ω . The estimated uncertainty of resistance measurements is ± 0.02 m Ω . Resistance values ranged between about 2 and 20 m Ω , depending on L and A , and thus had a relative uncertainty between 1 and 0.1 percent. Leads were sanded with 600 grit paper, cleaned, dried, and coated with a contact enhancer DeoxIT® (CAIG Laboratories, Inc.) prior to testing. If the wire was made with a HIP can, only the center section of wire was tested so that the pure Cu ends could be avoided. In order to keep the wire straight during testing, fine springs were attached to the wire ends to hold the wire in tension. The location of the sensing clips was marked on the wire with a fine felt-tipped marker. After R was measured, clips were removed and L was measured using a magnifying glass and 24-in. calipers. The uncertainty of L is estimated to be ± 0.003 in., which was less than 0.1 percent for most L measurements.

Results and Discussion

Material Workability and Wire Quality

As seen in the larger piece of the sectioned ingot in Figure 1, occasional voids (characteristic of shrinkage voids) were present in the Cu.4C ingot. An unusual aspect of the voids in the Cu.4C ingot was that the void interiors were black. Normally, shrinkage voids in Cu are clean and bright. Typical voids do not significantly affect wire processing, since they are evacuated and welded closed during rolling and drawing. The voids in the Cu.4C ingot, however, which appeared to be coated with C powder, did negatively affect workability. Figure 4 shows the pure Cu and Cu.4C HIPed ingot (HIPed without using a tube) sections after several rolling steps. The pure Cu sample worked easily. However, the covetic sample split and broke in some areas, and frequently black powder decanted from the breaks and splits. Since this black powder had the characteristics of carbon powder, and C additions were the only difference between the samples, it was believed that the black powdery material was C. Figure 5 shows this was confirmed by SEM and EDS analyses of the wire's internal surface, which was exposed when the wire split during rolling. Figure 5 shows the opened pore to be coated with C. The C-coated voids in the Cu.4C material get elongated during wire working, but they do not weld shut, creating a permanent defect in the material. This makes the wire very weak. Still, voids did not dominate the ingot, so some wire sections in the Cu.4C sample were acceptable for testing. Figure 6 shows optical images of good sections of wire made from the as-received ingot sections. Figure 7 shows examples of below-average quality wire made from ingot sections that were HIPed but not sealed in tubes. Conductivity and density measurements were made using only sections of wire that were judged to be free of significant flaws.



Figure 4.—Hot isostatically pressed and rolled pure Cu sample (top) and Cu-0.4C (wt%) (bottom). In both cases, the sections were HIPed as is, without being placed in a copper tube prior to HIPing; the lines on the paper are 7 mm apart.

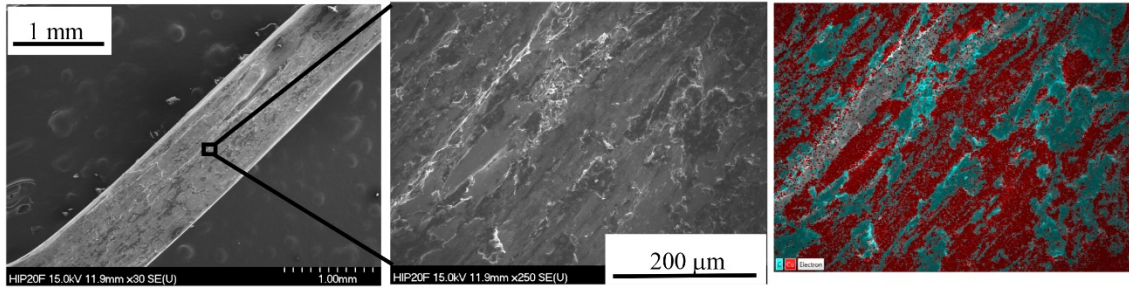


Figure 5.—SEM and EDS of the Cu-0.4C (wt%) wire HIPed without a tube that split open during rolling; in the layered EDS element map C is teal and Cu is red.

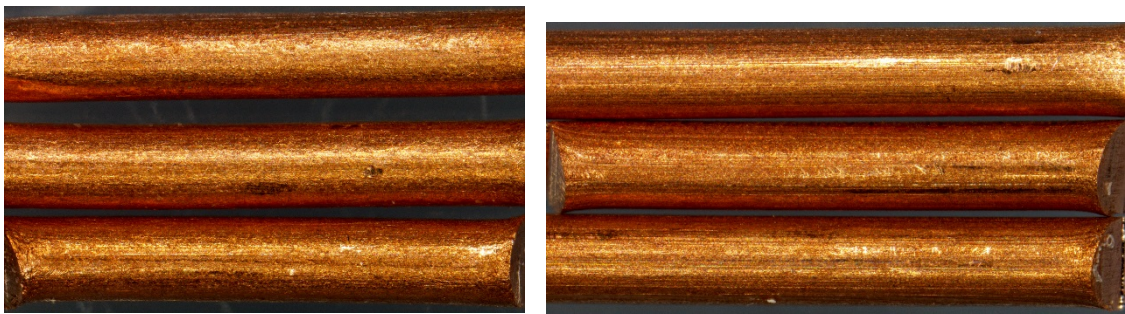


Figure 6.—Sections of above-average-quality 0.67-mm-diameter wire made from as-received (not HIPed) pure Cu (left) and covetic Cu-0.4C (wt%) (right).

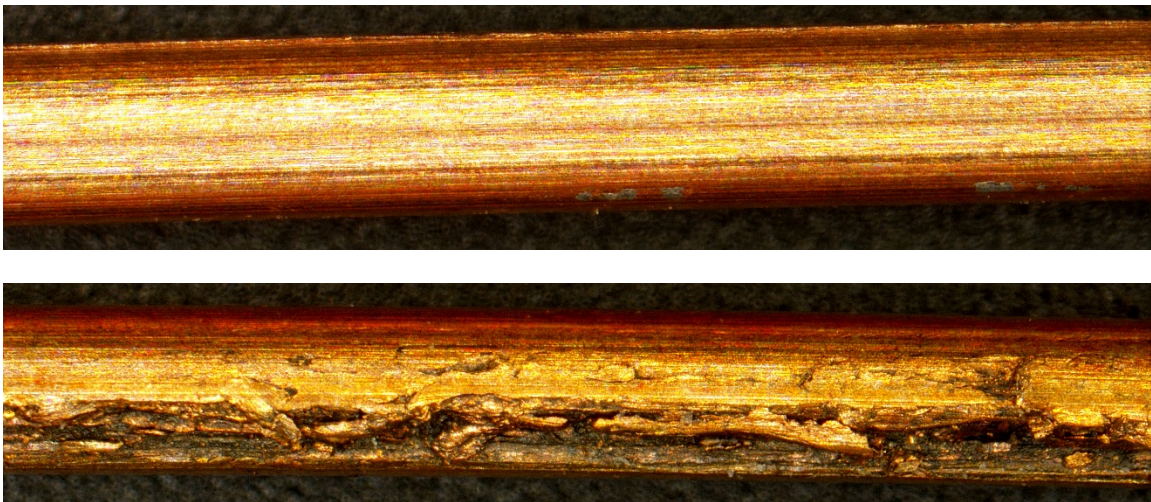


Figure 7.—Examples of below-average-quality wire made from sections HIPed without tubes: pure Cu on top, covetic Cu-0.4C (wt%) on the bottom; wires have 0.93-mm diameters.

Figure 8 shows longitudinal and transverse cross sections of wire made from ingot sections HIPed in Cu tubes, wherein the tube became part of the wire. The pure Cu sample appears to be fully dense and single phase, although with close examination some second-phase inclusions were found at what is believed to be the sample-tube interface (Fig. 8). The Cu.4C covetic (HIPed in a tube) wire had large areas that did not appear to be fully dense, and they had a much higher concentration of what appeared to be a second phase. The presence of the second phase coincided with the regions riddled with the C-coated voids. The black lacy structure in the Cu.4C wire is consistent with other observations made during sectioning and drawing, which indicated that voids in the material were lined with powdery carbon. The concentration of C in the collapsed voids of the covetic samples was confirmed by SEM and EDS analysis, the results of which are shown in Figure 9. Based on the longitudinal and transverse sections in Figures 8 and 9 it can be seen that these C-peppered voids do not weld closed during rolling and drawing and appear to result in a high void fraction. However, as will be shown, a significant difference in density was not found among the samples.

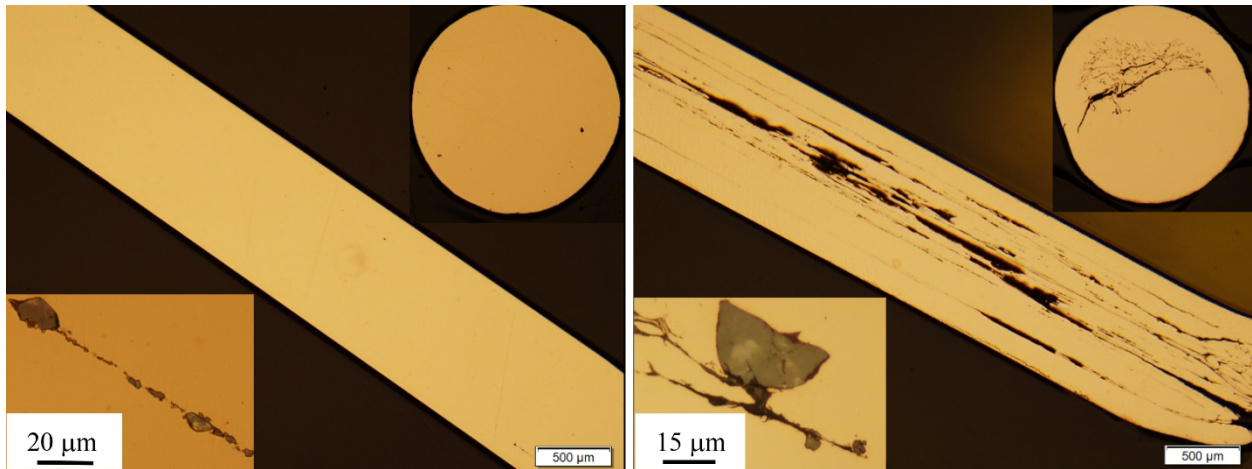


Figure 8.—Longitudinal and transverse cross sections of pure Cu (left) and Cu-0.4C (wt%) (right) 1-mm-diameter wires made from samples sealed in Cu tubes and HIPed; the inclusions in the high-magnification inserts are Si.

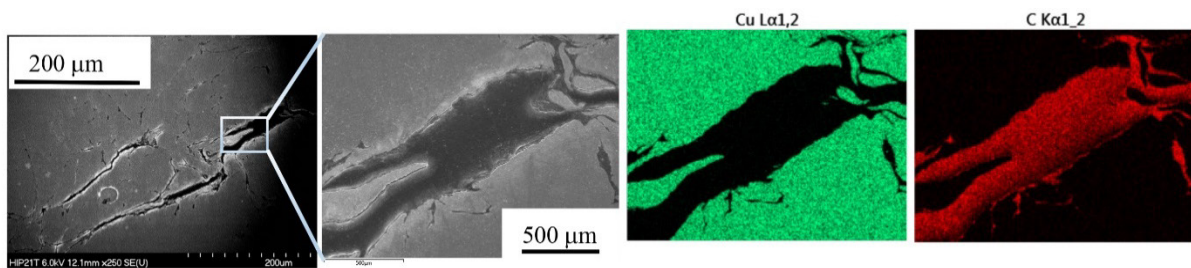


Figure 9.—SEM and EDS of the transverse cross section of Cu-0.4C (wt%) (HIPed in a tube) wire showing collapsed void coated with C.

Compositional Analyses

Analysis results for trace elements after various stages of processing of the nominally pure Cu and the covetic Cu.4C ingots are shown in Table I. The nominal amount of C in the covetic Cu.4C material does not appear to be achieved; only small amounts of C were detected in the Cu.4C wire samples, and low amounts of C were found in the original ingot. Trace elements were about 3× higher in the Cu.4C ingot and wire compared to in the pure Cu samples. The elements Fe, Mn, and Al are expected to be most deleterious, since the conductivity of Cu is quite sensitive to these elements (Refs. 11 and 18). Still, based on the literature, a total of 40 ppm of these damaging impurities is expected to lower conductivity no more than 4 percent (Refs. 11 and 18).

Density and Void Fraction

The measured densities of wires made from the three sections cut from each ingot are shown in Table II. The uncertainty of the density measurements was approximately $\pm 0.1 \text{ g/cm}^3$; thus all samples were not distinguishable from the full density of pure Cu (8.96 g/cm^3) or the commercial Cu wire included for comparison. Therefore, the void fractions in all wires appear to be negligibly small. The Cu.4C section that was HIPed in a Cu tube had the lowest density, which implies a void fraction of about 1 percent, which seems consistent with the appearance of the wire interior shown in Figure 8. Still, even this sample, given the estimated error, is barely distinguishable from pure fully dense Cu. A density decrease of about 1.4 percent was expected based on the nominal composition of Cu-0.4C (wt%, or 1.77 vol%); however, chemical analysis indicates less than half of the nominal C amount, and a large amount of C segregation to surfaces and pores was observed in the metallographic and SEM examinations (Figs. 5, 8, and 9).

TABLE I.—ANALYSIS OF TRACE METALLIC ELEMENTS AND CARBON IN AS-RECEIVED INGOTS OF PURE Cu AND COVETICALLY ALLOYED Cu-0.4C (wt%) AND IN WIRES MADE FROM AS-RECEIVED INGOTS, SECTIONS OF THESE INGOTS THAT WERE VACUUM SEALED IN Cu TUBES AND HOT ISOSTATICALLY PRESSED (HIPed), AND HIPed EMPTY Cu TUBE^a

Element	Unit	Pure Cu			Cu-0.4C (wt%)			Cu tube
		Ingot	Wire	Canned and HIPed wire	Ingot	Wire	Canned and HIPed wire	HIPed wire
Cu	wt%	>> 99	>> 99	>> 99	> 99	>> 99	> 99	>> 99
Ag	ppmw	3	3	20	10	10	25	30
Al	ppmw	(b)	(b)	5	10	(b)	50	(b)
Fe	ppmw	14	11	(b)	29	31	(b)	(b)
Mn	ppmw	0.4	0.4	13	2.0	2.0	21	6
Na	ppmw	1	4	20	3	14	40	50
Zr	ppmw	(b)	(b)	(b)	(b)	(b)	(b)	47
C	wt%	0.004	0.005	0.003	0.025	0.006	0.208	0.011
C	wt%	-----	-----	0.001	0.184	-----	0.226	-----

^aTrace metals were analyzed with inductively couple plasma atomic emission spectroscopy (ICP–AES), and carbon was analyzed with combustion infrared detection.

^bElement was not detected.

TABLE II.—DENSITY OF WIRE SAMPLES

Sample	Density, g/cm^3
Commercial Cu wire	8.91
Pure Cu as received	8.98
Pure Cu as received, HIPed	9.00
Pure Cu HIPed in tube	8.91
Cu-0.4C (wt%) as received	9.00
Cu-0.4C as received, HIPed	8.90
Cu-0.4C HIPed in tube	8.86

TABLE III.—CONDUCTIVITY OF
BEST WIRE SECTIONS

Sample	Conductivity, MS/m
Commercial Cu wire	57.47
Pure Cu as received	58.97
Pure Cu as received, HIPed	57.49
Pure Cu HIPed in tube	57.08
Cu.4C as received	53.69
Cu.4C as received, HIPed	51.02
Cu.4C HIPed in tube	54.09

Electrical Conductivity

The measured electrical conductivity of the wires processed by the different methods from sections of each ingot are presented in Table III. The uncertainty of the conductivity measurements is approximately ± 1 MS/m, where MS/m are mega-siemens per meter. All of the pure Cu wires had conductivities approximately equal to 100 percent of the International Annealed Copper Standard (IACS) of 58 MS/m, as did the commercial Cu wire tested. The density and conductivity measurements together indicate that the rolling and drawing process sufficiently collapses voids, resulting in fully dense wire; HIPing did not increase conductivity or measurably decrease void fraction. The conductivity of the covetic Cu.4C wires was on average 9 percent lower compared to the wires similarly processed but without added C. Given the consistently low void fractions estimated based on density and chemistry measurements, only a small portion (~1 out of 9 percent) of this conductivity difference can be attributed to void fraction in the wire. The added trace elements found in the Cu.4C wires are expected to cause a conductivity decrease of about 3 percent (Ref. 18). The remaining 5 percent may be caused by poorly conducting interfaces created by collapsed voids lined with elemental C. The microstructures shown in Figures 5, 8, and 9 are consistent with this scenario.

Conclusions

The distribution of C in the covetic ingot and resulting wires was not homogeneous. Voids were found in the as-received ingots. These voids might be from solidification shrinkage or trapped gas resulting from vigorous mixing during processing. These voids were lined with powdery C and did not weld closed during cold working or hot isostatic pressing (HIPing). This resulted in a structure of elongated C-lined interfaces in the covetic wires, making the material weak and difficult to work into wire. The electrical conductivity of wires made from the nominal Cu-0.4C (wt%) covetic ingot were 9 percent lower than the pure Cu wires similarly processed. This is a very large decrease considering the (1) small amount of C added, (2) high level of Cu purity even in the Cu-0.4C wires, and (3) low void fraction (very close to full density). The electrical conductivity of most C phases is in the range characteristic of semiconductors; however, moderate C conductivity alone cannot explain the observed conductivity decline. It is concluded that the conductivity decline resulted from (1) impurities from the added C, (2) void fraction, and most significantly by (3) a structure of poorly conducting interfaces created by C-lined voids.

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