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Deformation-Processed Copper-Chromium Alloys: Optimizing Strength and Conductivity

S.T. Kim, P.M. Berge, and J.D. Verhoeven*

A developmental research program has been carried out to produce deformation-processed copper-chromium wires with optimum combinations of ultimate strength and electrical conductivity. Properties are improved by use of deformation to assist in the precipitation of chromium from solid solution. Various combinations of deformation, solution heat treatment plus quenching, and aging have been studied and an optimum processing scheme determined. Using this processing scheme, it is shown that deformation-processed Cu-7 vol% Cr wires have strengths on the order of 50% higher than commercial copper alloys available in the same conductivity range of 75 to 90% IACS.

Keywords
copper-chromium alloys, deformation processing, electrical conductivity

1. Introduction

RESEARCH on deformation-processed Cu-X alloys, where X is a body-centered cubic element, has shown (Ref 1, 2) that wires of this material can be produced that have better combinations of strength and electrical conductivity than are available in the best commercial copper alloys. Deformation processing consists of deforming a precursor billet to a very large deformation, usually a true strain, η (defined as the natural log of the original over the final area), of greater than around 3 (reduction in area of 95%). At these large deformations, the X phase deforms into aligned ribbon-shaped filaments in the copper matrix, producing essentially a metal/matrix composite material. Initial studies were done with niobium or tantalum as the X element. These elements have very little solubility in copper; therefore, precursor billets could be prepared by solidification techniques without reducing conductivity due to electron scattering from solid-solution elements in the copper matrix. When X elements that have significant solubility in copper are used, a severe reduction in conductivity occurs. Both iron and chromium are attractive X elements because of their low costs. Work on iron (Ref 3), however, found that the dissolved iron could not be effectively precipitated from the copper, making it necessary to employ the more costly powder processing techniques to achieve properties comparable to copper-niobium alloys. This paper presents a study of copper-chromium alloys using chill-cast precursor billets.

Initial studies were done on Cu-15 vol% Cr alloys prepared as 50 mm diam chill castings. Figure 1 presents conductivity versus temperature data for a sample cut from the casting (solid points). The conductivity was measured using the standard four-probe technique in a controlled-atmosphere furnace as the temperature was ramped up to 810 °C and back down to room temperature at a rate of approximately 1 °C/min. It is seen that upon heat-up the conductivity drops monotonically with temperature except over a range from around 400 to 500 °C, where it rises significantly. This rise results from the precipitation of chromium, which had been quenched into the copper matrix in the chill casting. (If the as-cast sample is heated back up to 810 °C after the first heat cycle, it then follows the upper curve on both heat-up and cool-down). The second set of data in Fig. 1 was measured after the cast ingot was deformed by $\eta = 3.3$. Here, the precipitation of chromium begins at a lower temperature, and after cool-down the conductivity is higher than it was for the undeformed material. The first two rows of Table 1 present the conductivity values for the two alloys of Fig. 1 at room temperature before and after the cycle to 810 °C. The remaining rows present similar data for samples given different pretreatments. In the heat-treated material, the cast ingot was heated to 750 °C for 24 h and then program-cooled to room temperature in 24 h. It is evident that this treatment is less effective in precipitating chromium from the copper matrix than the deformation processing followed by heat cycling to 810 °C. Two wires were prepared with a deformation of $\eta = 6.0$—one deformed directly from the cast alloy and the other from the cast alloy after the heat treatment. Deforming after the heat treatment produces increased conductivity.

These experiments illustrate two important factors involved in the control of conductivity of cast copper-chromium alloys:

- A significant increase in conductivity occurs with removal of chromium from solid solution upon heating to the 400 to 500 °C range.
- Thermomechanical treatments are more effective than thermal treatments alone in improving conductivity.

In addition, it has been reported (Ref 4), and was confirmed here, that the deformability of copper-chromium alloys is enhanced by an initial solution and quenching treatment. This property is quite beneficial to deformation processing because of the large deformation desired. In view of these facts, a developmental research program was undertaken to develop an optimal thermomechanical processing scheme for preparing copper-chromium alloys with maximum combinations of strength and conductivity. The work was done on 7 vol% Cr alloys because this lower concentration of chromium would be more economical and yet would be high enough to produce significant strength increases over the commercial age-hardening chromium-copper family of alloys, C18200 to C18500.

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2. Experimental Method

Chill-cast ingots of Cu-7 vol% Cr (5.7 wt%) were prepared by melting oxygen-free high-conductivity copper and commercially pure chromium in a vacuum induction melting furnace in either graphite or yttria-coated graphite crucibles. The melt was released through a 6 mm diam hole in the bottom of the crucible and poured into a 25 mm (1 in.) diam water-cooled copper mold. The hole was initially plugged with a hard-fired high-purity alumina tube containing a type B thermocouple used to monitor the melt temperature. The charge was heated to 900 °C under vacuum and backfilled with high-purity argon for further heating. Initial problems involved difficulty in getting the chromium to dissolve into the copper and excessive subsurface porosity in the ingots. Complete dissolution of the chromium required ramping the temperature to 1600 °C with the 3 kHz power source to produce good stirring. The porosity problem was overcome by outgassing the melt for 10 min at 1600 °C under a pressure of 10 torr. The chamber was then backfilled with argon and the melt cooled to 1300 °C and poured from that temperature. The 50 mm (2 in.) diam 15 vol% Cr ingots discussed in section 1 were made with the same procedure using a 50 mm (2 in.) diam copper chill mold.

Table 1 Room-temperature electrical conductivity of several Cu-15 vol% Cr alloys

Material	Conductivity, % IACS Before heating to 810 °C	After heating to 810 °C
As cast	47	76
Deformed to $\eta = 3.3$	46	83
HT (heat treated)	74	74
Deformed to $\eta = 6.0$	49	83
HT + deformed to $\eta = 6.0$	83	88

The 25 mm (1 in.) diam ingots were deformed initially by swaging and later by wire drawing as discussed later. The solution treatments involved heating the samples in a vacuum furnace backfilled with argon and quenching directly into water with vigorous stirring. Aging treatments were also done in a vacuum furnace backfilled with argon.

Conductivity measurements were made using the standard four-probe technique to measure resistivity at room temperature. The conductivities, in units of %IACS (International Annealed Copper Standard), were calculated using the standard 20 °C pure copper resistivity of 1.7241 $\mu\Omega \cdot$ cm. The small correction from the measured room temperature value to 20 °C was made using a resistivity temperature coefficient of 7×10^{-3} $\mu\Omega \cdot$ cm/°C determined from the slope of data of Fig. 1 at 20 °C. Reported conductivities are the average of three measured values. The tensile tests were performed at a strain rate of 6.7×10^{-4}/s, and the reported values of the ultimate tensile strengths

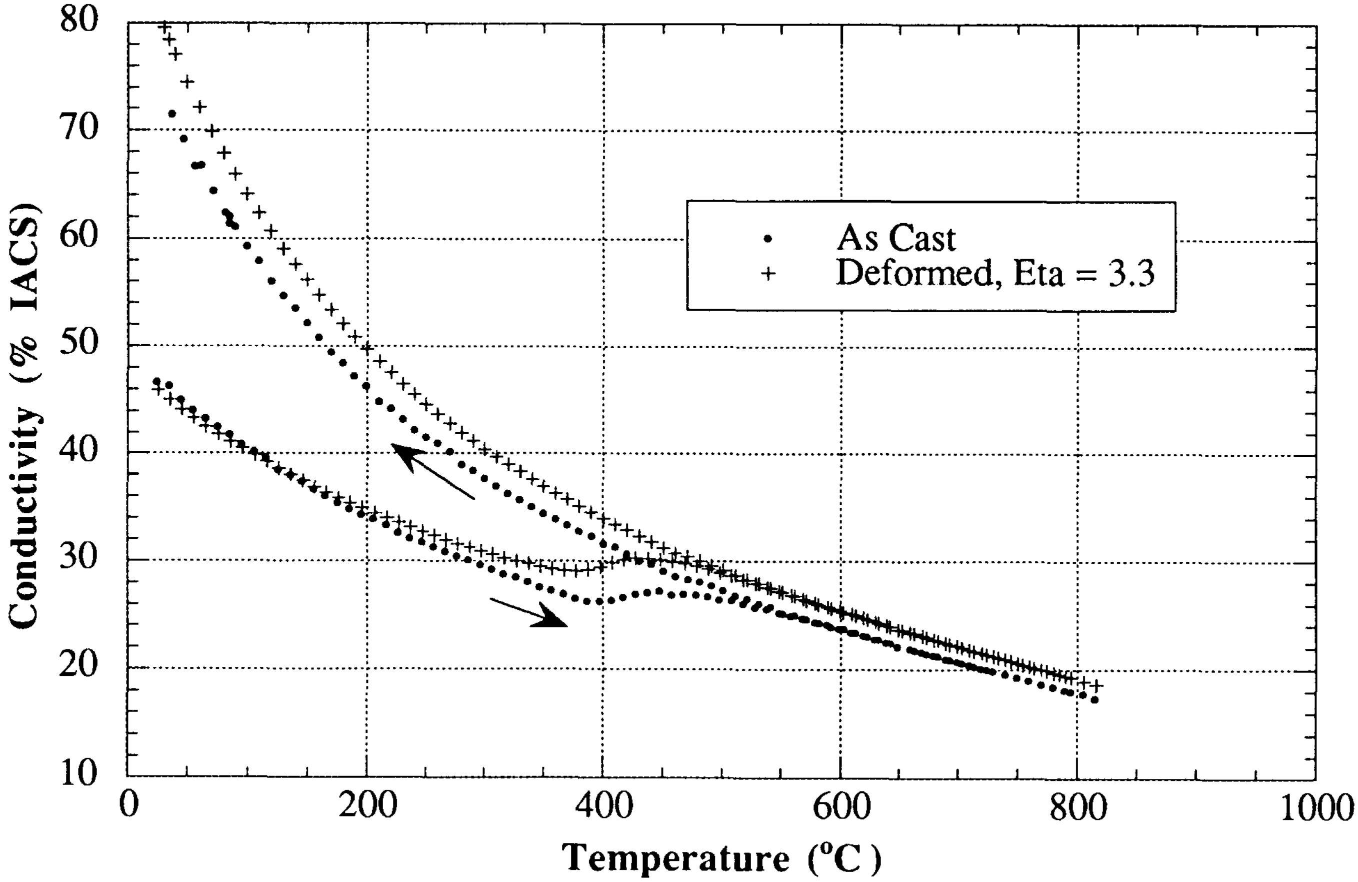

Fig. 1 Electrical conductivity versus temperature plot for two Cu-15 vol% Cr alloys heated to and cooled from 810 °C

are the average of three samples. It was necessary to use special grips for wires with diameters smaller than 0.1 mm.

3. Results and Discussion

3.1 *Part I*

As has been discussed, initial work showed that optimum conductivity is achieved through a combination of thermal and mechanical processing. In order to determine which combinations of thermal and mechanical processing would lead to the best combination of strength and conductivity, various combinations of the following four types of processes were examined:

- Deformation (D): produced by swaging or drawing
- Solution treatment (S): 1010 °C for 1 h + water quenching
- Aging (A): 420 °C for 12 h
- Heat treatment (H): 750 °C for 3 h + program cool to 21 °C in 48 h

A series of eight combinations were studied and are summarized in Table 2. The code used in Table 2 will be explained for the first series, DSDAD(1). Three deformation steps were employed, with the solution heat treatment between the first two

Table 2 Summary of experiments done in part I study

Process	η_1 (Diam, mm)	η_2 (Diam, mm)	A or H (Diam, mm)	η_3 (Diam, mm)	η_{total} (Diam, mm)	UTS, MPa	% IACS
DSDAD(1) (3-3-3)	2.8 (25 → 6.3)	2.7 (1.6)	420 °C/12 h (1.6)	3.0 (0.36)	8.5 (0.36)	925 ± 11	71.8 ± 0.9
DSD (3-5-0)	2.8 (25 → 6.3)	4.6 (0.63)	None	None	7.4 (0.63)	835	35.9
DSDA (3-5-0)	2.8 (25 → 6.3)	4.6 (0.63)	420 °C/12 h (0.63)	None	7.4 (0.63)	687	84.5
DSDAD(2) (3-5-1)	2.8 (25 → 6.3)	4.6 (0.63)	420 °C/12 h (0.63)	1.1 (0.36)	8.5 (0.36)	841	79.5
DHD (6-0-3)	5.5 (25 → 1.6)	None	750 °C/3 h/48 h (1.6)	3.0 (0.36)	8.5 (0.36)	789	85.0
DSDAD(3) (1-5-3)	0.6 (25 → 19)	4.9 (1.6)	420 °C/12 h (1.6)	3.0 (0.36)	8.5 (0.36)	816	75.3
DSDHD (1-5-3)	0.6 (25 → 19)	4.9 (1.6)	750 °C/3 h/48 h (1.6)	3.0 (0.36)	8.5 (0.36)	780	85.4
DSADHD (1-5-3)(a)	0.6 (25 → 19)	4.9 (1.6)	750 °C/3 h/48 h(a) (1.6)	2.8 (0.41)	8.3 (0.41)	739	84.0

(a) The aging treatment was done at 15 mm diameter with the condition of 420 °C/5 h.

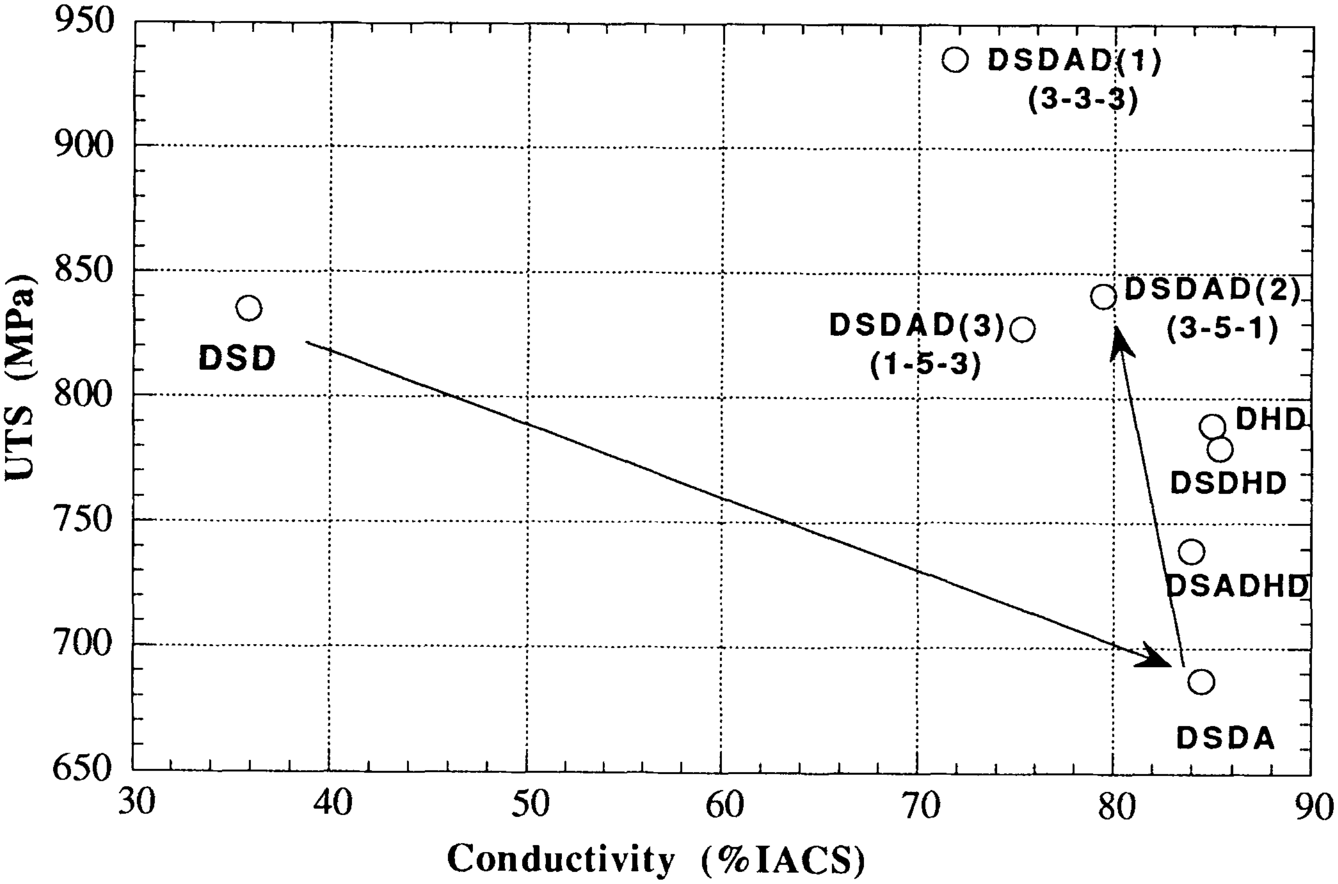

Fig. 2 Strength versus conductivity data for samples listed in Table 2

and the aging treatment between the last two: hence, DSDAD. The amount of strain on the first deformation is labeled η_1, and the value of 2.8 corresponds to a swaging reduction of the casting from 25 to 6.3 mm. The 6.3 mm rod was now given the solution treatment and wire drawn to 1.6 mm. This second deformation strain of $\eta_2 = 2.7$ followed the solution treatment. The 1.6 mm rod was then given the aging treatment followed by drawing to a final diameter of 0.36 mm. The final deformation is termed η_3. The total deformation strain for this series is simply the sum of $\eta_1 + \eta_2 + \eta_3$, which is listed as 8.5. The values of the ultimate tensile strength and the conductivity of the final 0.36 mm diam wire are listed in the right two columns. The plus or minus deviations are average values and are typical for all of the data. The label for this first series includes the term (3-3-3), which is a listing of the three strains used in the three deformations, rounded to integers. This code has been included in the labels for each series; it is evident that a total strain of roughly $\eta = 8$ was used for all of the experiments.

The effects of the various combinations of processes can be evaluated by plotting the data as shown in Fig. 2. As expected, the DSD processing has the lowest conductivity because it was not heated following the quench from the solution temperature. Therefore, the chromium trapped in solid solution by the quench reduces the conductivity. When the DSD treatment is followed by the aging step, DSDA, the conductivity rises to the highest value of around 85% and the ultimate tensile strength falls to the lowest observed value. Apparently the loss of solid-solution strengthening is not compensated for by an age-hardening reaction. The solid-solution chromium is probably precipitating on the preexisting chromium particles that were elongated into filaments by the two deformation steps. When the DSDA processing is followed by the final drawing step, DSDAD, a significant increase in strength is obtained with only a small loss in conductivity. The final drawing must reduce the chromium filament size and spacing to increase the strength. Previous work on deformation-processed copper-niobium alloys (Ref 5) has shown that electron scattering from copper/niobium filament interfaces becomes the dominant mode of loss of conductivity in these alloys at high strength levels. Apparently, at the strength levels of these copper-chromium alloys, the final drawing step does not reduce the filament spacing enough to provide a large increase in electron scattering, but it does reduce it enough to provide significant increases in strength. The relative amounts of strain in the three deformation steps in the DSDAD processing were varied in the series labeled with suffixes (1), (2), and (3). The highest strengthening occurs with only a small loss in conductivity for series (1), where the strains are roughly equal in all three steps.

The H heat treatment was utilized because it was thought to be an effective method for precipitating the chromium from solid solution. It appeared to be so, as the conductivities of these samples are consistently high. However, it is evident that drawing after an H treatment is not as effective for strengthening as is drawing after the A treatment. A possible explanation is that much more filament coarsening would be expected during the 750 °C H treatment compared to the 420 °C A treatment.

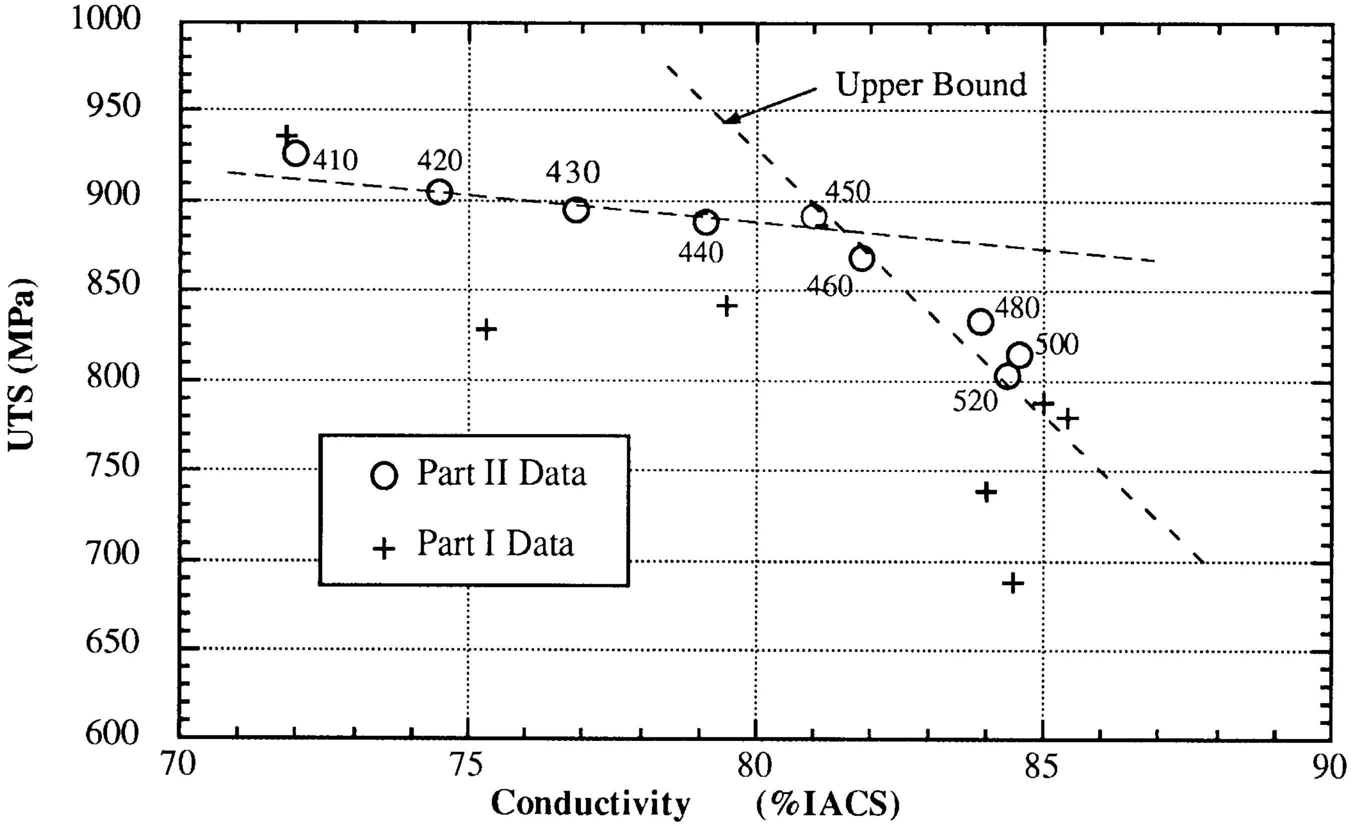

Fig. 3 Effect of aging temperature on strength versus conductivity data in the DSDAD process

3.2 *Part II*

The major conclusion of the part I study is that the DSDAD treatment appears to provide the best combination of strength and conductivity. Therefore, experiments were done to evaluate the optimum temperature for the aging step in the DSDAD process. The processing procedure employed was that shown in Table 2 for DSDAD(1), except that the aging treatment was carried out for 4 h at temperatures ranging from 410 to 520 °C. The resulting strength versus conductivity data are shown in Fig. 3 (dashed lines). As the aging temperature is increased from 410 to 450 °C, a significant increase in conductivity is found with little loss in strength. At aging temperatures above 450 °C, the strength starts to drop more with increasing aging temperature. What appears to be happening is that below 450 °C the conductivity is rising due to the loss of solid-solution chromium from the copper matrix, but strength does not fall much because of negligible coarsening of the chromium filaments. Above 450 °C the larger slope of the dashed line is probably due to a coarsening of the chromium filaments.

One reasonable explanation of these data is that at aging temperatures near 450 °C the solid-solution chromium has been fully removed, and at higher aging temperatures the increase in conductivity and loss of strength both result primarily from increased filament size and spacing due to coarsening effects. If such were the case, then one would expect that the upper line in Fig. 3 might represent an upper bound that characterizes optimum combinations of strength and conductivity. Notice that the dashed line through the higher-temperature data also passes through the data from part I for the DHD and DSDHD experiments. One expects these samples to have coarser chromium filaments with lower strengths and higher conductivities, and they might represent two more data points on an upper bound line.

Additional evidence that the high-temperature line in Fig. 3 might define an upper bound is presented in Fig. 4, where the line is plotted on literature data for deformation-processed Cu-15 vol% X alloys of copper-niobium, copper-tantalum, and copper-chromium. The slopes of the lines are essentially parallel, with the Cu-7Cr line displaced to slightly higher values.

3.3 *Part III*

Additional variations in the processing were studied in part III. Experiments confirmed reports (Ref 4) that solution treating of copper-chromium ingots improves drawability. Therefore, the 25 mm (1 in.) diam Cu-7Cr ingots were solution treated as the initial step in this work. To determine whether the upper bound line could be extended to higher strengths, the total deformation was increased to strains of around 9.5. This was about as high as it was possible to go and still obtain wires large enough for convenient testing (diameters of approximately 0.2 mm). Two series of tests, termed A and B, were performed.

In series A (first two rows of Table 3), aging treatments were used between the first two reduction steps, giving the processing sequence of SDADAD. The first aging treatment was done at either 450 °C/6 h or 500 °C/6 h, and the second aging treatment was at 500 °C/6 h. There was little problem with breakage

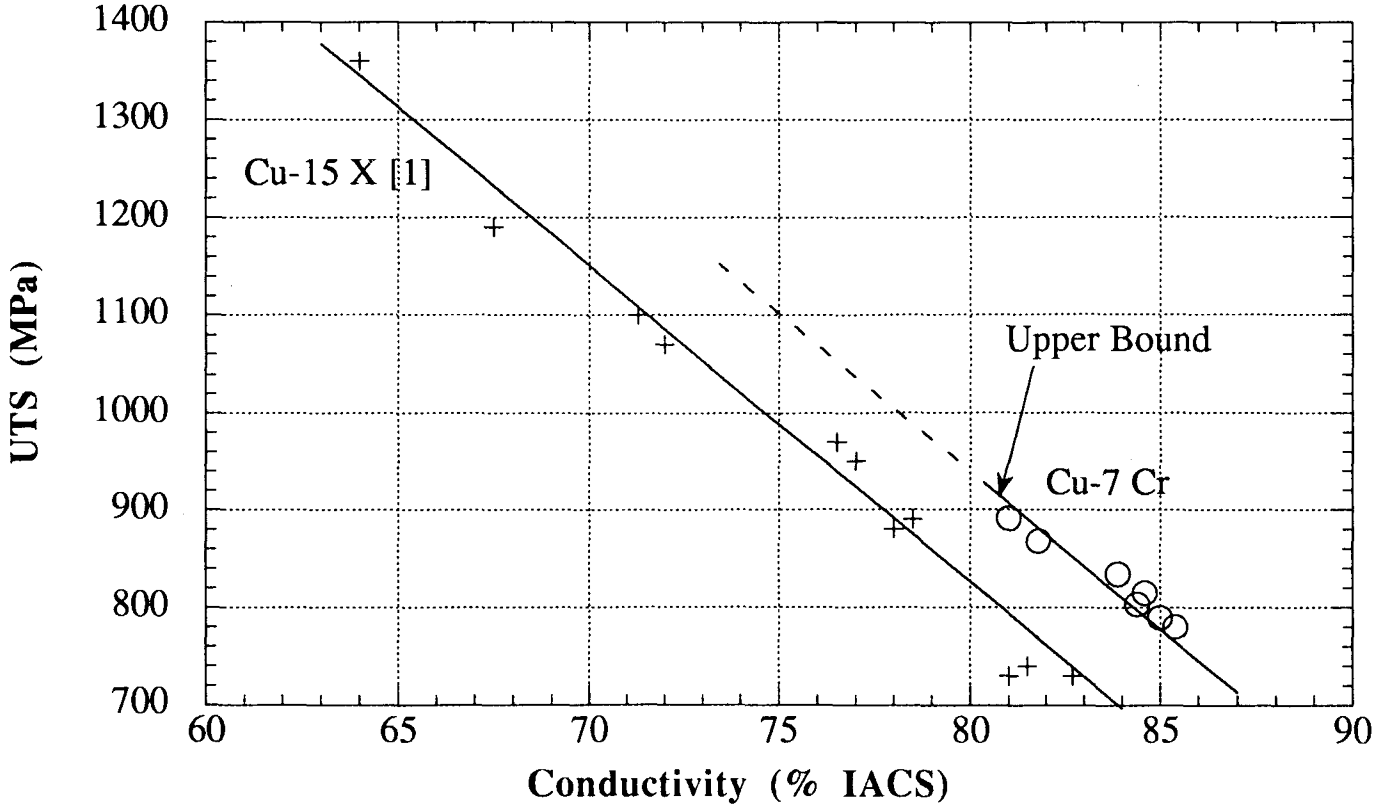

Fig. 4 Comparison of strength versus conductivity of Cu-7 vol% Cr data to literature data on Cu-15 vol% X alloys (where X = niobium, tantalum, and chromium)

on drawing in these doubly aged samples after either aging treatment, but the strength/conductivity properties of these samples were well below the upper bound line (Fig. 5).

In series B (final two rows of Table 3), the solution-treated ingots were given the DSDAD treatment, similar to the work in parts I and II. The effect of aging time was examined in the SDSDAD (450) samples by aging at 450 °C for 6 to 48 h. As shown in Fig. 5, this produced strength/conductivity data that run down the extension of the upper bound line. The series B sample aged at 500 °C/6 h is also seen to fall on the upper bound line. Hence, this series of tests is consistent with the idea that the upper bound line represents the optimum combination of strength and conductivity that can be produced in the Cu-7Cr alloy and that it might possibly be extended to higher strengths by starting with larger ingots, which would allow larger total strains in small-size wires.

It was expected that the series A samples would have finer filaments than series B samples because of the much lower temperature of the first aging step compared to the 1000 °C solution temperature employed in series B at this same stage of processing. It was also thought that the series A samples might have higher conductivities because the double aging treatments

Table 3 Summary of experiments done in part I study

Process	η_1 (Diam, mm)	η_2 (Diam, mm)	A or H (Diam, mm)	η_3 (Diam, mm)	η_{total} (Diam, mm)	UTS, MPa	%IACS
Series A							
SDADAD (450)	4.6 (25 → 2.5)	1.8(a) (1.0)	500 °C/6 h (1.0)	3.2 (0.20)	9.6 (0.20)	823	76.0
SDADAD (500)	4.6 (25 → 2.5)	1.8(b) (1.0)	500 °C/6 h (1.0)	3.2 (0.20)	9.6 (0.20)	810	74.0
Series B							
SDSDAD	4.6	2.5	450 °C/6 h	2.3	9.4	975	77.0
(450)	(25 → 2.5)	(0.71)	450 °C/24 h	(0.23)	(0.23)	950	79.0
			450 °C/36 h			932	80.0
			450 °C/48 h			896	80.0
			(1.0)				
SDSDAD (500)	4.6 (25 → 2.5)	2.5 (0.71)	500 °C/6 h (1.0)	2.3 (0.23)	9.4 (0.23)	953	78.5

(a) Aging condition: 450 °C/6 h. (b) Aging condition: 500 °C/6 h

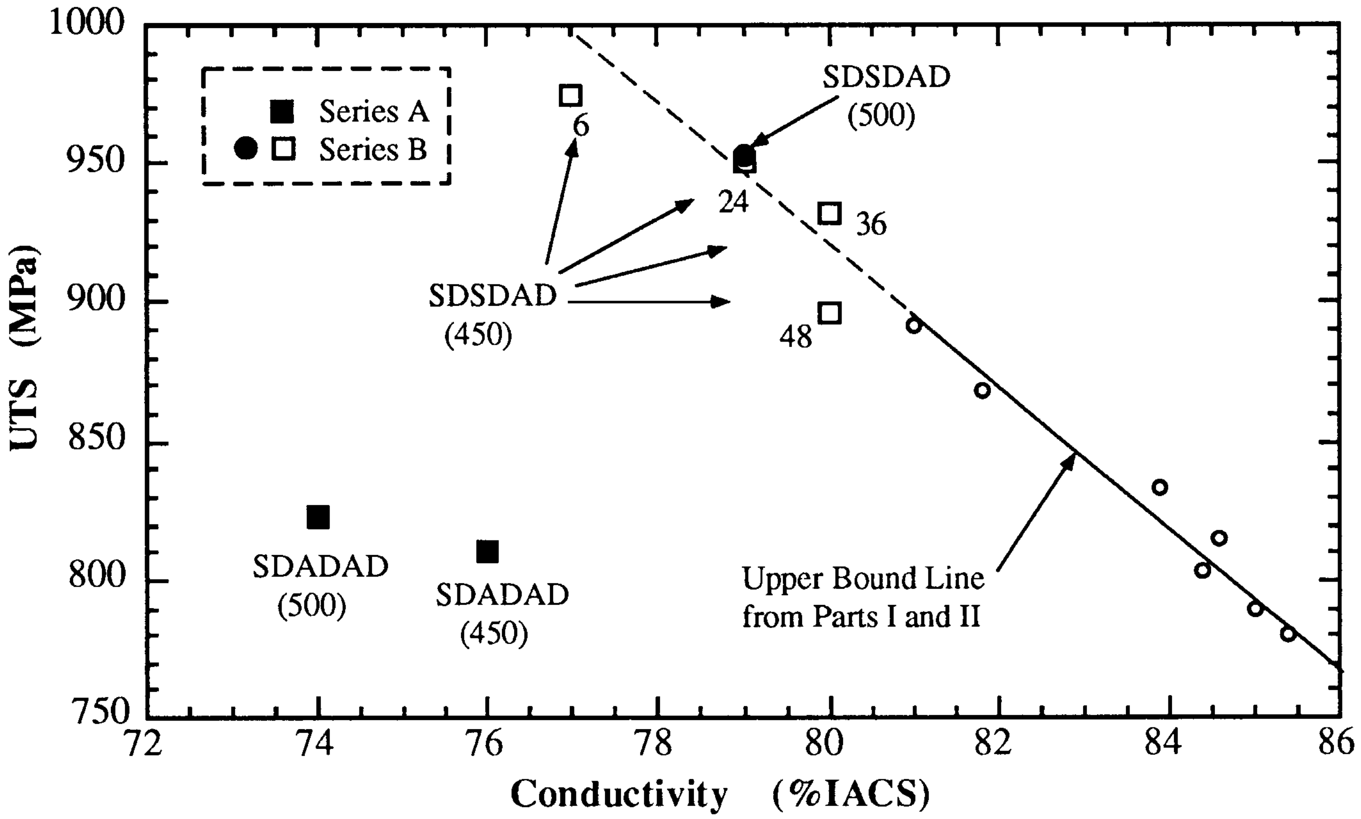

Fig. 5 Strength versus conductivity data for samples listed in Table 3

would be more effective in removing chromium from solid solution following the initial solution treatment. The low values of both strength and conductivity revealed that neither of these effects occurred. Examination of the filaments on deeply etched samples in the scanning electron microscope (SEM) showed that most of the chromium particles had been elongated into the ribbon-shaped filaments characteristic of these deformation-processed alloys (Ref 1, 2). However, the elongated filaments in series A samples revealed serrated edges not present in series B filaments, but the resolution of the SEM was not adequate to pin down the nature of the serrations.

Therefore, filaments were extracted for transmission electron microscope (TEM) analysis from the copper matrix in a solution of 50% nitric acid in water using standard filtering techniques. Figure 6 presents TEM micrographs of the extracted filaments from series A and B samples. The edges of the series A filaments were consistently found to be jagged, with transverse cracks extending inward at frequent intervals along their length, as indicated by the arrows in Fig. 6(a). In contrast, the filaments of the series B samples were significantly smoother and less cracked (Fig. 6b). The stress-strain curves for the series A samples showed roughly the same shapes in the plastic flow regions prior to fracture; thus, the serrated filaments did not lower the tensile strengths due to early onset of fracture. The lower strength of the series A samples probably results from fragmentation of the filaments and less elongation of the filaments compared to the series B samples.

It is not obvious why the series A samples also have a lowered conductivity. Subsequent work (Ref 6) has confirmed that deformation following the second solution treatment produces a strong precipitation of chromium from solid solution. Perhaps the lower conductivity in the B samples results from a reduction of this effect by replacement of the second solution with an aging treatment in the B samples.

Commercial copper alloys available in the same conductivity range as these deformation-processed Cu-7 vol% Cr alloys achieve a large component of strength from age hardening. Figure 7 compares the strength-conductivity of several such alloys to the deformation-processed alloys of this study. The present alloys provide an approximate 50% increase in strength at a given level of conductivity. It is believed that the reason for the improved properties of the deformation-processed alloys is that the electron scattering from the particles of age-hardened alloys plus scattering from remnant solid-solution effects produces a larger loss in conductivity than does the electron scattering from the elongated filaments of the deformation-processed alloys. Because the deformation-processed alloys of this study that produced optimum properties had been solution treated and aged, it would seem reasonable that these alloys might also have some component of age hardening contributing to their strength. The role of age hardening and microstructural development in the optimally processed alloys has been examined in a subsequent study (Ref 6).

4. Conclusions

It has been found that deformation-processed copper-chromium alloys prepared from chill-cast ingots achieve optimum combinations of strength and conductivity by utilizing a combination of mechanical deformation and thermal treatments. Of the processing schemes studied, the DSDAD process was found to produce optimum properties. This scheme includes three deformation steps, with a solution treatment between the first two steps and an aging treatment between the final two steps.

When the temperature/time of the aging step was controlled, the strength/conductivity values tended to move along a common line, which appears to be an upper bound for the best combination of properties in the Cu-7 vol % Cr alloys studied here. Comparison of this upper bound line strength/conductivity properties of commercial copper alloys in the same range of conductivities demonstrates that the deformation-processed Cu-7Cr wires have strengths that are greater by roughly 50%.

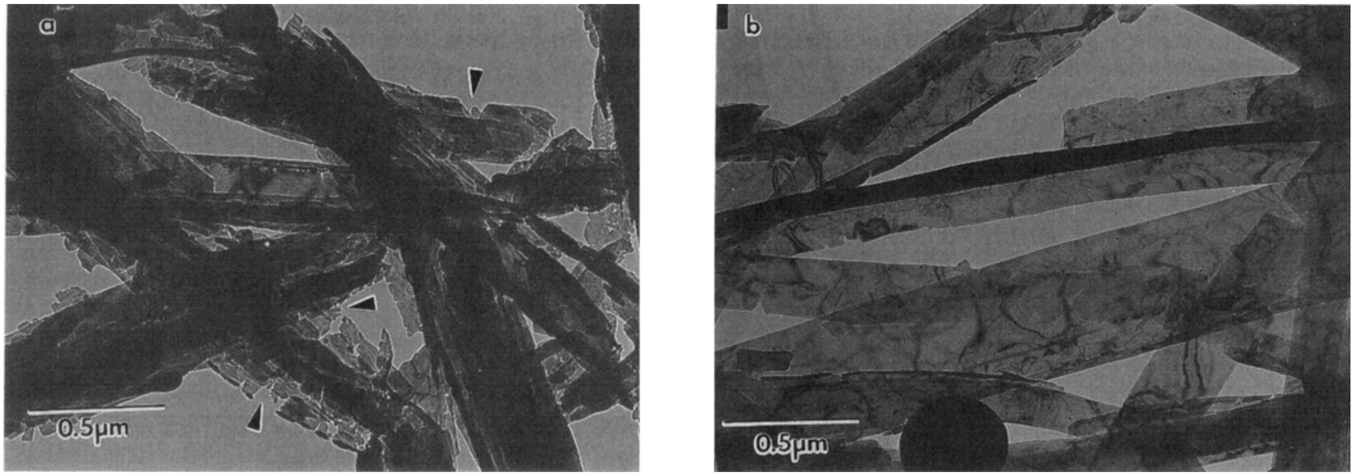

Fig. 6 TEM bright-field micrographs at an original magnification of 40 kx. (a) Filaments from a series A sample. (b) Filaments from a series B sample

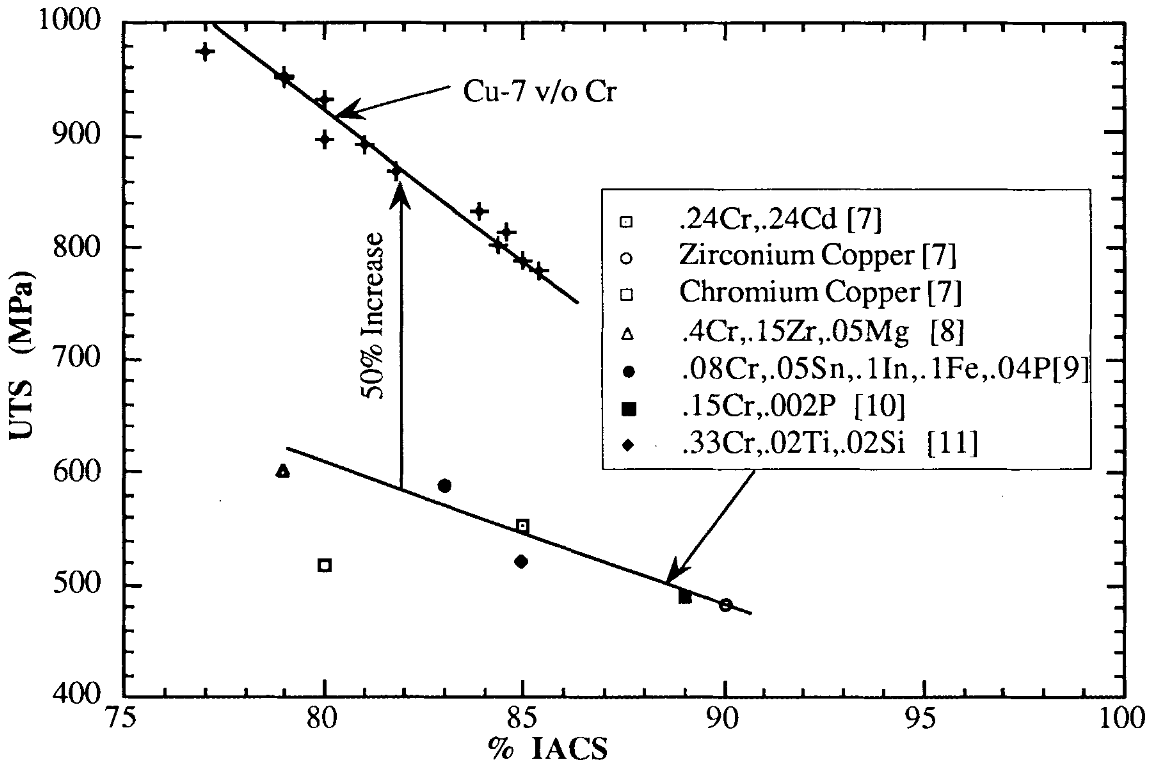

Fig. 7 Comparison of strength versus conductivity data for the Cu-7 vol% Cr wires and for commercial copper alloys having the same range of conductivity

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References

1. J.D. Verhoeven, W.A. Spitzig, L.L. Jones, H.L. Downing, C.L. Trybus, E.D. Gibson, et al., Development of Deformation Processed Copper-Refractory Metal Composite Alloys, *J. Mater. Eng.*, Vol 12, 1990, p 127-139
2. W.A. Spitzig, C.L. Trybus, and J.D. Verhoeven, Chap. 7 in *Metal Matrix Composites: Processing and Interfaces*, R.K. Everett and R.J. Arsenault, Ed., Academic Press, London, 1991
3. G.A. Jerman, I.E. Anderson, and J.D. Verhoeven, Strength and Electrical Conductivity of Deformation Processed Cu-15% Fe Alloys Produced by Powder Metallurgical Techniques, *Metall. Trans. A*, Vol 24A, 1993, p 35-42
4. *ASM Handbook*, Vol 4, *Heat Treating*, ASM International, 1991, p 894
5. J.D. Verhoeven, H.L. Downing, L.S. Chumbley, and E.D. Gibson, The Resistivity and Microstructure of Heavily Drawn Cu-Nb Alloys, *J. Appl. Phys.*, Vol 65, 1989, p 1293-1301
6. T.W. Ellis, S.T. Kim, and J.D. Verhoeven, Deformation-Processed Copper-Chromium Alloys: Role of Age Hardening, *J. Mater. Eng. Perform.*, in this issue
7. H.J. Fisher, D.A. Hay, and W.L. Finlay, The Development and Properties of a New High-Conductivity/High-Strength Copper Alloy, *J. Inst. Met.*, Vol 98, 1970, p 368-375
8. P.W. Taubenblat, W.R. Opie, and Y.T. Hsu, A New Copper Alloy with High Strength and Conductivity, *Met. Eng. Q.*, Vol 12 (No. 4), 1972, p 41-45
9. T. Kawahara and M. Tsuji, "Copper Alloy Leads for Semiconductor Devices," Japanese Patent 63,167,832, 24 July, 1987
10. Y. Oyama, M. Asai, T. Sato, S. Shiga, and S. Shinozaki, "Copper Alloy for Electronic Leads and Its Heat Treatment," Japanese Patent 6,338,561, 19 Feb 1988
11. W. Duerrschnabel, F. Puckert, and M. Bletschacher, "Copper-Chromium-Titanium-Silicon Alloys for Electrical Apparatus," European Patent 264,463, 27 April 1988