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Deformation-Processed Copper-Chromium Alloys: Role of Age Hardening

T.W. Ellis, S.T. Kim, and J.D. Verhoeven*

A processing technique was developed previously to optimize strength and electrical conductivity in deformation-processed copper-chromium wires. It consists of deformation treatments alternated with a solution plus quench treatment and then with an aging treatment. In the present study, samples were examined by transmission electron microscopy at each stage of the optimized process to follow the evolution of microstructure. It was shown that this type of processing develops maximum reduction in size of the chromium dendrite phase without breakage and that the deformation produces a strong precipitation of the chromium from solid solution. The aging treatment does not produce an age-hardening effect. Rather, it produces precipitation of chromium on the existing chromium filaments and relieves the strain in them so that additional reduction by deformation is possible. Additional experiments on copper-niobium alloys, which are not expected to show age hardening, also support these conclusions.

Keywords

age hardening, copper-chromium alloys, deformation processing, electrical conductivity

1. Introduction

CHROMIUM-COPPER alloys are used for applications requiring modest improvements in strength relative to pure copper, while maintaining fairly high electrical conductivities in the 80 to 90% IACS (International Annealed Copper Standard) range. Such alloys are currently designated C18X00 (X = 2 to 5) in the United States by the Copper Development Association (Ref 1). The alloys obtain a significant component of their strength by age hardening. The maximum solubility of chromium in copper is approximately 0.7 wt% at 1077 °C and falls to near zero at room temperature, and the C18X00 alloys utilize chromium levels from 0.40 to 1.2 wt%. The deformation-processed Cu-X alloys were initially developed with the X element being niobium and later tantalum, both of which have little solubility in the copper matrix. Early work (Ref 2) showed that copper-chromium alloys could also be deformation processed to produce elongated filaments of chromium in the copper matrix, similar to the niobium and tantalum alloys. It was then apparent that deformation-processed copper-chromium alloys might have an advantage over the copper-niobium and copper-tantalum alloys because the greater high-temperature solubility of chromium in copper, compared to niobium and tantalum, might allow use of age hardening to achieve an additional strengthening component. A recent study of copper-chromium alloys (Ref 3) utilized an aging treatment to achieve optimum strength/conductivity properties. The role played by age hardening in this optimized processing has been studied using transmission electron microscopy (TEM) techniques, and the results are presented here.

After the solution treating and quenching of an age-hardenable alloy, resistivity is high because of increased electron scattering from the solid-solution solute atoms trapped in the matrix. Upon aging, one would expect the resistivity to drop as the solute atoms are removed from solid solution to form the precipitates that produce the age hardening. In many age-hardenable alloys, however, resistivity is observed to rise to maximum values at near the same conditions that produce peak hardness. This effect is called the anomalous increase in resistivity, and theoretical models (Ref 4, 5) have shown that it is due to essentially a diffraction of the electrons, considered now as waves, from the arrays of very fine precipitates, such as Guinier-Preston (GP) zones, that produce maximum strengths in many age-hardenable alloys. Copper-beryllium alloys display this anomalous increase in resistivity, with the highest-strength alloys having fairly low conductivities of only around 20 to 25% IACS (Ref 1).

A very large body of literature is devoted to the study of the precipitation reaction in copper-chromium alloys (Ref 6-16). These studies have all examined alloys with low chromium levels (less than 1 wt%) and find that optimum strengthening occurs with age-hardening temperatures in the range of 400 to 500 °C. The anomalous increase in resistivity is often not found in copper-chromium alloys, but Fig. 1 presents data (Ref 14) showing a small anomalous increase in resistivity for short aging times. Note, however, that the peak hardness is obtained

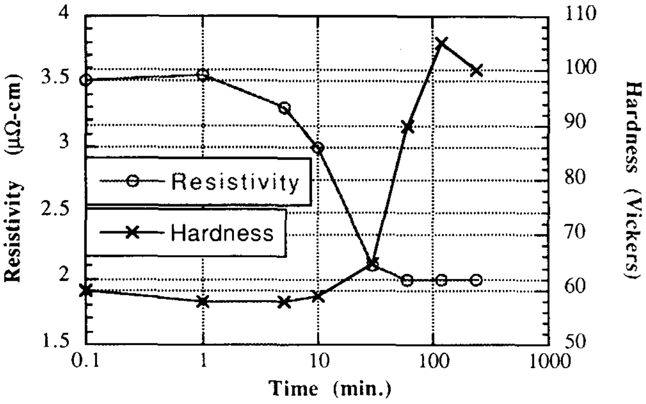

Fig. 1 Resistivity and hardness versus aging time for a Cu-0.75 wt% Cr alloy aged at 400 °C. Source: Ref 14

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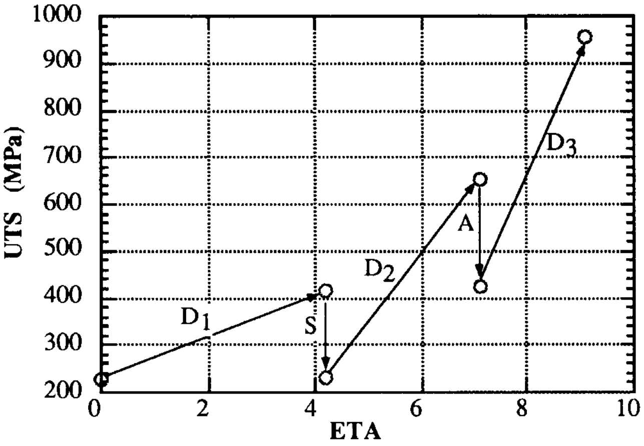

Fig. 2 Ultimate tensile strength versus η during the various steps of the SDSDAD process in Cu-7 vol% Cr

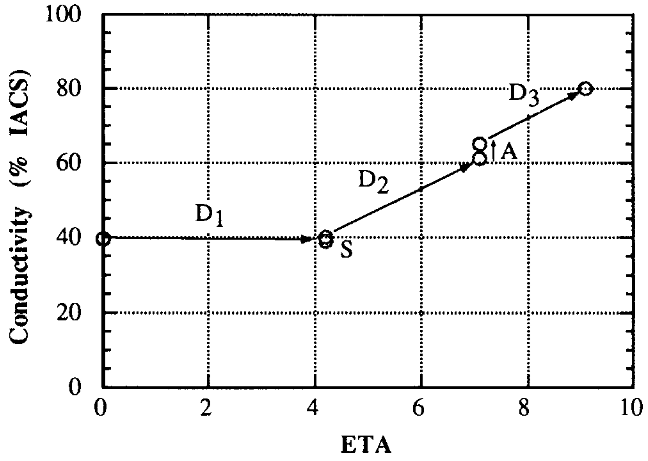

Fig. 3 Percent IACS versus η during the various steps of the SDSDAD process in Cu-7 vol%Cr

Table 1 Details of the steps in the DSDAD processing

Processing stage	Total η	Processing step
S	0	Solution treat ingot at 1025 °C/12 h and water quench
SD_1	4.3	Swage and draw solution-treated 26 mm ingot to 3 mm rod
SD_1S	4.3	Solution treat 3 mm rod at 1025 °C/12 h and water quench
SD_1SD_2	7.1	Draw from 3 mm rod to 0.75 mm wire
SD_1SD_2A	7.1	Age 0.75 mm wire at 430 °C/6 h
$SD_1SD_2AD_3$	9.1	Draw aged 0.75 mm wire to final 0.27 mm wire

well after the resistivity has dropped to low values. The average chromium particle size at peak hardness was found to be approximately 0.3 μm, which is significantly larger than in many age-hardenable alloys; this probably accounts for the absence of a significant anomalous resistivity at the highest strength levels for the copper-chromium alloys.

These considerations indicate that the addition of age hardening to deformation-processed copper-chromium would hold good promise for increasing strength with little loss of electrical conductivity. However, an obvious question remains: Would the chromium filaments present in the deformation-processed alloys act as precipitation sites for the chromium in the aging process and eliminate nucleation of the particles responsible for age hardening? This work is an attempt to evaluate the role of age hardening in deformation-processed copper-chromium alloys by examination of the evolution of the microstructures during the aging step and other steps of the optimized processing technique recently developed (Ref 3).

2. Experimental Method

2.1 *Series 1: TEM Study*

The experimental work was carried out in two stages, which will be referred to as series 1 and 2. In the first series, experiments were performed to reproduce the optimum processing technique (Ref 3). The same techniques were used to prepare a 26 mm diam chill-cast Cu-7 vol% Cr alloy, which was then solution treated at 1025 °C for 12 h and water quenched. The processing can be understood by arranging the steps in tabular form (Table 1). The optimum processing was coded SDSDAD (Ref 3). Table 1 uses subscripts on the three deformation steps to distinguish among them. The processing consists of the three deformation steps, with a second solution treatment between the first two and an aging step between the last two. The code for the processing stage listed in the first column of Table 1 simply adds the processing steps as they accumulate: S for the solution treatment plus quench, D for deformation, and A for the aging heat treatment. The deformation strain, η, is defined as the natural log of original over final area; thus, the total η at a given stage is the sum of the η values of previous deformations.

Ultimate tensile strength and electrical conductivity were measured at each stage in the processing in the manner described in Ref 3. In addition, samples were prepared from each stage for examination in the TEM in order to follow the evolution of the microstructures with the processing. The microstructural features proved to be too small to allow unambiguous measurement with the scanning electron microscope (SEM).

2.2 *Series 2: Copper-Niobium Alloy*

In the second series of experiments, Cu-7 vol% Nb alloys were prepared for comparison with the copper-chromium alloys. Age hardening is not expected to occur in these copper-niobium alloys because of the very low solubility of niobium in copper; therefore, they can be used as a standard to evaluate possible increments in strength due to age hardening. The 26 mm diam copper-niobium ingots were prepared by two different methods. In the first, the same bottom-pour chill (BPC) cast technique previously employed (Ref 3) was utilized. It was necessary, however, to heat the sample 50 °C hotter (1650 versus 1600 °C) to obtain complete dissolution of the niobium filaments. Because of impurity pickup problems (discussed later), a second method was also employed. The ingots were prepared by the consumable arc method (arc cast), which has been previously discussed (Ref 2). This method melts a composite Cu + Nb electrode into a water-cooled copper mold, producing an in-

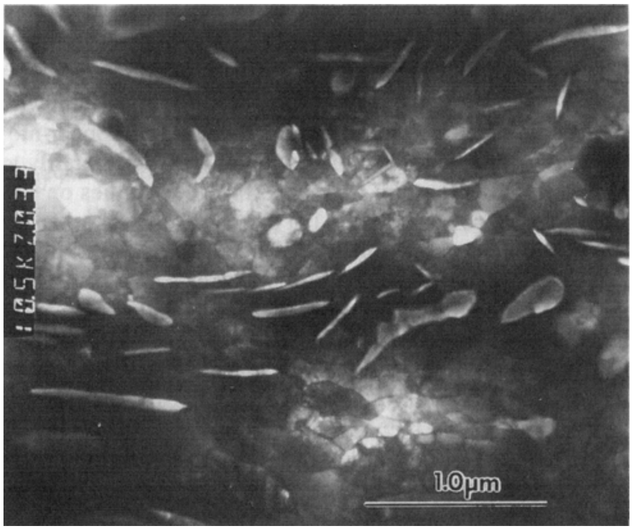

Fig. 4 TEM micrograph of sample from the SD_1 stage of processing (η = 4.2)

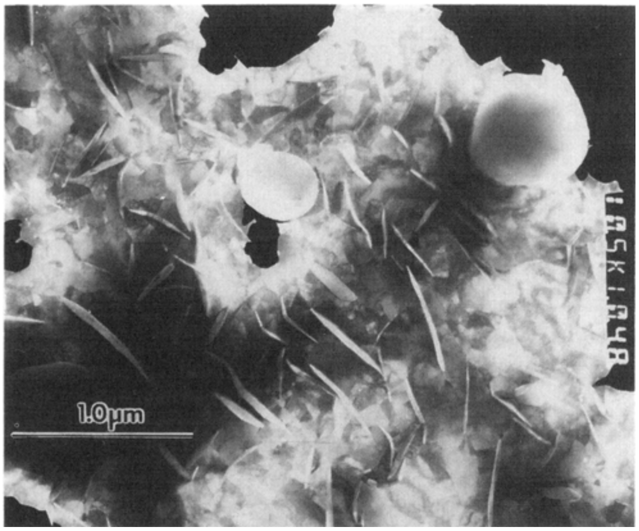

Fig. 5 TEM micrograph of sample from the SD_1SD_2 stage of processing (η = 7.1)

Table 2 Size of microstructural features at each stage of the SDSDAD processing

Processing stage	Total η	Figure	Copper grain size, µm	Chromium spacing, µm	Chromium thickness, µm
S	0	...	50	...	5
SD_1	4.3	4	0.34	1.3	0.333
SD_1S	4.3	...	4.17	2.70	1.53
SD_1SD_2	7.1	5	0.22	0.48	0.09
SD_1SD_2A	7.1	...	0.17	1.1	0.14
$SD_1SD_2AD_3$	9.1	6	0.14	0.18	0.03

got with a dendrite size similar to that of the BPC cast ingot while avoiding impurity pickup from a liquid-containment vessel.

3. Results and Discussion

3.1 *Series 1: TEM Study*

After each stage in the $SD_1SD_2AD_3$ processing, the strength and conductivity were measured; the results are presented in Fig. 2 and 3, respectively. Typical TEM micrographs for samples at selected stages in the processing are shown in Fig. 4 to 6. The TEM micrographs were used to measure average values of (1) the grain size of the copper matrix, (2) the average spacing between chromium filaments, and (3) the average thickness of the chromium filaments (Table 2).

All of these data can be used to evaluate how the microstructural changes that occur at each step in the processing give rise to the changes observed in strength and conductivity. The original as-cast chromium dendrite size and copper grain size do not change significantly in the initial solution treatment. The dendrites are not distributed very uniformly, as was also found in studies on Cu-5Nb (vol%) alloys (Ref 17), and thus an initial chromium spacing was not measured. As shown in Fig. 2 and 3, during the D_1 deformation the strength rises with a constant conductivity. The copper grain size and the thickness of the chromium particles undergo dramatic reductions, which would account for the increase in strength. The constant conductivity during the D_1 deformation indicates that no significant loss of solid-solution chromium occurred during the first deformation.

The second solution treatment at η = 4.3 produces a significant drop in strength with very little change in conductivity. The increase in copper grain size and chromium filament size and spacing shown in Table 2 would account for the loss in strength. One would expect the second solution treatment to produce the same amount of solid-solution chromium as the first. Hence, the essentially constant value of conductivity after the second solution step is consistent with the conclusion that the first deformation has not removed chromium from solid solution induced by the first solution treatment.

The second deformation, D_2, causes significant increases in strength and conductivity. The large refinement of the microstructure in this step (Table 2) would account for the increase in strength. It is surprising that this deformation produces such a large increase in conductivity. This result must mean that the deformation is causing precipitation of the chromium from solid solution. Previous studies (Ref 12, 15) on chromium precipitation in low-chromium alloys have also indicated that mechanical deformation is effective in promoting precipitation. The large increase in conductivity is observed here (from 40 to 62% IACS) is surprising because the deformation is occurring

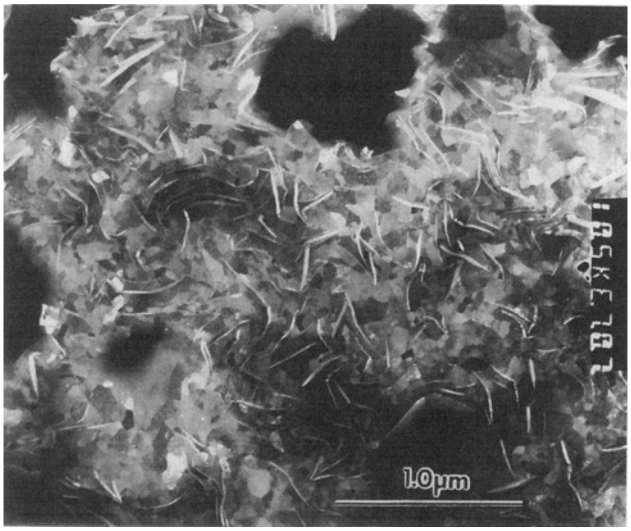

Fig. 6 TEM micrograph of sample from the $SD_1SD_2AD_3$ stage of processing ($\eta = 9.1$)

at room temperature, where the mobility of chromium in copper is expected to be so low that precipitation would not occur. The very large reduction in grain size during D_2 (from 4.17 to 0.22 μm) is evidence of the recrystallization of the copper matrix previously shown to occur (Ref 18) during room-temperature deformation of these types of alloys. Perhaps the reduction of solid-solution chromium in the copper matrix is occurring as the recrystallization front moves along the chromium filaments, and the reason that this effect does not occur during D_1 may be that chromium filaments remain too large at this stage.

The aging treatment after the second deformation, A, produces a significant drop in strength. Clearly, no age hardening is occurring in this so-called aging step. The data in Table 2 show that the copper grain size is essentially constant but that a significant coarsening of the chromium filaments has occurred. Careful examination of the TEM images revealed no evidence for precipitate particle formation during this aging step. As previously discussed, during the aging step of conventional low-chromium alloys, particles with diameters of approximately 0.3 μm form at peak hardness. The chromium filaments that exist in these deformation-processed alloys are already smaller than this dimension before the aging heat treatment begins. It is reasonable to expect that these preexisting chromium filaments would serve as growth fronts for the precipitation of chromium during the aging treatment, with no additional particle nucleation being produced. The small rise in conductivity during this aging step is evidence that additional removal of chromium from solid solution in the copper matrix is occurring. It is apparent that the aging step in this processing treatment is serving mainly to coarsen the chromium filaments and to remove additional chromium from solid solution. (Although the bulk of the chromium was found to be in the form of fine filaments throughout the processing, the TEM micrographs reveal that some fairly spherical particles were consistently present in the microstructures. The lack of deformation of these particles is not understood.)

During the final deformation step, D_3, a quite large percentage increase in strength occurs, just as in the second deformation. Again, this increase can be attributed to the refinement of the microstructure shown in Table 2. Although very little change occurs in the copper grain size, the chromium filament size and spacing are reduced significantly. It is consistent with previous studies (Ref 2) on deformation-processed copper-niobium alloys that the high strength values are due primarily to fine, elongated chromium filaments. Previous studies on Cu-20Nb alloys have shown (Ref 19) that electron scattering became the dominant component of resistivity when the filament size became small. This occurred at η values above 6, which corresponded to ultimate strength levels above 600 MPa. Hence, one would expect that the refinement of the chromium filaments in this final step, accompanied by the strength increase to values well above 600 MPa, would cause a reduction in conductivity. The fact that the conductivity has increased from 65 to 80% IACS in the last deformation step indicates that additional removal of chromium from solid solution must be occurring in the final deformation. The final strength and conductivity of the alloy examined here are plotted as the point labeled TEM on Fig. 7, and the properties are seen to be equivalent to those of the best optimized wires (Ref 3).

3.2 *Series 2: Copper-Niobium Alloy*

The 26 mm diam copper-niobium ingots were processed to 0.57 mm diam wire using the three methods shown in Table 3, so that in each case the total deformation strain was $\eta = 7.6$. In the D process, the ingot was drawn directly to the final wire size. In the DSDAD process, the ingot was drawn to wire using three deformation stages, with the solution treatment between the first two stages and the aging treatment between the second two stages. The solution treatment was a 1 h hold at 1010 °C plus water quenching, and the aging treatment was a 6 h hold at 500 °C. The amount of strain in each of the three deformation stages is shown in Table 3 as η_1, η_2, and η_3; these strains, rounded to the nearest integers, are given after DSDAD as (3-3-2). The DHD processing is described in Table 3 in a similar fashion. In this case, only two deformation steps were used; the H refers to a heat treatment of holding 3 h at 750 °C and program-cooling to room temperature in 48 h. The purpose of this treatment was to remove the niobium from solid solution in the copper matrix, as previous work on copper-niobium (Ref 17) has shown this treatment to be effective.

In Fig. 7, the strength versus conductivity data from the copper-niobium alloys are plotted on the data of the Cu-7Cr (vol%) alloys prepared with the optimized DSDAD processing of the previous study (Ref 3). Consider first the arc cast alloys. When the H heat treatment is used, the strength/conductivity data match that of the optimized copper-chromium alloys, whereas direct deformation of the as-cast ingot produces a lower value. This is consistent with a recent study on Cu-5Nb (vol%) alloys (Ref 17), which found that the H treatment produced a small improvement in the strength/conductivity data due to removal of the small amount of niobium dissolved in the copper matrix in the cast alloy. Interestingly, the DSDAD processing did not produce strength/conductivity values as high as the optimized copper-chromium samples. It seems likely that the reduction results from a lowered conductivity due to niobium remaining in solid solution following the S treatment. Whereas the mobility of chromium in copper has been found adequate to allow

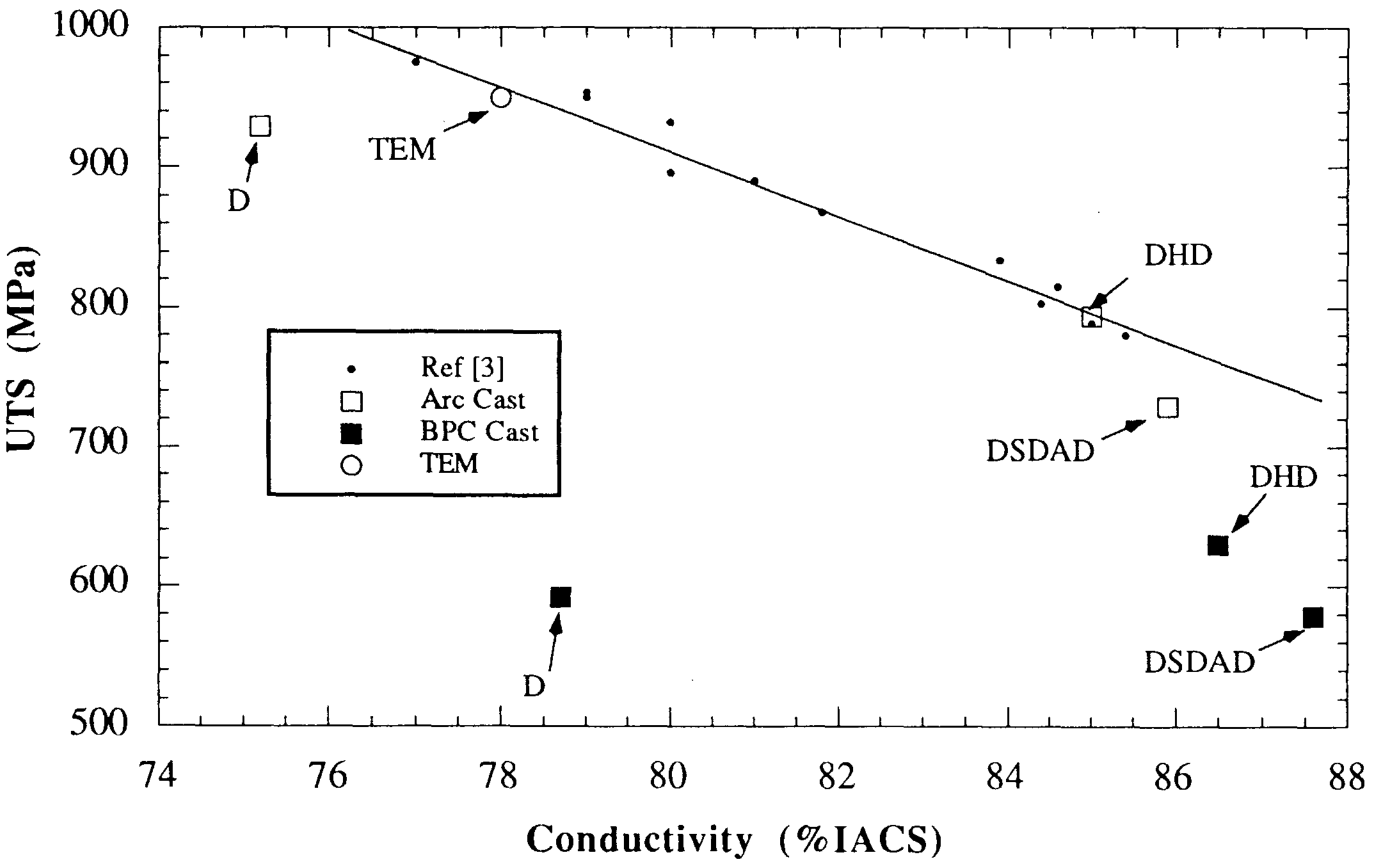

Fig. 7 Strength versus conductivity data for samples from this study plotted with data from Ref. 3.

Table 3 Strength, conductivity, and processing data for Cu-7 vol% Nb alloys

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
Arc cast							
D (8)	None	None	None	None	7.6 (0.57)	929	75.2
DSDAD (3-3-2)	2.8 (25 → 6.3)	2.7 (1.6)	500 °C/6 h (1.6)	η_A = 2.1 (0.57)	7.6 (0.57)	729	85.9
DHD (3-5)	2.8 (25 → 6.3)	None	750 °C/3 h/48 h (6.3)	η_H = 4.8 (0.57)	7.6 (0.57)	794	85.0
BPC cast							
D (8)	None	None	None	None	7.6 (0.57)	592	78.7
DSDAD (3-3-2)	2.8 (25 → 6.3)	2.7 (1.6)	500 °C/6 h (1.6)	η_A = 2.1 (0.57)	7.6 (0.57)	579	87.6

full precipitation from solid solution during the drawing and aging steps, apparently the mobility of niobium is too low to allow full precipitation.

The recent study on 5 vol% Nb alloys (Ref 17) utilized a resistivity analysis to show that following a heat treatment quite similar to the H treatment used here, the niobium is fully precipitated from the copper matrix. Hence, since the data for the DHD sample of copper-niobium fall on top of the optimized copper-chromium data, and since both alloys have the same volume fraction of copper, it seems likely that all of the chromium has been removed from the copper matrix by the optimized processing and that the filament sizes and distribution must be quite similar in the two alloys. The latter conclusion is confirmed by the TEM work of this study; the chromium filaments shown in Fig. 6 (and in Fig. 6b of Ref 3) are qualitatively the same as the niobium filaments examined in previous studies (Ref 18). Hence, these results are additional confirmation that the aging treatments of the optimized copper-chromium process is not producing an increment of strength, because aging is not expected in the copper-niobium alloys due to the very small niobium solubility in this system.

The BPC cast alloys of copper-niobium are represented by the solid squares in Fig. 7. These alloys are consistently shifted to lower strengths and higher conductivities than the arc cast alloys for the three processing schemes examined. Longitudinal samples examined in the SEM showed conclusively that the niobium filaments of the BPC cast alloys were significantly shorter than those of the arc cast alloys. It was suspected that

Table 4 Combustion analyses for oxygen, nitrogen, and carbon in alloys studied

Element	Analysis, ppmw Cu-7Cr (BPC cast)	Cu-7Nb (BPC cast)	Cu-7Nb (arc cast)
Oxygen	178	226	<1
Nitrogen	<1	<1	<1
Carbon	11	58	108

the BPC casting technique might have been contaminating the niobium by reduction of the Al_2O_3 crucible material due to the larger chemical reactivity of niobium and the slightly higher temperatures required to fully dissolve the niobium into the molten copper. Combustion analyses for oxygen, nitrogen, and carbon were carried out; the results are presented in Table 4. It is seen that the BPC cast copper-niobium alloy does have a significantly higher interstitial content of oxygen and carbon. It seems likely that the reduced filament size in these alloys has resulted from loss of ductility from the high interstitial content, because it is well established that the ductility of body-centered cubic elements is strongly reduced by interstitial impurities. These results show that even in copper-niobium alloys the optimum strength and conductivity properties require that the ductility of the refractory element phase be high enough to allow maximum elongation upon deformation.

4. Conclusions

The previous work (Ref 3) investigated several alternate processing schemes for the Cu-7 vol% Cr alloys, none of which produced as good a combination of strength and conductivity as the DSDAD process. In the series 1 experiments of this study, a few additional schemes were also examined and they too proved inferior. As in the previous study (Ref 3), the problem with the inferior samples was traced to breakage of the chromium filaments. It was also found in the oxygen-contaminated studies on copper-niobium alloys that formation of optimum lengths of the niobium filaments during deformation is critical to the production of optimum strength and conductivity.

The optimum properties of deformation-processed copper-chromium alloys apparently require processing schemes that are able to produce the finest spacing and size of the chromium filaments along with complete removal of the chromium from solid solutions. The alternating treatments of deformation, solution treatment plus quench, deformation, aging, and deformation appear to accomplish this goal. The two thermal treatments following the deformations allow the chromium filaments to be deformed more fully than any other combinations of treatments studied. In addition, the deformation treatments appear to assist the precipitation of the chromium from solid solution remarkably well, perhaps due to the deformation-induced recrystallization in the presence of fine chromium filaments.

Finally, it has been shown that the aging step in the processing does not produce an age-hardening effect, which must be because precipitation of chromium occurs on the fine chromium filaments present in these materials. The function of the aging step appears to be to provide sufficient stress relief to the chromium filaments to allow additional deformation without breakage and to remove chromium from solid solution.

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