

# Strength and conductivity of *in situ* Cu-Fe alloys

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Alloys of Cu-Fe with iron contents from 10 to 30 wt% have been prepared by casting plus mechanical reduction. A series of heat treatments was done at various stages of the mechanical reduction to promote precipitation of the iron from the copper matrix with the hope of optimizing electrical conductivity at a given strength level. A curve of optimum tensile strength against electrical conductivity was determined. It was found to lie significantly below the available data for Cu-Nb alloys and it is suggested that further improvements may be possible in Cu-Fe alloys by improved thermal mechanism processing.

## 1. Introduction

As a result of research directed at producing superconducting alloys about a decade ago it was discovered that cast Cu-Nb alloys could be drawn extensively to produce a composite of niobium fibres in a copper matrix. Bevk *et al.* [1] first demonstrated that such heavily drawn Cu-Nb alloys with around 15 to 20 vol% Nb can have very high tensile strengths, approaching 2000 MPa. Upon solidification of these alloys, niobium dendrites form in a copper matrix and the subsequent mechanical reduction reduces the dendrites to aligned filaments having a ribbon-shaped cross-section. Recent studies by Spitzig and co-workers [2, 3] have demonstrated that the tensile strength correlates with the reciprocal square root of the niobium filament spacing which suggests that the high strength results from dislocation blockage at the copper matrix/niobium fibre interfaces. Funkenbusch and co-workers [4, 5] have proposed an alternate model for these materials which attributes the strength to increased dislocation densities. These alloys are often termed *in situ* alloys because the filamentary composite structure is produced by the production process. The particularly attractive feature of these alloys is the combination of high strength plus high electrical and thermal conductivity. A recent study by Renaud *et al.* [6] produced a Cu-18 wt% Nb alloy having  $\sigma(\text{UTS}) = 1450$  MPa with an electrical conductivity of 66.6% IACS. Commercial Cu-Be alloys can achieve  $\sigma(\text{UTS})$  values in this range, but with a conductivity of only around 30% IACS. Other Cu-X alloys may be produced by this *in situ* processing when the X component forms as nearly pure dendrites having good ductility and the remaining liquid freezes as nearly pure copper. This occurs with the body centred cubic alloys, and recent studies have demonstrated mechanical properties similar to Cu-Nb in cast and drawn Cu-V [7], Cu-Cr [8, 9], Cu-Ta [8] and Cu-Fe [7, 10] alloys.

The Cu-Fe system is of particular interest because of the relatively low cost of iron compared to the other possible X components. A literature search revealed that the potential for high strength in drawn Cu-Fe alloys had been studied several decades prior to the recent interest in these so called *in situ* alloys. In an effort to develop high-strength high conductivity wires for the US Army a research programme was carried out at Battelle Columbus Ohio in the late 1940s. This study [11, 12] was directed at the development of alloys possessing maximum strength plus electrical conductivity. Wires were produced by techniques similar to those employed in the recent *in situ* studies; ingots of around 10 cm diameter were produced in cast iron moulds and then hot forged and hot rolled to 4.3 mm square stock. This material was reduced to wire by a combination of drawing and heat-treatment processes. Alloys containing 15 wt% Fe plus 0.1 wt% Mg had tensile strengths of 1080 MPa with conductivity of 56% IACS. There have also been other studies of Cu-Fe alloys prior to the recent *in situ* work and these are summarized in Table I, along with the recent Cu-Nb data for comparison.

The solidification processing of these Cu-X alloys is controlled by the phase equilibria, and the Cu-Fe diagram [16] is given in Fig. 1. The Cu-Fe diagram differs from other Cu-X systems such as Cu-Nb in two important factors. The solid state  $\gamma$ - $\alpha$  phase transition occurs in the iron phase and the solubility of iron in copper and copper in iron is higher at high temperatures. The nature of the precipitation of iron from copper is quite interesting and has been widely studied [17-21]. Rapid cooling can produce formation of metastable fcc iron which reverts to bcc iron upon subsequent mechanical deformation or thermal treatment. Iron has one of the highest resistivity decrements in copper ( $9.2 \mu\Omega \text{ cm/wt \% Fe}$  [19]) and for this reason it is important to remove as much iron from solid solution in the copper as is possible.

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TABLE I Literature data on Cu-Fe alloys prior to 1978

| Reference                | Tensile strength (MPa) | Conductivity (% IACS) | Composition (wt %) |
|--------------------------|------------------------|-----------------------|--------------------|
| Renaud <i>et al.</i> [6] | 1450                   | 66                    | Cu-18 Nb           |
| Hodge <i>et al.</i> [11] | 1080                   | 56                    | Cu-15 Fe-0.1 Mg    |
| Smith and Palmer [13]    | 1170                   | 35                    | Cu-43 Fe-0.2 Mg    |
| Ivanova and Myuller [14] | 1080                   | 31                    | Cu-35 Fe-0.04 Al   |
| Fukui <i>et al.</i> [15] | 1450                   | -                     | Cu-30 Fe           |

Hansen and Anderko [16] have recommended the data of Tammann and Oelsen [22] for the low-temperature-iron solubility in copper, and a recent study [23] is in good agreement with this choice. Extrapolating these data on an  $\ln x-1/T$  plot shows that the iron solubility is less than 1 p.p.m. at 233°C; using the above resistivity decrement, if the predicted solubility at 253°C could be achieved the conductivity of the copper phase would be reduced by only 1% IACS.

The relatively high solubility of iron in copper at high temperature, coupled with the slow kinetics of iron precipitation at low temperatures make it difficult to achieve the low equilibrium solubility levels by thermal treatment alone. For this reason studies aimed at optimizing strength and conductivity [12, 14] have employed thermal/mechanical treatments. That is, instead of simply cooling an alloy very slowly, the alloy is cooled slowly, then cold worked, reheated, and cooled again. Such treatments are complicated by the fact that high strengths require very fine filament thicknesses and the reheating process causes these fine filaments to coarsen. The present work is a preliminary study directed at evaluating the effectiveness of various thermal/mechanical treatments at improving the strength plus electrical conductivity of Cu-Fe alloys.

## 2. Experimental details

Alloys of Cu-Fe were made by solidifying small

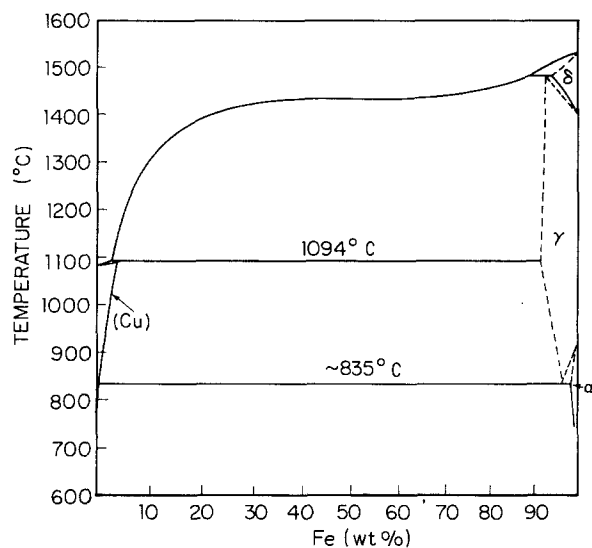


Figure 1 The Cu-Fe phase diagram [16].

2.54 cm diameter by 2.5 cm high melts in high-purity hard-fired  $\text{Al}_2\text{O}_3$  crucibles. The initial starting materials were 99.999% pure copper rod and electrolytic sheets of Glidden iron. Spark source mass spectroscopy of two batches of the iron subsequent to melting in  $\text{Al}_2\text{O}_3$  crucibles revealed the major heavy element impurities to be germanium, nickel, cobalt, sulphur, copper and phosphorus at levels of 48, 29, 22, 20, 16 and 7 parts per million by weight, p.p.m.w. The initial alloys were made by induction melting the chemically cleaned copper and iron sheets directly in the  $\text{Al}_2\text{O}_3$  crucibles using a tantalum susceptor. A vacuum of around  $10^{-6}$  torr was maintained to temperatures of 1000°C and heating was then continued under  $\sim 1$  atm argon gas. The melt was held for 5 min at 1550°C and after removing the sensing thermocouple the alloys were solidified directly in the crucible by furnace cooling. The initial Cu-20 wt % Fe alloys were dendritic, except near the top of the crucible, where two-phase spheroids of Cu + Fe were observed, indicating that a liquid-phase immiscibility had occurred. It is well established that impurities can cause such an effect in Cu-Nb [24] and Cu-Fe [12] alloys. Therefore, the as-received iron sheets were electron-beam melted to eliminate volatile impurities and when this iron was used no spheroids were observed. The dendrites were uniformly distributed throughout the volume of the ingots. The average iron dendrite arm diameter in the cast alloy was evaluated by standard optical metallography to be 6.8, 8.4 and 10.0  $\mu\text{m}$  in alloys of 10, 20 and 30 wt % Fe, respectively. These sizes are very close to the niobium dendrite sizes found in Cu-Nb *in situ* studies [2].

It was thought that the reason for spheroid formation with the as-received iron was the presence of oxygen or carbon impurities. Therefore oxygen, nitrogen and hydrogen were determined by vacuum fusion analysis and carbon by combustion analysis on ingots with and without spheroids. Within the limits of the analysis both ingots gave the same levels of impurity content, oxygen 10 p.p.m.w., carbon 16 p.p.m.w., and hydrogen and nitrogen both 1 p.p.m.w. Although it seems likely that the spheroid formation was due to an impurity effect, the responsible impurity is unknown. It may have been sulphur, but this was not checked.

The electrical resistivity was measured by the standard four-probe technique. Tensile tests were carried out on 0.25 and 0.5 mm wires at a cross-head speed of 0.254  $\text{mm min}^{-1}$ . Both techniques are described in detail elsewhere [25].

## 3. Results and discussion

Because the 2.54 cm diameter ingots were so short, they were reduced to wire by enclosing them in a stainless steel tube and then swaging. Two treatments were investigated. (A) In this case the ingot was first annealed under argon at 1000°C for 12 min and slowly cooled to room temperature over 108 h to maximize precipitation of the iron. It was then cold swaged to 2.54 mm. The stainless jacket was removed as soon as the Cu-Fe was long enough to hold for insertion into the swager. (B) In this case the as-cast ingot was hot swaged to 13.6 mm diameter in the

TABLE II Electrical conductivity (% IACS) and tensile strength of two Cu-20 wt % Fe alloys after initial mechanical reduction by treatment A (slow cool) and B (hot swage)

| (a) Heat treatment 1 at 2.54 mm diameter |                  |                  |                   |  |
|--|------------------|------------------|-------------------|--|
|  | Process          |                  |                   |  |
|  | I, 840° C/1 h    | II, 630° C/1 h   | III, 540° C/1 h   | IV, 540° C/1 h<br>2 day cool to 440° C   |
| A  | 40.1%            | 41.8%            | 47.02%            | 53.0%                                    |
| B  | 38.8%            | 47.2%            | 47.78%            | 55.1%                                    |
| Draw to 1 mm diameter                    |                  |                  |                   |  |
| A  | 38.9%            | 38.0%            | 44.1%             | 49.7%                                    |
| B  | 35.6%            | 44.9%            | 46.2%             | 52.2%                                    |
| (b) Heat treatment 2 at 1.0 mm diameter  |                  |                  |                   |  |
|  | Process          |                  |                   |  |
|  | I, 540° C/1.3 h  | II, 540° C/1.3 h | III, 440° C/1.3 h | IV, 440° C/1.3 h<br>2 day cool to 340° C |
| A  | 58.9%            | 56.5%            | 63.1%             | 70.2%                                    |
| B  | 58.0%            | 60.1%            | 65.0%             | 72.2%                                    |
| Draw to 0.25 mm diameter                 |                  |                  |                   |  |
| A  | 54.6% (1090 MPa) | 52.4% (1250 MPa) | 54.1% (1220 MPa)  | 61.2% (950 MPa)                          |
| B  | 58.9% (1000 MPa) | 57.7% (1010 MPa) | 58.8% (1120 MPa)  | 68.8% (950 MPa)                          |

stainless jacket. The jacket was then removed and the ingot was cold swaged to 2.54 cm. The electrical conductivities of the 2.54 mm rod from treatments A and B were 36.9 and 22.7% IACS respectively, where the standard resistivity for conversion to % IACS was taken as  $1.724 \mu\Omega \text{ cm}$ . Material from treatments A and B were reduced to 0.25 mm wire by four different thermomechanical processes, labelled I to IV in Table II.

All the processes involved two heat treatments and two mechanical reductions. In all cases the cooling after the heat treatment was a 15 h cool to room temperature and the mechanical reduction was by drawing. The electrical conductivity was evaluated after each step of the processing but the tensile strength was measured only after the final step. Process I is described in the left-hand column of the Table. The initial heat treatment was a 1 h hold at 850° C followed by the 15 h cool to room temperature which increased the conductivities of A and B from 36.9 to 40.1% IACS and 22.7 to 38.8% IACS, respectively. The material was then drawn from 2.54 to 1 mm and the conductivity of A dropped from 40.1 to 38.9% IACS and B from 38.8 to 35.6% IACS. The 1 mm diameter wires were then held at 540° C for 1.3 h which raised the conductivity of A from 38.9 to 58.9% and B from 35.6 to 58.0%. Finally, the wire was drawn from 1.0 to 0.25 mm diameter which lowered the conductivity of A from 58.9 to 54.6% IACS and raised B from 58.0% to 58.9% IACS. The tensile strengths of A and B material at this point were measured to be 1089 and 1003 MPa, respectively. The property variation for the other three processes are similarly described in the table.

The tensile strength and electrical conductivity of the final wire given in Table II may be summarized graphically as shown in Fig. 2. The solid line in the graph represents the upper limit of the best combination of strength and conductivity achieved in these experiments and is termed the optimum curve.

Process I did not give optimum results for treatments A or B. Apparently, too much iron dissolves into the copper matrix in the 840° C treatment for the subsequent 1.3 h, 550° C anneal to produce adequate precipitation. Process IV gave the highest conductivities but the lowest strengths. Apparently the 2-day coolings utilized in IV were effective at precipitating more iron from the copper matrix, which would account for the increased conductivity. The reduced strength is most probably a result of coarsening of the iron filaments during the 2-day coolings. It is also possible, however, that the reduced strength results from reduced work hardening of the cleaner copper matrix, but electron microscopy studies would be required to differentiate clearly between these two mechanisms. Treatment A optimized the strength at low conductivities, while treatment B optimized the conductivities at low strengths. It was expected that the very slow cool from 1000° C in the A ingot would

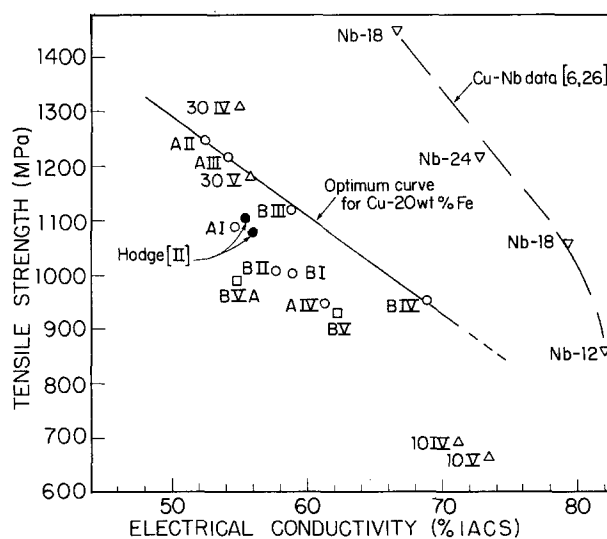


Figure 2 Data on tensile strength plotted against electrical conductivity.

TABLE III Electrical conductivity and tensile strength after initial mechanical reduction by treatment B: processes V and VA

| Step | Treatment                 | Diameter (mm) | Conductivity (% IACS) | Tensile strength (MPa) |
|------|---------------------------|---------------|-----------------------|------------------------|
| 1    | 540° C/1 h-2d to 440° C   | 2.5 mm        | 55.1%                 | -                      |
| 2    | Draw                      | 1.5           | 52.8%                 | -                      |
| 3    | 440° C/1.3 h-2d to 340° C | 1.5           | 72.0%                 | -                      |
| 4    | Draw                      | 1.0           | 53.7%                 | -                      |
| 5    | 440° C/1.3 h-2d to 340° C | 1.0           | 73.9%                 | -                      |
| 6    | Draw                      | 0.50          | 54.2%                 | 730                    |
| 7    | 340° C/1.3 h-2d to 240° C | 0.50          | 56.7%                 | -                      |
| 8    | Draw                      | 0.25          | 62.2%                 | 930                    |
| 6A   | Draw                      | 0.25          | 54.8%                 | 990                    |

maximize iron precipitation and lead to higher conductivities. This was true only for the early stages of process I. The reason why treatments A and B give such different properties is not clear and would require further studies of the microstructure and strength changes which occur during the various steps of the process. It is also not clear why process II produced higher strengths than process III for treatment A and not for treatment B.

In an effort to improve further the strength/conductivity properties, wires were given additional heat treatments at lower temperatures after drawing to see if such thermomechanical treatments would precipitate more iron and give increased conductivities. These treatments, termed processes V and VA are described in Table III. Eight steps were involved in process V which included four heat treatments followed by four reductions. The resulting properties, 62.2% IACS and 930 MPa, are shown in Fig. 1 as point BV, which is seen to be well below the optimum curve. In process VA the final heat treatment, step 7, was omitted, which resulted in properties even poorer than found with process V.

Alloys of both 10 and 30 wt % Fe were also prepared by treatment B (hot and cold swaging the ingot to 2.5 mm diameter) and then examined by processes IV and V. The final properties are shown for the 30% alloys by the points labelled 30 IV and 30 V on Fig. 1, while the 10% results are labelled 10 IV and 10 V. It is seen that some improvement over the optimum 20 wt % Fe curve was obtained for the 30 wt % alloys, but only at low conductivities. The 10 wt % alloys produced increased conductivities, as expected because of the reduced iron content, but unfortunately the strengths fell off significantly below the optimum curve for 20 wt % Fe alloys.

A very interesting result was observed in process V which is illustrated in Table III. In all cases the drawing step had caused the conductivity to drop, but notice that the drawing in step 8 actually increased the conductivity. This same effect was observed in both the 10 and 30 wt % alloys. Unfortunately the tensile strength at step 7 was not evaluated so it is not clear whether some age hardening might have occurred by the step 7 heat treatment. A possible explanation of the increase

in conductivity is that age hardening occurred in the 340° C/240° C heat treatment of step 7 and the subsequent mechanical reduction caused a loss of coherency strains with an increase in conductivity.

The best previous data on Cu-Fe alloys are those of Hodge *et al.* [11], see Table I, and their data are shown on Fig. 1. The present results are somewhat better but additional studies are clearly required to understand further the quite complex mechanisms which are occurring in the thermal mechanical processing of these Cu-Fe alloys. Available data for thermomechanically treated Cu-Nb alloy [6, 26] are shown on Fig. 1 for alloys of 12, 18 and 24 wt % Nb and it is seen that these data lie considerably above the Cu-Fe data. It does not seem reasonable that the higher strengths of the Cu-Nb alloys at a given conductivity are due to higher strengths of the niobium fibres, because the modulus of niobium is less than that of iron by a factor of 1.9. More likely, the reduced conductivities of the Cu-Fe alloys at a given strength level are due to a combination of the much higher solubility of iron in copper at the higher temperatures coupled with the higher resistivity decrement of iron. As shown above, the equilibrium solubilities of iron in copper are low enough at temperatures below 253° C to reduce the % IACS of the copper matrix by only 1%. Hence, it would appear that one should be able to raise the optimum curve for Cu-Fe alloy closer to the Cu-Nb data if additional precipitation of the iron could be achieved. It would be interesting to do further studies utilizing hot drawing in the temperature range 200 to 400° C.

An interesting high volume potential application for Cu-Fe alloys would be transmission wire cable. These are presently made from aluminium wires cabled around stainless steel. A typical cable, having six aluminium wires wound on one steel wire, has a tensile strength of 317 MPa, a conductivity of 58.8% IACS and a density of 3.42 g cm<sup>-3</sup> [27]. Taking the ratio of TS × conductivity/density as a figure of merit, FM, for this application the cable has FM = 5500. If one chose the same conductivity for a Cu-Fe cable, taking the density of Cu-20 wt % Fe as 8.72 g cm<sup>-3</sup>, the value of FM from Fig. 1 is 7600, somewhat better than the aluminium steel cable. If one could improve the Cu-Fe properties to approach the Cu-Nb alloys the FM would be nearly doubled that of the aluminium steel cable. A possible problem with Cu-Fe for the application would be corrosion due to the presence of the iron. However, because chromium alloys with copper in essentially the same way as iron, ternary alloys of Cu-Fe-Cr should display the same microstructure and similar properties to Cu-Fe alloys. This fact was realized long ago by Hodge *et al.* [12] who demonstrated that an alloy of Cu-18 wt % Fe-2.5% Cr was rust-resistance. They present data points on strength and conductivity, 758 MPa at 50% IACS which gives FM of only 5180, but perhaps this could be improved by optimum thermomechanical processing.

#### 4. Conclusion

A literature survey has found that development studies on cast and deformed Cu-Fe alloys to optimize

the combination of high strength plus electrical conductivity was done as long ago as the 1930s and 1940s [11–13]. The microstructure and strengthening mechanisms in these alloys is the same as for the *in situ* Cu–Nb alloys which have recently been studied quite extensively [1–3, 6, 7, 26]. The present work examined several different thermomechanical processes aimed at optimizing strength plus ductility on Cu–Fe alloys of compositions 10, 20 and 30 wt % Fe and an optimum curve was found which is slightly better than achieved in the older work [11]. The mechanisms which control the strength/conductivity properties are not understood and will require further studies. Comparison of the data to the best available data on Cu–Nb suggests that additional improvement might be possible with Cu–Fe if methods could be found to reduce the iron dissolved in the copper matrix to its equilibrium levels at around 250°C. It is suggested that hot drawing at near this temperature might produce the desired improvement. The present results show that tensile strength/electrical conductivity combinations of around 950 MPa/69% IACS may be achieved in Cu to 20 wt % Fe alloys and 1310 MPa/55% IACS in Cu–30 wt % Fe alloys. If the properties could be improved to match the Cu–Nb alloys, the conductivity at 950 MPa could be increased to over 80% IACS and at 1310 MPa to over 70% IACS. At these levels the alloys might be attractive for such applications as transmission lines.

### Acknowledgements

This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, US Department of Energy and it was performed at the Ames Laboratory which is operated for the US Department of Energy by Iowa State University under contract no. W-7405-ENG-82.

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Received 22 February  
and accepted 14 June 1988