JOURNAL OF MATERIALS SCIENCE **36** (2001) 2711–2719

Precipitation hardening of Cu-Fe-Cr alloys

Part I *Mechanical and electrical properties*

H. FERNEE, J. NAIRN, A. ATRENS
Department of Mining Minerals and Materials Engineering,
The University of Queensland, Brisbane Qld Australia 4072
E-mail: atrens@minmet.uq.oz.au

This research is part of a project whose scope was to investigate the engineering properties of new non-commercial alloy formulations based on the Cu rich corner of the Cu-Fe-Cr ternary system with the primary aim of exploring the development of a new cost-effective high-strength, high-conductivity copper alloy. The literature indicated that Cu rich Cu-Cr and Cu-Fe alloys have been thoroughly investigated. A number of commercial alloys have been developed and these are used for a variety of applications requiring combinations of high-strength, high-conductivity and resistance to softening. Little evidence was found in the literature that the Cu rich corner of the Cu-Fe-Cr system had previously been investigated for the purpose of developing high-strength, high-conductivity copper alloys resistant to softening. The aim of these present investigations was to explore the possibility that new alloys could be developed that combined the properties of both sets of alloys, ie large precipitation hardening response combined with the ability to stabilise cold worked microstructures to high temperatures while at the same maintain high electrical conductivity. To assess the feasibility of this goal the following alloys were chosen for investigation: Cu-0.7wt%Cr-0.3wt%Fe, Cu-0.7wt%Cr-0.8wt%Fe, Cu-0.7wt%Cr-2.0wt%Fe. This paper reports on the mechanical property investigation which indicated that the Cu-0.7wt%Cr-0.3wt%Fe, and Cu-0.7wt%Cr-2.0wt%Fe alloys were worthy of further investigation.

1. Introduction

Copper and copper-based alloys are among the most commercially important metals because of their excellent properties, ease of manufacture and numerous applications. They are normally used because of their excellent electrical and thermal conductivity, outstanding resistance to corrosion and ease of fabrication. Copper alloys are generally non-ferromagnetic with medium values of strength and fatigue resistance. Copper alloys can range in colour from white through gold to purple. They can be polished, textured, plated or coated to provide a wide variety of functional or decorative surfaces. Pure copper and low-alloyed copper are used extensively for cables and wires, electrical contacts and a wide variety of other parts that are required to pass electrical current. Applications for copper and copper alloys which take advantage of their high thermal conductivity include heat exchangers, radiators, home heating systems, solar panels and any other application requiring rapid conduction of heat. Bronzes (Cu-Sn), Brasses (Cu-Zn) and Cupronickels (Cu-Ni) all have an outstanding ability to resist corrosion. These alloys along with copper are commonly used for pipes, valves and fittings in water based carrying systems. The ease with which copper and copper alloys can be shaped to the required form means that any of the common fabricating processes such as machining, forging, rolling, drawing and stamping can be used. Copper and copper alloy are readily joined and assembled by mechanical means, and are easily welded, soldered and brazed. Typical applications for cold worked materials include springs, fasteners, plates, small gears and cams. The development of the electronics industry has led to a number of new applications for copper alloys including lead frames, connectors and other electronic components. These applications require alloys with unique combinations of strength and conductivity coupled with temperature stability.

The largest quantity of copper is consumed by the electrical industry. This has grown from 45% to 47% of total copper consumption [1]. More recent data from the United States has shown that 58% of copper consumed is selected for its electrical conductivity [2].

This research is part of a project whose scope was to investigate the engineering properties of new non-commercial alloy formulations based on the Cu rich corner of the Cu-Fe-Cr ternary system with the primary aim of exploring the development of a new cost-effective high-strength, high-conductivity copper alloy.

The literature [3] indicated that Cu rich Cu-Cr and Cu-Fe alloys have been thoroughly investigated. A number of commercial alloys have been developed and these are used for a variety of applications requiring combinations of high-strength, high-conductivity and resistance to softening. In most instances trace element additions are required to achieve optimum properties in these binary alloys.

Commercial Cu-Cr alloys couple high strength with very high electrical conductivity in the optimally aged condition. These family of alloys (Cu-(0-1%) Cr + minor additions) have a large precipitation hardening response. This is because in the solution treated condition the super saturation of Cr in the Cu matrix creates a high degree of thermodynamic meta-stability, thus providing a high chemical potential for the precipitation reaction of Cr. The high strength is derived from the distribution of nano-sized Cr rich precipitates in the Cu – matrix, due to the fine precipitate size in the peak-aged condition. Conductivity is close to that of pure Cu due to the low concentration of Cr in Cu solid solution after aging.

For commercial Cu-Fe alloys, relatively little strengthening is achieved due to precipitation hardening. It is conventional to rely on CW for improving the strength of these alloys. Fe rich precipitates serve to stabilise the cold worked microstructure. Properties comparable to Cu-Cr alloys can be achieved in the cold worked condition. Cu-Fe alloys also have the advantage of being easier to process than Cu-Cr alloys. Conductivity is lowered by the high equilibrium solid solubility of Fe in Cu at the ageing temperatures.

Little evidence was found in the literature that the Cu rich corner of the Cu-Fe-Cr system had previously been investigated for the purpose of developing high-strength, high-conductivity copper alloys resistant to softening. The combined effect of Fe and Cr in a ternary Cu rich Cu-Fe-Cr alloy was not known, but appeared to be worth investigating.

The effect of Fe and Cr upon each other's solid solubility in the Cu matrix was not known. In principle, increased solid solubility that may be provided by the addition of Fe to Cu-Cr would lead to an increased volume fraction of precipitate and ordinarily should increase strength. The effect of Fe additions to Cu-Cr on the precipitation potential is not known. Any net decrease in precipitation potential (of Cu-Cr) would lead to a dramatic drop in conductivity. On the other hand, the high chemical affinity of Cr for Fe may encourage co-precipitation of Fe-Cr, either as separate phases, solid solutions in one another or as a Fe/Cr intermetallic. In which case, the net precipitation potential would be much larger than that of the binary Cu-Fe and higher conductivity would be anticipated. The effect of Fe and Cr upon the size and morphology of the precipitates formed in the copper matrix was similarly not known. The Fe-Cr equilibrium phase diagram [4] shows that Fe and Cr have complete solid solubility in one another at elevated temperatures. Would this be the case in the copper matrix or would two populations of precipitates exist? How would this effect the mechanical properties? Would the CrFe intermetallic (σ) form in the Cu matrix and how would this affect the properties?

Another factor that encouraged further investigation into this system was that commercially available ferro-chrome could be used as the source of Cr for these alloys as opposed to the traditional practise of using more expensive electrolytic Cr or copper chrome master alloys for commercial Cu-Cr alloys. Ferro-chrome is a comparatively cheap (compared to chromium) alloying addition widely used in the steel industry. It consists of a ~70 : 30 mixture of Cr and Fe.

The aim of these present investigations was to explore the possibility that new alloys could be developed that combined the properties of both sets of alloys, ie large precipitation hardening response combined with the ability to stabilise cold worked microstructures to high temperatures while at the same maintain high electrical conductivity. To assess the feasibility of this goal the following alloys were chosen for investigation:

- Cu-0.7wt%Cr-0.3wt%Fe
- Cu-0.7wt%Cr-0.8wt%Fe
- Cu-0.7wt%Cr-2.0wt%Fe

The Cu-0.7wt%Cr-0.3wt%Fe composition was selected to determine if an alloy could be developed from this system with properties comparable to existing Cu-Cr alloys. The ratio of Fe to Cr was the same as that of the ferro-chrome alloying addition. This alloy would be simple to produce as ferro-chrome would be added directly to the copper melt. The maximum equilibrium solubility of Cr in Cu is 0.73 wt% at 1076.2 °C. From the Cu-Cr phase diagram [4] it is apparent that it is impractical to solution treat at a temperature to achieve this due to the risk of formation of some liquid phase. At a safe solution treatment temperature no more than 0.7 wt% Cr could be expected to go into solid solution. The addition of more Cr than 0.7 wt% Cr would serve no purpose in the precipitation hardening of the alloy. This same Cr content was maintained for each of the alloys investigated as it was necessary to maximise the Cr content in solid solution in order to maximise the precipitation hardening response in each alloy.

The Cu-0.7wt%Cr-2.0wt%Fe alloy was selected in order to try and develop an alloy with properties comparable to existing Cu-Fe alloys, ie the ability to retain cold work strengthening to high operating temperatures and at the same time maximising electrical conductivity. As a result a high Fe content was selected. The maximum solubility of Fe in Cu is 4.1 wt% [4], however in literature it is reported that the maximum practical limit is ~2.5 wt% [5] due to the formation of non-uniform distributions of precipitates. An Fe content of 2 wt% was selected based upon this and because of the unknown effect of 0.7 wt% Cr upon the solid solubility of Fe in Cu.

The Cu-0.7wt%Cr-0.8wt%Fe was chosen in order to be able to fully investigate the properties of this system. The ratio of Fe to Cr in this alloy is approximately mid way between that of the other two compositions selected. This composition was selected to explore the possibility that the properties of this alloy would combine both a large precipitation hardening response and resistance to recrystallisation at elevated temperatures while at the same time maintaining high electrical conductivity. In addition, this ratio of Fe to Cr coincides with the stoichiometric concentrations for the formation of the Fe-Cr intermetallic σ phase as predicted in the Fe-Cr equilibrium phase diagram. It is thought that this composition would have the highest thermodynamic driving force for the precipitation reaction into the FeCr σ phase. The effect this phase would have upon the engineering properties was unknown.

The scope of this research program is too large to report in one paper. This first paper explores the precipitation response. As there was a significant response, the microstructure was investigated and is reported as part II of this paper [6]. It was also worthwhile continuing the program with a thorough investigation of the effect of cold work upon the properties of the alloys, and that study is reported in a second paper [7]. The effect of trace quaternary additions was also investigated in order to further improve the mechanical and electrical properties [8].

2. Experimental

Three alloys were studied: Alloys A, B and C with nominal compositions Cu-0.7wt%Cr-0.3wt%Fe; Cu-0.7wt%Cr-0.8wt%Fe and Cu-0.7wt%Cr-2.0wt%Fe. For each alloy, the following were studied: the precipitation hardening behaviour, and the electrical and mechanical properties. The effect of cold working upon the precipitation hardening reaction and the resultant properties were also examined and are reported in a later paper in this series [7]. Two binary alloys were included in the study as reference alloys: Cu-1wt%Fe (Alloy Y) and Cu-1wt%Cr (Alloy Z). Both these commercial alloys have been widely studied and the results of the present measurements were used to validate the testing methods.

The alloys were melted and cast in a vacuum induction furnace. The copper base was electrolytic sheet copper that was 99.999% pure. All alloys were made with additions of low carbon ferro-chrome (70wt%Cr-30wt%Fe), with the supplied composition as shown in Table I. For alloys where additional iron was required, "chips" of electrolytic iron (99.98% pure) were used. The two reference alloys, Cu-1wt%Fe and Cu-1wt%Cr were made using electrolytic iron chips and Cu-10wt%Cr master-alloy.

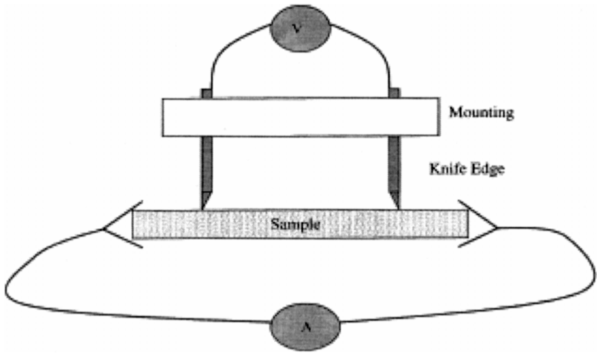

Figure 1 Experimental arrangement used for conductivity measurements.

The castings were sealed in Vical glass to prevent oxidation and solution treated for two hours at 1050°C, followed by water quenching. Solution treated castings were machined into hardness blocks and tensile specimens. Spark emission spectroscopy (SES) gave the compositions as in Table II.

Conductivity testing was carried out on the gauge length of tensile specimens prior to tensile testing. The same equipment and testing technique was used for testing all samples. All testing was carried out at a uniform temperature of 23°C. Prior to testing the surface of each specimen was polished with 1200 grit SiC paper to remove any oxide. The dimensions for calculating the cross sectional area (a) were carefully measured with a digital vernier to the nearest 0.01 mm. The arrangement is shown schematically in Fig. 1. Two knife edges made from mild steel were applied to the surface of the specimen with sufficient force so that they could not be

TABLE I Composition of raw material used to make alloys

	Alloy Composition (wt%)							
Alloy	Cu	Cr	Fe	C	Si	P	Pb	Y
Low C ferro-chrome		70.31	29.64	0.043	0.063	0.18		
High C ferro-chrome		66.06	24.81	7.90	1.17	0.2		
Cu-15wt%P		<0.01	<0.035			14.84	<0.01	
Cu-10wt%Cr		9.492	0.075		0.018	0.003	0.018	
Cu-Y	58.4							41.6

TABLE II Alloy compositions

			Analysed Compositions (wt%)	
Nominal Composition (wt%)	Designation		%Cr	%Fe
Cu-0.7%Cr-0.3%Fe (casting 1)	Cu0.7Cr0.3Fe	Alloy A	0.70	0.27
Cu-0.7%Cr-0.3%Fe (casting 2)	Cu0.7Cr0.3Fe	Alloy A	0.67	0.27
Cu-0.7wt%Cr-0.8wt%Fe	Cu0.7Cr0.8Fe	Alloy B	NA*	NA
Cu-0.7%Cr-2.0%Fe (casting 1)	Cu0.7Cr2.0Fe	Alloy C	0.63	1.85
Cu-0.7%Cr-2.0%Fe (casting 2)		Alloy C	0.63	1.86
Cu-1%Fe	Cu1Fe	Alloy Y	0.05	0.95
Cu-1%Cr	Cu1Cr	Alloy Z	0.81	<0.01

* NA not analysed.

easily moved. The distance, l, between the knife edges was measured to the nearest 0.01 mm, using a digital vernier. To either end of the sample were attached two large alligator clips. These were connected to a DC power supply. A ~3 amp current was passed through the sample, this was measured to the nearest milliamp using a digital multimeter. The knife edges were connected to a high accuracy Keithley digital multimeter (model : 195A) that had a maximum resolution of 100 nV and a zeroing facility. This was used to measure the voltage between the two knife edges.

The resistivity ρ is given by:

$$\rho = (\mathrm{R} \cdot \mathrm{a})/\mathrm{l}\ (\mathrm{n}\Omega \cdot \mathrm{m}) \qquad (1)$$

where R ($R = \mathrm{VI}$) is the resistance of the alloys. The standard conductivity of pure copper is assigned a value of 100% IACS corresponding to an electrical resistivity of 1.724 $\mu\Omega \cdot \mathrm{cm}$. The conductivity of the each sample is given by

$$\%\mathrm{IACS} = 1724/\rho\ (\mathrm{n}\Omega \cdot \mathrm{m}) \qquad (2)$$

3 independent measurements were conducted on each sample and the results averaged. The conductivity of alloys in the peak aged and solution treated condition was measured using 2 samples.

In order to ensure that that the results were accurate the conductivity of a number of high purity standard materials were tested. Tests on 99.99% pure Cu, Al, Ni and Co resulted in reproducible conductivity readings that were within 1% IACS of those quoted in literature. During the course of testing additional tests were carried out periodically on the Cu standard to ensure the results were accurate.

3. Results

3.1. Isochronal aging

Solution treated hardness blocks were aged for one hour at 50°C intervals to determine the optimum aging temperature of each alloy. The optimum aging temperature was considered to be that which produced the maximum age hardening response after aging for one hour, Fig. 2. Error bars show the range of hardness values recorded for each specimen.

Isochronal aging curves for the Cu-1%Cr (Alloy Z) and the Cu-0.7%Cr-0.3%Fe alloy (Alloy A) followed a similar trend. Both alloys had a large hardening response. Hardness increased up to an optimum aging temperature of 500°C, above which over aging occurred. The averaged maximum hardness for Alloy A after being aged at 500°C for one hour was 144 HV, compared to 160 HV for Alloy Z. This hardness value is ~15 HV higher than that reported by other authors [9, 10] for comparable Cu-Cr alloys. These authors used a solution treatment temperature of 1000°C compared to 1050°C used in the present study. This significantly reduced the amount of Cr in solid solution that was available for precipitation strengthening. The hardness of both alloys after aging at 550°C and higher were comparable. However the rate of over aging of Alloy A appeared to be less than that of Alloy Z. The higher solution treated hardness of Alloy A in comparison to all other alloys could have been due to a slightly slower quenching rate after solution treatment which may have resulted in some precipitation during cooling. However the solution treated conductivity of this alloy was less than that of the other two Cu-Fe-Cr alloys which would seem to indicate otherwise. An alternative explanation may be that the ratio of Fe to Cr in solid solution is conducive to solid solution strengthening. The higher solution treated hardness would also be expected to have affected the hardness of specimens aged at 350 and 400°C.

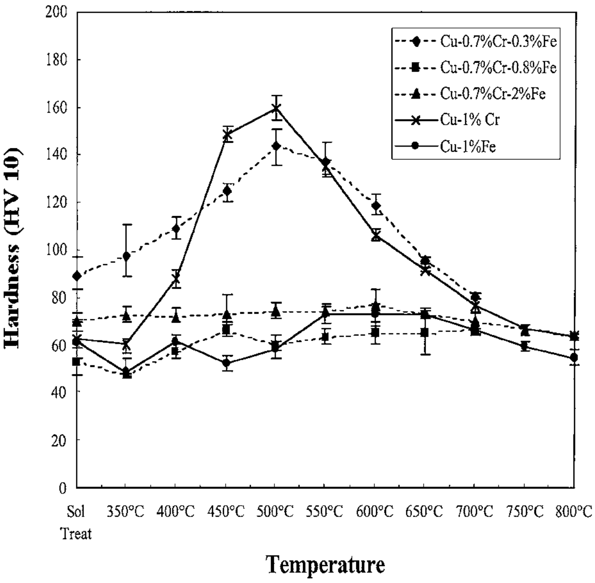

Figure 2 One hour isochronal aging curves for the solution treated alloys.

One hour isochronal aging curves for the Cu-0.7%Cr-0.8%Fe (Alloy B), Cu-0.7%Cr-2.0%Fe (Alloy C) and Cu-1%Fe (Alloy Y) alloys all showed very small age hardening responses. The increase in average hardness from the solution treated condition to the peak aged condition was less than 18 HV for these alloys. The hardness of these alloys did not change appreciably with exposure to elevated temperatures.

Alloy Y showed only a very small age hardening response. This is in agreement with literature and is the reason that these alloys are only used in cold worked condition [11]. The peak hardness of 73 HV was in good agreement with the results of [12]. Overlap of error bars make it difficult to determine the optimum aging temperature; 600°C was chosen.

The isochronal aging curve for Alloy B showed that this alloy has only a very small hardening response. Average hardness increased from 53 HV in the solution treated condition up to a maximum of 69 HV at 500°C. Thus 500°C was chosen as the optimum aging temperature. Peak hardness was less than that recorded for Alloy Y. Overaging occurred for temperatures above 550°C, however the amount of overaging in all cases up to 700°C was less than 6 HV.

Alloy C did not seem to show any appreciable age hardening response. The average hardness of Alloy C increased from 70 HV in the solution treated condition up to a peak of 77 HV after one hour at 600°C. The peak hardness was 67 HV less than that of Alloy A, but 8 HV higher than that of Alloy B. Over aging at higher temperatures was slow, the average hardnesses after aging at 700 and 800°C for 1 hour were still 70 and 64 HV. Such a small increase in hardness and overlap of error bars for each heat treatment temperature made it difficult to determine an optimum aging temperature. However the high temperature stability of this alloy was worth investigating, therefore 600°C, the temperature which had the maximum average hardness, was chosen as the optimum aging temperature.

3.2. Isothermal aging

Isothermal aging curves for the alloys, at the selected optimum aging temperatures (Table III), are shown in Fig. 3. Solution treated specimens of each alloy were plotted as having an aging time of one minute. Tests were carried out in duplicate on peak aged and selected under aged and over aged specimens.

The results of isothermal aging curves support those of the isochronal aging curves. Only Alloy A showed a significant age hardening response, approaching that of Alloy Z. Alloy B and Alloy C had similar age hardening responses to Alloy Y. Alloy C was resistant to softening after prolonged exposure to elevated temperatures. Average peak hardness recorded for all alloys on both isochronal and isothermal curves were very similar. The results of the isothermal aging data are summarised in Table IV.

Fig. 3 shows that the hardness of all of the alloys fell slightly when aged for short periods, 2–10 minutes. This behaviour was most pronounced for Alloy Y and Alloy B where even after 10 minutes of aging the hardness was still less than that in the solution treated condition. In the early stages of precipitation the amount of precipitation strengthening does not make up for the loss of solid solution strengthening. Similar trends have been reported for Cu-Fe alloys by [12, 13].

TABLE III Optimum aging temperatures selected for each alloy

Alloy (wt%)	Optimum aging temperature (°C)
Cu-0.7%Cr-0.3%Fe (Alloy A)	500
Cu-0.7%Cr-0.8%Fe (Alloy B)	500
Cu-0.7%Cr-2%Fe (Alloy C)	600
Cu-1%Cr (Alloy Z)	500
Cu-1%Fe (Alloy Y)	600

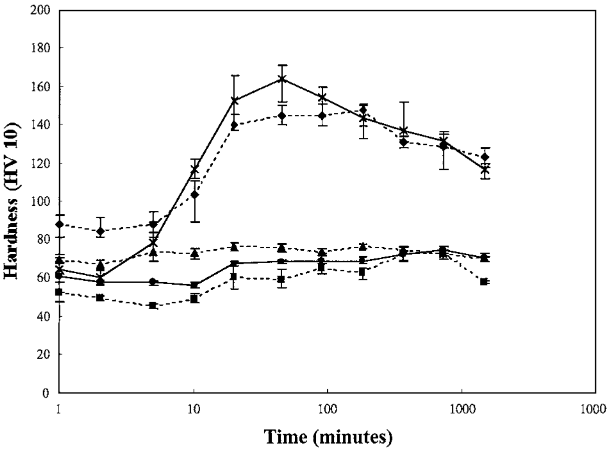

Figure 3 Isothermal aging curves.

TABLE IV Summary of hardness results for isothermal aging curves

Alloy	H_{ST}	H_{peak}	ΔH
Cu-0.7%Cr-0.3%Fe (Alloy A)	89	148	60
Cu-0.7%Cr-0.8%Fe (Alloy B)	53	72	19
Cu-0.7%Cr-2%Fe (Alloy C)	70	76	6
Cu-1%Cr (Alloy Z)	63	164	101
Cu-1%Fe (Alloy Y)	61	74	13

H_{ST}: hardness in solution treated condition.
H_{peak}: peak hardness reached.
ΔH: Increase in hardness from solution treated condition to peak hardness.

Alloy A age hardened rapidly at 500°C. Hardness increased from 89 HV in the solution treated condition to 139 HV after 20 minutes aging. Further aging increased the hardness to a maximum of 148 HV after 180 minutes at 500°C. There was a broad maximum in the aging curve. Over aging occurred gradually, with hardness falling to 123 HV after 1440 minutes. Alloy Z in comparison had a peak hardness of 164 HV after aging for 45 minutes at 500°C, however the rate of overaging was higher. The results seem to suggest that the conventional Cu-1%Cr (i.e. Alloy Z) is more susceptible to over aging compared with the experimental Alloy A. These results were in good agreement with those from isochronal aging.

The age hardening response of Alloy B aged at 500°C was minimal. Hardness increased from 53 HV in the solution treated condition up to a maximum of 72 HV which was measured after aging for 360 and 720 minutes. The optimum aging time for this alloy would be expected to exist somewhere between these two aging times. Overaging occurred after aging for 1440 minutes, with hardness falling to 58 HV.

Alloy C was aged at 600°C. The age hardening response of this alloy was very small, increasing from 70 HV in the solution treated condition to a maximum of 76 HV after 180 minutes. The higher solution treated hardness of this alloy meant that the increase in hardness associated with aging, ~6 HV, was less than half that which occurred in both Alloy Y and Alloy B. The peak aged hardness of this alloy was approximately the same as that of Alloy Y and Alloy B aged at 600°C and 500°C respectively. The temperature stability of this alloy was high. Only minimal over-aging occurred. The hardness was still 70 HV after aging for 1440 minutes.

3.3. Tensile properties

Tensile specimens were machined from solution treated castings. Prior to tensile testing hardness tests were carried out on each tensile specimen in order to ensure that each specimen had received the correct heat treatment. Hardness data from the tensile specimens were plotted against aging time and the results compared to the data used in the isothermal aging curve. It was found that the hardness of all tensile specimens were very similar to that of the aged hardness blocks. This confirmed that the heat treatments given to the tensile specimens were correct.

Results of tensile tests are summarised in Figs 4 and 5, which respectively present plots of ultimate tensile stress (σ_{uts}) and 0.5% yield stress (σ_{y}) versus aging time. Solution treated specimen data have been plotted with an aging time of 1 minute. Results summarised in Fig. 4 were consistent with the hardness values (Fig. 2). The σ_{uts} of both Alloy Z and Alloy A increased significantly with aging time and then decreased with overaging. Also consistent with hardness measurements, Alloys B, C and Y showed small increases in σ_{uts} with aging time.

The σ_{uts} of Alloy A reached a peak of 365 MPa after aging for 45 minutes at 500°C. Peak strength based upon the isothermal hardness curve was expected after 180 minutes aging, at this aging time a σ_{uts} of 340 MPa was recorded. The average peak σ_{uts} measured for Alloy Z was 413 MPa after aging for 45 minutes at 500°C. As for the hardness results the peak σ_{uts} was higher than those quoted in literature for Cu-1%Cr, typically ~350 MPa [14, 15]. This was attributed to the higher solution temperature used, 1050°C compared to 1000°C. The solution treated σ_{uts} of Alloy A was high in comparison to that Alloy Z as was the case for the solution treated hardness.

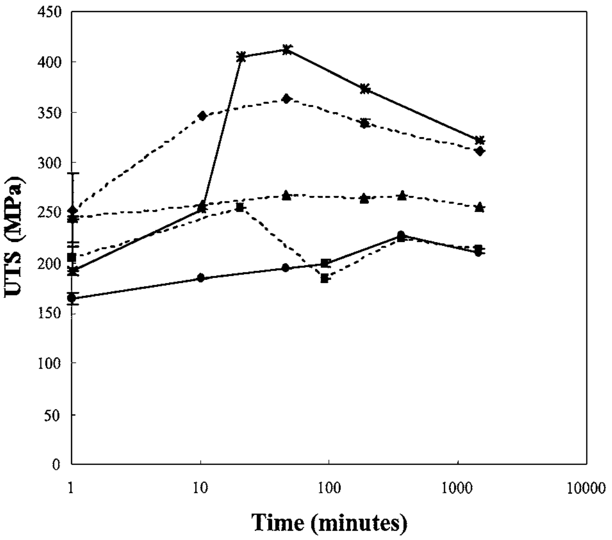

Figure 4 Ultimate tensile stress (σ_{uts}) versus aging time.

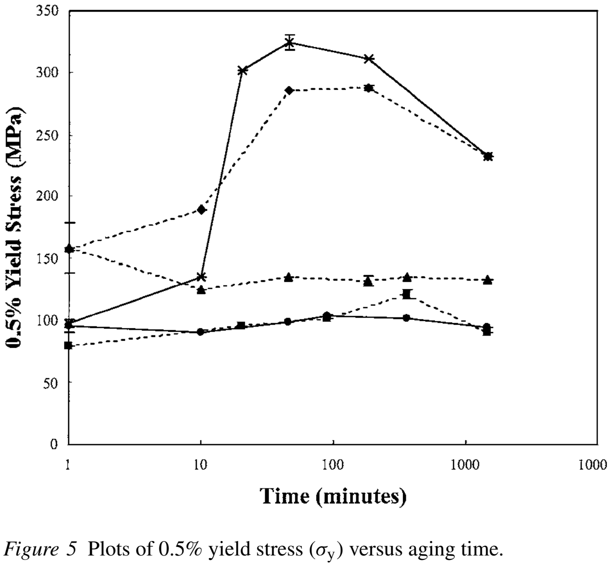

Figure 5 Plots of 0.5% yield stress (σ_{y}) versus aging time.

The plot of σ_{uts} versus aging time at 500°C for Alloy B appeared to contain an anomalous data point, ie. for the specimen aged for 90 minutes. A peak σ_{uts} of 256 MPa was recorded after aging for only 20 minutes. Duplicate tests on tensile specimens aged for 360 minutes, where peak σ_{uts} was anticipated, gave average σ_{uts} of 226 MPa. Solution treated and peak σ_{uts} were higher than those of the Alloy Y, unlike the hardness measurements. The maximum recorded σ_{uts} was similar to that of the Alloy C aged at 600°C. Aging for extended periods at 500°C appeared to cause overaging as observed in the isothermal aging curve.

For Alloy C the σ_{uts} showed only a minimal increase with aging at 600°C as did hardness. The σ_{uts} increased from 245 MPa in the solution treated condition up to a peak of 269 MPa after 360 minutes aging. This was only 96 MPa less than the peak σ_{uts} recorded for Alloy A. Duplicate tests after aging for 180 minutes gave σ_{uts} of 265 and 266 MPa. The σ_{uts} was still 257 MPa after 1440 minutes aging.

The 0.5% yield stress (σ_{y}) is widely used in the literature when reporting the properties of high-strength, high-conductivity copper alloys [11, 14]. The results of σ_{y} plotted against aging time for each alloy at their selected optimum aging temperature are plotted in Fig. 5. For Alloy A and Alloy B projected σ_{y} values have been plotted. These have been derived from hardness results.

It was anticipated that the plots of σ_{y} versus aging time would show relationships similar to those shown by the plots of hardness and σ_{uts} versus aging time. This was true for all of the alloys investigated. Plots of σ_{y} and hardness vs aging time were almost identical, both showed the same aging behaviour. The plot of σ_{uts} versus aging time (Fig. 4) showed that the difference in σ_{uts} of each alloy in all aged conditions was not as great as the difference in σ_{y} and hardness. The reason for this was the greater amount of strain that occurred in Alloy Y, Alloy B and Alloy C at their σ_{uts} in all aged conditions in comparison to Alloys A and Z. This meant more work hardening occurred in these alloys which made up for their lack of precipitation strengthening.

Fig. 5 shows that the σ_{y} of Alloy C was not significantly affected by aging at 600°C. Maximum σ_{y} of 159 MPa was recorded in the solution treated condition. After aging for 1440 minutes σ_{y} was 133 MPa. These results supported hardness results for this alloy which showed essentially no age hardening response.

σ_{y} for Alloy Y increased marginally with aging time at 650°C from an average of 96 MPa in the solution treated condition to a peak value of 104 MPa after 90 minutes followed by comparatively slow overaging down to 95 MPa. Results were in good agreement with hardness results which showed a very small age hardening response for the alloy. There was a slight decrease in σ_{y} after 10 minutes aging corresponding to a similar decrease recorded for the hardness. This behaviour was thought to be due to a transition between solution strengthening and precipitation hardening.

For Alloy Z, σ_y increased from 98 MPa in the solution treated condition up to a peak of 325 MPa after 45 minutes at 500°C. Overaging occurred after 180 minutes with σ_y falling to a value of 312 MPa. After 1440 minutes σ_y had fallen to 233 MPa. Again the peak σ_y for Alloy Z was slightly higher than that reported in literature, 275 MPa [15]. This was consistent with how σ_{uts} and HV compared with reported values.

For Alloy A, σ_y increased from 160 MPa in the solution treated condition to a peak of 288 MPa after 180 minutes at 500°C. This was 37 MPa less than the peak recorded for Alloy Z. This was followed by overaging with σ_y falling to 233 MPa after 1440 minutes.

The σ_y of Alloy B increased from 80 MPa in the solution treated condition to a peak of 122 MPa after 360 minutes aging. The σ_y of Alloy B was similar to that observed for Alloy Y for all aging times.

Table V shows the measured values of strain at the peak stress and at specimen failure, for the Alloys C, X and Y.

Values of strain obtained for these alloys are indicative of their high ductility. No relationship could be determined between the aging time and the value of ε_p or ε_f for Alloy C or Alloy Y. For Alloy Z there was a trend that both ε_p and ε_f decrease with aging time. It can be safely assumed from these results that the ductility of Alloy A and Alloy B would be similarly high.

3.4. Conductivity

Conductivity testing was carried out on the gauge lengths of tensile specimens. Based upon the results of isochronal and isothermal aging curves, aging times were chosen so as to maximise the amount of information that could be obtained from the number of samples available. Conductivity (δ) measurements on each sample were repeated three times to ensure consistency of results. Multiple δ tests on individual samples were found to give identical results. Where possible two overaged and two underaged specimens, aged for different lengths of time as well as peak aged and solution treated specimens, were used to generate curves. A minimum of two specimens were used to measure the peak aged δ.

In order to be able to directly compare the δ of the three Cu-Fe-Cr alloys (Alloys A, B & C), δ curves for each alloy were needed at the same aging temperature. 500°C was selected as this had been chosen as the optimum aging temperature for both Alloys A and B. The solution treated δ of each tensile specimen was measured prior to aging and the results are shown in Table VI.

TABLE VI Conductivity (% IACS) of solution treated Cu-Fe-Cr alloy tensile specimens prior to aging at 500°C

Specimen	Cu-.7%Cr-.3%Fe (Alloy A)	Cu-.7%Cr-.8%Fe (Alloy B)	Cu-.7%Cr-2.%Fe (Alloy C)
1	25	25	27
2	26	28	27
3	26	27	27
4	27	29	30
5	26	29	27
6	—	23	30
Average	26	27	28

Results in Table VI show that the conductivity (δ) of solution treated tensile specimen for each alloy were similar. This was a strange result as it was anticipated that the δ of Alloy B would be considerably lower than that of Alloy A. The conductivity of Alloy C was expected to be considerably lower again. This was due to the higher concentration of iron atoms expected in solid solution after quenching. An explanation for the observed behaviour is that precipitation occurs during quenching reducing the concentration of solute atoms in solid solution. This explanation was supported by the findings that it was impossible to prevent precipitation during water quenching after solution treatment for binary Cu-Cr [16, 17] and Cu-Fe alloys [18, 19].

The results of conductivity (δ) measurements on tensile specimens aged at 500°C are plotted in Fig. 6. The δ of each alloy initially increased rapidly with aging time as solute elements precipitated out of solution. As aging times increased the rate of increase in δ began to decrease as the solute concentration in the copper approached equilibrium. The increase in δ was greatest for Alloy A. After 20 minutes of aging the δ of Alloy A was 64% IACS compared to 56% IACS for Alloy B and 54% IACS for Alloy C. The average solution treated δ of each alloy were all within 3% IACS. Increasing iron content resulted in lower final δ for the three Cu-Fe-Cr alloys. After aging for 360 minutes the δ of the Alloy A was 75% IACS compared to 64% IACS for Alloy B

TABLE V Percent strain at the peak stress (ε_p) and at failure (ε_f) for Alloys C, Y and Z

	Cu-0.7%Cr-2%Fe (C)		Cu-1%Cr (Alloy Z)		Cu-1%Fe (Alloy Y)	
Time (min)	Peak (ε_p)	Failure (ε_f)	Peak (ε_p)	Failure (ε_f)	Peak (ε_p)	Failure (ε_f)
0	27	38	23	29	24	31
	22	31	29	37	34	39
10	34	45	24	29	29	40
45	30	34	12	17	21	26
			11	15		
90					33	43
					26	31
180	27	37	12	20		
	36	46				
360	35	45			28	36
1440	28	37	11	19	35	42

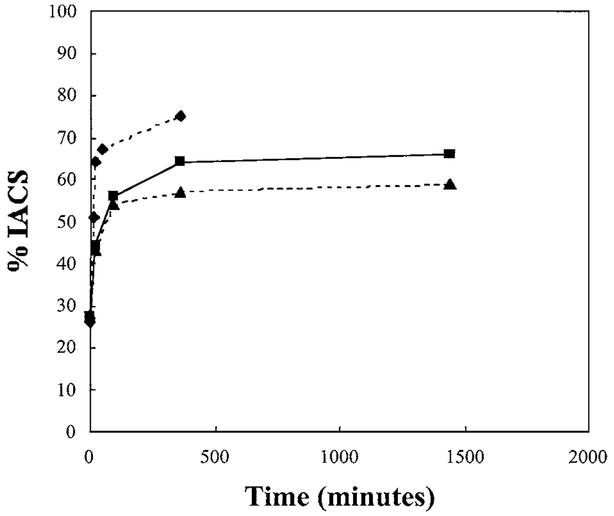

Figure 6 Plot of conductivity (% IACS) versus aging time at 500°C.

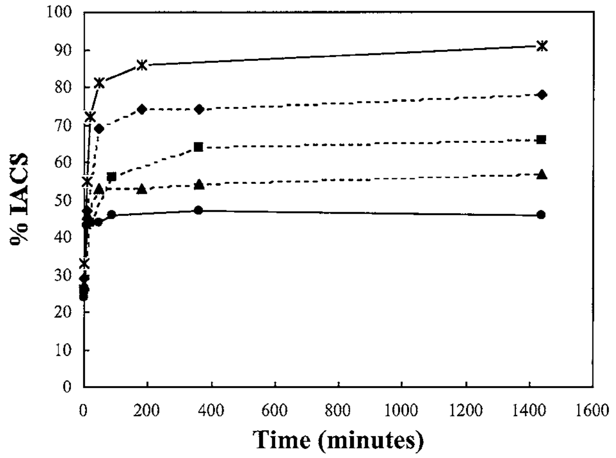

Figure 7 Plot of conductivity (% IACS) versus aging time for the alloys at their selected optimum aging temperatures.

and 58% IACS for Alloy C. This was attributed to the increasing iron content which resulted in a higher solid solubility of Fe in Cu after aging which reduced the equilibrium conductivity.

Conductivity (δ) curves were also produced for each alloy at their optimum aging temperatures. These results are shown in Fig. 7. For Alloy A the measurements were repeated on different samples. 650°C was used for the δ curve of Alloy Y rather than 600°C because very little overaging had been observed when Alloy Y was aged at 600°C. Aging at 650°C would be more likely to produce the equilibrium δ level.

Results plotted in Fig. 7, (showing aging behaviour at optimum aging temperature) follow the same trends as those of Fig. 6 (showing aging behaviour at the arbitrary aging temperature of 500°C). Conductivity (δ) curves for Alloy A in both figures were identical because the arbitrary aging temperature is coincident with the optimum aging temperature. The lower δ of Alloy C in Fig. 7 was due to the higher aging temperature which resulted in higher equilibrium concentration of solute in solution. After 1440 minutes of aging the δ of Alloy C aged at 500°C was 62% IACS compared to 57% IACS when aged at 600°C.

The δ determined for aged Alloy Z was higher than that of Alloy A for all aging times. After 45 minutes aging at 500°C the δ of Alloy Z was 81% IACS compared to 69% IACS for Alloy A, after 180 minutes the δ values were 86 and 74% IACS respectively. The δ values determined for Alloy Z agreed well with those reported by authors who have investigated this system [20]. In the case of the Alloy B aged at 500°C, δ was considerably lower; after 360 minutes of aging δ for this alloy was only 64% IACS, marginally increasing to 66% IACS after 1440 minutes. This was consistent with earlier results (Fig. 6) that showed that increasing iron content decreased the conductivity of Cu-Cr alloys. In the case of Alloy Y peak δ of 47% IACS was recorded after 1440 minutes of aging at 650°C. The δ was low due to the high aging temperature. This compares well with previous results (Bojarski *et al.* [19]) where it was reported that after 1 hour aging at 650°C, δ for a Cu-0.55wt%Fe and a Cu-1.49wt%Fe alloy were 43 and 41% IACS respectively. The present work although consistent with Bojarski *et al.* [19], on the effect of Fe can not be directly compared to the δ for the other Cu-Fe-Cr alloy due to the higher aging temperature used.

3.5. Summary for alloys solution treated and aged

Results of the investigation of the properties of the three Cu-Fe-Cr alloys (A, B & C) revealed that their properties differ widely. Comparison of the properties of the two standard alloys (Y & Z) to those values published in literature showed that that the present results were accurate, thereby validating the methods employed in the present study. In the solution treated and aged condition Alloy A had properties approaching that of Alloy Z. The alloy had a large age hardening response as illustrated by hardness and tensile results. The peak hardness and maximum ultimate tensile stress of 148 HV and 365 MPa were recorded; for Alloy Z the corresponding values were 164 HV and 413 MPa. The conductivity of Alloy A in the peak aged condition (ie. at peak hardness) was 74% IACS compared to 81% IACS for Alloy Z. The lower conductivity is the result of the 0.3 wt% Fe, a significant proportion of which is thought to remain in solid solution after aging.

Results for Alloy B indicated limited potential for this alloy as a high strength, high conductivity alloy. Only a small increases in hardness and tensile properties occurred with aging. Peak hardness and maximum ultimate tensile stress of only 72 HV and 256 MPa were recorded. In the peak aged condition the conductivity of this alloy was 64% IACS, while in the overaged condition the conductivity was 66% IACS.

Alloy C was also observed to have only a small age hardening response. The properties of Alloy C, both electrical and mechanical, were considerably less than those of Alloy A. The mechanical properties recorded were superior to those of Alloy B, however electrical conductivity after aging was not as high, due to the higher iron content. Peak hardness recorded was 76 HV. The maximum tensile and yield stress were 269 and 159 MPa respectively. The peak aged conductivity of this alloy when aged at 500°C was 58% IACS compared to 53% IACS when the alloy was aged at 600°C. The optimum aging temperature selected for this alloy was 600°C, similar to that of Alloy Y for which 650°C was chosen. At this elevated temperature the properties of the alloy were stable even after prolonged exposure. After 1440 minutes the hardness of this alloy was still 70 HV and the ultimate tensile stress was 257 MPa, ∼10 MPa higher than that of the solution treated specimen. This observation was supported by isochronal aging results which showed that the hardness of the alloy was still 64 HV after 1 hour exposure to 800°C.

4. Discussion

4.1. Validity of test method

Throughout the results section four major parameters, hardness (HV), ultimate tensile stress (σ_{UTS}), 0.5% yield stress (σ_{y}) and conductivity (δ) were consistently measured to evaluate the alloys properties. Results were reproducible and contained little scatter. Numerous examples were given showing that the aging response and peak aged properties of the two reference alloys, Cu-1wt%Cr and Cu-1wt%Fe were equivalent to those reported in literature.

There was however one minor discrepancy between literature values and the properties measured in this study. This was the higher peak aged mechanical properties of the solution treated and aged Cu-1%Cr alloy. The mechanical properties (HV, σ_{y}, σ_{UTS}) of the alloy solution treated and peak aged were ∼15 % higher than those reported in the literature [9, 10, 12, 14, 15].

The improved mechanical properties of the reference alloy were attributed to the higher solution treatment temperature used in the present study, 1050°C as opposed to 1000°C for the alloys in the literature. The Cu-Cr phase diagram indicates that the solubility of Cr in Cu decreases rapidly as the temperature drops. At the higher solution treatment temperature used in the present study, more Cr would dissolve into solid solution and as a result the volume fraction of Cr available for strengthening would be higher.

Apart from this minor difference, the properties of the two reference alloys as determined from this study were in good agreement with those of equivalent compositions in literature. This, together with the reproducibility of the results, indicates that the experimental methods used were appropriate and that the experimental results determined for the three Cu-Fe-Cr alloys investigated are valid and can be confidently compared with results from the literature.

5. Conclusions

This paper reports on the mechanical property investigation which indicated that the Cu-0.7wt%Cr-0.3wt%Fe, and Cu-0.7wt%Cr-2.0wt%Fe alloys were worthy of further investigation.

Acknowledgements

This work was supported by the Australian Research Council and by Copper Refineries Pty Ltd.

References

1. "The World of Metals, Copper" (Metallgesellschaft (Publishers), Frankfurt, 1993).
2. "Metals Handbook - Desk Edition," 2nd ed., edited by J. R. Davis (ASM International (Publishers), Metals Park, Ohio, 1985).
3. A. ATRENS, J. NAIRN, H. FERNEE, G. SKENNERTON and A. OLOFINJANA, *Materials Forum* **21** (1997) 57.
4. "Alloy Phase Diagrams," ASM Handbook, vol. 3, 10th ed. (1990).
5. S. F. HAGER, *Metal Progress* **107** (1975) 85.
6. H. FERNEE, J. NAIRN and A. ATRENS, part II, Microstructural Characterisation, *J. Mater. Sci.* **36** (2001) 2721.
7. H. FERNEE, J. NAIRN and A. ATRENS, Cold Worked Cu-Fe-Ce alloys, submitted for publication to *Journal of Materials Science*.
8. H. FERNEE, J. NAIRN and A. ATRENS, Influence of Quaternary Additions to Cu-Fe-Cr Alloys, submitted for publication to *Journal of Materials Science*.
9. N. Y. TANG, D. M. R. TAPLIN and G. L. DUNLOP, *Materials Science and Technology* **1** (1985) 270.
10. J. RYS and Z. RDZAWSKI, *Metals Technology* January 1980, 32.
11. Alloy Digest, "Alloy Digest, Engineering Alloy Digest" (New Jersey (Publisher), April 1979).
12. S. NISHIKAWA and K. NAGATA, Report of the Industrial Science, The University of Tokyo, vol. 28, no. 2, serial no. 181, 1980.
13. J. M. DENNEY, *Acta Metallurgica* **4** (1956) 586.
14. D. T. PETERS and J. A. KUNDIG, *Advanced Materials and Processes* **6** (1994) 20.
15. Metals Handbook, ASM Handbook, vol. 2, 10th ed. (1990).
16. R. O. WILLIAMS, *Transactions of the ASM* **52** (1960) 530.
17. J. SZABLEWSKI and R. HAIMANN, *Materials Science and Technology* **1** (1985) 1053.
18. A. BOLTAX, *Transactions AIME* **218** (1960) 812.
19. Z. BOJARSKI, W. BABINSKI, H. MORAWIEC, T. PANEK, J. RASEK and D. STROZ, *Metals Technology* (1980) 248.
20. M. K. BANERJEE, *Cast Metals* **6** (1994) 204.

Received 25 April
and accepted 3 November 2000