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Cold worked Cu-Fe-Cr alloys

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The aim of this project was to investigate the properties of copper rich Cu-Fe-Cr alloys for the purpose of developing a new cost effective, high-strength, high-conductivity copper alloy. This paper reports on the influence of cold work. The age hardening response of the Cu-0.7%Cr-2.0%Fe alloy was minimal, but the resistance to softening was superior to that reported for any commercial high-strength, high-conductivity (HSHC) copper alloy with comparable mechanical and electrical properties. For example, an excess of 85% of the original hardness of the 40% cold worked alloy is retained after holding at 700°C for 1 hour, whereas commercial HSHC Cu-Fe-P alloys have been reported to soften significantly after 1 hours exposure at less than 500°C. The Cu-0.7Cr-2.0Fe alloy would therefore be expected to be more suitable for applications with a significant risk of exposure to elevated temperatures. Optical microscope examination of cold worked and aged microstructures confirmed the high resistance to recrystallization for Cu-0.7%Cr-2.0%Fe. The Zener-Smith drag term, predicting the pinning effect of second phase particles on dislocations in cold worked microstructures, was calculated using the precipitate characteristics obtained from TEM, WDS and resistivity measurements. The pinning effect of the precipitate dispersions in the peak-aged condition was determined to be essentially equivalent for the Cu-0.7%Cr-0.3%Fe and Cu-0.7%Cr-2.0%Fe alloys. A lower recrystallisation temperature in the Cu-0.7%Cr-0.3%Fe alloy was therefore attributed to faster coarsening kinetics of the secondary precipitates resulting from a higher Cr concentration in the precipitates at lower iron content. © *2001 Kluwer Academic Publishers*

1. Introduction

The results of experiments on solution treated and aged Cu-Fe-Cr alloys were sufficiently encouraging [1] to warrant investigation into the effect of cold work upon their properties, ie to investigate the properties produced by cold work plus peak age (CW + PA). This was reinforced by the fact that Cu-Fe binary alloys are only used in the cold worked condition where Fe precipitates are used to stabilise the cold worked microstructure to elevated temperatures [2]. It was expected that Fe precipitates would have the same effect in the Cu-Fe-Cr alloys. The effect of cold work plus aging was investigated for Cu-0.7% Cr-0.3%Fe (Alloy A) and Cu-0.7%Cr-2.0%Fe (Alloy C). The properties of Alloy A had been found to approach those of Cu-1%Cr alloy (Alloy Z) in the solution treated and aged condition [1]; it was considered that in the cold worked condition they may equal or exceed them. In the solution treated and aged condition Alloy C was resistant to softening at elevated temperatures [1], in particular more resistant than the binary reference Alloy Y (Cu-1%Fe). Whether this stability translated into the precipitates being able prevent recrystallisation and therefore enable the retention of cold work strengthening to elevated temperatures was investigated in this work. The properties of the two reference alloys (Alloys Y and Z) were also investigated in the cold worked condition. This was done so the results could be validated by comparison to published values and also to compare the effect of cold work on Cu-Fe-Cr alloys to binary alloys that were subjected to similar thermo-mechanical treatments.

The literature indicates that high strength, high conductivity (HSHC) copper alloys are widely used for applications such as lead frames and electrical connectors after being first peak aged and then cold worked (PA + CW) [3, 4]. Conductivity (δ) and hardness can be maximised prior to CW and no loss of CW strengthening can occur due to recovery or recrystallisation during aging. This can result in a better combination of mechanical and electrical properties. The properties of Cu-0.7%Cr-0.3%Fe (Alloy A) and Cu-0.7%Cr-2.0%Fe (Alloy C) were therefore also investigated in the PA + CW condition. This would also enable comparison of the properties in the CW + PA versus PA + CW conditions.

2. Experimental

The experimental procedures were as in the prior research [1], except for Differential Scanning Calorimetry (DSC). Chemical compositions of all alloys are also given in [1].

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To investigate the CW + PA conditions, samples of solution treated castings for each of the four alloys were cold rolled by 40 and 90%. These two reductions were selected because, for copper alloys such as Cu-Be, 40% cold work (CW) is the recommended optimum for mechanical properties [5] whereas high reductions are found to be beneficial for alloys such as Cu-Fe where strengthening relies only on CW [5, 6]. Rolled samples were machined into hardness blocks and aged at 50°C intervals from 350°C through to 800°C in order to determine the optimum aging temperature. Aging at temperatures above 600°C was carried out to provide information about the softening resistance of each alloy. Subsequently isothermal aging curves were determined at the optimum aging temperature.

Conductivity (δ) was measured on the gauge lengths of tensile specimens prior to tensile testing. Cold worked tensile specimens were aged at what had been selected as their optimum aging temperature.

Optical microscopy was used to determine the recrystallisation temperature of the 40 and 90% cold worked Alloy A and Alloy C. Cold worked hardness blocks that had been used to determine the isochronal aging curves were mounted, polished and then etched with alcoholic ferric chloride to reveal the grain structure. 40% cold worked samples were examined transverse to the direction of rolling while 90% cold worked samples were examined longitudinally.

DSC was used to determine the recrystallisation temperatures of the cold worked Cu-Fe-Cr alloys. All scans were performed using a Perkin Elmer DSC-7 instrument. The calorimeter was calibrated with indium and zinc standards by comparing the scan results at 20°C a minute with the published equilibrium data for the standards. Transformation temperature measurements after calibration were accurate to ±1°C. The samples used were typically between 20–60 mg in weight. They were rectangular pieces cut from hardness blocks with a Buehler Isomet low speed diamond saw to ensure no heating or coldworking of the specimens. All scans were acquired using aluminium sample pans. A heating rate of 20°C per minute was used over a temperature range of ~100 to ~550°C. The possibility of the aluminium sample pans alloying with the platinum sample holder cell precluded scan temperatures higher than 550°C.

For the PA + CW investigations, the various treatment conditions are summarised in Table I. Pieces of solution treated castings were PA + CW and then machined into tensile specimens and hardness blocks. Alloy A was aged for 180 minutes at 500°C prior to cold working. This aging temperature and time were selected based upon the isothermal aging results for the solution treated alloys discussed in [1]. Alloy C was aged at 500°C for 3 hours. The lower aging temperature was selected (compared to 600°C that was selected as the optimum aging temperature for the other Cu-0.7%Cr-2%Fe alloys) to try and increase the δ by reducing the concentration of solute atoms in the copper matrix after aging. As this alloy had shown only a minimal age hardening response, aging at 500°C would not affect the strength. Hardness, electrical δ, tensile properties and the resistance to softening were investigated.

For Alloy C, CW + PA, peak mechanical properties (hardness, σ_y, σ_{UTS}) were recorded in the unaged condition. The mechanical properties in this condition were almost identical to those when the alloy was PA + CW. Aging to increase δ caused recovery and resulted in a decrease in the mechanical properties. The mechanical properties listed in following sections to compare with those when the alloy is PA + CW are those recorded after the alloy had been aged and δ was approaching equilibrium. These better represented the actual properties of the alloy when in service.

3. Results

3.1. Isochronal aging of CW samples

Fig. 1 shows that after 40% CW the age hardening response of both Alloy Z and Alloy A were almost

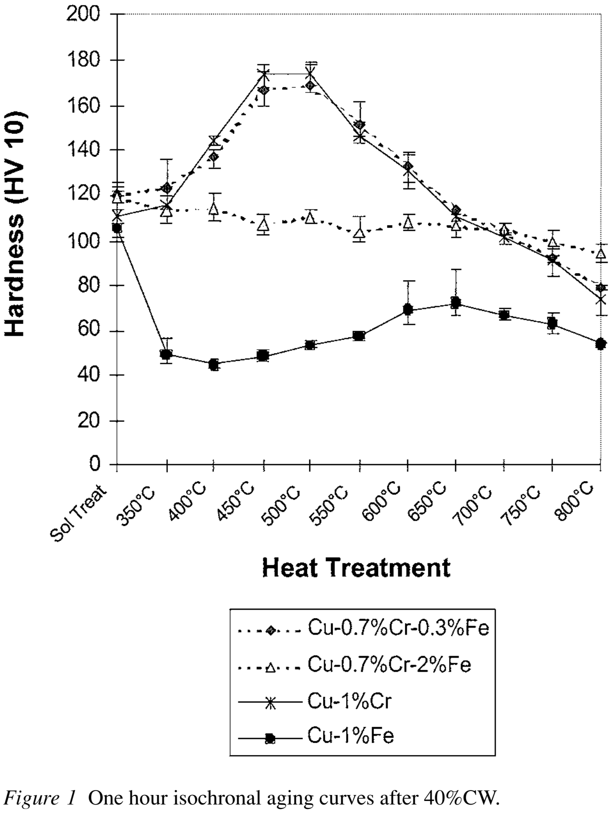

Figure 1 One hour isochronal aging curves after 40%CW.

TABLE I Treatment conditions

	Cu-0.7%Cr-0.3%Fe (Alloy A)		Cu-0.7%Cr-2.0%Fe (Alloy C)	
Condition	40% CW	90% CW	40% CW	90% CW
Peak Age (PA) + CW	180 min 500°C + 40%CW	180 min 500°C + 90%CW	180 min 500°C + 40%CW	180 min 500°C + 90%CW
CW + PA	40%CW + 360 min 450°C	90%CW + 90 min 450°C	40%CW + 45 min 600°C	90%CW + 45 min 600°C

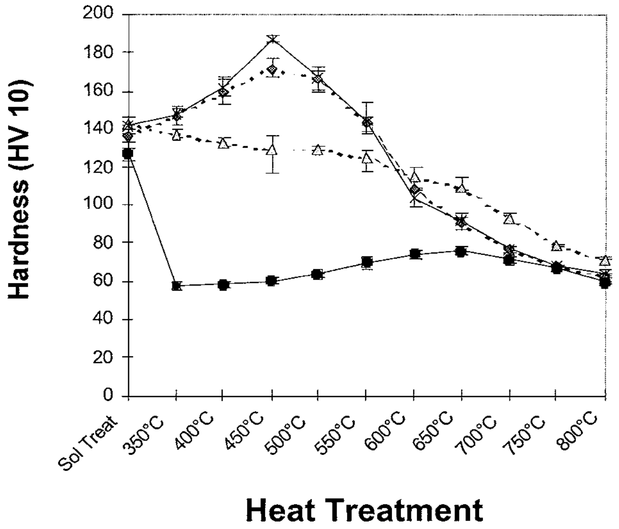

Figure 2 One hour isochronal aging curves after 90%CW, symbols as for Fig. 1.

identical. The hardness of both alloys increased significantly with increasing aging temperature, peaking after being aged at 500°C for 1 hour. Aging at temperatures higher than 500°C caused overaging, hardness decreased almost linearly down to a minimum of 74 HV for Alloy Z and 79 HV for Alloy A after aging at 800°C for 1 hour. These hardness values were higher than those of the equivalent solution treated and aged specimens indicating that the strengthening effect of CW is not completely lost even after significant overaging. The optimum aging temperature selected for both of these alloys was 450°C. The reason was that the hardness of both alloys after aging at 450°C was near the peak hardness, (only less than 2 HV lower than that recorded after aging at 500°C).

Fig. 2 shows that similar age hardening behaviour was displayed by both Alloys A and Z after 90% cold work. The size of the age hardening response of both alloys was reduced due to the higher hardness of the initial sample. The peak hardness of both alloys was modestly increased from that of the 40% cold worked alloys and occurred at a lower aging temperature, 450°C. After aging at 500°C and above the isochronal aging curves of both alloys were essentially identical. Peak hardness occurred at a lower aging temperature after 90% CW because the higher dislocation density of the microstructure provided more sites for precipitation. This provided a thermo-kinetic advantage for the precipitation reaction, so the peak hardness occurred at lower aging temperature. The lower hardness of the overaged 90% cold worked Alloy Z and Alloy A at temperatures greater than 450°C compared to when 40% cold worked was attributed to a combination of accelerated overaging and recovery/recrystallisation. The optimum aging temperature selected for both 90% cold worked alloys was 450°C.

For Alloy C in both the 40% and 90% cold worked conditions there was no age hardening response. However in both cold worked conditions the resistance to softening at elevated temperatures exceeded that of Alloy Z and Alloy A. The precipitation reaction did not strengthen the alloy, however it did stabilise the cold worked microstructure.

TABLE II Optimum aging temperatures for the cold worked alloys

Alloy (wt%)	40% CW	90% CW
Cu-0.7%Cr-0.3%Fe	450°C	450°C
Cu-0.7%Cr-2%Fe	600°C	600°C
Cu-1%Cr	450°C	450°C
Cu-1%Fe	650°C	650°C

For the binary Alloy Y, exposure of the 40 and 90% cold worked samples to 350°C for 1 hour caused complete recrystallisation of the cold worked microstructure and the loss of all strengthening due to CW. This complete recrystallisation was contrary to literature data [2, 5, 7]. Recrystallisation temperatures between 350–550°C are reported for commercial Cu-Fe alloys depending upon the amount of CW and exposure time. Commercial alloys contain trace additions of P (0.1–0.03 wt%) which form Fe_2P precipitates during solidification. These precipitates are reported to be effective at stabilising cold worked microstructures [7]. Another important difference is that these commercial alloys have been aged prior to cold working so that a significant proportion of precipitates are already present to stabilise the microstructure, unlike when the alloy is aged after being solution treated and cold worked.

Table II gives the optimum aging temperatures selected for the cold worked alloys.

3.2. Isothermal aging of the CW samples

Figs 3 and 4 show the isothermal aging curves, at the selected optimum aging temperatures, for the alloys after 40 and 90% cold work and critical values are summarised in Table III. Figs 3 and 4 show that the age hardening response of cold worked Alloy A is comparable to that of the Alloy Z. However the size of the age hardening response and peak hardness of Alloy A was slightly less than that of Alloy Z. The hardness peak was flat for Alloy A, prior to overaging occurring. Alloy Z in comparison had a more distinct optimum aging temperature. The partial substitution of Fe for Cr in

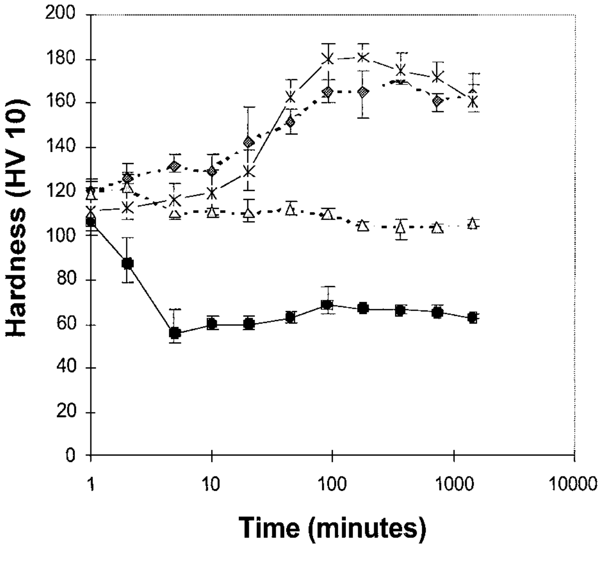

Figure 3 Isothermal aging curves after 40%CW, symbols as for Fig. 1.

TABLE III Vickers hardness results for cold worked isothermal aging

Alloy	Condition	H_{ua}	H_{peak}	ΔH
Cu-0.7%Cr-0.3%Fe, (Alloy A)	Sol treated + age 500°C	89	148	60
	40%CW + age 450°C	120	171	51
	90%CW + age 450°C	134	171	37
Cu-0.7%Cr-2.0%Fe (Alloy C)	Sol treated + age 600°C	70	76	6
	40%CW + age 600°C	119	122	2
	90%CW + age 600°C	142	142	–
Cu-1%Cr (Alloy Z)	Sol treated + age 500°C	63	164	101
	40%CW + age 450°C	111	181	70
	90%CW + age 450°C	140	184	44
Cu-1%Fe (Alloy Y)	Sol treated + age 650°C	61	74	13
	40%CW + age 650°C	106	106	–
	90%CW + age 650°C	128	128	–

H_{ua}: hardness in unaged condition, H_{peak}: peak hardness, ΔH: Increase in hardness from solution treated condition to peak hardness.

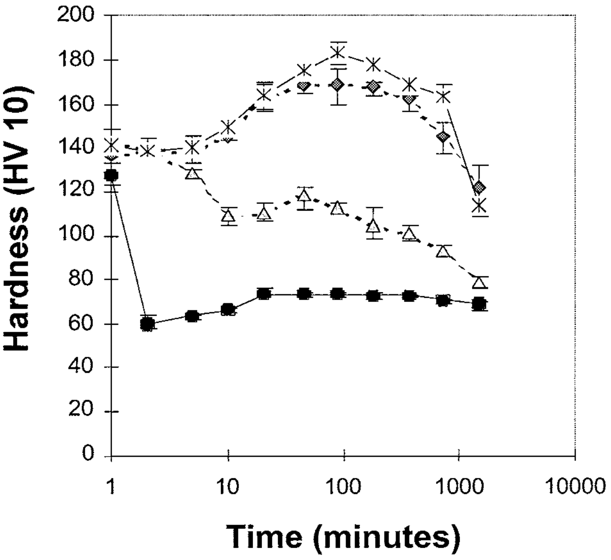

Figure 4 Isothermal aging curves after 90%CW, symbols as for Fig. 1.

the Cu-1%Cr was attributed as responsible for slowing down the precipitation kinetics.

Comparison of the effect of 40 and 90% CW upon the age hardening response of Alloy A and Alloy Z revealed that the effect of the two different amounts of cold work upon the peak hardness was small. For Alloy A, the peak hardness was the same after both the 40 and 90% CW, only the time to reach peak hardness was different, 360 minutes after 40% CW and 90 minutes after 90% CW. In both Alloys A and Z, CW accelerated the precipitation reaction so that peak hardness was reached after shorter aging times. Higher amounts of CW also accelerated the rate of recrystallisation so that softening occurred more rapidly in the 90% cold worked condition.

Isothermal aging curves for cold worked Alloy C showed similar results to those of the isochronal aging curves. Again there was no sign of any age hardening, however the 40% cold worked alloy did show excellent resistance to softening with prolonged exposure to elevated temperatures. The hardening due to 40% CW was maintained even after prolonged aging times, average hardness of the unaged 40% cold worked alloy was 119 HV, after 1440 minutes at 600°C the hardness was still 105 HV. This indicated that recovery and little recrystallisation occurred in the copper matrix. In comparison, the 90% cold worked alloy had a quite different isothermal aging curve at 600°C.

Isothermal aging curves for the cold worked Alloy Y show complete recrystallisation occurred after very short aging times. They also show that the higher the amount of cold work the faster the rate of recrystallisation. In the 90% cold worked condition complete recrystallisation occurred after only 2 minutes at 650°C whereas after 40% CW 5 minutes was required. Once recrystallisation had occurred, both isothermal aging curves were the same as that of the solution treated alloy.

3.3. Tensile properties

Figs 5 and 6 present plots of aging time versus the σ_{UTS} for each alloy. These showed trends similar to the equivalent plots of hardness vs aging time. Cold worked Alloy A showed a strengthening response similar to that of Alloy Z. Alloy C was resistant to softening with exposure to elevated temperatures and had higher σ_{UTS} than Alloy Y. All the cold worked alloys had higher σ_{UTS} than the solution treated alloys. The major difference between the plots of σ_{UTS} vs aging time and hardness vs aging time was that 90% CW resulted in a

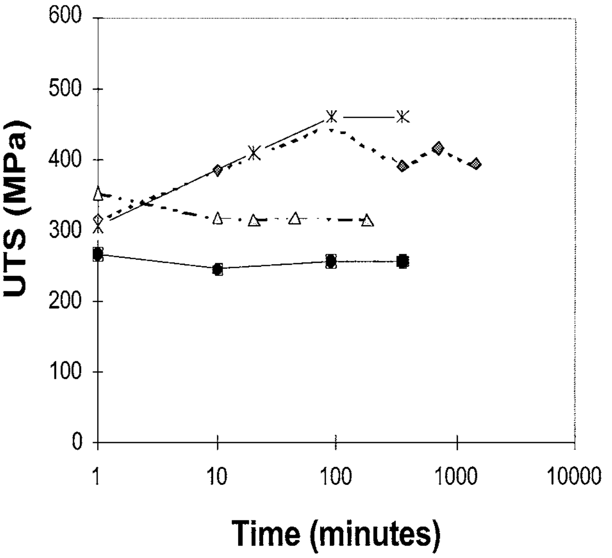

Figure 5 Plot of σ_{UTS} (MPa) versus aging time for 40%CW alloys at their optimum aging temperature, symbols as for Fig. 1.

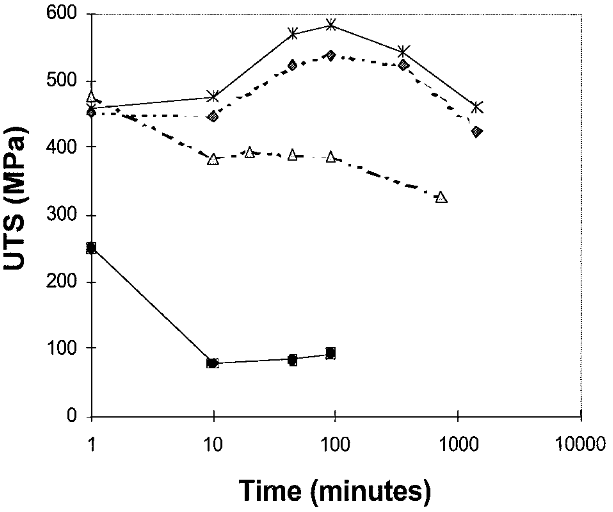

Figure 6 Plot of σ_{UTS} (MPa) versus aging time for 90%CW alloys at their optimum aging temperature, symbols as for Fig. 1.

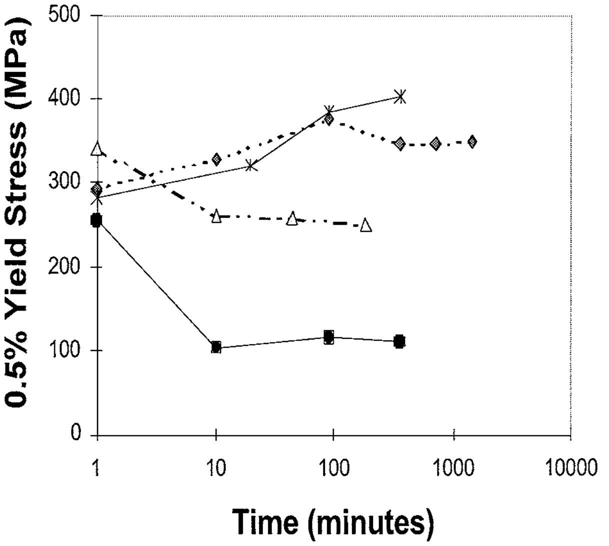

Figure 7 Plot of 0.5% yield stress (MPa) versus aging time for 40%CW alloys at their optimum aging temperature, symbols as for Fig. 1.

significantly higher σ_{UTS} than that recorded when 40% cold worked. This trend was maintained after aging for each alloy. In contrast, the increase in hardness due to 90% CW compared to 40% CW was lost during aging for each alloy. The values of peak σ_{UTS} for the cold worked reference Alloy Z compare well with those reported in literature, for 90% cold worked Cu-0.8%Cr alloy, σ_{UTS} of 593 MPa was reported whereas for the 50% cold worked alloy, σ_{UTS} of 462 MPa [8].

Figs 7 and 8 plot σ_y vs aging time for the four alloys after 40 and 90% CW at their selected optimum aging temperatures. The plots of σ_y vs aging time for Alloys A and Z after 40 and 90% CW showed similar aging behaviour to the equivalent plots of hardness and σ_{UTS} vs aging time. The values for σ_y determined in the present work compare well with those reported in literature. For a Cu-0.8%Cr alloy, 50% cold worked and aged at 450°C for 3 hours, a σ_y of 408 MPa was reported. For the same alloy 90% cold worked the σ_y was 531 MPa [8]. For cold worked Alloy C, the peak σ_y was recorded in the unaged condition consistent with the trend observed for peak hardness and peak σ_{UTS}. Aging for 10 minutes caused a large decrease in cold worked σ_y. For Alloy Y the effect of cold working upon the σ_y was lost after only 10 minutes aging at 650°C.

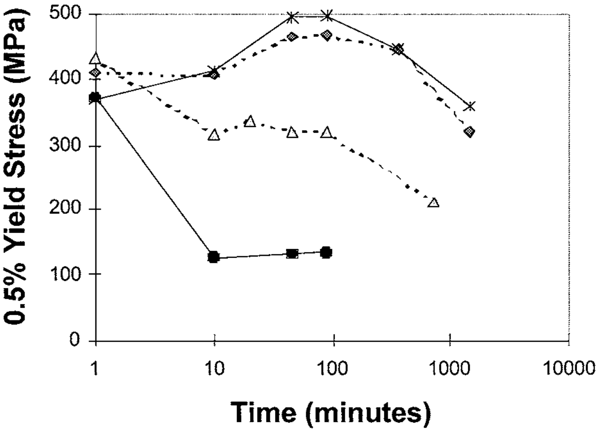

Figure 8 Plot of 0.5% yield stress (MPa) versus aging time for 90% CW alloys at the optimum aging temperature, symbols as for Fig. 1.

Our prior paper [1] on the tensile properties of each alloy when solution treated and aged, showed the percent strain at the σ_{UTS} and at fracture. The high strains recorded illustrated the high ductility of these alloys. In this section only the strain at peak tensile strength are discussed.

For 40 and 90% cold worked Alloy A the ε at the σ_{UTS} increased as the alloy was aged up to 90 minutes. The increase in ε was greater for the 90% cold worked alloy indicating that more recovery was occurring. Further aging for 360 minutes decreased the ε at the σ_{UTS} of both cold worked alloys. This was attributed to be the result of the precipitation hardening reaction which caused increased strength but also decreased ductility. For the 90% cold worked tensile aged for 1440 minutes the ε at the σ_{UTS} increased to 23%. This indicated that recrystallisation had occurred in this specimen which supports indications from trends observed in the σ_y and hardness plots.

For the Cu-0.7%Cr-2%Fe alloy (Alloy C) the plot of ε at the σ_{UTS} vs aging time indicated that the ductility of the solution treated alloy was little affected by aging. The strain (ε) was between 22 and 37% in all aged conditions. For both the 40 and 90% cold worked alloys the plots of ε vs aging time at 600°C were essentially identical. For both cold worked alloys there was an increase in ε from ~1 to ~10% after 10 minutes aging at 600°C. With further aging ε continued to increase from ~10% to ~14% after 360 minutes. For the 90% cold worked alloy ε further increased to 20% after aging for 720 minutes, indicating recrystallisation had occurred. This was also evident in the trend observed for σ_y and hardness with aging time.

3.4. Conductivity

The measured conductivity values, Figs 9 and 10, show that cold working marginally decreased the conductivity. Scattering of conducting electrons by dislocations would be expected to lead to a reduction of the order of 1–3% IACS [9]. The magnitude of δ decrease from cold working recorded in the present work is in conformity with this prediction.

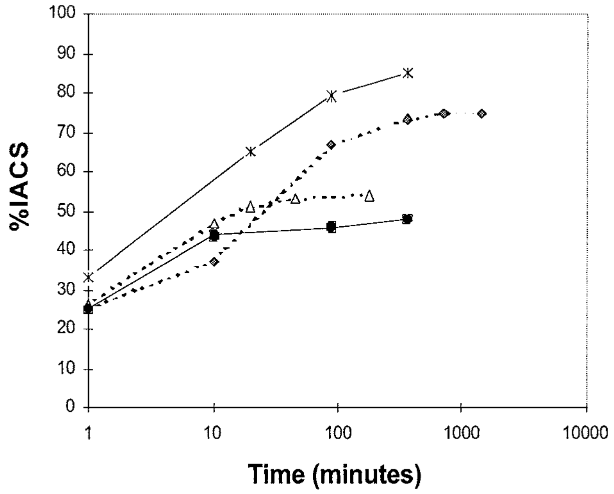

Figure 9 Plot of conductivity (% IACS) versus aging time for 40% CW alloys at the optimum aging temperatures, symbols as for Fig. 1.

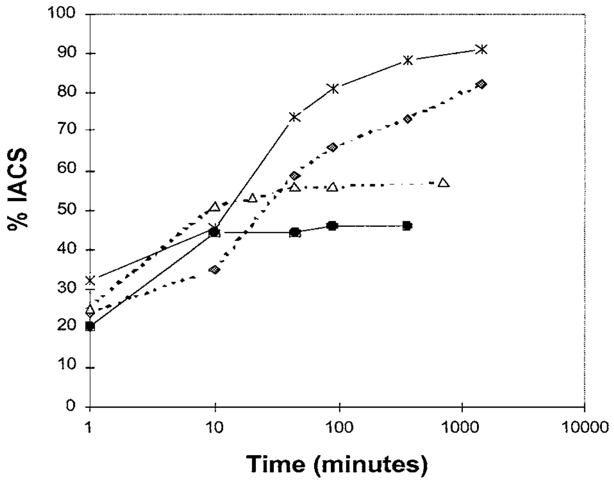

Figure 10 Plot of conductivity (% IACS) versus aging time for 90% CW alloys at the optimum aging temperatures, symbols as for Fig. 1.

For Alloy A, CW had only a small effect upon the plot of % IACS vs aging time. The lower aging temperature (450°C) used for the cold worked alloys caused a slower rate of increase in conductivity due to slower precipitation kinetics. This apparently overrides any increase in precipitation kinetics due to cold working. Similar behaviour was observed for Alloy Z. The lower δ of the 90% cold worked Alloy A in comparison to the 40% cold worked alloy for aging times up to 90 minutes was attributed to the higher dislocation densities. After aging for 360 minutes the δ of the 40 and 90% cold worked alloys were both 73% IACS, indicating that the dislocation density in the 90% cold worked alloy had decreased. After aging for 1440 minutes, the conductivities of specimens with 90% CW, 40% CW and solution treated, were respectively, 82, 75 and 78% IACS. Aging cold worked specimens at 450°C was expected to have resulted in a higher δ due to a lower concentration of solute atoms, compared to aging at 500°C. The low δ of the 40% cold worked alloy indicated that recrystallisation had not occurred. This result is supported by aging curves.

Figs 9 and 10 both show that the conductivity of Alloy A was less than that of Alloy Z for all aging times. This was the same result as reported for the solution treated alloy aged at 500°C. The δ of the cold worked Cu-1%Cr alloy agreed well with those quoted in Literature for similar alloys [8, 10]. The reason for the difference in δ between the two alloys was due to the 0.3 wt% Fe, a large part of which was thought to remain in solid solution after aging.

The plot of conductivity (δ) vs aging time for Alloy C was similar to all other alloys investigated, CW had only a small effect upon the δ.

3.5. Combination of mechanical properties and conductivity

The properties of the 40 and 90% CW Cu-0.7%Cr-0.3%Fe (Alloy A) and Cu-0.7%Cr-2%Fe (Alloy C) approached or were equivalent to those of other commercial CW high strength, high conductivity copper alloys currently in service.

Table IV summarises the effect of cold work prior to aging upon the peak aged properties of Alloy A. It is evident that CW significantly improved the peak aged mechanical properties of Alloy A. The effect of cold working upon the peak aged σ_{UTS} was most significant. It is clear that the increased strength was accompanied by a decreased δ in the peak aged condition. Aging the cold worked alloys for longer than 90 minutes improved the δ to 73% IACS with only a minor reduction to the mechanical properties due to overaging. A comparison of the properties of the peak aged Alloy A to those of the Cu-1%Cr (Alloy Z) can be made with reference to Table V. Comparison of the peak aged properties of Alloy Z to those of Alloy A showed that in all cold worked conditions, the mechanical properties of Alloy Z were marginally superior to those of the Alloy A. The electrical δ of the peak aged Alloy Z was considerably higher than that of the Alloy A, this difference decreases with further aging. The mechanical and electrical properties recorded for Alloy Z in all conditions agreed well with those reported in literature. This indicated that the testing techniques used were accurate and that the values recorded for the Cu-Fe-Cr alloys were

TABLE IV Properties of peak aged Cu-0.7%Cr-0.3%Fe

Property	Solution treated + aged 500°C 180 min	40% CW + aged 450°C 90 min	90% CW + aged 450°C 90 min
σ_y (MPa)	288	377	467
σ_{uts} (MPa)	340	460	537
Hardness (HV)	148	165	171
Cond (% IACS)	74	67	66

TABLE V Properties of peak aged Alloy Z Cu-1.0%Cr

Property	Solution treated + aged 500°C 45 min	40% CW + aged 450°C 90 min	90% CW + aged 450°C 90 min
σ_y (MPa)	325	386	497
σ_{uts} (MPa)	365	460	583
Hardness (HV)	165	184	184
Cond (% IACS)	81	78.5	80.5

TABLE VI Properties of peak aged Cu-0.7%Cr-2.0%Fe

Property	Solution treated + aged 600°C 45 min	40% CW + aged 600°C 45 min	90% CW + aged 600°C 45 min
σ_y (MPa)	135	258	322
σ_{uts} (MPa)	268	316	391
Hardness (HV)	75	112	118
Cond (% IACS)	53	52.5	55.5

correct. The lower strength and lower δ of Alloy A was the result of the 0.3 wt% Fe.

For Alloy C, Table VI summarises typical properties. Peak mechanical properties were recorded in the cold worked condition, for the 90% cold worked alloy. However in this condition δ was at a minimum. Aging at 600°C for 10 minutes caused some loss of mechanical properties for both cold worked alloys after which further aging had little effect upon the properties. Extended aging did result in some additional softening in the 90% cold worked alloy. Conductivity (δ) increased rapidly with aging at 600°C and was found to be almost at equilibrium after only 20 minutes, 51% IACS–40% cold worked, 53% IACS–90% cold worked. Continued aging caused further slight improvements. The optimum aging times for cold worked Alloy C were a compromise between strength and δ.

From Table VI it was apparent that Alloy C was dependant upon CW for strengthening. The mechanical and electrical properties were inferior to those of Alloy A and Alloy Z, however this alloy was able to retain its mechanical properties in the cold worked condition after extended exposure at 600°C. Isochronal aging curves for the 40 and 90% cold worked alloy showed that at elevated temperatures Alloy C is better able to retain its mechanical properties. The low δ of this alloy is partly a result of the high aging temperature, by aging at 500°C a δ of 62% IACS was produced for the solution treated alloy. It is thought that better combinations of mechanical and electrical properties would result if the alloy was aged at a lower temperature (∼450°C) to produce a higher δ and then cold worked.

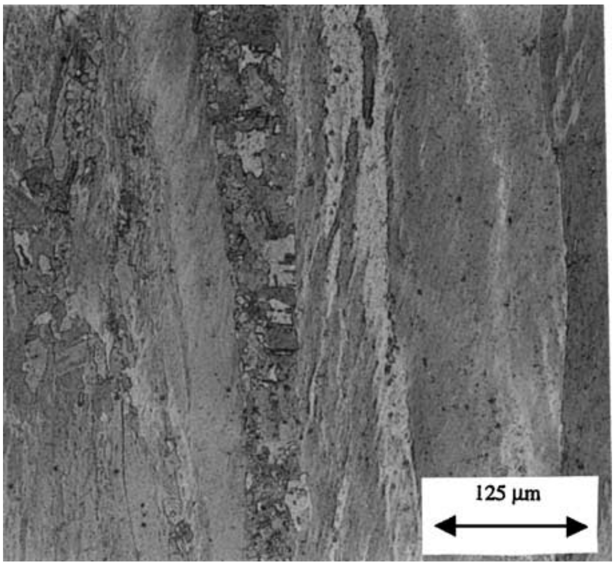

Figure 11 Optical micrograph of 40%CW Cu-0.7%Cr-0.3%Fe aged for 1 hour at 550°C showing some recrystallised grains. Etched ferric chloride.

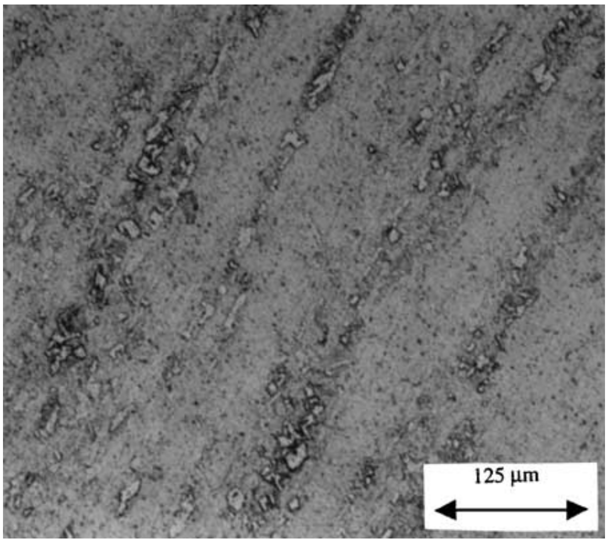

Figure 12 Optical micrograph of 40%CW Cu-0.7%Cr-2.0%Fe alloy aged at 800°C for 1 hour showing some recrystallised grains. Etched ferric chloride.

3.6. Recrystallisation temperature

For the 40% cold worked Alloy A, recrystallisation was first observed in the sample aged at 550°C for 1 hour as shown in Fig. 11. New grains had nucleated within the original cold worked grains. At higher aging temperatures, the amount of recrystallisation increased, however, even after aging at 700°C for 1 hour, recrystallisation was still not complete.

For 90%CW Alloy A, recrystallisation was first seen in the specimen aged at 550°C for 1 hour. At aging temperatures higher than 550°C, the amount of recrystallisation in the 90%CW specimens was significantly higher than that in the 40%CW specimens. This was due to the higher driving force for recrystallisation in the 90%CW alloy. For the 90%CW specimen aged at 700°C for 1 hour, recrystallisation was almost complete.

The temperatures at which recrystallisation occurred in CW samples of Alloy C were significantly higher than those of the equivalent Alloy A samples. For 40%CW Alloy C, the only evidence of recrystallisation was observed in the specimen aged at 800°C for 1 hour. Only slight recrystallisation had occurred in this specimen as shown in Fig. 12. This supported the isochronal aging results which showed the 40%CW alloy to be very resistant to softening at elevated temperatures up to 800°C. 90%CW Alloy C was not as resistant to recrystallisation. This was as expected based upon the aging curves of the cold worked alloys. Recrystallisation was first observed in the specimen aged at 650°C for 1 hour. After aging at 750°C recrystallisation was almost complete; after aging at 800°C no evidence of the original grain structure remained.

The temperature at which recrystallisation was first observed, in the present work, after 1 hour exposure for cold worked alloy A and alloy C are summarized in Table VII.

TABLE VII Temperature at which recrystallisation was first observed after 1 hour exposure for 40 and 90% CW Cu-0.7%Cr-0.3%Fe and Cu-0.7%Cr-2.0%Fe alloys

Condition	Cu-0.7%Cr-0.3%Fe (Alloy A)	Cu-0.7%Cr-2.0%Fe (Alloy C)
40% Cold worked	550°C	800°C
90% Cold worked	550°C	650°C

3.7. Differential scanning calorimetry

Initial scans were carried out on 40 and 90% CW pure copper samples. Typical scans, eg Fig. 13, showed that recrystallisation could be measured using DSC. Recrystallisation was typically observed to begin at less than 200°C. This was in agreement with recrystallisation temperatures for pure copper quoted in literature [11].

Repeated scans on CW Alloys A and C, Fig. 14, showed no evidence of recrystallisation at temperatures of up to 550°C. These results supported observations made during the optical investigation of the cold worked microstructures.

3.8. Alloys peak aged then cold worked (PA + CW)

3.8.1. Hardness

The results of hardness tests, Table VIII, shows that the peak hardness of Alloy A was higher when CW + PA

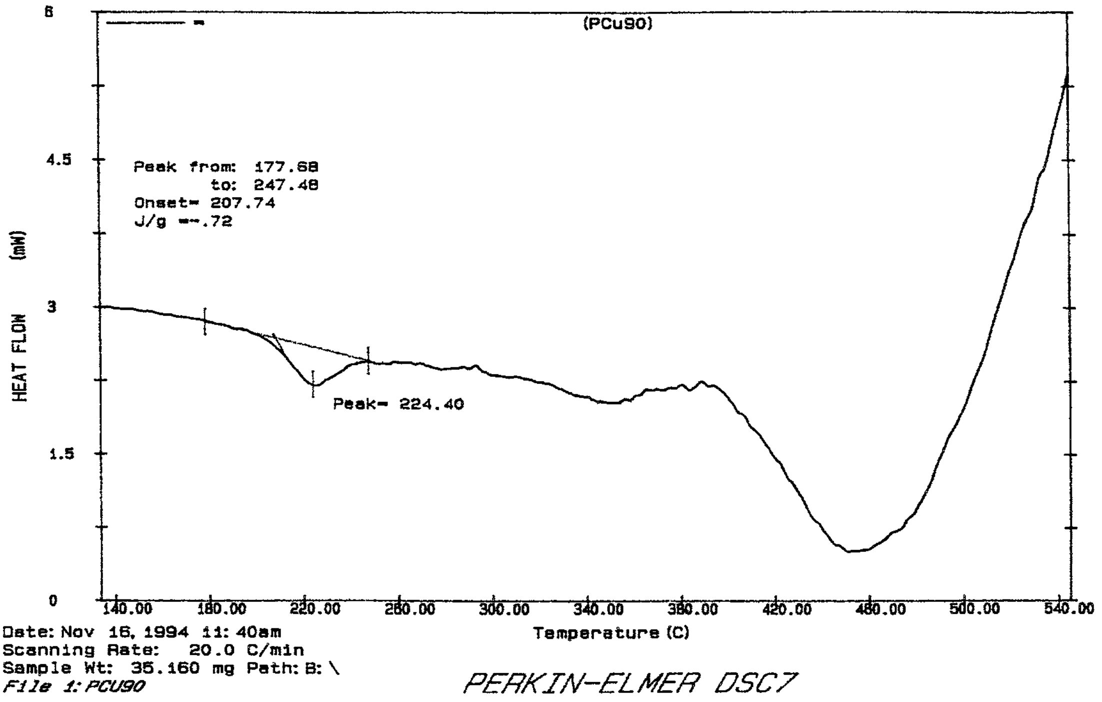

Figure 13 DSC scan of 90% CW pure Cu. Recrystallisation peak can be seen at 224°C.

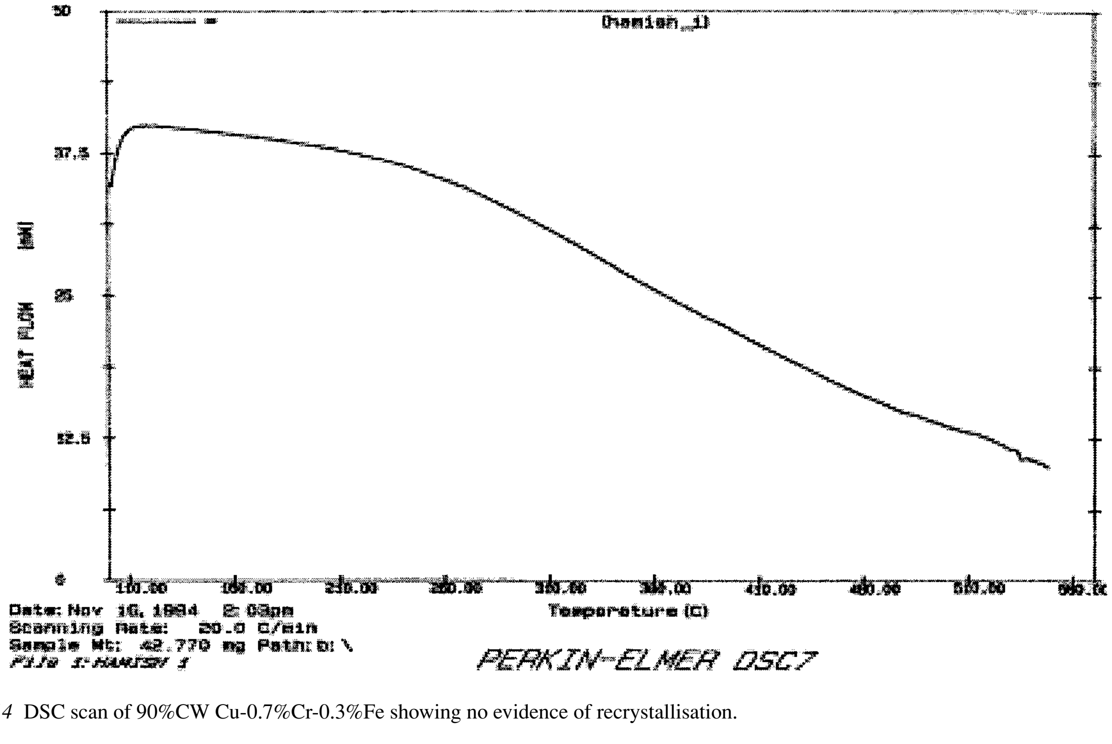

Figure 14 DSC scan of 90%CW Cu-0.7%Cr-0.3%Fe showing no evidence of recrystallisation.

TABLE VIII Hardness values

	Cu-0.7%Cr-0.3%Fe (Alloy A)		Cu-0.7%Cr-2.0%Fe (Alloy C)	
Condition	40% CW	90% CW	40% CW	90% CW
PA + CW	156	159	129	144
CW + PA	171	171	112	118

TABLE IX Ultimate tensile stress (MPa) for conditions listed in Table I

	Cu-0.7%Cr-0.3%Fe (Alloy A)		Cu-0.7%Cr-2.0%Fe (Alloy C)	
Condition	40% CW	90% CW	40% CW	90% CW
PA + CW	448	546	374	484
CW + PA	447[a]	537	316	390

[a] Aged for 90 minutes not 360 minutes.

TABLE X 0.5% yield stress (MPa) for conditions listed in Table I

	Cu-0.7%Cr-0.3%Fe (Alloy A)		Cu-0.7%Cr-2.0%Fe (Alloy C)	
Condition	40% CW	90% CW	40% CW	90% CW
PA + CW	404	474	356	420
CW + PA	377[a]	467	258	322

[a] Aged for 90 minutes not 360 minutes.

rather than PA + CW. An explanation for this was that CW prior to aging resulted in more precipitates being nucleated causing a finer distribution of precipitates in the peak aged condition and therefore an increased age hardening response. This was supported by σ_{UTS} and σ_{y} measurements which showed very little difference between PA + CW or CW + PA. For Alloy C in which the age hardening response was minimal the hardness after PA + CW was considerably higher than when CW + PA.

3.8.2. Tensile properties

Table IX presents the σ_{UTS} values. For Alloy C the σ_{UTS} after PA + CW was markedly higher than the equivalent CW + PA alloys. For Alloy A, σ_{UTS} for PA + CW and CW + PA alloys were very similar. The σ_{y} of Alloy A and Alloy C in the PA + CW and CW + PA conditions are given in Table X. For both alloys, σ_{y} was higher for PA + CW. This was as expected since no recovery, which would reduce the amount of stress within the crystal lattice, could have occurred. This is reflected in the low strain (ε) where peak strength occurs and at fracture. For Alloy C, σ_{y} for PA + CW was ~100 MPa higher than for CW + PA. In contrast the increase in σ_{y} of Alloy A was small.

The ε at the σ_{UTS} of Alloy A and Alloy C in the PA + CW and CW + PA conditions are presented in Table XI. The ε at the σ_{UTS} was low for alloys PA + CW. This was as expected since little additional work hardening of these alloys could occur. For both alloys when CW + PA, the ε at the σ_{UTS} was significantly higher. Optical microscopy was necessary to determine whether this was the result of recovery alone or recrystallisation as well. For Alloy A, 40% CW + PA, the 1.7% strain at the σ_{UTS} was markedly lower than the other CW + PA alloys. This was attributed to the combination of low aging temperature (450°C) and 40% CW providing little driving force for recrystallisation and/or recovery.

TABLE XI Strain (%) at the σ_{UTS} for conditions listed in Table I

	Cu-0.7%Cr-0.3%Fe		Cu-0.7%Cr-2.0%Fe	
Condition	40% CW	90% CW	40% CW	90% CW
PA + CW	0.9	1	1.1	0.9
CW + PA	1.7[a]	9	11	11

[a] Aged for 90 minutes not 360 minutes.

TABLE XII Conductivity (% IACS) for conditions listed in Table I

	Cu-0.7%Cr-0.3%Fe (Alloy A)		Cu-0.7%Cr-2.0%Fe (Alloy C)	
Condition	40% CW	90% CW	40% CW	90% CW
PA + CW	74	66	61	57
CW + PA	73	66	53	56

3.8.3. Electrical conductivity

Table XII shows that, for Alloy A it was apparent that the sequence of CW and PA had little or no effect on δ in the PA condition. For Alloy C, δ was considerably higher for PA + CW. This was attributed to the lower aging temperature (ie. 500°C as opposed to 600°C). When Alloy C was CW + PA, δ of the 90%CW alloy was 3% IACS higher than that of the 40%CW alloy. This was attributed to recrystallisation having occurred in the 90%CW alloy. When the alloy was PA + CW, δ of the 90%CW alloy was lower than the 40%CW alloy indicating that the CW microstructure has been retained. For both alloys, higher conductivity could have been achieved by aging at lower temperatures ie. 450°C. However, the amount of time required to reach peak hardness becomes excessive which would make the cost prohibitive in commercial practice.

3.8.4. Resistance to softening

The softening resistance of Alloy A and Alloy C after PA + CW was determined using hardness blocks that were aged at 50°C intervals from 400 to 800°C for 1 hour, Figs 15 and 16. The softening resistance of both alloys was extremely high. The half softening temperature was greater than 700°C for both alloys after both 40 and 90% CW.

For the 40 and 90%CW Alloy A, the average hardness fell less than 15 HV from that in the peak aged cold worked condition after 1 hour at 550°C. Aging at higher temperatures caused hardness to fall more rapidly. This was more pronounced for the 90%CW alloy as expected. After aging at 600°C for 1 hour the hardness of the 40%CW alloy fell 26 HV from that in

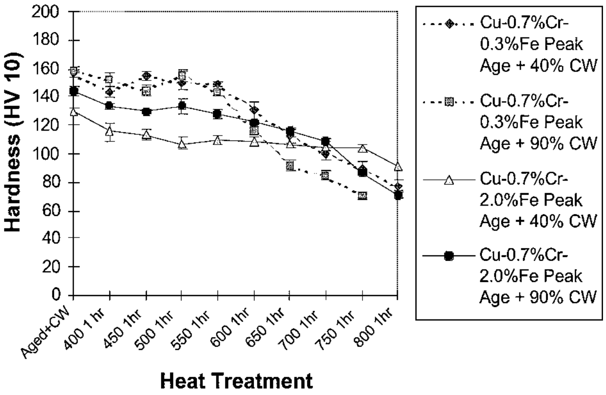

Figure 15 Softening curves for peak aged, 40 and 90% CW Cu-0.7%Cr-0.3%Fe and Cu-0.7%Cr-2.0%Fe alloys aged for 1 hour at 50°C intervals from 400 to 800°C.

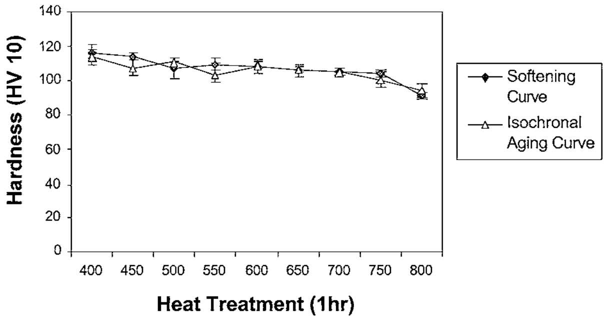

Figure 16 Softening curve and isochronal aging curve for 40% CW Cu-0.7%Cr-2.0%Fe (Alloy C). Specimens aged at 50°C intervals from 400 to 800°C.

the PA + CW condition, while for the 90%CW alloy hardness fell 42 HV. The shape of the plots indicated that aging at 600°C and above resulted in some recrystallisation and grain growth.

For Alloy C, the hardness after PA + CW was not as high as the equivalent Alloy A specimens. However, the amount of softening that occurred after exposure to high temperatures was less than that of Alloy A. After exposure to temperatures greater than 600°C the hardness of the 90%CW Alloy C exceeded that of both the 40 and 90%CW Alloy A. The hardness of the 90%CW alloy fell only 25 HV after 1 hour exposure at 700°C. The softening resistance of the 40%CW Alloy C was equivalent to the 90%CW alloy although hardness was lower. After exposure to temperatures greater than 700°C the hardness of the 40%CW alloy exceeded that of the 90%CW alloy.

4. Discussion

4.1. Mechanical properties

Investigation into the effect of cold work (CW) upon the properties was encouraged by literature on binary Cu-Fe alloys, which showed that these alloys are only ever used in the cold worked condition, where the function of the Fe precipitates is not to strengthen but to stabilise the cold worked microstructure [2]. After the investigation of the properties of the solution treated Cu-Fe-Cr alloys, the effect of cold work upon the properties of Alloy A and C was determined. The mechanical and electrical properties of Alloy A in the solution-treated and aged condition approached those of the Cu-1%Cr reference alloy, and consequently it was interesting to determine if these properties could be further improved with the aid of CW. The mechanical properties for Alloy C were stable after prolonged exposure to elevated temperatures, and consequently it was interesting to determine whether this translated into the precipitates being able to stabilise the cold worked microstructures at elevated temperatures. The effect of CW on the properties of the Cu-1%Fe and Cu-1%Cr alloys were also investigated for reference and comparison purposes.

In this section the discussion is limited to the effect of CW upon the properties of the alloys investigated and the interpretation of these results. The levels of CW investigated were 40 and 90%. The reasoning behind this selection was discussed previously. Results showed that the peak aged mechanical properties (HV, σ_y, σ_{UTS}) of Alloys A and C were significantly improved by cold working prior to aging. Similar results were shown by the two reference alloys. Plots of HV, σ_y & σ_{UTS} vs aging time for each of the alloys showed the same relationships between properties and aging time (ie. equivalent optimum aging times). Similarly, the aging curves illustrated how the driving force for recrystallisation increases as the percentage cold work increases. The σ_y of the peak aged Alloy A increased from 288 MPa for the unworked sample to 377 to 467 MPa respectively for the 40 and 90% CW. The increase in σ_y due to cold working was retained in the peak aged condition (90 minutes at 450°C) indicating that no recrystallisation had occurred. With extended aging time, the σ_y of the 90% CW alloy falls below that of the 40% CW alloy indicating recrystallisation has occurred. This was supported by results of the investigation into the recrystallisation temperature of Alloy A. Differences in yield stress for Alloy A were greatest in the solution treated condition. This is because no recovery had occurred in this condition. The plots of σ_y v age time for Alloy C showed the same results, however due to the small age hardening response in this alloy the highest σ_y occurred in the cold worked solution treated condition prior to aging.

Plots of conductivity (δ) versus aging time showed that the effect of CW upon the δ of Alloy A, Alloy C and the two reference alloys was to lower δ by ~1–3% IACS in all aged conditions prior to recrystallisation occurring. This is illustrated in Table VI where the increase in δ due to cold work on solution treated and peak aged samples of alloy C is presented. This supports literature results which indicate that CW is expected to contribute to a reduction of the magnitude of 1–3% IACS in the δ of precipitation hardened copper alloys in which the concentration of solute atoms is low [12]. The concentration of solute elements is low even in the solution treated condition based upon the results of resistivity testing. Results indicate that some precipitation had occurred during quenching of Alloy A and C and the actual concentration of alloying elements in solid solution was comparatively low, particularly for Alloy C (0.21 wt% Cr and 0.68 wt% Fe in solid solution).

The improved mechanical properties of the cold worked alloys (prior to any recrystallisation occurring) was not solely due to retained cold work strengthening. The higher σ_{UTS} and σ_{y} were also due to a refinement of the size of the precipitates in the peak aged condition. As reported in the literature [13], cold working prior to aging provides more sites for nucleation; this results in a finer dispersion of precipitates and therefore greater strengthening. Similar results are exhibited when alloys are aged at lower temperatures. The best proof of this is shown by figures which plot HV, σ_{UTS} and σ_{y} versus aging time for the Cu-1%Fe reference alloy. Plots show that recrystallisation occurred after very short aging times; however the σ_{UTS} and σ_{y} of the 90% CW alloy were higher than the 40% CW alloy which were higher than the solution treated and aged alloy for all aged conditions. The reason for this was attributed to be a refinement in the precipitate size.

As mentioned above, cold working prior to aging significantly increased the peak aged mechanical properties of each of the alloys except Alloy Y which recrystallised after very short aging times. Comparison of the peak aged cold worked properties of Alloy A (see Tables IV and V) show that cold working prior to aging did not improve the properties of Alloy A relative to Alloy Z. Isochronal and isothermal aging curves show that Alloy A was no more resistant to softening than Alloy Z. Based upon these results the 0.3 wt% Fe in Alloy A did not increase the resistance of the secondary precipitates to coarsening. CW prior to aging did not refine the size of the Fe-Cr secondary precipitates in the peak aged condition relative to those of Alloy Z. Comparison of the peak aged cold worked properties show that the conductivity (δ) of Alloy A decreased relative to that of Alloy Z as the amount of CW increased. The difference in peak aged conductivity, (δ) increased from 7 to 11.5 to 14.5% IACS as the percentage cold work increased, the actual peak aged δ of Alloy A fell from 74 to 67 to 66% IACS. The reason for this drop is attributed to a combination of slower precipitation kinetics in Alloy A relative to Alloy Z and the shorter aging times to reach peak aged mechanical properties of Alloy A when cold worked compared to when solution treated and aged. Plots of % IACS vs aging time for solution treated and aged alloys indicated that increasing Fe content decreases the rate of precipitation ie. decreases the precipitation kinetics. This is supported by the plots of % IACS v aging time for the 40 and 90% cold worked Alloy A and Alloy Z. Plots show that the δ of Alloy Z increases considerably quicker than that of Alloy A. Therefore if peak mechanical properties of CW Alloy A are being reached after shorter aging times compared to when solution treated and aged, then the concentration of alloying elements still in solid solution is higher relative to Alloy Z and the difference in δ is larger.

The effect of CW on the Cu-0.7%Cr-2.0%Fe alloy (Alloy C) was investigated to determine whether the temperature stability of this alloy in the solution treated condition translated into the alloy being able to retain strengthening due to cold working to elevated temperatures ie. prevent recrystallisation of the cold worked microstructure. The small age hardening response of this alloy has been discussed as has the lower electrical conductivity of this alloy in relation to Alloy A. Isochronal aging curves for 40 and 90% CW alloys are shown in Figs 1 and 2. Plots show that CW Alloy C is more resistant to recrystallisation than CW'ed Alloy A and Z. This is supported by the results of the investigation into the recrystallisation temperature of Alloy A & C, the results of which are shown in Table VII.

Isothermal aging curves of CW Alloy C also show that the alloy is resistant to recrystallisation at elevated temperatures. 600°C was chosen as the aging temperature to test the resistance of the alloy to softening. More softening was seen in the 90% CW alloy due to the higher driving force for recrystallisation.

The pinning effect of dispersed second phase particles on recrystallisation is usually considered in terms of the Zener-Smith drag term [14, 15]:

$$Z = 3f/2r \tag{1}$$

Where f is the volume fraction of precipitate and r is the precipitate radius. The equation assumes precipitates are spherical, of uniform size and evenly distributed. It provides a guide to the resistance to recrystallisation provided by a particular precipitate distribution, however this is a complex function dependant on a number of factors including the percentage cold work and precipitate morphology. Z has been calculated for each of the three Cu-Fe-Cr alloys in the peak aged condition using the same values of f and r as were used in the calculation of the Orowan-Ashby equation [1]. The Z parameters so determined are given in Table XIII.

The Z term obtained for Alloy B supports the decision not to investigate the cold work properties of this alloy. The value of the Z term suggests that the recrystallisation resistance of this alloy would have been very low based upon the precipitate volume fraction and size. In the peak aged condition the recrystallisation resistance of Alloy A and C are predicted to be equivalent. The higher volume fraction of precipitate in Alloy C compensates for the larger precipitate size. The lower recrystallisation temperature of Alloy A is attributed to faster coarsening kinetics of the secondary precipitates. As the precipitates coarsen, the Z term decreases (assuming the volume fraction of precipitate remains constant) meaning that the pinning effect of the precipitate decreases making it easier for recrystallisation to occur. Based upon the compositions of the secondary precipitates, the slower coarsening rate of precipitates in Alloy C is expected, ie. higher Fe content translates into slower coarsening kinetics. This is supported by the isochronal aging curves which show that the Cu-1%Fe

TABLE XIII Zener-Smith Drag terms calculated for the alloys in the peak aged condition

Alloy	Zener–Smith drag term, Z (nm)$^{-1}$
Cu-0.7%Cr-0.3%Fe (Alloy A)	177
Cu-0.7%Cr-0.8%Fe (Alloy B)	99
Cu-0.7%Cr-2.0%Fe (Alloy C)	174

TABLE XIV Comparative properties of 40%CW Cu-0.7%Cr-2.0%Fe alloy (Alloy C)

Property	Peak age + cold work	Cold work + peak age
HV	129	112
σ_{UTS} (MPa)	374	316
σ_{y} (MPa)	356	258
% Strain	1.1	11
% IACS	61	53

alloy required the highest aging temperature of the alloys investigated. It should be noted that the TEM investigation into the microstructure of Alloy A showed little coarsening of precipitates in the overaged condition. The reason for this is because specimens of Alloy A investigated in the TEM were aged at 500°C for 12 hours. A higher aging temperature or longer aging time is required for indisputable evidence of coarsening.

The properties of Cu-0.7%Cr-0.3%Fe (Alloy A) and Cu-0.7%Cr-2.0%Fe (Alloy C) were also investigated after being peak aged and then cold worked (PA + CW). A better combination of mechanical and electrical properties were expected because conductivity could be maximised prior to cold working and no loss of cold work strengthening would occur due to recovery or recrystallisation during aging. It was also expected that the softening resistance of alloys may be improved as a dispersion of secondary precipitates would be there from the start to stabilise the CW'ed structure. Results showed that the peak aged mechanical properties of Alloy A were not significantly improved with no change to the electrical conductivity. For Alloy C there were significant improvements in both peak aged mechanical and electrical properties. This is illustrated in Table XIV.

The reason for the improvement in mechanical properties for Alloy C and not for Alloy A was because Alloy C has a very small age hardening response and derives most of its strength through stabilisation of the cold worked microstructure. When solution treated and CW Alloy C is aged to increase conductivity, recovery within the CW microstructure occurs which lowers the peak aged mechanical properties as evidenced in the results. This is exacerbated by the higher isothermal aging temperatures required for Alloy C compared to Alloy A due to the higher Fe content of the secondary precipitates, ie. 600°C compared to 450°C. If the alloy is aged first to optimise the conductivity then all of the CW strengthening can be retained. The higher conductivity for Alloy C when aged then cold worked was due to the lower aging temperature used, 500°C as opposed to 600°C. For Alloy C, optimum combination of mechanical and electrical properties is obtained when peak aged and then cold worked, however ductility is significantly reduced.

The softening resistance of both Alloy A and Alloy C was high. Properties are discussed in regard to other commercial alloys in the following sections. Alloy A in both CW conditions started softening after exposure to 600°C for 1 hour. Alloy C was more resistant to softening with little softening after exposure to 700°C for 1 hour. Comparison of the softening curves of Alloys A and C (Fig. 15) to the isochronal aging curves of these Alloys in the 40 and 90% CW condition (Figs 1 and 2) show that the resistance to softening was comparable for both processing routes. This is illustrated in Fig. 16 for 40%CW Cu-0.7%Cr-2.0%Fe (Alloy C).

Direct comparison of the two sets of data is not strictly appropriate as the isochronal aging curves were generated from samples in the CW solution treated condition as opposed to samples CW and peak aged. However results from isochronal aging curves give a reasonable indication of the softening resistance of the alloys when CW then aged, particularly at elevated temperatures. For Alloy A at temperatures less than 450°C the hardness of isochronal samples of Alloy A were lower than those of specimens peak aged then CW because the precipitates in these samples were underaged. For Alloy C, hardness was comparable for all aging temperatures. There was no improvement in the softening resistance of cold worked Alloys A and C when cold worked after peak aging. The reason for this could be attributed to two reasons:

1. Precipitation occurs during quenching of these alloys, meaning some precipitates are present in the solution treated condition.
2. Precipitation occurs very rapidly during aging as evidenced by the plots of aging time v conductivity (Figs 9 and 10).

For the reasons given above there is no net benefit gained by having the precipitates present to stabilise the cold worked microstructure prior to aging.

Results showed that cold working prior to aging significantly improves the mechanical properties of Alloy A and Alloy C. Alloy Z showed similar results; however Alloy Y lost all cold work strengthening due recrystallisation after very short aging times. The mechanical and electrical properties of cold worked Alloy A were only slightly lower than those of cold worked Cu-1%Cr alloy (ie. Alloy Z) and the resistance to softening (ie. recrystallisation) was comparable. Mechanical and electrical properties of cold worked Alloy C were inferior to Alloy A. However, the resistance to recrystallisation of Alloy C at elevated temperatures was higher than that of Alloy A. The reason for this was attributed to the slower coarsening kinetics of the Fe rich secondary precipitates in Alloy C. Comparison of the optimum combination of electrical and mechanical properties attainable when Alloy A and Alloy C were cold worked either before or after aging, showed that equivalent properties were obtained for Alloy A using both processing routes, however for Alloy C a better combination of mechanical and electrical properties were obtained when aged before cold working. The reason for this was that Alloy C unlike Alloy A derived most of its strengthening through the stabilisation of the cold worked microstructure.

4.2. Comparison with existing commercial alloys

Unlike the Cu-0.7%Cr-0.3%Fe alloy the properties of the Cu-0.7%Cr-2.0%Fe alloy can not be directly compared to a reference alloy whose properties were

TABLE XV Optimum combination of mechanical and electrical properties of peak aged then 40 and 90% CW Cu-0.7%Cr-2.0%Fe alloy. The properties of some commercial Cu-Fe alloys in equivalent tempers (based upon elongation) are listed for comparison

UNS no.	Comp (wt%)	σ_y (MPa)*	σ_{UTS} (MPa)	Elong %	Cond (% IACS)
–	Cu-0.7%Cr-2.0%Fe	356	374	1.1	61
–	Cu-0.7%Cr-2.0%Fe	420	484	0.9	57
C19200	Cu-1%Fe-0.03%P	480	490	2	60
C19400	Cu-2.35%Fe-0.03%P-0.12%Zn	507	530	2	65
C19500	Cu-1.5%Fe-0.1%P-0.8%Co-0.6%Sn	650	670	2	50
C19700	Cu-0.6%Fe-0.2%P-0.05%Mg	490	500	2	80

Note that σ_y listed for Cu-0.7%Cr-2.0%Fe alloy is 0.5%σ_y while for other alloys it is the 0.2%σ_y.

investigated during the course of this thesis. The reason is that the Cu-1%Fe binary alloy did not contain trace additions of P, so its properties were not equivalent to those of commercial HSHC wrought Cu-Fe binary alloys. The age hardening response of the solution treated Cu-0.7%Cr-2.0%Fe alloy was low, however it was thought that the large volume fraction of precipitate and high Fe content may translate into a high recrystallisation temperature in the cold worked condition. It was hoped that the Cu-0.7%Cr-2.0%Fe alloy could compete with commercial Cu-Fe-P and Cu-Fe-P-X alloys which are used for applications which require excellent formability and high softening temperatures coupled with high strength and electrical conductivity [16].

The mechanical and electrical properties of cold worked Cu-0.7%Cr-2.0%Fe alloy and those of other commercial Cu-Fe alloys containing trace additions of P are shown in Table XV. Properties listed for commercial Cu-Fe alloys come from the [5]. The combination of mechanical and electrical properties of the Cu-0.7%Cr-2.0%Fe alloy (Alloy C) were not as high as those reported for Cu-Fe-P alloys that had received equivalent thermo-mechanical treatments. Equivalent results were seen for all thermo-mechanical treatments investigated. The electrical conductivity of Alloy C was lower than the values reported for comparable HSHC Cu-Fe-P alloys with equivalent mechanical properties. The reason for the lower conductivity of Alloy C is that Alloy C does not contain any trace additions of P which form Fe_2P compounds [7] and reduce the concentration of Fe in solid solution. Additions of P to the Cu-0.7%Cr-0.3%Fe alloy were found to preferentially form intermetallics with Cr which decreased the peak aged mechanical properties and did not improve the electrical conductivity.

High recrystallisation temperatures were recorded for the Cu-0.7%Cr-2.0%Fe alloy. For samples solution treated, cold worked then aged, the first evidence of recrystallisation after 1 hours aging was seen in samples aged at 800°C when 40% cold worked and 650°C when 90% cold worked. Recrystallisation temperatures of the commercial HSHC Cu-Fe-P alloys are not published in the Metals Handbook [5] due to the recrystallisation temperature being a function of the amount of cold work received and the time of exposure. Similarly, recrystallisation temperatures are not widely published in literature, for the Cu-2.4%Fe-0.03%P-0.12%Zn alloy (UNS no. 19400); Awata and Futasuka [2] reported that the recrystallisation temperature was between 350 and 500°C depending upon the temper. This is significantly less than the recrystallisation temperatures measured for the Cu-0.7%Cr-2.0%Fe alloy.

The softening resistance of the Cu-0.7%Cr-2.0%Fe alloy was measured after the alloy had been peak aged then cold worked by 40 and 90%. Results show that very little softening occurred after aging at 700°C for 1 hour for the 90% cold worked alloy and 750°C for the 40% cold worked alloy. These softening temperatures are higher than those reported for commercial Cu-Fe-P alloys in the literature. Watanabe [17] reported half softening temperatures of 475 and 450°C for C19400 and C19500 alloys (composition are given in Table XV) when in hard temper. Hard temper is equivalent to ~40% cold work (Metals Handbook [5]). The softening temperatures of the Cu-0.7%Cr-2.0%Fe alloys are in excess of the 600°C softening temperature reported by Yamaguchi and Yamasaki [18, 19] for Cu-0.69%Fe-0.36%Ti-0.06%Mg alloy, which they claim to have the highest resistance to softening among comparable HSHC Cu-Fe alloys. It should be noted that the electrical and mechanical properties of this alloy are higher than those recorded for Alloy C.

Based upon these results it is apparent that although the combination of mechanical and electrical properties of the Cu-0.7%Cr-2.0%Fe alloy are not as high as those of existing commercial HSHC Cu-Fe-P alloys, the resistance to softening and recrystallisation at elevated temperatures is superior. This is attributed to the large volume fraction of Fe-Cr precipitates which are resistant to coarsening at elevated temperatures. It is thought that there would be numerous applications for which Cu-Fe-P alloys are currently used which could take advantage of the increased resistance to softening at elevated temperatures provided by this alloy. Such applications would include those where there is significant risk of exposure to elevated temperatures such as heat exchangers, electrical connectors and electrical terminals. In addition Cu-0.7%Cr-2.0%Fe alloy would be no more expensive to produce than other commercial Cu-Fe-P alloys as the Cr additions could be made using ferro-chrome which by weight is less expensive than copper.

Comparison of the properties of Alloys C to those of commercial HSHC Cu alloys has shown that there is potential for this alloy to find commercial applications. The alloy is a possible alternative to UNS No. alloys C19400 and C19500 both of which are used for applications requiring high strength and high electrical conductivity coupled with excellent softening resistance.

5. Conclusions

The aim of this project was to investigate the properties of copper rich Cu-Fe-Cr alloys for the purpose of developing a new cost effective, high strength, high conductivity copper alloy. Three alloys were initially selected for the investigation: Cu-0.7%Cr-(0.3, 0.8 and 2.0) %Fe. Two of these alloys have been shown to display unique sets of properties that could make them suitable for a range of commercial applications. The alloy containing 0,3%Fe was discussed in the prior paper [1].

The age hardening response of the Cu-0.7%Cr-2.0%Fe alloy was minimal, but the resistance to softening in the wrought condition was superior to that reported in literature for any other commercial high strength, high conductivity copper alloy with comparable mechanical and electrical properties. For example, an excess of 85% of the original hardness of the 40% cold worked alloy is retained after holding at 700°C for 1 hour, whereas commercial HSHC Cu-Fe-P alloys have been reported to soften significantly after 1 hours exposure at less than 500°C. The Cu-0.7Cr-2.0Fe alloy would therefore be expected to be more suitable for applications with a significant risk of exposure to elevated temperatures.

Optical microscopy showed that the microstructure was dendritic surrounded by a rod-like eutectic. The as-cast grain size was in excess of 70 μm in all samples, the Hall-Petch equation indicated that the increase in yield stress that could be expected for this grain size was of the order of 16 MPa. Examination of cold worked and artificially aged microstructures confirmed that the Cu-0.7%Cr-2.0%Fe alloy was more resistant to recrystallisation than the Cu-0.7%Cr-0.3%Fe alloy. The Cu-0.7%Cr-0.3%Fe alloy, cold worked to both 40% and 90% reduction, showed the first evidence of recrystallisation after aging at 550°C for 1 hour. No evidence of recrystallisation was observed in the Cu-0.7%Cr-2.0%Fe alloy, for 1 hour treatments, until a temperature of 650°C for the 90% cold worked condition and 800°C for the 40%.

The Zener-Smith drag term, predicting the pinning effect of second phase particles on dislocations in cold worked microstructures, was calculated using the precipitate characteristics obtained from TEM, WDS and resistivity measurements [1]. The pinning effect of the precipitate dispersions in the peak-aged condition was determined to be essentially equivalent for the Cu-0.7%Cr-0.3%Fe and Cu-0.7%Cr-2.0%Fe alloys. A lower recrystallisation temperature in the Cu-0.7%Cr-0.3%Fe alloy was therefore attributed to faster coarsening kinetics of the secondary precipitates resulting from a higher Cr concentration in the precipitates at lower iron content. The interparticle distance was calculated for all alloys in the peak-aged condition and was found to always be larger than 75 nm, well above the mean free path of electrons in copper (42 nm). The precipitates therefore do not significantly effect the electrical conductivity of any of the alloys investigated. The decrease in conductivity of the peak-aged alloys with increased Fe content was found to be caused by an increase in the concentration of Fe in solid solution after ageing.

It is clear that the properties of the Cu-0.7%Cr-2.0%Fe alloy warrant further investigation. More detailed analysis of the optimum aging temperatures and times is required. Similarly further work is recommended in order to determine the optimum cold reduction prior to aging.

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