

Quaternary Cu-0.7%Cr-0.3%Fe-X alloys

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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 aim of the present work was to increase the electrical conductivity and strength of the Cu-0.7wt%Cr-0.3wt%Fe alloy through selective minor additions (≤ 0.15 wt%) of elements expected to promote precipitation of dissolved Fe: Ti, B, P, Ni & Y. Such quaternary alloys with reduced Fe in solid solution would be expected to have properties equivalent to or better than those of the Cu-1%Cr reference alloy (Alloy Z). The investigation showed that none of the trace element additions significantly improved the size of the age hardening response or the peak aged electrical conductivity of Alloy A, although further work is required on the influence of Ti. Additions of P and B were detrimental. Other trace additions had little or no effect apart from causing some slight changes to the precipitation kinetics. The mechanical properties of the Cu-0.7%Cr-0.3%Fe alloy made with less expensive high carbon ferrochrome were found to be inferior to those of the equivalent alloy made with low carbon ferrochrome.

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1. Introduction

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, i.e. 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. Our first paper [1] reported 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.

Our second paper [2] reported on the microstructural characterisation of these alloys and discussed the mechanical and electrical properties of these alloys in terms of their microstructure, particularly the formation of precipitates. These alloys have evinced properties that warrant further investigation. Cost modelling has shown that Cu-0.7wt%Cr-0.3wt%Fe is approximately 25% cheaper to produce than commercial Cu-1%Cr. It has also been shown to be more cost efficient on a yield stress and % IACS per dollar basis. The reason for the cost saving is that the Cu-0.7%Cr-0.3%Fe alloy can be made with low carbon ferro-chrome additions as the source of chromium rather than the more expensive Cu-Cr master-alloy. For applications in which cost is one of the primary materials selection criteria, it is envisaged that there would be numerous applications in both cast and wrought form, where the Cu-0.7%Cr-0.3%Fe alloy would be more suitable than Cu-1%Cr.

Our third paper [3] showed that 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 in literature 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 was 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.

Our fourth paper [4] reported on the determination of the copper rich corner of the ternary Cu-Fe-Cr phase diagram using wavelength dispersive spectroscopy and resistivity measurements.

The aim of the present work was to investigate increasing the electrical conductivity and strength of the Cu-0.7wt%Cr-0.3wt%Fe alloy (Alloy A) through selective minor additions (≤ 0.15 wt%) of elements expected to promote precipitation of dissolved Fe. Such quaternary alloys with reduced Fe in solid solution would be expected to have properties equivalent to or better than those of the Cu-1%Cr reference alloy (Alloy Z).

Simple binary Cu-Fe alloys are rarely used in commercial practice. The reason for this being: (1) the slow kinetics of the precipitation reaction in the binary alloy; and (2) the difficulties in subsequent processing caused by alpha iron formed during solidification (Willet [5]). Ternary Cu-Fe alloys are used which contain trace additions of P (~ 0.03 wt%). The addition of P causes the formation of Fe₂P intermetallic precipitates which produces an increased precipitation hardening effect and also results in increased conductivity (δ) through a reduction in the solid solubility of Fe [6]. Awata *et al.* [7] and Murakami *et al.* [8] have investigated trace element additions to improve both the mechanical and electrical properties of high strength, high conductivity (HSHC) Cu-Fe alloys. Ohashi *et al.* [9] has patented a number of Cu-Fe-P-X alloys in which trace additions (< 0.1 wt%) of Si, B, and Ni are reported to form intermetallics with Fe which lead to increases in δ of $\sim 7\%$ IACS. The age hardening response of binary Cu-Fe alloys is essentially non-existent as seen from the results presented in [1] and in the literature [10]. Ternary alloy additions such as Ti, Co and Si have been shown to allow considerable increases in the strength of binary Cu-Fe through intermetallic formation without having any negative effect upon the δ [11, 12]. Ti additions to Cu-Fe alloys allow the formation of Fe₂Ti intermetallic precipitates, the resultant mechanical properties are equivalent to Cu-1%Cr alloys [13].

The mechanical and electrical properties of Cu-0.7%Cr-0.3%Fe alloy (Alloy A) were found [1] to approach those of the reference Cu-1%Cr alloy (Alloy Z).

The characterisation [2] of the Cu-Fe-Cr alloys showed that Alloy A had a conductivity (δ) lower than Alloy Z because of the 0.3 wt% Fe in Alloy A, some of which remained in solid solution after aging. A research strategy was therefore formulated to seek a trace element addition that would reduce the amount of Fe that remained in solid solution through intermetallic formation and as a result increase the δ in the peak aged condition. Microstructural characterisation of the Cu-Fe-Cr alloys had indicated that both the primary and secondary precipitates contained both Fe and Cr which resulted in strength values slightly lower than those of the Cu-1%Cr alloy, as discussed previously [1, 2]. If Fe were to form intermetallics with trace element additions, secondary precipitates could contain less Fe and more Cr which could result in improved strength. In addition it was possible that any Fe intermetallics formed could further improve the mechanical properties of the alloys. The quaternary alloying additions were chosen based upon literature and an examination of the relevant phase diagrams [14], as discussed in the following section.

Results of the investigation into the properties of alloys containing trace quaternary alloying additions showed that the δ and age hardening response of the alloy containing 0.13 wt% Ti were equivalent to those of the reference Cu-0.7%Cr-0.3%Fe alloy. This was attributed to the Ti additions forming intermetallics, as a decrease in δ would otherwise be expected if Ti additions remained in solid solution after aging. Cold worked high strength, high conductivity Cu-Fe-Ti alloys have been reported [8] to have a softening temperature in excess of 600°C, i.e. higher than any other HSHC copper alloy. In addition, work by Yamaguchi and Yamasaki [13] indicated that the δ of HSHC Cu-Fe-Ti alloys in the peak aged condition was greatly increased when cold worked prior to aging. As a result, investigation was also made of the age hardening response and electrical properties of solution treated Cu-0.7%Cr-0.3%Fe-0.13%Ti alloy, which had been 40 and 90% cold worked prior to aging.

1.1. Selection of quaternary alloying elements

Examination of phase diagrams revealed a number of alloying elements also had the potential to form intermetallic phases with Cr. Whether these elements would preferentially form intermetallics with Cr or Fe while in a copper matrix could only be determined experimentally. The weight percent of trace element addition selected where this could be the case was based upon the assumption that the alloying elements would preferentially form intermetallics with Fe and not Cr. There was also the possibility that any Cr intermetallics formed may also improve the properties of the Alloy A. The trace alloying additions selected are shown in Table I.

Titanium was chosen based upon literature which showed that the addition of Ti to Cu-Fe alloys allowed the formation of Fe₂Ti precipitates which resulted in a precipitation hardening response greater than that of Cu-Fe. Yamaguchi and Yamasaki [13] reported that for maximum δ , the optimum Fe/Ti ratio by weight was

TABLE I Trace alloying additions added to the Cu-0.7%Cr-0.3%Fe alloy

Alloying element	Weight percent (wt%)
Titanium (Ti)	0.05
"	0.13
Phosphorus (P)	0.055
"	0.083
Boron (B)	0.03
"	0.05
Nickel (Ni)	0.02
"	0.05
Yttrium (Y)	0.02
"	0.05
Ti + Y	0.15 + 0.02
P + Y	0.083 + 0.02

2.33. This suggested a Ti level of 0.13 wt% for Alloy A which contained 0.3 wt% Fe. A lower Ti content of 0.05 wt% was also studied. For both Ti additions there would be an excess of Fe in solid solution if Fe₂Ti precipitates are formed. An excess of Fe was chosen because Ti additions in solid solution decrease the δ of Cu more than an equivalent concentration of Fe [15].

Phosphorus was chosen because the addition of P to Cu-Fe alloys allows the formation of Fe₂P precipitates [5]. Based upon the stoichiometric ratio of Fe₂P and the atomic weights of Fe and P, 0.083 wt% P is required for the 0.3 wt% Fe in Alloy A. The results of Stanley [16] shows that excess P in solid solution decreases δ more than Fe. Therefore 0.055 wt% P was also selected in order to ensure no P remained in solid solution after aging. The Fe-P phase diagram [14] shows that in addition to Fe₂P intermetallics it was also possible to form Fe₃P intermetallics, although based upon the temperature stability of this phase it was not thought that these precipitates were as likely to form as Fe₂P. In addition they had not been reported in literature. 0.055 wt% P was stoichiometrically correct if Fe₃P precipitate did form instead of Fe₂P.

Boron was selected because of the existence of the two stable intermetallics phases: FeB and Fe₂B. Ohashi [9] detected iron boron intermetallics when B was added to HSHC Cu-Fe-P alloy, the composition of the intermetallics formed was not given. 0.03 wt% B was chosen based upon the stoichiometric ratio of Fe to B required to form FeB. For Fe₂B intermetallics, 0.06 wt% B was required, however only 0.05 wt% was chosen as this corresponded to the maximum solubility of B in Cu. No data was found in the literature on the influence of B in solid solution upon the conductivity (δ) of Cu. However because B occupies the same column as Al in the periodic table (and therefore has a similar electron configuration), like Al, the effect of B in solid solution might be minimal. Further more B has a very low solid solubility in Cu, 0.01 wt% at room temperature.

Ni was reported by Ohashi [9] to form Ni-Fe intermetallics when added to Cu-Fe-P alloys. The composition of the intermetallics formed was not given. The Fe-Ni phase diagram shows the existence of a Fe₃Ni intermetallic, which is only stable up to 517°C, above which Fe and Ni are completely soluble in each other.

The low temperature stability of this phase indicates a low driving force for its formation. Ni is completely soluble in Cu and more importantly the effect of Ni in solid solution upon the δ is significantly less than that of Fe [16]. Ni additions of 0.02 and 0.05 wt% were chosen in the expectation that Ni in solid solution might reduce the concentration of Fe and Cr in solid solution in the peak aged condition. This would increase the δ and might also provide some increased solid solution strengthening and precipitation strengthening due to an increased volume fraction of precipitate. Some improvement in strength might also result from the formation of Fe₃Ni intermetallics although the Ni levels are not based stoichiometrically on Fe₃Ni formation.

Additions of 0.02 and 0.05 wt% Yttrium (Y) were chosen based on the paper by Banerjee [17] which reported that the addition of trace amounts of rare earth elements such as Y (~0.02 wt%) to HSHC Cu-Cr-Zr had refined the size of the precipitates in the peak aged condition thereby increasing the size of the age hardening response. Conductivity (δ) was also increased through the removal of impurity atoms such as oxygen from solid solution.

The literature and phase diagram analysis indicated greatest promise for the alloys containing trace additions of 0.083 wt% P and 0.13 wt% Ti. Two additional alloys were chosen that contained these trace element and also 0.02 wt% Y in order to investigate the possibility of a synergistic effect.

Twelve Cu-0.7%Cr-0.3%Fe alloys were cast containing trace element additions. Cu-0.7%Cr-0.3%Fe alloy (Alloy A) was cast as a reference alloy. Also an additional Cu-0.7%Cr-0.3%Fe alloy was cast using high carbon ferro-chrome rather than low carbon ferro-chrome which had been used for all other alloys. High carbon ferro-chrome is a considerably cheaper alloying addition than low carbon ferro-chrome. For the rest of this paper each Cu-0.7%Cr-0.3%Fe alloy containing trace element additions is referred to based upon its trace elements, i.e. Cu-0.7%Cr-0.3%Fe-0.083%P alloy is referred to as the 0.083% P alloy.

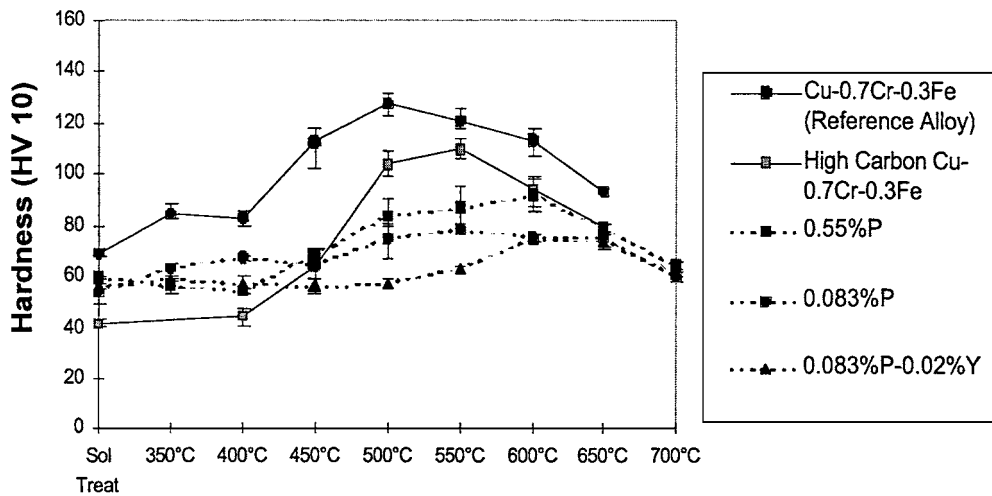
2. Experimental

The twelve quaternary alloys, the reference alloy and the reference alloy made with high carbon ferro-chrome were cast according to the procedure outlined previously [1–3]. Castings were machined into hardness blocks and rods for conductivity (δ) testing prior to solution treatment. Hardness blocks and δ rods were sealed in Vical glass and solution treated for two hours at 1050°C, followed by water quenching. Specimens were then aged in an inert gas atmosphere.

3. Results

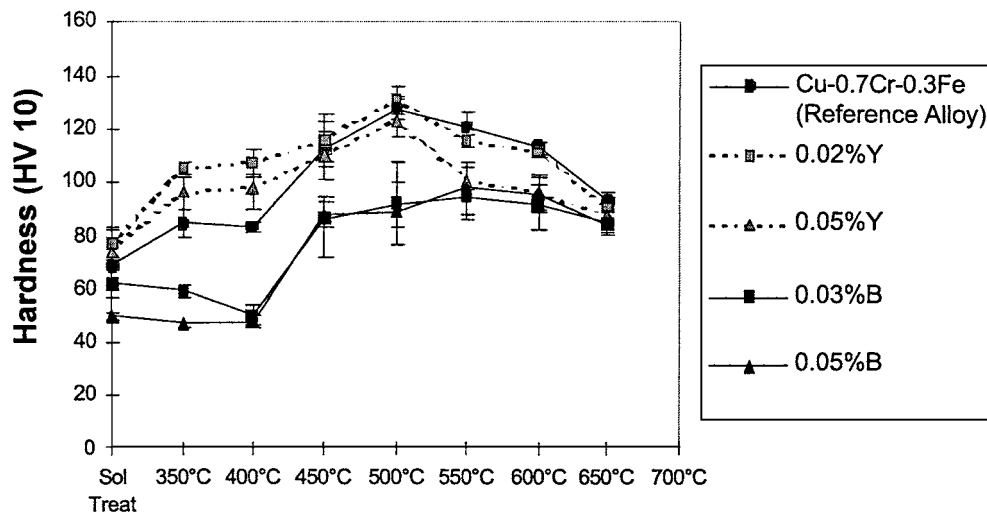
3.1. Isochronal aging

Solution treated hardness blocks of each alloy were aged for one hour at 50°C intervals to determine their optimum aging temperature. It was already known that the optimum aging temperature for Alloy A was 500°C. However, the effect of the trace element additions upon the ageing behaviour was unknown. The results are plotted in Fig. 1A–C. It should be noted that the peak



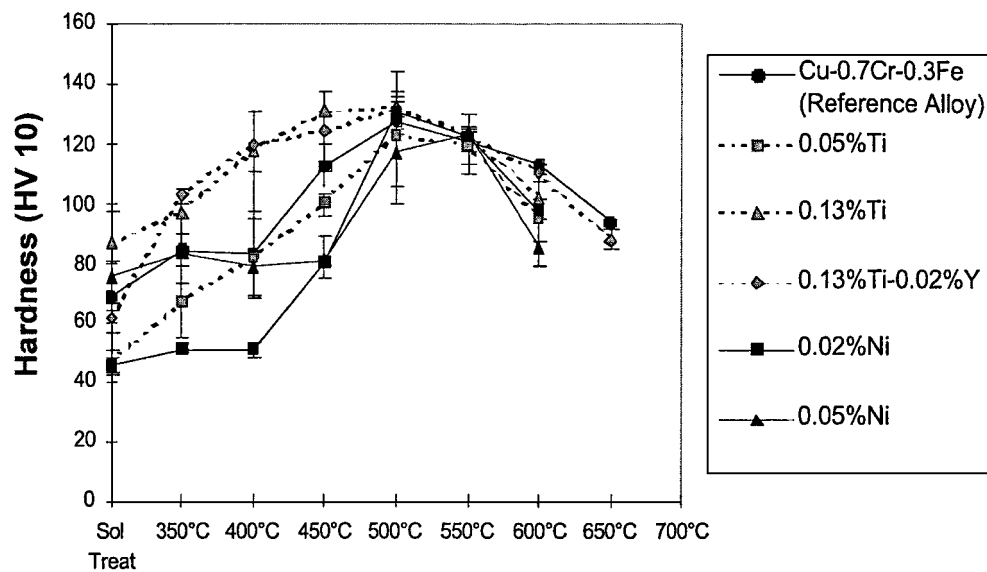
Heat Treatment

(A)



Heat Treatment

(B)



Heat Treatment

(C)

Figure 1 One hour isochronal aging curves (A) for the solution treated Cu-0.7%Cr-0.3%Fe alloys containing trace element additions of P, and for the alloy made with high carbon ferro-chrome; (B) for the solution treated Cu-0.7%Cr-0.3%Fe alloys containing trace element additions of Y and B; (C) for the solution treated Cu-0.7%Cr-0.3%Fe alloys containing trace element additions of Ti and Ni.

hardness of the reference Alloy A was ~ 15 HV less than that previously recorded [1] for the same alloy. Apart from the lower peak hardness, the age hardening behaviour of this alloy was similar to that previously recorded. The reason for the lower peak hardness was associated with the specimen preparation procedure; in the present work alloys were machined into hardness blocks and rods for δ measurements prior to being solution treated as opposed to the whole casting being solution treated. The significance is explained below. Since each of the quaternary alloys investigated in this section were machined prior to being solution treated comparison of their properties to those of the reference Alloy A is valid.

Fig. 1A shows that the peak hardness of the alloy made with high carbon ferro-chrome was 20 HV less than that of reference Alloy A. Peak hardness also occurred at a higher aging temperature. The addition of P and Y to Alloy A had a negative effect upon the age hardening response.

Fig. 1B shows that the addition of 0.02 and 0.05 wt% Y to Alloy A did not change the optimum aging temperature (500°C), nor did they have any significant effect upon the peak hardness. It does appear that Y additions may have accelerated the age hardening response as judged by the higher hardness values for aging temperatures of 350 and 400°C . The effect of B additions was detrimental to the age hardening response of Alloy A.

Fig. 1C shows that the addition of 0.05 wt% Ti had a slight effect upon the age hardening response of Alloy A. The addition of 0.13 wt% Ti increased the hardness of samples aged for 350 , 400 and 450°C compared to Alloy A, and moreover, the peak aged hardness was 5 HV higher than the reference alloy. The addition of 0.02 wt% Y to the alloy containing 0.13 wt% Ti had no effect upon the age hardening response. The rate of overaging of the alloys containing additions of Ti was higher than that of Alloy A. The addition of 0.02 and 0.05 wt% Ni to Alloy A had some effect upon the age hardening response, but peak hardness values were comparable to that of Alloy A.

500°C was selected as the optimum aging temperature for all alloys except those containing P and B. For alloys containing B, 550°C was selected while for those containing P, 600°C was chosen.

3.2. Isothermal aging

Isothermal aging curves for the high carbon Cu-0.7%Cr-0.3%Fe alloy and each of the Cu-0.7%Cr-0.3%Fe alloys containing trace element additions are shown in Fig. 2A–C. The isothermal aging curve for the reference Cu-0.7%Cr-0.3%Fe alloy (Alloy A) was the same as that previously recorded [1] apart from lower peak hardness.

Fig. 2A shows that the use of high carbon ferro-chrome significantly reduced the size of the age hardening response and that trace additions of P to Alloy A had a large negative effect upon the age hardening response.

Fig. 2B shows that the addition of both 0.02 and 0.05 wt% Y to Alloy A had a small negative effect upon

the age hardening response, and that the B additions had a large negative effect.

Fig. 2C shows that the age hardening response of the 0.05% Ti alloy was initially slower than that of Alloy A but rapidly increased such that the average peak hardness after 90 minutes aging was 130 HV almost the same as that of Alloy A. Overaging of the 0.05% Ti alloy was more rapid than that of Alloy A. For the 0.13% Ti alloy the isothermal aging curve showed a peak hardness of 129 HV after 90 minutes aging. The age hardening response of the 0.13%Ti-0.02%Y alloy was almost identical to that of Alloy A.

Additions of both 0.5 and 0.2 wt% Ni appeared to delay the initial age hardening response, after which rapid aging occurred. Both alloys reached peak hardness after 45 minutes aging as opposed to 90 minutes for Alloy A. Peak hardness of both alloys was equivalent to that of Alloy A. Overaging of the 0.05% Ni alloy at 500°C was considerably faster than that of the Alloy A.

3.3. Effect of sample preparation upon peak aged properties

As was reported, the peak aged hardness of the reference Alloy A was ~ 15 HV less than that recorded for the same alloy previously [1]. This is attributed to the fact that this alloy was solution treated after first being machined into hardness blocks and conductivity rods as opposed to being solution treated as a whole casting and then machined. Because the specific surface (i.e. surface area/mass) is much higher in the hardness blocks than the castings, a greater loss of temperature would have occurred in the time it took to remove the samples from the furnace and quench into water. As a result, the precipitation of secondary precipitates (responsible for hardening) would be more advanced, i.e. more precipitates nucleated, or nucleated precipitates would have grown to a larger size. This would have negatively affected the age hardening response when the hardness blocks were aged.

Conductivity results (as reported in following section) show that the solution treated conductivity of Alloy A was approximately the same when solution treated as a casting and when solution treated as individual conductivity rods. This indicates that the concentration of alloying elements in solid solution was essentially the same.

In order to determine whether the lower peak hardness was the result of the different methods of sample preparation, a large As-Cast section of the Cu-0.7%Cr-0.3%Fe reference alloy was solution treated. Hardness blocks were then machined from this piece. In addition an As-Cast piece of Cu-0.7%Cr-0.3%Fe alloy, which had previously been shown to have a peak aged hardness of 150 HV when aged after being solution treated as a casting, was machined into hardness blocks and solution treated. Hardness blocks of both Cu-0.7%Cr-0.3%Fe alloys were then aged at 500°C for 20, 45, 90 and 180 minutes. The results are plotted in Fig. 3.

Fig. 3 shows that the lower hardness of the reference Cu-0.7%Cr-0.3%Fe alloy compared to the prior work [1] was due to the reference alloy being solution

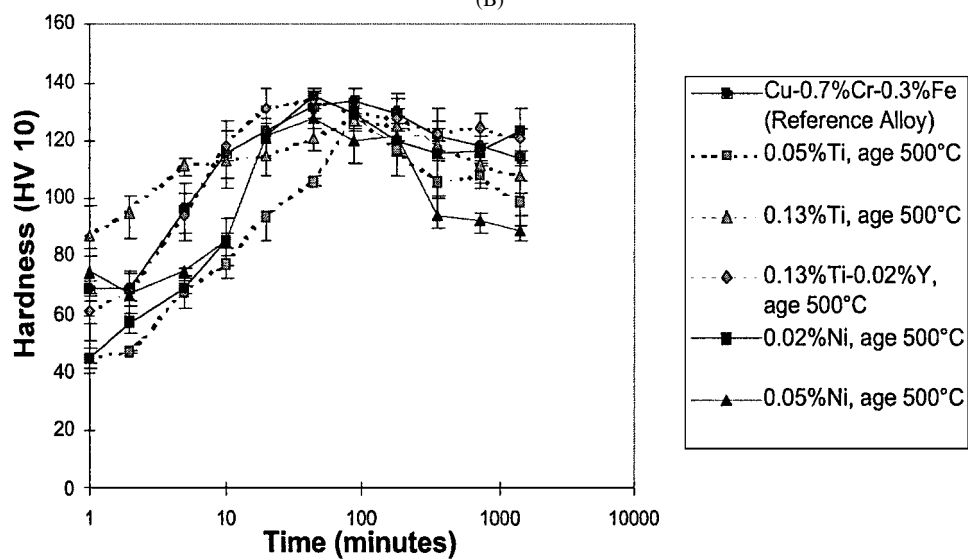
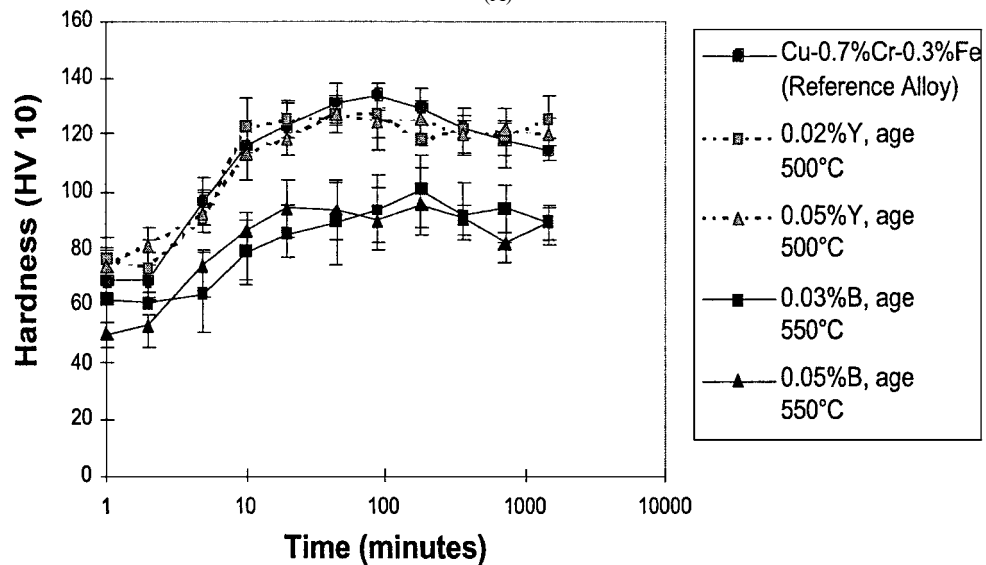
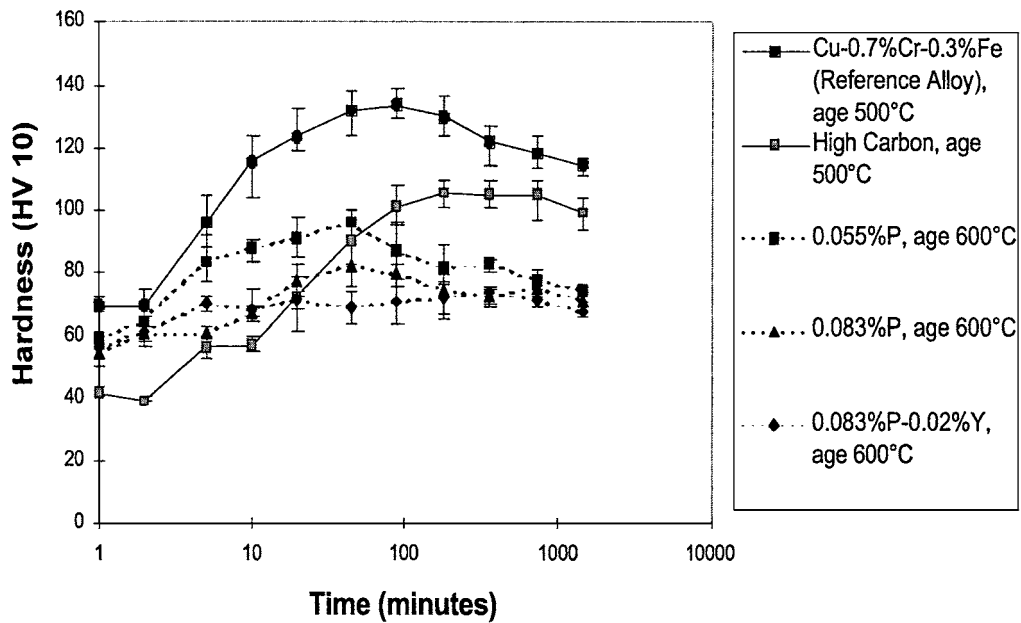


Figure 2 Isothermal aging curves (A) for solution treated Cu-0.7%Cr-0.3%Fe alloys containing trace additions of P and the alloy made with high carbon ferro-chrome; (B) for solution treated Cu-0.7%Cr-0.3%Fe alloys containing trace additions of Y and B; (C) for solution treated Cu-0.7%Cr-0.3%Fe alloys containing trace additions of Ti and Ni.

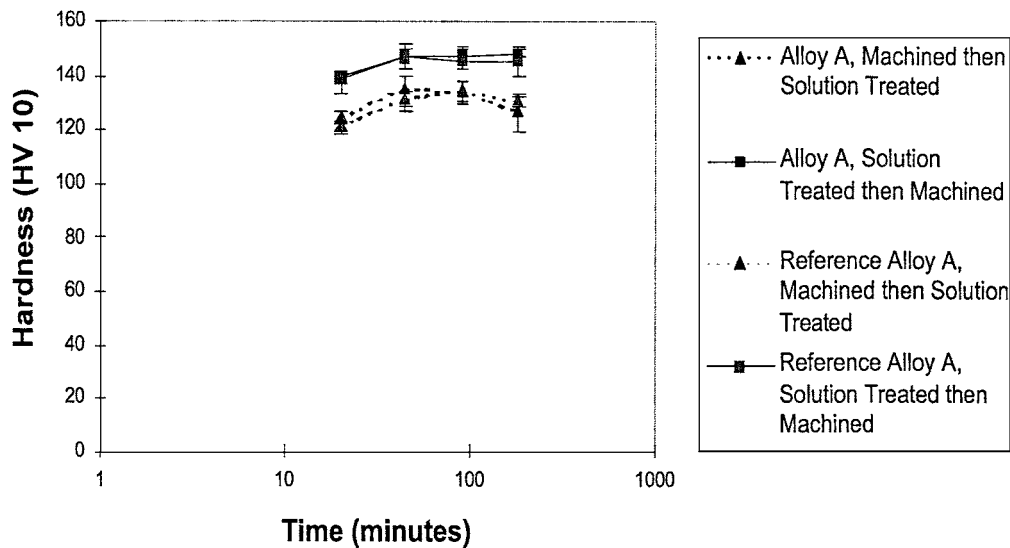


Figure 3 Effect upon the age hardening response of solution treating the Cu-0.7%Cr-0.3%Fe alloy casting as a whole or solution treating individual hardness blocks. Investigation used the Cu-0.7%Cr-0.3%Fe alloy whose properties were investigated previously [1] and the Cu-0.7%Cr-0.3%Fe alloy used as a reference in Sections 3.1 and 3.2. Aging temperature was 500°C.

treated as hardness blocks rather than as a casting prior to machining.

3.4. Conductivity

Conductivity testing was carried out on rods which had been machined from castings prior to solution heat treatment. Results are plotted in Fig. 4A–C. For all of the alloys investigated the conductivity (δ) initially increased rapidly after which further aging resulted in only minor δ increase. The effect of aging upon the δ of the reference Alloy A aged at 500°C was the same as that previously measured [1] for the Cu-0.7%Cr-0.3%Fe alloy, which was solution treated as a casting. Based upon this, it is apparent that the machining of rods for δ testing from castings prior to solution heat treatment has not affected the δ . This is as expected based upon the fact that δ is primarily dependant upon the concentration of alloying elements in solid solution after aging which would not be affected by differences in initial solution heat treatment.

Fig. 4A shows that the δ of the Cu-0.7%Cr-0.3%Fe alloy made with high carbon ferro-chrome was marginally higher than that of reference Alloy A after being aged. Trace additions of P decreased δ . The addition of 0.02 wt% Y to the 0.083% P alloy had no effect upon the δ .

Fig. 4B shows that the δ of Alloy A was not significantly affected by the addition of 0.02 or 0.05 wt% Y. The plots of δ versus aging time for the 0.03% B and 0.05% B alloys were almost identical. Conductivity (δ) after aging each alloy for 90 and 720 minutes was 3–4% IACS less than that of reference Alloy A. This is thought to be the result of the higher temperature (550°C) that was used to age these alloys and not the addition of B. B was therefore thought to have little effect upon the δ .

The effect of trace additions of Ti upon the δ of Alloy A are shown in Fig. 4C. In the peak aged condition (aged 90 minutes, 500°C) the δ of the 0.13% Ti and

0.05% Ti alloys were equivalent to that of Alloy A. After overaging for 720 minutes, the δ of both alloys was within 1% IACS of the reference Alloy A. The addition of 0.02 wt% Y to the 0.13% Ti alloy had no significant effect upon the δ .

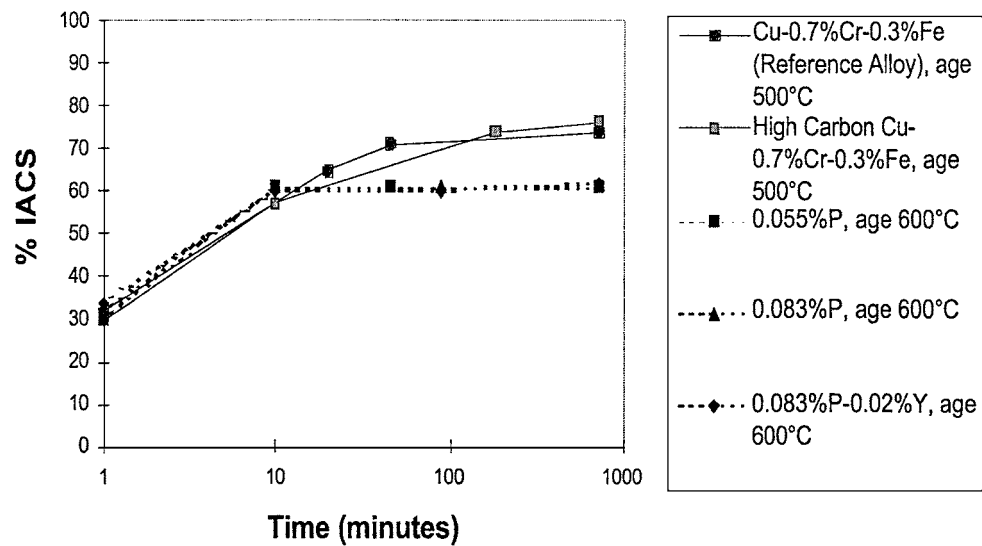
The addition of trace amount of Ni to Alloy A had some effect upon the δ . In the peak aged condition (aged 45 minutes, 500°C) the δ of both the 0.02% Ni and 0.05% Ni alloys was lower than that of reference Alloy A, the reduction in δ was proportional to the Ni content.

3.5. CW quaternary

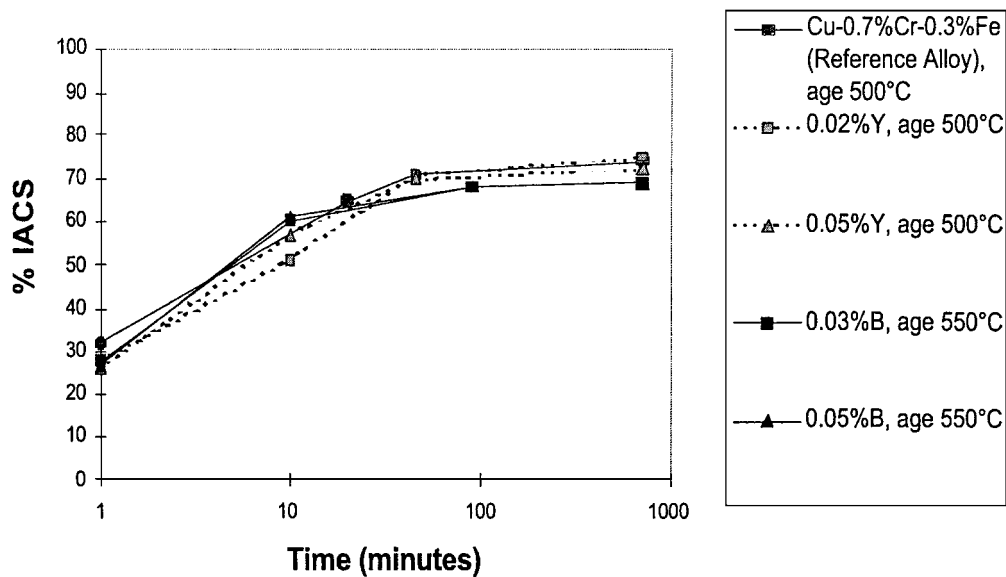
Cu-0.7%Cr-0.3%Fe-0.13%Ti alloy

For these experiments the whole casting was solution treated at 1050°C for 2 hours. Higher peak aged hardness of the alloy in this condition would further confirm the negative effect upon peak aged hardness of machining hardness blocks from castings prior to solution heat treatment.

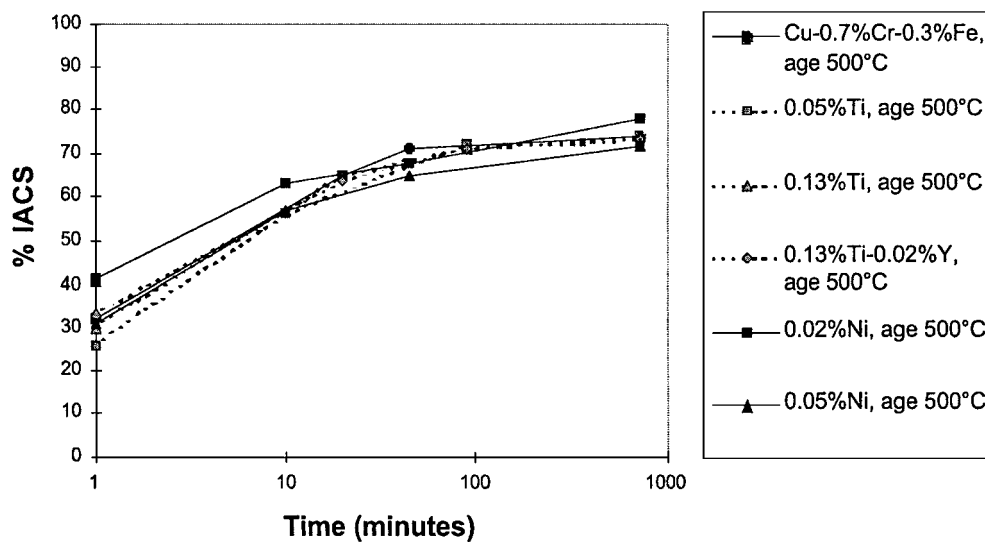
Fig. 5 shows that the addition of 0.13 wt% Ti to the Cu-0.7%Cr-0.3%Fe alloy had essentially no affect upon the age hardening response of the 40 and 90% cold worked alloys. For the solution treated and aged 0.13% Ti alloy, peak hardness of 153 HV was recorded after aging at 500°C for one hour. This was 9 HV higher than the equivalent peak aged hardness recorded for Alloy A. Result had previously shown the peak aged hardness of the of the solution treated 0.13% Ti alloy to be equivalent to that of Alloy A. The peak aged hardness of this alloy was also 21 HV higher than that of the same alloy investigated in Sections 3.1 and 3.2. This result further supports the explanation given in Section 3.3 that the low peak hardness of the alloys investigated in Sections 3.1 and 3.2 was due to them being solution treated as hardness blocks and not castings. Apart from higher peak aged hardness the addition of 0.13 wt% Ti to Alloy A had no effect upon the shape of the isochronal aging curve.



(A)



(B)



(C)

Figure 4 Plot of conductivity (% IACS) versus aging time for (A) solution treated Cu-0.7%Cr-0.3%Fe alloys containing trace additions of P and made with high carbon ferro-chrome; (B) for solution treated Cu-0.7%Cr-0.3%Fe alloys containing trace additions of Y and B; (C) for solution treated Cu-0.7%Cr-0.3%Fe alloys containing trace additions of Ti and Ni.

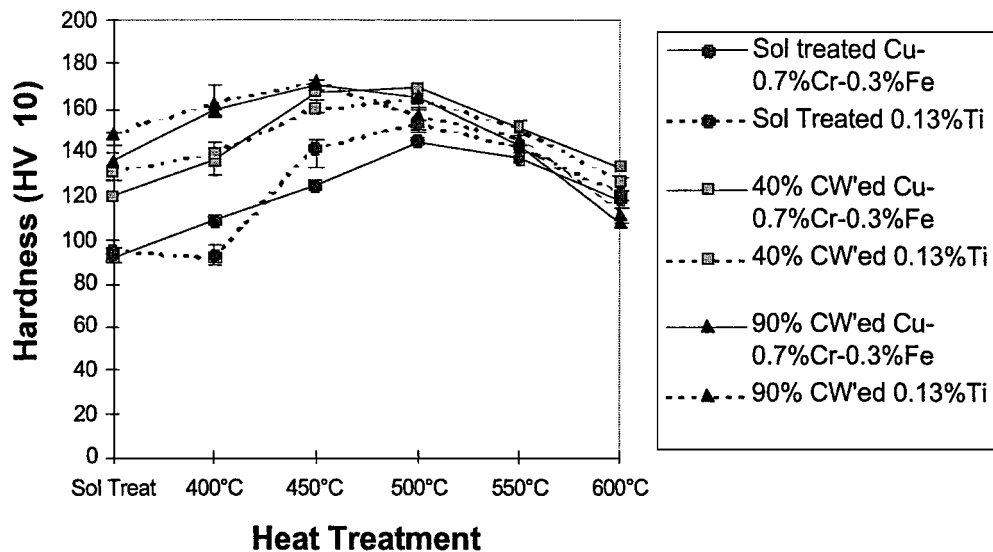


Figure 5 One hour isochronal aging curves for solution treated, 40% CW and 90% CW Cu-0.7%Cr-0.3%Fe-0.13%Ti and Cu-0.7%Cr-0.3%Fe alloys.

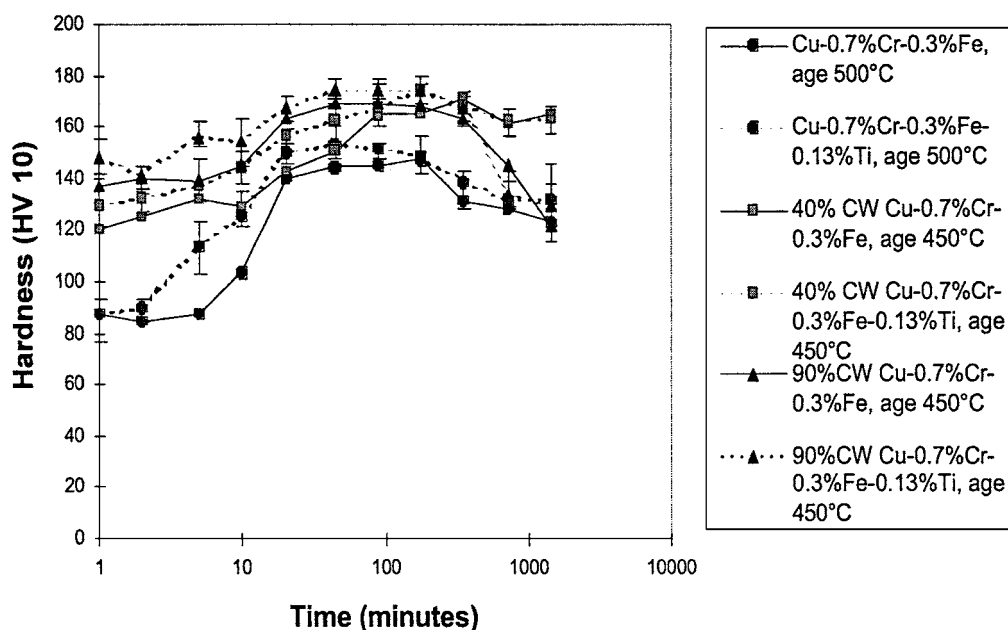


Figure 6 Isothermal aging curves for Cu-0.7%Cr-0.3%Fe-0.13%Ti alloy and Cu-0.7%Cr-0.3%Fe alloy in the solution treated, the 40% cold worked and the 90% cold worked condition.

Isothermal aging curves for the 0.13% Ti alloy in the solution treated, the 40% cold worked and the 90% cold worked condition, Fig. 6 shows that the addition of 0.13 wt% Ti had no significant effect upon the isothermal age hardening curves.

Conductivity (δ) testing was carried out on rods machined from solution treated pieces of the 0.13% Ti alloy which had been cold worked 40 and 90%. Results are plotted in Fig. 7. The δ of the 40% cold worked 0.13% Ti alloy was between 2–4% IACS lower than that of the Cu-0.7%Cr-0.3%Fe alloy (Alloy A) in the peak aged condition.

For the 90% cold worked 0.13% Ti alloy, the δ for aging times up to ~600 minutes was slightly higher than that of Alloy A. With continued aging however the difference in δ between the two alloys continued to decrease until after 1440 minutes when the δ of Alloy A reached 82% IACS, 2% IACS higher than that of the 0.13% Ti alloy.

The addition of 0.13 wt% Ti to the Cu-0.7%Cr-0.3%Fe alloy (Alloy A) did not result in any significant increase in electrical or mechanical properties. Some minor improvements in hardness were recorded. Similarly some minor improvement in δ were recorded in certain conditions, particularly when 90% cold worked. As for Alloy A, the best combination of δ and hardness were recorded for the 0.13% Ti alloy when 40% cold worked in the solution treated condition prior to aging.

3.6. Microstructure

For each of the quaternary alloys peak aged samples were examined to determine whether any of the trace alloying additions had had any optically observable effect upon the microstructure compared to that of the Cu-0.7%Cr-0.3%Fe alloy. For most of the peak aged quaternary alloys examined no difference could be observed between their microstructure and that of the

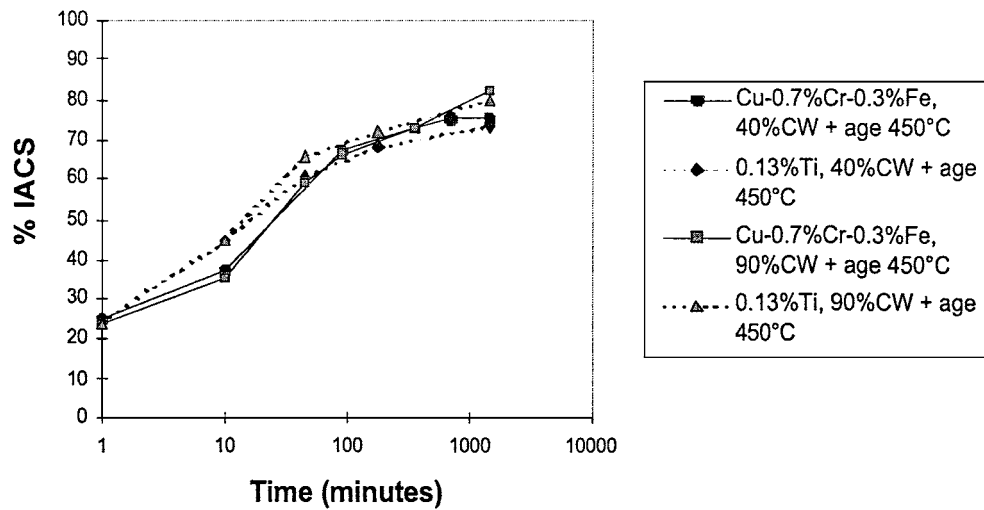


Figure 7 Plot of conductivity (% IACS) vs aging time at 450°C for 40 and 90% cold worked Cu-0.7%Cr-0.3%Fe-0.13%Ti alloys. Equivalent data for Cu-0.7%Cr-0.3%Fe alloy has been included for comparison.

peak aged Cu-0.7%Cr-0.3%Fe alloy (Alloy A). The microstructure of peak aged Alloy A is shown in Fig. 8. Only for those alloys containing trace additions of P and B was there an obvious difference in microstructure. This is illustrated for the 0.083% P alloy in Fig. 9. The microstructure of all alloys containing P and B were observed to contain a disproportionately high amount of eutectic. No difference could be seen between the microstructures of the 0.03% B, 0.05% B, 0.055% P, 0.083% P and 0.083%P-0.02%Y alloys.

The results in Sections 3.1 and 3.2 showed that the peak aged hardness of those alloys containing trace additions of P and B was significantly reduced compared to that of the reference Alloy A. Other alloying additions caused only small differences in peak aged hardness. There is obviously a connection between the effect of these alloying additions upon the peak aged hardness and their effect upon the microstructure.

Analysis of the Cr-B binary phase diagram [14] revealed the existence of a number of different Cr-B in-

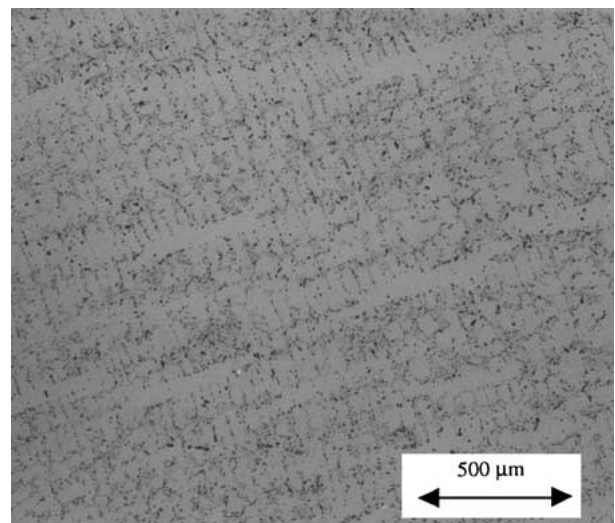


Figure 9 Optical micrograph of peak aged Cu-0.7%Cr-0.3%Fe-0.83%P alloy showing dendritic microstructure and increased volume fraction of eutectic compared to that of the Cu-0.7%Cr-0.3%Fe alloy seen in Fig. 8. Unetched.

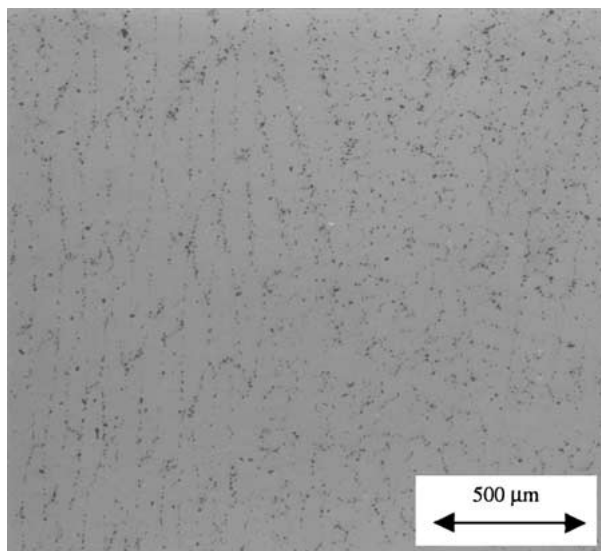


Figure 8 Optical micrograph of peak aged Cu-0.7%Cr-0.3%Fe alloy showing dendritic microstructure and eutectic. Unetched.

termetallics. No binary Cr-P phase diagrams have been reported in literature. It is proposed that in alloys containing B and P additions, intermetallics have formed between these elements and Cr which have caused the observed increased volume fraction of eutectic. The reduced peak hardness was thought to be linked to the increased volume fraction of eutectic.

3.7. Energy dispersive spectroscopy analysis

Energy Dispersive Spectroscopy (EDS) was carried out on primary precipitates of the peak aged Cu-0.7%Cr-0.3%Fe alloys that contained trace additions of P. This was done in order to determine whether P was present in eutectic precipitates which would support the formation of Cr-P intermetallics. It was not possible to carry out similar measurements for the alloys that contained B additions because of the relatively low atomic weight of B (B-10.8, Cu-63.5). All EDS spectra were obtained

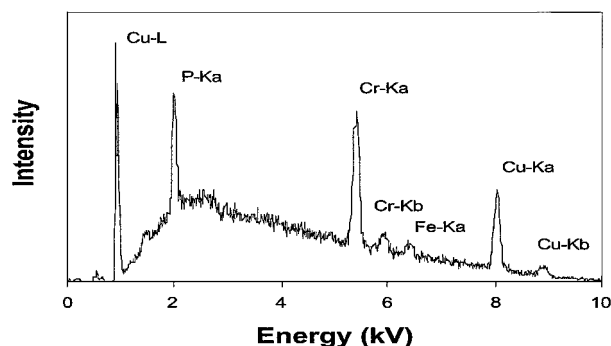


Figure 10 EDS spectra of primary precipitate in peak aged Cu-0.7%Cr-0.3%Fe-0.083%P alloy, 10 kV.

using an accelerating voltage of 10 kV in order to minimise the size of the interaction volume. Spectra shown are typical for the multiple tests that were carried out.

Fig. 10 shows the EDS spectra taken from a large eutectic precipitate in the 0.083% P alloy. It is evident that P is present in the eutectic precipitates. A large P peak is visible in addition to a large Cr peak. EDS spectra taken from the matrix of the same alloy showed only Cu peaks. Similar results were obtained for the 0.055% P alloy. This showed that P additions were concentrated in eutectic precipitates. This indicates Cr-P intermetallic formation.

3.8. Wavelength dispersive spectroscopy

Wavelength Dispersive Spectroscopy (WDS) was used to quantitatively determine the concentration of Fe and Cr in the matrix of each quaternary alloy. Where possible the concentration of trace alloying addition was also measured. These measurements were carried out in order to explain the effect of different alloying additions upon the mechanical properties of the Cu-0.7%Cr-0.3%Fe alloy. Solution treated hardness blocks from each alloy were analysed. Tests were carried out according to the experimental procedure as described previously [1]. The results of analyses of solution treated alloys are shown in Table II. Peak aged hardness as recorded in isothermal aging curves has been included

in Table II for comparison. For the alloys containing Ti additions, values reported are those for sample solution treated as hardness blocks after having been machined.

For the reference Cu-0.7%Cr-0.3%Fe alloy (Alloy A) the concentration of Cr and Fe in solid solution was slightly higher than that reported for other equivalent alloys previously investigated [2]. The concentration of Cr in solid solution was actually 0.01 wt% higher than that previously reported for the Cu-1%Cr reference alloy. An explanation for this is that the solution treatment temperature may have been slightly higher than 1050°C. This would account for the higher concentration of Cr, since at elevated temperatures the solubility of Cr in Cu increases significantly with increased temperature.

For the high carbon alloy, the concentration of Cr in solid solution after solution heat treatment was only slightly more than half that of the reference alloy. This correlates with the lower peak aged hardness of this alloy.

Trace additions of P to reference Alloy A greatly reduced the amount of Cr in solid solution. The reduction in Cr concentration was dependant upon the amount of P added as was the reduction in peak aged hardness. No evidence of P was found in the solution treated matrix of these alloys. The amount of Fe in solid solution compared to Alloy A was also reduced marginally. The reduction was greater for the alloys containing 0.083 wt% P. Results indicate that P may be forming intermetallics with Fe, however based upon the reduced Cr concentration in solid solution it is thought that P is forming intermetallics preferentially with Cr.

The addition of Y to Alloy A had essentially no effect upon the amount of Fe and Cr in solid solution and had no effect upon hardness and δ . Analysis of Y in the matrix found only trace amounts in a few of the analyses. It is possible that Y additions were preferentially oxidised during casting or Y was concentrated in the eutectic.

The addition of B to Alloy A decreased the amount of Cr in solid solution. The decrease was dependant upon the amount of B added. The reduction was not as significant as that caused by P additions, however neither

TABLE II Concentration of alloying elements (wt%) in the matrix of the quaternary Cu-0.7%Cr-0.3%Fe alloys after solution treatment at 1050°C for two hours

Alloy	%Cr	%Fe	%X	Hardness (HV)
Cu-0.7%Cr-0.3%Fe (Ref Alloy)	0.59	0.31	—	134
High C, Cu-0.7%Cr-0.3%Fe	0.29	0.22	—	105
Cu-0.7%Cr-0.3%Fe-0.055%P	0.38	0.28	0.00	96
Cu-0.7%Cr-0.3%Fe-0.083%P	0.23	0.26	0.00	82
Cu-0.7%Cr-0.3%Fe-0.083%P-0.02%Y	0.23	0.26	—	75
Cu-0.7%Cr-0.3%Fe-0.02%Y	0.52	0.29	~0.003	127
Cu-0.7%Cr-0.3%Fe-0.05%Y	0.58	0.29	~0.004	127
Cu-0.7%Cr-0.3%Fe-0.03%B	0.47	0.29	^a	101
Cu-0.7%Cr-0.05%B-0.05%B	0.35	0.30	^a	96
Cu-0.7%Cr-0.3%Fe-0.05%Ti	0.52	0.29	0.005	130
Cu-0.7%Cr-0.3%Fe-0.13%Ti	0.52	0.28	0.004	129
Cu-0.7%Cr-0.3%Fe-0.13%Ti-0.02%Y	0.55	0.29	—	134
Cu-0.7%Cr-0.3%Fe-0.02%Ni	0.54	0.30	0.02	136
Cu-0.7%Cr-0.3%Fe-0.05%Ni	0.55	0.31	0.05	128

^aCould not be measured using WDS.

Peak hardness values obtained in isothermal ageing curves are also included.

was the reduction in peak aged hardness. The amount of Fe in solid solution for both alloys was equivalent to that of Alloy A. The concentration of B in the matrix could not be analysed due to difficulties associated with measuring the concentration of trace element additions with low atomic weights using WDS. As for P containing alloys, the reason for the reduction in peak aged hardness is believed to be due to the formation of Cr-B intermetallics.

The concentration of Cr in the matrix of both the 0.05% Ti and 0.13% Ti alloy was 0.52 wt% compared to 0.59 wt% in Alloy A. For the 0.13%Ti-0.02%Y alloy the concentration of Cr in the matrix was 0.55 wt%. The concentration of Fe in solid solution was essentially unchanged for each alloy. The peak hardness recorded for all Ti containing alloys were equivalent to Alloy A. It is not possible to say whether the small reduction in Cr concentration in these alloys was due to the Ti additions or due to experimental variations.

For the alloys containing additions of 0.02 and 0.05 wt% Ni the concentration of Cr in solid solution was 0.54 and 0.55 wt%. The concentration of Fe in solid solution was the same as that in Alloy A. For both alloys the concentration of Ni in solid solution was the same as the amount added. Peak aged hardness was also equivalent to that of Alloy A as was conductivity. As for Ti containing alloys it is not possible to say whether the lower Cr concentration was a result of the Ni additions or experimental variation.

WDS results show that for each of the alloys the peak aged hardness was dependant upon the amount of Cr in solid solution. For alloys containing additions of P and B the reduction in peak aged hardness was dependant upon the reduction in percent Cr in solid solution. Similarly the reduced peak hardness of the Cu-0.7%Cr-0.3%Fe alloy made with high carbon ferrochrome could also be related a reduced concentration of Cr in solid solution. Other alloys containing additions of Ti, Y and Ni had peak hardness equivalent to Alloy A and also had equivalent concentrations of Cr in solid solution after solution treatment.

4. Discussion

Experimental results on the ternary Cu-0.7%Cr-0.3%Fe alloy had shown that the mechanical and electrical properties of this alloy approached those of the Cu-1%Cr alloy. It is known that trace element additions (≤ 0.15 wt%) could improve mechanical and electrical properties of binary Cu-Fe alloys. As a result, a number of trace element additions were selected to determine whether they would have a similar effect on the properties of the Cu-0.7%Cr-0.3%Fe alloy. The minor additions considered were Titanium (Ti), Phosphorus (P), Boron (B), Nickel (Ni) and Yttrium (Y). The detailed rationale behind each of these additions and the wt% selected was discussed in the Introduction. Ti, B & P additions were selected with the intention of promoting the formation of Fe-X type intermetallics. Ni additions were expected to improve conductivity by displacing Fe in solid solution after aging and Y was expected to increase the age hardening response by refining the peak

aged precipitate size. For intermetallic forming additions, the concentration of trace elements selected was based upon the assumption that all of the trace alloying additions would preferentially react with the Fe.

The investigation showed that none of the trace element additions significantly improved the age hardening response or the peak aged electrical conductivity of Alloy A. Additions of P and B were detrimental. Other trace additions had little or no effect apart from causing some slight changes to the precipitation kinetics. The mechanical properties of the Cu-0.7%Cr-0.3%Fe alloy (Alloy A) that had been made with less expensive high carbon ferrochrome were found to be inferior to those of the equivalent alloy made with low carbon ferrochrome.

Results in Sections 3.1 and 3.2 showed that the peak aged hardness of the 0.055% and 0.083% P alloys were significantly reduced relative to the reference alloy; similar results were reported for the two alloys containing boron additions. WDS results showed that as the concentration of P and B increased, the amount of Cr in solid solution decreased but the amount of Fe remained unchanged. The reduction in the amount of Cr in solid solution was reflected in the increased volume fraction of eutectic in alloys containing P and B trace additions. EDS on eutectic precipitates in the P alloys showed that they contained predominantly Cr and P. Based upon the results of the characterisation of the quaternary alloys, the cause for the reduction in peak aged hardness of the P and B containing alloys was that the trace element additions preferentially form Cr-B and Cr-P eutectic precipitates which reduce the amount of Cr in solid solution. The high temperature stability of these precipitates indicates that they are stable and that there would be a high driving force for their formation. The reduction in the concentration of Cr in solid solution means that the secondary precipitates which have been shown to be primarily responsible for strengthening/hardening in Alloy A, contain proportionally more Fe. The higher the Fe:Cr ratio, the larger the precipitates in the peak aged condition and the smaller the age hardening response. The higher Fe content of the secondary precipitates in the P and B alloys, relative to the other quaternary alloys, is supported by isothermal aging curves (Fig. 1A and B) which show that the optimum 1 hour aging temperatures were 600 and 550°C, compared to 500°C for the reference alloy. Higher optimum 1 hour aging temperatures reflect the slower precipitation kinetics of the Fe rich precipitates. The lower concentration of Cr in solid solution also means that the volume fraction of secondary precipitate is decreased which according to precipitation hardening theory reduces the amount of strengthening. The lower peak aged hardness of the high carbon Cu-0.7%Cr-0.3%Fe alloy (105 HV) is attributed to the same cause: impurities such as C, Si and P in the high carbon ferrochrome forming Cr-X type intermetallics during solidification which reduces the amount of Cr that dissolves into solid solution to 0.29 wt%.

For each of the other quaternary alloys containing additions of Y, Ti and Ni, the peak aged hardness was equivalent to that of the reference Alloy A. WDS results

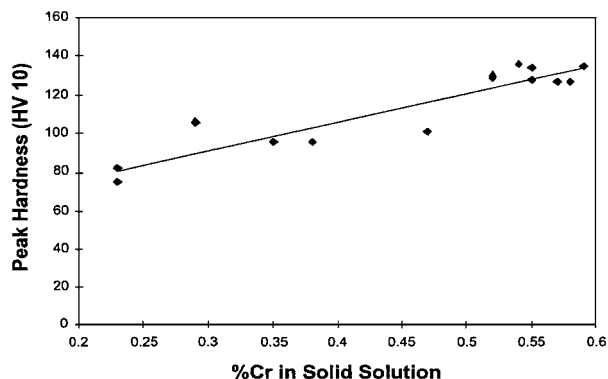


Figure 11 Plot of peak aged hardness v % Cr in solid solution for solution treated Cu-0.7%Cr-0.3%Fe alloys containing trace quaternary alloying additions. Data taken from Table II.

showed that for these alloys, the concentration of Cr in solid solution prior to aging was equivalent to that of the reference Alloy A. For the alloys containing additions of Y this result indicates that no refinement of the peak aged Fe-Cr secondary precipitates occurred as was expected based upon the views of Banerjee [17]. The relationship between % Cr in solid solution and peak aged hardness is illustrated in Fig. 11. The peak aged hardness of each of the quaternary alloys is proportional to the concentration of Cr in solid solution prior to aging. This indicates that none of the trace alloying additions investigated had a significant effect upon the morphology or composition of the secondary precipitates which have been shown to be primarily responsible for strengthening of these alloys. For example if Fe-X intermetallics formed during aging then there would be less Fe available to form Cr-Fe secondary precipitates, a higher age hardening response would be expected for a given Cr:Fe ratio. The opposite would hold if secondary Cr-X intermetallics formed. The fact that the peak aged hardness of the quaternary alloys is proportional to the solution treated Cr:Fe ratio indicates that this does not occur. This is illustrated in Fig. 12 which plots peak HV of the quaternary alloys v Cr:Fe ratio in the solution treated matrix. The relationship is linear.

The effect of P and B additions could be clearly seen upon the microstructure and mechanical properties of the quaternary Cu-0.7%Cr-0.3%Fe alloys. WDS on P

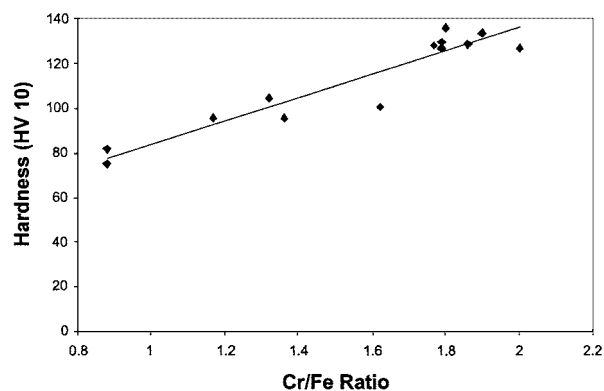


Figure 12 Plot of peak aged hardness v Cr:Fe ratio in solid solution for Cu-0.7%Cr-0.3%Fe alloys containing trace quaternary alloying additions. Results taken from Table II.

alloys indicated little P in solid solution in the matrix. However, the conductivity (δ) results showed that the averaged δ of the P containing alloys was $\sim 13\%$ IACS lower than that of the overaged reference Alloy A (Fig. 4A). The difference in δ is too large to be accounted for based upon the differences in aging temperatures alone, 600°C as opposed to 500°C . Stanley [16] has shown that P is one of the most effective elements at reducing the electrical δ of copper. Thus the conductivity decrease in the P containing alloys is attributed to a small increase in P content in solid solution, at a concentration below that detected by WDS. For quaternary B alloys, the trace concentrations of B were below the detection limit of WDS due to the low atomic weight of B. The 4% IACS lower δ of the overaged B containing alloys (Fig. 4B) was attributed to the higher aging temperature, 550°C as opposed to 500°C . The actual effect of B in solid solution upon the δ of copper has not been reported in literature but is expected to be minimal based upon boron's low solid solubility in Cu, 0.05 wt\% at 1013°C [14] and its similar valence to Cu [18]. For each of the other quaternary alloys investigated, the δ in the peak aged and overaged conditions were equivalent to the reference Alloy A. The one major exception was the overaged δ of the 0.02 wt\% Ni alloy. The purpose of the 0.02 and 0.05 wt\% Ni additions had been to try and improve the δ in the peak aged condition by reducing the concentration of Fe in solid solution after aging. Ni in solid solution in Cu is known to have less of an effect upon δ than Fe [16]. WDS results show that for both alloys all of the Ni additions have gone into solid solution. After aging for 720 minutes at 500°C the δ of the 0.02 wt\% Ni alloy was 77% IACS, 3% IACS higher than that of the reference Alloy A. This was initially attributed to a reduced concentration of Fe in solid solution. However, the δ of the overaged 0.05% Ni alloy was 2% IACS less than that of the reference Alloy A. If Ni addition did improve the δ then the improvement would be expected to be at least equal or greater for the 0.05 wt\% Ni alloy. The fact that it is not, indicates that the higher conductivity (δ) of the 0.02 wt\% Ni alloy is not statistically significant and is within experimental variability.

For the quaternary alloys containing trace Ti additions, the mechanical and electrical properties of the solution treated alloys were equivalent to those of Alloy A (Figs 1C, 2C & 3C). Based upon this, the properties were investigated of the 0.13 wt\% Ti alloy when 40 and 90% CW prior to aging. It was expected that since the δ of the 0.13 wt\% Ti alloy in the peak aged condition was not decreased relative to reference Alloy A, then Ti must be forming intermetallics. This was because it was known that Ti in solid solution has a more negative effect upon the δ of copper than Fe and some decrease in δ would be expected if there was Ti remaining in solid solution after aging [19]. Further investigation was also encouraged by results reported by Yamaguchi and Yamasaki [13] which had shown that for Cu-Fe-Ti alloys the δ in the peak aged condition was significantly improved by cold working prior to aging. Similarly Murakami *et al.* [8] had reported that the softening resistance of

HSHC Cu-Fe-Ti alloy was higher than any equivalent HSHC copper alloys. The results of the investigation into the properties of the 0.13% Ti alloy when CW showed no improvement in peak aged hardness or softening resistance relative to the reference Alloy A in either CW condition. Isochronal and isothermal aging curves were almost identical (Figs 5 and 6). There were slight changes to the plots of conductivity versus aging time relative to the reference Alloy A (Fig. 7). These, however, were minor and were thought due to experimental variation and not the result of trace Ti additions.

Optical examination of the microstructures of the Ti containing alloys revealed that Ti additions had had no optically observable effect upon the microstructure. WDS results showed that the %Cr and %Fe in solid solution were equivalent to Alloy A. Concentrations of Ti less than 0.01% were measured for each of the Ti containing alloys in the solution treated condition. Equivalent Ti concentrations were recorded when the Ti concentration in the Cu standard was measured. If Ti was not in solid solution because it had formed intermetallics with Cr, then an observable increase in the eutectic volume fraction would be expected based upon what was observed for the P and B containing alloys. Similarly the %Cr in solid solution would have been reduced. Based upon the above evidence, combined with the equivalent mechanical and electrical properties of the Ti containing alloys and the reference Alloy A, the Ti additions did not dissolve into the copper melt but were oxidised during the casting process.

The reason that Ti additions did not dissolve into solid solution is believed to be due to a combination of the large driving force for oxidation and also the method with which Ti additions were added to the alloy. Thermochemical modelling of copper melts has shown that of the trace alloying additions investigated only Yttrium additions are more prone to oxidation than Ti [20]. Ti additions were elemental consisting of a Ti sponge of 99.5 wt% purity that was added to the crucible prior to melting. It is thought that during melting and the period in which the melt was held molten all of the Ti additions were oxidised. In hindsight a similar practise should have been employed as was used for the P and Yttrium additions in which Cu-P and Cu-Y masteralloys were added to melt just prior to casting so as to minimise the amount of oxidation of the alloying additions.

5. Conclusions

A number of trace quaternary alloying additions were tested to investigate if further improvements of the mechanical and electrical properties of the Cu-0.7%Cr-0.3%Fe alloy could be achieved. Additions of Ti, B and P were expected to form intermetallics with Fe that could result in improved electrical conductivity by reducing the concentration of Fe in solid solution after ageing, intermetallics may also possibly contribute to additional strengthening. Ni additions were expected to improve conductivity by displacing Fe in solid solution. Additions of Ti and Ni did not have a significant effect, where the Ti additions may have oxidised during

melting and holding. Additions of B and P were found to significantly reduce the age hardening response because they preferentially formed primary intermetallics with Cr rather than Fe. This reduced the amount of Cr in solid solution after solution heat treatment, resulting in secondary precipitates containing proportionally less Cr and therefore being less efficient at strengthening. Additions of Y were investigated alone and in combination with other trace elements. Y was expected to refine the size of the precipitates in the peak aged condition, thus increasing the age hardening response. No evidence of precipitate refinement was found.

The effect of adding chromium in the form of high carbon ferro-chrome instead of low carbon ferro-chrome was investigated for the Cu-0.7%Cr-0.3%Fe alloy. The mechanical properties of this alloy were found to be inferior to those of the same alloy made with low carbon ferro-chrome additions, because impurities such as C, S and P introduced with the high carbon ferro-chrome formed primary intermetallics with Cr and reduced the amount of Cr in solid solution.

During the investigation it had been thought that additions of Ti, along with P, had the greatest potential to further improve the mechanical and electrical properties of the Cu-0.7%Cr-0.3%Fe alloy. This view has not changed. It is recommended that further work be carried out to evaluate the effect of Ti additions, Ti additions should be added in the form of Cu-Ti master-alloy just prior to casting rather than as elemental Ti sponge prior to melting.

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