JOURNAL OF MATERIALS SCIENCE **39** (2004) 1579–1587

Precipitation hardening of Cu-4Ti-1Cd alloy

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Precipitation hardening of Cu-4Ti-1Cd alloy has been studied using hardness measurements and transmission electron microscopy. This alloy exhibited hardness of 238 Hv in solution treated (ST) condition and attained peak hardness of 318 Hv after ageing at 450°C for 40 h. Electrical conductivity of Cu-4Ti-1Cd alloy increased from 5.7 %IACS (International Annealed Copper standard) in ST condition to 8.9 %IACS on ageing at 450°C for 16 h. This alloy exhibited markedly higher yield strength (751 MPa in the peak-aged condition) compared to Cu-4.5Ti alloy but the increase in UTS due to cadmium addition was less significant. The higher yield strength of ternary alloy in peak aged condition is due to the solid solution strengthening of cadmium as well as the presence of β'-Cu_4Ti precipitate. On over-ageing the alloy showed a decrease in hardness as a result of formation of equilibrium precipitate, β-Cu_3Ti. Optical microscopy reveals single phase with equiaxed grains in solution treated condition. A coherent, metastable phase β'-Cu_4Ti is responsible for high strength and hardness in peak aged condition. The over-ageing in this alloy shows the formation of cellular structure at the grain boundaries of the matrix phase.

1. Introduction

Copper and copper-base alloys are widely used for numerous applications demanding good mechanical properties, resistance to corrosion, good electrical conductivity, color and ease of fabrication [1, 2]. Among the alloys having a good combination of high strength and high thermal as well as electrical conductivity, age hardenable Cu-Be alloys are most widely used but they have the limitation of toxicity and high cost of production.

Cu-Ti alloys are precipitation strengthened by spinodal decomposition mechanism [3–5] involving composition modulations and long-range ordering in the initial stages of ageing. The peak hardening is associated with modulated structure along with the precipitation of coherent and metastable phase β'-Cu_4Ti, which has an ordered body centered tetragonal structure ($a = 0.584$ nm and $c = 0.362$ nm) [6]. Over ageing is characterised by the formation of equilibrium phase β-Cu_3Ti in the form of cellular precipitates with an orthorhombic structure ($a = 0.516$ nm, $b = 0.435$ nm and $c = 0.453$ nm) [7]. The earlier work on Cu-Ti alloys showed that they exhibit mechanical properties comparable to those of Cu-Be alloys, though the electrical conductivity was slightly inferior [8–10].

Earlier investigators [11–15] have studied the effect of various alloying additions like V, Al, Sn, B and Co on the age hardening behaviour of Cu-Ti alloys. Vanadium is a grain-refining element but retards the continuous precipitation of the intermetallic phase β' while accelerating the discontinuous precipitation of β [11]. The presence of dispersed particles of TiB_2 in addition to the development of modulated structure and the precipitation of metastable Cu_4Ti caused much higher strength in the Cu-Ti-B alloys [12]. When Co is added to Cu-Ti alloys, formation of intermetallic phases like Ti_2Co and TiCo depleted the Ti content in the matrix on ageing to result in lower strength and conductivity [13].

The addition of cadmium to copper resulted in considerable solid solution strengthening with only a slight reduction in electrical conductivity [14]. Addition of 1.0 wt% Cd is known to improve the tensile strength as well as creep and fatigue resistance of copper [15]. The present work has therefore been taken up to study the effect of 1 wt% cadmium addition to binary Cu-4Ti alloy on the precipitation hardening and structure-property relationship in Cu-4Ti-1Cd alloy.

2. Experimental procedure

Cu-4 wt%Ti-1 wt%Cd was prepared by melting in a graphite crucible in a stokes vacuum induction melting (VIM) furnace and cast as 30 kg ingot. Oxygen-free high-conductivity (OFHC) copper, pure titanium and cadmium were used as raw materials. After homogenization at 800°C for 24 h, the ingots were analysed for its cadmium and titanium concentrations. The ingot was initially hot forged and then rolled at 850°C to 10 mm thick plates and 14 mm diameter rod. Specimens were cut from rods and solution treated at 860°C for 2 h and quenched rapidly in water. These samples were aged at 400, 450 and 500°C temperatures for different times. Vickers hardness (Hv) measurements using 10 kg load were made for solution treated samples at different times of ageing.

Threaded tensile samples, as per ASTM E8M-97 standard, with a gauge diameter of 6 mm and length 40 mm, were prepared in solution treated as well as peak aged (at 450°C) conditions and tested for tensile properties at ambient temperature in an Instron Universal Testing machine at the strain rate of 10^{-3} s^{-1}.

Optical microscopy of the alloy in solution treated, peak aged and over-aged conditions was carried out by mechanical polishing followed by etching in a solution of 10 gms $K_2Cr_2O_7$, 5 ml conc. H_2SO_4, 80 ml distilled water and 2 drops of HCl. Slices of 0.5 mm thickness cut from the alloys using a Buehler's Isomet low speed saw were mechanically polished to 50 μm thickness. Discs of 3 mm diameter were punched out from the thin slices and electropolished in a twin jet electro-polisher using an electrolyte of 30 vol% HNO_3 and 70 vol% methanol at −35°C and 30 V. The thin foils were examined at 120 kV/160 kV in a Jeol 200CX Transmission Electron Microscope. The fractured surfaces of tensile tested samples were examined in a Jeol 840A Scanning Electron Microscope.

The solution treated alloy rods were cold drawn to 2 mm diameter wire with intermittent annealing. Electrical resistance of 300 mm long wire in solution treated and aged conditions were measured using Microohmmeter, model no. OM-15 and electrical conductivity was evaluated as per ASTM B193-95 specifications.

3. Results

3.1. Hardness

Fig. 1 shows the influence of ageing time at different temperatures on the hardness of solution treated Cu-4Ti-1Cd alloy. The hardness of 238 Hv was obtained for solution treated Cu-4Ti-1Cd alloy, which on ageing at 400°C did not reach a peak value even after 48 h. The alloy attained a peak hardness of 318 Hv after ageing for 40 h at 450°C. A lower peak hardness of 290 Hv was recorded after ageing for 4 h at 500°C beyond which over-ageing was rapid.

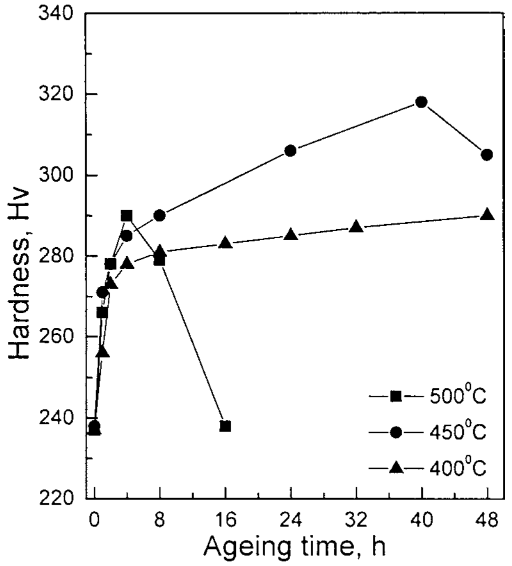

Figure 1 Age hardening behaviour of Cu-4Ti-1Cd alloy.

The effect of 1.0 wt% cadmium addition to Cu-4Ti alloy on age hardening is shown in Fig. 2. The hardening curves for the alloy Cu-4Ti-1Cd aged at 400, 450 and 500°C are respectively shown in Fig. 2a, b and c. The age hardening curves of binary Cu-4.5Ti alloy, as reported by Nagarjuna [16], are included in Fig. 2 for comparison. The hardness value of Cu-4Ti-1Cd alloy in solution treated condition is nearly same as that of Cu-4.5Ti alloy. The maximum hardness of ternary Cu-4Ti-1Cd alloy was observed to be similar to binary Cu-4.5Ti alloy in peak aged condition but the peak ageing time was very long (40 h) compared to binary alloy (16 h) at 450°C . However, over-ageing was very rapid in ternary Cu-4Ti-1Cd alloy after attaining peak hardness at 500°C compared to binary Cu-4.5Ti alloy.

3.2. Tensile properties

The tensile properties along with hardness and electrical conductivity of Cu-4Ti-1Cd alloy are compared with that of binary Cu-4.5Ti alloy [16] in Table I. The yield strength (YS) and ultimate tensile strength (UTS) of Cu-4Ti-1Cd alloy are higher than that of binary alloy in solution treated as well as peak aged conditions. The YS of the Cu-4Ti-1Cd alloy increased from 528 MPa in solution treated condition to 751 MPa on peak ageing while the corresponding increase in UTS has been from 754 to 894 MPa. These results show that the YS in Cu-4Ti-1Cd alloy has increased by 42% on peak ageing, while the corresponding increment in UTS was 18%.

The Cu-4Ti-1Cd alloy exhibited similar ductility as that of Cu-4.5Ti in solution treated and peak aged conditions. Ductility of solution treated Cu-4Ti-1Cd alloy was reduced by 38% on peak ageing.

The fractographs of the ternary alloy (Fig. 3) showed microvoid coalescence in all the conditions studied indicating that they are ductile in both solution treated and peak aged conditions.

3.3. Electrical conductivity

The effect of ageing time on electrical conductivity (%IACS) of Cu-4Ti-1Cd alloy at 400, 450 and 500°C is shown in Fig. 4a, b and c respectively. The electrical

TABLE I Mechanical properties of Cu-4Ti-1Cd, Cu-4.5Ti [16] and Cu-2Be-0.5Co alloys [19]

	Cu-4Ti-1Cd		Cu-4.5Ti		Cu-2Be-0.5Co	
	ST	ST+PA	ST	ST+PA	ST	ST+PA
YS (MPa)	528	751	350	680	170	1035
UTS (MPa)	754	894	630	850	415	1105
Hardness (Hv)	238	318	212	340	63Rb	43Rc
El (%)	29	18	29	20	35	1
EC (%IACS)	5.7	10.1	8.0	11.0	19	25

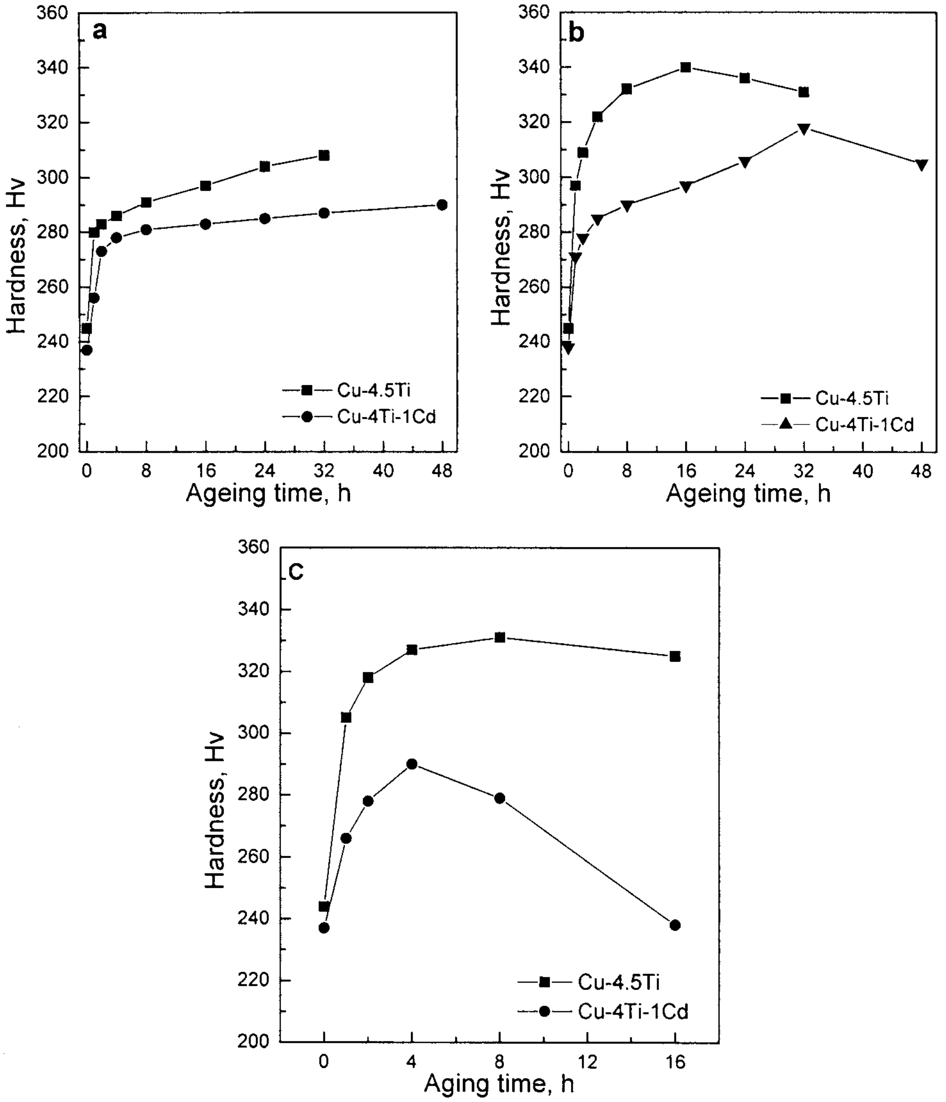

Figure 2 Age hardening of Cu-4.5Ti and Cu-4Ti-1Cd alloys at (a) 400°C, (b) 450°C, and (c) 500°C.

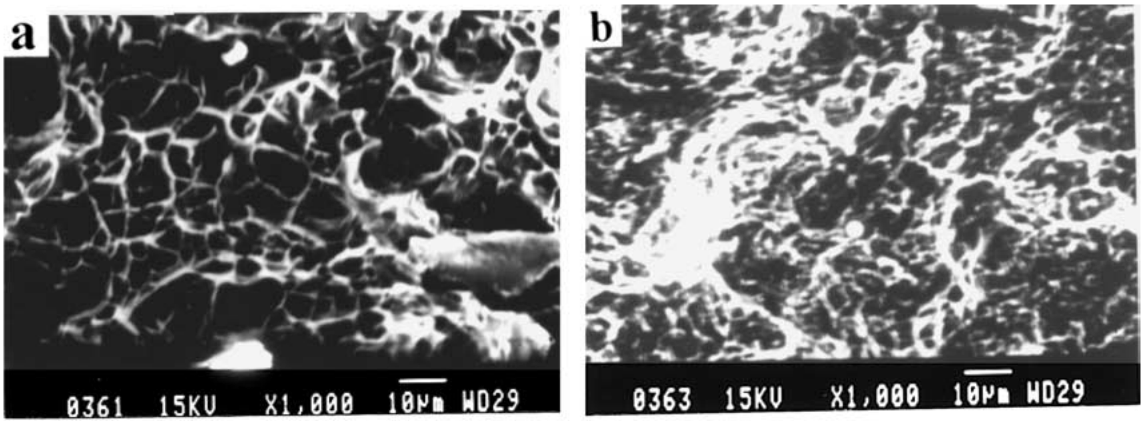

Figure 3 Fractographs of Cu-4Ti-1Cd alloy in (a) Solution treated and (b) Peak aged conditions.

conductivity curves of binary Cu-4.5Ti alloy with respect to ageing time are also included in these figures for comparison [16]. The EC of ternary Cu-4Ti-1Cd alloy was much lower than that of the binary Cu-4.5Ti alloy in solution treated as well as aged conditions. The solution treated Cu-4Ti-1Cd alloy exhibited an electrical conductivity of 5.7 %IACS, while it was 8.0 %IACS for the Cu-4.5Ti alloy. Ageing at 500°C for 2 h resulted in a considerable increase in conductivity i.e., from 5.7 to 9.5 %IACS for the ternary alloy. On further ageing at the same temperature to 16 h EC of ternary alloy has gone to 14.4 %IACS. On ageing at 450°C for 16 h, the Cu-4Ti-1Cd alloy exhibited an EC of 8.9 %IACS. Similarly, Cu-4Ti-1Cd alloy on ageing at 400°C for 16 h exhibits 7.1 %IACS. The addition of 1.0 wt% Cd to binary Cu-Ti alloy has thus resulted in a decrease in electrical conductivity in solutionised as well as aged conditions, while the effect was not so significant on

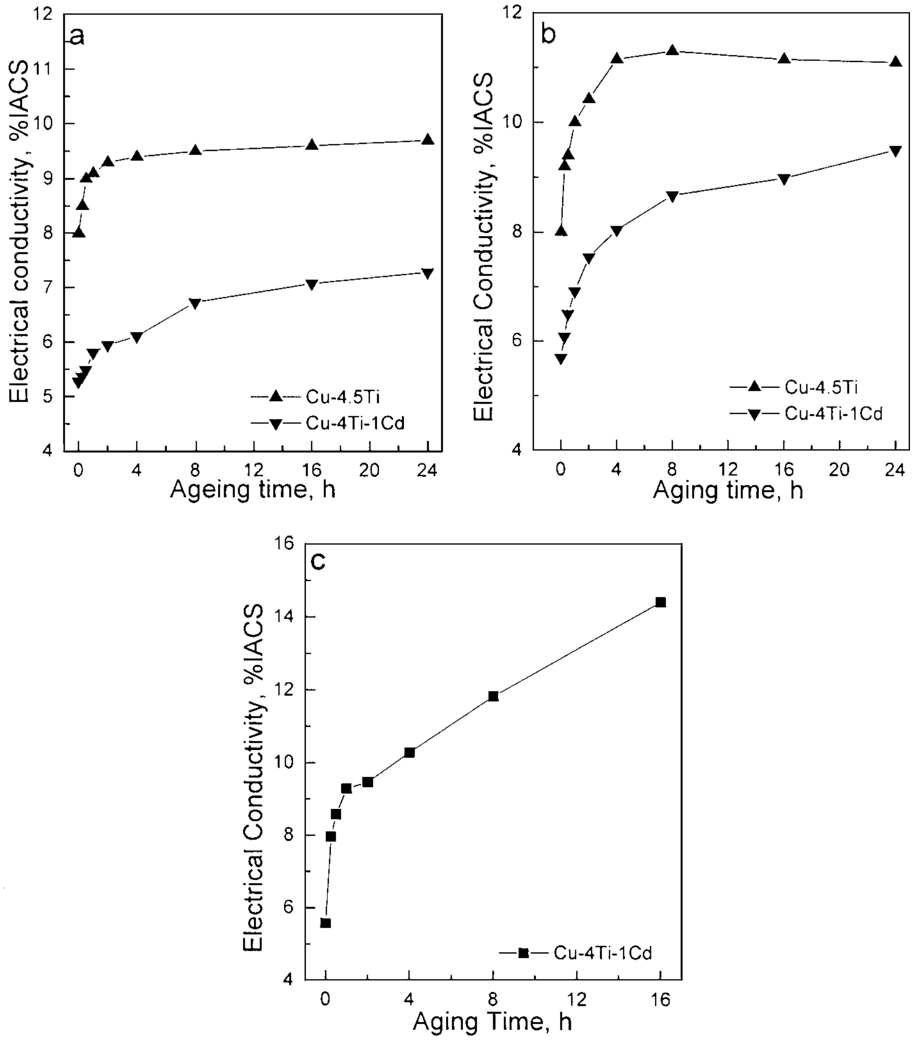

Figure 4 Variation in electrical conductivity of Cu-4.5Ti and Cu-4Ti-1Cd alloys at (a) 400°C, (b) 450°C, and (c) 500°C.

electrical conductivity when cadmium was added to copper [17].

3.4. Optical microscopy

Fig. 5 shows the optical micrographs of Cu-4Ti-1Cd alloy in solution treated, peak aged and over-aged conditions. Equiaxed grain structure with about 50 μm grain size was revealed for ST condition (Fig. 5a). For the ST+PA condition (450°C/40 h), few grain boundaries revealed signs of discontinuous precipitation (Fig. 5b). On further ageing at the same temperature a good amount of discontinuous precipitation was formed (Fig. 5c). Ageing at 500°C for 32 h resulted in more than 50% discontinuous precipitation (Fig. 5d).

3.5. Transmission electron microscopy

Transmission Electron Microscopy studies have been carried out to study the microstructural changes that took place on ageing the Cu-4Ti-1Cd alloy and also to evaluate precipitate-matrix orientations.

The transmission electron micrographs (TEMs) of Cu-4Ti-1Cd alloy in solution treated condition are shown in Fig. 6. Modulated structure with fine precipitates in bright field (BF) and dark field (DF) images are seen in Fig. 6a and b respectively. The corresponding selected area diffraction (SAD) pattern in Fig. 6c along with its schematic in Fig. 6d identifies the precipitate to be β' phase, with a stoichiometric composition of Cu_4Ti, having body-centered tetragonal (bct) structure with lattice parameters of $a = 5.84$ Å and $c = 3.62$ Å. The orientation relationships found for matrix and the precipitate are given below:

$$(1\ 0\ 1)_{\alpha}\ /\!/\ (1\ 3\ 2)_{\beta'}$$

$$(1\ 1\ 5)_{\alpha}\ /\!/\ (-1\ 2\ 1)_{\beta'} \quad \text{and}$$

$$[1\ -4\ 1]_{\alpha}\ /\!/\ [1\ 3\ -5]_{\beta'}$$

This agrees with the orientation relationships proposed by Datta and Soffa [6].

Fig. 7 shows the presence of annealing twins in the peakaged alloy (at 450°C). The BF and DF are shown in Fig. 7a and b respectively. The SAD given in Fig. 7c and its schematic in Fig. 7d reveals twinning of {1 1 1} type. Tweed structure with copious amount of precipitation was observed as shown in the BF and DF images, Fig. 7e and f. Fig. 7g was the corresponding SAD with its schematic in Fig. 7h, which identify the precipitate to be β'. A fine scale precipitation of β'-Cu_4Ti with modulated structure was also reported for Cu-4.5Ti alloy in

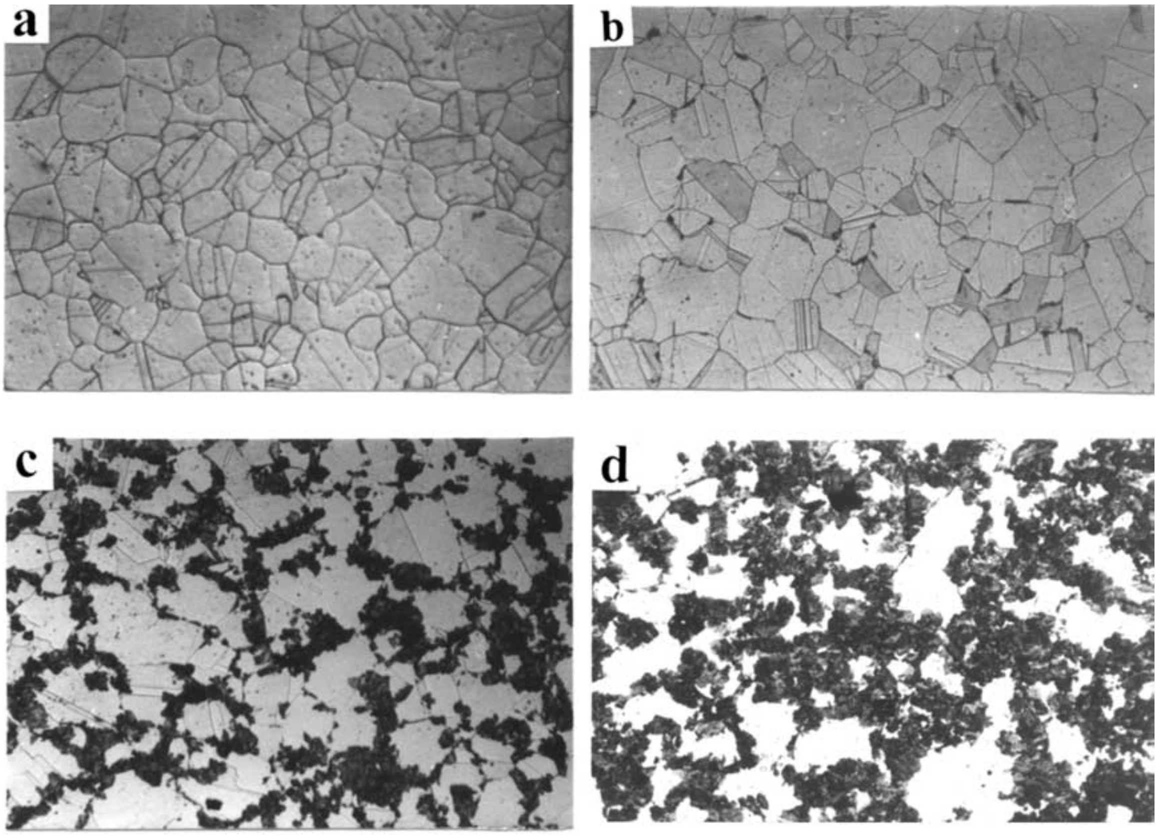

Figure 5 Optical micrographs of Cu-4Ti-1Cd alloy: (a) Solution Treated, (b) Peak aged at 450°C, (c) Overaged at 450°C, and (d) Overaged at 500°C.

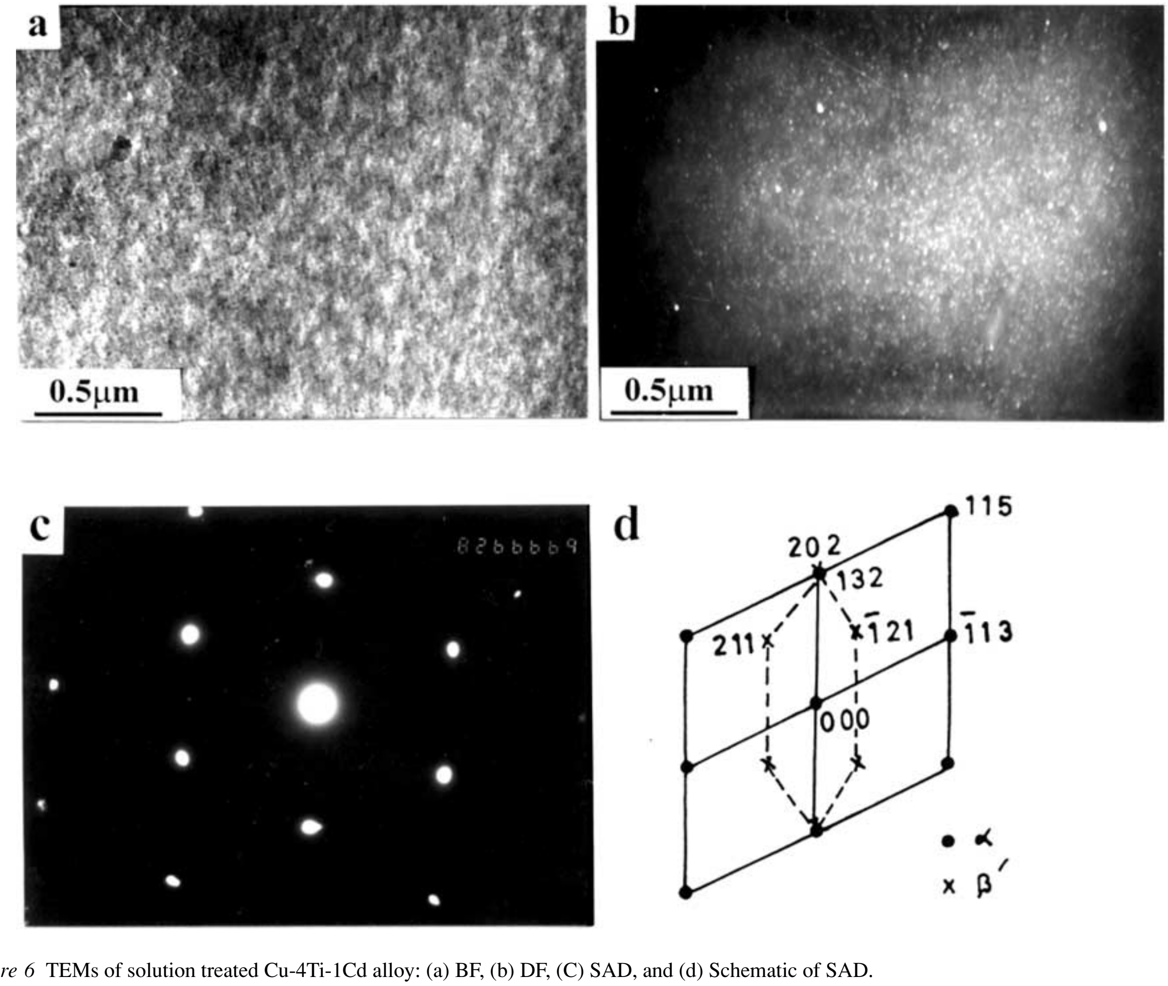

Figure 6 TEMs of solution treated Cu-4Ti-1Cd alloy: (a) BF, (b) DF, (C) SAD, and (d) Schematic of SAD.

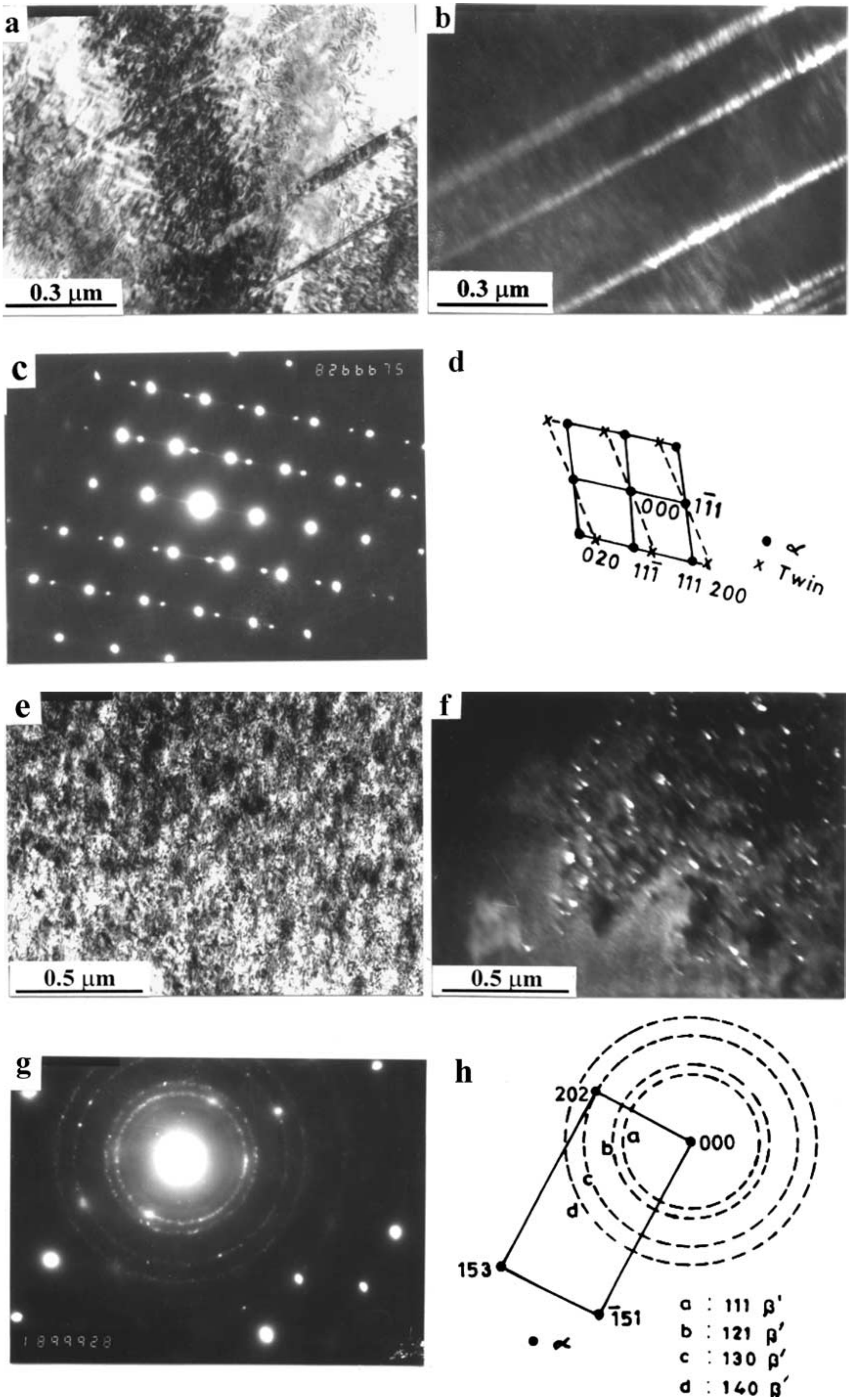

Figure 7 TEMs of peak aged Cu-4Ti-1Cd alloy showing annealing twins: (a) BF, (b) DF, (c) SAD, (d) Schematic of SAD; and modulated structure, (e) BF, (f) DF, (g) SAD, and (h) Schematic of SAD.

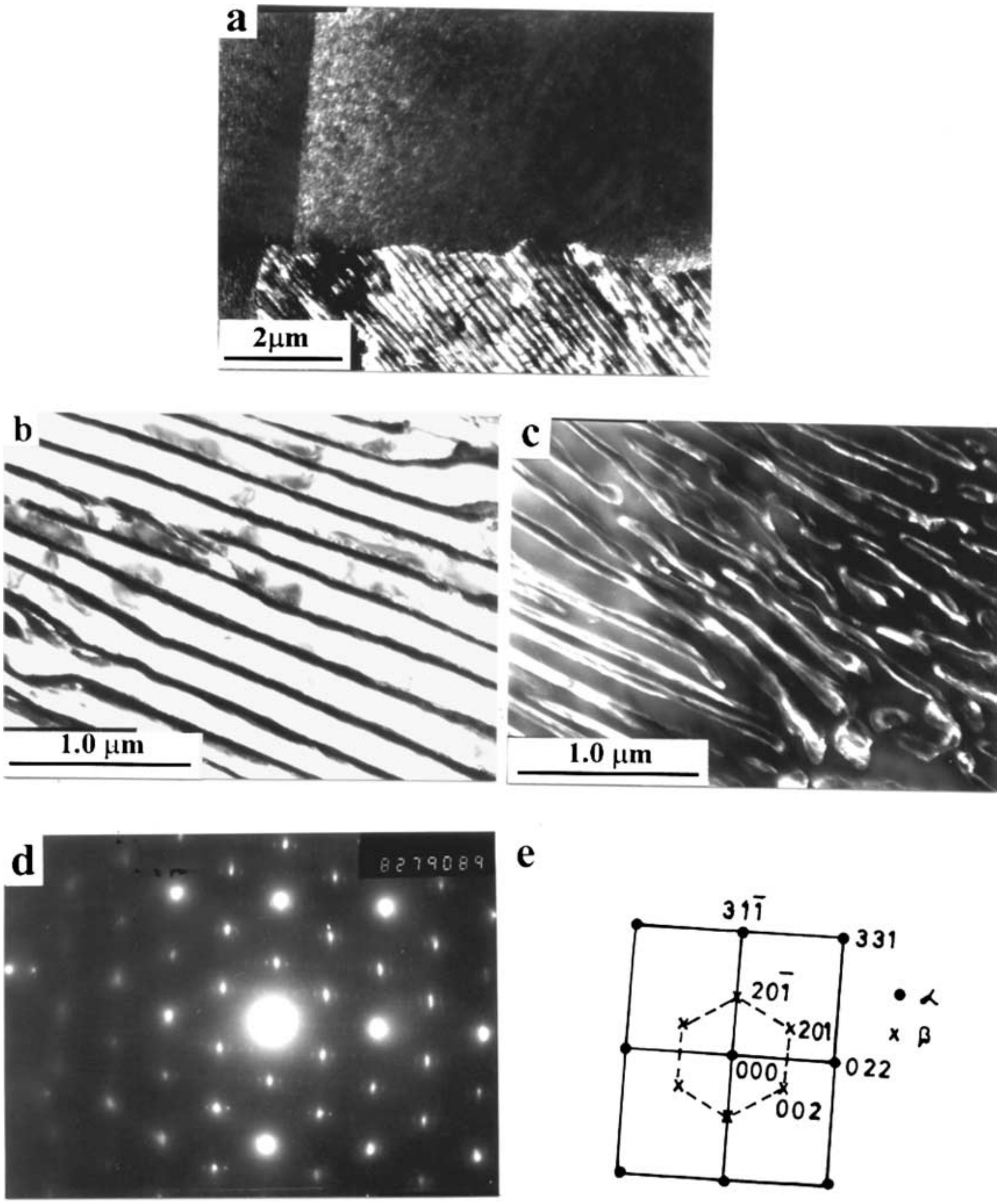

Figure 8 TEMs of Cu-4Ti-1Cd alloy overaged at 450°C. (a) Grain boundary between matrix and discontinuous precipitation. (b) & (c) BF and DF of discontinuous precipitation. (d) & (e) SAD and Schematic of SAD of equilibrium phase, β.

solution treated condition; while on peak aging copious amount of fine precipitate β'-Cu_4Ti were present [10].

When the alloy was over-aged at 450°C for 88 h, in addition to the continuous precipitation in the matrix, discontinuous precipitation was observed in several locations as could be seen in Fig. 8a. Fig. 8b and c show BF and DF from a grain boundary region exhibiting the discontinuous precipitation. The SAD and its schematic shown in Fig. 8d and e respectively identify the precipitate to be the equilibrium β phase having an orthorhombic crystal structure having lattice parameters $a = 5.162$ Å, $b = 4.347$ Å and $c = 4.53$ Å. On overaging (450°C/32 h) discontinuous precipitation with an equilibrium phase β-Cu_3Ti was reported for the binary alloy [10].

Peak ageing was observed in a short duration (4 h) of ageing the ternary alloy at 500°C as compared to 450°C (40 h in case of Cu-4Ti-1Cd alloy) accompanied by slight coarsening of modulated structure but with a predominant fraction of discontinuous precipitation. Fig. 9 shows the TEMs of the alloy aged at 500°C for 16 h where over-aging was observed. Fig. 9a and b are BF and DF images of discontinuous precipitation in Cu-4Ti-1Cd alloy, while Fig. 9c and d are SAD of the precipitate and its sketch respectively.

4. Discussion

4.1. Solution treatment

The present investigation shows that the addition of 1% cadmium has resulted in a substantial increase in yield

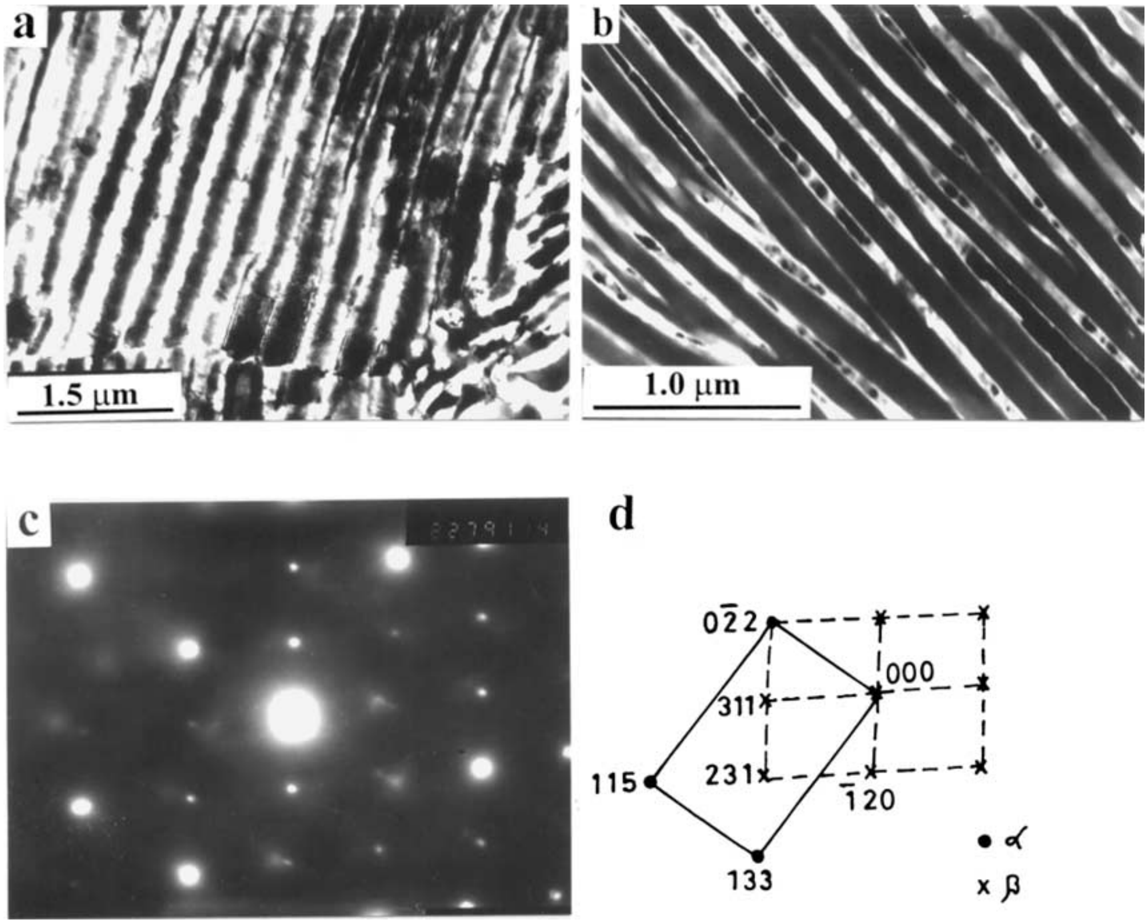

Figure 9 TEMs of Cu-4Ti-1Cd alloy over aged at 500°C showing discontinuous precipitation. (a) BF, (b) DF, (C) SAD, and (d) Schematic of SAD.

strength and tensile strength in 4 wt% titanium alloy in the solution treated condition (Table I). The YS of the Cu-4Ti-1Cd alloy was higher by 51% compared to the Cu-4.5Ti alloy in solution treated condition studied by Nagarjuna *et al.* [10], which corresponding increase in tensile strength was 20%. Tweed structure was seen in the present alloy during quenching itself. Like in the binary Cu-Ti alloy, the Cu-4Ti-1Cd alloy had higher YS because of the modulated structure in the solution treated condition.

The atomic misfit between copper and cadmium is 16.4%, which is the primary reason for the large solid solution strengthening effect in copper. The amount of titanium present in ternary alloy is also less than that of the alloy studied by Nagarjuna *et al.* [10]. The increase in YS and UTS is, however, much higher in Cu-4Ti-1Cd alloy in the solution treated condition because of the solid solution strengthening effect of cadmium.

The solubility of cadmium in copper at 549°C (eutectic temperature) is 3.72 and <0.5 wt% at room temperature [17]. Since 1.0 wt% Cd is added to the ternary alloy, all the cadmium is expected to retain in solid solution on water quenching during solution treatment. Datta and Soffa reported that modulated structure cann't be obtained on solution treatment in binary Cu-Ti alloys up to 4 wt% Ti in Cu [6]. In the present investigation, the modulated structure has formed in solution treated condition itself (Fig. 5) in ternary alloy, which is in agreement with earlier study on binary alloys by Piotrowski and Gawrouski [11].

The presence of fine spherical precipitates of metastable β'-phase with a stoichiometric composition of Cu_4Ti in the solution treated condition itself reveals that the precipitation kinetics is very rapid in the Cu-4Ti-1Cd alloy. The strains associated with the modulated structure as well as β' precipitates have increased the YS considerably but decreased the electrical conductivity. The conductivity has gone down by 30% for the ternary alloy compared to binary Cu-4.5Ti alloy in solution treated condition.

The Cu-4Ti-1Cd alloy has shown good ductility with 29%El in the solution treated condition and is similar to that of Cu-4.5Ti alloy studied by Nagarjuna *et al.* [10].

4.2. Peak ageing

The YS and UTS of the present Cu-4Ti-1Cd alloy are considerably increased on ageing. The increments in YS and UTS are 42 and 18% compared to 94 and 35% for the binary Cu-4.5Ti alloy studied by Nagarjuna *et al.* [10]. The increments in Cu-4Ti-1Cd alloy are low since the YS and UTS increased considerably during solution treatment itself by solid solution strengthening as well as the formation of modulated structures.

The peak ageing time got considerably delayed due to 1% Cd addition, from 16 to 40 h at 450°C, though the mechanism of age hardening is not changed. The precipitation of metastable β'-Cu_4Ti phase by spinodal decomposition is responsible in both binary and ternary alloys [8–10], as shown in Fig. 8. The increase in YS due to Cd addition is attributed primarily to its solid solution strengthening effect.

The electrical conductivity of Cu-4Ti-1Cd alloy is comparable to that of binary Cu-4.5Ti alloy in aged condition. Addition of 1.0 wt% cadmium to pure copper lowered the electrical conductivity to 90 %IACS [18] where as Cu-4Ti-1Cd alloy has shown 10 %IACS on peak ageing as compared to 11 %IACS for Cu-4.5Ti alloy [10]. Therefore, the addition of cadmium to Cu-Ti alloy has improved the strength properties, but lowered the electrical conductivity. During ageing, as the titanium comes out of the matrix (solid solution) to form precipitation of metastable phase (β'), the electrical conductivity increases.

4.3. Over ageing

The discontinuous precipitation at grain boundaries of the matrix can be seen in optical micrographs (Fig. 5c and d) of the ternary alloy in the over-aged condition. The loss of coherency strains associated with the precipitation of Cu_3Ti (β) with in the matrix α-phase as well as discontinuous precipitation at the grain boundaries seen in the present over-aged ternary alloy (Fig. 9) are responsible for the decrease in the hardness and strength of the alloy (Table I). Datta and Soffa [6] have also attributed the over-aging in binary Cu-4Ti alloy to the cellular precipitation occurring along the grain boundaries.

There have been a few earlier investigations to evaluate the effects of ternary alloying elements on the structure and properties of Cu-Ti alloys. Piotrowski and Gawrouski [11] observed that 0.23% vanadium retards continuous precipitation of metastable phase β' in Cu-Ti alloys and increased the rate of kinetics of discontinuous precipitation. Bozic and Mitkov [12] studied Cu-Ti-B alloys via rapid solidification route and reported that development of modulated structure, precipitation of metastable Cu_4Ti and the dispersion of primary TiB_2 resulted in a good combination of strength and conductivity.

Nagarjuna *et al.* [13] reported that the addition of cobalt up to 1.8% to Cu-4.5Ti alloy resulted in the formation of Ti_2Co and TiCo phases as undissolved particles while the hardening precipitate was Cu_4Ti. The undissolved particles depleted Ti from solid solution and reduced both the strength and electrical conductivity of the alloy.

5. Conclusions

1. A modulated structure with fine scale precipitation of Cu_4Ti (β') is obtained in Cu-4Ti-1Cd alloy resulting in improved yield and tensile strengths in solution treated condition. The role of cadmium is in causing substitutional solid solution strengthening in the ternary alloy.
2. Peak ageing at 450°C is delayed in the ternary Cu-4Ti-1Cd alloy compared to corresponding Cu-4.5Ti binary alloy. The precipitation of β'-Cu_4Ti is responsible for age hardening behaviour in the ternary alloy.
3. Discontinuous precipitation is noticed in the ternary alloy when the alloy is over-aged at 450 and 500°C.
4. The electrical conductivity of Cu-4Ti-1Cd alloy is less than that of Cu-4.5Ti alloy in both solution treated and aged conditions.

Acknowledgements

The authors greatly acknowledge the Head, Department of Metallurgical Engineering, IT, BHU, Varanasi, for providing laboratory facilities. The authors are thankful to the Defence Research and Development Organisation, New Delhi, for financial support. The authors wish to thank Director, Defence Metallurgical Research Laboratory, Hyderabad, for permission to carry-out some experimental work. One of the authors (RM) is thankful to Jawaharlal Nehru Technological University, Hyderabad for granting leave under QIP.

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Received 16 June
and accepted 28 October 2003