

Effect of prior cold work on mechanical properties and structure of an age-hardened Cu–1.5wt% Ti alloy

S. NAGARJUNA, K. BALASUBRAMANIAN*

*Defence Metallurgical Research Laboratory, and *Non-Ferrous Materials Technology Development Centre, Kanchanbagh-PO, Hyderabad 500 058, India*

D. S. SARMA

Department of Metallurgical Engineering, Banaras Hindu University, Varanasi 221 005, India

The effects of prior cold work on hardness, tensile properties, electrical conductivity and microstructure of an aged Cu–1.5 wt % Ti alloy have been studied by employing hardness and resistivity measurements, tensile tests and scanning and transmission electron microscopy. The hardness increased from 80 VHN in the solution-treated condition, to 210 VHN on peak ageing and 280 VHN with prior cold work followed by ageing. While a similar trend has been observed in yield and tensile strengths, the ductility (percentage elongation) decreased from 45% to 9%. The electrical conductivity of the alloy also increased up to 26% International annealed copper standard upon ageing the cold-worked alloy. Maximum strengthening of the alloy was associated with the precipitation of metastable, coherent and ordered Cu_4Ti , β' phase having body-centred tetragonal structure. The differences in the properties and microstructural evolution between low and high titanium alloys (for example, the absence of composition modulations and deformation twins in Cu–1.5 Ti alloy, while they are present in Cu–4.5 Ti alloy) have been discussed. Prior cold work did not change the fracture mode of microvoid coalescence.

1. Introduction

Worldwide research on Cu–Ti alloys has been mainly aimed at developing a substitute for Cu–Be alloys which are highly expensive and pose health hazards during manufacture and processing, due to toxicity of beryllium metal. It is now well established that Cu–Ti alloys containing up to about 5.5 wt % Ti, can develop very high strength levels through precipitation hardening [1]. The following sequence of decomposition was found to occur in these alloys [2–5]:

- (i) spinodal decomposition leading to long-range composition fluctuations and modulated structures;
- (ii) formation of ordered, metastable and coherent Cu_4Ti , β' precipitates;
- (iii) growth of the Cu_4Ti precipitates;
- (iv) loss of coherency and formation of the equilibrium phase, $\beta\text{Cu}_3\text{Ti}$.

Earlier studies on Cu–Ti alloys were confined to mechanisms of spinodal decomposition, structure and property (mostly hardness and tensile properties, up to some extent) changes during ageing [6–17]. Further, work on the effects of prior cold work was limited to hardness and microstructural investigations in high titanium containing Cu–Ti alloys [1, 18–21]. However, little work has been reported on the effects of prior cold deformation on tensile properties and electrical conductivity in Cu–Ti alloys with low titanium contents. Therefore, we have undertaken a project to

investigate the effects of prior cold work on hardness, tensile properties, electrical conductivity and microstructure during ageing of Cu–Ti alloys containing low (< 3 wt %) and high (> 3 wt %) titanium contents. Results on a Cu–4.5 wt % Ti (high titanium content) alloy have been reported [22] recently, in which we have shown that the properties of the cold-worked and aged alloy approach those of the commercial Cu–2Be–0.5Co alloys.

The aim of the present investigation was to study the influence of ageing on the structure and properties of a Cu–1.5 wt % Ti alloy with and without prior cold work and also to determine if the properties are comparable with those of the commercial Cu–0.5Be–2.5Co alloy. This paper presents the results obtained on age-hardening curves, tensile properties, electrical conductivity and transmission electron microscopy (TEM) of the alloy in different tempers.

2. Experimental procedure

A 30 kg melt of Cu–Ti alloy with an aimed titanium content of 1.5 wt % was made in a vacuum induction melting (VIM) furnace with Cu–Ti master alloy and 99.99% purity oxygen-free electronic copper (OFEC) as charge material. The liquid alloy was poured into a graphite mould and cooled in the mould chamber of the VIM furnace. The ingot was homogenized and

analysed for titanium content. The chemical analysis showed that the analysed composition matched the aimed titanium content with ± 0.1 wt % accuracy. The ingot was hot forged and rolled at 800 °C to obtain 10 mm thick plates and 12 mm diameter rods.

Samples from hot-rolled plate were solution treated at 900 °C for 2 h and rapidly quenched in water. These samples were aged at different temperatures (400, 450, 500 and 550 °C) and their hardness (VHN) was measured. The solution-treated samples were cold-rolled giving different amounts of cold deformation. The hardness of the cold-deformed samples was measured after ageing at 400, 450 and 500 °C. Flat tensile samples with 25 mm gauge length, as per the ASTM specification E 8M-89b [23] (sub-size specimen) were made from the solution-treated and cold-rolled strips, peak aged at 400 °C and tested for tensile properties. The tensile-tested specimens were observed under a scanning electron microscope (SEM) to identify the mode of fracture occurring in this alloy with and without prior cold deformation.

Rod samples after solution treatment (900 °C/2 h/WQ), were cold drawn giving 30% and 95% reduction in area, to a final diameter of 2 mm. Electrical resistance of these wires was measured using Kelvin Bridge apparatus at room temperature in solution-treated, aged, as-cold drawn, and cold drawn and aged (at 400 and 450 °C) conditions. Electrical conductivity was determined according to the ASTM specification B 193-89 [24].

Optical metallography of the alloy was carried out in solution-treated (ST), peak-aged (PA), overaged, solution-treated + cold-worked (CW) and ST + CW + PA conditions. Thin foils for TEM were prepared both from sheet and rod materials. Discs and sheet samples were mechanically polished to 10–15 μm . Discs, 3 mm in diameter, were punched out from the thinned specimens and electropolished in a twin-jet electropolisher, using a solution of 30 vol % nitric acid and 70 vol % methanol at -45 °C and at a voltage of 10 V. The thin foils were examined at 160 kV using Jeol 200 CX TEM.

3. Results

3.1. Mechanical properties

The effect of ageing time on the hardness of solution-treated Cu–1.5 wt % Ti alloy at different temperatures is shown in Fig. 1. While the alloy has not attained peak hardness at 400 °C even after ageing for 32 h, a peak hardness of 210 VHN was reached after ageing at 450 °C for 16 h beyond which the hardness decreased gradually with increasing time. The peak hardness was slightly lower (198 VHN) and overageing was rapid on ageing at 500 °C. The overageing was drastic and peak hardness was further lowered to 180 VHN when aged at 550 °C.

The influence of prior cold work on the hardness of the alloy after ageing at 400, 450 and 500 °C is shown in Fig. 2–4, respectively. At all ageing temperatures, increasing the amount of cold work (20% to 80%) caused an improvement in the peak hardness (the

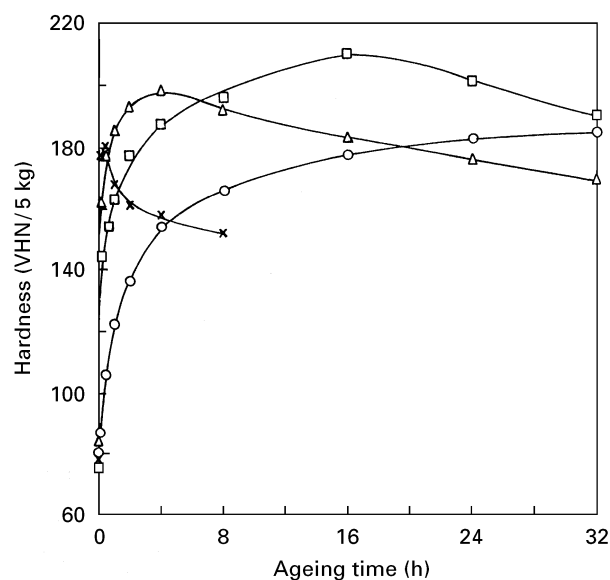


Figure 1 Age hardening in Cu–1.5 wt % Ti alloy at (○) 400 °C, (□) 450 °C, (△) 500 °C, (×) 550 °C.

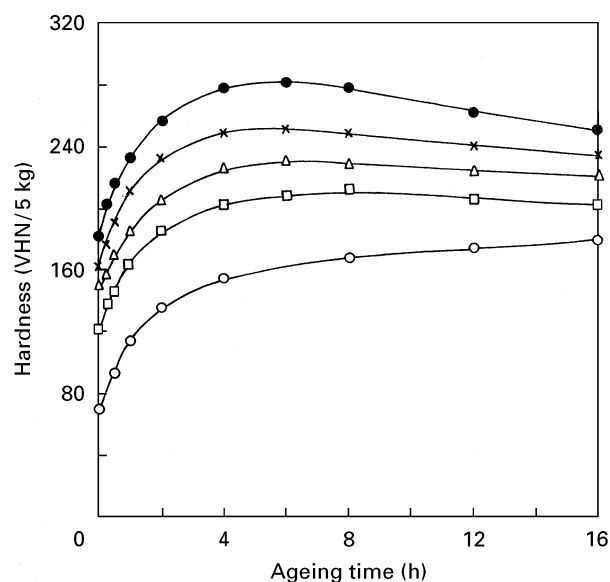


Figure 2 Effect of prior cold work on age hardening in Cu–1.5 wt % Ti at 400 °C: (●) 80%, (×) 60%, (△) 40%, (□) 20% and (○) 0% cold rolled.

highest hardness measured was 280 VHN after 80% cold work followed by ageing at 400 °C for 6 h). The overageing of cold-worked alloy was marginal at 400 °C, considerable at 450 °C and drastic at 500 °C. For example, the hardness of the 80% cold-worked alloy aged at 500 °C for 12 h was lower than that of the undeformed and aged one.

The variation of tensile properties of the alloy with prior cold-work followed by peak ageing at 400 °C, are shown in Fig. 5. As seen from the hardness curves, the increasing amount of cold work has raised the yield strength from 350 MPa to 680 MPa and tensile strength, from 520 MPa to 760 MPa. The elongation, however, decreased from 23% in the undeformed state, to 9% with 90% cold work and peak ageing at 400 °C.

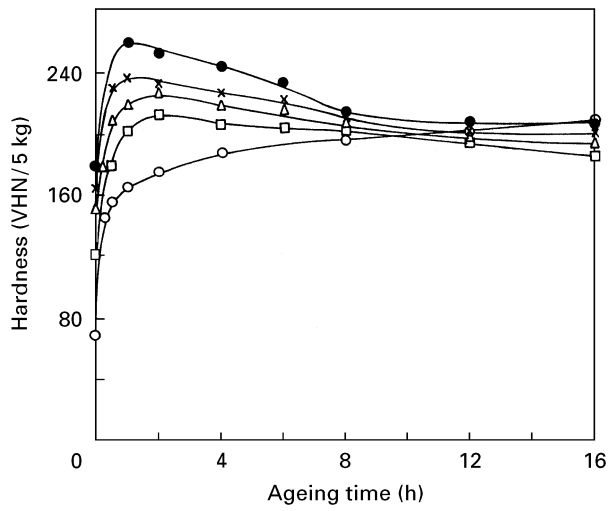


Figure 3 Effect of prior cold work on age hardening in Cu-1.5 wt % Ti alloy aged at 450 °C: (●) 80%, (×) 60%, (△) 40%, (□) 20% and (○) 0% cold rolled.

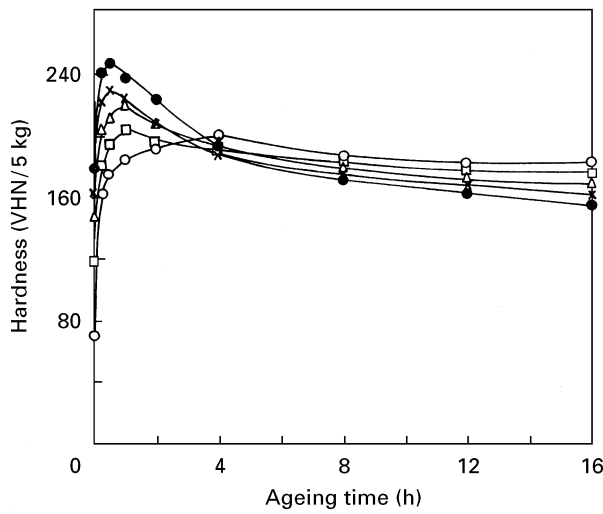


Figure 4 Effect of prior cold work on age hardening in Cu-1.5 wt % Ti alloy aged at 500 °C: (●) 80%, (×) 60%, (△) 40%, (□) 20% and (○) 0% cold worked.

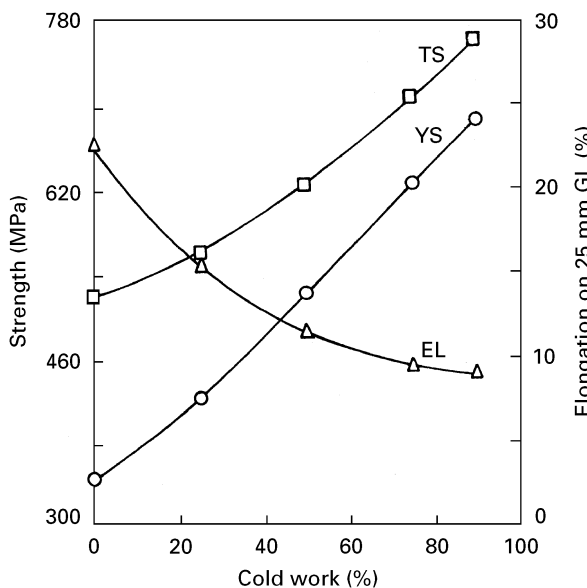


Figure 5 Effect of prior cold work on tensile properties of Cu-1.5 wt % Ti alloy peak aged at 400 °C .

3.2. Electrical conductivity (EC)

The influence of ageing time at 400 and 450 °C on the EC of the alloy in the undeformed as well as cold-drawn conditions is shown in Fig. 6. The EC of the alloy was found to be 15.5% International Annealed Copper Standard (IACS) in the solution-treated condition and reduced to 13.5% and 10.5% IACS, respectively, with 30% and 95% cold deformations. During ageing, the EC of the undeformed alloy increased to 22.5% IACS at 400 °C and 24.5% IACS at 450 °C for 12 h and remained constant thereafter.

The 30% deformed alloy exhibited similar trend on ageing, showing an increase in the EC up to 23% IACS at 400 °C and 25% IACS at 450 °C. The change in EC due to ageing of the alloy with 95% deformation

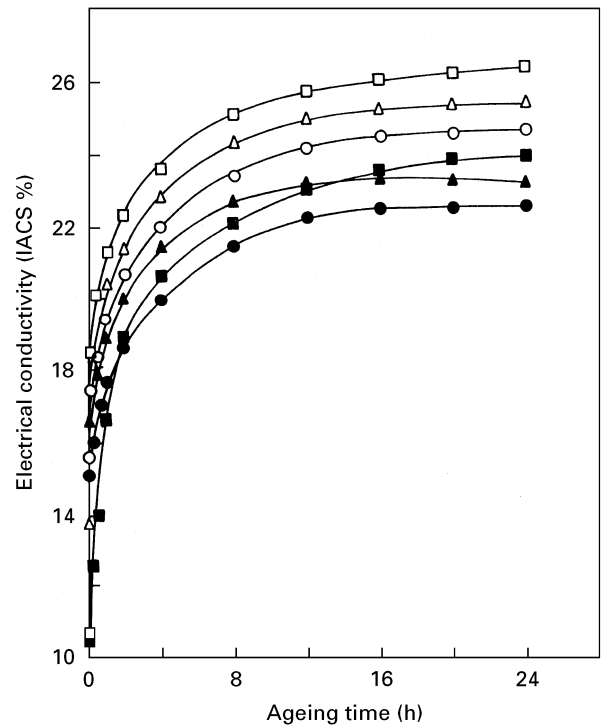


Figure 6 Effect of ageing time and (●, ○) 0%, (▲, △) 30% and (■, □) 95% prior cold work on electrical conductivity in Cu-1.5 wt % Ti alloy at (●, ▲, ■) 400 °C and (○, △, □) 450 °C.

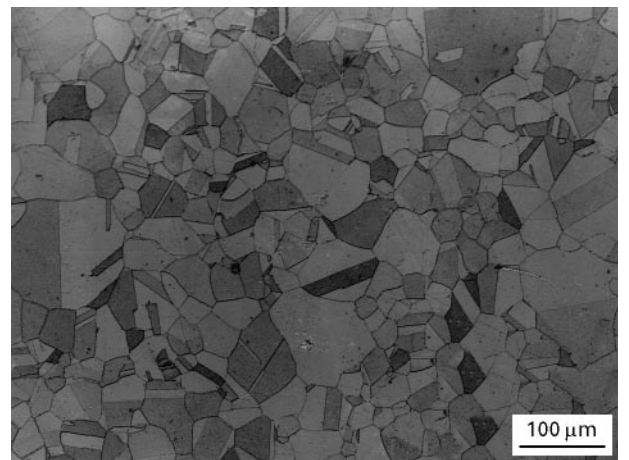


Figure 7 Optical microstructure of Cu-1.5 wt % Ti alloy overaged at 500 °C for 16 h.

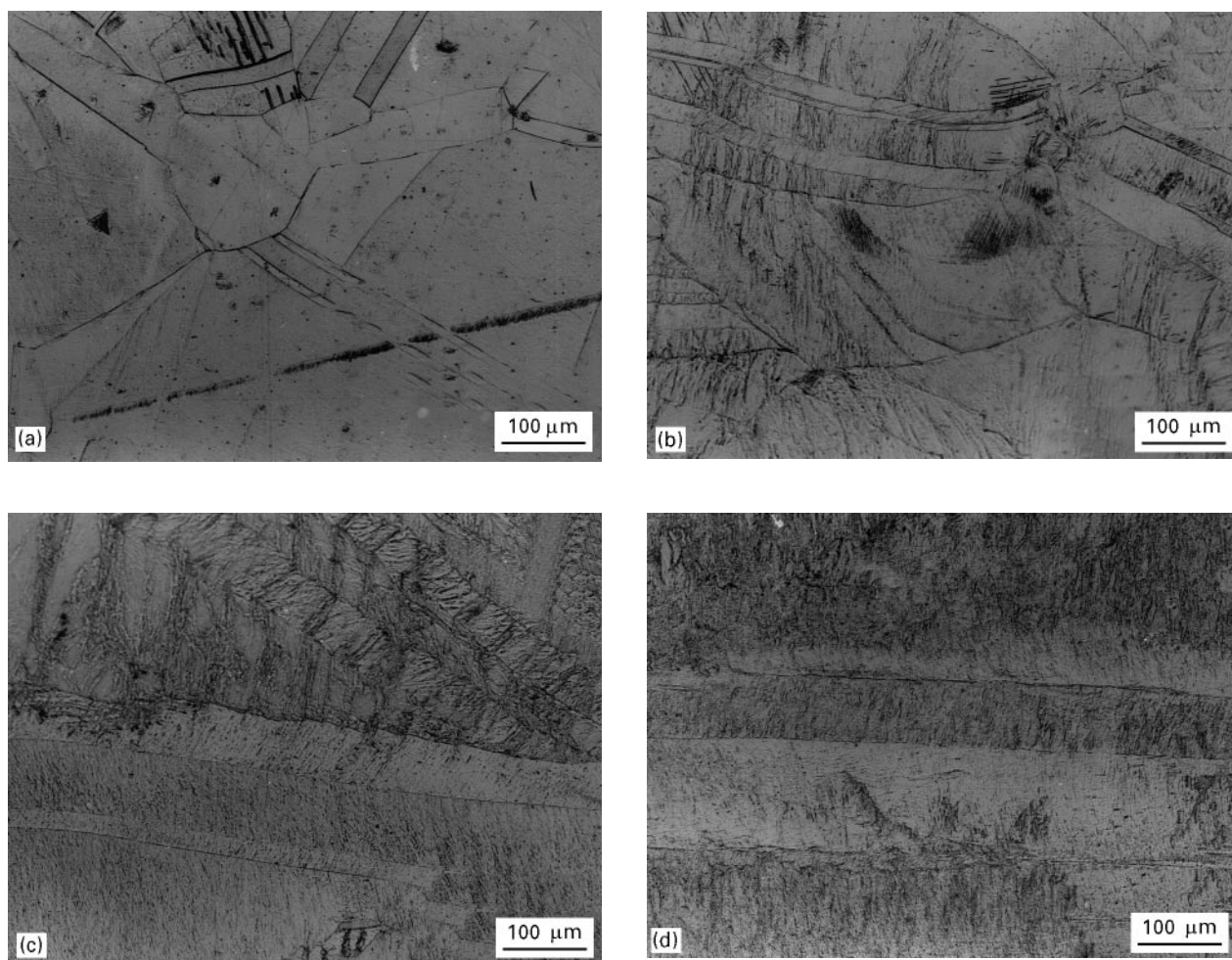


Figure 8 Optical microstructures of Cu–1.5 wt % Ti alloy with different amounts of cold work. (a) 25%, (b) 50%, (c) 75%, and (d) 90%.

was also similar to the trends shown above, exhibiting values of 24% IACS at 400 °C and 26.5% IACS at 450 °C for 24 h ageing.

3.3. Microstructural observations

Optical microscopy of the alloy in the solution-treated (900 °C) as well as peak-aged (450 °C) conditions, revealed equiaxed grains containing annealing twins. The optical microstructure of the alloy overaged at 500 °C for 16 h is shown in Fig. 7, which is also observed to be similar to that of the solution-treated or peak-aged alloy. Further, no discontinuous precipitation has been noticed in the overaged alloy. Optical micrographs of the alloy with different amounts of cold work are shown in Fig. 8. Deformation of grains has started in the alloy cold-worked by 25% (Fig. 8a) and fully elongated grains are seen in the 90% worked sample in Fig. 8d. The grain size in Fig. 8a–d is coarse, because these samples were solution treated at 900 °C. However, the optical micrograph in Fig. 7 shows a fine grain size which corresponds to the solution treatment at 750 °C. The solution-treatment temperatures resulting in the finest grain size possible in Cu–Ti alloys, have been established with extensive studies on grain-size strengthening by the present authors [25–28]. Ageing of the cold-worked alloy at 400 °C did not have any significant effect on the optical microstructure.

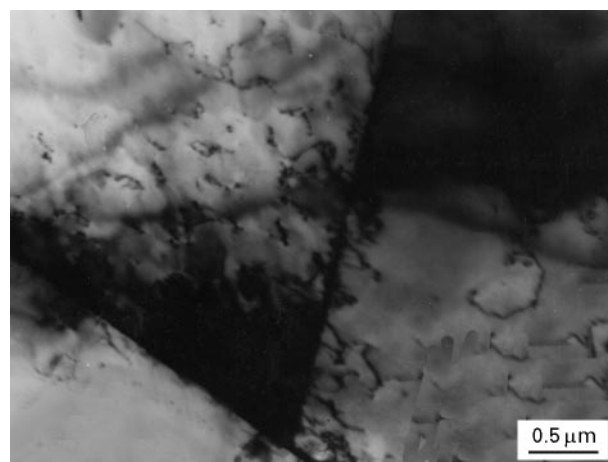


Figure 9 Transmission electron micrograph of Cu–1.5 wt % Ti alloy in the solution-treated condition.

A transmission electron micrograph of the solution-treated alloy is shown in Fig. 9. Grain boundaries with a triple junction and dislocations within the grain are seen here. Further, the microstructure does not reveal any modulations or precipitates. Fig. 10 shows the microstructure of the alloy peak aged at 400 °C for 96 h. The bright-field (BF) image shows an annealing twin and fine precipitates (Fig. 10a) of β' phase (Cu_4Ti) with a body-centred tetragonal (bct) crystal structure ($a = 0.584$ nm and $c = 0.362$ nm), as

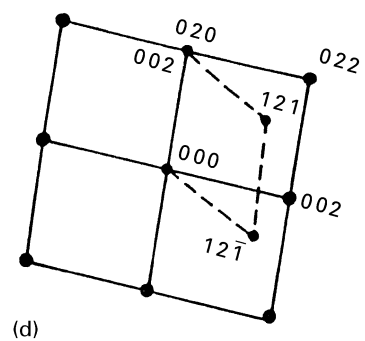
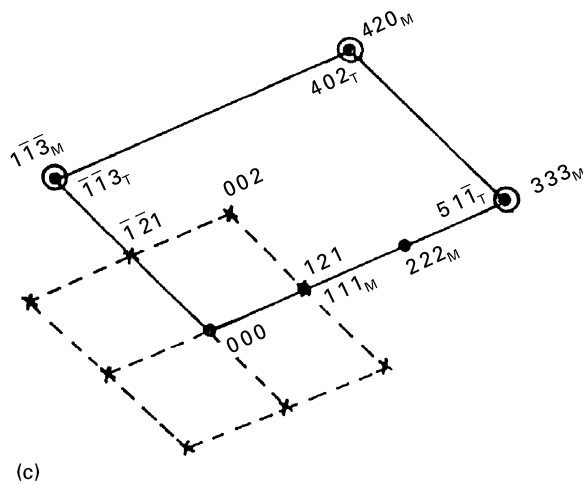
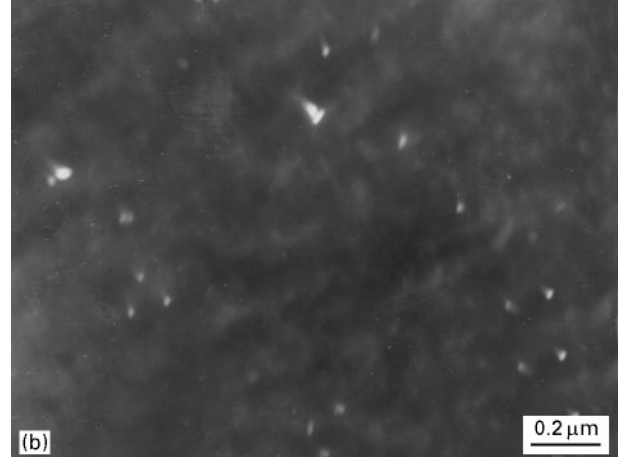
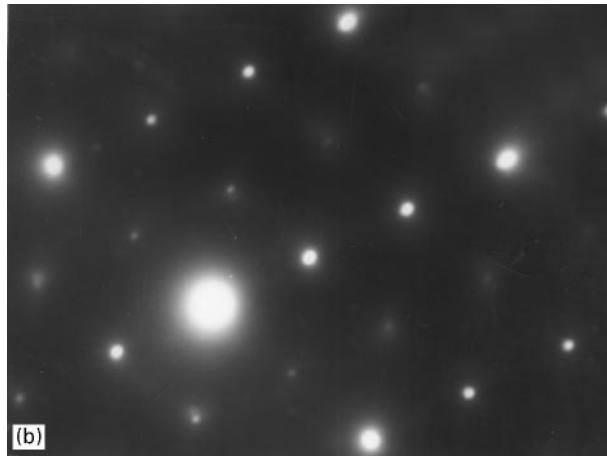
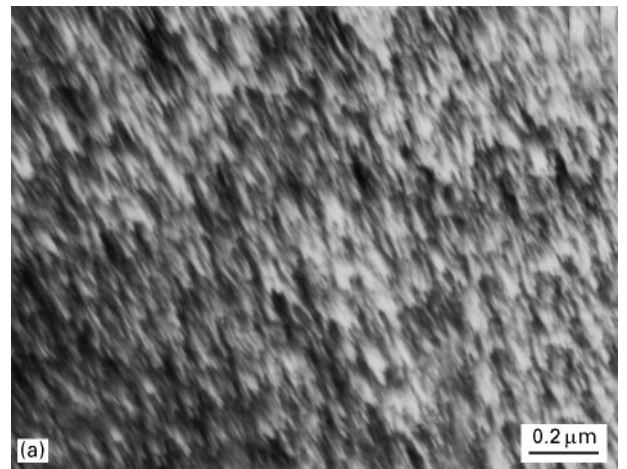
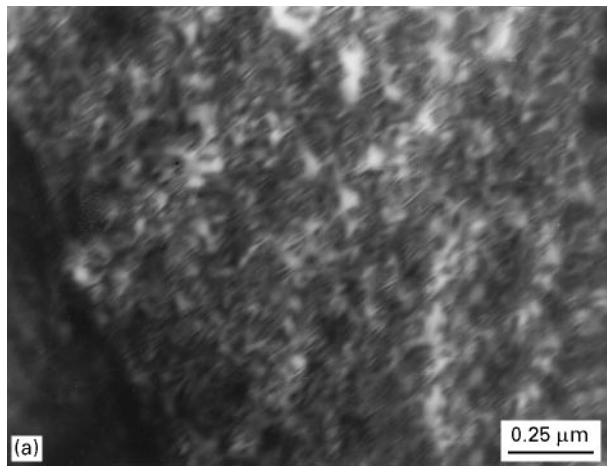


Figure 10 Transmission electron micrographs of Cu-1.5 wt % Ti alloy peak aged at 400 °C for 96 h: (a) BF image, (b) SAD pattern, and (c) schematic drawing of the SAD pattern: (—○) matrix, M, (—●) twin, T, (---) precipitate β' .

confirmed by the selected-area diffraction (SAD) pattern (Fig. 10b) and its schematic drawing (Fig. 10c). Reflections due to the annealing twin are also seen in Fig. 10b and c. Ageing of the solution-treated alloy at 450 °C for 16 h (peak ageing) also resulted in the precipitation of β' (Cu_4Ti) phase. Fig. 11a shows the BF image and Fig. 11b, the dark-field (DF) image of the precipitates. The SAD pattern and its schematic drawing in Fig. 11c and d confirm the precipitates to be β' (Cu_4Ti).

Figure 11 Transmission electron micrographs of Cu-1.5 wt % Ti alloy peak aged at 450 °C for 16 h: (a) BF image, (b) DF image, (c) SAD pattern, and (d) schematic drawing of the SAD pattern: (—) matrix, (---) precipitate β' .

The β' precipitates have coarsened upon overageing at 450 °C for 50 h, as seen in Fig. 12a and b, the BF and DF images, respectively. It is evident from the SAD pattern and its schematic drawing (Fig. 12c and d) that even after overageing at 450 °C for 50 h, only β' phase is seen and equilibrium phase has not formed. Overageing of the alloy at 500 °C for 16 h has, however, resulted in the formation of the equilibrium precipitate. The BF and DF images in Fig. 13a and b reveal the presence of coarse precipitates. From the SAD pattern and its schematic drawing in Fig. 13c and d, the precipitates have been identified to be the equilibrium phase, β , Cu_3Ti , having an orthorhombic crystal structure with lattice parameters $a = 0.5162$ nm, $b = 0.4347$ nm and $c = 0.453$ nm.

On cold rolling to 25% reduction in thickness after solution treatment, the alloy exhibited dislocation cells, as revealed by the BF image in Fig. 14a. Ageing the cold-worked (25%) alloy at 400 °C for 8 h (peak ageing) revealed fine-scale precipitates of β' , Cu_4Ti phase (Fig. 14b). Overageing of the 25% cold-worked alloy at 400 °C for 16 h has only coarsened the precipitates.

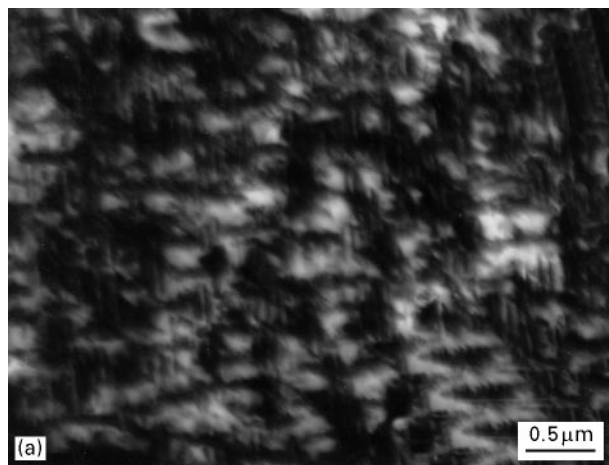


Fig. 15 shows transmission electron micrographs of 90% cold-worked alloy. While elongated grains are revealed in Fig. 15a in the cold-rolled condition, the BF image in Fig. 15b shows fine-scale precipitation of β' Cu_4Ti phase in the alloy, with 90% cold work and peak aged at 400 °C. Overageing of the 90% cold-worked alloy at 400 °C for 16 h resulted in the coarsening of these precipitates.

3.4. Fractography

The SEM fractographs of the undeformed as well as 90% cold-worked alloy in the peak-aged condition, revealed round dimples characterizing ductile fracture, as seen in Fig. 16a and b.

4. Discussion

4.1. Mechanical properties

The present investigation confirms the findings of earlier workers [1–22, 29] that the Cu–Ti alloys are age-hardenable with substantial improvements in hardness and strength. In the peakaged condition and

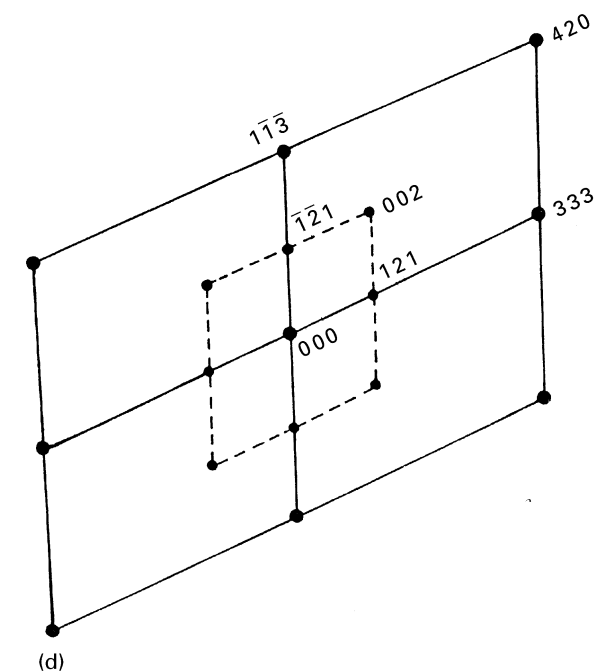
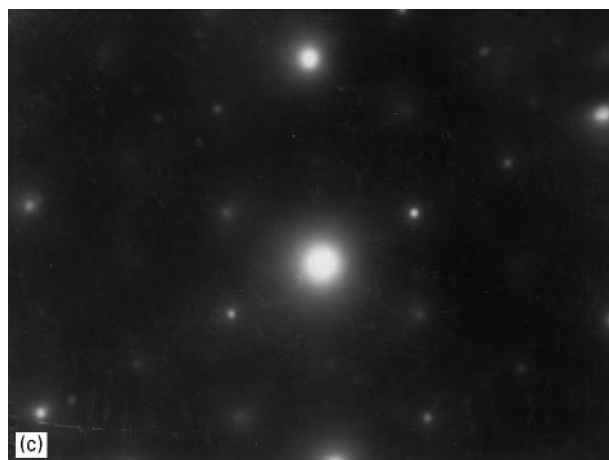
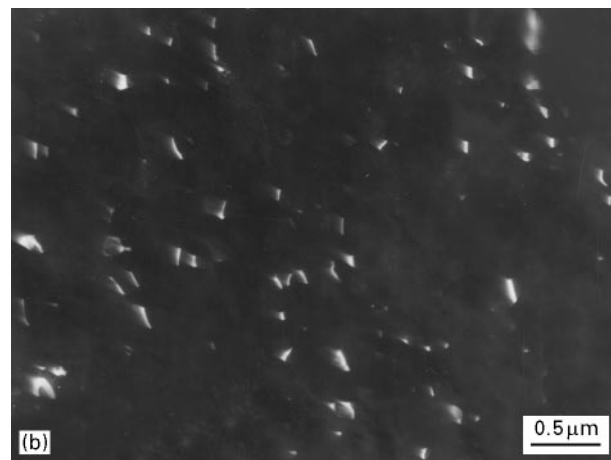


Figure 12 Transmission electron micrographs of Cu–1.5 wt % Ti alloy overaged at 450 °C for 50 h: (a) BF image, (b) DF image, (c) SAD pattern, and (d) schematic drawing of the SAD pattern: (—) matrix, (---) precipitate β' .

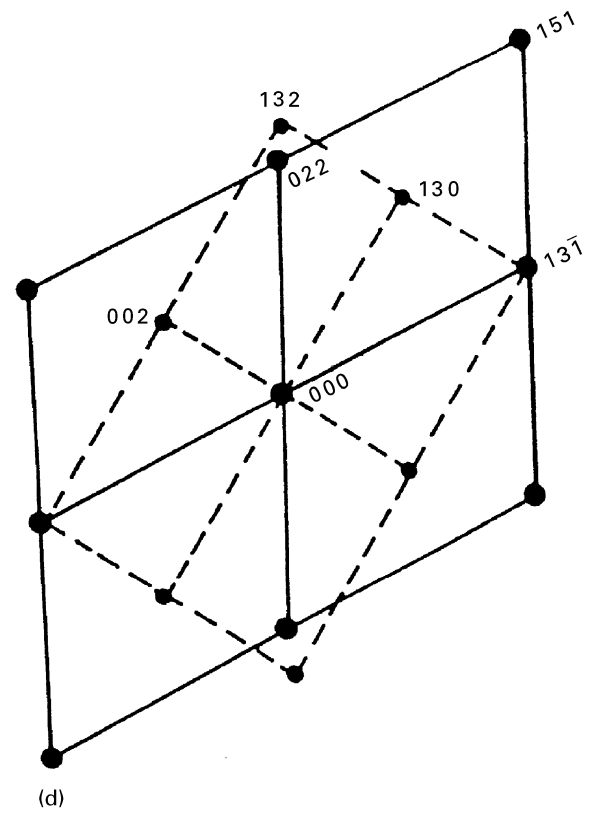
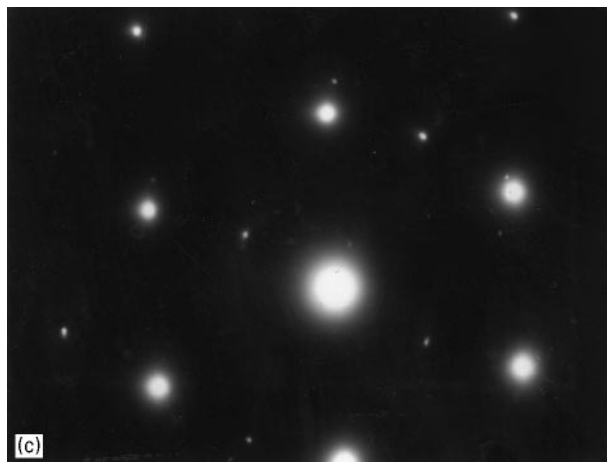
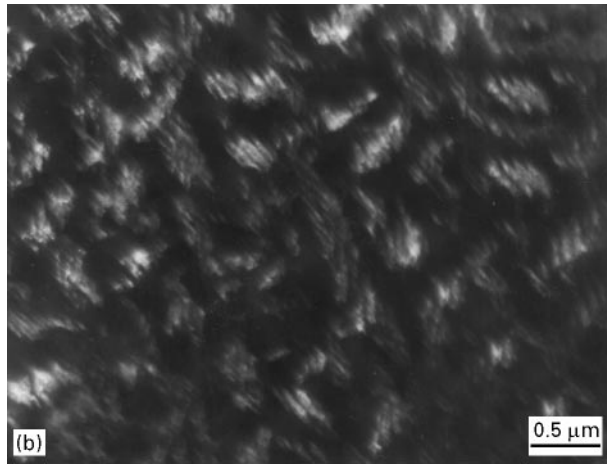
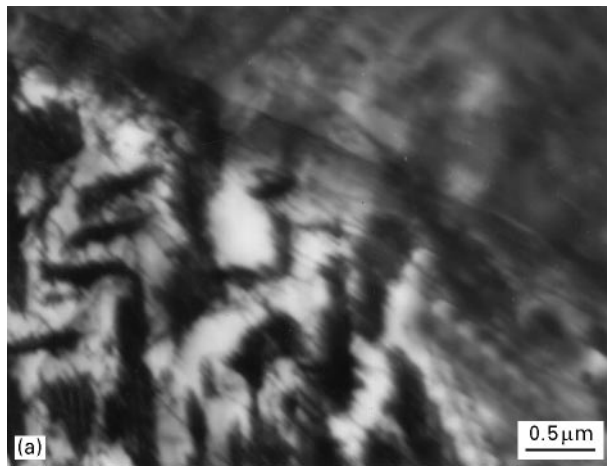


Figure 13 Transmission electron micrographs of Cu-1.5 wt % Ti alloy overaged at 500 °C for 16 h: (a) BF image, (b) DF image, (c) SAD pattern, and (d) schematic drawing of the SAD pattern (—) matrix, (---) precipitate, β .

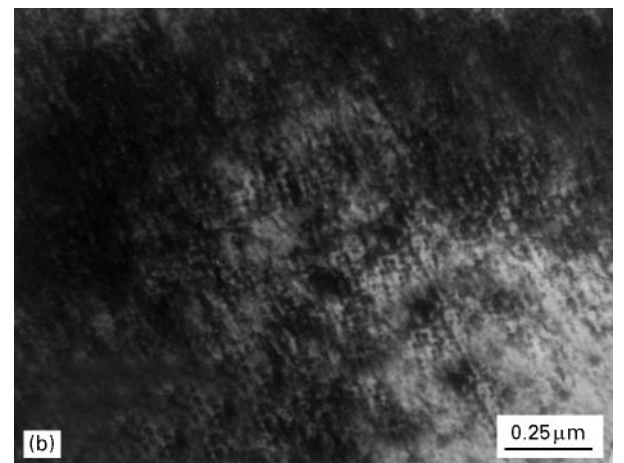
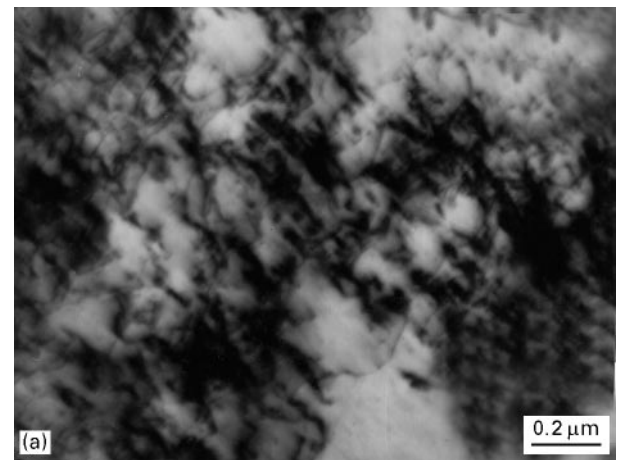


Figure 14 Transmission electron micrographs of Cu-1.5 wt % Ti alloy with 25% cold work; (a) as-cold worked, and (b) cold worked and peak aged at 400 °C for 8 h.

in the absence of any prior cold work, the Cu-1.5 wt % Ti alloy can attain a maximum hardness of 210 VHN (Fig. 1) and a tensile strength of 520 MPa with attendant elongation of 23% (Fig. 5). The hardness and strength are further improved by cold work prior to ageing; hardness increased to 280 VHN (Fig. 2) and the tensile strength, to as high as 760 MPa, while ductility reduced to 9% (Fig. 5). The mechanical properties and electrical conductivity of Cu-1.5 Ti (low titanium) and Cu-4.5 Ti (high titanium) [22] alloys are compared in Table I. Critical examination of the hardness values of both alloys reveals that the magnitude of increase in hardness in the peak-aged condition, is higher for low titanium

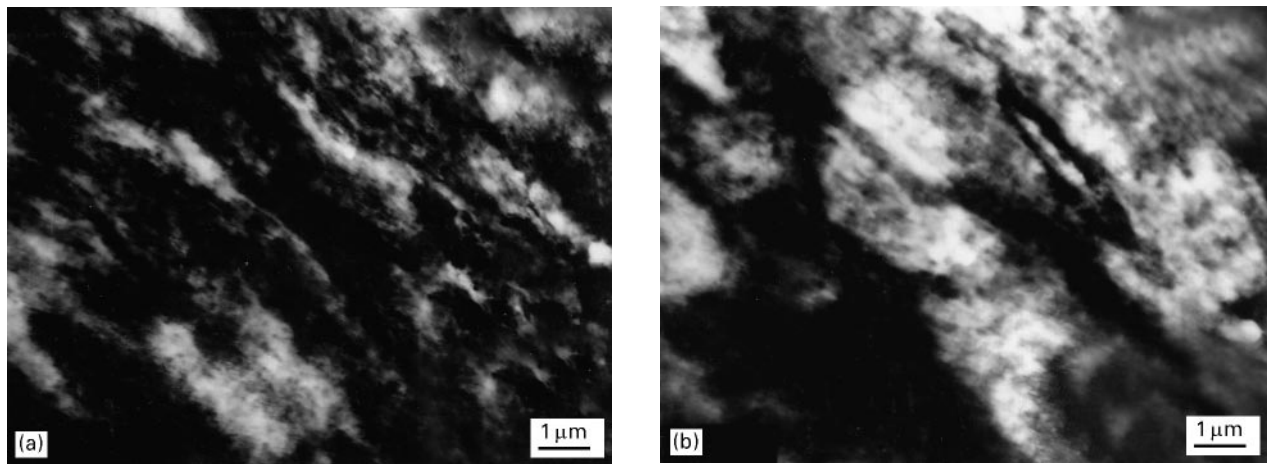


Figure 15 Transmission electron micrographs of Cu-1.5 wt % Ti alloy with 90% cold work; (a) as-cold worked, and (b) cold worked and peak aged at 400 °C for 6 h.

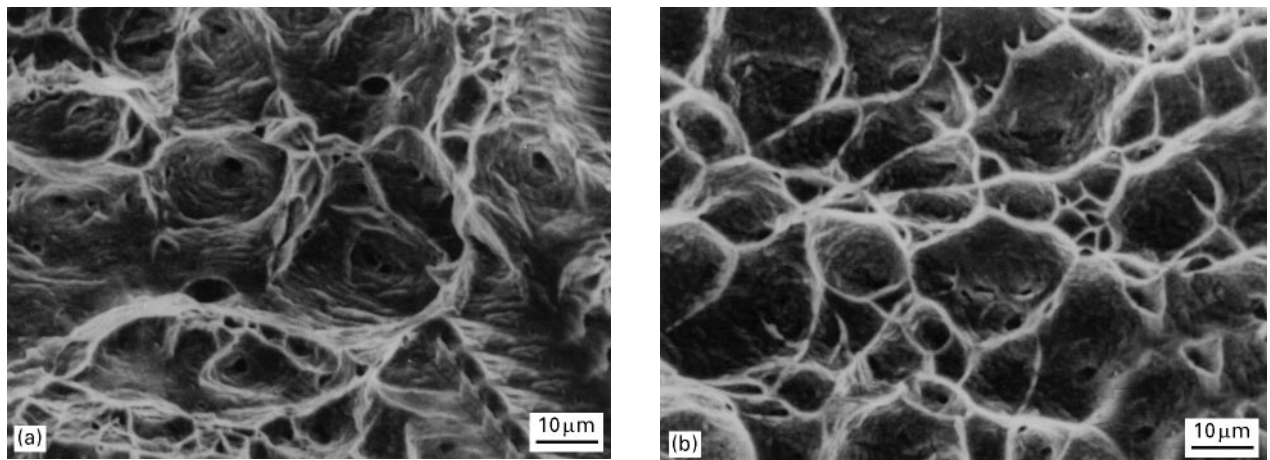


Figure 16 SEM fractographs of Cu-1.5 wt % Ti alloy: (a) undeformed and peak aged at 450 °C for 16 h, and (b) 90% cold worked and peak aged at 400 °C for 6 h.

TABLE I Comparison of mechanical properties and electrical conductivity of Cu-1.5 Ti with Cu-4.5 Ti [22] alloy

Property	Cu-1.5 Ti			Cu-4.5 Ti		
	ST	ST + PA ^a	ST + 90% CW + PA ^b	ST	ST + PA ^a	ST + 90%CW + PA ^c
1. Yield strength ^d (MPa)	112	348	670	470	720	1280
2. Tensile Strength (MPa)	292	520	760	680	890	1380
3. Elongation ^e (%)	45	23	9	24	17	2
4. Hardness (VHN)	75	210	280	245	340	425
5. Electrical conductivity (% IACS)	15.5	23.0	24.5 (26.5 ^f)	8	11	8 (25 ^f)

^a Aged at 450 °C/16 h.

^b Aged at 400 °C/6 h.

^c Aged at 400 °C/1h

^d 0.2% offset.

^e GL: 25 mm,

^f Aged at 450 °C/24 h

alloy, and smaller for the high titanium one, i.e. the increase in hardness from the ST to PA condition is 180% for Cu-1.5 Ti and 39% for Cu-4.5 Ti alloy. This can be explained on the basis that composition modulations that form during quenching in Cu-4.5 Ti alloy, raise its hardness and hence the increase in hardness after peak ageing, is smaller than that for Cu-1.5 Ti

alloy in which no composition modulations were observed in the solution-treated condition. Further, a similar trend is followed in the case of yield and tensile strengths also in both low and high titanium alloys. Our results on mechanical properties of Cu-1.5 Ti alloy are compared with those of Cu-2.0 Ti and Cu-0.5Be-2.5Co alloys in Table II. The mechanical

properties of Cu–1.5 Ti alloy compare well with those of Cu–2.0 Ti alloy obtained without any prior cold work, by Knights and Wilkes [16] and also with the commercial Cu–0.5Be–2.5Co alloy [30] of grade C 17500 in full hard and aged condition.

4.2. Electrical conductivity (EC)

The changes in electrical conductivity (EC) of the Cu–1.5 wt % Ti alloy with ageing temperature and time and prior cold work reveal that the maximum achievable conductivity in the present study is 26% IACS. The EC in the solution-treated condition was 15.5% IACS and it increased to 22.5% IACS and 24.5% IACS on ageing at 400 and 450 °C, respectively. Prior cold deformation (90%) increased the EC only marginally, to 23.5% and 26.5% IACS upon ageing at 400 and 450 °C, respectively. However, in the high titanium content Cu–4.5 wt % Ti alloy [22], the increase in conductivity on account of prior cold work and ageing, was significantly higher, namely 8% IACS (ST) → 11.3% IACS (PA at 450 °C) → 25.6% IACS (ST + 90%CW + PA at 450 °C). Considering the results of age hardening as well as EC, it is clear that the increase in electrical conductivity in these alloys is predominantly due to the combined effects of recovery that has taken place in the cold-worked matrix and enhanced precipitation of titanium as Cu₄Ti phase due to prior cold deformation, which is marginal in low titanium alloys (24.5% → 26.5% IACS) and significant in high titanium alloys (11.3% → 25.6% IACS). The different levels of increase in EC of low and high titanium alloys is explained on the basis of the solute titanium content in the solid solution (α -copper). Most of the solute titanium is removed from the solid solution during ageing of the undeformed alloy which accounts for significant increase in the EC of Cu–1.5 Ti alloy (15.5% → 24.5% IACS). The marginal increase in EC in the prior cold-worked and aged alloy is probably due to recovery occurring in the matrix. However, in the high titanium Cu–4.5 Ti alloy, ageing of the undeformed alloy removes the same amount of solute titanium (as in Cu–1.5 Ti alloy) from the solid solution but due to the high titanium con-

tent, considerable amount of titanium still remains in the solid solution. The prior cold work followed by ageing therefore, takes out the remaining amount of solute titanium from the matrix, thus resulting in a large increase in EC (11.3% → 25.6% IACS). Further, the maximum achievable EC in both Cu–1.5 Ti and Cu–4.5 Ti alloys is around 25% IACS after 90% CW and ageing at 450 °C for 24 h, which indicates that this level of conductivity corresponds to the minimum possible solute titanium available in the solid solution after precipitation of Cu₄Ti phase in these alloys. An EC greater than 25% IACS can be achieved in Cu–Ti alloys, if the remaining solute titanium is further removed by some means, namely the addition of a ternary alloying element which will readily combine with titanium and can reduce its solubility in the α -copper. The electrical conductivity of the Cu–1.5 Ti alloy is less than that of Cu–0.5Be–2.5Co alloy (Table II), and therefore needs further improvement in order to compare favourably with the commercial Cu–Be–Co alloy for high-conductivity applications. Alternatively, Cu–1.5 Ti alloy can be used in those applications where high strength is the essential requirement and not the conductivity.

4.3. Microstructure and precipitation sequence

There have been several investigations [2–5, 8, 12, 22] on the mechanisms and precipitation sequence in the age-hardening process in Cu–Ti alloys. The differences in the precipitation reactions in the low and high titanium content Cu–Ti alloys are discussed here.

The decomposition in higher titanium alloys starts with the formation of composition modulations during quenching itself [3, 4, 13, 22] and proceeds with further ageing through spinodal decomposition [3, 4] with clustering of titanium atoms along $\langle 100 \rangle$ directions. Ordering of titanium-rich regions precedes [2] or coincides [3] with the formation of a coherent and metastable phase, β' , having the stoichiometry of Cu₄Ti, a bct *D*1a structure [2–4, 14, 22] with particles still aligned along $\langle 100 \rangle$. Prolonged ageing or

TABLE II Comparison of mechanical properties and electrical conductivity of Cu–1.5 wt % Ti alloy with Cu–2.0 Ti [16] and Cu–0.5 Be–2.5 Co [30] alloys

Property	Cu–1.5 Ti			Cu–2.0 Ti			Cu–0.5 Be–2.5 Co		
	ST	ST + aged	ST + 90% CW + aged	ST	ST + aged	ST + CW + aged	ST	ST + aged	ST + full hard + aged
1. Yield strength ^a (MPa)	112	350	670	104	392	N.I. ^c	140–205	550–690	690–825
2. Tensile Strength (MPa)	292	520	760	308	592	N.I.	240–380	690–825	760–895
3. Elongation ^b (%)	45	23	9	58	13	N.I.	20–35	10–20	8–15
4. Hardness (VHN)	75	210	280	90	225	N.I.	72–92	188–215	206–225
5. Electrical conductivity (% IACS)	15.5	24.5	26.5	N.I.	N.I.	N.I.	20–30	45–60	50–60

^a0.2% offset for Cu–1.5 Ti and 0.1% for Cu–2.0 Ti alloy.

^bGL, 25 mm for Cu–1.5 Ti and 50 mm for Cu–Be alloy.

^cN.I., not investigated.

ageing at high temperatures results in the formation of the equilibrium phase β , with stoichiometric composition of Cu_3Ti [6, 7, 29] or Cu_4Ti [10] by discontinuous or cellular reaction.

In the present investigation on Cu–1.5 Ti alloy, composition modulations have not been observed in the solution-treated Cu–1.5 wt % Ti alloy, which means that the decomposition in low titanium alloys is suppressed during quenching due to the limited extent of supersaturation. This observation is in agreement with the reported behaviour for Cu–Ti alloys up to 2.7 wt % Ti [4, 13, 16, 17]. Decomposition in Cu–1.5 Ti alloy starts only with ageing and maximum strengthening is obtained when the alloy is aged at 450 °C for 16 h (peak ageing). The β' Cu_4Ti precipitate is observed to occur predominantly in the peak-aged condition. This observation is in agreement with the findings by most of the investigators that β' Cu_4Ti precipitate with $D1a$ bct structure is responsible for maximum hardening [2–4, 12, 22] in Cu–Ti alloys because it is dominant at the peak-hardening time. The equilibrium phase β (Cu_3Ti) in Cu–1.5 wt % Ti alloy starts forming as coarse precipitates at 500 °C aged for 16 h and has an orthorhombic structure [22, 29]. However, the equilibrium precipitate was observed at 450 °C itself (aged for 16 h) in the Cu–4.5 wt % Ti alloy.

Several earlier workers [8, 14, 16] attributed overageing to the discontinuous precipitation leading to alternate (lamellar) distribution of α and β phases. However, such discontinuous precipitation has not been observed in Cu–1.5 wt % Ti alloy, even after overageing at 500 °C for 16 h (Fig. 7). It may be stated here that Knights and Wilkes [16] reported the occurrence of cellular reaction in a Cu–2.0 Ti alloy only after ageing for 3 h at 600 °C. Thus, it is concluded that the β' phase is only responsible for peak hardening in Cu–1.5 wt % Ti alloy at 400 and 450 °C and the precipitation of equilibrium phase β occurs at 500 °C causing considerable overageing, while the discontinuous precipitation may occur only at higher temperatures (> 550 °C).

In the prior cold-worked Cu–1.5 Ti alloy, dislocation cells are observed in the initial stages of deformation (25% CW) and considerably elongated grains on 90% cold work (Figs 14 and 15). Dislocation cells have been reported to occur in low titanium alloys with tensile deformation [26]. On ageing, the cold work causes enhanced precipitation of metastable and coherent β' Cu_4Ti phase which is responsible for increase in strength. In contrast to the formation of dislocation cells in low titanium alloys, deformation twinning was observed in Cu–4.5 wt % Ti alloy in the solution-treated condition by the present authors [22, 26]. The twinning mode of deformation is expected to be due to fine-scale precipitation present in the high titanium alloys in the solution-treated condition itself.

Regarding the fracture behaviour, the alloy deformed by shear mode of fracture (microvoid coalescence) in the undeformed as well as prior cold-worked and aged alloy. The observation of nearly equiaxed dimples even in the 90% cold-worked and peak-aged

condition, confirms the ductile mode of fracture in the Cu–1.5 Ti alloy. The ductile mode of fracture was also reported in Cu–4.5 Ti alloy by the present authors [22].

5. Conclusions

1. Considerable strengthening of the alloy occurs on ageing at 400 and 450 °C. The hardness increased from 80 VHN in the solution-treated state, to a peak value of 210 VHN on ageing, in the undeformed condition and 280 VHN, with 80% prior cold work and ageing. The peak values of yield strength for the corresponding conditions are 112, 350 and 680 MPa, while those of UTS are 292, 520 and 760 MPa.

2. While no composition modulations were observed after quenching in the solution-treated condition, the principal strengthening mechanism of age hardening is the precipitation of the metastable, ordered and coherent β' phase, having body-centred tetragonal (bct) crystal structure at the peak-hardening time. The equilibrium phase β , with the orthorhombic structure, forms during overageing at 500 °C for 16 h.

3. The electrical conductivity increased from 15.5% IACS in the solution-treated condition, to 26.5% IACS when slightly overaged at 450 °C for 24 h after 95% prior cold deformation. The increase in EC in the aged alloy with prior cold work is marginal in Cu–1.5 Ti alloy, whereas it is significant in high titanium alloy (Cu–4.5 wt % Ti [22]). However, the maximum achievable EC in both low and high titanium alloys is around 25% IACS.

4. The properties and microstructural evolution in low titanium alloys are contrasted with that in high titanium alloys in terms of the absence of (i) the development of modulations during quenching itself, and (ii) deformation twins after solution treatment and cold work.

5. Neither ageing treatment nor prior cold work changed the mode of fracture, i.e. microvoid coalescence in the alloy.

Acknowledgements

The authors are grateful to the Director, DMRL, for permission to publish this paper and the Head, Department of Metallurgical Engineering, Banaras Hindu University, Varanasi, for providing TEM facilities. One of the authors (S.N.) thanks Dr A. Venugopala Reddy, Scientist DMRL, for assistance in the experimental work and helpful discussions.

References

1. M. J. SAARIVIRTA and H. S. CANNON, *Met. Prog.* **76** (1959) 81.
2. T. HAKKARAINEN, PhD thesis, Helsinki Technical University, (1971).
3. D. E. LAUGHLIN and J. W. CAHN, *Acta Metall. Mater.* **23** (1975) 329.
4. A. DATTA and W. A. SOFFA, *ibid.* **24** (1976) 987.
5. R. WAGNER, in "Proceedings of the 5th International Conference on Strength of Metals and Alloys", edited by P. Haasen, V. Gerold and G. Kostorz, Vol. 1 (Pergamon Press, Oxford, 1979) p. 645.

6. U. HEUBNER and G. WASSERMANN, *Z. Metallkde* **53** (H3) (1962) 152.
7. H. T. MICHELS, I. B. CADOFF and E. LEVINE, *Metall. Trans. A* **3** (1972) 667.
8. J. A. CORNIE, A. DATTA and W. A. SOFFA, *ibid.* **4** (1973) 727.
9. J. GREGGI and W. A. SOFFA, in "Proceedings of the 5th International Conference on Strength of Metals and Alloys", edited by P. Haasen, V. Gerold and G. Kostorz, Vol. 1 (Pergamon Press, Oxford, 1979) p. 651.
10. R. C. ECOB, J. V. BEE and B. RALPH, *Phys. Status Solidi* (a) **52** (1979) 201.
11. P. KRATOCHVIL, M. SAXLOVA and J. PESICKA, in "Proceedings of 5th International Conference on Strength of Metals and Alloys", edited by P. Haasen V. Gerold and G. Kostorz, Vol. 1, (Pergamon Press, Oxford, 1979) p. 687.
12. W. A. SOFFA and D. E. LAUGHLIN, in "Proceedings of the International Conference on Solid → Solid Phase Transformations", edited by H. I. Aaronson (The Metallurgical Society of AIME, Warrendale, PA, 1982) p. 159.
13. K.-E. BIEHL and R. WAGNER, *ibid.*, p. 185.
14. A. W. THOMPSON and J. C. WILLIAMS, *Metall. Trans.* **15A** (1984) 931.
15. R. KAMPMANN and R WAGNER, in "Proceedings of the Conference on Decomposition of Alloys: The Early Stages", edited by P. Haasen, V. Gerold, R. Wagner and M. F. Ashby (Pergamon Press, Oxford, 1984) p. 91.
16. R. KNIGHTS and P. WILKES, *Acta Metall. Mater.* **21** (1973) 1503.
17. L. V. ALVENSLEBEN and R. WAGNER, in "Proceedings of Conference on Decomposition of Alloys: The Early Stages", edited by P. Haasen, V. Gerold, R. Wagner and M. F. Ashby (Pergamon Press, Oxford, 1984) p. 143.
18. U. ZWICKER, *Z. Metallkde* **53** (1962) 709.
19. J. DUTKIEWICZ, *Metall. Trans.* **8A** (1977) 751.
20. S. SAJI and E. HORNBOKEN, *Z. Metallkde* **69** (1978) 741.
21. N. J. GRANT, A. LEE and M. LOU, in "Proceedings of Symposium on High Conductivity Copper and Aluminium Alloys", edited by E. Ling and P.W. Taubenblat (The Metallurgical Society of AIME, Warrendale, PA, 1984) p. 103.
22. S. NAGARJUNA, K. BALASUBRAMANIAN and D. S. SARMA, *Mater. Trans. JIM* **36** (1995) 1058.
23. "Standard Test Methods for Tension Testing of Metallic Materials", ASTM: E 8M-89b Vol. 03.01, edited by P. C. Fazio, M. Gorman, E. L. Gutman, C. T. Hsia, G. Jones, J. Kramer, C. M. Leinweber, P. A. McGee, S. P. Milligan and K. W. O'Brien (Annual Book of ASTM Standards, Philadelphia, PA, 1990), p. 146.
24. "Standard Test Method for resistivity of Electrical Conductor Materials", ASTM: B 193-89, Vol. 02.01, edited by P. C. Fazio, M. Gorman, E. L. Gutman, C. T. Hsia, G. Jones, J. Kramer, C. M. Leinweber, P. A. McGee, S. P. Milligan and K. W. O'Brien (Annual Book of ASTM Standards, Philadelphia, PA, 1990), p. 330.
25. S. NAGARJUNA, M. SRINIVAS, K. BALASUBRAMANIAN and D. S. SARMA, *Scripta Metall. Mater.* **30** (1994) 1593.
26. *Idem, ibid.* **33** (1995) 1455.
27. *Idem, Acta Mater.* **44** (1996) 2285.
28. S. NAGARJUNA, K. BALASUBRAMANIAN and D. S. SARMA, *Scripta Mater.* (1996) **35** (1996) 147.
29. N. KARLSSON, *J. Inst. Metals* **79** (1951) 391.
30. "Properties and Selection: Non-Ferrous Alloys and Special Purpose Materials, Metals Hand Book" 10th edn, Vol. 2, L. A. Abel, R. T. Kieppura, P. Thomas, H. F. Lampman and N. D. Wheaton (ASM International, Ohio, USA, 1990) p. 228.

*Received 11 July 1996
and accepted 7 January 1997*