

# Age hardening studies in a Cu–4.5Ti–0.5Co alloy

S. Nagarjuna <sup>a,\*</sup>, K.K. Sharma <sup>a</sup>, I. Sudhakar <sup>b</sup>, D.S. Sarma <sup>c</sup>

<sup>a</sup> Defence Metallurgical Research Laboratory, Kanchanbagh-PO, Hyderabad 500058, India

<sup>b</sup> Department of Metallurgical Engineering, Regional Engineering College, Warangal 506004, India

<sup>c</sup> Department of Metallurgical Engineering, Banaras Hindu University, Varanasi 221005, India

Received 16 August 2000; received in revised form 11 October 2000

---

## Abstract

Age hardening in a Cu–4.5Ti–0.5Co alloy has been studied at different aging temperatures and times. It has been observed that this alloy exhibits considerable age hardening with hardness increasing from  $225H_V$  to a peak value of  $320H_V$  on aging. Yield strength increases from 360 to 710 MPa and tensile strength from 610 to 890 MPa on aging the solution treated alloy for peak strength. The electrical conductivity of the alloy is found to be 4 and 8% International Annealed Copper Standard (IACS) in solution treated and peak aged conditions, respectively. Addition of cobalt to Cu–4.5Ti alloy reduces the aging temperature and time for attaining peak hardness. Ordered, metastable and coherent  $Cu_4Ti$  ( $\beta^1$ ) precipitate is found to be responsible for maximum strengthening of the alloy. Interestingly, absence of equilibrium precipitate  $Cu_3Ti$  and presence of  $Cu_4Ti$  phase have been noticed in the overaged condition. The absence of  $Cu_3Ti$  is attributed to the addition of cobalt. In addition, intermetallic phases of Ti and Co like  $Ti_2Co$  and  $TiCo$  have been observed in solution treated, peak aged and overaged conditions. Cold work prior to aging enhances the hardness, strength and electrical conductivity of the alloy. For example, 90% cold work followed by aging at  $400^\circ C$  for 1 h increases the hardness from 320 to  $430H_V$ ; yield and tensile strengths, from 710 to 1185 and 890 to 1350 MPa, respectively, and electrical conductivity, marginally by 1% IACS. While mechanical properties are comparable, electrical conductivity of Cu–4.5Ti–0.5Co is less than that of the binary Cu–4.5Ti alloy in the solution treated as well as peak aged conditions. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Copper titanium cobalt alloy; Solution treatment; Aging; Age/precipitate hardening and mechanical properties

---

## 1. Introduction

Copper and copper alloys are widely used because of their excellent electrical and thermal conductivities, outstanding resistance to corrosion, ease of fabrication as well as good strength and fatigue resistance [1]. Age hardenable copper beryllium (Cu–Be) alloys exhibit the highest strength levels among the family of copper alloys and also possess medium electrical conductivity. However, they have serious disadvantages of toxicity and high cost, which limit their use. Worldwide efforts have, therefore, been concentrated on developing a substitute for the Cu–Be alloys and copper titanium (Cu–Ti) alloys have a good potential in this respect.

Earlier studies have shown that the binary Cu–Ti alloys are strengthened by spinodal decomposition and age hardening and exhibit mechanical properties comparable to those of the Cu–Be alloys [2–9].

Studies on ternary alloying additions such as vanadium, aluminum, alumina, boron and nickel to binary Cu–Ti alloys have been carried out by earlier investigators [10–14], but have not resulted in significantly better properties than the binary ones. Though either Co or Ni or both are added to commercial Cu–Be alloys for improved properties [15], little work has been done on the addition of cobalt to the Cu–Ti alloys, except for a patent on Cu–0.5–0.6%Ti–0.5–0.6Co alloy by Duerrschnabel et al. [16]. A detailed study was, therefore, undertaken to investigate the age hardening behaviour of a Cu–4.5Ti–0.5Co alloy and this paper presents the findings of this investigation.

\* Corresponding author. Fax: +91-40-4441439.

E-mail address: sn@dmr1.ernet.in (S. Nagarjuna).

## 2. Experimental

A 30 kg melt of the Cu–Ti–Co alloy was made in STOKES Vacuum Induction Melting (VIM) furnace with oxygen free electronic (OFE) copper, Cu–26wt.%Ti master alloy and pure cobalt metal as charge materials. The ingot was homogenized at 850°C for 24 h and analysed for titanium and cobalt contents. The analysed composition of the ingot was found to be 4.5 wt.% Ti and 0.5 wt.% Co. The homogenized ingot was hot forged and rolled into rods and flats of suitable sizes. Specimens from the hot rolled rod were solution

treated (860°C/2 h/WQ) and aged at 400, 450 and 500°C for different times. Vickers hardness ( $H_V$ ) of these specimens was measured at 10 kg load. The solution treated specimens were also cold rolled giving different amounts of deformation. Hardness ( $H_V$ ) of the cold rolled specimens was measured after aging at different temperatures and times. Round headed cylindrical specimens with a gauge diameter of 4.0 mm and length of 25 mm were tested for tensile properties as per ASTM specifications (E: 8M-97) [17] at ambient temperature, at a nominal strain rate of  $10^{-3} \text{ s}^{-1}$  using INSTRON 1185 ball screw driven universal testing system. Flat specimens with 25 mm gauge length, made as per the above specification (sub-size specimen), were used to determine the tensile properties of cold worked and aged alloys. Samples from the hot rolled rods were cold drawn to 2 mm diameter wires with intermittent solution treatments. Electrical conductivity of the wire samples was determined as per the ASTM specification B 193-95 [18].

Thin discs of  $\sim 0.10$  mm thickness were sliced from the heat-treated samples using an ISOMET saw and they were further reduced to  $\sim 20$   $\mu\text{m}$  by mechanical polishing. Discs of 3 mm diameter were punched out from these thinned sections and electropolished in a Fischionne twin jet electropolisher using a solution of 30 vol%  $\text{HNO}_3$  and 70% methanol at  $-45^\circ\text{C}$  and at a voltage of 10V. The thin foils were examined at 160 kV using JEOL-200CX transmission electron microscope.

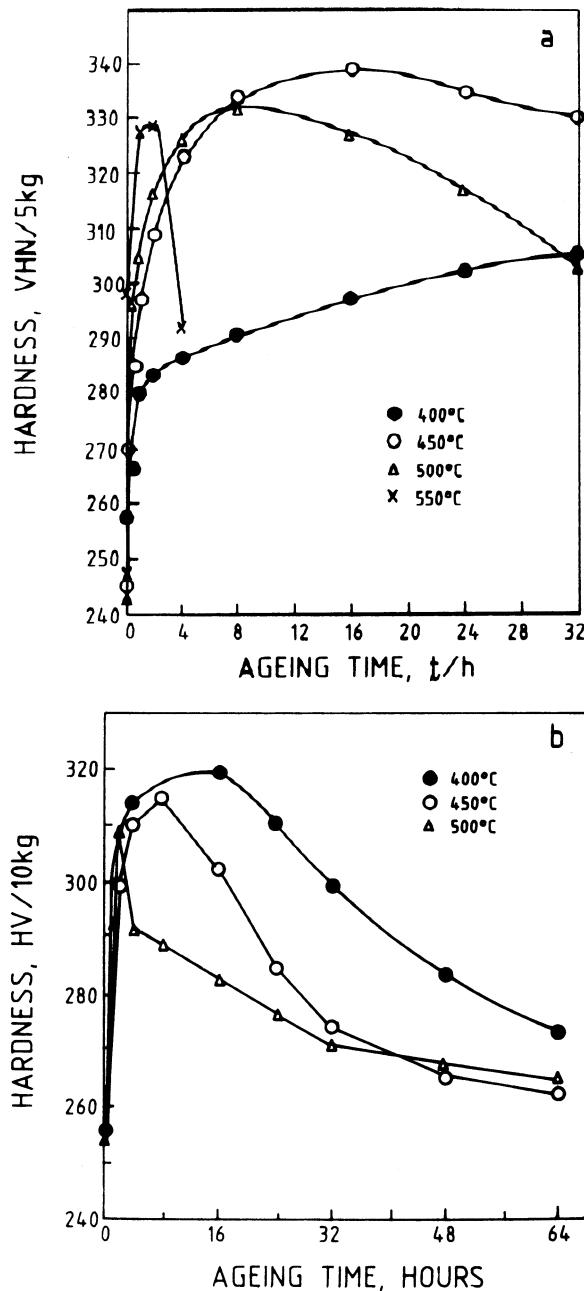


Fig. 1. Age hardening in Cu–4.5Ti–0.5Co alloy compared with Cu–4.5Ti alloy [5]. (a) Cu–4.5Ti and (b) Cu–4.5Ti–0.5Co.

## 3. Results and discussion

### 3.1. Mechanical properties

#### 3.1.1. Hardness

The influence of aging time on hardness of the solution treated Cu–4.5Ti–0.5Co alloy compared with the binary Cu–4.5Ti [5] alloy is shown in Fig. 1. In the ternary Cu–4.5Ti–0.5Co alloy, a peak hardness of  $320 H_V$  is observed after aging at 400°C for 16 h, beyond which it decreased with aging time. At 450°C, the peak hardness is found to be slightly lower, i.e.  $314 H_V$ , but the over aging is faster. The peak hardness is further lowered to  $308 H_V$  and overaging is drastic on aging at 500°C. While peak hardness in the binary Cu–4.5Ti alloy [5] ( $340 H_V$ ) is attained after aging at 450°C for 16 h, the peak ( $320 H_V$ ) is observed at 400°C aged for 16 h in Cu–4.5Ti–0.5Co alloy. Further, the peak was not attained in the binary alloy aged at 400°C even after 32 h. At 450°C, the peak hardness in Cu–4.5Ti–0.5Co alloy is obtained even earlier (in 8 h) and the peak hardness value is lower than that obtained at 400°C. A similar behaviour is observed at 500°C as well in the ternary alloy. It is, therefore, evident that a cobalt addition of 0.5wt.% to the Cu–4.5Ti alloy has

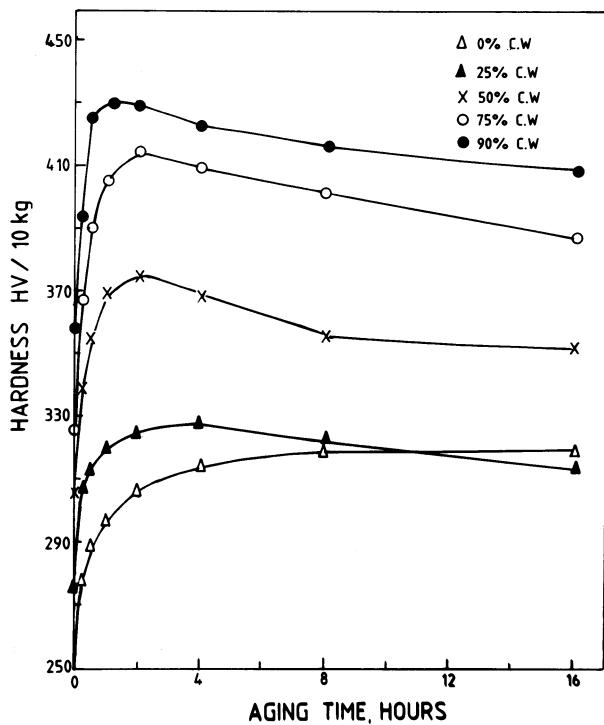


Fig. 2. Effect of prior cold work on age hardening at 400°C in Cu-4.5Ti-0.5Co alloy.

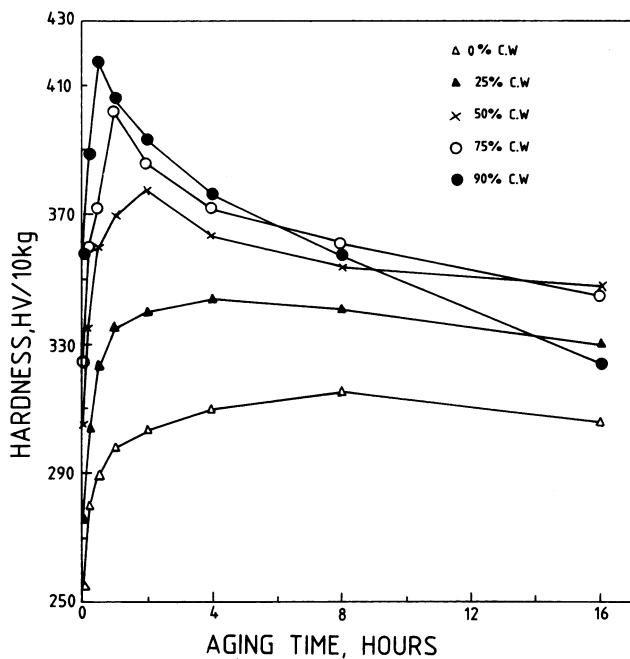


Fig. 3. Effect of prior cold work on age hardening at 450°C in Cu-4.5Ti-0.5Co alloy.

not only decreased the aging time and temperature for attaining peak hardness but also reduced the peak hardness marginally.

The effect of cold work on aging at 400, 450 and 500°C is shown in Figs. 2–4, respectively. In all cases,

increase in cold work in the range of 0–90% has increased the peak hardness. The highest hardness noted was  $430\text{HV}$  after 90% cold work and aging at 400°C for 1 h. In the case of binary Cu-4.5Ti alloy, the peak hardness corresponding to 90% cold work and peak aged condition is reported to be  $425\text{HV}$  [5]. The peak hardness value obtained for Cu-4.5Ti-0.5Co alloy is comparable with that of the Cu-4.5Ti alloy. While the extent of over aging is marginal at 400°C, it is moderate at 450°C and drastic at 500°C. For instance, aging the alloy at 500°C for about 16 h after 50–90% cold work has lowered the hardness well below that of the as-quenched alloy.

### 3.1.2. Tensile properties

The influence of prior cold work on the tensile properties of the present alloy after peak aging for maximum hardness at 400°C is shown in Fig. 5. As expected from the hardness behaviour, the yield and tensile strengths increased continuously with increasing amount of deformation, raising the yield strength from 710 to 1185 MPa and tensile strength from 890 to 1350 MPa. The elongation has, however, decreased after peak aging, from 25% in the undeformed state to  $\sim 3\%$  after 90% deformation.

The tensile properties and electrical conductivity of the Cu-4.5Ti-0.5Co alloy are compared with those of Cu-4.5Ti and Cu-5.4Ti alloys [9] in Table 1. It is seen here that hardness as well as yield and tensile strengths of solution treated Cu-4.5Ti-0.5Co alloy are lower

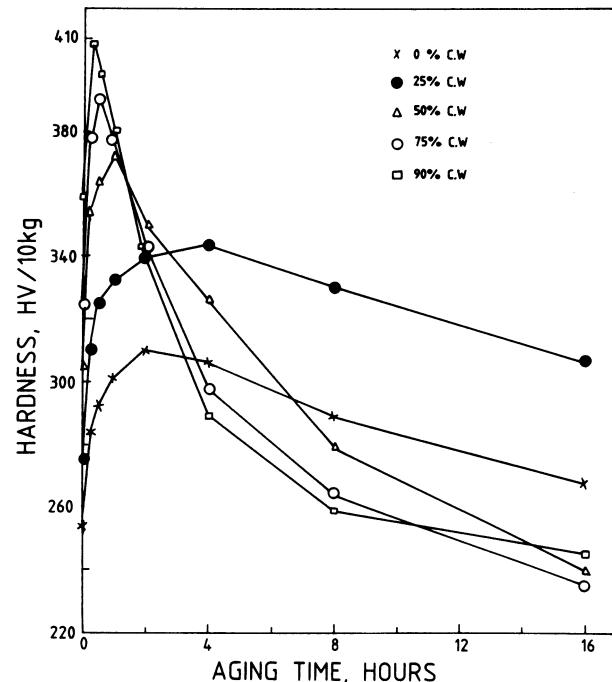


Fig. 4. Effect of prior cold work on age hardening at 500°C in Cu-4.5Ti-0.5Co alloy.

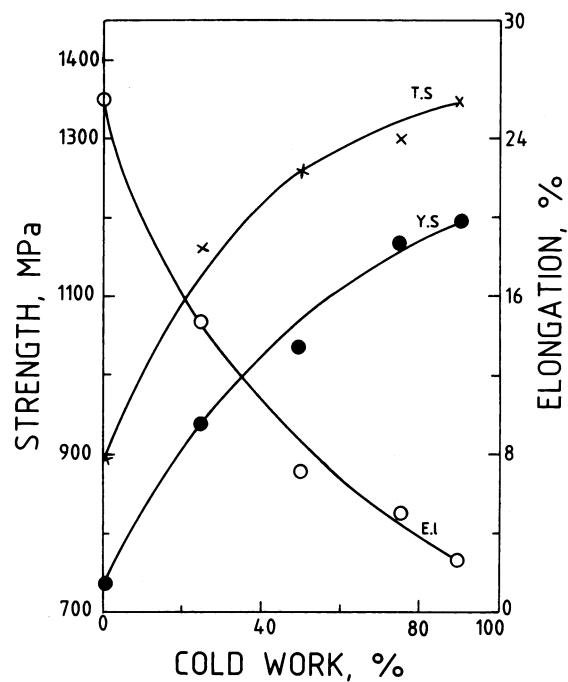


Fig. 5. Influence of prior cold work on the tensile properties of Cu-4.5Ti-0.5Co alloy after peak aging for maximum hardness at 400°C.

than those of the binary Cu-4.5Ti alloy. It was reported earlier that in solution treated binary Cu-Ti alloys, fine scale precipitation in the form of modulations in Cu-4.5Ti and Cu<sub>4</sub>Ti  $\beta^1$  precipitates in Cu-5.4Ti alloy formed during quenching [9]. Though the Cu<sub>4</sub>Ti,  $\beta^1$  precipitate is found in Cu-4.5Ti-0.5Co alloy as well, the strength levels of the ternary alloy are lower than that of binary Cu-Ti alloys due to removal of additional Ti from the matrix to form intermetallic phases containing Co and Ti. The formation of these phases is dealt with, in the following sections. Addition of Co to Cu-4.5Ti alloy increases its strength due to solid solution strengthening. However, the strength increase after aging due to solid solution strengthening as

a result of Co addition is marginal because only a small amount of the total Co added remains in solid solution and the balance is utilized for the formation of intermetallic phases with Ti. The solid solubility of Co in Cu at room temperature was reported to be  $\leq 0.2\%$  [19]. Since the strength decrease due to lowering of Ti content in the matrix and subsequent formation of Co-Ti phases is considerably higher than the increase in strength due to solid solution strengthening, the net result is an overall decrease in the strength of the Cu-4.5Ti-0.5Co alloy.

In the peak-aged condition, the strengths of the Cu-4.5Ti-0.5Co alloy and of the binary Cu-4.5Ti alloy [9] are nearly the same. The increase in strength in the ternary alloy is attributed to enhanced precipitation of Cu<sub>4</sub>Ti ( $\beta^1$ ) phase. In the cold worked and peak aged condition too, the hardness and strength levels of ternary alloy are comparable with those of the binary Cu-4.5Ti alloy, although the yield strength of the ternary alloy is lower. The strength as well as hardness of Cu-4.5Ti-0.5Co alloy is lower than that of Cu-5.4Ti alloy. However, the elongation of the ternary alloy is higher than that of the Cu-4.5Ti and Cu-5.4Ti alloy.

The electrical conductivity (EC) of the Cu-4.5Ti-0.5Co alloy is lower than that of the binary Cu-4.5Ti and Cu-5.4Ti alloys in both solution treated and peak aged conditions. In the solution treated condition, the EC of the ternary alloy is found to be 4.0% IACS which is lower than that of the binary Cu-4.5Ti alloy by nearly 50%. However, it increased to 8.0% IACS on peak aging, the extent of increase being 50% of the solution treated alloy. The lower levels of EC in Cu-4.5Ti-0.5Co, as compared to the binary Cu-4.5Ti alloy are mainly attributed to the Co being in solid solution in copper. Gregory et al. [19] have reported that in copper, synergistic effects occur when more than one solute is present simultaneously. Further, some elements show a much more serious effect on decreasing the EC than others. They also concluded that a

Table 1  
Comparison of properties of Cu-4.5Ti-0.5Co alloy with Cu-4.5Ti and Cu-5.4Ti alloys [9]

Property	Cu-4.5Ti			Cu-5.4Ti			Cu-4.5Ti-0.5Co		
	ST	ST+PA	ST+90CR+PA	ST	ST+PA	ST+90CR+PA	ST	ST+PA	ST+90CR+PA
Yield strength <sup>a</sup> (MPa)	440	700	1280	590	790	1400	360	710	1185
Tensile strength (MPa)	680	890	1380	780	930	1450	610	890	1350
Elongation <sup>b</sup> (%)	29	20	2	23	15	1.5	32	25	3
Hardness ( $H_V$ )	245	340	425	310	366	455	225	320	430
Electrical conductivity (%IACS)	8	11.3	8 <sup>c</sup> , 25.6 <sup>d</sup>	9	10.8	4.8 <sup>c</sup> , 14.5 <sup>d</sup>	4	8	9 <sup>c</sup> , 12 <sup>d</sup>

<sup>a</sup> 0.2% offset.

<sup>b</sup> Gauge length = 25 mm.

<sup>c</sup> Value reported for deformed alloy aged at 400°C/1 h.

<sup>d</sup> Values reported for deformed alloys aged at 450°C/24 h.

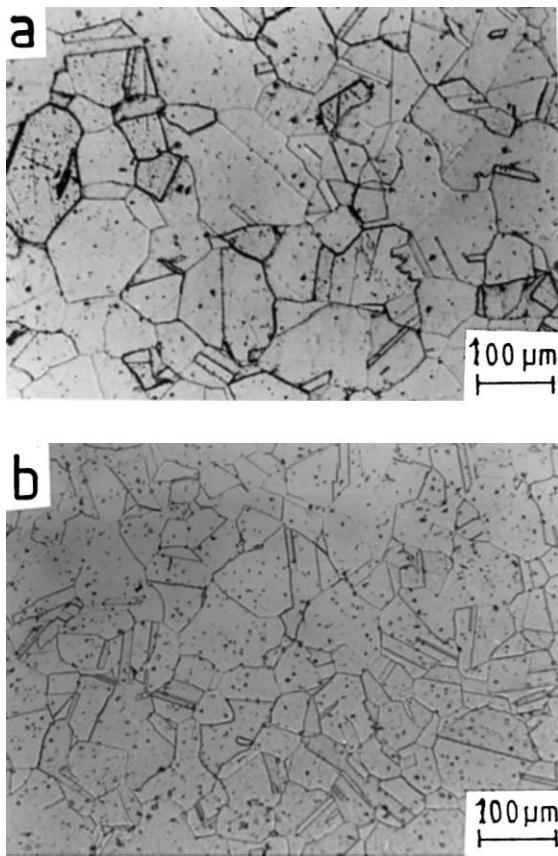


Fig. 6. Optical micrographs depicting the grain size of the solution treated alloys. (a) Cu–4.5Ti [20], grain size = 75  $\mu\text{m}$ . (b) Cu–4.5Ti–0.5Co, grain size = 55  $\mu\text{m}$ .

solute in solid solution with copper has a much more powerful effect on decreasing the EC than when it is present as partly or wholly of a second phase. When a solute is present as a non-conducting second phase, the decrease in EC depends on the form and distribution of the phase. If dispersed, the decrease is equal to the volume fraction of the phase and is much smaller than when the solute is in solid solution. In the present study, copper has two solutes, viz. Ti and Co in solid solution and therefore, the EC decreased considerably in the solution treated condition because of their combined effect. Further, these two elements have been reported to cause greater increase in electrical resistivity than others like Cd, Ag, Zn, Ni, Sn, Be, etc. [6,19]. Though the presence of the  $\text{Cu}_4\text{Ti}$  ( $\beta^1$ ) phase and intermetallic phases containing Ti and Co was noticed in the solution treated alloy, their contribution to enhance the EC of the alloy is negligible compared to the decrease in EC due to the solid solution of Ti and Co in copper. The increase in EC of the peak-aged alloy is attributed to removal of considerable quantity of Ti and Co from the copper solid solution to form  $\text{Cu}_4\text{Ti}$  ( $\beta^1$ ) phase and intermetallic phases containing Ti and Co. Further, the volume fraction of these phases is considerably higher than that of the solution treated alloy, which

contribute significantly to the EC of the Cu–4.5Ti–0.5Co alloy.

### 3.2. Microstructure

#### 3.2.1. Grain size

The optical micrographs depicting the grain size of the solution treated binary Cu–4.5Ti [20] and ternary Cu–4.5Ti–0.5Co alloys are shown in Fig. 6. It is seen here that the grain size of the ternary Cu–4.5Ti–0.5Co alloy (55  $\mu\text{m}$ ) is less than that of the binary Cu–4.5Ti alloy (75  $\mu\text{m}$ ) [20]. The observed behaviour is in agreement with the reported results that Co addition to binary Cu–Be alloys resulted in refinement of grain size by restricting the grain growth during solution annealing by establishing a dispersion of beryllide particles in the matrix [15]. A fine dispersion of the intermetallic phases containing Ti and Co could have caused the refinement of grain size in the ternary Cu–4.5Ti–0.5Co alloy.

#### 3.2.2. Optical metallography

The optical microstructures of Cu–4.5Ti–0.5Co alloy in solution treated and peak aged conditions are shown in Fig. 7. In the solution treated condition (Fig. 7a), the microstructure mainly consists of equiaxed

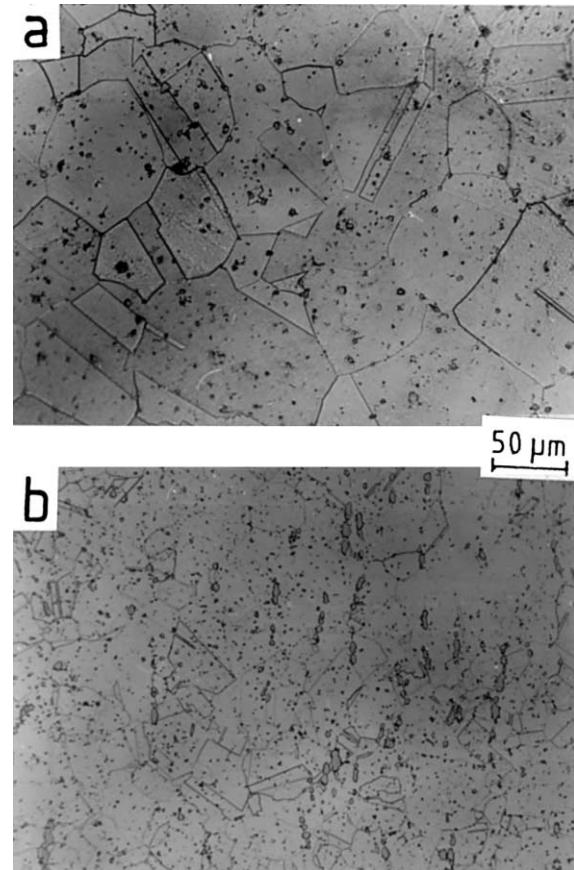


Fig. 7. Optical microstructures of Cu–4.5Ti–0.5Co alloy. (a) Solution treated, and (b) peak aged.

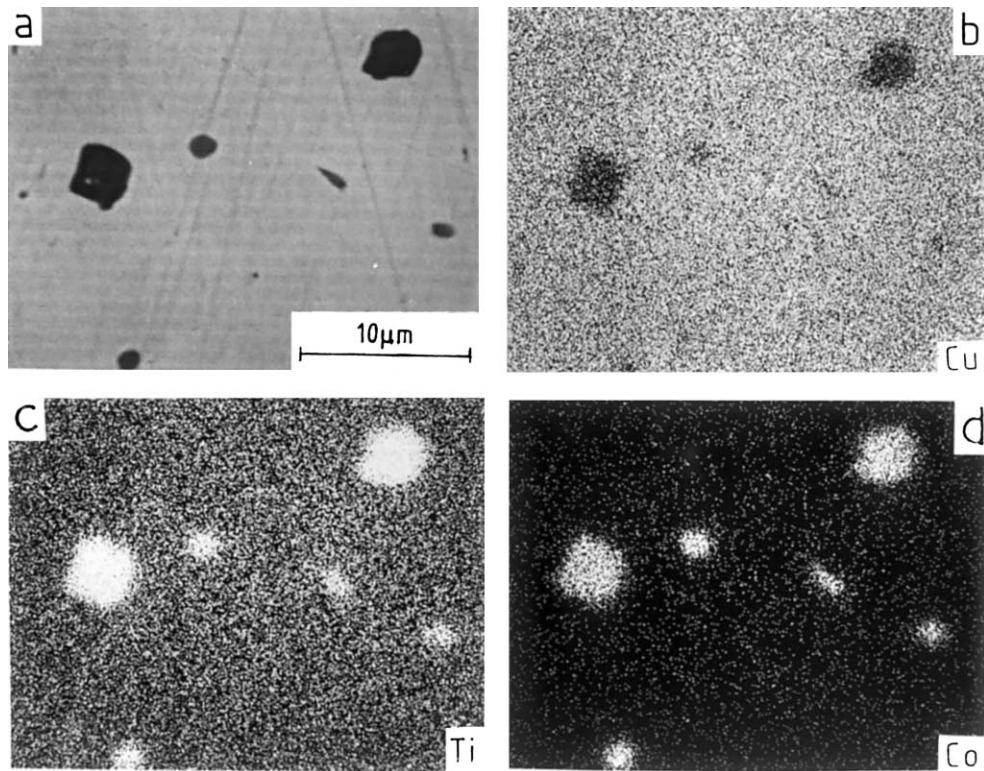


Fig. 8. EPMA microstructure and mapping of elements of solution treated Cu–4.5Ti–0.5Co alloy.

grains with annealing twins. Further, small and round precipitate particles are spread uniformly. Fig. 7b shows the microstructure of peak aged Cu–4.5Ti–0.5Co alloy, wherein equiaxed grains with annealing twins are seen. In addition, round as well as string-type elongated precipitates are found. These precipitate particles appear to have grown larger in size compared to those in the solution treated condition.

### 3.2.3. Electron probe micro analysis (EPMA)

Fig. 8 shows the EPMA microstructure and mapping of elements in the solution treated Cu–4.5Ti–0.5Co alloy. The back-scattered electron image in Fig. 8a showed globular as well as string-like elongated particles. The elemental mapping in Fig. 8b–d revealed that these precipitate particles are rich in Ti as well as Co.

### 3.2.4. Transmission electron microscopy

The transmission electron micrographs (TEMs) of the solution treated Cu–4.5Ti–0.5Co alloy are shown in Fig. 9. Grain boundaries with fine precipitate are seen in the bright field image in Fig. 9a. Fig. 9b shows the selected area diffraction (SAD) pattern of the precipitate particles and the schematic of SAD pattern is in Fig. 9c. From the SAD pattern and its schematic, the precipitates have been identified to be:

1. Ordered, metastable and coherent  $\beta^l$  phase with a stoichiometric composition of  $\text{Cu}_4\text{Ti}$  having body-centered tetragonal (bct) crystal structure with lattice parameters of  $a = 0.584$  nm and  $c = 0.362$  nm.

2. An intermetallic phase having stoichiometric composition of  $\text{Ti}_2\text{Co}$ , an ordered FCC structure having a lattice parameter of 1.127 nm.
3. One more intermetallic phase having stoichiometric composition of  $\text{TiCo}$  with  $\text{CsCl}$  structure (cubic) having a lattice parameter of 0.2986 nm.

It is surprising that solution treatment followed by rapid quenching of Cu–4.5Ti–0.5Co alloy has not suppressed the formation of these phases. Formation of composition modulations and fine scale precipitation ( $\text{Cu}_4\text{Ti}$ ,  $\beta^l$ ) has been reported in solution treated binary Cu–Ti alloys containing more than 4.0wt.% Ti by Laughlin and Cahn [3], Datta and Soffa [4], and Nagarjuna et al. [5–9] and our observation that  $\text{Cu}_4\text{Ti}$ ,  $\beta^l$  is present in the solution treated Cu–4.5Ti–0.5Co alloy is in agreement with the reported behaviour. However, it is to be noted here that in solution treated binary Cu–4.5Ti alloy, only composition modulations were observed and the  $\text{Cu}_4\text{Ti}$ ,  $\beta^l$  phase was not yet precipitated [5], whereas addition of Co to the binary Cu–4.5Ti alloy has resulted in the formation of fully developed  $\text{Cu}_4\text{Ti}$ ,  $\beta^l$  phase, thereby indicating that Co has advanced the kinetics of precipitation of  $\text{Cu}_4\text{Ti}$ ,  $\beta^l$  phase. In the case of binary Cu–Be–Co alloys, the addition of cobalt was reported to enhance the magnitude of the age-hardening response and retard the tendency to overage or soften at extended aging times and higher aging temperatures [15]. Such a behaviour was not observed in the Cu–4.5Ti–0.5Co alloy. It is

evident from the Ti–Co phase diagram [21] that a eutectoid reaction  $(\text{Ti}) = (\alpha\text{Ti}) + \text{Ti}_2\text{Co}$  occurs at 685°C. Formation of  $\text{Ti}_2\text{Co}$  phase was noticed in the present study also, which is due to the above eutectoid reaction occurring in the Cu–4.5Ti–0.5Co alloy. The SAD pattern and its schematic in Fig. 9b and c confirm the presence of  $\text{Ti}_2\text{Co}$  phase. Further, the phase diagram also shows a congruent reaction, viz.  $\text{L} \rightarrow \text{TiCo}$  occurring at a temperature of 1325°C. Formation of  $\text{TiCo}$  intermetallic phase was also found in Cu–4.5Ti–0.5Co alloy of the present study (Fig. 9). The presence of Ti and Co in the precipitate particles as revealed by the EPMA studies (Fig. 8), further confirms the presence of  $\text{Ti}_2\text{Co}$  and  $\text{TiCo}$  phases in the solution treated Cu–4.5Ti–0.5Co alloy.

Fig. 10 shows the transmission electron micrographs of the Cu–4.5Ti–0.5Co alloy peak aged at 400°C for 16 h. The bright field image in Fig. 10a and the dark field image in Fig. 10b reveal fine precipitates, while Fig. 10c and d show SAD pattern and its schematic respectively of the precipitates. The phases present in the peak aged Cu–4.5Ti–0.5Co alloy have been identified from the SAD pattern and its schematic as the same observed in the solution treated alloy. The  $\beta'$ ,  $\text{Cu}_4\text{Ti}$  phase with body-centered tetragonal structure is responsible for precipitation strengthening, as observed earlier in binary Cu–Ti alloys [3–9]. In the Cu–4.5Ti–0.5Co alloy too, the  $\beta'$ ,  $\text{Cu}_4\text{Ti}$  phase is responsible for maximum strengthening, as it is predominantly present in the peak aged condition. It is also observed that in addition to  $\beta'$ ,  $\text{Cu}_4\text{Ti}$  phase,  $\text{Ti}_2\text{Co}$  and  $\text{TiCo}$  phases are present in the peak aged Cu–4.5Ti–0.5Co alloy.

The transmission electron micrographs of Cu–4.5Ti–0.5Co alloy over aged at 450°C for 64 h are shown in Fig. 11. Fig. 11a reveals fine precipitates as seen in the bright field image. The SAD pattern of the precipitate particles and its schematic are shown in Fig. 11b and c, respectively. From the SAD pattern and its schematic, the precipitates have been identified to be the same as those observed in the solution treated or peak aged alloy. It is interesting to note that only the transition phase  $\beta'$ ,  $\text{Cu}_4\text{Ti}$  is present in the overaged alloy even after overaging for 64 h at 450°C. It has been reported by Nagarjuna et al. [9] that equilibrium precipitate,  $\text{Cu}_3\text{Ti}$  formed in binary Cu–4.5Ti and Cu–5.4Ti alloys after overaging at 450°C for 50 h. The precipitation of equilibrium phase,  $\text{Cu}_3\text{Ti}$  has not been observed in Cu–4.5Ti–0.5Co alloy in the present study even after aging for 64 h at 450°C. The addition of Co has resulted in the formation of  $\text{Ti}_2\text{Co}$  and  $\text{TiCo}$  phases, which reduces the Ti content of the matrix. In the binary Cu–Ti alloys, the  $\beta'$ ,  $\text{Cu}_4\text{Ti}$  metastable phase transforms to,  $\text{Cu}_3\text{Ti}$  equilibrium phase on over aging when sufficient Ti is available in the matrix. However, if Ti content in the matrix is lower, only  $\beta'$ ,  $\text{Cu}_4\text{Ti}$  precipitate is observed and such a behaviour was reported for Cu–1.5Ti alloy overaged at 450°C for 50 h [7] and Cu–4.3Ti–2Ni–2Al alloy aged at 500°C for 700 min [14]. Therefore, the present observation that only  $\beta'$ ,  $\text{Cu}_4\text{Ti}$  phase is present in overaged Cu–4.5Ti–0.5Co alloy is in agreement with the reported results. It is seen from Fig. 1 that hardness decreased with prolonged aging after a peak value. Formation of the equilibrium precipitate,  $\text{Cu}_3\text{Ti}$  has been reported to cause decrease in hardness and strength due to the overaging phe-

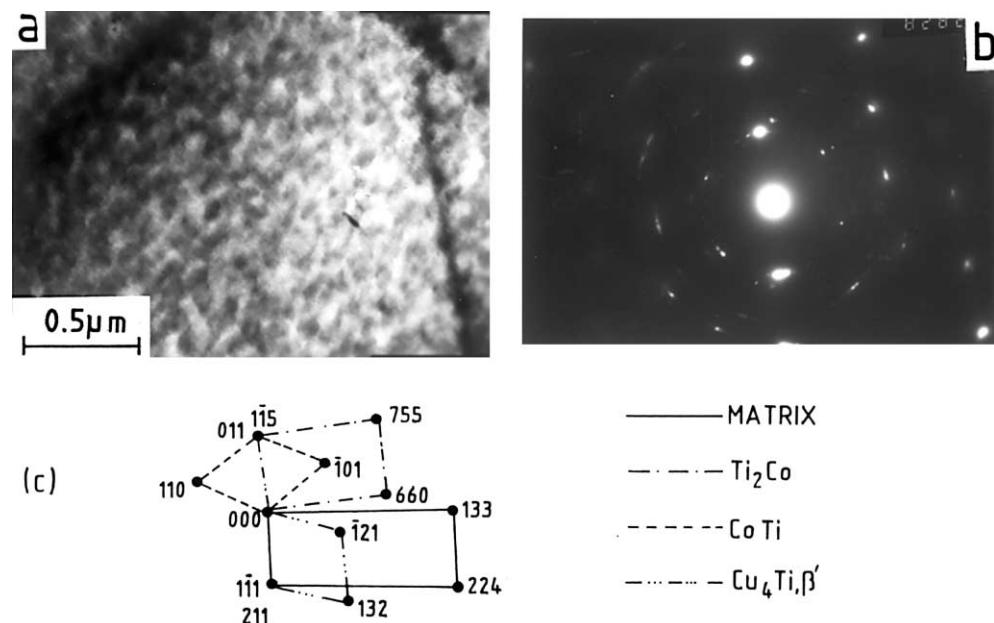


Fig. 9. Transmission electron micrographs (TEMs) of solution treated Cu–4.5Ti–0.5Co alloy. (a) Bright field image, (b) SAD pattern and (c) schematic of SAD pattern.

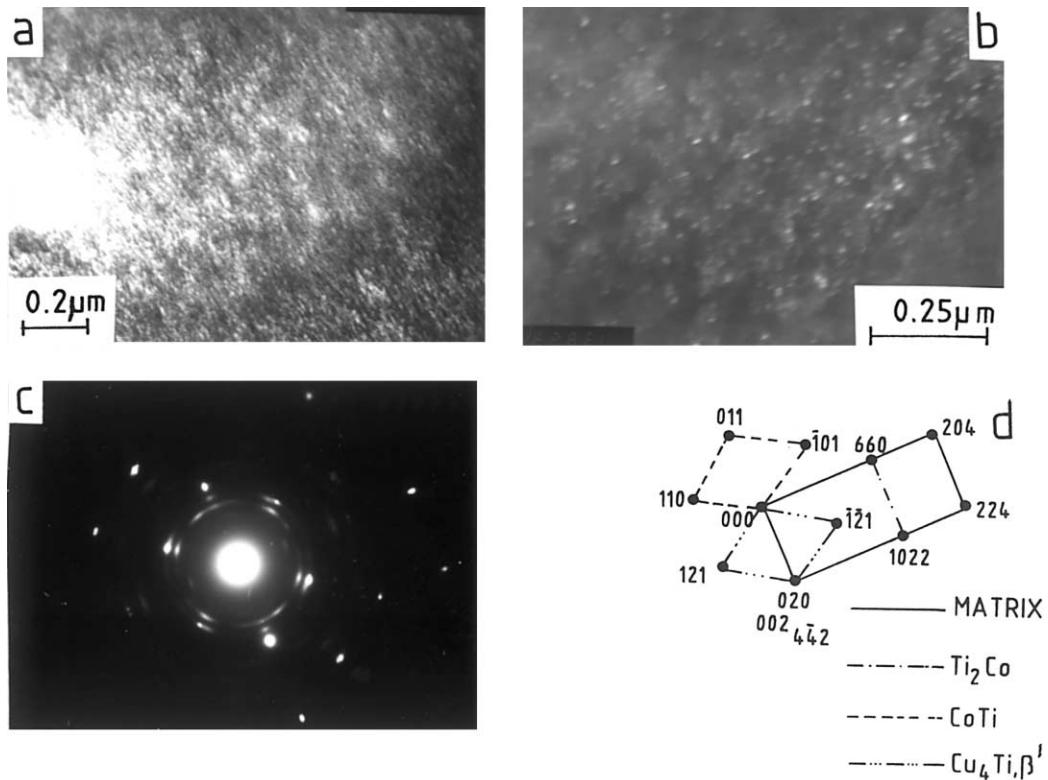


Fig. 10. Transmission electron micrographs (TEMs) of peak aged Cu–4.5Ti–0.5Co alloy. (a) Bright field image, (b) dark field image, (c) SAD pattern, and (d) schematic of SAD pattern.

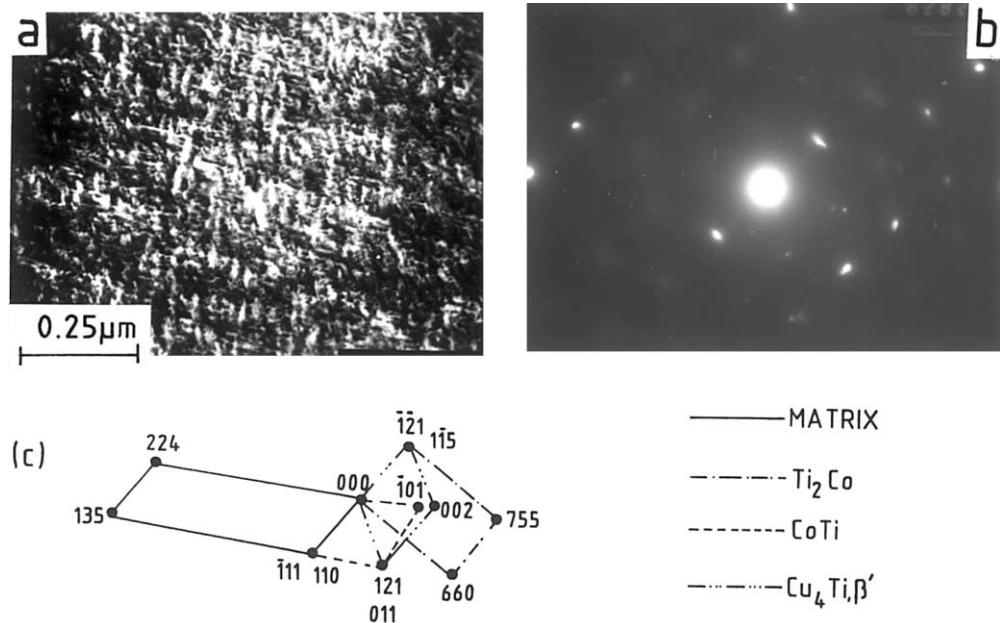


Fig. 11. Transmission electron micrographs (TEMs) of overaged Cu–4.5Ti–0.5Co alloy. (a) Bright field image, (b) SAD pattern, and (c) schematic of SAD pattern.

nomenon in binary Cu–Ti alloys [2–5,7,9]. Because equilibrium phase,  $\text{Cu}_3\text{Ti}$  is not found in Cu–4.5Ti–0.5Co alloy, the reason for decrease in hardness on prolonged aging/overaging could be due to further low-

ering of Ti content in the matrix, which was caused by the formation and further growth of  $\text{Ti}_2\text{Co}$  and  $\text{TiCo}$  precipitates. It is, therefore, concluded that Co additions up to 0.5% to binary Cu–4.5Ti alloy suppress the

formation of equilibrium phase,  $\text{Cu}_3\text{Ti}$  by lowering the Ti content in the matrix, which is utilized for formation and growth of  $\text{Ti}_2\text{Co}$  and  $\text{TiCo}$  precipitates.

Fig. 12 shows the transmission electron micrograph of the  $\text{Cu}-4.5\text{Ti}-0.5\text{Co}$  alloy in ST + 90%CW + PA condition (peak aged at  $400^\circ\text{C}$  for 1 h). The microstructure essentially consists of elongated grains and fine precipitates. Hardness and strength of the cold worked and peak aged  $\text{Cu}-4.5\text{Ti}-0.5\text{Co}$  alloy are higher than those of the as-quenched and peak aged alloy. Cold work increases the dislocation density of the solution treated alloy. An annealed metal/alloy contains  $\sim 10^6-10^8$  dislocation  $\text{cm}^{-2}$  while plastically deformed material contain about  $10^{12}$  dislocation  $\text{cm}^{-2}$  [22]. Dutkiewicz [23] concluded that in a highly deformed  $\text{Cu}-4.29\text{wt.\%}$  alloy heterogeneous precipitation of transitional  $\beta^1$  phase occurred on dislocations and other structural defects. In the present study also, nucleation of intermediate precipitate ( $\beta^1$ ,  $\text{Cu}_4\text{Ti}$ ) in solution treated and cold worked  $\text{Cu}-4.5\text{Ti}-0.5\text{Co}$  alloy occurred on aging at crystal defects such as dislocations that act as heterogeneous sites and the volume fraction of the precipitates increased. As a result, both hardness and strength increased considerably and are higher than that of the solution treated and peak aged alloy. The electrical conductivity too increased slightly in the ST + 90%CW + peak aged alloy due to enhanced removal of Ti from the solid solution as well as increased volume fraction of  $\beta^1$   $\text{Cu}_4\text{Ti}$ ,  $\text{Ti}_2\text{Co}$  and  $\text{TiCo}$  phases.

#### 4. Conclusions

Age hardening behaviour of  $\text{Cu}-4.5\text{Ti}-0.5\text{Co}$  alloy has been studied at different temperatures and times

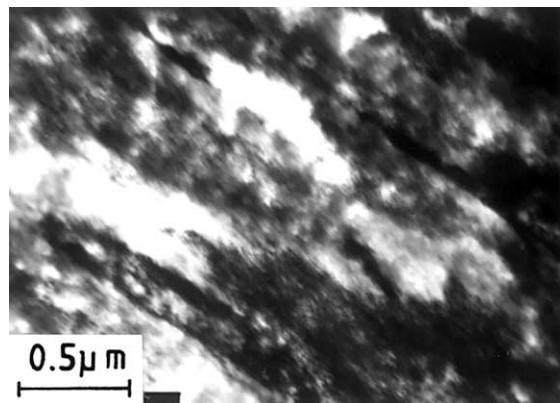


Fig. 12. Transmission electron micrograph (TEM) of  $\text{Cu}-4.5\text{Ti}-0.5\text{Co}$  alloy in ST + 90%CW + PA condition (peak aged at  $400^\circ\text{C}$  for 1 h).

and the following conclusions have been drawn on the present investigation:

(1) Cobalt addition to the binary  $\text{Cu}-4.5\text{Ti}$  alloy results in the refinement of grain size.

(2) Considerable strengthening occurs on aging of the solution treated  $\text{Cu}-4.5\text{Ti}-0.5\text{Co}$  alloy with hardness increasing from 250 to  $320 \text{ H}_\text{V}$  after aging at  $400^\circ\text{C}$  for 16 h.

(3) Cobalt addition to  $\text{Cu}-4.5\text{Ti}$  alloy reduces not only the aging temperature and time for attaining peak hardness but also the magnitude of peak hardness slightly. It also advances the kinetics of precipitation of transition phase  $\text{Cu}_4\text{Ti}$ ,  $\beta^1$ .

(4) Yield and tensile strength follow the trend of hardness, with yield strength increasing from 360 to  $710 \text{ MPa}$  and tensile strength, from 610 to  $890 \text{ MPa}$  on aging the solution treated alloy for peak strength. The ductility (% elongation) however, decreases from 32 to 25%.

(5) Ordered, metastable and coherent  $\text{Cu}_4\text{Ti}$ ,  $\beta^1$  phase is found to be mainly responsible for maximum strengthening, as it is predominantly present in the peak aged condition.

(6) In the overaged condition, absence of equilibrium precipitate  $\text{Cu}_3\text{Ti}$ , and presence of transition phase  $\text{Cu}_4\text{Ti}$ ,  $\beta^1$  are observed which shows that the addition of cobalt to  $\text{Cu}-4.5\text{Ti}$  alloy suppresses the precipitation of equilibrium phase  $\text{Cu}_3\text{Ti}$ .

(7) Two intermetallic phases containing Ti and Co with stoichiometric composition of  $\text{Ti}_2\text{Co}$  and  $\text{TiCo}$  are found to form in all the conditions studied, i.e. solution treated, peak aged and overaged.

(8) Cold work prior to aging further increases the hardness and strength; hardness from  $320$  to  $430 \text{ H}_\text{V}$ , yield strength from  $710$  to  $1185 \text{ MPa}$  and tensile strength, from  $890$  to  $1350 \text{ MPa}$  on aging the solution treated and 90% cold deformed alloy for peak strength. The ductility (% elongation), however, decreases from 25 to 3%.

(9) The electrical conductivity of the  $\text{Cu}-4.5\text{Ti}-0.5\text{Co}$  alloy is found to be 4 and 8% IACS, respectively, in the solution treated and peak aged conditions.

(10) While the mechanical properties are comparable, the electrical conductivity of the  $\text{Cu}-4.5\text{Ti}-0.5\text{Co}$  alloy is inferior to the binary  $\text{Cu}-4.5\text{Ti}$  alloy.

#### Acknowledgements

The financial support of the Defence Research and Development Organisation is gratefully acknowledged. The authors thank Dr D. Banerjee, Director, DMRL for permission to publish this paper. The services rendered by different Groups of DMRL are acknowledged with thanks.

## References

- [1] Metals Hand Book, Desk edition, ASM, OH, 1984, p. 7.1.
- [2] M.J. Saarvista, H.S. Cannon, *Met. Prog.* 76 (1959) 81.
- [3] D.E. Laughlin, J.W. Cahn, *Acta Metall.* 23 (1975) 329.
- [4] A. Datta, W.A. Soffa, *Acta Metall.* 24 (1976) 987.
- [5] S. Nagarjuna, K. Balasubramanian, D.S. Sarma, *Mater. Trans. JIM* 36 (8) (1995) 1058.
- [6] S. Nagarjuna, K. Balasubramanian, D.S. Sarma, *Mater. Sci. Eng.* A225 (1997) 118.
- [7] S. Nagarjuna, K. Balasubramanian, D.S. Sarma, *J. Mater. Sci.* 32 (1997) 3375.
- [8] S. Nagarjuna, M. Srinivas, K. Balasubramanian, D.S. Sarma, *Mater. Sci. Eng.* A259 (1999) 34.
- [9] S. Nagarjuna, K. Balasubramanian, D.S. Sarma, *J. Mater. Sci.* 34 (1999) 2929.
- [10] W. Piotrowski, Z. Gawronski, *Metals Technol.* 12 (1980) 502.
- [11] J. Dutkiewicz, L. Litinska, S. Salwa, *Pr. Inst. Met. Nizelaz* 13 (1–2) (1984) 10.
- [12] E.P. Daneliya, M.I. Doperchuck, G.I. Kandhba, I.P. Pazyuk, *Fiz. Met. Metalloved.* 57 (2) (1984) 335.
- [13] D.S. Arensburger, S.M. Letunovich, *Poroshk. Metall.* 6 (1988) 49.
- [14] Y.H. Hong, J.H. Lee, S.H. Hong, *Proceedings of PRICM-1, Advanced Materials and Processing, The Minerals and Materials Society, Warrendale, PA*, 1993, p. 579.
- [15] Metals Hand Book, Properties and Selection: Nonferrous Alloys and Special purpose materials, Vol.2, 10th edn., ASM International OH, 1990, p. 404.
- [16] Duerrschnabel, Wolfgang, Puckerd, Franz, Stueer, Heinrich, Use of a Cu–Ti–Co alloy as a material for electronic components, Patent no. US 4734255, 1986.
- [17] Standard Test Method for Tension Testing of Metallic Materials (Metric), ASTM E8M-97, Annual book of ASTM standards, vol. 03.01., 1997, p.77.
- [18] Standard Test Method for Resistivity of Electrical Conductor Materials, ASTM B193-95, Annual book of ASTM standards, vol. 02.03., 1997, p.73.
- [19] P. Gregory, A.J. Bangay, T.L. Bird, *Metallurgia* 71 (1965) 207.
- [20] S. Nagarjuna, M. Srinivas, K. Balasubramanian, D.S. Sarma, *Acta Mater.* 44 (1996) 2285.
- [21] J.L. Murray, L.H. Bennett, H. Baker, *Binary Alloy Phase diagrams*, vol. 1, ASM, Metals Park, OH, 1986, p. 809.
- [22] G.E. Dieter, *Mechanical Metallurgy*, McGraw–Hill Book, New York, 1987, p. 230.
- [23] J. Dutkiewicz, *Metall. Trans. A* 8 (1977) 751.