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Effect of cobalt additions on the age hardening of Cu-4.5Ti alloy

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The effects of 0.9 and 1.8 wt% cobalt additions on the age hardening behaviour of Cu-4.5Ti alloy have been investigated. It has been observed that though Co addition results in the refinement of grain size and the Cu-Ti-Co alloys exhibit age hardening (giving rise to peak hardness on aging at 400°C for 16 hours), the peak hardness as well as the corresponding yield and tensile strengths were found to decrease with increasing cobalt content. The electrical conductivities of 0.9 and 1.8 wt% Co alloys were found to be 6% and 10% International Annealed Copper Standard (IACS) and 7% and 14% IACS in solution treated and peak aged conditions, respectively. Like in the binary Cu-Ti alloys, precipitation of ordered, metastable and coherent $Cu_4Ti(\beta^1)$ precipitate was found to be responsible for maximum strengthening in these alloys. In addition, coarse intermetallic phases of Ti and Co, viz. Ti_2Co and TiCo particles have been observed in all the conditions studied. The inferior mechanical properties of Cu-Ti-Co alloys compared with those of the binary Cu-Ti alloys are attributed to the depletion of Ti from matrix, which is consumed to form Ti_2Co and TiCo phases. © *2002 Kluwer Academic Publishers*

1. Introduction

Immense research is directed at developing new and improved copper base alloys with the aim of achieving better combination of properties such as high strength and good electrical conductivity. Age hardenable Cu-Be alloys possess the combination of high strength and medium electrical conductivity [1]. However, they have serious disadvantages of toxicity and high cost, which limit their use. Cu-Ti alloys have good potential as a substitute for the Cu-Be alloys. Binary Cu-Ti alloys are strengthened by age hardening through spinodal decomposition and our earlier work shows that they exhibited mechanical properties comparable to those of the Cu-Be alloys [2–7], though the electrical conductivity was slightly inferior.

There have earlier been some investigations to study the influence of ternary alloying additions such as vanadium, aluminum, alumina, boron and nickel to binary Cu-Ti alloys carried out by several earlier investigators [8–12]. Though either Co or Ni or both are added to commercial Cu-Be alloys for improved properties [13], 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.* [14] and our recent investigation on a Cu-4.5Ti-0.5Co alloy [15]. While the patented alloy was reported to possess a combination of strength (UTS: 479–570 MPa), electrical conductivity (74–77% IACS) and softening resistance [14], Cu-4.5Ti-0.5Co alloy was shown to exhibit better strength (UTS: 890–1350 MPa) but suffered from poor electrical conductivity (8–12% IACS) [15]. Therefore, a detailed study was undertaken to investigate the effects of additions of cobalt greater than 0.5 wt% to binary Cu-4.5Ti alloy with the aim of development of alloys exhibiting a good combination of strength and electrical conductivity. This paper presents the findings of the investigation.

2. Experimental

A 30 kg melt each of the Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys was made in the graphite crucible of STOKES Vacuum Induction Melting (VIM) furnace. The ingots were homogenized at 850°C for 24 hours and analysed for titanium and cobalt contents. The analysed composition of the ingots is given in Table I. The homogenized ingots were hot forged and rolled into rods and flats of suitable sizes. Specimens from the hot rolled rods were solution treated at 860°C/2h/WQ and aged at 400, 450 and 500°C for different times. Vickers hardness (Hv) of these specimens was measured at 10 kg load. 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) [16] at ambient temperature, at a nominal strain rate of 10^{-3}/sec using INSTRON 1185 ball screw driven universal testing system. 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 [17].

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TABLE I Analyzed composition of Cu-Ti-Co alloys

Ingot Id. No.	Titanium (wt%)	Cobalt (wt%)	Oxygen (ppm)	Copper
CTC - 2	4.5	0.9	6.3	Balance
CTC - 3	4.5	1.8	7.5	Balance

Samples from solution treated as well as aged alloys were polished, etched and examined under optical microscope. Electron Probe Micro Analysis (EPMA) was carried out on the solution treated samples of both the alloys. Thin discs of about 0.10 mm thickness were sliced from the heat-treated samples using an ISOMET saw and they were further reduced to about 20 μm by mechanical polishing. Discs of 3 mm diameter were punched out from these thinned sections and electropolished in a Fischionne twin jet electro-polisher using a solution of 30 vol% HNO_3 and 70% methanol at −45°C and at a voltage of 10 V. The thin foils were examined at 160 kV using JEOL-200CX Transmission Electron Microscope.

3. Results

3.1. Mechanical properties

3.1.1. Hardness

The influence of aging time on hardness of the solution treated Cu-Ti-Co alloys is shown in Fig. 1. As seen in Fig. 1a, a hardness of about 170 Hv was recorded for solution treated Cu-4.5Ti-0.9Co alloy, which after aging at 400°C for 16 hours, reached a value of 310 Hv and remained nearly constant even after aging for 32 hours. The hardness increased to 300 Hv after aging at 450°C for 16 hours, beyond which it decreased with aging time. A slightly lower peak hardness of 296 Hv was obtained at 500°C after just 2 hours of aging beyond which overaging (decrease in hardness with aging time) was rapid. The age hardening curves of Cu-4.5Ti-1.8Co alloy are shown in Fig. 1b. The alloy had a hardness of 120 Hv in the solution treated condition and attained hardness values of 250, 238, 238 Hv after aging at 400°C for 16 hours, 450°C for 4 hours and 500°C for 2 hours respectively. Further, overaging was insignificant at 450°C but more drastic at 500°C when compared to that in Cu-4.5Ti-0.9Co alloy.

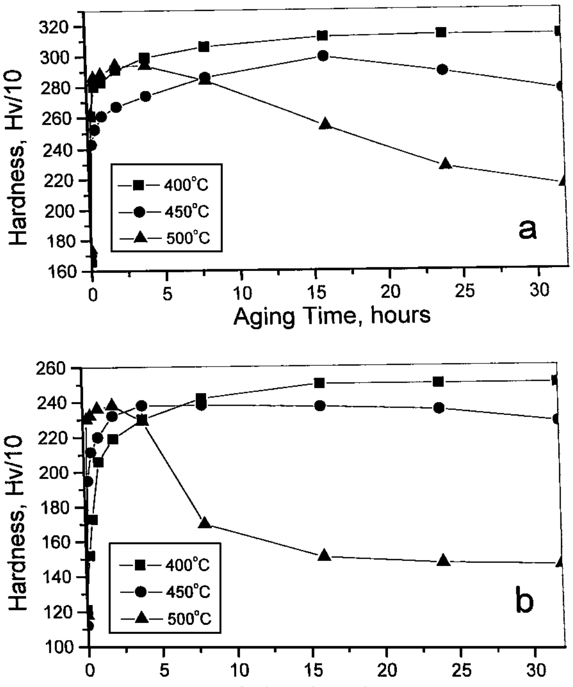

Figure 1 Age hardening in Cu-Ti-Co alloys. (a) Cu-4.5Ti-0.9Co and (b) Cu-4.5Ti-1.8Co.

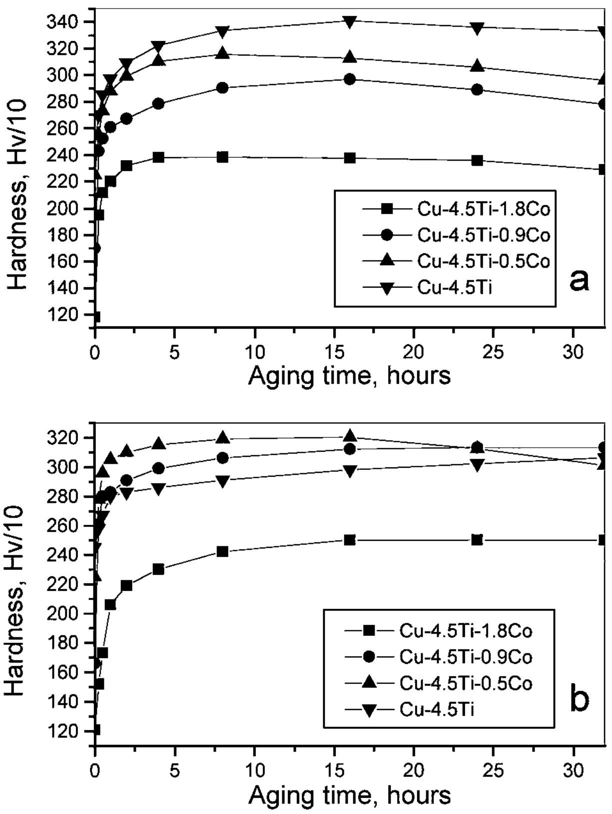

Figure 2 Effect of cobalt additions to Cu-4.5Ti alloy on age hardening. (a) Aged at 450°C and (b) aged at 400°C.

The effect of Co additions on age hardening in the alloys studied is shown in Fig. 2. Fig. 2a and b reveal the age hardening curves for the alloys aged at 450°C and 400°C respectively. The peak hardness was the highest (340 Hv) in the binary Cu-4.5Ti alloy [5], which got lowered to 320 Hv in Cu-4.5Ti-0.5Co alloy [15]. The present study shows that the peak hardness got further reduced to 310 Hv for the Cu-4.5Ti-0.9Co alloy and 250 Hv for the Cu-4.5Ti-1.8Co alloy.

Co additions to Cu-4.5Ti alloy have also lowered the aging temperature at which maximum hardness is obtained, from 450°C for binary Cu-4.5Ti alloy to 400°C in the ternary Cu-Ti-Co alloys, as shown in Fig.3. Further, this temperature was constant irrespective of the amount of cobalt added. The aging time for attaining maximum hardness was found to be constant at 16 hours for the three Cu-Ti-Co alloys at 400°C as well as for the binary Cu-4.5Ti alloy at 450°C. It is, therefore, evident that cobalt additions to the binary Cu-4.5Ti alloy decreased both the peak hardness as well as aging temperature to achieve this peak hardness.

3.1.2. Tensile properties

The hardness, tensile properties and electrical conductivity of the two present Cu-Ti-Co alloys are compared

TABLE II Comparison of properties of Cu-Ti-Co alloys with binary Cu-4.5Ti alloy [5]

Alloy	Condition	Hardness (Hv/10)	Yield strength[a] (MPa)	Tensile strength (MPa)	Elongation[b] (%)	Electrical conductivity (% IACS)	Reference
Cu-4.5Ti-1.8Co	ST	120	210	430	34	7.0	Present work
	PA	250	575	745	16	14.2	
Cu-4.5Ti-0.9Co	ST	170	280	530	40	5.8	Present work
	PA	310	610	795	19	10.0	
Cu-4.5Ti-0.5Co	ST	225	360	610	32	4.0	Nagarjuna *et al.* [15]
	PA	320	710	890	25	8.0	
Cu-4.5Ti	ST	245	440	680	29	8.0	Nagarjuna *et al.* [5]
	PA	340	700	890	20	11.0	

ST: Solution treated. PA: Peak aged.
[a] 0.2% offset.
[b] GL = 25 mm.

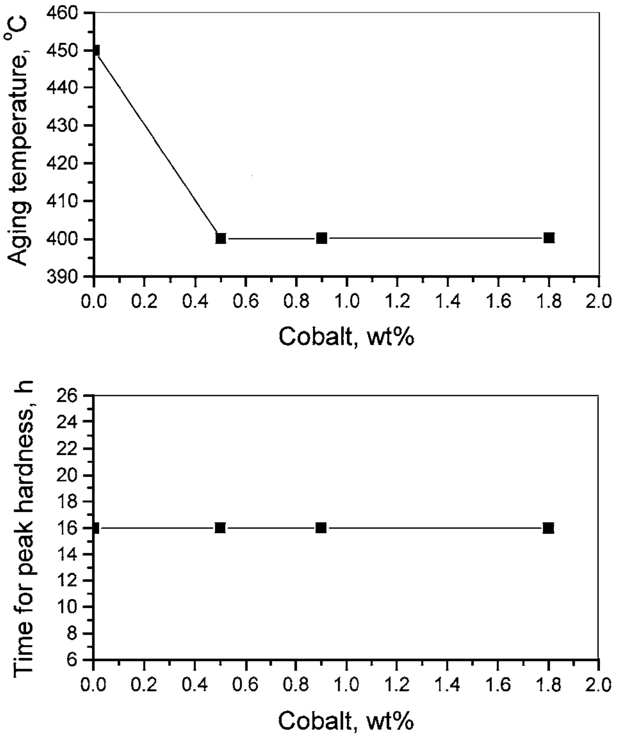

Figure 3 Effect of cobalt additions to Cu-4.5Ti alloy on aging parameters.

with our earlier results on Cu-4.5Ti alloy [5] and Cu-4.5Ti-0.5Co [15] in Table II. The yield and tensile strengths of Cu-4.5Ti-0.9Co alloy increased respectively from 280 and 530 MPa in solution treated condition to 610 and 795 MPa in peak aged condition and the corresponding elongation reduced from 40% to 19%. The yield and tensile strengths of Cu-4.5Ti-1.8Co alloy were found to be further lowered to 210 and 430 MPa in solution treated and 575 and 745 MPa in peak aged conditions respectively, while the elongation decreased from 34% for the solution treated alloy to 16% on aging. It is therefore seen here that the hardness as well as yield and tensile strengths of solution treated Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloy are lower than those of Cu-4.5Ti [5] as well as Cu-4.5Ti-0.5Co [15] alloys in either the solution treated or peak aged conditions. The variation of hardness and tensile properties with cobalt content is shown in Fig. 4. Hardness, yield strength and tensile strength decreased with increasing cobalt while elongation showed an initial increase followed by a peak at 0.9% Co in solution treated condition and at 0.5% Co in aged condition and decreased thereafter to 1.8% Co. The over all effect of addition of cobalt to Cu-4.5Ti alloy is a decrease in the hardness and tensile properties.

3.1.3. Electrical conductivity

The electrical conductivity (EC) of the Cu-Ti-Co alloys investigated is recorded in Table II. The solution treated Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys exhibited an electrical conductivity of 6 and 7% IACS, which increased on aging for peak hardness, to 10 and 14% IACS respectively. Fig. 5 shows the variation of electrical conductivity with cobalt in Cu-Ti-Co alloys. EC decreased initially with a minimum at 0.5% Co and increased thereafter, with increasing cobalt up to 1.8% in both solution treated and peak aged conditions. The cobalt additions have therefore, increased the EC in Cu-4.5Ti-1.8Co alloy on peak aging to 14% IACS which is greater than that of the Cu-4.5Ti alloy (11% IACS) [5]. The EC of both Cu-4.5Ti-0.5Co and Cu-4.5Ti-0.9Co alloys is less than that of the binary alloy in the corresponding condition, i.e. solution treated or peak aged.

3.2. Microstructure

3.2.1. Optical microscopy

The optical micrographs depicting the grain size of the solution treated binary Cu-Ti and Cu-Ti-Co alloys are shown in Fig. 6 (Fig. 6a shows the microstructure of Cu-4.5Ti [15]; Fig. 6b, Cu-4.5Ti-0.5Co [5]; Fig. 6c, Cu-4.5Ti-0.9Co and Fig. 6d, Cu-4.5Ti-1.8Co alloy). The grain sizes of the binary Cu-4.5Ti alloy and ternary Cu-4.5Ti-0.5Co alloy have been reported as 75 μm and 55 μm respectively [5, 15]. The Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys revealed grain sizes of 24 μm and 20 μm respectively. It is seen here that the grain size decreased with increasing amount of cobalt. Fig. 7 shows a plot of variation of grain size with cobalt content. The grain size decreased considerably from 75 to 24 μm with cobalt increasing from 0 to 0.9% and only marginally from 24 to 20 μm beyond 0.9% and up to 1.8% Co.

The optical microstructures of Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys are shown in Fig. 8 in solution treated and peak aged conditions. In the solution treated Cu-4.5Ti-0.9Co alloy (Fig. 8a), the microstructure mainly consists of equiaxed grains with annealing twins. Further, small spherical as well as

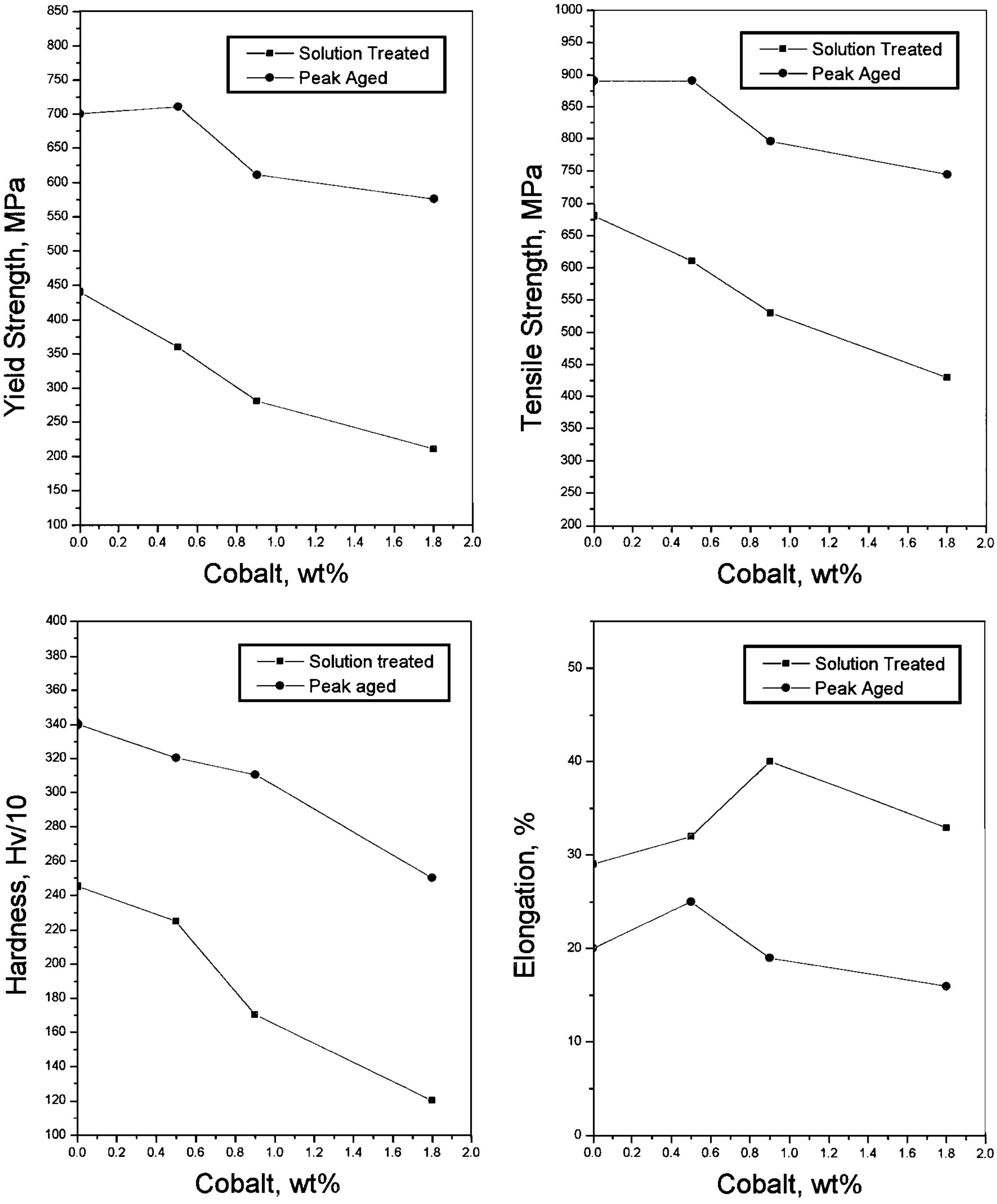

Figure 4 Variation of mechanical properties with cobalt content in Cu-Ti-Co alloys.

irregular shaped particles are spread uniformly throughout the matrix. Fig. 8b shows the microstructure of the Cu-4.5Ti-0.9Co alloy on aging and the structure is similar to that in Fig. 8a. Fig. 8c and d show the microstructure of the Cu-4.5Ti-1.8Co alloy in the solution treated and aged conditions respectively. They are similar to that found in Fig.8a and b except that the particles are larger in size compared to those in Cu-4.5Ti-0.9Co alloy (Fig. 8a or b). Such particles were also observed in Cu-4.5Ti-0.5Co alloy [15], wherein they were identified as Ti_2Co and TiCo.

3.2.2. Electron probe micro analysis (EPMA)

Fig. 9 shows the back-scattered electron image and mapping of elements in the solution treated Cu-4.5Ti-0.9Co alloy obtained from EPMA. The BSE image in Fig. 9a shows globular as well as string-like elongated particles. The elemental mapping in Fig. 9b–d revealed that these precipitate particles are rich in Ti as well as Co. The observed behaviour is similar to that reported for Cu-4.5Ti-0.5Co alloy [15]. EPMA was also carried out on solution treated Cu-4.5Ti-1.8Co alloy which showed similar images and presence of Ti and Co in elemental mapping.

3.2.3. Transmission electron microscopy

The transmission electron micrographs (TEMs) of the solution treated Cu-4.5Ti-0.9Co alloy are shown in Fig. 10. Fig. 10a shows the bright field image of the intertwined modulated structure with fine precipitates and Fig. 10b reveals the coarse particles of 0.1–0.3 μm.

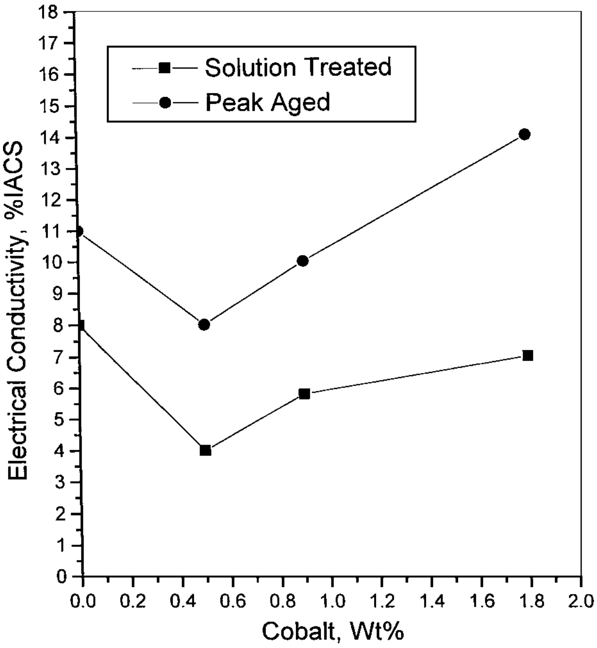

Figure 5 Variation of electrical conductivity with cobalt content in Cu-Ti-Co alloys.

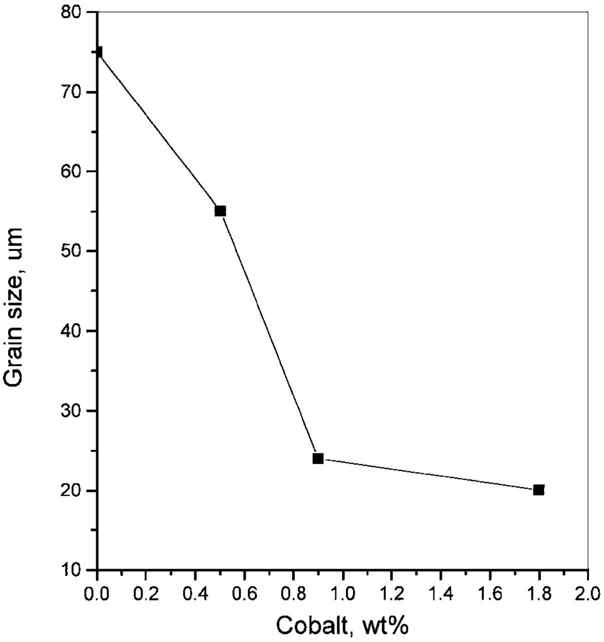

Figure 7 Variation of grain size with cobalt content in solution treated Cu-Ti-Co alloys.

Fig. 10c shows selected area diffraction (SAD) pattern of the precipitate particles and Fig. 10d, the schematic of SAD revealing the presence of

(i) ordered, metastable and coherent β^1 phase with a stoichiometric composition of Cu_4Ti having body-centered tetragonal (bct) crystal structure with lattice parameters of $a = 0.584$ nm and $c = 0.362$ nm.

(ii) an intermetallic phase having stochiometric composition of Ti_2Co, an ordered FCC structure having a lattice parameter of 1.127 nm.

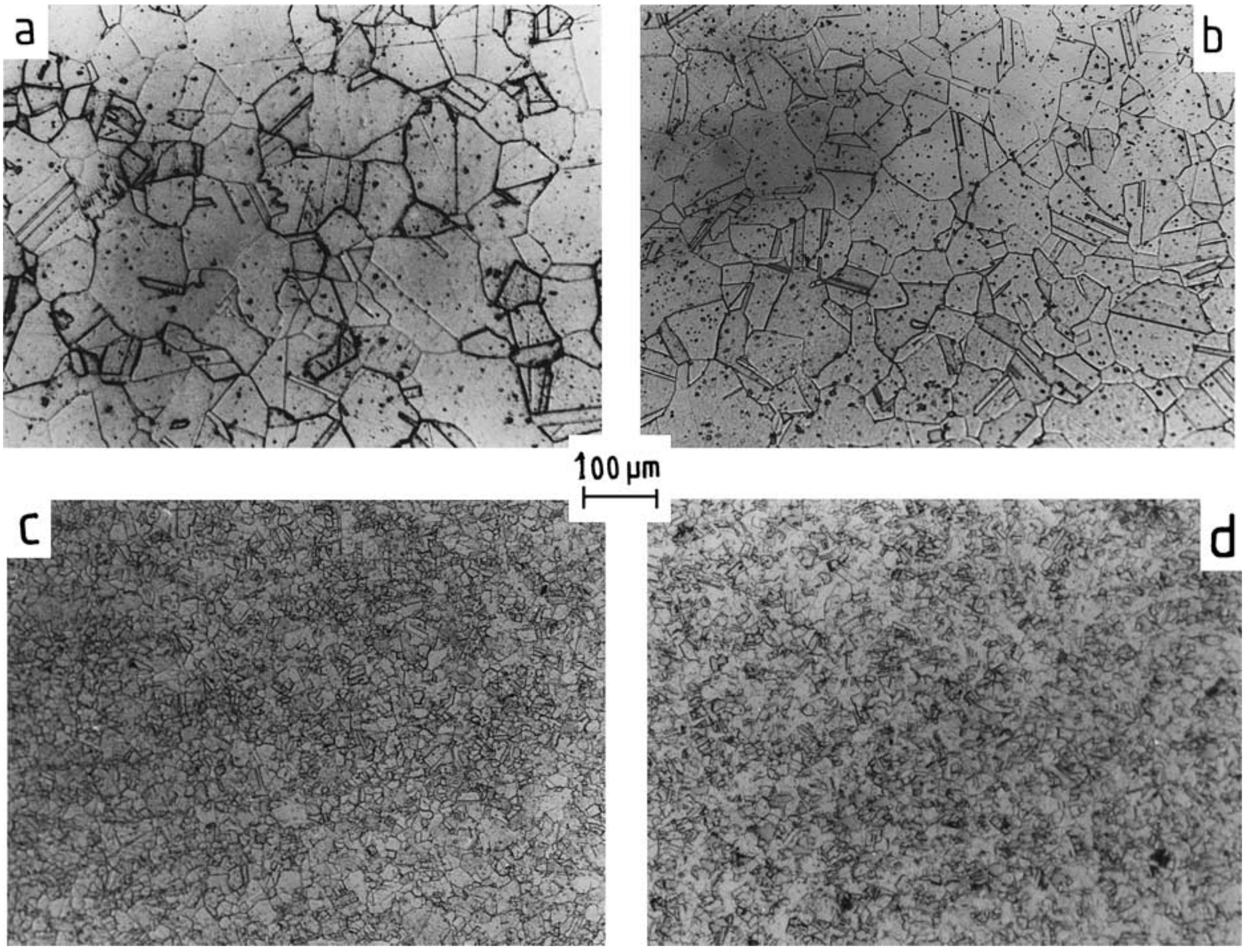

Figure 6 Optical micrographs showing grain refinement as a result of Co additions to Cu-4.5Ti alloy. (a) Cu-4.5Ti[5], (b) Cu-4.5Ti-0.5Co[15], (c) Cu-4.5Ti-0.9Co and (d) Cu-4.5Ti-1.8Co.

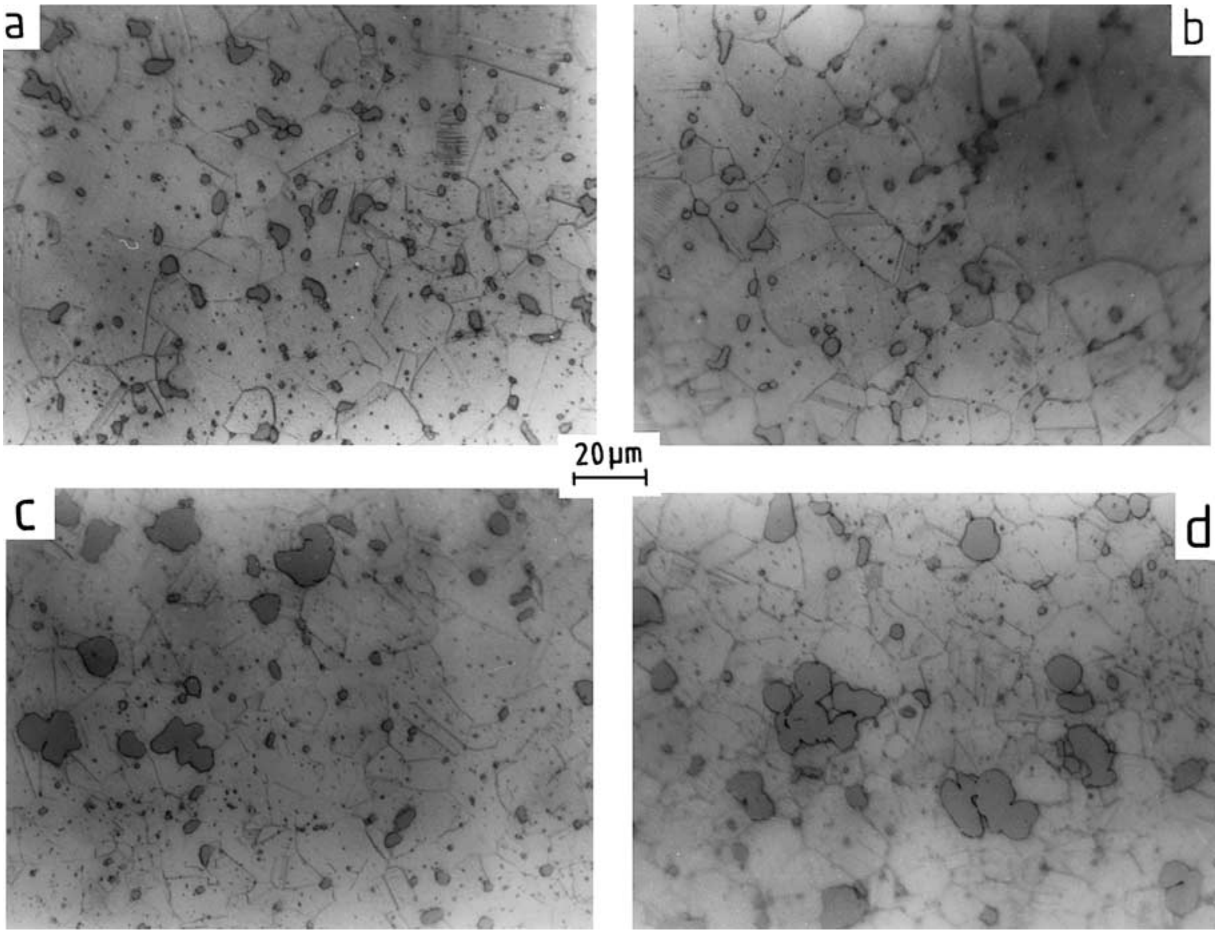

Figure 8 Optical micrographs of solution treated and peak aged Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys. (a) Solution treated Cu-4.5Ti-0.9Co (b) peak aged Cu-4.5Ti-0.9Co. (c) solution treated Cu-4.5Ti-1.8Co and (d) peak aged Cu-4.5Ti-1.8Co.

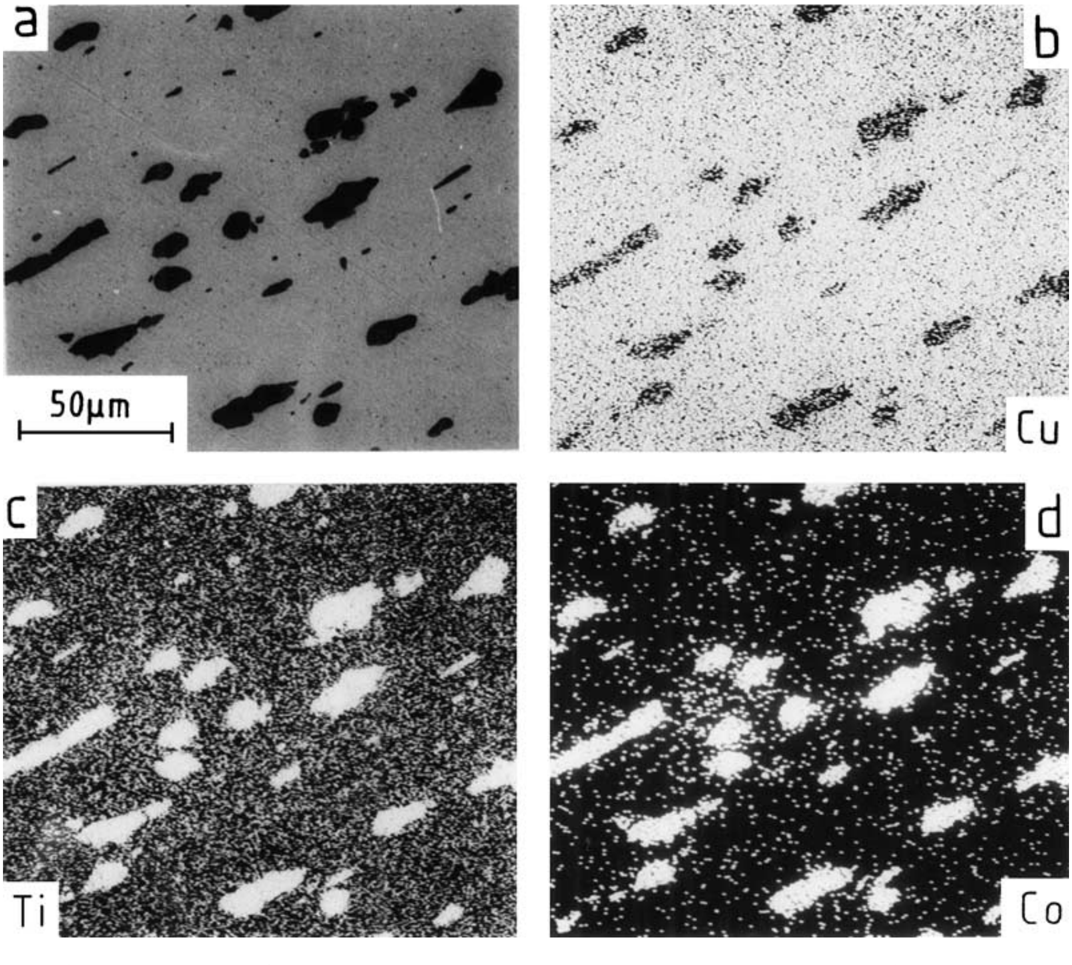

Figure 9 EPMA of solution treated Cu-4.5Ti-0.9Co alloy. (a) Back scattered image (b, c and d) elemental mapping for Cu, Ti & Co.

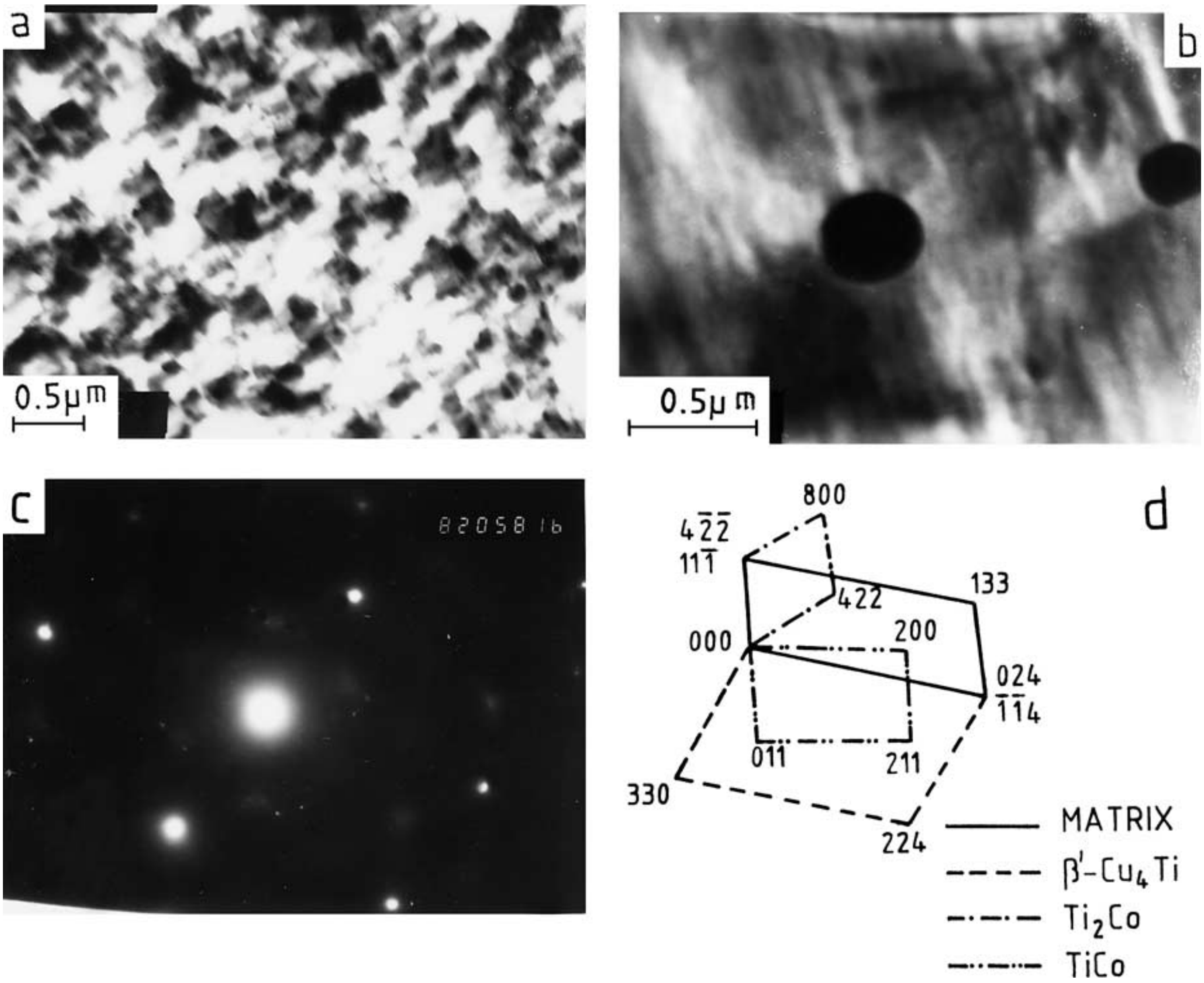

Figure 10 TEMs of solution treated Cu-4.5Ti-0.9Co alloy. (a) and (b) Bright field images, (c) SAD pattern and (d) schematic of SAD pattern.

(iii) one more intermetallic phase having stoichiometric composition of TiCo with CsCl structure (cubic) having a lattice parameter of 0.2986 nm.

Fig. 11 shows the transmission electron micrographs of the Cu-4.5Ti-0.9Co alloy aged at 400°C for 16 hours. The bright field images in Fig. 11a and b show a coarse particle and precipitates respectively, while Fig. 11c reveals the dark field image of the precipitates. Fig. 11d and e show SAD pattern and its schematic respectively of the precipitates. The phases present in the peak aged Cu-4.5Ti-0.9Co alloy have been identified from the SAD pattern and its schematic as the same observed in the solution treated alloy. The β^1, Cu_4Ti phase with body-centered tetragonal structure is responsible for precipitation strengthening, as observed earlier in binary Cu-Ti alloys [3–7]. In the Cu-4.5Ti-0.9Co alloy too, the β^1, Cu_4Ti phase is responsible for maximum strengthening, as it is predominantly present in the peak aged condition. In addition to β^1, Cu_4Ti phase, Ti_2Co and TiCo phases are present in the peak aged Cu-4.5Ti-0.9Co alloy.

The transmission electron micrographs of solution treated Cu-4.5Ti-1.8Co alloy are shown in Fig. 12. Fig. 12a–c reveal a coarse particle and fine precipitates as seen in the bright field images. The SAD pattern of the precipitate particles and its schematic are shown in Fig. 12d and e, respectively. After indexing the SAD pattern and from its schematic, the precipitates have been identified to be the same as those observed in the solution treated or peak aged Cu-4.5Ti-0.9Co alloy. The transmission electron micrographs of Cu-4.5Ti-1.8Co alloy aged at 400°C for 16 hours are shown in Fig. 13. Fig.13a and b are the bright field and dark field images respectively of fine precipitates as well as a coarse particle. The SAD pattern of the precipitate particles and its schematic are shown in Fig. 13c and d, 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 Cu-4.5Ti-0.9Co alloy or solution treated Cu-4.5Ti-1.8Co alloy. It is therefore, evident from the TEM studies that only β^1 Cu_4Ti, Ti_2Co and TiCo phases are present in the solution treated and aged Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys.

4. Discussion

The present work shows that the addition of cobalt to Cu-4.5 wt% Ti alloy has resulted in a decrease in hardness as well as strength in both the solution treated and peak aged conditions. The effects of Co additions to Cu-4.5Ti alloy on age hardening revealed in Fig. 2 show that the peak hardness was the highest (340 Hv) in the binary Cu-4.5Ti alloy [5], which got lowered to 320 Hv in the Cu-4.5Ti-0.5Co alloy [15]. The present study shows that the peak hardness got further lowered

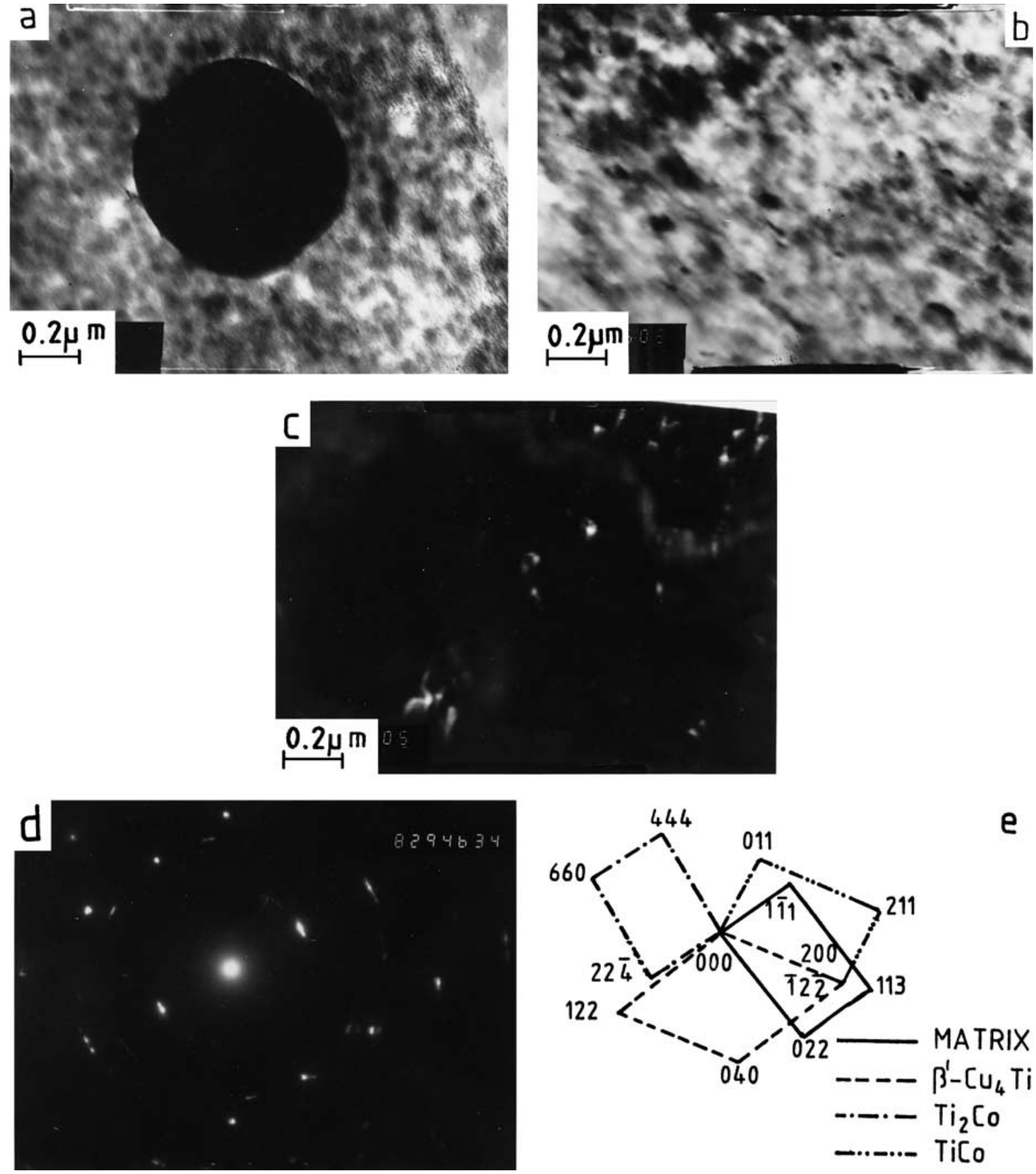

Figure 11 TEMs of peak aged Cu-4.5Ti-0.9Co alloy. (a) and (b) Bright field images, (c) dark field image, (d) SAD pattern, and (e) schematic of SAD pattern.

to 310 Hv for the Cu-4.5Ti-0.9Co alloy and 250 Hv for the Cu-4.5Ti-1.8Co alloy.

In the binary Cu-4.5Ti alloy, the peak hardness (340 Hv) was obtained after aging at 450°C for 16 hours, whereas the same was observed at 400°C aged for 16 hours in the Cu-4.5Ti-0.5Co alloy [15]. In the alloys of present study also, the peak hardness was obtained at 400°C aged for 16 hours. Further, the peak was not attained in the binary alloy aged at 400°C even after 32 hours. While the magnitude of hardness obtained at the aging temperature of 400°C is significantly higher than at 450°C in Cu-Ti-Co alloys, it is the reverse in the binary Cu-4.5Ti alloy [5]. At 450°C, the peak hardness in Cu-4.5Ti-0.9Co alloy (300 Hv) is obtained in 16 hours in contrast to that in 8 hours in Cu-4.5Ti-0.5Co alloy (315 Hv). Moreover, the peak hardness value is lower than that obtained at 400°C or at 450°C in Cu-4.5Ti-0.5Co alloy [15].

Co additions to Cu-4.5Ti alloy have also lowered the aging temperature at which maximum hardness was obtained, from 450°C for binary Cu-4.5Ti alloy to 400°C in the ternary alloys (Fig. 3). Further, this temperature was constant irrespective of the amount of cobalt added. The aging time for attaining maximum hardness was found to be constant at 16 hours for the three Cu-Ti-Co alloys at 400°C as well as for binary Cu-4.5Ti alloy at 450°C. It is, therefore, evident that cobalt additions to the binary Cu-4.5Ti alloy decreased both the peak

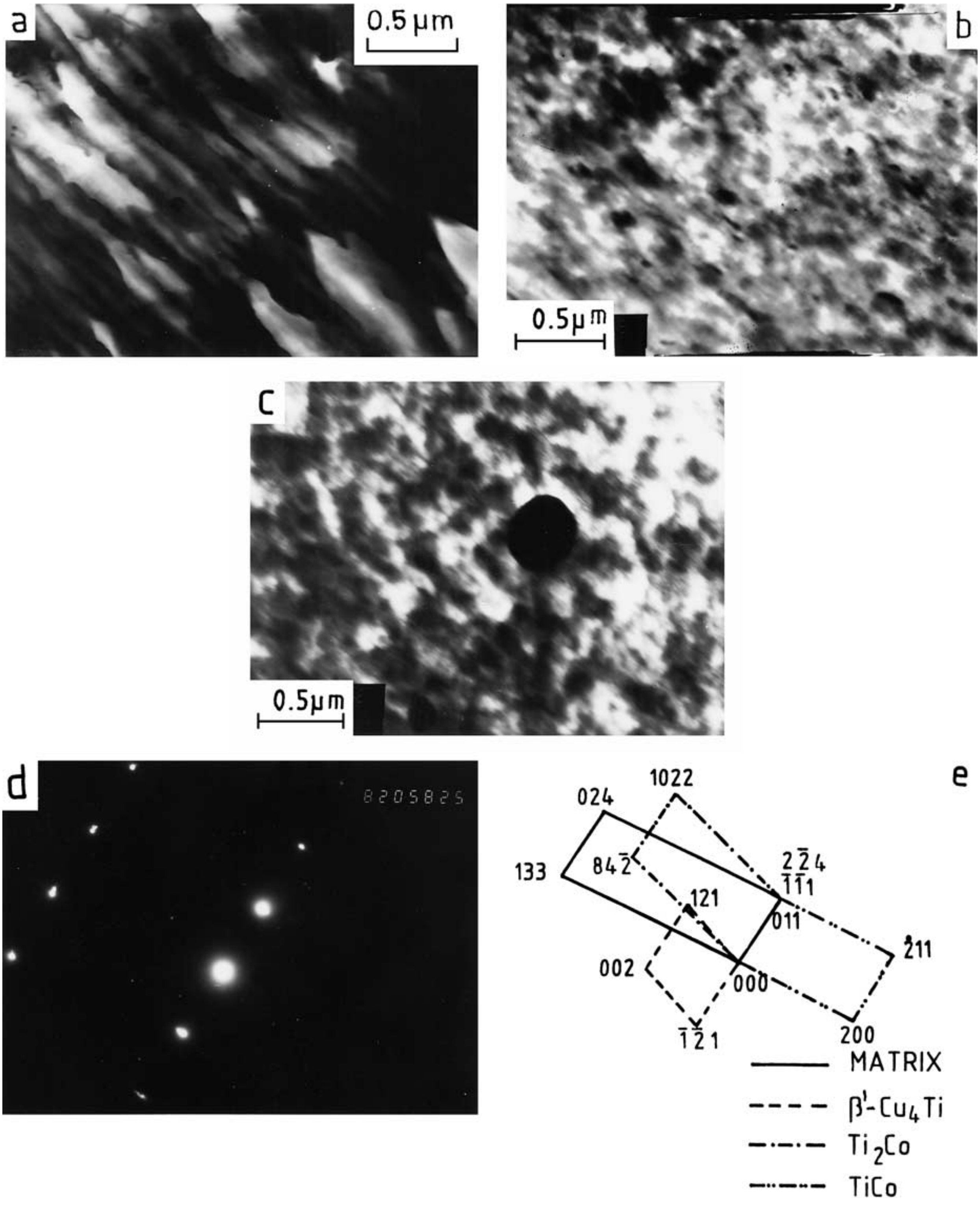

Figure 12 TEMs of solution treated Cu-4.5Ti-1.8Co alloy. (a), (b) and (c) Bright field images, (d) SAD pattern, and (e) schematic of SAD pattern.

hardness as well as aging temperature to achieve this peak hardness.

It was reported earlier that in the solution treated condition, fine scale precipitation in the form of modulations formed during quenching in Cu-4.5Ti alloy, which resulted in sharp increase in hardness and strength [7]. Though the Cu_4Ti (β^1) precipitate is found to be present in the solution treated condition in the three Cu-Ti-Co alloys studied, the strength levels of the ternary alloys are lower than that of binary Cu-4.5Ti alloy due to the removal of 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 is expected to increase its strength due to solid solution strengthening. However, the strength increase 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 0.2% [18]. Since the strength decrease due to lowering of Ti content in the matrix due to the formation of Ti-Co phases is considerably higher than the increase in strength due

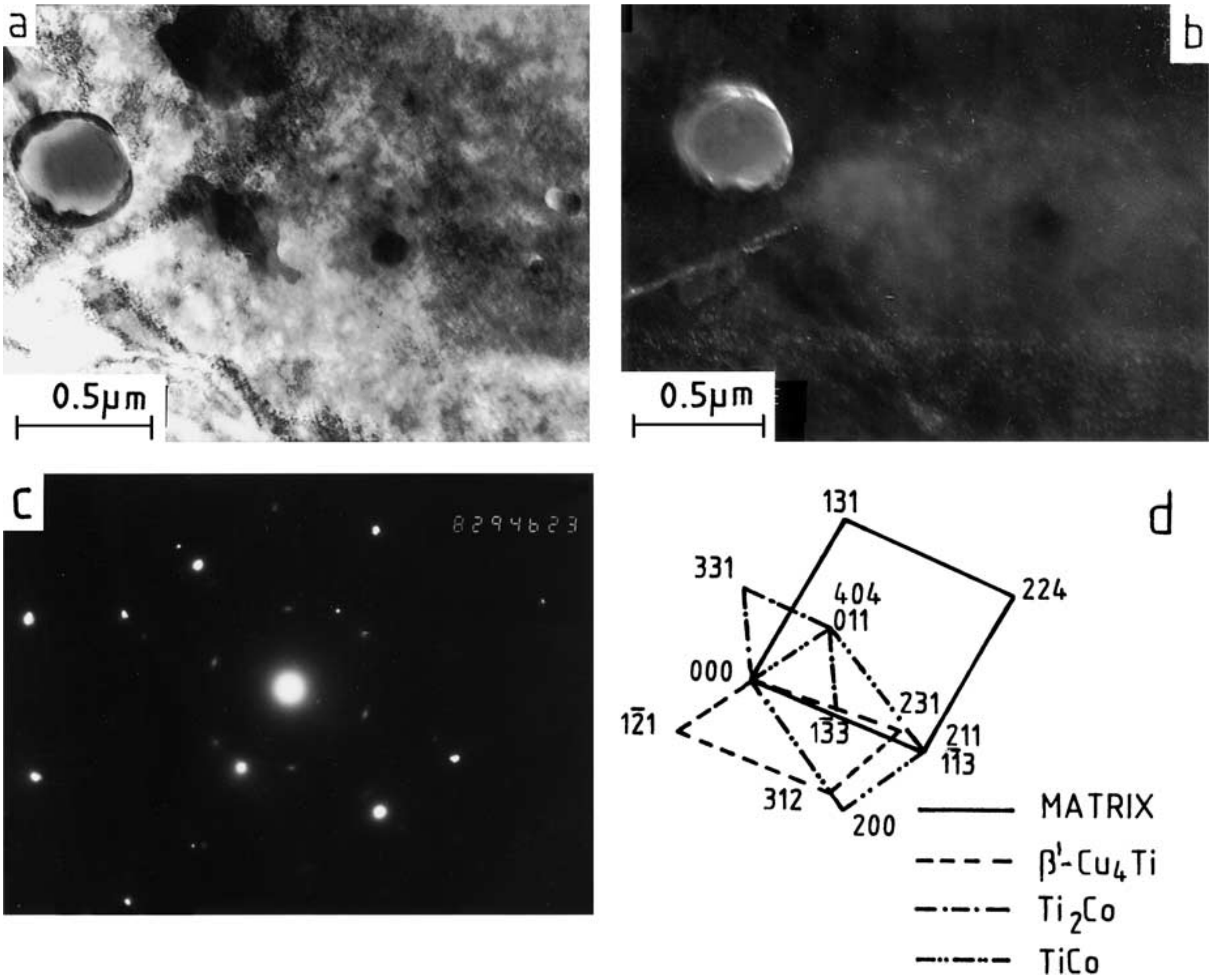

Figure 13 TEMs of peak aged Cu-4.5Ti-1.8Co alloy. (a) Bright field image, (b) dark field image, (c) SAD pattern, and (d) schematic of SAD pattern.

to solid solution strengthening, the net result is an overall decrease in the strength of the Cu-Ti-Co alloys. The elongation of Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys is however, higher than that of the binary Cu-4.5Ti [5] as well as Cu-4.5Ti-0.5Co alloy [15].

In the peak aged condition, hardness as well as strength of Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys is higher than that of the solution treated ones and the increase is attributed to precipitation of Cu_4Ti (β^1) phase. Our observation in the present study is in agreement with the reported results by Nagarjuna *et al.* [5–7] that precipitation of Cu_4Ti (β^1) phase was found to be responsible for strengthening in aged binary Cu-Ti alloys. The hardness and strength of Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co are however, found to be lower than those of Cu-4.5Ti and Cu-4.5Ti-0.5Co alloys studied by us earlier [5, 15] due to the reduced Ti content in the matrix. As the Co content in Cu-4.5Ti is increased from 0.5 to 1.8%, Ti_2Co and TiCo phases have formed by consuming more Ti from the matrix which reduced the Ti required for precipitation of β^1 Cu_4Ti phase, thereby resulting in inferior tensile properties in Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys. The elongation of the aged Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys is lower than that of not only the solution treated ones but also that of Cu-4.5Ti and Cu-4.5Ti-0.5Co alloys [5, 15].

The variation of hardness and tensile properties with cobalt content (Fig. 4) revealed that hardness followed a decreasing trend with increasing amount of Co in both solution treated and aged conditions. A similar behaviour was observed in the variation of yield and tensile strengths in solution treated condition. In aged condition, however, the strengths are found to be constant up to 0.5% Co and decreased thereafter, up to 1.8% Co. The overall result is that the Co additions to Cu-4.5Ti alloy have led to the decrease in hardness and strength. Elongation in solution treated condition increased with increasing Co up to 0.9% and decreased thereafter, up to 1.8% Co. The elongation of Cu-4.5Ti-1.8Co alloy is greater than that of binary Cu-4.5Ti [5] or Cu-4.5Ti-0.5Co alloy [15]. In the aged condition, Cu-4.5Ti-0.5Co alloy [15] exhibited higher elongation (25%) than binary Cu-4.5Ti (20%) [5]. The elongation decreased beyond 0.5% Co up to 1.8% Co.

The EC of the solution treated Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys is much lower than that of the binary Cu-4.5Ti but higher than that of Cu-4.5Ti-0.5Co alloy. The lower values of EC of the alloys of the present study in solution treated condition compared to Cu-4.5Ti [5] is attributed to cobalt in solid solution with copper, as the cobalt atoms restrict the free movement of electrons in the lattice. However, it is higher for Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys than Cu-4.5Ti-0.5Co [15] due to enhanced removal of Ti from matrix as a result of increased additions of cobalt. As more and more Ti is depleted from matrix to form intermetallic phases with Co, the movement of electrons becomes easy and thus, EC increases.

In the aged condition, the EC is higher than that of the solution treated alloys due to the precipitation of Cu_4Ti (β^1) phase, which also reduces the amount of Ti from matrix. The EC of peak aged Cu-4.5Ti-0.9Co is greater than that of the Cu-4.5Ti-0.5Co alloy [15], but lower than that of binary Cu-4.5Ti [5] and Cu-4.5Ti-1.8Co alloy. The Cu-4.5Ti-1.8Co alloy exhibits the highest value of EC (14% IACS) among the four alloys studied which is attributed to the removal of Ti from matrix by the combined phenomena of precipitation of Cu_4Ti (β^1) phase and formation of intermetallic phases of Ti and Co. Variation of electrical conductivity with Co content (Fig. 5) indicates that in both solution treated and aged conditions, EC decreased to a minimum at 0.5% Co and increased thereafter, up to 1.8% Co. The decrease in EC up to 0.5% Co is due to the addition of cobalt, which restricts the free movement of electrons in the lattice, as explained in detail in our earlier work on Cu-4.5Ti-0.5Co alloy [15]. Further, the quantity of Co here is not sufficient enough to pull out more Ti from the matrix compared to the other two Cu-Ti-Co alloys. The increase in EC beyond 0.5% Co is due to the removal of more and more Ti from matrix by the formation of intermetallic phases of Ti and Co in the solution treated condition and the combined phenomena of precipitation of Cu_4Ti (β^1) phase and formation of intermetallic phases of Ti and Co in aged condition. This effect is more pronounced in aged alloys than the solution treated ones. Therefore, the overall effect of addition of Co to Cu-4.5Ti alloy shows a decrease in EC in the solution treated condition and increase in the aged condition.

Our observation that Co additions to Cu-4.5Ti alloy decreases the grain size is in accordance 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 [13]. A fine dispersion of the intermetallic phases containing Ti and Co could have caused the refinement of grain size in the ternary Cu-Ti-Co alloys. Increasing the Co content would lead to increased volume fraction of Ti-Co intermetallic phases, which in turn, have restricted the grain growth during solution treatment and subsequently resulted in finer grain sizes in Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys.

It is surprising that solution treatment followed by rapid quenching of Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys has not suppressed the formation of the Cu_4Ti (β^1), Ti_2Co and TiCo phases. Formation of composition modulations and fine scale precipitate (Cu_4Ti, β^1) has been reported in solution treated binary Cu-Ti alloys containing more than 4.0 wt% Ti by Laughlin and Cahn [3], Datta and Soffa [4], and Nagarjuna *et al.* [5–7] and our observation that Cu_4Ti, β^1 is present in the solution treated Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys is in agreement with the reported behaviour. Presence of Cu_4Ti, β^1 phase was also reported in solution treated Cu-4.5Ti-0.5Co alloy [15]. However, it is to be noted here that in solution treated binary Cu-4.5Ti alloy, only composition modulations were observed and the Cu_4Ti, β^1 phase was not yet precipitated [5], whereas the addition of Co to the binary Cu-4.5Ti alloy has resulted in the formation of fully developed Cu_4Ti, β^1 phase, thereby indicating that Co has advanced the kinetics of precipitation of Cu_4Ti, β^1 phase in the solution treated condition. 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 [13]. Such behaviour was not observed in both the Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys, as hardness and strength are less than that of the binary Cu-4.5Ti alloy. It is evident from the Ti-Co phase diagram [19] that a eutectoid reaction (β Ti) $\rightarrow$ (α Ti) + Ti_2Co occurs at 685°C. Formation of Ti_2Co phase was noticed in the present study also, which is due to the above eutectoid reaction occurring in the Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys. The SAD pattern and its schematic in Fig. 10c and d and Fig. 12c and d confirm the presence of Ti_2Co phase. Further, the phase diagram also shows a congruent reaction, viz. $L \rightarrow TiCo$ occurring at a temperature of 1325°C. Formation of TiCo intermetallic phase was also found in Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys of the present study (Figs 10 and 12). The presence of Ti and Co in the precipitate particles as revealed by the EPMA studies (Fig. 9), further confirms the presence of Ti_2Co and TiCo phases in the solution treated Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys. The same phases have been reported to be present in Cu-4.5Ti-0.5Co alloy [15] as well. In summary, the Co additions have not been found to be beneficial in improving the strength of the Cu-4.5Ti alloy. Though considerable grain refinement has occurred, formation of intermetallic phases depleted Ti from solid solution to decrease its strength in general and increase electrical conductivity, in particular, in Cu-4.5Ti-1.8Co alloy.

5. Conclusions

The precipitation hardening behaviour of Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys has been studied by aging at different temperatures and times and the following conclusions have been drawn on the present investigation:

1. Cobalt additions to Cu-4.5Ti alloy result in considerable refinement of grain size from 75 μm in the binary alloy to 20 μm in the Cu-4.5Ti-1.8% Co alloy.
2. Cobalt additions to Cu-4.5Ti alloy also reduce the aging temperature for attaining peak hardness from 450°C for the binary alloy to 400°C for Cu-Ti-Co alloys.
3. Significant strengthening occurs on aging of the solution treated Cu-4.5Ti-0.9Co and Cu-4.5Ti-1.8Co alloys with hardness increasing from 170 to 310 Hv and 120 to 250 Hv respectively on peak aging (400°C/16 h). However, cobalt additions to Cu-4.5Ti alloy decrease the hardness and strength.

4. Ordered, metastable and coherent Cu_4Ti, β^1 phase has been found to be mainly responsible for maximum strengthening in these alloys.

5. The electrical conductivity of the Cu-4.5Ti-0.9Co alloy has been found to be 6 & 10% IACS, while that for Cu-4.5Ti-1.8Co alloy is 7 & 14% IACS respectively, in the solution treated & peak aged conditions. The EC of the peak aged (400°C/16 h) Cu-4.5Ti-1.8Co is superior to that of the binary Cu-4.5Ti alloy (450°C/16 h).

6. The intermetallic phases containing Ti and Co with stochiometric composition of Ti_2Co and TiCo are found to form as coarse undissolved particles in solution treated and peak aged conditions, which are responsible for the decrease in hardness and strength as the Co content in Cu-4.5Ti alloy increases.

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