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Thermo-Mechanical Treatments of Cu-Ti Alloys

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***Abstract*—**This paper aims to study the effect of cold work condition on the microstructure of Cu-1.5wt%Ti, and Cu-3.5wt%Ti and hence mechanical properties. The samples under investigation were machined, and solution heat treated. X-ray diffraction technique is used to identify the different phases present after cold deformation by compression and also different heat treatment and also measuring the relative quantities of phases present. The metallographic examination is used to study the microstructure of the samples. The hardness measurements were used to indicate the change in mechanical properties. The results are compared with the mechanical properties obtained by previous workers. Experiments on cold compression followed by aging of Cu-Ti alloys have indicated that the most efficient hardening of the material results from continuous precipitation of very fine particles within the matrix. These particles were reported to be β`-type, $Cu_4Ti$ phase. The β`-β transformation and particles coarsening within the matrix as well as long grain boundaries were responsible for the overaging of Cu-1.5wt%Ti and Cu-3.5wt%Ti alloys. It is well known that plate-like particles are β –type, Cu_3Ti phase. Discontinuous precipitation was found to start at the grain boundaries and expand into grain interior. At the higher aging temperature, a classic Widmanstätten morphology forms giving rise to a coarse microstructure comprised of α and the equilibrium phase β. Those results were confirmed by X-ray analysis, which found that a few percent of Cu_3Ti, β precipitates are formed during aging at high temperature for long time for both Cu- Ti alloys (i.e. Cu-1.5wt%Ti and Cu-3.5wt%Ti).

***Keywords*—**Metallographic, hardness, precipitation, aging.

I. 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. Age hardenable copper beryllium (Cu- Be) alloys exhibit the highest strength levels among the family of copper alloys and also possess medium electrical conductivity [3], [4]. 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. The worldwide research acknowledged that binary Cu- Ti alloys could serve as a substitute for expensive and toxic Cu-Be and Cu-Be-Co alloys. There are only two principal methods for increasing the strength and hardness of a given alloy: cold working or heat treatment. The most important heat– treating process for nonferrous alloys is age hardening or precipitation hardening. In order to apply this heat treatment, the equilibrium diagram must show partial solid solubility, and the slope of the solvus line must be such that there is greater solubility at higher temperature than at lower temperature [1]. These alloys that satisfy their conditions are named age hardenable alloy. The other hardening process termed thermomechanical treatment (TMT) or thermomechanical processes (TMP) which include high temperature thermomechanical (HTMT) and low-temperature thermomechanical treatment (LTMT) which will be discussed later. Thermo-mechanical processes are defined in the broadest sense to include any combination of thermal and mechanical processes that give rise to interactive microstructural features. Thermomechanical processing, which combines deformation and heat treatment is very effective for microstructure control and hence for the improvement of mechanical properties of the metallic material [2]. An extensive research was carried out by several researchers on the mechanism of spinodal decomposition and precipitation strengthening in Cu-Ti alloys. Nagarjuna et al. [3], [4] have studied the structure – property correlations of Cu-Ti alloys in various conditions, viz., solution treatment, solution treatment and aging, and solution treatment, cold work and aging. It was reported that compositional modulations would occur during solution treatment itself in Cu-Ti alloys containing Ti $\geq$ 4.0 wt% and age hardening takes place by the formation of metastable β`, Cu_4Ti phase in both deformed and undeformed alloys. The effect of prior deformation on the microstructure and properties of age hardenable Cu-Ti alloy is still a matter of investigation. The complex sequence of precipitation process and the different type of phase formed, and their morphology in these alloys make it very interesting.

During last year's attention has been given to the interaction between deformation process and diffusion controlled phase transformation process. To test both continuous and discontinuous precipitation interaction with deformation process, Cu-Ti alloys were chosen [5], [6].Thus, the most interesting purpose of experiments described below was to study the interaction between the precipitation process and the material defects introduced by mechanical deformation. Emphasis was placed on the interaction of precipitation process with structural inhomogeneties that may develop during deformation.

II. Experimental Procedure

Cold compression tests were performed on two copper–titanium alloys, of different chemical composition as given in Table I.

The vacuum melted and casted alloys were received in the form of cylindrical ingots of 18.6 mm in diameter and 145 mm

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long. The ingots were homogenized for two hours at 900°C, water quenched, and then cold rolled. Intermediate annealing at 900°C for half an hour followed by water quenching before final cold drowning to an average diameter of 9.4mm was used. The ingots were perfectly wrapped in copper foils to prevent the surface oxidation during heat treatments. The samples were subsequently sectioned along the compression axis using a spark erosion machine, after that, the samples were aged at different temperatures (550, 600, 650) for Cu-1.5 wt% Ti and at (450, 500, 600, 750) for Cu-3.5wt%Ti. Vickers hardness was measured using a Buehler hardness tester (Buehler, UK, Ltd., CO.,) with a 1 kg load. Optical metallography of the alloys were carried out in solution–treated (ST), peak – aged (PA), overaged, solution–treated+cold–worked (CW) and ST+CW+PA conditions. X–ray diffraction were obtained using X-ray diffractometer type PHILIPS–binary (scan) (.RD) with Cu Kα radiation with a wavelength of 1.5406 A°, the voltage was 40KV, and filament current was 30 mA. The scans were performed over the range of 2θ from 10 to 140°.

TABLE I
CHEMICAL COMPOSITION OF ALLOYS (WT% BY PPM)

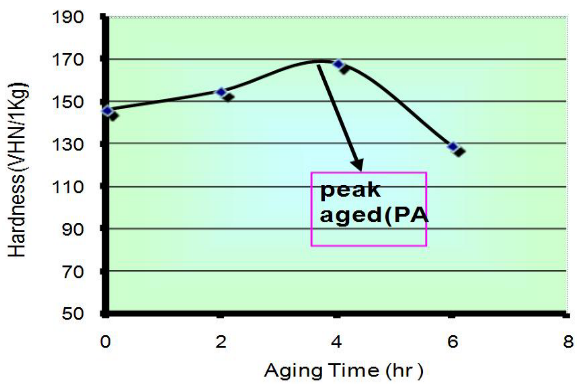
Element Alloy	P	Ag	Sb	Zn	Fe	As	S
1.5Ti	187ppm	3	10	13	87	13	66
3.5Ti	83	<1	18	<1	37	12	56
Element Alloy	Cd	Pb	Ni	Sn	Ti	Cu	
1.5Ti	4	<1	77	8	1.5	In bal.	
3.5Ti	5	<1	68	1	3.5	In bal.	

III. RESULTS AND DISCUSSION

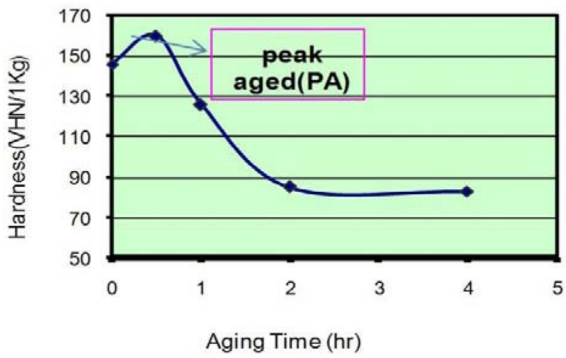
A. Hardness

The hardness measurements were used to follow the interaction of static precipitation process with structural components introduced by cold deformation.

Figs. 1 (a), (b), and (c) show the effect of pre cold work on hardness of Cu – 1.5 Ti wt% alloy during aging at 550, 600 and 650° C.



(a)



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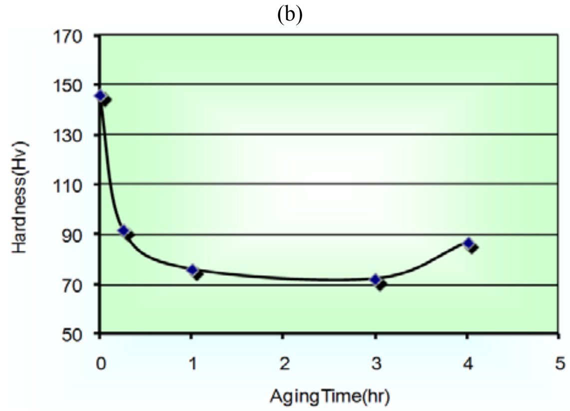

(c)

Fig. 1 Effect of prior cold work on age hardening in Cu- 1.5 wt% Ti alloy aged at (a) 550ºC, (b) 600ºC, (c) 650ºC

Fig. 1 include variation in hardness with aging time of deformed alloy at the above aging temperatures. Cold work increased the hardness of Cu- 1.5 Ti alloy in the solution treated (ST +CW) as well as peak aged (ST+CW+PA) conditions.

The maximum hardness for Cu- 1.5Ti alloy varied from 70 Hv in the solution treated condition to 168Hv for 50 %deformation and aging at 550°C Fig. 1 (a). Similarly, the peak hardness obtained for 50 % deformed Cu- 1.5 Ti alloy aged at 600°C was 160 Hv and decrease drastically. It is seen from Fig. 1 (b). That hardness decreased with prolonged aging after a peak value. Formation of the equilibrium precipitate, Cu_3Ti has been reported to cause a decrease in hardness due to the overaging phenomenon in binary Cu- Ti alloys [7]. The overaging was observed at 650° C it is seen from Fig. 1 (c).

The influence of prior cold work on the hardness of the Cu-3.5 Ti at (450) and (500°C) in the Figs. 2 (a) and (b) Cold work followed by ageing at (450°C) for (8hr) was marginal and at (500°C) , considerably and drastic at (600) and (750°C) Fig. 2 (c) and (d).

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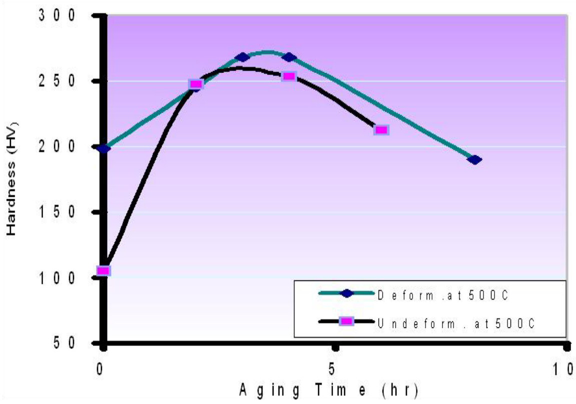
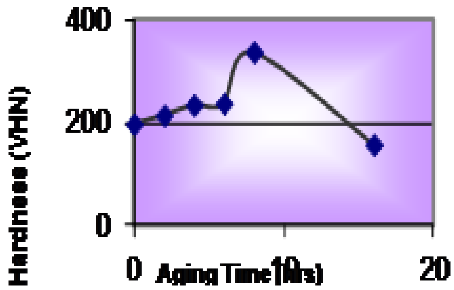


(a)



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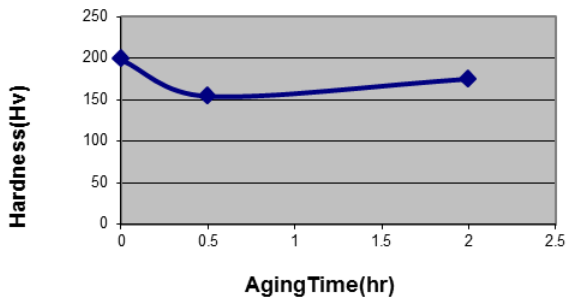

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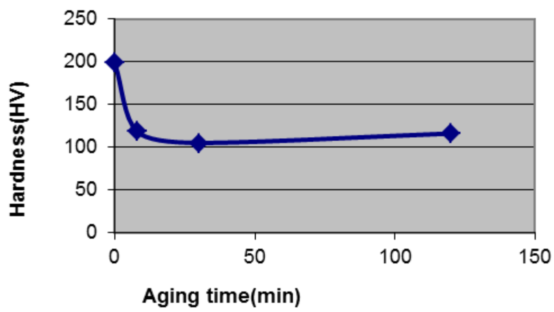


(d)

Fig. 2 Effect of prior cold work on age hardening on Cu-3.5wt%Ti alloy aged at (a) 450ºC, (b) 500ºC, (c) 600ºC, (d) 750ºC

B. Microstructure

Fig. 3 shows optical microstructures of Cu- 3.5wt. %Ti, solution heat–treated at 900°C for 1hr followed by water quenching Fig. 3 (a) and subsequently 50% deformed Fig. 3 (b). The structure shown consists of large equiaxed grains of α phase with annealing twins and many uniformly distributed particles. The particles are Cu_3Ti with a body-centered tetragonal (bct) crystal structure and that they are formed during casting and remain undissolved in the solution – treated state [8]. After cold compression of the solution treated samples; compression test mainly flats the grains shown and aligned in a direction perpendicular to the compression axis.

(a)

(b)

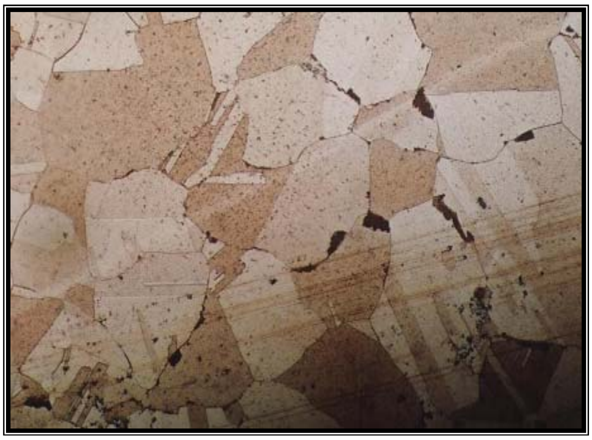
Fig. 3 Optical micrographs of Cu-3.5wt% Ti alloys: (a) solution treated at 900°C, (b) cold deformed 50% without aging (300X)

Cold compression after solution treatments leads to a deformed supersaturated solid solution. During subsequent aging, the processes of precipitation, recovery, and recrystallization may occur simultaneously and may interact with each other [9].

In Fig. 4 (a) the specimen which contains 3.5 wt. %Ti aged for (170 mins) at 500°C after the 50% deformation; it showed a precipitates at grain boundaries (as cellular colonies). Fig. 4 (b) displays the microstructure of Cu-3.5wt. %Ti aged at 500°C without pre deformation. It reveals that many of the particles are at the grain boundary and structural defects. Similar results are obtained for 4hrs aging of same sample (Fig. 4 (c)).

(a)

(b)



(c)

Fig. 4 Optical micrographs of Cu-3.5 wt. %Ti alloys (a) 50% cold deform. With aging at 500°C for 170 mins., (b) Aging at 500°C for 2hrs without deform (300x), (c) Aging at 500°C for 4hrs without deforms (300X)

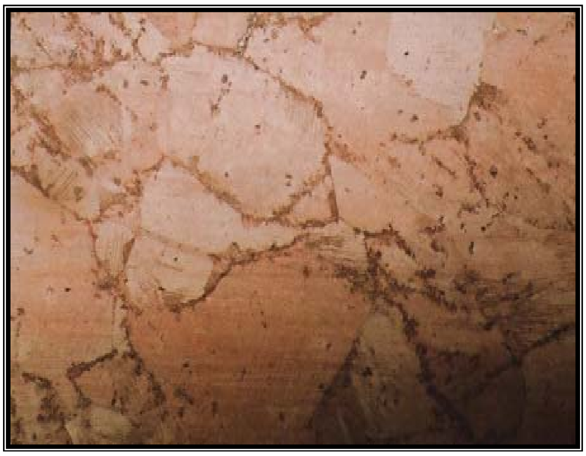
The alloy tested aged at 500°C without deformation for 2hrs and 4hrs show equiaxed grains with annealing twin (see Figs. 4 (b) and (c). Lamellar precipitation of equilibrium phase β at the grain boundaries as dark colonies growing into the grains which is attributed to overaging of the alloy at this temperature since the optical micrographs of peak aged alloy are quite similar to those of the solution treated one.

The optical micrograph for the Cu-3.5 wt. %Ti alloy aged for 8 hrs at 500°C after it has been given a 50% deformation (overaging stage) is given in Fig. 5 (a).

This micrograph shows deformed grains of α-phase. The equilibrium precipitates can be observed along the grain boundaries as well as on the structural defects, introduced by prior deformation: It is clear that deformation has affected morphology and distribution of precipitates, and equilibrium precipitates in the grain boundaries which appear as dark nodules in a light matrix. Striations in alpha matrix are the result of the concurrent metastable precipitate formation, not resolved by optical microscopy.

The deformed Cu- Ti alloys gets overaged with the formation of the incoherent and equilibrium precipitate of β-Cu_3Ti in the matrix as well as lamellar type discontinuous precipitation at the grain boundaries of the matrix. This is observed in X-ray analysis of Cu-3.5wt. %Ti aging is at 500°C for 8hrs (see later in X- ray results).

Over aging occurs at 500°C after 8hrs for Cu- 3.5wt. %Ti and at 600°C after 30 mins for Cu- 1.5wt%Ti alloy, also at 650°C after (1/4hr). The lamellar morphology of discontinuous precipitation is converted to the globular morphology of coarse β needle-like structure within the α–matrix that are concentrated in the highly deformed areas as shown in Figs. 5 (b) and (c) this means the large strains induced by severe deformations are completely deformation are completely released on long time aging at high temperature of (600°C and 650°C) for Cu-1.5wt. %Ti and promoted the lamellar type discontinuous precipitation to dissociate into dual phase structure of coarse precipitate β surrounded by α –matrix.



(a)

(b)

(c)

Fig. 5 Optical micrographs of Cu-3.5wt%Ti alloy: a) deformed and aging at 500°C for 8 hrs (300X) (b) Optical micrographs of Cu-1.5 wt. %Ti alloy, cold deform, and aging at 600°C for 1/2 hr; (c) Cu-1.5wt%Ti, cold deform and aging at 650 °C for 1/4hr (600X)

In Figs. 6 (a), (b), and (c) show a large amount of precipitation which clearly distributed all over the matrix and does not restrict to the grain boundaries, this also indicated that the cold work has affected the morphology and distribution of precipitates. The morphology of precipitates becomes a needle- like structure distributed all over the matrix. The microstructure is responsible for the overaging of this alloy composition.

Fig. 7 (a) shows the microstructure of non-uniform distribution of grain size, which observed to be similar to that of the solution–treated condition. In this case, no discontinuous precipitation has been noticed in the overaged of Cu-3.5wt%Ti alloy at 750°C. During the deformation, the pinning effect of precipitates may have led to a significant multiplication of dislocations so that the specimen contains a higher density of dislocations. The deformed alloy with a higher density of dislocation has more potential to recrystallization due to the higher driving force [10]. This could be the reason behind why could not observe the needle-like structure for the alloy under these conditions. In this case, recrystallization process is much faster, due to high density of dislocation than precipitation process that could lead the inhalation of many defects introduced by deformation that might assist precipitation process.

(a)

(b)

(c)

Fig. 6 (a) Optical microstructure of Cu-1.5wt%Ti def and aging at 650°C for 4hrs (1000X), (b) Cu-1.5wt.%Ti, cold def and aging at 650°C for 4hrs (400X), (c) Cu-1.5wt. %Ti, def and aging at 600°C for 4hrs (1000X)

The precipitates formed during the aging after deformation can act as the barrier that retard the recrystallization, however, they would coarsen and have increased interparticle spacing with increasing time during aging. In Fig. 7 (b) shows striation in the interior grain due to a concurrent metastable precipitate formation at this temperature (450°C).

(a)

(b)

Fig. 7 (a) Micrographs of Cu- 3.5 wt. %Ti alloy deformed then aged at 750°C for 2hrs (600 X), (b) Cu- 3.5wt%Ti deformed then aged at 450°C for 4hrs (300X)

C. Solution Treatment and Cold Work (ST+CW)

The present investigation reveals that hardness of Cu- Ti alloys is significantly improved by cold working in solution treated condition, the hardness was increased by about 30% when cold compressing to 50% reduction. Cold working results in plastic deformation of the alloy, which produces an increase in the number of dislocations. An annealed metal or solution treated alloy contains about 10^6- 10^8 dislocations per centimeter square, and severe cold working increases the same to 10^{12}/ cm^2 [3]. As a consequence, hardness and strength increase significantly as per the following expression [8].

$$\sigma = \sigma_o + \alpha\ G\ b\ \rho^{1/2} \quad (1)$$

where σ is flow stress, σ_o is friction stress, α is a constant, G is shear modulus and ρ is the dislocation density. Cold working by 50% further increased the hardness of Cu – 3.5 wt %Ti alloy from 198 Hv to 338Hv as shown in Fig. 2 (a).

D. Solution Treatment, Cold Work and Peak Aging (ST + CW+PA)

The hardness of Cu-Ti alloy was improved by 30% reaching a maximum hardness of 338 Hv Fig. 2 (a). On 50% deformation and aging at 450ºC. Whereas undeformed (Cu-3.5 wt %Ti) alloy exhibited the highest peak hardness when aged at 500ºC for 4hr as shown in Fig. 2 (b). The kinetics of aging is found accelerate resulting in maximum hardness at a lower temperature (450ºC) promoting the precipitation of very fine metastable phase $\beta^{`}$ in increased volume fraction [7].

E. Solution Treatment, Cold Work and Overaging (ST+CW+OA)

The decrease in hardness reflects overaging of Cu- Ti alloys. Aging at 500°C for 8hr of Cu- 3.5Ti resulted in drastic fall in hardness after 50% deformation. This indicates that considerable recovery of the matrix has occurred in 50% deformed alloy on aging at 500°C. This can be observed in optical images of the deformed alloy in Fig. 4 (a). It was reported earlier [7] that on aging of solution treated and cold worked Cu- 1.81Be- .28Co alloy at 500°C produced faster rates of recovery, recrystallization and subgrain structure in the matrix. The deformed Cu- Ti alloys gets overaged with the formation of the incoherent and equilibrium precipitate of β Cu_3Ti in the matrix as well as lamellar type discontinuous precipitation at the grain boundaries of the matrix. This is observed in 50% deformation of Cu- Ti alloys. They are overaged at 500°C for 8hr of Cu- 3.5Ti and at 600°C after 30 min of Cu- 1.5Ti alloy. The lamellar morphology of discontinuous precipitation is converted to the globular morphology of coarse β surrounded by the α–matrix. That means the large strains induced by severe deformations are completely released on long time aging at high temperature (600 and 650°C) of Cu–1.5 wt %Ti and promoted the lamellar type discontinuous precipitation to dissociate into dual phase structure of coarse precipitate β surrounded by α – matrix.

The microstructure shows the nonuniform distribution of grain size, and also observed to be similar to that of the solution –treated condition. Further, no discontinuous precipitation has been noticed in the overaged of Cu-3.5wt%Ti alloy at 750°C as shown in Fig. 7 (a).

F. X-Ray Diffraction Results

X-ray diffraction patterns obtained for various heat treatments. All diffraction patterns show that peaks that consist of Cu (α_{ss} solid solution), Cu_3Ti and Cu_4Ti phases. These last two phases are readily identified in XRD diffraction patterns β-Cu_3Ti which is characterized by diffraction lines from planes (020), (100), (002), (021) and (111), while the α solid solution planes with lines from (111),(200), (220).

The peak positions and intensities of the diffraction data reveal that the sample consists mainly of the α phase (92%) and a small amount (8%) of Cu_3Ti. The presence of Cu_3Ti phase is essential to accelerate during a long time.

G. Effect of Aging Temperature, Time, and Composition on Quantity of Cu_3Ti

The effect of aging temperature on a quantity of Cu_3Ti is shown in Figs. 8 (a) and (b). Selected XRD spectra of samples containing different amount of Cu_3Ti and α ss can be seen as well. On aging at 500°C for 8hr of Cu-3.5wt%Ti, the quantity of Cu_3Ti was 8%, whereas on aging at 600°C for 4hr of Cu-1.5 wt%Ti the β- Cu_3Ti content is reduced to 2% as shown in Fig. 8 (b). This comparison showed that β become more stable with aging time and temperature. This behavior indicates that the Cu_3Ti could be stable at high temperature and long aging time for the high content of Ti.

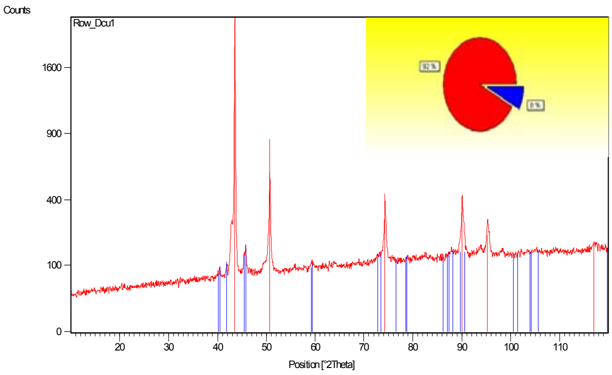


Fig. 8 (a) XRD pattern of Cu-3.5wt%Ti aged at 500°C for 8hr after 50% cold work

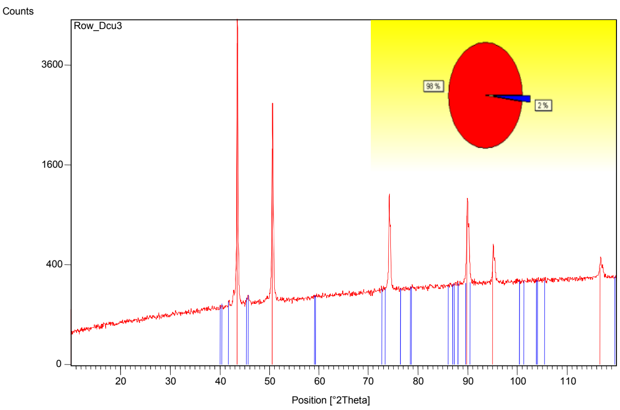


Fig. 8 (b) XRD pattern of Cu-1.5wt%Ti aged at 600°C for 4hr after 50% cold work

IV. Conclusion

1. The hardness increased from 70VHN in the solution treated state of Cu-1.5wt. %Ti to a peak value of 168VHN on aging at 550°C with prior cold deformation, while the hardness increased from 105VHN in the solution treated state of Cu-3.5wt. %Ti to a peak value of 338VHN on aging at 450°C with prior cold deformation.
2. At high aging temperature, (650°C) over aging were found to take place at the very short aging time for Cu-1.5wt%.Ti. While over aging occurs at 600 and 750°C for Cu-3.5wt. %Ti.
3. The deformation after aging treatment may disintegrate very fine precipitates and may induce partial re-dissolution of the solute atoms into the copper matrix.
4. During static aging, pre-existing grain boundaries are the preferable sites for the nucleation of discontinuous precipitation and cellular growth of plate-like particles of Cu_3Ti phase in undeformed high titanium content alloys.
5. X-ray analysis, reveals the presence of equilibrium β, Cu_3Ti precipitate and a few of metastable β`, Cu_4Ti, when tested Cu-3.5wt. %Ti at 500°C for 8hr, and equilibrium precipitate Cu_3Ti, β at the aging temperature of 450°C for 8hr of Cu-3.5wt. %Ti.
6. The quantity of β, Cu_3Ti, phase is related to Ti content and aging temperature, for high Ti content and high temperature (750°C), it reveals 8% percent of Cu_3Ti, for Cu-3.5wt. %Ti, while at Cu-1.5wt. %Ti, it is only 2% of Cu_3Ti.

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