

Resoftening and Resistivity Variations in Thermally Deformed Cu-Sn and Cu-Sn-Zn Alloys

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Resistometric and tensile characteristics were studied for both Cu-Sn and Cu-Sn-Zn alloys in the temperature range from 573 K to 773 K. Resistivity saturation was found to take place through two annealing stages. The time exponent n for ϵ -precipitate dissolution during annealing within stage I in Cu-Sn alloy and stages I and II for Cu-Sn-Zn alloy decreased with increasing working temperature. The values of the rate constant K increased with increasing deformation temperature. *A softening behaviour was observed at higher stresses and temperatures. This was deduced from both the decreasing values of the strength parameters σ_y , σ_f , σ_c , σ_u with increasing temperature and the sharp change in strain hardening at the critical stress σ_c . Above σ_c , the second hardening stage behaviour appeared during tensile testing. The results were explained in view of the mode of dislocation interaction with both the lattice defects and the different inclusions existing in the matrix. The associated atomic rearrangement and the formation of deformation twins, thermally activated by 0.24 eV in Cu-Sn alloy and 0.28 eV in Cu-Sn-Zn alloy, were also considered.*

Introduction

The resistivity of metals and alloys arises from the change of electron velocities due to scattering at different obstacles such as crystal imperfections, chemical impurities and the formation of different phases.

Being a structure sensitive property, electrical resistivity measurements are commonly used to trace thermally induced structure variations caused by different processes such as precipitation process in super saturated solid solutions, dissolution of precipitates, structure ordering, deformation irradiation and alloying effects. The effect of ϵ -phase dissolution on electrical resistivity was studied [1] for torsionally deformed Cu- 5 wt.% Sn alloy.

Work hardening is usually attributed to the hindering of dislocation motion. The addition of alloying elements to a given base metal, leads to a wide variety of strengthening mechanisms. In twinning as a process of deformation other than slipping [2], the concentration of the generated deformation twins increased with increasing working temperature while the work hardening rate decreased once the twinning process began.

The present work aims at studying the effect of isothermal annealing, mechanical deformation and Zn addition on the characteristics of Cu-5 wt.% Sn alloy. This is carried out through resistivity measurements, stress-strain relations and X-rays diffraction technique.

Experimental Procedure

Two copper alloys with the compositions, Cu-5 wt.% Sn and Cu-5 wt.% Sn-0.5wt.%Zn were prepared from electrolytic copper of purity 99.99%, zone refined tin (99.999%) and Zn of purity 99.99%. The rod ingots were homogenized at 973 K for 3 days. The rod of each alloy was reduced in diameter to wires of 0.3 mm. The working length of the samples was 50 cm for resistivity measurements and 5 cm for tensile tests. All the samples were annealed at 973 K for 1 h to anneal out the effect of deformation then water quenched to bring them to the same initial state with the supersaturated α -solid solution structure [1]. The specimens of both alloys were then isothermally annealed at 473 K for 7 days to allow the formation of a certain volume fraction of the ϵ -precipitate such that the samples contain the double phase ($\alpha + \epsilon$) structure.

Resistivity measurements for wire samples, doubly wound to eliminate the induction effect, were carried out using a Kelven double bridge at temperatures, in the solid solution region of the alloys, from 573K to 773 K in steps of 50 K with sensitivity $\pm 10^{-9} \Omega$ cm.

The stress-strain experiments were carried out at an average strain rate of $6.6 \times 10^{-6} \text{ s}^{-1}$ at the same working temperatures used for resistivity measurements. A conventional type machine was used and the elongations obtained in the tested wires during deformation were measured by a dial gauge to $\pm 10^{-5} \text{ m}$. The time from the start of the tensile test till fracture was recorded for each stress strain curve. The true strain ϵ_t was obtained as:

$$\epsilon_t = \ln (1 + \epsilon) \dots\dots\dots (1)$$

where ϵ is the linear strain. The true stress was obtained as:

$$\sigma_t = [P/A_0] (1 + \epsilon) \dots\dots\dots (2)$$

where P/A_0 is the nominal stress (= applied load / initial cross sectional area)

The microstructure of the tested samples was examined by using Philips X-rays Diffractometer type (PW 1050/70) with K_α radiation of wavelength 1.542 Å.

3. Results and Discussion

All the tested samples which have the two phases, $\alpha + \epsilon$ precipitate structure were found to have the same R. T. initial resistivity ρ_0 .

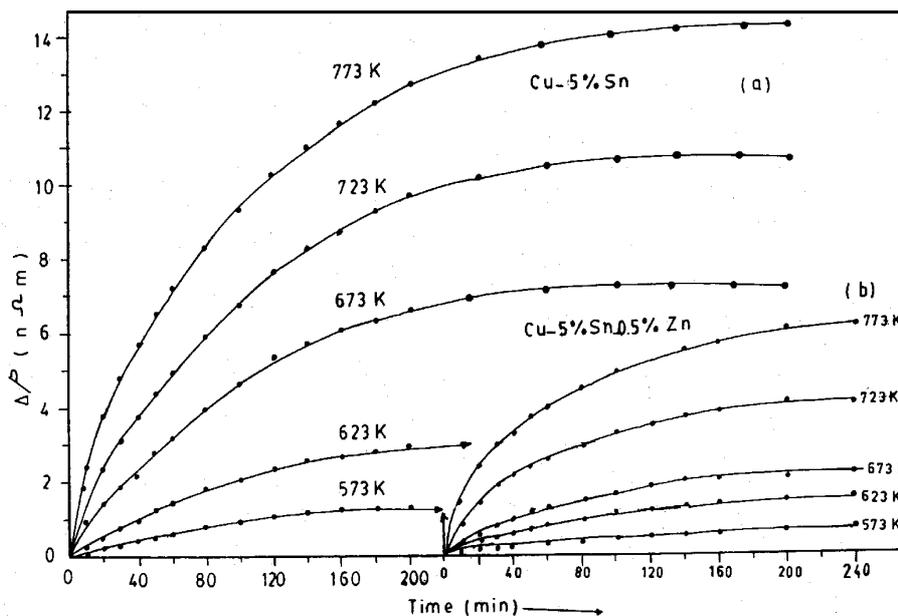


Fig.(1) Time dependence of isothermal resistivity change at different temperatures for (a) Cu-Sn alloy, (b) Cu-Sn-Zn alloy.

During isothermal annealing the resistivity ρ_t as a function of time t was measured for each working temperature. The time dependence of resistivity change $\Delta\rho_t$ ($= \rho_t - \rho_0$) at different temperatures is shown in Fig. (1a, b). It is observed that increasing annealing time and/or working temperature produced higher values of resistivity increase $\Delta\rho$ until asymptotic saturation value ρ_∞ was attained. The saturation levels of resistivity change in the tested temperature range were less for Cu-Sn-Zn samples and in general increased for both alloys with increasing working temperature.

The stress-strain curves till fracture obtained are given in Fig. (2a, b). It is clear that higher flow stresses are needed for Cu-Sn-Zn samples to attain the same amount of strain in Cu-Sn samples. In Fig.(2), increasing working temperature decreased both the fracture strain ϵ_f and the yield stress σ_y , which is taken as the stress corresponding to the first deviation from linearity in the stress strain curve, as shown in Fig.(3a, b). It is clear from Fig.(3a,b) that Zn addition increased the strength of the Cu-Sn alloy and reduced its ductility.

According to the similarity observed in the general shape of the curves in (Figs. 1 and 2) the following conclusions may be considered:

- 1-The initial parts of both resistivity and stress strain curves are linear. The points on the curves of Fig.(1) at which the first deviation from linearity starts can be taken as the critical resistivity increase values $\Delta\rho_c$, as to

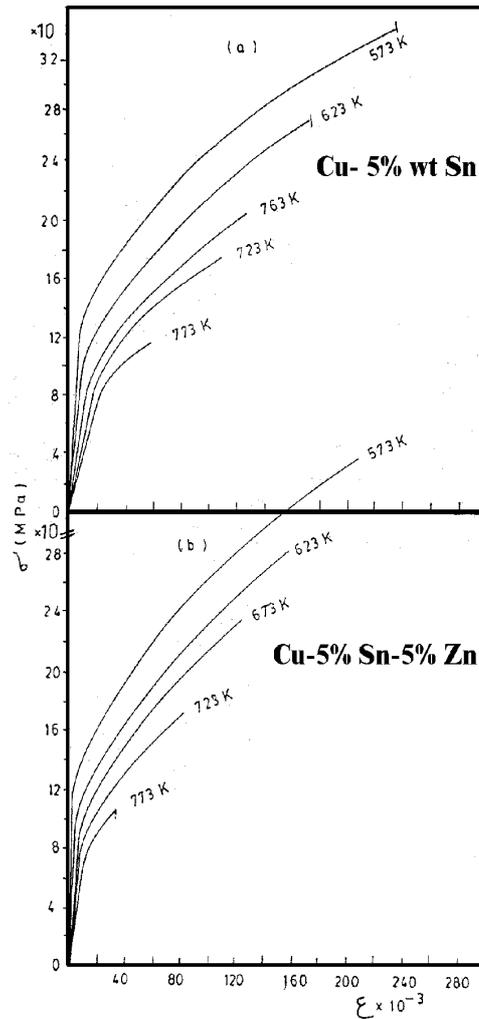


Fig.(2) Stress-strain curves at different deformation temperatures for: (a) Cu-Sn alloy, (b) Cu-Sn-Zn alloy.

correspond to the yield stress values on the curves of Fig.(2). The time to reach $\Delta\rho_c$ in Fig.(1), is taken as the critical time t_c . Therefore, the slope of the straight line ending at $\Delta\rho_c$ indicates the rate of resistivity increase ($\Delta\rho_c/\Delta t_c$). This rate, as calculated from Fig.(1) was found to increase with increasing deformation temperature and has higher values for Cu-Sn samples than those of Cu-Sn-Zn samples at the same temperature as shown in Fig. (4a).

2- For the parabolic part of Fig.(1) curves, the plots between $(\Delta\rho)^2$ values and the corresponding annealing time t gave straight lines for all the working temperatures. The temperature dependence of the slope $\frac{(\Delta\rho)^2}{t}$ given in Fig.(4b)

shows low values of the slope at low annealing times and temperatures. Besides, it shows a higher level for Cu-Sn samples over that of Cu-Sn-Zn samples. Marked increase is observed for $\frac{(\Delta\rho)^2}{t}$ at the second stage, which

may correspond to the parabolic part of the curves of fig.1 above nearly 650K for Cu-Sn samples and above 700 K for Cu-Sn-Zn samples.

3- The temperature dependence of the critical annealing time t_c given in Fig.(4c) was found to be greater for Cu-Sn samples above 623 K. In general, for both types of the samples t_c decreased with increasing working temperature.

It was found that the rate of diffusion of Sn in Cu is very low [3], and therefore, the dissolution of ϵ -precipitate in Cu-Sn alloy is expected to be very low. The relative resistivity change X given as:

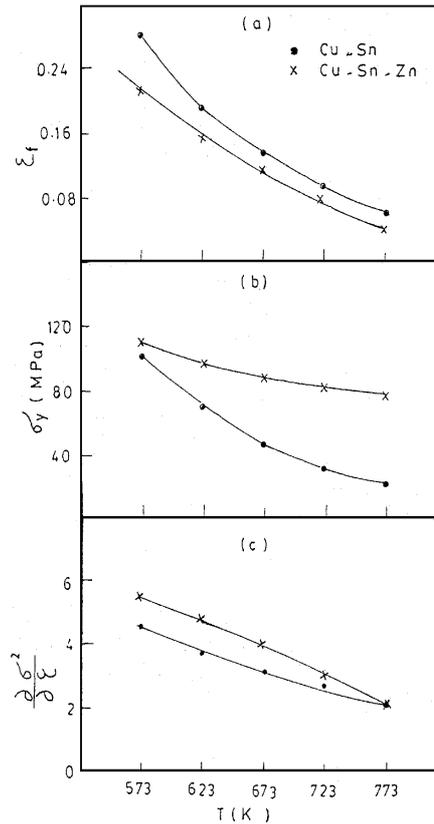


Fig.(3) Temperature dependence of (a) Fracture strain ϵ_f , (b) Yield Stress σ_y , (c) Coefficient of work hardening χ for Cu-Sn and Cu-Sn-Zn alloys.

$$X = (\rho_t - \rho_0) / (\rho_\infty - \rho_0) = \Delta\rho / \Delta\rho_\infty \dots\dots\dots(3)$$

is therefore proportional to the amount of the dissolved precipitate such that the rate of dissolution of the precipitate follows Avrami type equation of the form [4]:

$$X = 1 - \exp(-Kt^n) \dots\dots\dots(4)$$

where K is the rate constant of the dissolution process and n is the time exponent.

In terms of resistivity changes, the relation between $\ln\left(\frac{1}{1-X}\right)$ and $\log t$ at different annealing temperatures given in Fig.[5] shows straight lines with two linear parts of different slopes. This indicates that annealing is completed through two stages and each stage extends over a certain annealing time. The slope of the linear part gives the time exponent **n**. For each stage at any deformation temperature the corresponding rate constant K is calculated from the intercept of the linear part with the vertical axis. The slope of the linear part gives the time exponent **n**. The obtained values for the time exponent **n** for precipitate dissolution process gave an average relatively high value of 0.88 in stage I (at low annealing times). This may be due to the increased number of Sn atoms resulting from the dissolution of the second phase (ϵ -precipitate) particles. The Sn atoms disperse in

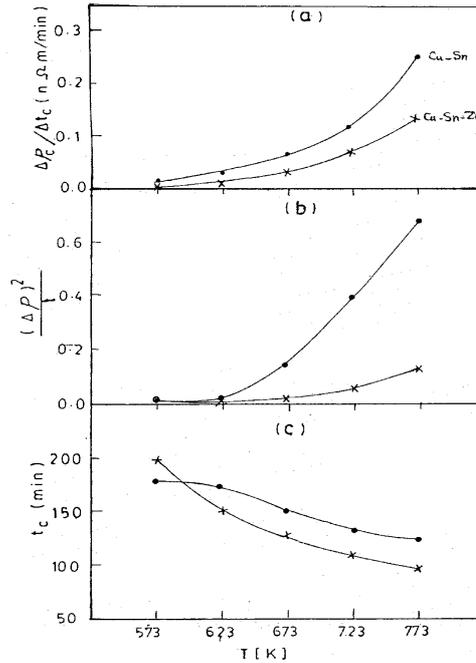


Fig.(4) Temperature dependence of (a) $\Delta\rho_c / \Delta t_c$, (b) $(\Delta\rho)^2 / t$, (c) Critical annealing time for Cu-Sn and Cu-Sn-Zn alloys as deduced from fig.1.

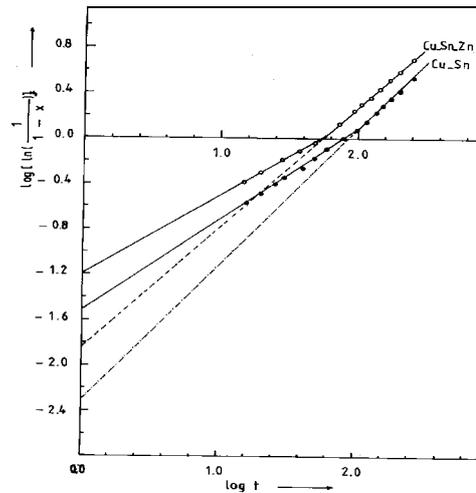


Fig.(5) Representative example for $\log [\ln 1/(1-x)]$ and $\log t$ relation for Cu-Sn alloy deformed at 773 K.

the matrix at a high rate and act as isolated scattering centers for conduction electrons. This leads to the high rate of resistivity increase in this stage. This average value of n being around unity may point to segregation of the freed Sn atoms on long thin cylinders, such as dislocations.

In the second stage (at high annealing times) the obtained n values gave an average value of 0.68 indicating that the dissolution process in this stage follows a power law of nearly $t^{2/3}$. This agrees well with previous results[5]. The decrease of n indicates that the transformation process moves gradually from sporadic to predetermined one.

In general, the data showed that n decreased with increasing deformation temperature except for the second stage of the binary alloy (Cu-Sn) samples where it increased. It seems that the longer annealing times enhanced the thermally activated structural variations in Cu-Sn samples. This effect showed itself through the relatively high K values and the increasing values of n with increasing deformation temperature. The values of the rate constant K increased with increasing deformation temperature in consistence with the corresponding resistivity increase in the same temperature range. The increase of the rate constant K might be due to the formation and growth of small Sn-vacancy clusters, many of which have sizes available for effective interaction with electron flow and retarding the mobile lattice defects [6].

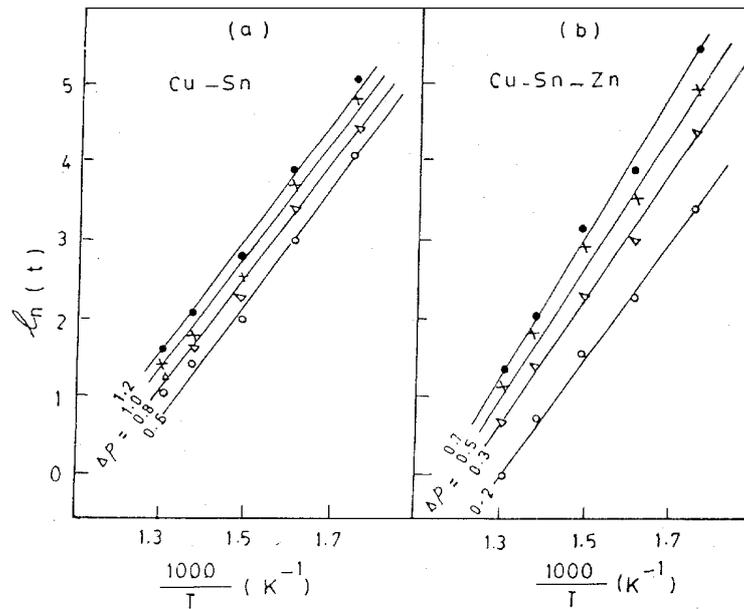


Fig.(6) Relations between $\ln(t)$ and $1000/T$ at different values of $\Delta\rho$ for (a) Cu-Sn alloy, (b) Cu-Sn-Zn alloy as deduced from fig.1.

The segregation of Sn atoms produced from the ϵ -phase, at grain boundaries, decreases apparently the concentration of Sn in the matrix. This leads to the observed reduction in resistivity increase at longer annealing times. In the used annealing temperature range, besides precipitate dissolution, many processes such as migration and clustering of Sn atoms at grain boundaries and vacancy formation may take place. To find the energy activating these processes, some values of $\Delta\rho$ in Fig.(1) were considered and the corresponding annealing times t at different temperatures were obtained. The relation between $\ln t$ and $1000/T$ gives the straight lines of Fig.(6). The activation energy was calculated from the slopes of these lines. The activation energy 1.47 eV was obtained from Fig. (6a) for Cu-Sn samples. For Cu-Sn-Zn samples the role of Zn atoms seems to be effective and the relation in Fig.(6b) showed a dependence of the calculated activation energy on the corresponding $\Delta\rho$ values considered for calculations. In this case an average value of 1.7 eV was obtained for Cu-Sn-Zn alloy samples.

As the deformation temperatures lie in the one phase region (α -solid solution), the dissolution of the existing second phase is expected and the dissolved fraction will therefore depend on the annealing time and the working temperature. Resistivity changes and deformation characteristics at different temperatures will depend mainly on the structural variations taking place in the samples. This viewpoint is supported by analyzing the stress dependence of Young's modulus $Y (= \frac{\partial\sigma}{\partial\varepsilon})$, Fig.(7a,b), at different temperatures for both the

Cu-Sn and Cu-Sn-Zn samples. For any testing temperature, Y decreased with increasing stress pointing to a softening behaviour for the tested samples.

Three distinct stages can be easily distinguished in Fig.(7a, b), and the effect of the deformation temperature and stress is observed markedly in the second stage. At a certain critical stress σ_c , depending on the deformation temperature a sharp drop in the values of Y takes place. This sudden drop might be due to the beginning of the formation of deformation twins [7]

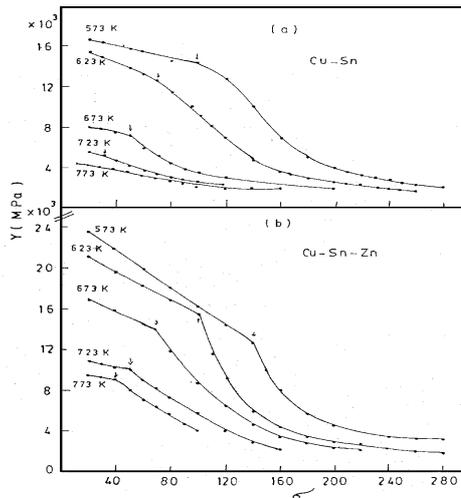


Fig.(7) Relation between Young's modulus Y against σ at different deformation temperatures for (a) Cu-Sn alloy, (b) Cu-Sn-Zn alloy.

in the tested Cu-Sn samples with an activation energy, obtained from a relation between $\ln\sigma_c$ and $1000/T$, as 0.24 eV. The activation energy for twin formation in Cu-Sn-Zn samples increased slightly to 0.28.

Twin formation is associated with an increase in strain without affecting the flow stress. Once the twin formation begins, the work hardening rate decreases. As the working temperature increases, twin concentration increases leading to the further decrease in work hardening rate. This agrees well with previous results for Cu-Sn alloy samples [7,8].

In view of the considered working conditions, the ductility drop observed in (Fig. 2) at higher temperatures cannot be explained as being due to dynamic strain, aging or strain induced precipitation [9], since none of these mechanisms occurs in the present alloy under the considered working conditions. It is therefore proposed that this ductility drop may be the result of twins formation on intersecting planes in the deformed samples. This leads to earlier fracture at higher working temperatures (Fig. 3a), rather than to an increase of the flow stress as a result of creation of microcracks at the regions of grain boundaries with high concentration of stress induced twins.

Considering the parabolic region observed in (Fig. 2a, b), the temperature dependence of the parabolic work hardening coefficient χ calculated [10] from, $\chi \left(= \frac{\partial \sigma^2}{\partial \epsilon} \right)$, is given in (fig. 3c). In general, χ decreased with increasing temperature pointing to the softening behaviour expected from Fig.(7a, b).

The behaviour of strain hardening during tensile testing can also be cleared out by using Hollomon equation [11]:

$$\sigma_t = A \epsilon_t^m \dots\dots\dots (5)$$

where σ_t is the true stress, ϵ_t is the true strain, A is the strain hardening coefficient and m is the strain hardening exponent (or the strain hardening rate).

The relation between $\log \sigma_t$ and $\log \epsilon_t$ given in Fig. (8), yields a straight line with two parts for all the tested samples at all deformation temperatures (in the range 573K–773K). This relation shows a “double – m “ or two stage strain hardening behaviour [12] . It is therefore concluded that the investigated samples undergo a sharp change in strain hardening rate during tensile testing

at a certain critical stress σ_c , which was obtained assuming that the strain hardening rate at the critical strain ϵ_c can be expressed as [12] :

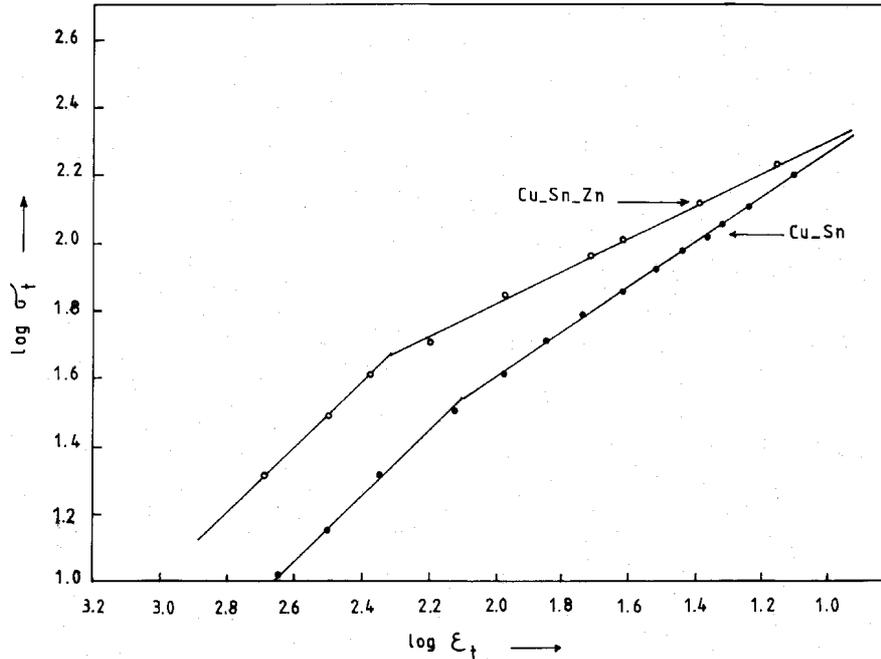


Fig.(8) Representative example for $\log \sigma_t$ and $\log \epsilon_t$ relation for Cu-Sn alloy deformed at the temperatures indicated on the lines.

$$m_1 - m_2 = \log (A_2 / A_1) / \log \epsilon_c \dots\dots\dots (6)$$

or

$$m_1 / m_2 = \log (\sigma_c / A_1) / \log (\sigma_c / A_2) \dots\dots\dots (7)$$

was nearly the same as that obtained from fig.6a at all the testing temperatures.

As a result of strain hardening there is an enormous increase in the dislocation density. A corresponding decrease in the ease with which these dislocations can glide takes place. As these dislocations move they become tangled. It is then more difficult for other dislocations to glide through the material specially at lower deformation temperatures. Increasing the applied stress and/or the deformation temperature will initiate rearrangement of the dense dislocation networks formed by strain hardening into simple and more ordered ones. This reduces the lattice energy. Accordingly the strain hardened structure which passes its maximum strength at the temperature dependent critical stress σ_c will be replaced by a new atomic ordered structure of reduced strain hardening. This state represents the start of the second stage of strain hardening where softening is supposed to take place.

Zn atoms, seem to have a strong tendency to segregate on deformed grain boundaries [13]. This greatly affected the work hardening and retarded softening due to slowing down the initial rate of precipitate formation. The improved mechanical properties for Cu-Sn-Zn samples may be due to the grain refining effect of Zn, since larger area of grain boundaries should be more effective as impeding agent for dislocation motion.

Due to the binding between vacancies and Zn atoms, the nucleation of cracks should be difficult and therefore, their formation should be retarded. The thermal enhancement of crack formation together with the associated defects at higher temperatures may explain the increased resistivity change at higher temperatures (Fig. 1a, b). The stabilization of defects by Zn atoms in the testing temperature range and the small amount of ϵ -precipitate formed in the presence of Zn in the alloy may explain the higher resistivity changes Fig.(1a), the increased fracture strain Fig.(3a), the decreased hardness level (Fig.3b, c) observed for the Zn free samples. This might be due to the enhanced nucleation rate of ϵ -precipitate [14] induced by the existing dislocations.

X-rays diffraction patterns for samples deformed in tension at different deformation temperatures are given in Fig.(9). From Fig.(9), it is observed that the lattice parameter (a) and the integral intensity (I) deduced from the (111) plane for Cu are given in Fig.(10). It is clear from Fig.(10) that Zn atoms have a large effect on the distribution of vacancy clusters and modifying the structure of ϵ -precipitate. This is thought to take place by eliminating the coarse planar features and the non-uniformity within the microstructure [15]. This increased the hardness of the alloy and consequently increased the lattice parameter and decreased the integral intensity.

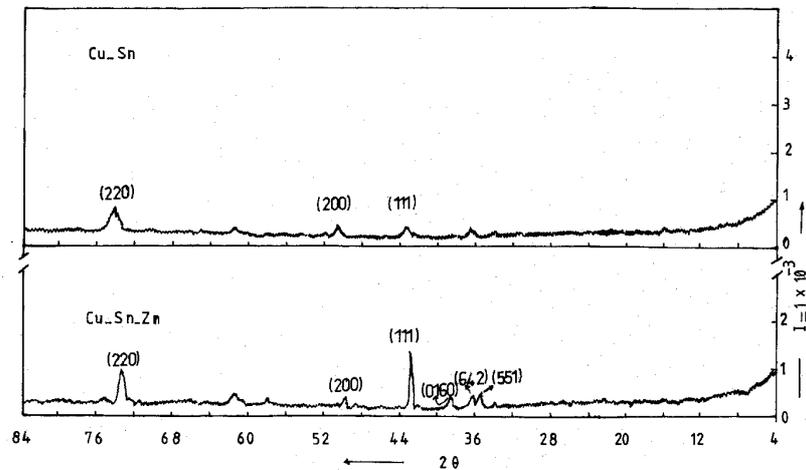


Fig.(9) Representative X-rays diffraction patterns of undeformed Cu-Sn and Cu-Sn-Zn alloys.

The higher values of the lattice parameter (a) in Fig.(10) at 673 K, points to a higher deformation level occurring in the Cu-Sn alloy with the result of higher residual strain in Cu-Sn alloy over that in Cu-Sn-Zn alloy.

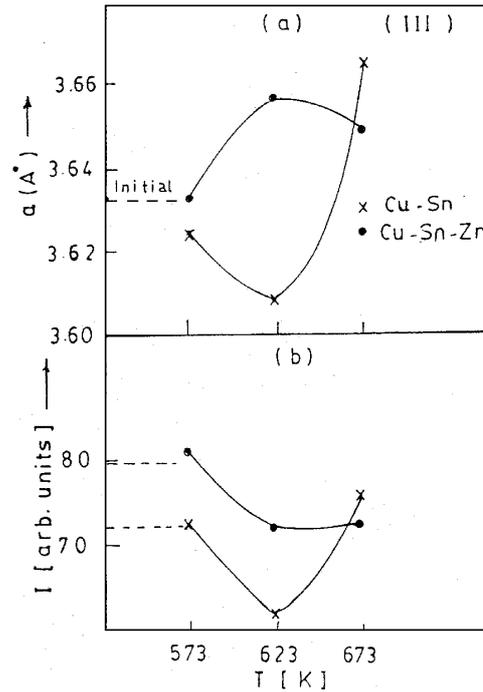


Fig.(10)
The effect of working temperature on
a) Lattice constant (a),
b) X-ray integral intensity, for the Cu-Sn and Cu-Sn-Zn alloys.

The increased concentration of vacancies created as a result of precipitate dissolution might also be a cause of the observed increase in the lattice parameter (a).

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