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Effect of Alloying with Copper on the Microstructure and Mechanical Properties of Al–30wt% Zn Alloy

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***Abstract*— This paper describes the microstructure and mechanical properties of a series of Al-Zn-Cu alloys ranging from 0 to 2 wt% Cu. Optical microscopy (OM) and X-ray diffraction patterns (XRD) were used for microstructural characterization, and creep tests for a preliminary assessment of mechanical properties. The results showed that the steady state creep rate, $\acute{\varepsilon}_{st}$, of the ternary alloys decreased with increasing copper content up to 1 wt%, but above this level, it increased as the copper content increased. Furthermore, the results of the steady state creep indicated two deformation temperature regions (below and above 548 K). The energies activating the steady state creep were found to have the value of 39.2 kJ/mol in the low range of temperature (508-538 K) and 87.6 kJ/mol in the high range of temperature (558-557 K). The values of the activation energies in the first range of temperatures suggest the grain boundary sliding mechanisms while in the second range one it can be attributed to dislocation climb mechanism.**

***Index Terms*— Al-Zn based alloys; creep; microstructure; dislocations**

I. INTRODUCTION

The effect of micro-alloying elements on the behavior of age-hardenable alloys is an interesting physical problem addressing the mechanisms of transport and aggregation of the solute, which has important technological applications (such as optimization of the thermal treatments, nucleation of precipitates, stability of the microstructure [1].

The microstructure, mechanical, and physical properties of the Al-Zn system, with respect to the composition and applied heat treatment, have been studied by many authors. According to the phase diagram [2] of the Al-Zn system, slowly cooled Al-30wt% Zn alloy consists of two phases, namely α-solid solution (Al-rich phase of fcc structure) and considerable amounts of β-phase (Zn-rich phase of hcp structure) forms at the boundaries of α-phase [3,4].

Aging characteristics of the Al-10 wt% Zn alloy have been investigated [5] in the temperature range 383–503 K by electrical resistivity measurements. The resistometric study delineated two distinct stages. The first stage characterized by a decrease in resistivity, whereas an increase was observed in the second stage. The activation energy was found to have a value of ~ 48 kJ/mol in accordance with that expected to activate vacancy or atom migration in Al. The creep behavior of Al-40 wt% Zn alloy, with and without different degrees of torsional pre-deformation, has been studied [6] under constant stresses ranging from 42 to 50.3 MPa and at different temperatures ranging from 513 to 593 K. The energy activating the steady state creep was found to be 78 kJ/mol and 105.7 kJ/mol, in the low and high temperature range, respectively, characterizing a grain boundary diffusion mechanism of Zn and Al atoms.

The effect of Cu addition on the spinodal decomposition of the Al–Zn alloy has been investigated by X-ray diffraction analysis [7]. It is found that the required time for spinodal decomposition in the Al-Zn-Cu alloy extended up to 20 times more than that in the Al-Zn alloy when isothermally aged at 300 ^{o}C. This indicated that the spinodal decomposition of supersaturated α-phase in Al-Zn alloy can be retarded due to the addition of Cu under the three-phase equilibrium temperature. Govindaraju et al [8] investigated the fatigue crack growth behavior of Al-Zn and Al-Zn-Ce alloys. They found that the addition of Ce had very strong influence on fatigue strength. Ce eliminates the porosities and refines microstructures of the alloy, showing the improved fatigue crack growth behavior.

Till now, a systematic study of the effect of Cu addition on the microstructure and creep properties of Al-30 wt% Zn alloy has not been studied. Therefore, the present investigation was initiated in order to elucidate the influence of Cu addition and heat treatment on the microstructure and mechanical properties of Al-30 wt% Zn alloy.

II. EXPERIMENTAL PROCEDURES

A. Sample preparation

One binary Al-30 wt% Zn and four ternary Al-30 wt% Zn-Cu alloys with different copper contents (0.5, 1.0, 1.5 and 2.0 wt%) were prepared by Al, Zn, and Cu of 99.99% purity by melting under vacuum in a high-purity graphite crucible. After annealing for homogenization at 813 K for 4 days, the ingots were swaged and cold drawn into wires of 0.8mm in diameter for creep measurements and sheets of 0.6mm in thickness for microstructural examinations. The chemical composition of the alloys was verified by means of energy dispersive X-ray analysis (EDX). After solution heat treatment at 698 K for 4 h to eliminate the cold work introduced during swaging, wires and sheets specimens were

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slowly cooled to room temperature with a cooling rate of $11x10^{-3}$ K/s. Such heat treatment allowed the double ($\alpha + \beta$) phase to exist [9].

B. Creep measurements

A conventional tensile testing machine described elsewhere [10] equipped with a strain resolution equal to 10^{-5} was employed. Creep experiments have been performed under a constant load corresponding to the stress of 21.20 MPa and at deformation temperatures ranging from 508 to 578 K (0.54 ~ 0.62; T_m where T_m is the absolute melting temperature of the matrix). The accuracy of temperature measurements is of the order of ±1K.

C. Microstructure observations

Two powerful tools are used to investigate the microstructure of the present alloys. Optical microscope and X–ray diffractometer are utilized. Prior to the optical microscope observation, a solution of 2ml HF+3ml HCl+5ml HNO_3+250ml H_2O was prepared and used to etch the samples. The X-rays diffraction data (XRD) were recorded at room temperature on a Philips PW3710 X-ray diffractometer using Cu K_α radiation (of wave length λ= 0.15406 nm) at 40 kV and 40 mA settings.

III. RESULTS

Typical creep curves for Al-Zn-Cu samples strained at different deformation temperatures under a constant applied stress of 21.20 MPa are shown in Fig. 1. It can be seen that the Al-Zn-Cu samples showed characteristics of well-defined steady state creep directly after loading with little primary creep duration. This implies that the hardening of the matrix was recovered immediately and balanced at an extended deformation rate. Nevertheless, the variation in steady state creep rate, $\acute{\varepsilon}_{st}$, suggested that the creep behavior of investigated alloys is strongly affected by the deformation temperature. A monotonic shift towards higher strains is observed with increasing the deformation temperature interrupted with a sudden decrease at about 548 K, followed by a rapid increase afterwards above 548 K.

The deformation temperature dependence of the steady state creep rate, $\acute{\varepsilon}_{st}$, (determined by differentiating the creep strain of the linear parts of the creep curves shown in Fig. 1 with respect to time) is shown in Fig.2. It can be seen that $\acute{\varepsilon}_{st}$ increases with increasing the deformation temperature exhibiting minimum value at 548 K above which a continuous increase occurs.

Figure 3 demonstrates the influence of Cu content on the steady state creep rate, $\acute{\varepsilon}_{st}$, at different deformation temperatures. It can be observed that, for all deformation

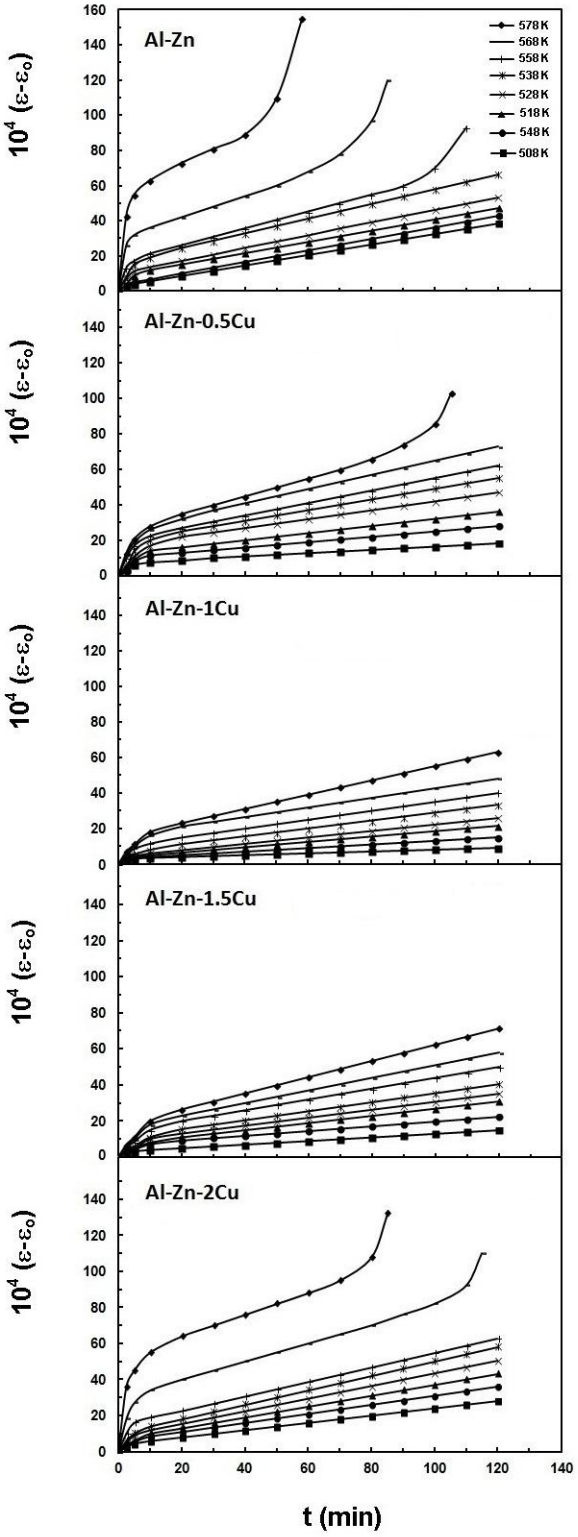

Fig.1: Creep curves of the investigated alloys with different Cu contents under constant applied stress of 21.20MPa at different deformation temperatures as indicated. ε_o is an instantaneous creep strain at time = 0

temperatures applied, the values of the steady state creep rate, $\acute{\varepsilon}_{st}$, are characterized by two distinct stages. In the first stage, the steady state creep rate, $\acute{\varepsilon}_{st}$, decreased continuously with increasing copper content up to 1.0 wt%. However, when the copper content exceeded 1.0 wt%, a second stage

characterized by the increase in the steady state creep rate, $\acute{\varepsilon}_{st}$, with increasing Cu content is observed.

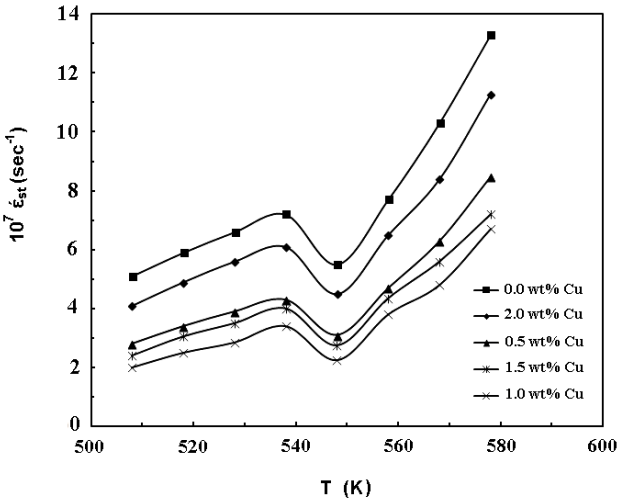

Fig.2: The deformation temperature dependence of the steady state creep rate, $\acute{\varepsilon}_{st}$, for different Cu contents as indicated.

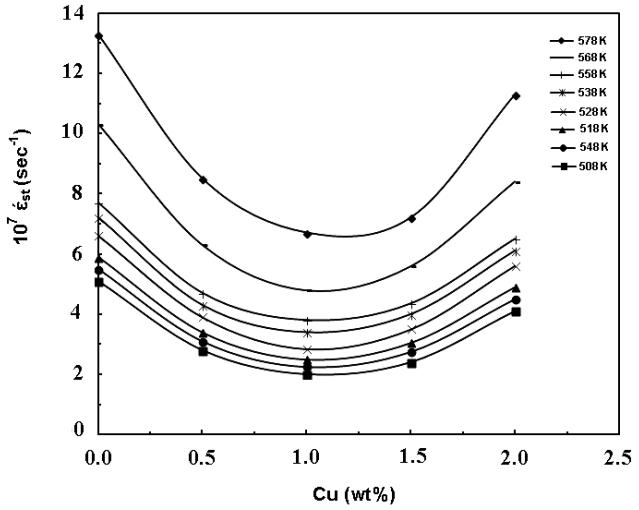

Fig.3: The Cu content dependence of the steady state creep rate, $\acute{\varepsilon}_{st}$, at different deformation temperatures indicated.

Figure 4(a and b) shows the optical micrographs of the Al-Zn alloy samples at various deformation temperatures. The microstructure of the Al-Zn alloy heated at 528 K basically comprise a mixture of two phases, namely α Al-rich phase and β Zn-rich phase which forms at the grain boundaries of α - phase (Fig. 4a). As the temperature increases from 528 to 558 K, the microstructure of the Al-Zn alloy consists of one α Al-rich phase (Fig.4b). The addition of Cu to Al-Zn alloy resulted in the formation of copper rich θ-phase (CuAl2). This can be seen in the microstructures of the alloys containing 0.5-2wt% Cu (Fig. 5(a-c). The observed particles were identified to be copper rich θ-phase through analysis of X-ray diffraction (see Fig. 6). This is in agreement with the previous results in the Al-Zn-Cu alloy system [11].

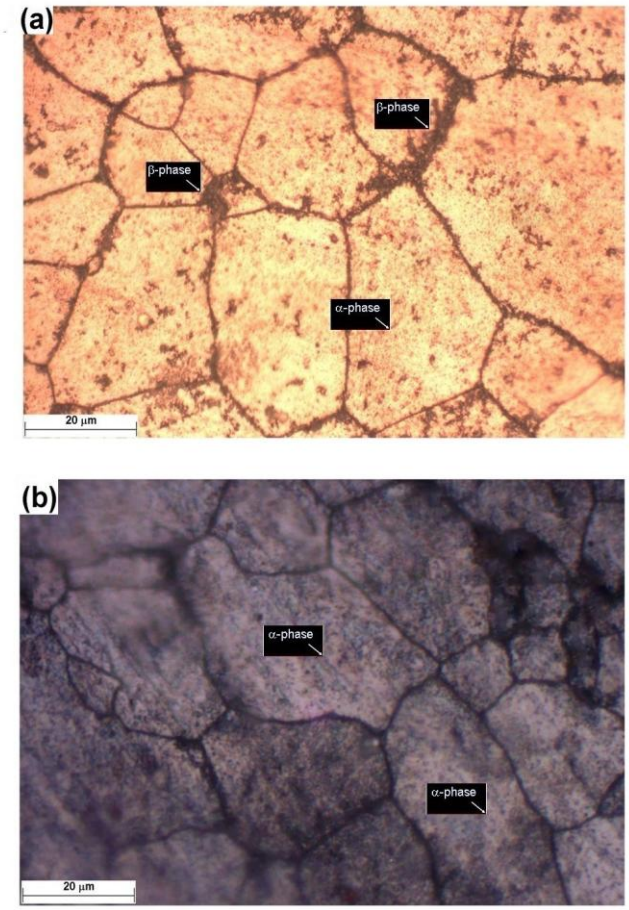

Fig.4. Optical micrographs for Al-30wt% Zn heated at (a) 528K showing the presence of β-phase at the grain boundaries (b) 558K showing the dissolution of β-phase.

A representative example of X-ray diffraction patterns of Al-Zn-Cu alloys is depicted in Fig.6. The Al-Zn alloy was mainly composed of α Al-rich phase and β-Zn rich phase, while the alloys with Cu additions were composed of three phases, i.e., α Al-, β Zn- and θ Cu-rich phases. The X-ray diffraction pattern obtained from a metallic sample gives information about imperfections in the material i.e. dislocations, crystallite size, and lattice strain within the grains due to dislocations and stacking faults [12]. The crystallite size (η) was calculated from the Scherer's formula from the full width at half maximum (FWHM) (β) of the peaks expressed in radians [13]:

$$\eta = \frac{0.94\,\lambda}{\beta \cos\theta} \qquad (1)$$

where λ is the wavelength of the X–ray used and is θ is Bragg's angle. The lattice strain (ε) is calculated from the slope of (β cosθ)/ λ versus (sinθ)/ λ plot using the relation [14]:

$$\frac{\beta \cos\theta}{\lambda} = \frac{1}{\eta} + \frac{(2\varepsilon \sin\theta)}{\lambda} \qquad (2)$$

The dislocation density (δ) is defined as the length of dislocation lines per unit volume of the crystal and calculated by using the formula [15]:

$$\delta = \frac{1}{\eta^2} \quad (3)$$

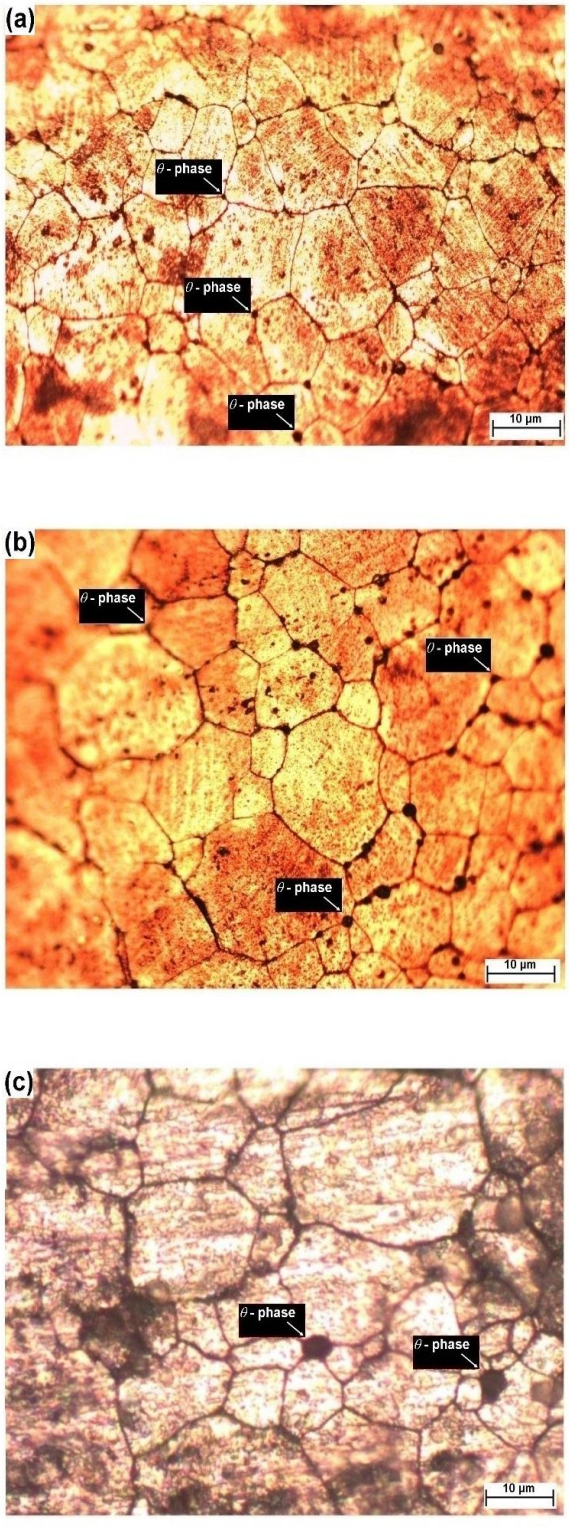

Fig. 5: Optical micrographs for (a) Al–30 wt% Zn–0.5 wt% Cu, (b) Al–30 wt% Zn–1.0 wt% Cu and (c) Al–30 wt% Zn–1.5 wt% Cu alloys at different deformation temperature of 548K showing the presence of copper rich θ – phase at grain boundaries.

The deformation temperature dependence of the lattice strain ε, the crystallite size, η, and the dislocation density, δ, for different Cu contents is given in Fig. 7.

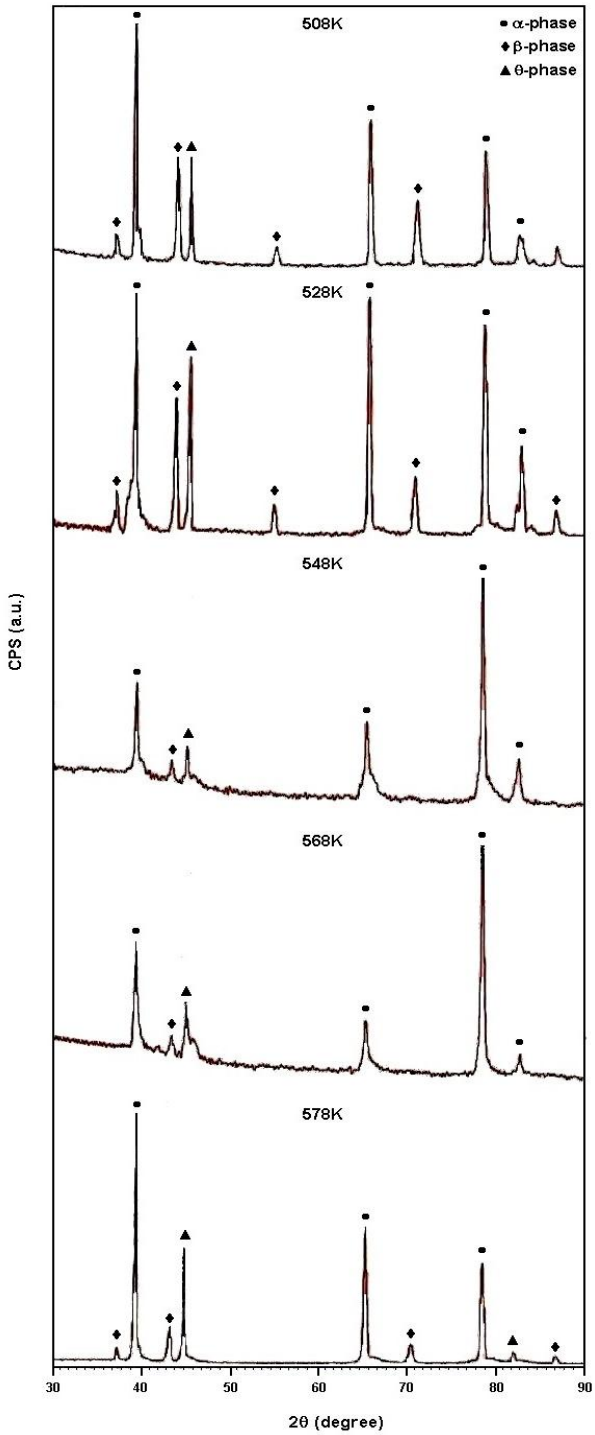

Fig.6: Representative example for X-ray diffraction patterns of the Al-30wt% Zn-0.5wt% Cu alloy after creep measurements at different deformation temperatures as indicated.

IV. DISCUSSION

Creep of materials is classically associated with time-dependent plasticity under a fixed stress at an elevated temperature. At temperatures above about half the absolute melting point (T_m), most metals and alloys exhibit normal creep curves, i.e., following the initial strain on loading (ε_o), the creep rate decays during the primary stage, reaching a minimum or secondary value before accelerating during the tertiary stage that leads to fracture [16]. The steady state creep at constant stress results from the balance of the simultaneous operation of the processes of work hardening and recovery. Because of this balance, which gives rise to a "steady state", the rates of these two processes are coupled to each other in such a manner as to establish a dynamic equilibrium of generation of dislocations (associated with work hardening) and annihilation of dislocations (associated with recovery) [17].

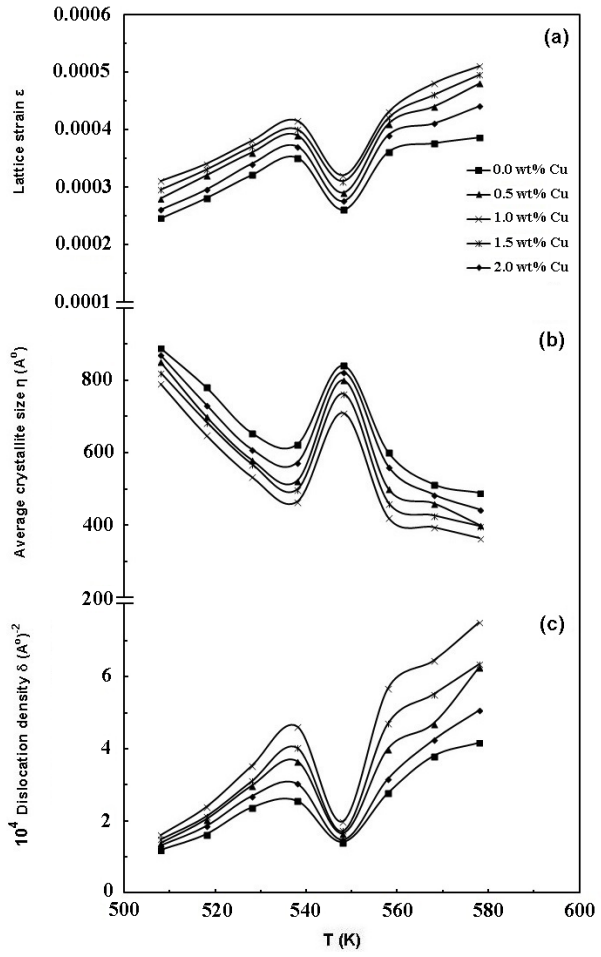

Fig.7: The deformation temperature dependence of (a) the lattice strain ε, (b) the crystallite size η ,and (c) the dislocation density δ for different Cu contents as indicated.

Creep characteristics are known to depend on the applied stress, deformation temperature and internal microstructure of the tested material [18,19]. The variation of the steady state creep rate, $\acute{\varepsilon}_{st}$, with deformation temperature for alloys under investigation can be referred to the different microstructures taking place during the heating process. From the experimental data shown in Fig. 2, it can be seen that the values of $\acute{\varepsilon}_{st}$ increase continuously with increasing deformation temperature in the first temperature range below 548K. This behavior is in good agreement with a previously reported conclusion obtained from stress-strain measurements on the same alloys [20]. This behavior can be explained as due to the coarsening of β - phase, as seen in Fig. 4a, which lowers the interaction between the β–phase and dislocations and consequently leads to softening [21].

The anomalous behavior in $\acute{\varepsilon}_{st}$ values was found at the temperature 548K which could be attributed to the dissolution of the β - phase, thus causing free Zn atoms which consequently move towards the generated mobile dislocations and pinning them. The rapid increase of the steady state creep rate, $\acute{\varepsilon}_{st}$, in the high temperature range (558-578K) could be a result of the further heating which completely dissolves the Zn-rich phase (see Fig.4b) [22].

The present results clearly demonstrate that Cu addition has a significant effect on the creep behavior of the Al-Zn alloy. It was found that the steady state creep rate, $\acute{\varepsilon}_{st}$, of the Al-30wt% Zn-Cu alloys decreased continuously with increasing copper content up to 1 wt%, above which the trend reversed (Fig. 3). These results may be explained in terms of microstructural features and solution strengthening mechanism. The addition of copper resulted in the formation of stable θ - intermetallic phase ($CuAl_2$) in the ternary alloys (Fig. 5). The number and size of the θ-phase particles increased as the copper content of the Al-30 wt% Zn-Cu alloys increased up to 1wt% Cu (Fig. 6a and b). These fine precipitates of θ - phase act as barrier to dislocation motion and thus causing retardation of their movement, i.e. enhancing the work hardening in the alloys. It appears that replacing zinc with copper in Al-Zn-Cu system results in the formation of θ-phase in place of β-phase particles. These observations are in agreement with the results of previous investigations and can be related to Al-Zn, Al-Cu, and Zn-Al-Cu phase diagrams [23-25].

The subsequent increase in the steady state creep rate, $\acute{\varepsilon}_{st}$, with increasing Cu content for all deformation temperatures is believed to be due to the coarsening of θ - phase (Fig.6c). The formation of coarsening θ - phase weakens the interdendritic regions of the alloys and gives rise to cracking tendency. Thus the matrix gets clean and the movement of dislocations should be much easier. Similar explanations have also been offered previously in the literature [23,24].

From Fig. 7, it can be observed that the deformation temperature dependence of both lattice strain ε, and dislocation density δ are in contrary to the behavior of the crystallite size η. The increase in both lattice strain ε, and dislocation density δ values with increasing deformation temperature for different Cu contents was attributed to the increase of the coarsening process of the β-phase in the

Al-rich phase by thermally activated process. Above the transformation temperature (548 K) the dissolution of the second phase (β-phase) in the α-phase matrix leading to the increase in the homogeneity of the α-phase matrix and the homogeneity of the distribution of Zn atoms in the α-phase matrix with increasing deformation temperature may contribute to the observed increase in both ε and δ.

One of the most common ways to identify the micro-mechanisms responsible for creep process is to establish the creep activation energy [26]. The activation energy of steady state creep was calculated from the slopes of the straight lines relating ln $\acute{\varepsilon}_{st}$ and 1000/T (see Fig. 8) [27]. The average activation energies were found to be ~ 39.2 and 87.6 kJ/mol in the low and high deformation temperature regions, respectively. The activation energy of 39.2 kJ/mol obtained in the low deformation temperature range (508-538K) , is close to 34.5 kJ/ mol reported for the creep of the Al-40 wt% Zn alloy at slightly low temperatures (503-533 K). The former value of activation energy consistent with the activation energies for the grain boundary sliding mechanism [9]. The value of activation energy (87.6 kJ/mol) in the high deformation temperature range (558-578K) indicates that the dominant operating mechanism is a dislocation climb [9].

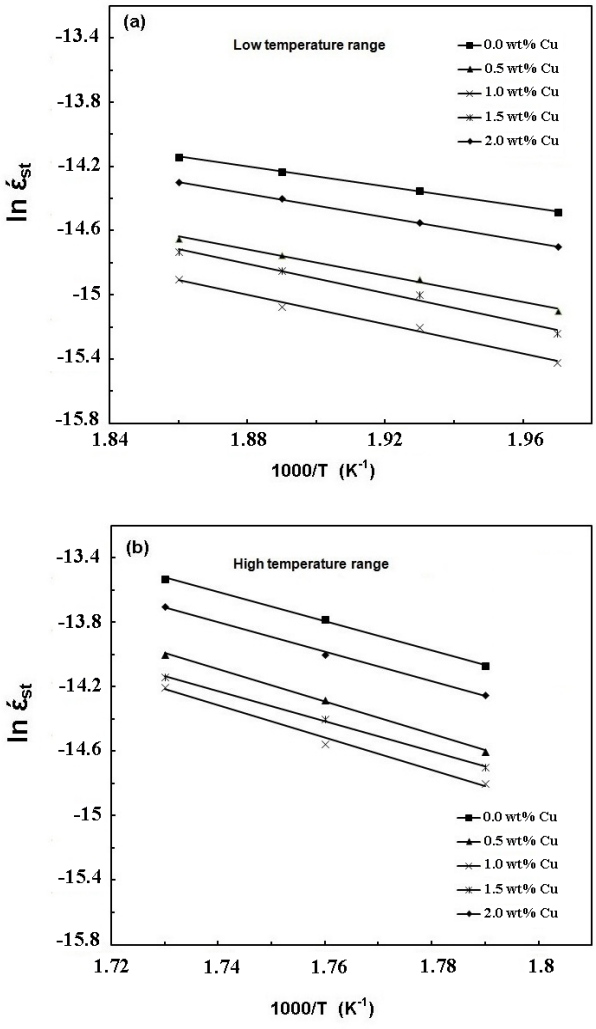

Fig.8. Relation between ln $\acute{\varepsilon}_{st}$ and 1000/T in (a) the low temperature range, and (b) the high temperature range for different Cu contents as indicated.

V. CONCLUSIONS

The effect of Cu addition of the creep behavior of Al–Zn alloy and its relationship to microstructure evolution are systematically investigated at different temperatures ranging from 508 to 578 K in the present study. The obtained results of the steady state creep rate revealed that a transition point at 548 K. The steady state creep rate of Al–30 wt% Zn–Cu alloys decreased continuously with increasing copper content up to 1 wt%, but above this level, it increased as the copper content increased.

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