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Anomalous creep behaviour of a Ni–22 at % Cu alloy and the miscibility gap

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The purpose of this study is to understand the anomalous creep behaviour of Ni–22 at % Cu alloy at the suggested critical miscibility gap temperature, below 598 K (0.36 T_m). The Cu–Ni system is classified as a class II solid solution at temperatures above 0.4 T_m, and it is also experimentally verified by the authors that the characteristic creep behaviour of the alloy used for this work is that for a class II solid solution. However, at low temperatures, this particular alloy shows different creep behaviours, with small stress increment in the steady state, sigmodial creep deformation is observed while with large stress increases normal primary creep occurs. When unloading the stress during creep and ageing at the test temperature, no softening due to recovery is observed but the same creep rate is achieved. The activation energy of the creep for the quenched and aged specimen is anomalously high, 326 kJ mol^{-1}, however, for the annealed specimen it was 167 kJ mol^{-1} which is the same for that of pipe diffusion. On the basis of the observed experimental results and proper analysis, it is hypothesized that, at the test temperature, the possible formation of the solute clustering is responsible for the high activation energy and stress exponent for the creep deformation. Using the mechanical testing, creep test, it is experimentally verified that Cu–Ni system has a miscibility gap at low temperature.

1. Introduction

On the basis of the various reports [1–6] it has been shown that the enthalpies of formation of solid Cu–Ni alloys are positive, and it has been suggested that there is a possibility that a miscibility gap is formed in these alloys at low temperatures. That is to say, at low temperatures the free energy of alloy formation is governed by the enthalpy term which favours decomposition of the solid solution alloys into two phases.

The fact that a miscibility gap exists in the Cu–Ni alloys at low temperatures was presumed to explain the anomalous increase in specific heat [7, 8], electrical resistivity [9, 10], elastic modulus [11] and magnetism [12, 13] compared with those values expected from the isomorphous solid solution in which copper and nickel atoms are assumed to be distributed randomly. In fact the direct experimental evidence for nonrandomness of Cu–Ni solid solutions at low temperature was confirmed by neutron measurement [14] and X-ray diffraction technique [15, 16]. In 1969, from thermodynamic calculation [2], the critical temperature and composition of the miscibility gap were reported to be 595 K and 78 at % Ni, respectively.

The creep behaviour of the alloys having a miscibility gap have been reported for Au–Ni [17] and Al–Zn [18] solid solution alloys. In these alloys, a dislocation glide process was found to be the most predominant rate controlling mechanism of the creep deformation even above the misci-

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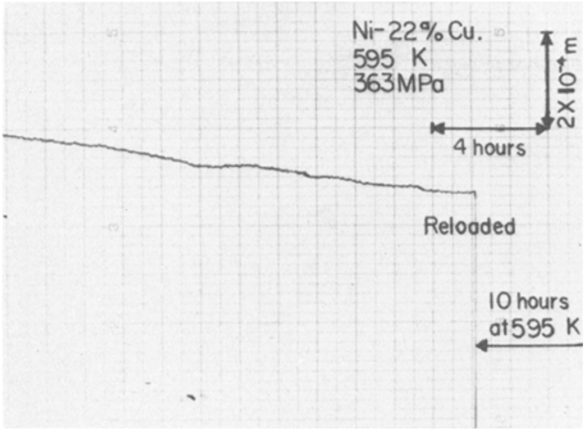

Figure 1 Creep behaviour upon reloading the original creep stress after the specimen was unloaded and left for 10 h at the test temperatures.

bility gap temperature range. However, the fact that the Cu–Ni solid solution is much more ideal than these alloys at above 0.5 T_m (since the miscibility gap occurs at a lower temperature) it has been classified as a class II alloy on the basis of the creep data tested above 0.5 T_m [19, 20]. Recently, Nam *et al.* [21] reconfirmed that at the temperature range well above the critical miscibility gap tempterature, i.e. 0.4 to 0.6 T_m, Ni–22 at% Cu alloy behaved as a class II alloy.

However, according to the thermodynamic concept it is presumed that creep behaviour at low temperatures may be different from its behaviour at high temperatures. This is based on the fact that at high temperatures the contribution of the entropy term becomes predominant to cause random distributions of atoms (solid solution) but at low temperatures the effect of the enthalpy term becomes very significant to cause segregation of atoms (hard to mixing). In fact, Yi [22] has measured the creep rates of a series of Cu–Ni alloys at a temperature slightly higher than the proposed critical miscibility gap temperature and found that the minimum creep rate was observed for the alloy Ni–22 Cu.

The purpose of the present work is to clarify the cause of the anomalous creep behaviour of Ni–22 at% Cu alloy at the proposed critical miscibility gap temperature.

2. Experimental procedure

The alloy for the specimen was fabricated by melting electrolytic nickel and copper of purity not lower than 99.9%. The chemical composition of the specimen was; 21.5 at% Cu, 78.2 at% Ni, 0.18 at% Mn, 0.02 at% Fe, 0.002 at% Pb and 0.14 at% Co. The slabs were homogenized for 12 h at 1173 K and cold rolled to a sheet of 1 mm thickness and machined along the rolling direction in the form of a plate-type tensile creep specimen to give the dimension of gauge length and width as 25 and 4 mm, respectively.

Prior to testing, most of them were fully annealed at 1073 K in vacuum for 2 h and quenched into liquid nitrogen and then annealed at 573 K for a week.

The creep tests were performed using a creep machine equipped with an Andrade–Chalmers constant stress arm. Stress change and intermittent stress tests were conducted to investigate the creep behaviour at low temperature. Activation energy for the creep deformation process was measured during the second stage of creep with the temperature change method in the neighbourhood of the temperature range where the presence of the miscibility gap is expected.

The extension of the specimen was measured by the Schaevitz model HR 1000 LVDT with an accuracy of 0.5×10^{-5} m. The test temperature was below 598 K (0.36 T_m) and the stress level was lower than 390 MPa.

3. Experimental results and discussion

A specimen was crept under a stress of 333 or 363 MPa at the test temperature of 595 K (0.36 T_m) for a certain period of time until the creep deformation rate reaches that for a steady state, and it was unloaded to be left for 10 h at the test temperature. Upon reloading to the original stress, the steady state was achieved immediately and no transition was observed (Fig. 1).

Pavlov and Pereturina [23] have reported the

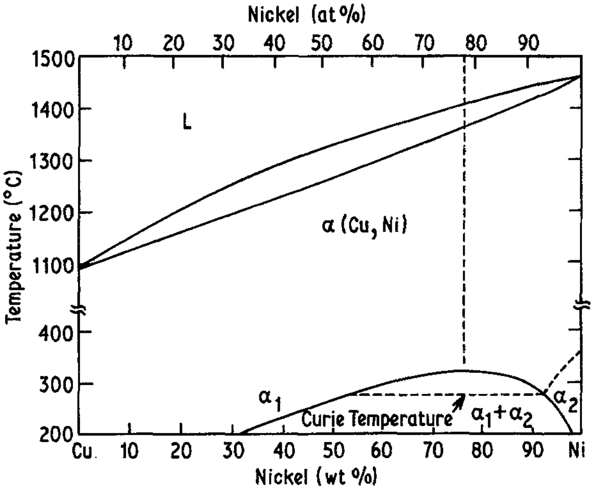

Figure 2 Equilibrium phase diagram of Cu–Ni alloy system (from Metals Handbook, Vol. 8, 8th edition, ASM, Metals Park, Ohio, 1973).

experimental observation of the strengthening effect due to short range order clustering in Cu–Ni alloys, which have been pulled in tension for a certain value of strain, the test stopped, unloaded, kept at low temperature and pulled again. On the basis of this strengthening effect, it is hypothesized that the present experimental result of no transition upon reloading is not due to lack of recovery at low temperature but due to solute cluster formation. This assumption may also be supported by the suggestion of the possible existence of the miscibility gap [1–6] and the proposed phase diagram of Cu–Ni system [24] in which the miscibility gap is shown (Fig. 2).

To confirm the effect of negative short range order (cluster) in the steady state, the specimens have been unloaded and maintained in the unloading condition at the test temperature for 10 h and then reloaded. The results after reloading show that when a small stress (6 MPa) was applied, a sigmoidal transient creep curve was observed (Fig. 3b) and when large stress (15 MPa) was applied, the normal transient curve was recorded (Fig. 3a). These phenomena may also be explained by the effect of solute clusters. Namely, upon a small stress increase, dislocations may gradually escape from the clusters and as the dislocations move and multiplicate new dislocations, which are free from the short range clusters, the creep rate may be enhanced. As a consequence of this faster or easier dislocation motion, the specimen will be strain hardened during creep strain and the hardening

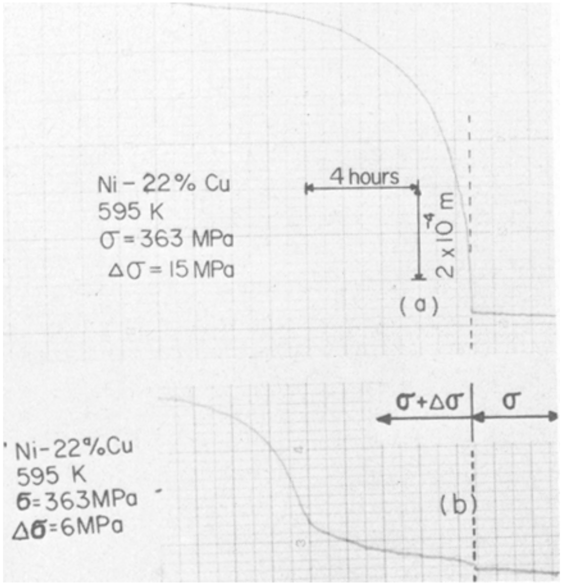

Figure 3 Transient creep behaviour with the amount of creep stress reloaded. Specimen is unloaded, left for 10 h at the test temperature, and reloaded to the original creep stress. Creeping 5 h after the specimen is reloaded and (a) the creep stress is suddenly increased by 15 MPa, (b) it is increased by 6 MPa.

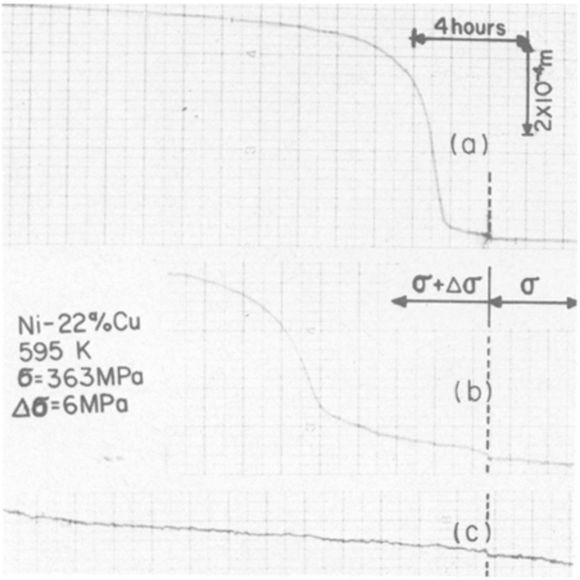

Figure 4 Transient creep behaviours with the duration of unloading time at the test temperature for (a) 2 h, (b) 10 h and (c) 24 h. For these tests specimens were unloaded for each time duration and reloaded to the original stress and then crept for 5 h before the stress increment.

may cause the gradual decrease in the creep rate. With a large stress increase, a dislocation can overcome the clusters at one and accordingly normal transient curves are observed, as in the case for class II alloys.

In a further effort to examine whether the clusters are responsible for this behaviour, another set of tests was performed. In the steady state the specimen was unloaded, annealed at test temperature for 2, 10 or 24 h and reloaded. It took a longer time to obtain acceleration of the creep rate with increased annealing time, and, in the case of the specimen which was maintained for 24 h, the acceleration of creep rate was not observed (Fig. 4). Such experimental results are explained by the mobile dislocation density decrease due to the increase of cluster formation and the growth of clusters with the increase of annealing time. This hypothesis is supported by the TEM observations reported by Karashima and his associates [25]. They observed that, at the early stage of sigmoidal creep, the multiplication of the mobile dislocations had been inhibited to give a very low creep rate. As the creep rate generally increases and reaches the transition stage in which the creep rate becomes maximum the generation of mobile dislocations becomes very significant. As has been previously mentioned, the authors [21] have tested the same alloy but it has been fully annealed in the temperature range of $0.36 \sim 0.64\,T_m$ and under a constant stress condition of 10 to 392 MPa. However, in this higher temperature range all the tests, including stress change tests, show no evidence of "anomalous creep behaviour".

To see the possible effect of solute clustering, the activation energy of the creep deformation is measured by means of the temperature increment method proposed by Movchan and Nerodenko [26] for the solid solutions in which low temperature phase transformation is occurring.

Specimens, which have been heat treated the same as those used for the creep tests (annealed at 1073 K for 2 h in vacuum, quenched into liquid nitrogen and then annealed at 573 K for one week for convenience, and referred to as "specimen A") were used to measure the activation energy. The measured activation energy of this test was observed to be 326 kJ mol^{-1}, which was very much larger than that usually observed (Fig. 5). For the purpose of comparison, other specimens have been annealed at 1073 K for 2 h in vacuum and then furnace cooled (these specimens are referred to as "specimen B"). The measured activation energy for this fully annealed specimen is 167 kJ mol^{-1} which is a similar value to that for pipe diffusion [21]. These results are shown in Fig. 5.

Many of the experimental observations have been reported [27–29] for this kind of anomalously high value of the activation energy for creep in solid solution alloys which show phase transition at low temperatures. However, in this present work the value of the activation energy is dependent on the heat treatment of the specimen.

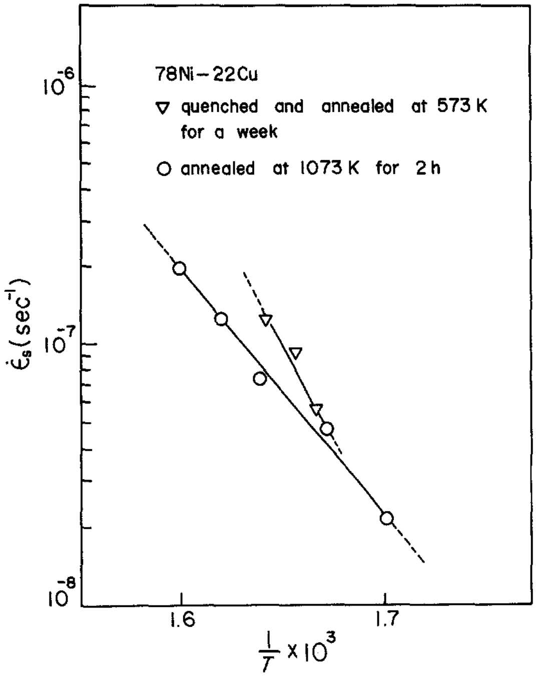

Figure 5 Arrhenius plot of the steady state creep rates as a function of the inverse of the temperature for the specimens of annealed and quench-annealed.

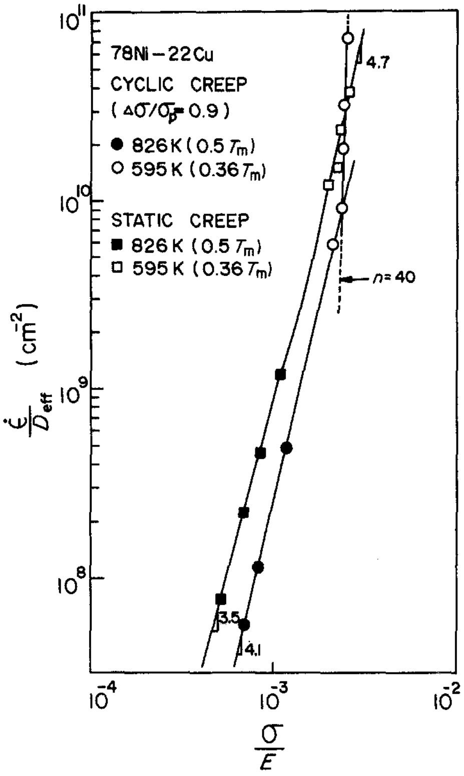

Figure 6 The plot of temperature normalized creep rate against Young's modulus normalized creep stress for static and cyclic creep tests [34].

Therefore, it will be very helpful for us to know the effect of heat treatment on the internal structure of this alloy system. To explain this anomaly, one may refer to the reports [30–32] which show that the effects of heat treatment were observed at low temperatures in Cu–Ni system.

Several investigators [30–32] have reported the effects of heat treatment of Cu–Ni systems at low temperature. These reports support the idea that low temperature phase separation in these alloy systems may not be possible if it is cooled slowly because of the low diffusivity. However, the excess vacancies introduced artificially by quenching or straining are not annihilated easily [33] owing to the binding energy of vacancies with solute atoms, but instead promote clusters formation [13, 32]. Numakura *et al.* [32] also reported that the elastic modulus is more sensitive to temperature at low temperatures where the strong effect of the clusters is observed.

It will be very helpful for us to understand the anomalies if we can explain the higher activation energy for the specimen solutionized, quenched and aged at 573 K for one week (specimen A).

Recently, Han [34] has observed a very high value for the stress exponent of $n = 40$ for Ni–22 at % Cu alloy cyclically crept in the present investigation. In Fig. 6, the experimental data were plotted along with the results for $0.5\,T_m$. The stress exponent for the static tests at $0.36\,T_m$ were observed to be 4.7, which is much lower than 40. It is very interesting to note that the stress exponents for static and cyclic creep at $0.5\,T_m$ are very close, i.e. only at low temperature is another anomaly observed for the cyclic creep.

This anomaly may be explained by the report of Miller and Sherby [35] in which they claim that a very large value of the stress exponent is predicted in metals that are solute strengthened. This idea has also been experimentally confirmed by many investigators [36, 37]. According to this evidence, it is clear that the increase in stress exponent for the cyclically crept specimens at low temperature can be related to the solute clusters which are promoted in the presence of excess vacancies that are mechanically generated by the cyclic stress [38, 39]. As far as the role of excess vacancy is concerned, there is common support for the enhanced diffusion of solute by vacancies for these specimens cyclically crept and solutionized, quenched and aged. This enhanced diffusion is

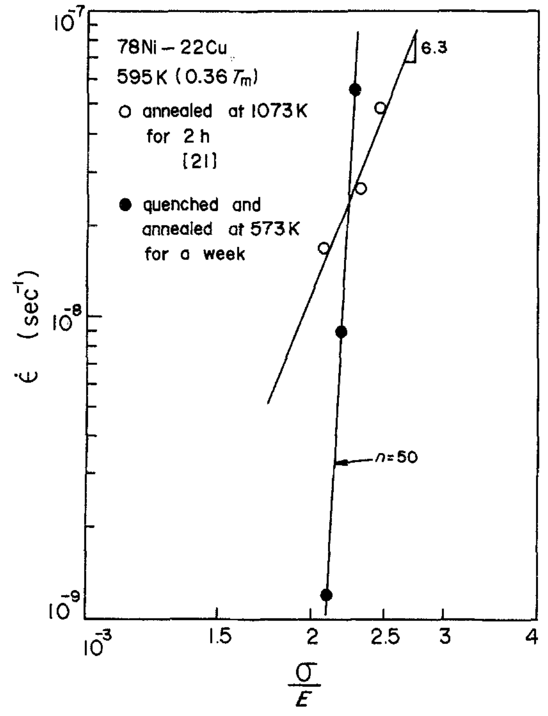

Figure 7 Steady-state creep rate as a function of Young's modulus normalized creep stress at 0.36 T_m.

supported by works from Schüle *et al.* [40] and Poerschke *et al.* [41] in that the maximum temperature and the miscibility gap for Cu–Ni alloy were enhanced by neutron or electron irradiation.

To see if there is the possibility of obtaining a higher value of stress exponent for "specimen A", one set of static creep tests were conducted at 595 K (0.36 T_m) for the stress range of $(\sigma/E) = 2 \sim 2.5 \times 10^{-3}$ and these creep rates during the steady state were plotted in Fig. 7 along with the data for the "specimen B" from [21]. From this plot it is clearly seen that the exponent is very much higher ($n = 50$) for the quenched, aged specimen ("specimen A") which is believed to have solute clustering as compared to that of the fully annealed one ("specimen B") from [21], ($n = 6.3$).

It has been quoted already [32] that the elastic modulus is known to be very sensitive to temperature where a strong effect of solute clustering is observed. Therefore, the anomalously high value of activation energy may be explained by the temperature-dependent elastic modulus combined with the high value of stress exponent.

Under the condition of constant (σ/E), the creep rate equation can be expressed as Equation 1,

$$\dot{\epsilon}_s = AD_{\text{eff}}\left(\frac{\sigma}{E}\right)^n \qquad (1)$$

where A is the temperature insensitive constant, D_{eff} is the effective diffusivity including the coefficients of lattice and pipe diffusion and E is the elastic modulus of the specimen at the given temperature. Therefore, one may get the value of the stress exponent, n, from the plot of $\ln \dot{\epsilon}$ against $\ln(\sigma/E)$.

Also, from Equation 1, one can get an expression for the effective activation energy for the creep deformation, shown below,

$$Q_{\text{eff}} = -R\left[\frac{\partial \ln \dot{\epsilon}}{\partial\left(\frac{1}{T}\right)}\right]_\sigma - nR\frac{\mathrm{d}\ln E}{\mathrm{d}\left(\frac{1}{T}\right)}$$

$$Q_{\text{eff}} = Q_c + nR\frac{T^2}{E}\frac{\mathrm{d}E}{\mathrm{d}T} \qquad (2)$$

where Q_{eff} is the effective activation energy for creep deformation under constant (σ/E), Q_c is the apparent creep activation energy obtained under constant stress (actually, this is obtained from the plot of $\ln \dot{\epsilon}$ against $\ln(1/T)$, shown in Fig. 5). It is apparent that the magnitude of the stress exponent and temperature dependence of the elastic modulus have significant effects on the activation energy of creep as shown in Equation 2.

Assuming that the increments of the stress exponent and the elastic modulus are due to the effect of solute clustering the necessary calculations from Equation 2 are made and they are tabulated in Table I. The effective activation energies for the creep deformation are calculated to be 187 and 160 kJ mol^{-1} for "specimen A" and "specimen B", respectively. Both of these values correspond to the activation energy for the pipe diffusion (188 kJ mol^{-1}) in Ni–22 at% Cu alloy [42]. The fact that those effective activation energies calculated in this analysis are similar to that of pipe diffusion in this alloy supports the phenomenological validity of this attempt.

From the above arguments, it may be suggested that the increase of activation energy is related to the increase of the elastic modulus and stress exponent which are all originally affected by the formation of solute clustering.

Consequently, the observed phenomena from the creep tests may support the possible existence of the miscibility gap in Cu–Ni system at low temperature.

TABLE I Comparison of the effective activation energies between fully annealed and quenched, aged specimens of Ni–22 at % Cu alloy at the temperature range of around $0.36\ T_m$

	Annealed at 1073 K and furnace cooling	Quenched and aged at 573 K
Elastic modulus $E(T)$	$-57.3 \times T + 1.97 \times 10^6$ [21]	$-214 \times T + 3.64 \times 10^5$ [32]
Stress, σ/E	2.3×10^{-3}	2.3×10^{-3}
$nR\ (T^2/E)(\mathrm{d}E/\mathrm{d}T)$ (kJ mol^{-1})	-5	-139
Apparent activation energy, Q_c (kJ mol^{-1})	167	326
Effective activation energy, Q_{eff} (kJ mol^{-1})	162	187

4. Conclusions

1. During the stress intermittent test (a test in which stress is unloaded to zero and left at the temperature to allow a possible recovery process) the same steady state was attained immediately upon reloading to the original stress level. This is thought to be due to the hardening effect of clusters.

2. When conducting the stress increment tests, sigmoidal curves were observed when a small stress was applied while a normal transient curve was attained when a large stress was applied. This phenomenon may also give some indication of the effect of solute clusters.

3. The time required to accelerate the creep rate increased with increasing annealing time. This may be explained by the decreasing dislocation mobility due to cluster formation and their subsequent growth with increasing unloading time.

4. Anomalously high activation energy and stress exponent values for the creep deformation are assumed to be influenced by solute clusters.

5. All the results support the possible existence of solute clusters which is an indication of the presence of the miscibility gap at low temperature.

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