Microstructure and Mechanical Property of α -Al-Zn-Cu Alloys Aged at Room Temperature

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Al-Zn-Cu alloys with five different compositions in the α -phase region have been prepared and their microstructures have been characterised employing X-ray diffraction, optical and scanning electron microscopy. The mechanical property of the alloys has also been characterized from the measure of hardness. A close correlation between the microstructure and hardness of the alloys has been observed. X-ray studies of ageing at room temperature of the materials in the deformed state revealed faster stress-induced precipitation of Zn and Cu whereas the transformation is slow in the homogenized materials. The rate of G.P. zone formation is either very slow or not detectable. The results of phase-transformation study have been supplemented by DSC study along with subsequent measurement of hardness values which are reduced on completion of Zn and Cu-rich precipitations.

(Received June 23, 1994)

Keywords: microstructure, microhardness, grains, grain boundaries, ageing, aluminium-zinc-copper alloy, X-ray diffraction analysis

I. Introduction

The present investigation deals with the microstructural characterization and phase transformation study in the as-cast and deformed states of the α -phase Al-based Al-Zn-Cu alloy system. Extensive studies on the microstructure and transformation kinetics of a large number of binary Al-based alloys have already been made by a wide variety of experimental techniques, like SAXS (small angle X-ray scattering), TEM (transmission electron microscopy) and DSC (differential scanning calorimetry)⁽¹⁾⁻⁽⁵⁾. The objective of these investigations is primarily related to better understanding of the structure-property correlation. The aluminium-rich Al-Cu alloys are well-known to undergo temperature-dependent precipitation from the supersaturated solid solution $\alpha^{(2)}$, via the sequence:

where θ is the equilibrium second phase having body-centered tetragonal structure and chemical composition CuAl_2 . Similarly in supersaturated aluminium-rich Al-Zn solid solutions the process of Zn precipitation follows the continuous appearance of several metastable phases (G.P. Zones) before reaching the stable hcp phase⁽³⁾. It would be interesting to know how these two binaries influence the structure and properties of the corresponding ternary Al-Zn-Cu alloys prepared in the α -phase region as few such studies on Al-based ternary alloys appear to have been reported⁽⁶⁾⁻⁽⁹⁾ until now. With this broad objective in mind the present study has been conducted as follows:

1. To characterize the microstructure of the alloys in

the deformed and homogenized state by X-ray diffraction, optical and scanning electron microscopies, in continuation of our recent study⁽¹⁰⁾ on the microstructure in the plastically deformed state of Al-Zn-Cu alloys. The above study⁽¹⁰⁾ characterizes the microstructure of the alloys in the deformed state through the evaluation of the defect parameters such as stacking fault density $\langle \alpha \rangle$, coherent domain sizes (D_e), r.m.s. microstrain $\langle \epsilon_L^2 \rangle^{1/2}$, dislocation density (ρ) and stacking fault energy parameters (γ) etc. by applying the well known X-ray diffraction line broadening analysis⁽¹¹⁾.

2. To study the mechanical properties from the measure of hardness.

3. To identify the nature of the precipitates, their size and volume fraction and the composition of the remaining solid solution from the study of phase transformation of the deformed and annealed powder forms of the materials.

4. Finally, to correlate the microstructure with the mechanical properties, following an earlier approach⁽¹²⁾⁽¹³⁾, from the results of the above studies.

II. Experimental Procedure

1. Preparation of the alloys

Five ternary Al-Zn-Cu alloys in the α -phase (fcc) region⁽¹⁴⁾ were chosen for the study having the following compositions in mass%:

1. Al-5Zn-3Cu, 2. Al-15Zn-3Cu, 3. Al-30Zn-1Cu, 4. Al-30Zn-2Cu, 5. Al-30Zn-3Cu.

Accurately weighed quantities of the constituent metals (spec. pure: 99.999% from Johnson Matthey, England) required for the above compositions were placed

(a)

(b)

Fig. 1 Micrographs of Al-15Zn-3Cu showing (a) general grain structures (optical). (b) SEM micrograph showing the grain boundaries and precipitates of Zn [z] and CuAl_2 [c] within grains and in the boundaries.

(a)

(b)

Fig. 2 Micrographs of Al-30Zn-3Cu showing (a) general grain structures (optical). (b) precipitates within the grain (optical). [z=Zn; c= CuAl_2]

in graphite crucibles, vacuum-sealed inside silica tubes and the contents melted in a muffle furnace at about 1173 K with intermittent shaking. The resulting ingots were subsequently homogenized at 733 K for 10 d and later quenched by dropping the capsules into liquid N_2 to retain the crystal structure of the 733 K isotherm⁽¹⁴⁾. The mass loss during the process being negligible the nominal compositions were retained.

2. Experimental details

In order to reveal the microstructure of the homogenized bulk samples by optical and scanning electron microscopy (SEM), about 2 mm thick slices (parallel faced) of the as-cast alloy samples were cut using a Buehler Isomet low speed Diamond saw (Model No. MA 11-1108) and polished metallurgically using standard procedure, with final polishing done using 1 μm diamond paste. Some of these slices were etched using a modified Keller's solution:

2 m/ HF + 3 m/ HCl + 5 m/ HNO_3 + 190 m/ H_2O

Micrographs using a high resolution optical microscope with a DIK attachment (Carl Zeiss, Jenavert 2000X) and a scanning electron microscope (Hitachi, Model No S 2300) were taken for a number of specimens (Figs. 1 and 2) to reveal the microstructure of the homogenized materials aged at RT for 1 year.

In order to correlate the microstructural characteristics with mechanical properties⁽¹⁵⁾ hardness studies of some previously polished 2 mm thick samples aged at RT for about 1 year were undertaken using a Vickers hardness tester (Model mph 160) attached to the optical microscope. Up to 1.568 N of load for an indentation period of 20 s have been used and at least five indentations have been averaged for each datum to account for any local inhomogeneity of grain compositions. Vickers hardness values H_v were evaluated following the procedure as adopted earlier⁽¹²⁾⁽¹³⁾.

Study of phase transformation due to different periods of ageing at room temperature (RT) of the as-cast and deformed states was undertaken for the alloys as, unlike binary Al-base alloys⁽¹⁾⁻⁽⁴⁾, very few such studies for ternary alloys exist in the literature⁽⁶⁾⁻⁽⁸⁾. The precipitation/decomposition phenomena have been studied by X-ray diffraction (XRD) and differential scanning calorimetry (DSC) (using Perkin Elmer DSC-2) with annealed (strain free) powders (Sample I), partially deformed (by compression) bulk (Sample II) and drastically deformed (cold-worked) powders by hand-filing (Sample III). Alloys with high Zn composition have been preferred.

III. Results and Discussions

1. Microstructure of homogenized alloys

The micrographs (Figs. 1 and 2) reveal almost equiaxed grain structures for the alloys homogenized containing lower concentration of Zn and Cu showing Zn precipitates dispersed inside the grains and at the grain boundaries (Fig. 1(b)). However, with increasing Zn and Cu concentration the Zn precipitates are increasingly observed (Fig. 2(b)) compared to Cu-rich precipitates as has been confirmed by EDX studies. With increasing Cu and Zn solutes the EDX data for the as-cast aged materials show the respective solute concentrations varying between 4.31%–10.57% and 59.46%–90.25% (in mass%). These observations about the presence of Zn-rich and Cu-rich phases are also confirmed by X-ray studies from the appearance of Zn and also some CuAl_2 peaks in the X-ray diffractogram along with the diffraction pattern of Al-matrix after a long period of ageing at RT (Section III.3).

2. Microhardness and its correlation with microstructure

Vickers hardness values H_v were found to increase gradually with increasing load (P) reaching saturation at about 1.225–1.568 N of load indicating uniform hardening in the interior of the specimen for almost all the alloy compositions (Fig. 3). The penetration depth (h) of indentation has been evaluated to lie within 5.3 to 8.7 μm for the alloys⁽¹⁶⁾ (Table 1). The lower H_v values at lower loads may reflect heterogeneous microdeformations for smaller indentation as reported earlier for various materials⁽¹²⁾⁽¹³⁾ and/or may be related to the phenomenon of surface-softness⁽¹⁷⁾ which controls the fatigue strength of the materials. For alloys with fixed (3 mass%) Cu concentration the peak hardness values, H_v are found to lie between 794 and 1117 MPa for varying Zn (from 5–30 mass%) concentration. Similarly, for fixed Zn concentra-

Table 1 Stacking fault density, $\langle\alpha\rangle$, dislocation density, ρ_{av} , penetration depth (h) and peak hardness.

Alloys	$\langle\alpha\rangle \times 10^3$	$\rho_{av} \times 10^{-11} (\text{cm}^{-2})$	Range of penetration depth (h) for load 0.49–1.568 N (μm)	H_v (MPa) (Peak value)
Al–5Zn–3Cu	5.5	1.87	5.7–8.7	794
Al–15Zn–3Cu	11.6	4.06	5.6–7.7	980
Al–30Zn–1Cu	5.8	2.36	5.6–8.3	862
Al–30Zn–2Cu	7.6	3.43	5.4–7.8	1000
Al–30Zn–3Cu	17.6	5.09	5.3–7.3	1117

tions (30 mass%) the H_v values of the alloys are found to vary from 862–1117 MPa respectively for varying Cu (1–3 mass%) concentration. The H_v values for the materials are also found to increase at a faster rate for increasing Cu (from 1–3 mass%) than Zn (from 5–30 mass%). Thus accommodation of more Cu in the Al–Zn matrix has resulted in an increased rate of solution-strengthening as Cu addition to Al–Zn substantially reduces the amount of Zn precipitation⁽¹⁸⁾.

Thus precipitation-hardening, if any, at the initial stage of ageing appears to be primarily controlled by dispersed Zn-precipitates as is also evident from the X-ray study (Fig. 6). This further leads to the conclusion that Zn additions slow down the diffusion of Cu in Al inhibiting the formation of CuAl_2 precipitates⁽¹⁸⁾ unlike in binary Al–Cu alloys⁽¹⁹⁾. Another contributing factor to the hardness of the alloy is strain-hardening, the nature of which is reflected in the mode of variations of work-hardening exponent, n , as measured from Meyer's law⁽²⁰⁾, which relates indentation load, P , with indentation dimension, d , as such,

$$P = Kd^n$$

where K is a constant.

The values of ' n ' as evaluated in this study are found to increase at a faster rate for increasing Cu than Zn concentration (Fig. 4) predicting the cumulative influence of Cu and Zn precipitation in the increase of internal stress of the Al-matrix⁽²¹⁾. This nature of solute dependence of work hardening effect compares favourably with the similar nature of variations of dislocation density values, ρ_{av} , with respective solute (Cu and Zn) concentration as has been evaluated in the earlier X-ray line profile study⁽¹⁰⁾ on the deformed powder samples.

The values of the parameters, $\langle\alpha\rangle$ and ρ , have been evaluated as such: following the method of Warren⁽¹¹⁾ for X-ray line broadening studies, the stacking fault density parameter $\langle\alpha\rangle$ has been calculated for f.c.c structure from the relation,

$$\delta(\Delta 2\theta)_{hkl-h'k'l'} = H_{hkl-h'k'l'} \langle\alpha\rangle,$$

where $\delta(\Delta 2\theta)$ is the measured values of the relative X-ray peak-shifts of the neighbouring pairs of reflections hkl and $h'k'l'$. $H_{hkl-h'k'l'}$ is a constant and depends only on reflecting lattice plane. Dislocation density, ρ is evaluated from the following relation⁽¹¹⁾

Fig. 3 Vickers hardness, H_v vs load for Al–Zn–Cu alloys.

Fig. 4 Plots of work hardening coefficient (n) and average dislocation density (ρ_{av}) vs solute (Zn/Cu) concentration for Al-Zn-Cu alloys. [●: n vs Cu, □: n vs Zn, △: ρ_{av} vs Zn, ○: ρ_{av} vs Cu]

Fig. 5 Plots of (a) α vs H_v and (b) ρ_{av} vs H_v , [△: Al-30Zn-Cu, ○: Al-3Cu-Zn].

$$\rho = (\rho_D \rho_S)^{1/2}$$

where ρ_D (due to domain size) = $3/(D_e)^2$ and ρ_S (due to strain broadening) = $K\langle\epsilon_L^2\rangle/b^2$, $K=6\pi$ for the Gaussian strain distribution, D_e is the effective domain sizes, ϵ_L is the microstrain values and b is the Burger vector for unit dislocation.

Evaluating the values of the parameters, D_e and $\langle\epsilon_L^2\rangle$ from X-ray peak broadening analysis of Warren⁽¹¹⁾, the values of the dislocation density, ρ , for the alloys have been calculated along with those of stacking fault density, $\langle\alpha\rangle$, from peak shift studies.

The mechanical property of the alloys with varied compositions has further been correlated with the results of the X-ray line profile studies⁽¹⁰⁾ (Table 1) through the plots (Figs. 5) of H_v vs stacking fault density, $\langle\alpha\rangle$, and dislocation density, ρ_{av} , which show that the nature of

Fig. 6 Diffraction patterns from annealed (a) and hand-filed powders (b) of Al-30Zn-1Cu alloy.

solute dependence of the microstructural parameters, $\langle\alpha\rangle$ and ρ_{av} , closely resembles that of hardness values⁽¹⁵⁾. Thus a close correlation has been observed between the microstructure and mechanical property from the results of the two different methods of analyses.

3. Ageing of deformed alloys

Prolonged ageing at RT of annealed powders (Sample I) showed no evidence of any phase transformation in the X-ray study except for the appearance of a small hump of (101) Zn line which already appeared in the pre-aged as-cast state (Figs. 6). However, on further ageing for over a year and half some faint broad humps (Fig. 7) were noticed to develop close to the high-angle sides of some of the XRD peaks, namely (111) and (200) of the Al-matrix resembling the appearance of the GP zones as reported for binary Al-Zn alloys⁽⁵⁾ from XRD study. Samples II (partially deformed by compression) and III (drastically deformed by filing) however, showed faster rate of transformation starting within a week after deformation, possibly due to stress induced enhanced diffusion resulting in supersaturated Zn solute being precipitated out of the Al-rich matrix. The XRD peaks of both Zn and Al-matrix gradually became sharp reaching almost saturation within 6 months of ageing (Fig. 8(a)). The transformation process was found to be slower in Sample II than in Sample III. Continued RT ageing of Sample III (beyond 6 months) resulted in further transformation leading to the appearance of some more prominent CuAl_2 XRD lines (Fig. 9) resembling the equilibrium θ -phase structure of binary Al-Cu alloy system⁽²⁾. Late appearance of CuAl_2 phase is perhaps due to the lower diffusion rate of Cu in Al due to Zn additions⁽¹⁸⁾. It can thus be suggested that an increase in the dislocation density in the matrix, as a result of cold-working, resulted in accelerated ageing leading to the precipitation of the phases occurring in the corresponding constituent binary systems, Al-Cu⁽²⁾ and Al-Zn⁽³⁾. The possibilities of formation of GP zones are threefold: (i) slower, (ii) not detectable by XRD due to small volume fraction of their formation, (iii) hindered in some ternary alloys as has recently

Fig. 7 Diffraction pattern from annealed powders of Al-30Zn-1Cu aged at RT for 4.73×10^7 s.

Fig. 9 Diffraction pattern from deformed powders of Al-30Zn-1Cu aged at RT for 2.10×10^7 s.

Fig. 8 (a) Diffraction pattern from deformed powders of Al-30Zn-1Cu aged at RT for 1.58×10^7 s.
(b) Diffraction pattern of Al-30Zn-3Cu powders annealed at the DSC peak temperature (570 K) for 6×10^2 s.

been reported for the Al-Cu-Si alloy system⁽⁷⁾.

To supplement the results of the transformation study by XRD some of the deformed powder samples of Al-30Zn-1Cu and Al-30Zn-3Cu were subjected to a DSC scan from 323 to 680 K to identify any precipitation/dissolution peak in the thermograms. At least 3 test runs at the heating rate of 0.33 K/s were performed for each sample. Figure 10 shows such a thermogram for Al-30Zn-3Cu alloy showing a broad precipitation peak with the maximum at about 570(± 5) K. The samples were subsequently subjected to annealing for 10 min at the corresponding DSC peak temperatures and XRD patterns recorded. The XRD patterns resemble almost the fully transformed state of the materials as were evidenced after long ageing at RT (Fig. 8(b)). It can thus be inferred from this DSC scan that the associated exothermic effects are attributed to the combined precipitation of (β) Zn and CuAl₂ phases in the equilibrium state of the materials. No evidence of G.P zone formation was however found from the DSC scan possibly due to its slower rate of formation as has been predicted for the Al-Cu-Si

Fig. 10 DSC curve of Al-30Zn-3Cu powder.

alloy system⁽⁷⁾.

The composition in the equilibrium state of the deformed matrix was also studied by measuring the lattice parameters of the Al-matrix [$a_0 = 4.0493(\pm 0.0005)10^{-10}$ m] and Zn [$a = 2.6647(\pm 0.0005)10^{-10}$ m and $c = 4.9468(\pm 0.0005)10^{-10}$ m] from XRD pattern and comparing their integrated intensities with those of pure Al and Zn. The results of integrated intensity study reveal $65(\pm 5)$ mass% Al, $25(\pm 5)$ mass% Zn, balance CuAl_2 in the transformed matrix. It is thus found that the Al rich-matrix has almost been transformed to pure Al, most of the Zn and Cu being precipitated out of the parent lattice. The value of hardness H_v of the overaged sample (II) at RT for Al-30Zn-1Cu was found to be reduced to a value ($H_v = 725$ MPa) lower than the hardness value of the supersaturated solid solution ($H_v = 862$ MPa) which existed prior to the ageing treatment. The hardness values of the same sample in the deformed and as-cast states were further reduced to lower values ($H_v = 598$ MPa and 578 MPa respectively) after annealing at DSC peak temperature for 10 min. This is due to lowering of free energy on completion of all stages of precipitation as is usually the case in all age-hardenable materials.

IV. Conclusions

(1) The rate of phase transformation is slow at the early stage of deformation or during room temperature ageing of as-cast alloys. However, phase transformation proceeds at a faster rate in the deformed state of the materials due to stress induced diffusion in which case Zn diffuses out at a comparatively faster rate than Cu from the Al-matrix.

(2) No evidence of G.P. Zone formation could be found from DSC scan although XRD study of overaged (at RT) strain-free powders revealed some indication of

G.P. Zone formation.

(3) Cu influences the hardness of the as-cast alloys predominantly over Zn.

(4) Solute dependence of microstructural parameters as characterized by XRD/LPA closely resembles that of hardness values establishing a close correlation between the microstructure and mechanical property of the materials.

(5) DSC study revealed a broad exothermic peak attributed to the precipitation of β (Zn) and CuAl_2 phases accompanied by the reduction in hardness values. Further reduction in hardness on annealing at the DSC peak temperature shows completion of all stages of precipitation with the precipitating phases almost separating out of the Al-matrix.

Acknowledgement

The authors are thankful to Prof. S. P. Sen Gupta, Head of the Department of Materials Science and Prof. S. K. Sen for their co-operation and interest.

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