Microstructural evolution of annealed Al–5 wt % Ca–5 wt % Zn sheet alloy

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Microstructural evolution on annealing of Al–5 wt % Ca–5 wt % Zn sheet alloy has been systematically investigated by means of texture analysis and optical and transmission electron microscopy. Heat treatments in the temperature range of 100 to 540 °C for times between 0.11 (7 min) and 90.5 h have been performed. After annealing, the main texture component of the as- received material, $\{1\,1\,3\}\langle 3\,3\,2\rangle$, was retained, whereas the minor components, $\{0\,1\,3\}\langle 3\,1\,0\rangle$ and $\{0\,1\,1\}\langle 1\,0\,0\rangle$, showed clear changes depending on the annealing conditions. Additional minor components appeared upon heat treatments. Continuous recrystallization, subgrain accommodation by means of rotation and subsequent extensive grain growth are the processes which account for all the microstructural changes observed.

1. Introduction

Al–5 wt % Ca–5 wt % Zn is a two phase (Al and Al_3CaZn) alloy which, following specific thermomechanical processing, develops a fine microstructure material and shows superplastic behaviour when tested at high temperature (350–550 °C) and appropriate strain rates (1×10^{-5}–3×10^{-2} s^{-1}). Under these conditions a strain rate sensitivity value of $m \approx 0.5$ and tensile elongations up to 600% have been achieved [1]. This alloy shows also sharp and well-defined texture components which are remarkably sensitive to superplastic deformation. The study of superplasticity in this alloy with the help of texture analysis has been undertaken [2, 3], where it proved to be helpful in understanding the microscopic processes responsible for superplastic deformation. Texture changes which occur when the tensile direction is parallel or perpendicular to the rolling direction were investigated in [2] with the aid of pole figures. It was concluded that the final orientation would depend on the initial texture and on the position of the tensile axis with respect to the rolling direction. Superplastic deformation was explained by means of grain rotation and slip. Superplasticity has been correlated not only with grain rotation but also with grain growth at the expense of grains forming the major components of the Al-phase [3]. Although extensive effort has been applied to studying this alloy [1–3], further work is, however, needed to explain in detail the deformation mechanisms responsible for superplastic behaviour.

On the other hand, it is known that microstructural changes also take place in Al–5 wt % Ca–5 wt % Zn when heated at temperatures where superplasticity occurs [3], a phenomenon commonly observed in fine-grained materials [4]. The results obtained in [3], however, do not give a full description of this evolution. For a thorough understanding of the microscopic mechanisms involved during deformation at high temperatures, it is, therefore, necessary to know first the evolution of the microstructure at high temperature occurring under static conditions.

This work deals with the microstructural changes which take place in Al–5 wt % Ca–5 wt % Zn as a function of annealing temperature and annealing time. A systematic study, by means of texture analysis as well as optical and transmission electron microscopy, has been conducted.

2. Experimental procedure

The Al–5 wt % Ca–5 wt % Zn alloy studied was prepared from 99.99% aluminium by the Aluminium Company of Canada. Its composition is shown in Table I. Cast ingots were hot rolled and subsequently cold rolled to a 3.2 mm thick sheet [1].

Heat treatments were performed on 10×10 mm^2 specimens in a salt bath at temperatures ranging from 100 to 540 °C and different time intervals. Specifically, isochronal annealings of 1 h at temperatures ranging from 100 to 540 °C were made at increments of 100 °C up to 500 °C and of 20 °C from 500 to 540 °C. Also, heat treatments at 500, 520 and 540 °C for different annealing times ranging from 0.11 to 90.5 h were executed.

Texture measurements were carried out by means of the Schulz reflection method, using a Siemens diffractometer furnished with a D5000 goniometer and a closed Eulerian cradle. The X-radiation used was β-filtered CuK_α. The pole figures (1 1 1), (2 0 0), (2 2 0), and (3 1 1) were obtained. The polar angle ranged from

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TABLE I Composition in mass per cent of the Al–5 wt % Ca–5 wt % Zn sheet alloy

Ca	Zn	Fe	Mg	Si	Cu	Mn	Al
5.0	4.95	0.18	0.042	0.1	< 0.01	< 0.01	Bal.

0 to 90 ° in steps of 3 °. From the pole figures, the even part of the three-dimensional orientation distribution function (ODF), a function of Euler angles ϕ_1, Φ, and ϕ_2, was calculated by a series expansion method. The odd coefficients were approximated by an iterative procedure. The maximum rank of even and odd coefficients is 22 and 21, respectively. Textures were measured at about 50 μm depth. It was seen, however, that except for the central region of the sheet, the texture components were the same at different depths. From the ODF the different components of the texture were identified. Since the intensity of the texture components was very sensitive to surface condition, special care was taken with sample preparation in order to eliminate degradation effects derived from treatments in the salt bath. Surface preparation was performed by abrasion using successively finer silicon carbide papers and then polishing with 1 μm diamond paste. Final surface preparation was performed in Barker's reagent (4 ml HBF_4, 200 ml H_2O) at 18 V for 50 s.

In order to investigate further the microstructural changes occurring with heat treatments in this Al–5 wt % Ca–5 wt % Zn alloy, the evolution of microstructure was studied by means of optical and transmission electron microscopy (OM, TEM). Metallographic preparation of samples for OM was the same as that used for texture measurements. A Jeol JEM 2000 FX II electron microscope working at 200 kV allowed the observation of the substructure of the alloy. Sample preparation for TEM was performed in various stages: (a) initial mechanical thinning to a thickness of 500 μm by means of a diamond slitting wheel, (b) chemical thinning up to 150 μm in Keller's solution (0.5 ml HF, 1.5 ml HCl, 2.5 ml HNO_3 and 95 ml H_2O), (c) cutting of the samples to give 3 mm diameter discs and (d) final thinning to electron transparency in a double jet Struers TENUPOL electropolisher working at − 30 °C and 18 V. An electrolyte of nitric acid and methanol (1 : 3) was used.

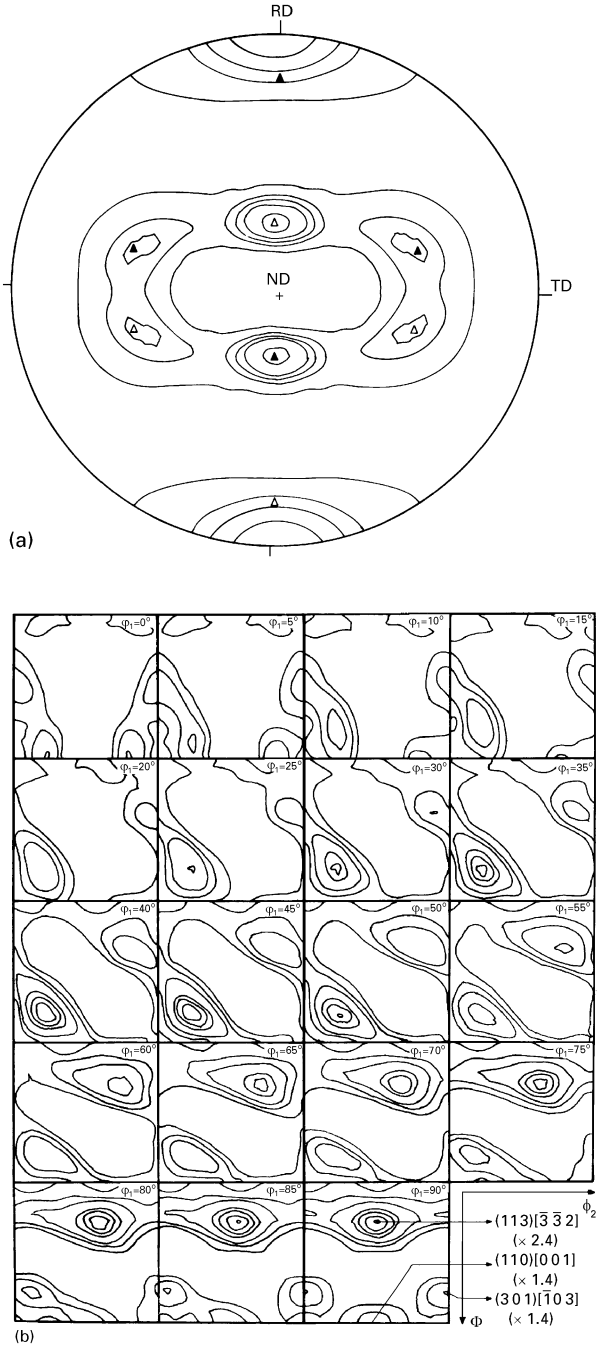

Figure 1 Texture of the as received Al–5 wt % Ca–5 wt % Zn sheet alloy. (a) (1 1 1) pole figure; ideal orientation $\{1\,1\,3\}\langle 3\,3\,2\rangle$ is represented by triangles. Rolling direction, normal to the rolling plane, and transverse direction are referred to as RD, ND, and TD, respectively. (b) ODF sections (ϕ_1 = constant.) at increments of $\Delta\phi_1 = 5°$.

3. Results and discussion

The texture of Al–5 wt % Ca–5 wt % Zn in the cold-worked state is shown in Fig. 1. The (1 1 1) pole figure (Fig. 1a) shows a well-defined component which was identified as $\{1\,1\,3\}\langle 3\,3\,2\rangle$. This ideal orientation (triangles in Fig.1a), close to the copper type C-component [5], has been previously reported as the dominant texture component in Al–5 wt % Ca–5 wt % Zn [3] and other aluminium sheet alloys [6]. The analysis by ODF, however, also allowed the identification of two other ideal orientations, namely the (3 0 1) $[\bar{1}\,0\,3]$ and the (1 1 0) [0 0 1], previously reported [3], both with 1.4 × random intensity (Fig. 1b). (1 1 3) $[\bar{3}\,\bar{3}\,2]$ is represented as the main component, with 2.4 × random intensity. All of them are located in the Euler space section corresponding to $\phi_1 = 90°$. Symmetric components are also found in different sections of the Euler space. Hereafter, families of planes and directions ($\{\}\langle\rangle$) will be used to designate texture components. It was seen that these components existed at different depths of the sheet, and formed the texture of most of the material. Therefore, this research only deals with the evolution of these components.

Important changes in texture have been detected in the annealed material depending on the heat-treatment conditions. Fig. 2 illustrates the $\phi_1 = 90°$ ODF

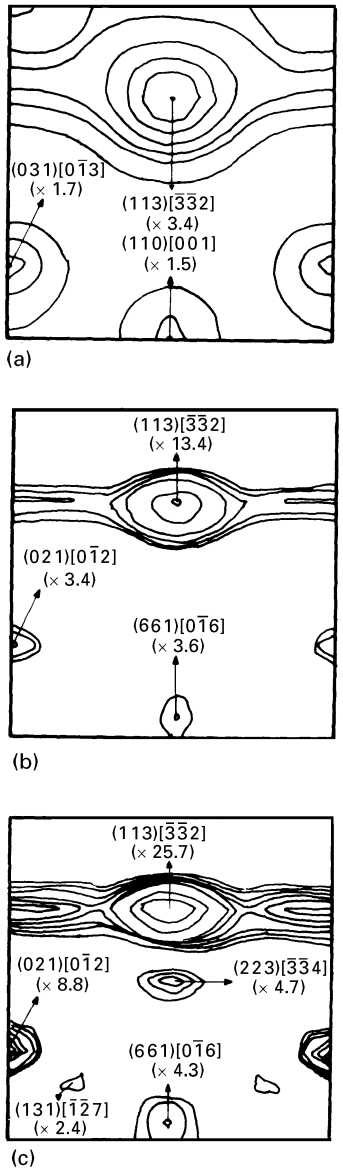

Figure 2 ODF sections ($\phi_1 = 90°$) of the Al–5 wt % Ca–5 wt % Zn sheet alloy for different heat treatments. (a) 200 °C/1 h; (b) 520°/4h; (c) 540°/24h.

sections corresponding to samples under three different heat treatments: (a) 200 °C/1 h; (b) 520 °C/4 h; (c) 540 °C/24 h. The components observed in Fig. 2a are the $\{1\,1\,3\}\langle 3\,3\,2\rangle$, the $\{0\,1\,3\}\langle 3\,1\,0\rangle$ and the $\{0\,1\,1\}\langle 1\,0\,0\rangle$. These are the same as those found in the as-received material, thus revealing little change of the microstructure with this heat treatment. After annealing at 520 °C/4 h, Fig. 2b, the main component is retained, but the other two components, the $\{0\,1\,3\}\langle 3\,1\,0\rangle$ and the $\{0\,1\,1\}\langle 1\,0\,0\rangle$, disappear and two new close components, the $\{0\,1\,2\}\langle 2\,1\,0\rangle$ and the $\{1\,6\,6\}\langle 6\,1\,0\rangle$, appear. The angles between the (0 3 1) and (0 2 1) planes and between the (1 1 0) and (6 6 1) planes are 8.1 and 6.7°, respectively. A similar behaviour can be inferred from Fig. 2c, which corresponds to the heat treatment at 540 °C/24 h. In addition to the changes occurring in Fig. 2b, new minor components appear with severity of heat treatment, namely the $\{2\,2\,3\}\langle 4\,3\,3\rangle$ and the $\{1\,1\,3\}\langle 7\,2\,1\rangle$. It is seen, then, that an increase of the annealing temperature/time, causes important changes in the components which describe the texture of the Al–5 wt % Ca–5 wt % Zn alloy. It is notable that the ideal orientation $\{1\,1\,3\}\langle 3\,3\,2\rangle$ remains as the dominant texture component of the material and that the intensity of the components increases with the severity of heat treatments.

Tables II and III summarize all texture components detected for the different annealing conditions. Different symbols are used to represent the texture components. Special attention was paid also to treatments at 500, 520 and 540 °C. From these tables several points can be seen. Firstly, the $\{1\,1\,3\}\langle 3\,3\,2\rangle$ ideal orientation is always present as the main component under all heat treatments, as was seen in Fig. 2 for three different annealing conditions. Secondly, changes of components, i.e. the disappearance of components and the appearance of new ones close to the former, take place with increasing annealing time and temperature. And thirdly, the number of components also rises with severity of heat treatment.

TABLE II Main texture components of the Al–5 wt % Ca–5 wt % Zn sheet alloy under heat treatments of one hour

100 °C	200 °C	300 °C	400 °C	475 °C	500 °C	520 °C	540 °C
▲◆●	▲◆●	▲◆●	▲◆●	▲◆●	▲◇●	▲◇○	▲◇○#

▲ = $\{1\,1\,3\}\langle 3\,3\,2\rangle$; ● = $\{0\,1\,1\}\langle 1\,0\,0\rangle$; ◆ = $\{0\,1\,3\}\langle 3\,1\,0\rangle$; ◇ = $\{0\,1\,2\}\langle 2\,1\,0\rangle$; ○ = $\{1\,6\,6\}\langle 6\,1\,0\rangle$; # = $\{2\,2\,3\}\langle 4\,3\,3\rangle$.

TABLE III Main texture components of the Al–5 wt % Ca–5 wt % Zn sheet alloy under heat treatments at 500, 520 and 540 °C

	Time (h)					
Temperature (°C)	0.11	1	4	24	41.33	90.5
500	▲◆●	▲◇●	▲◇○	▲◇○	–	▲◇○#
520	▲◇●	▲◇○	▲◇○	▲◇○#	▲◇○#	▲◇*# +
540	▲◇●	▲◇○#	▲◇○#	▲◇○# +	▲◇*# +	▲◇*# +

▲ = $\{1\,1\,3\}\langle 3\,3\,2\rangle$; ● = $\{0\,1\,1\}\langle 1\,0\,0\rangle$; ◆ = $\{0\,1\,3\}\langle 3\,1\,0\rangle$; ◇ = $\{0\,1\,2\}\langle 2\,1\,0\rangle$; # = $\{2\,2\,3\}\langle 4\,3\,3\rangle$; ○ = $\{1\,6\,6\}\langle 6\,1\,0\rangle$; * = $\{1\,4\,4\}\langle 8\,1\,1\rangle$; + = $\{1\,1\,3\}\langle 7\,2\,1\rangle$.

Regarding the disappearance/appearance of components, it is seen from Table II that these changes occur at 500 °C or above. At this temperature, $\{0\,1\,3\}\langle 3\,1\,0\rangle$ disappears and $\{0\,1\,2\}\langle 2\,1\,0\rangle$ appears. At 540 °C, interchange between $\{0\,1\,1\}\langle 1\,0\,0\rangle$ and $\{1\,6\,6\}\langle 6\,1\,0\rangle$ takes place. These two changes were studied in more detail under different annealing conditions as described in Table III. Whearas at 520 and 540 °C the $\{0\,1\,2\}\langle 2\,1\,0\rangle$ component (◇) has already appeared after annealing for 7 min, this occurs at 500 °C only after a 4 h treatment. The component $\{0\,1\,1\}\langle 1\,0\,0\rangle$ disappears and $\{1\,6\,6\}\langle 6\,1\,0\rangle$ appears, following 4 h at 500 and 520 °C, and after 1 h at 540 °C. It is to be noticed that the change ● → ○ requires more severe annealing conditions than ◆ → ◇, although the angle between the (0 1 3) and (0 1 2) planes is smaller. After annealing under extreme conditions (520 °C/90.5 h and 540 °C/41.3 h), a third change could be detected between the $\{1\,6\,6\}\langle 6\,1\,0\rangle$ and the $\{1\,4\,4\}\langle 8\,1\,1\rangle$ components. The angle between (6 6 1) and (4 4 1) planes is 3.3°.

The number of components increases up to five under certain conditions (520 °C/90.5 h, 540 °C/24 h, 540 °C/41.3 h, Table III). In 1 h isochronal annealings, $\{2\,2\,3\}\langle 4\,3\,3\rangle$ (#) appears at 540 °C (Table II and III). According to Table III this component also appeared after 90.5 h at 500 °C and after 24 h at 520 °C. One additional component was found with increasing time and temperature: $\{1\,1\,3\}\langle 7\,2\,1\rangle$ (+) appears after annealing for 90.5 h at 520 °C and after 24 h at 540 °C.

The intensity of all the components tends to increase with increasing annealing time and temperature, as shown in Fig. 2, except when a change in texture components takes place. This is more evident in Fig. 3, which shows this trend for samples annealed one hour at temperatures ranging from 100 to 540°C. In this figure the intensity of the $\{1\,1\,3\}\langle 3\,3\,2\rangle$, $\{0\,1\,3\}\langle 3\,1\,0\rangle$, and $\{0\,1\,1\}\langle 1\,0\,0\rangle$ components is represented as a function of annealing temperature. Whereas all intensities increase smoothly up to 475 °C, pronounced changes can be observed beyond this temperature. Firstly, the intensity of the main component (▲) increases noticeably (Fig 3a); secondly, the two changes between close components mentioned above take place. These changes indicate a sudden fall of intensity of the pre-existing components and an increase of the intensity of the new ones in a narrow interval of temperature. The intensity of the ideal orientation $\{0\,1\,3\}\langle 3\,1\,0\rangle$ drops rapidly and the intensity of the component $\{0\,1\,2\}\langle 2\,1\,0\rangle$ grows quickly up to a value close to that detected for $\{0\,1\,3\}\langle 3\,1\,0\rangle$ before it disappeared (Fig. 3b). A similar change can be seen in Fig. 3c for the components $\{0\,1\,1\}\langle 1\,0\,0\rangle$ and $\{1\,6\,6\}\langle 6\,1\,0\rangle$. The intensities of the minor components appearing under severe heat treatments (#, +) were rather low: typically 10–20 times smaller than the dominant ideal orientation (▲).

As reported previously [1], this alloy has a very fine and stable microstructure which could only be revealed by TEM. Fig. 4 shows a TEM micrograph of the microstructure after a heat treatment at 200 °C for 1 h. This microstructure is very similar to that of the as-received material. A subgrain of 0.9 μm was measured under these conditions versus the 0.7 μm measured for the non-heat-treated material. On the other hand, after more severe heat treatments (at 500, at 520 and at 540 °C), subgrain growth was clearly observed. Fig. 5 shows the subgrain structure of Al–5 wt % Ca–5 wt % Zn annealed at 520 °C for 90.5 h, where a subgrain diameter of 5.2 μm was measured. Under these extreme heat treatment conditions, optical microscopy also allowed the observation of the grain

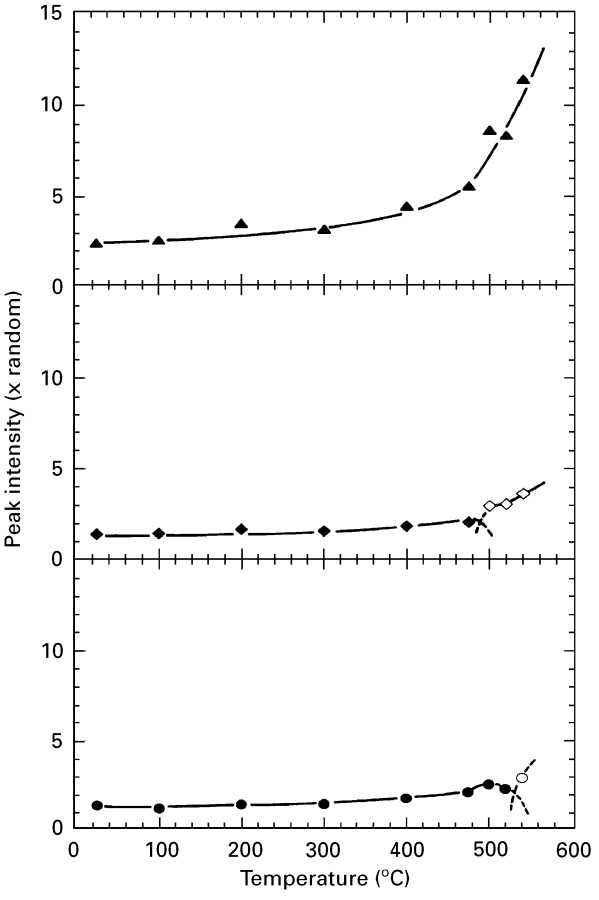

Figure 3 Peak intensity of the relevant components as a function of temperature for one-hour-annealed samples of the Al–5 wt % Ca–5 wt % Zn sheet alloy. ▲ $\{1\,1\,3\}\langle 3\,3\,2\rangle$; ◆ $\{0\,1\,3\}\langle 3\,1\,0\rangle$; ◇ $\{0\,1\,2\}\langle 2\,1\,0\rangle$; ● $\{0\,1\,1\}\langle 1\,0\,0\rangle$; ○ $\{1\,6\,6\}\langle 6\,1\,0\rangle$.

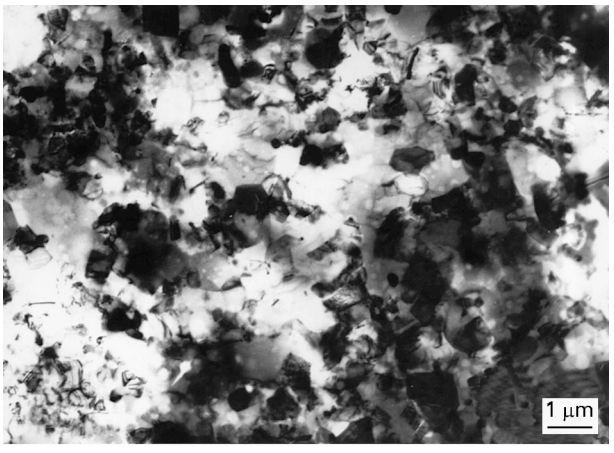

Figure 4 TEM micrograph of the subgrain structure of Al–5 wt % Ca–5 wt % Zn sheet alloy heat treated at 200 °C/1 h.

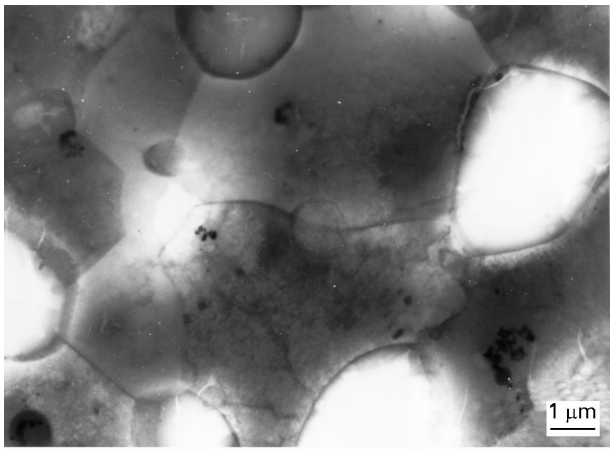

Figure 5 TEM micrograph of the subgrain structure of Al–5 wt % Ca–5 wt % Zn sheet alloy heat treated at 520 °C/90.5 h.

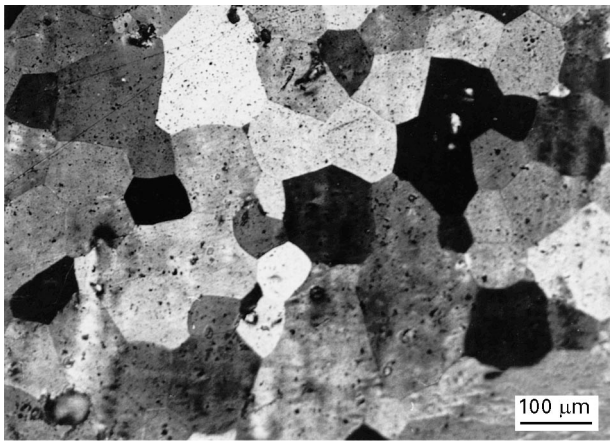

Figure 6 Optical micrograph of the grain structure of Al–5 wt % Ca–5 wt % Zn sheet alloy heat treated at 520 °C/90.5 h.

structure of this alloy. Subgrain size was taken as the mean intercept distance from photomicrographs. Fig. 6 shows an optical micrograph of the alloy under the same heat treatment as that of Fig. 5. It is clear that a well-defined grain and subgrain structure is developed in this alloy with severe heat treatments. At annealing temperatures below 520 °C and times shorter than 41.3 h, the grain structure, if it exists, could not be revealed by OM. This can be due either to the small grain size developed or to the presence of second phase particles, which somehow impede grain boundary observation, or both.

The evolution of subgrain size and the intensity of the main component $\{1\,1\,3\}\langle 3\,3\,2\rangle$ are shown in Fig. 7 as a function of annealing time for three different temperatures: 500, 520 and 540 °C. As can be seen, subgrain size increases with increasing annealing time and/or temperature. Furthermore, the intensity of the $\{1\,1\,3\}\langle 3\,3\,2\rangle$ component also increases with annealing time as a consequence of the coarsening of the structure. Similar trends are observed for the minor texture components. The drop in intensity detected when annealing at 540 °C for 90.5 h is attributed to the increasing effect of surface preparation on texture intensity as annealing is more severe, as a consequence

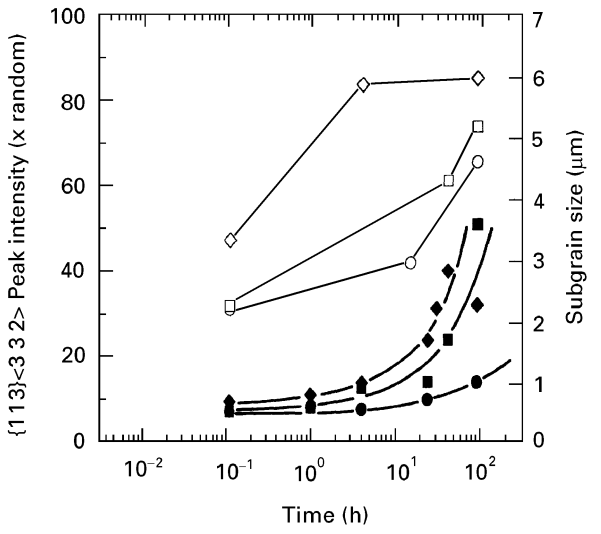

Figure 7 Peak intensity of the $\{1\,1\,3\}\langle 3\,3\,2\rangle$ component and subgrain size as a function of annealing time for samples of Al–5 wt % Ca–5 wt % Zn sheet alloy heat treated at 500, 520 and 540 °C. Key: Peak intensity: ● 500 °C; ■ 520 °C; ◆ 540 °C: subgrain size: ○ 500 °C; □ 520 °C; ◇ 540 °C.

of either the coarsening of the structure or the fact that surface damage becomes more accentuated with the severity of the heat treatment.

Texture analysis and TEM suggest that the evolution of the microstructure of Al–5 wt % Ca–5 wt % Zn when annealed under the different conditions used in this investigation consists of the following two steps. Initially, extended recovery or continuous recrystallization [7], a process already observed in other superplastic aluminium alloys [8], occurs. This would explain the retention of the main component of the rolling texture as well as a smooth intensity increase which was detected after annealing times for as long as 24 h. The presence of both a large volume fraction (20%) of second phase particles and only one main texture component in the as-received material are two typical factors that favour this phenomenon. By the process of continuous recrystallization, the dislocation cells present in the as-received material (a consequence of cold work) rearrange on annealing leading to a progressively more stable substructure. Hence, extensive homogeneous subgrain growth, whose kinetics is controlled by the coarsening of the second phase particles, occurs: i.e. the subgrain boundaries are gradually released since many particles are diminishing in size during Ostwald ripening [9]. After dissolution of these particles, the adjacent subgrains accommodate by small rotations [8] leading to the changes of the minor texture components observed as well as to the appearance of new minor texture components. An increase in subgrain size would cause the smooth texture intensity growth detected under these non-extreme annealing conditions. The intensity of the $\{1\,1\,3\}\langle 3\,3\,2\rangle$ component grows more rapidly in comparison to those of the minor components. Hence, growth of $\{1\,1\,3\}\langle 3\,3\,2\rangle$ oriented subgrains, at the expense of randomly oriented ones, would be more favoured than that of subgrains with other orientations. Hence, continuous recrystallization is followed by extensive

coarsening of the structure, leading to a large sharpening of texture.

At this stage, the annealing conditions, under which the grain structure of Al–5 wt % Ca–5 wt % Zn sheet alloy is well defined, are not clear. Thus, further work focused on revealing the grain structure under moderate annealing conditions is in progress. It is seen, however, that the microstructural evolution of Al–5 wt % Ca–5 wt % Zn under conditions of time/temperature at which superplasticity of this alloy takes place can be relevant when the material is annealed under static conditions. This suggests, therefore, that these changes should be taken into consideration when the dynamic mechanisms accounting for superplasticity in Al–5 wt % Ca–5 wt % Zn are investigated. These concepts could also be extended to other fine grained alloys.

4. Conclusions

Microstructural evolution of Al–5 wt % Ca–5 wt % Zn heat treated in the temperature range of 100–540 °C and for annealing times up to 90.5 h was systematically studied by texture analysis and optical and transmission electron microscopy. The major conclusions of this investigation are the following.

1. The texture of the as-rolled material is formed by three components: the main one is the $\{1\,1\,3\}\langle 3\,3\,2\rangle$ and the two minor components are the $\{0\,1\,1\}\langle 1\,0\,0\rangle$ and the $\{0\,1\,3\}\langle 3\,1\,0\rangle$. Retention and sharpening of the main component is observed on annealing under all conditions studied. The minor components, however, disappear with heat treatments and new ones, close to them, appear. In particular, the changes $\{0\,1\,3\}\langle 3\,1\,0\rangle \rightarrow \{0\,1\,2\}\langle 2\,1\,0\rangle$ and $\{0\,1\,1\}\langle 1\,0\,0\rangle \rightarrow \{1\,6\,6\}\langle 6\,1\,0\rangle$ were detected. Additional new minor components appear on increasing annealing temperatures and/or times. Smooth growth of texture intensity under moderate annealing conditions is followed by significant sharpening under more severe heat treatments.

2. A structure of both grains and subgrains has been observed following extreme heat treatment conditions. After moderate annealing treatments, however, only a subgrain structure, which coarsens with increasing annealing time and temperature, could be distinguished.

3. Continuous recrystallization, i.e. the formation and coarsening of subgrains, a process controlled by growth of second phase particles, accounts for the microstructural changes taking place under moderate heat treatments. Accommodation of subgrain growth is achieved by means of subgrain rotation. Extensive grain formation and growth occurs under severe heat treatments.

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