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Achieving superplastic properties in a Pb–Sn eutectic alloy processed by equal-channel angular pressing

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Abstract Experiments were conducted on a Pb-62% Sn eutectic alloy containing 160 ppm of Sb. The alloy was processed by equal-channel angular pressing (ECAP) through 1 to 5 passes at room temperature and then tested in tension at a temperature of 423 K using initial strain rates from 1.0×10^{-4} to 1.0×10^{-1} s^{-1}. Excellent superplastic elongations were achieved at intermediate strain rates with a maximum elongation to failure of 2,665%. It is shown that, for processing through similar numbers of ECAP passes, these elongations are higher than in an earlier investigation using a Pb-62% Sn alloy of higher purity. The results are presented pictorially in the form of a deformation mechanism map by plotting normalized grain size against normalized stress at a temperature of 423 K.

Introduction

Superplasticity describes the ability of some polycrystalline metals to pull out in tension to very high elongations prior to failure. Specifically, superplasticity requires elongations to failure of at least 400% and the measured strain rate sensitivities associated with this type of flow are generally close to ~0.5 [1]. There are two basic requirements for superplastic flow [2]. First, a high testing temperature within the diffusion-controlled regime, where this means a temperature of the order of ~0.5 T_m or greater, where T_m is the absolute melting temperature. Second, a grain size smaller than ~10 μm so that grain boundary sliding can occur easily. Since grain growth occurs readily at elevated temperatures, superplastic materials are in practice often two-phase alloys or they contain a fine dispersion of a second phase to restrict grain growth. The Pb-62% Sn eutectic alloy is a classic example of a highly superplastic metal. Earlier experiments showed the possibility of achieving elongations of up to >4,000% in a commercial Pb-62% Sn alloy [3] and later, by optimizing the testing conditions, the alloy was used to achieve a record superplastic elongation of 7,550% [4].

Much attention has focused recently on processing metals through the application of severe plastic deformation (SPD) in order to achieve exceptional grain refinement [5]. Equal-channel angular pressing (ECAP) is a typical SPD processing method [6] having the capability of producing very fine grain sizes and, if these small grains are reasonably stable at elevated temperatures, there is an opportunity for achieving superplastic flow. It was noted in an early analysis that, since the strain rate in superplasticity is inversely proportional to the grain size raised to the power of two [7], an ultrafine-grained material should exhibit superplasticity at exceptionally rapid experimental strain rates [8]. Subsequently, this prediction was confirmed in experiments on two commercial aluminum alloys [9] where superplasticity was achieved in the high strain rate superplastic regime which is defined as testing strain rates at and above 10^{-2} s^{-1} [10].

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A recent report tabulated data for superplasticity in metallic alloys processed by ECAP [11] but an examination shows this tabulation includes very few descriptions of superplastic properties in two-phase alloys. Specifically, there are reports to date of elongations to failure after ECAP of 1,970% [12], 2,230% [13, 14] and 2,380% [15] in the Zn-22% Al eutectoid alloy and an unusually high elongation of 3,060% in a Pb-62% Sn eutectic alloy processed by ECAP through 16 passes and tested at 413 K [16]. There is also a report of an elongation to failure of 230% in the Pb-62% Sn alloy after processing through 4 passes using a T-shaped form of ECAP and pulling to failure at 298 K with an imposed strain rate of 5×10^{-4} s^{-1} [17] where this latter elongation matches an earlier report for the same alloy tested at 298 K without processing by ECAP [18]. Accordingly, the present investigation was undertaken to examine the influence of the numbers of passes in ECAP on the superplastic ductilities attained in a Pb-62% Sn alloy and to examine the flow characteristics with reference to earlier experimental data.

Experimental material and procedures

The experimental alloy was prepared by casting Pb and Sn of commercial purity. The molten alloy, having a composition of 38% Pb and 62% Sn, was poured into a steel mould to give bars with dimensions of $15 \times 15 \times 200$ mm^3. A semi-quantitative analysis of the cast alloy revealed 160 ppm Sb and no other impurities in excess of 0.01%. Billets were machined from these bars for ECAP having square cross-sections of 14×14 mm^2 and lengths of 70 mm.

Processing by ECAP was conducted at room temperature using a die having an internal channel angle of 120° and an arc of curvature at the intersection of the channels of 0°. It can be shown by calculation that these angles lead to an imposed strain of ~0.67 on each pass [19]. The billets were pressed repetitively from 1 to 5 passes, equivalent to strains up to a maximum of ~3.3, using a pressing speed of 10 mm min^{-1} and processing route A in which the billets are not rotated between each separate pass [20]. Additional information on the ECAP processing facility was given in an earlier report [21].

Following ECAP, the specimens were etched for 20–30 s in a solution of 95 mL CH_3OH and 5 mL HNO_3 at room temperature and then examined using optical microscopy for determinations of the relevant grain sizes. To evaluate the superplastic properties, tensile specimens were cut from the billets with the tensile axes lying parallel to the pressing direction. These specimens had gauge lengths of 4 mm and cross-sectional areas of 3×2 mm^2. Each specimen was pulled to failure in tension at a temperature of 423 K using a furnace and testing machine operating at a constant rate of cross-head displacement. The specimens were tested at initial strain rates in the range from 1.0×10^{-4} to 1.0×10^{-1} s^{-1}.

Experimental results

Flow properties

The microstructure of the Pb-62% Sn alloy consists of a well-defined interpenetration of Pb-rich (α) and Sn-rich (β) phases. Table 1 shows the measured grain sizes for the as-cast alloy and for the samples taken through 1 to 5 passes of ECAP: the error bars for the latter specimens were estimated by separately measuring from 140 to 160 grains. These measurements show that processing by ECAP reduces the grain size from ~16 to ~6.0 μm and there is only a minor and essentially insignificant decrease in grain size with increasing numbers of ECAP passes.

Figure 1 shows representative plots of true stress against true strain for samples processed through 4 passes (4p) at

Table 1 Measured grain sizes in the Pb-62% Sn alloy

Condition	Grain size (μm)
As-cast	~16
1 pass	6.1 ± 0.2
2 passes	5.7 ± 0.2
3 passes	6.2 ± 0.4
4 passes	6.0 ± 0.3
5 passes	5.5 ± 0.2

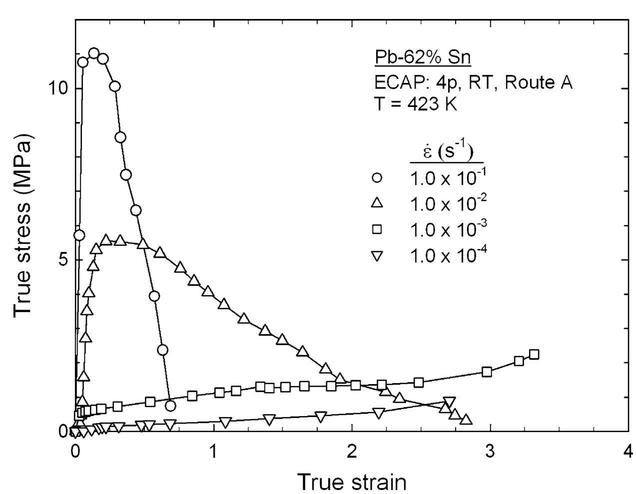

Fig. 1 Plots of true stress against true strain for samples processed through 4 passes of ECAP and pulled to failure at different initial strain rates

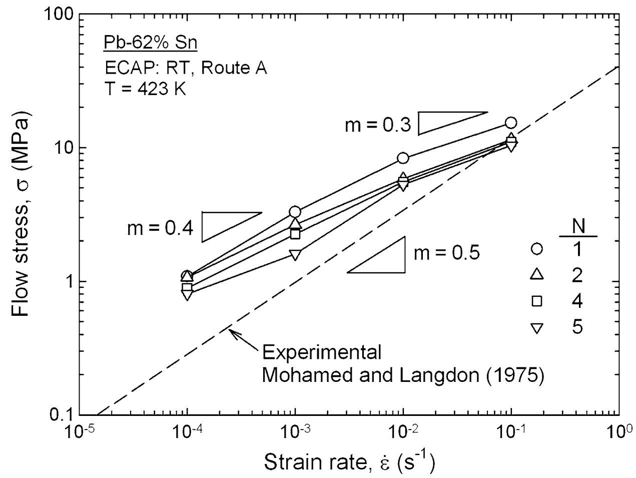

Fig. 2 Logarithmic plot of flow stress against strain rate for samples processed through different numbers of ECAP passes, *N*, and pulled to failure at 423 K: possible values for the strain rate sensitivity, *m*, are indicated

room temperature (RT) and then tested at 423 K using different values for the initial strain rate, $\dot{\varepsilon}$. These curves are similar to those shown in an earlier report for a Pb-62% Sn alloy tested in tension at 413 K [16].

Using these and other similar curves for samples processed through different numbers of passes, Fig. 2 shows the values of the measured flow stress, σ, plotted logarithmically against the strain rate, $\dot{\varepsilon}$, for samples subjected to different numbers of ECAP passes, *N*. Although this plot covers only three orders of magnitude of strain rate, there is evidence for the characteristic sigmoidal relationship between flow stress and strain rate where the strain rate sensitivity, m $(=\partial \ln \sigma/\partial \ln \dot{\varepsilon})$, has a low value at the lower strain rates in the non-superplastic region I, a higher value at intermediate strain rates in the superplastic region II and a low value at the higher strain rates in the non-superplastic region III [22]. For the present results, all datum points suggest $m \approx 0.3$ at the fastest strain rates and the evidence indicates $m \approx 0.5$ at intermediate strain rates in the samples pressed through 5 passes with a decrease in m at the lowest strain rates.

A comprehensive evaluation was presented earlier for superplastic flow in a Pb-62% Sn alloy having a grain size of 5.8 μm and tested without processing by ECAP [23]. The results obtained for this alloy in the superplastic region II at a testing temperature of 422 K are denoted by the dashed line in Fig. 2 and it is apparent that these earlier results are in excellent agreement with the data obtained after ECAP processing especially at the fastest strain rates. The slightly lower experimental strain rates measured in the alloy processed by ECAP cannot be due to a difference in grain size because the grain sizes in both alloys are essentially identical at ~6.0 and 5.8 μm, respectively. Instead, the difference is attributed to the presence of 160 ppm of Sb which is known to have a strengthening effect on the Pb–Sn alloy. For the alloy tested earlier without ECAP, the material was prepared from 99.999% Pb and 99.995% Sn and the total concentration of impurities was only <8 ppm [23].

Measurements of elongations to failure

The evidence in Fig. 2 for a possible sigmoidal relationship between the three regions of flow as in superplastic materials is supported by measurements of the elongations to failure as documented in Fig. 3 for the samples processed through from 1 to 5 passes of ECAP. These results show there is only limited ductility after processing through a single pass but there are significant increases in ductility at strain rates from 10^{-4} to 10^{-2} s^{-1} for samples processed through 2 to 5 passes. The increasing ductility with increasing imposed strain in ECAP is consistent with experimental evidence showing that the fraction of high-angle boundaries increases with increasing numbers of passes when processing by ECAP [24] because superplasticity occurs through flow by grain boundary sliding [25] and high-angle grain boundaries are a necessary prerequisite for the occurrence of sliding. The coincidence of all experimental measurements in Fig. 3 at the fastest strain rate of 1.0×10^{-1} s^{-1} is consistent with the occurrence of region III because the flow in this region is conventional dislocation creep where the grain size and the nature of the grain boundaries are not important [26].

The peak elongation recorded in Fig. 3 is 2,665% which was obtained at a testing strain rate of 1.0×10^{-3} s^{-1} after both 2 and 4 passes of ECAP. Figure 4 shows the specimens pulled to failure at different strain rates after 4 passes where the upper specimen is untested. It is clear that the

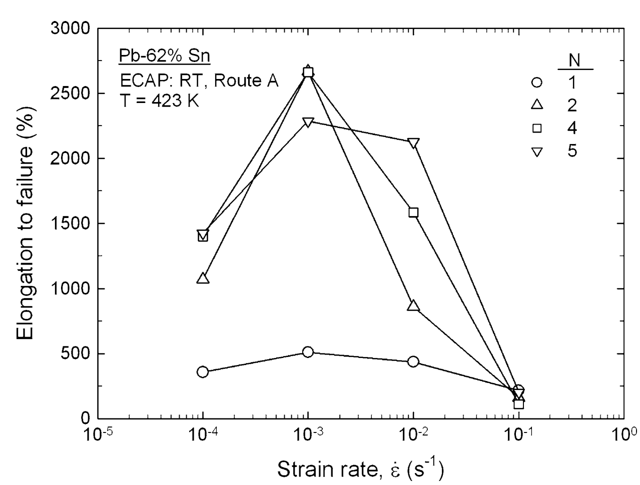

Fig. 3 Variation of the elongation to failure with the initial strain rate for samples processed through various numbers of passes and then pulled to failure at 423 K

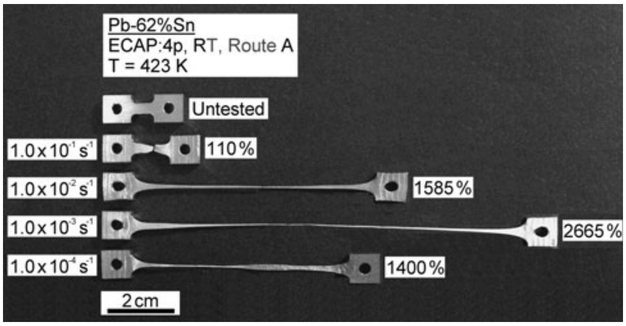

Fig. 4 Samples processed through 4 passes of ECAP and pulled to failure at different initial strain rates: these results cover only three orders of magnitude of strain rate but they indicate the occurrence of the three flow regions (regions I, II, and III) associated with superplastic alloys

highest elongation of 2,665% was achieved in a specimen which pulled out uniformly without any evidence for necking within the gauge length. This condition where $A_f/A_i \rightarrow 0$ is a characteristic of true superplastic behavior where A_f and A_i are the fracture area at the point of failure and the initial cross-sectional area within the gauge length, respectively [27]. Conversely, there is very clear evidence for the occurrence of necking at the lower strain rate of 1.0×10^{-4} s^{-1} where this is also consistent with superplastic materials deforming in the low stress region I [28, 29]. Finally, the abrupt failure at the fastest strain rate of 1.0×10^{-1} s^{-1} denotes quasi-brittle behavior which is a characteristic of behavior at high strain rates in region III [27]. Thus, the three conventional regions of flow in superplastic materials are well demonstrated by the measured elongations and the failure modes evident in Fig. 4.

Discussion

Comparison with earlier data for the Pb-62% Sn alloy

The present results show that the superplastic region is confined to strain rates close to $\sim 10^{-3}$ s^{-1} for the alloy tested at 423 K after processing through 4 ECAP passes using a die with a channel angle of 120° and processing route A. Table 2 compares these results with earlier data for the Pb-62% Sn alloy tested at the slightly lower temperature of 413 K after processing through 4 passes with a channel angle of 90° using processing route B_C where the billets are rotated about their longitudinal axes by 90° in the same sense between each pass [16].

It is apparent from Table 2 that the present elongations to failure are significantly higher than those recorded in the earlier study. These larger elongations are not due to the small difference in the testing temperature between the two sets of experiments or the relatively minor difference in the channel angle or the processing route. Instead, the difference is attributed to the variation in the purity levels between the two alloys because the alloy in the present investigation contained 160 ppm of Sb whereas the alloy used earlier contained a total of <8 ppm of impurities.

The presence of significant Sb in the alloy used in this investigation has three important effects. First, Sb is a strengthening additive so that, as shown in Fig. 2, the present strain rates are lower than those recorded earlier. Second, the presence of Sb is effective in inhibiting grain growth so that the grain size of $\sim$6.0 μm in this investigation is significantly smaller than the earlier measured grain size of 9.2 μm after processing by ECAP at room temperature. This smaller grain size leads to larger superplastic elongations. Third, the presence of a higher impurity content limits the ability for flow by grain boundary sliding and, as anticipated from theoretical considerations where region I entails an impurity-dominated threshold stress [30, 31], the advent of region I is displaced to faster strain rates and accordingly the range of strain rate for superplastic flow is reduced. This latter effect accounts for the rapid onset of region I even at a strain rate of 10^{-4} s^{-1}, as shown by the reduced elongation of 1,400% recorded under these conditions in Fig. 4. The effect of increasing impurity content on the occurrence of region I is well documented for the Zn-22% Al eutectoid alloy [32, 33] and the trend is similar in the present investigation.

Table 2 Elongations to failure for Pb-62% Sn alloys processed by ECAP through 4 passes

Processing route	Channel angle	d (μm)	Temperature (K)	Strain rate (s^{-1})	Elongation to failure (%)	Reference
B_C	90°	9.2	413	1.0×10^{-2}	350	Kawasaki et al. [16]
				3.3×10^{-3}	610	
				1.0×10^{-3}	1,515	
A	120°	6.0	423	1.0×10^{-1}	110	This investigation
				1.0×10^{-2}	1,585	
				1.0×10^{-3}	2,665	
				1.0×10^{-4}	1,400	

The construction of deformation mechanism maps

Deformation mechanism maps provide a simple process for constructing a pictorial display that provides direct information on the dominant flow process under any selected testing conditions. The earliest maps were constructed many years ago in the form of the normalized stress, σ/G, plotted against the homologous temperature, T/T_m, at a constant grain size, where G is the shear modulus, T is the absolute temperature and T_m is the melting temperature in degrees Kelvin [34] and these maps show fields in stress-temperature space within which a selected flow mechanism is rate-controlling. Subsequently, this approach was used to construct deformation mechanism maps for a large number of materials [35] including a Pb–Sn solder alloy having a grain size of 30 μm [36].

One difficulty with these maps is that the construction process is complicated because several of the field boundaries appear as curved lines. Therefore, an alternative approach was developed in which the normalized grain size, $d/\mathbf{b}$, is plotted against the normalized stress, σ/G, at a constant temperature [37], and this type of construction was used subsequently to prepare a map showing experimental data for the Pb-62% Sn eutectic alloy [38]. Figure 5 shows a map prepared for a testing temperature of 423 K where regions I, II, and III denote the three regions of flow associated with superplastic materials in the conventional sigmoidal plot [22] and the fields for Nabarro–Herring [39, 40] and Coble [41] diffusion creep are based on the theoretical relationships for these two mechanisms: for convenience, the absolute values of the stress and grain size are marked on the upper abscissa and the right ordinate, respectively.

The dashed line in Fig. 5 denotes the relationship

$$\frac{d}{\mathbf{b}} = 20\left(\frac{\sigma}{G}\right)^{-1} \tag{1}$$

where Eq. 1 is based on results obtained for the average subgrain size, δ, expressed as $\delta/\mathbf{b}$ and determined experimentally for a wide range of metals [42] and ceramics [43]. By placing the grain size d equal to the subgrain size δ into the conventional subgrain relationship, it follows that subgrains are formed under experimental testing conditions above the dashed line in Fig. 5 whereas below the dashed line the grain size is too small to permit subgrain formation. It is apparent that this dashed line lies almost coincident with the field boundary between regions II and III thereby confirming, as noted in an earlier report [38], that superplasticity requires a sufficiently small grain size that the accommodating dislocations are able to pass through the grains and thereby impinge upon, and climb into, the opposing grain boundaries: this concept is a fundamental characteristic of the theoretical model for superplastic flow [7].

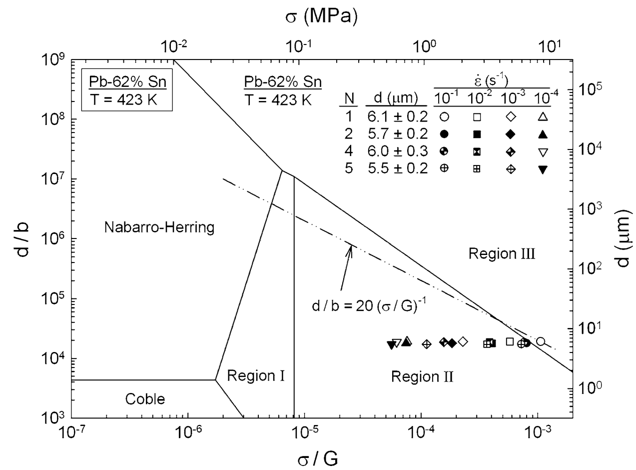

Fig. 5 A deformation mechanism map of normalized grain size versus normalized stress for the Pb-62% Sn alloy tested at 423 K: the experimental points are shown and the dashed line denotes the limiting condition for the formation of subgrains within the grains

Superimposed on Fig. 5 are the experimental points obtained in the present investigation. These points are in excellent agreement with the predictions of the map in two ways. First, only the experimental points at the fastest strain rates and highest stresses lie within region III. Second, the experimental points where the elongations are very high and up to >2,000% lie within the superplastic region II. A shortcoming of the map is that the boundary marking the transition between regions I and II is displaced to an exceptionally low stress and the evidence from Figs. 2 and 3 suggests that in this investigation the transition occurs at a higher stress level than predicted by the map. This apparent discrepancy arises because the map was constructed using creep data obtained from a Pb-62% Sn alloy having very high purity whereas the present data were obtained using an alloy having an Sb concentration of 160 ppm. This level of impurity has no influence on the boundary between regions II and III but it displaces the boundary between regions I and II to higher stress levels and thereby limits the total extent of the superplastic region II.

Thus, the experimental evidence is clear. An antimony addition in the Pb–Sn eutectic alloy leads to a strengthening effect, it gives smaller grain sizes when processing by ECAP because the Sb inhibits boundary movement and it expands the non-superplastic region I to higher stress levels so that the total range of strain rates associated with superplastic flow is reduced. In the present investigation, excellent superplastic ductilities were achieved at a strain rate in the vicinity of 10^{-3} s^{-1} after 2 and more passes of ECAP. Table 1 shows that, for samples pressed through 4 passes of ECAP, the measured elongations to failure, including the peak elongation of 2,665%, are higher than in an earlier study on a Pb-62% Sn alloy of much higher purity [16].

Summary and conclusions

1. Experiments were conducted on a Pb-62% Sn eutectic alloy, containing 160 ppm of Sb, to evaluate the superplastic properties after processing by equal-channel angular pressing through 1 to 5 passes at room temperature.
2. The results show the occurrence of excellent superplastic flow at a strain rate of 1.0×10^{-3} s^{-1} when testing in tension at 423 K with elongations to failure up to 2,665%. The measured elongations in this investigation are significantly higher than in an earlier investigation using a Pb-62% Sn alloy of higher purity.
3. The results are consistent with a deformation mechanism map showing normalized grain size against normalized stress. It is shown that apparent discrepancies between the present results and earlier data are due to differences in the purity levels in the two materials.

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