

## Letters

### *The tensile properties of a new superplastic aluminium alloy: Al–Al<sub>4</sub>Ca eutectic*

Several metals and alloys exhibit superplastic behaviour. Surveys of these materials are given in various extensive reviews [1–4]. It is observed that in the case of Al-base alloys only those containing intermetallic Al<sub>2</sub>Cu reveal superplastic effects, which are characterized by abnormal elongations and high strain-rate sensitivity (temperature  $\geq 400^\circ\text{C}$ ) [5–8]. Other systems such as Al–Si [9] and Al–Si–Cu [10] show high strain-rate sensitivity but limited elongation. The Al–Zn superplastic alloys are considered as Zn-base alloys.

In the frame of a recent research concerning the potential use of Ca metal [11] it appeared that superplasticity is attainable also in Al–Ca alloys containing a high percentage of the Al<sub>4</sub>Ca-second phase. Subsequent detailed investigations on a wide range of compositions and using different preparation methods led to the development of a new superplastic aluminium alloy, the Al–Al<sub>4</sub>Ca eutectic [12]. In this note some preliminary results concerning the tensile properties of this alloy are reported.

The Al–Ca eutectic (7.6 wt % Ca) presented here was prepared by induction melting in a graphite crucible under a positive pressure of argon, starting from slightly impure elements, respectively 99.9 Al and 99.0 Ca. The as-cast ingots were first extruded into 55 mm  $\times$  5 mm plates and then unidirectionally resolidified in a rectangular graphite crucible in order to minimize porosity and to obtain the fine regular lamellar structure (Fig. 1a) already described previously [13]. Finally the plates were hot-rolled (temperature  $\approx 300^\circ\text{C}$ ) into 1 mm thick sheets with the end effect of producing an intimate mixture of the two phase Al and Al<sub>4</sub>Ca with a very fine grains ( $\sim 5\ \mu\text{m}$  in size) (Fig. 1b). The volume fraction of the Al<sub>4</sub>Ca-second phase was 31%. Tensile specimens of 8 mm gauge-length and 1 mm  $\times$  2 mm gauge section were machined from the sheets. Tensile tests were carried out at temperatures varying from 20 to 600 $^\circ\text{C}$  on an Instron machine (model TTCML) capable of various constant cross-head speeds between  $0.83 \times 10^{-3}$  and  $8.33\ \text{mm sec}^{-1}$ . An Adamel air furnace was used with a constant temperature zone ( $\pm 2^\circ\text{C}$ ). The strain-rate sensitivity was determined at 450, 500 and 550 $^\circ\text{C}$  by calculating the slopes of the flow stress true strain-rate curves

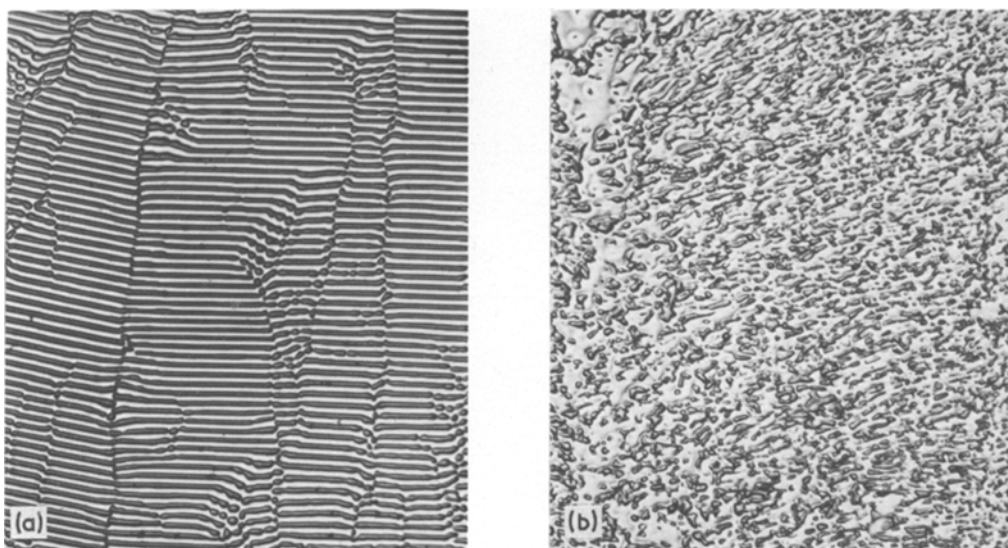


Figure 1 Microstructure of Al–7.8 wt % Ca eutectic alloy ( $\times 500$ ). (a) Unidirectionally solidified (transverse section), (b) superplastic (after casting and heavily hot-working).

TABLE I Superplastic tensile properties of the Al-Al<sub>4</sub>Ca eutectic

| Temperature (°C) | Cross-head speed (μm sec <sup>-1</sup> ) | Total plastic elongation (%)<br>(maximum values) | Maximum engineering stress (MN m <sup>-2</sup> )<br>(mean values) | Strain-rate sensitivity index ( <i>m</i> )<br>(maximum values) |
|------------------|--|--|---|--|
| 300              | 33.3                                     | 220  | 39.2  | —  |
| 400              | 33.3                                     | 351  | 14.7  | —  |
| 450              | 1.6, 3.3, 8.3, 16.7, 33.3, 83.3, 166.6   | 385  | 8.8   | 0.4  |
| 500              | 1.6, 3.3, 8.3, 16.7, 33.3, 83.3, 166.6   | 532  | 4.4   | 0.72   |
| 550              | 1.6, 3.3, 8.3, 16.7, 33.3, 83.3, 166.6   | 850  | 2.9   | 0.78   |
| 600              | 33.3                                     | 540  | 1.9   | —  |

following the method developed by Dunlop and Taplin [14] and used recently by Ducheyne and De Meester [15].

A summary of the superplastic tensile properties of the Al-Al<sub>4</sub>Ca eutectic is given in Table I. It appears clearly that the optimum temperature range for superplasticity lies between 500 and 600° C. This is actually expected for an eutectic alloy near to the melting point [4] (in our case 616° C). At lower temperatures the superplastic behaviour is still evident. This begins around 300° C = 0.64 *T<sub>m</sub>*, *T<sub>m</sub>* being the homologous temperature in Kelvin. This value is slightly above the minimum temperature for the occurrence of superplasticity, which is 0.5 *T<sub>m</sub>* = 171.5° C [1-4]. The maxi-

imum elongation (850% at 550° C) corresponds to a strain-rate of 1.3 × 10<sup>-2</sup> sec<sup>-1</sup>, while the maximum strain-rate sensitivity index (*m* = 0.78) corresponds to a strain-rate of 1.3 × 10<sup>-3</sup> sec<sup>-1</sup>. At this moment we cannot confirm the statement that maximum elongations occur frequently under conditions of maximum *m* [3].

The superplastic behaviour also emerges clearly from Figs. 2 and 3. Fig. 2 represents some typical engineering stress-strain curves obtained at different temperatures (400, 450 and 500° C) with an initial strain-rate of 4.1 × 10<sup>-3</sup> sec<sup>-1</sup>. Fig. 3a exhibits a sigmoidal relationship between log-stress and log-strain at 450, 500 and 550° C, with a region of high strain-rate sensitivity (*m* > 0.3) (*m* = δ log σ /

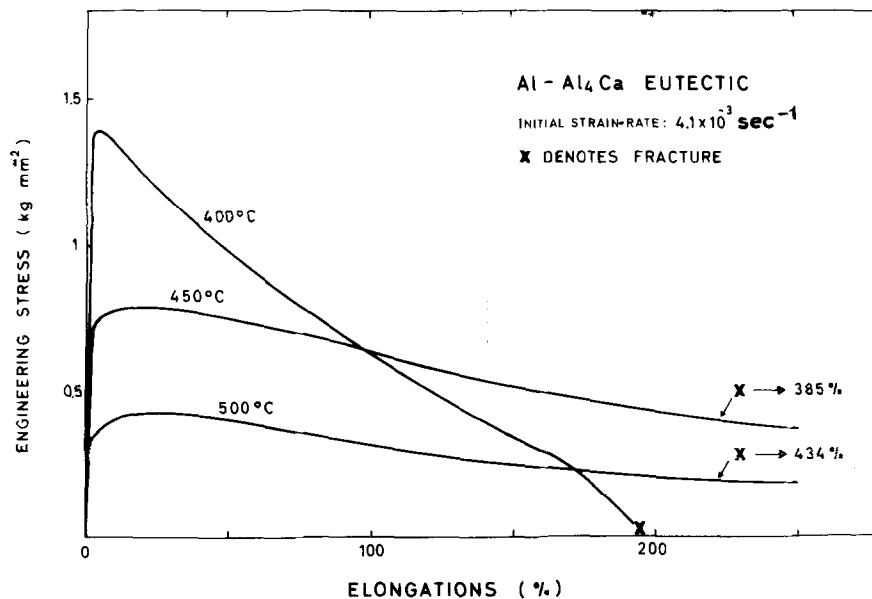


Figure 2 Engineering stress elongation curves for the Al-Al<sub>4</sub>Ca eutectic (1 kg mm<sup>-2</sup> = 9.806 65 MN m<sup>-2</sup>).

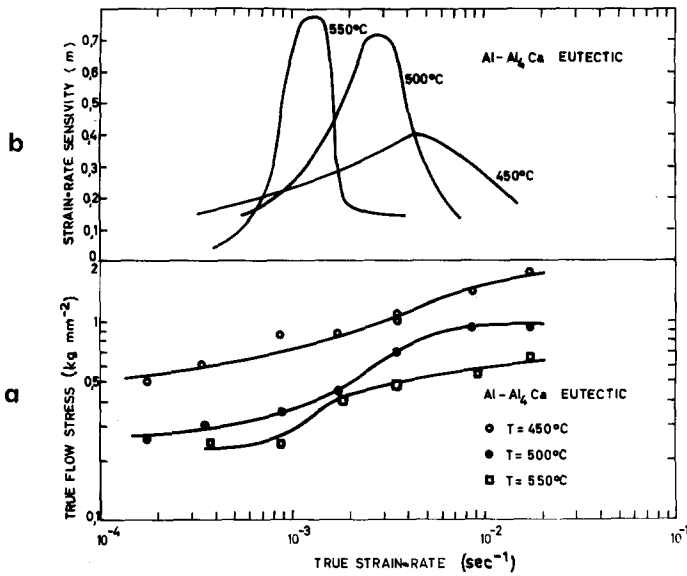


Figure 3 (a) The relationship (Dunlop and Taplin method) between flow stress and true strain-rate for Al–Al<sub>4</sub>Ca eutectic ( $1 \text{ kg mm}^{-2} = 9.80665 \text{ MN m}^{-2}$ ). (b) The dependence (derived from a) of strain-rate sensitivity index,  $m$ , on true strain-rate.

$\delta \log \dot{\epsilon}$  [16] where  $\sigma$  is the flow stress and  $\dot{\epsilon}$  the true strain-rate), in which superplasticity occurs. This region is bounded by two regions of low strain-rate sensitivity ( $m \sim 0.1$ ), both corresponding to conventional plasticity. This trend is typical of many other superplastic systems [3], as e.g. the eutectic Al–Al<sub>2</sub>Cu [5–6]. Fig. 3b shows the dependence of the strain-rate sensitivity  $m$  on the true strain-rate at different temperatures. As for other systems [3], the strain-rate sensitivity increases with increasing temperature and goes through a maximum with increasing strain-rate. A point worth noting is that the peak of  $m$  occurs at decreasing strain-rate as the temperature increases. On this point Al–Al<sub>2</sub>Cu [5] and Al–Al<sub>4</sub>Ca behave differently.

The tensile properties of the Al–Al<sub>4</sub>Ca eutectic at room temperature are given in Table II together with those obtained on the material after superplastic deformation (elongation 15%) at  $400^\circ\text{C}$ . For reasons of comparison the tensile properties

of an Al–Al<sub>4</sub>Ca unidirectionally solidified eutectic already described elsewhere [17] are also reported in the Table (column 4). Table II contains finally some data regarding the hardness and the density of the specimens used in the present investigations.

The eutectic Al–Al<sub>4</sub>Ca was also prepared by use of a second method based on a random solidification technique (chillcast into a graphite crucible) and subsequent hot-working (extrusion and hot-rolling). It is interesting to note that also the specimens prepared in this way revealed a very fine equiaxed grains duplex structure with superplastic behaviour. In this case, however, the superplasticity was tested on sheets at  $500^\circ\text{C}$  following to the method developed by Jovane [18–19]: a primary vacuum ( $10^{-1} \text{ mm Hg}$ ) is applied to one side of a test disc to form a dome, the increase in height of the dome being measured by a transducer and the depression by a vacuum gauge. The stress/strain-rate curves (Fig. 4a) were obtained from the theoretical approach of the deformation of a dome

TABLE II Room temperature characteristics of the Al–Al<sub>4</sub>Ca eutectic

| Properties                                       | Superplastic structures | Structures after superplastic deformation at $400^\circ\text{C}$ | Cast structures (unidirectionally solidified) [17] |
|--|-------------------------|--|--|
| Ultimate tensile strength ( $\text{MN m}^{-2}$ ) | 245–323                 | 196–235  | 225–255  |
| Total plastic elongation (%)                     | 3–6                     | 7–11   | 7–35   |
| Hardness ( $\text{kg mm}^{-2}$ )                 | 60–90 ( $H_V$ )         | 74 ( $H_V$ )   | 38–52 ( $H_B$ )                                    |
| Density ( $\text{g cm}^{-3}$ )                   | 2.59                    | –  | –  |

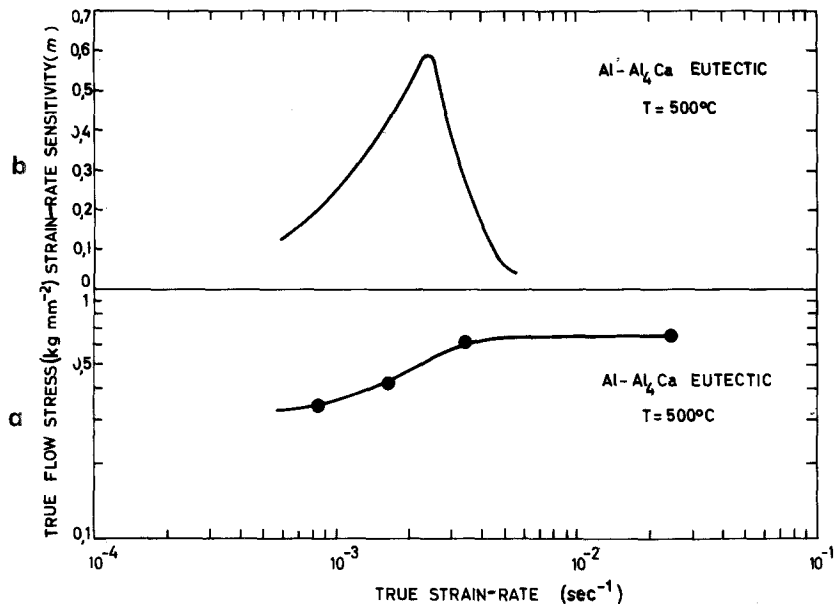


Figure 4 (a) The relationship between flow stress and true strain-rate for Al-Al<sub>4</sub>Ca eutectic (Jovane method) ( $1 \text{ kg mm}^{-2} = 9.80665 \text{ MN m}^{-2}$ ). (b) The dependence (derived from a) of strain-rate sensitivity index  $m$ , on true strain-rate.

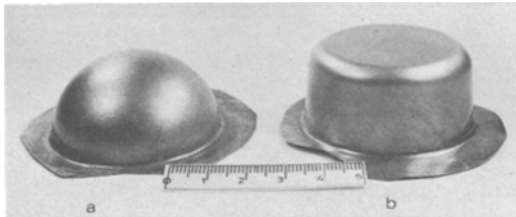


Figure 5 A dome vacuum (a) and a cup vacuum (b) formed into a die, both from superplastic Al-Al<sub>4</sub>Ca eutectic at 500° C.

in superplastics materials [18–19]. Fig. 4b shows the dependence of strain-rate sensitivity index,  $m$  on strain-rate. In Fig. 5 we show finally (a) a dome obtained from a test of 0.3 mm thickness at 500° C; (b) a cup of 0.07 mm thickness realized from an analogous disc by a deep vacuum forming at the same temperature.

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### Chemical characterization of a high-performance organic fibre

The high-performance and high-modulus fibre, Kelvar 49\*, is finding increasing military and commercial acceptance. When used for structural parts, the fibre is included in a matrix to form a composite. Since these structural parts must often be in contact with many different materials for long periods of time it is important to know the specific chemical structure of the fibre. The manufacturer has described the fibre as an aromatic amide, but there has been speculation as to its exact structure. Fig. 1 shows two possible alternative structures: a condensation product of *p*-aminobenzoic acid (or chloride derivative) monomers, polymer I, or of *p*-phenylene diamine with terephthalic acid (or acid chloride), polymer II. The manufacturer has in fact obtained patents on both polymers [1] and either structure would be consistent with the elemental analysis reported previously [2].

Proton nmr was appealing as a way to distinguish between polymer I and polymer II. The protons on the symmetrically substituted phenyl groups of polymer II would be expected to give a different aromatic proton spectrum from those on the asymmetrically substituted phenyl of polymer I. A spectrum of a saturated solution of the polymer in concentrated H<sub>2</sub>SO<sub>4</sub> was taken using computer-averaged transients to compensate for the diluteness of the solution. Unfortunately, the exceedingly slow-tumbling, large polymer molecules produced only a flat, broad, featureless peak. Thus traditional chemical means were necessary.

The yellowish fibre was chopped and dissolved in concentrated sulphuric acid, where it did not break into a monomer but assumed the form of a soluble polymer. When the yellow solution was diluted with water, a cottony white polymer appeared which was filtered, dried, and weighed. In this form, the polymer was treated further. A

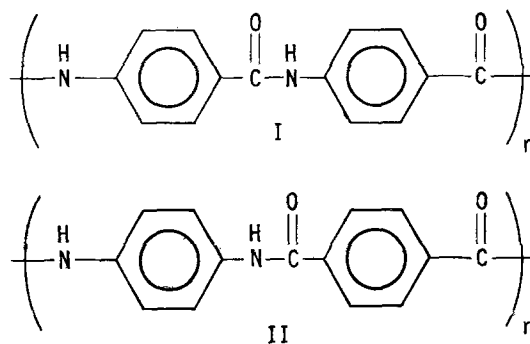


Figure 1 Two possible structures of the high modulus fibre, Kevlar.

mixture of 80% KOH (reagent grade, 85% pellets) and diethylene glycol was heated to 200°C. The water from the KOH pellets boiled off during heating, the KOH dissolved, and the solution turned amber. The weighed, dried polymer was placed in the hot solution and allowed to reflux for 8 h. The reaction mixture was then diluted with water and acidified with concentrated HCl. The white precipitate formed by the addition of HCl was isolated by filtration and washed thoroughly with water and acetone. The infra-red spectrum of the white crystals was exactly superimposable on that of known terephthalic acid.

If the fibre were polymer II, which would yield terephthalic acid as a monomeric breakdown product, the maximum obtainable terephthalic acid would be 0.697 g per g of polymer. In our laboratory, 0.490 g terephthalic acid per g polymer was produced, 70% of the theoretical maximum. Either the remainder was simply lost in the procedure, or it was never present in the original fibre. The possibility of some portion of the remaining weight being polymerized *p*-aminobenzoic acid was not experimentally disproven. Any other monomeric breakdown products from the fibre underwent sufficient change to become unidentifiable in the reaction mixture. Indeed, aromatic amines are known for their instability to harsh