



## Selective matrix dissolution in an Al–Si eutectic

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### ABSTRACT

The irregular structure of an Al–Si eutectic has been chemically modified by adding small amount of Sr (300 ppm). The initially coarse flake structure was converted into technologically preferable fine fibrous morphology. The selective phase dissolution has been investigated using two different electrochemical approaches, derived from superimposed Pourbaix diagrams. Anodisation at 0.3 V (SHE) in 1 M HCl led to pitting and was partially successful after an extended period of time (20 h). Electropolishing in a mixture of perchloric acid and methanol (10:90) at 0 °C proved successful in both the partial and the complete matrix dissolution, without affecting silicon structures.

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### 1. Introduction

Aluminium–silicon based foundry alloys are of great importance to the automotive, aerospace and engineering industries [1]. Owing to the high fluidity imparted by the presence of relatively large volumes of the Al–Si eutectic, it is possible to cast complex shapes with high dimensional precision. The eutectic is composed of  $\alpha$ -Al cells in which Si plates are interconnected, forming a Si network. However, the silicon needle-like particles are brittle reducing impact strength and ductility in cast structures. Therefore, eutectic modification is a common process performed to improve mechanical properties, particularly tensile elongation, by promoting a structural refinement of the inherently brittle eutectic silicon phase. It was reported earlier that the Al–Si interface can be modified by trace additions of strontium (a few hundred parts per million, ppm) to hypoeutectic aluminium–silicon alloys resulting in a transformation of the eutectic silicon morphology from a coarse plate-like structure to a well-refined fibrous structure [2–6]. Other elements including sodium and several rare earth elements are also known to result in varying degrees of modification [7–9]. Strontium offers clear advantages over sodium- or antimony-based alloy additives, including safer addition, better recovery, reduced fade and a fume-free application.

The Al–Si phase diagram has been recently assessed by Muray and McAlister [10]. The system is a simple binary eutectic with limited solid solubility. The maximum solubility of silicon in aluminium is 1.5 at.% at the eutectic temperature, and decreases to 0.05 at.% at 300 °C. The solubility of aluminium in silicon is much lower and reaches 0.016% at 1190 °C. This is still high in terms of silicon doping. Fig. 1 depicts the contemporary Al–Si phase dia-

gram [11]. The eutectic reaction takes place at 577 °C and at a silicon content of 12.6 wt.%.

According to the theory of crystal growth [12], the morphology of the eutectic structure depends upon the volume fractions of the constituent phases. When the volume fractions ( $V_f$ ) of one of the phases is <30% a fibrous structure is preferred because it exhibits lower total interface energy than the lamellar morphology. Although the volume fraction of silicon in the Al–Si eutectic is less than 30% (14.3%) the typical Al–Si eutectic is closer to a lamellar structure than to a fibrous one. This is usually attributed to the strong anisotropy of growth of silicon and to the relatively low interfacial energy between silicon and aluminium [13]. In such form it is inconvenient for producing Si nanostructures. However, a morphological modification by Sr addition can make it feasible, as it will be shown in this study.

Present work is concerned with a selective dissolution of the matrix phase in an Al–Si eutectic with and without Sr. The basic aim is to establish a well controlled procedure for dissolving the Al by using an electrochemical approach. This issue is important from two distinct points of view. Firstly, deeply etched structures enable a better view of the phase morphology and an insight into nucleation and growth mechanisms of eutectic Si. On the other hand, the extraction of silicon micro and nanostructures becomes possible, which may be further used for studying confinement effects in these one-dimensional nanostructures aiming at an application in modern semiconductor industry.

### 2. Experimental methods

#### 2.1. Eutectic alloy preparation

Prealloys were prepared from electrolytic aluminium (99.9999 wt.%), silicon (99.999 wt.%) and strontium (99.99 wt.%)

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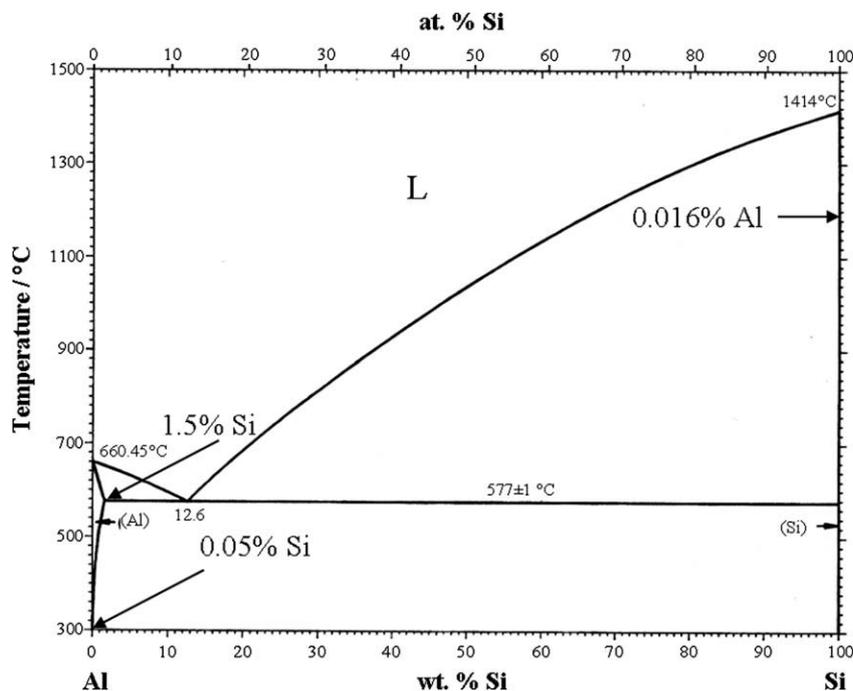


Fig. 1. Al-Si phase diagram adapted from [11].

by induction melting under an inert argon atmosphere. They were drop cast into a cylindrical copper mould and subsequently enclosed in evacuated quartz vials. A vial was suspended within the channel of a cylindrical furnace heated to  $650 \pm 5^\circ\text{C}$  and then allowed to melt. A motor lowered the vial at a constant rate through the furnace and into a glass funnel at its base. The motor used was manufactured by Faulhaber (Schönaich, Germany) running at 14,400 rpm combined with a 1:235,067 ultra low translation gears in order to realize constant and slow movement. This movement from the heat of the furnace into the funnel provided the temperature gradient necessary for directional solidification (*ds*). The glass funnel reduced air currents within the furnace's channel, which stabilized its temperature. Further details and a schematic drawing of the equipment are given elsewhere [14]. A rate of  $245 \text{ mm h}^{-1}$  ( $68.1 \mu\text{m s}^{-1}$ ) was employed. Samples for further investigations were cut from the *ds*-ingot perpendicular to the growth direction to allow a top view of the structure. After standard mechanical grinding with subsequently finer emery papers, the directionally solidified samples were treated electrochemically to selectively dissolve the aluminium matrix.

## 2.2. Electrochemical measurements

Electrochemical measurements were carried out in a conventional three-electrode electrochemical glass cell. Potentials were measured against a commercial reference electrode (Metrohm, Germany). The electrode used was a  $\text{Ag}|\text{AgCl}|\text{3 M KCl}$  electrode with a potential of 207 mV vs. SHE. The counter electrode was a strip of platinum foil with a surface area of  $1 \text{ cm}^2$ .

Initially, the aluminium phase was dissolved by exposing the sample to 1.0 M HCl (pH slightly above 0), and applying a potential of 0.3 V (SHE). Alternatively, the samples were electropolished in a mixture of perchloric acid and methanol (10:90) at a potential of 7 V (SHE) and a temperature of  $0^\circ\text{C}$ . The strategies used for this selective dissolution are discussed in detail in the results section. All chemicals were of p.a. grade and purchased from Merck, Darmstadt, Germany.

## 2.3. Electronics

Electrochemical investigations of the samples were conducted with a VoltaLab PST050 potentiostat manufactured by Radiometer Analytical SAS, Lyon, France. Scanning electron microscopy was performed using a Leo 1550 VP microscope (Leo Elektronenmikroskopie GmbH, Oberkochen, Germany) fitted with an INCA Energy Dispersive System (EDS) (Oxford Instruments, Oxford, UK).

## 3. Results and discussion

### 3.1. Microstructures

Silicon crystals may exhibit a remarkable variety of morphologies in an Al-Si alloy, depending on the crystallization conditions [15,16]. Fig. 2a displays the microstructure of a directionally solidified (*ds*) Al-Si eutectic alloy. It consists of coarse flake-like Si embedded in an Al matrix. The silicon particles seem to be disconnected. This is the typical morphology of irregular eutectic, frequently observed in faceted/non-faceted systems. Kobayashi and Hogan [17] suggested that nucleation of flat plate silicon (flake silicon) occurs by merging two groups of silicon atoms arranged in a tetrahedron into an embryo. Once formed, the embryo develops into a nucleus of critical size by the attachment of single silicon atoms to its surfaces. In this arrangement, the central mirror plane between the two tetrahedrons becomes a  $\{111\}$  twin plane. More tetrahedrons can add to the growing nucleus, which minimizes its surface energy by forming  $\{111\}$  planes at its corners. This mechanism, resulting in a plate-like morphology is known as the twin plane re-entrant edge mechanism (TPRE). The TPRE mechanism was first introduced by Hamilton and Seidensticker [18] to explain the growth of germanium dendrites and was later extended to the growth of silicon.

In an attempt to gain control over the morphology of the solidifying Al-Si eutectic an intentional modification of the interface energy was achieved by adding Sr to the melt. The addition of 300 ppm of strontium modified the morphology from flake-like to fibrous, as depicted in Fig. 2b. It can be observed that the Al-

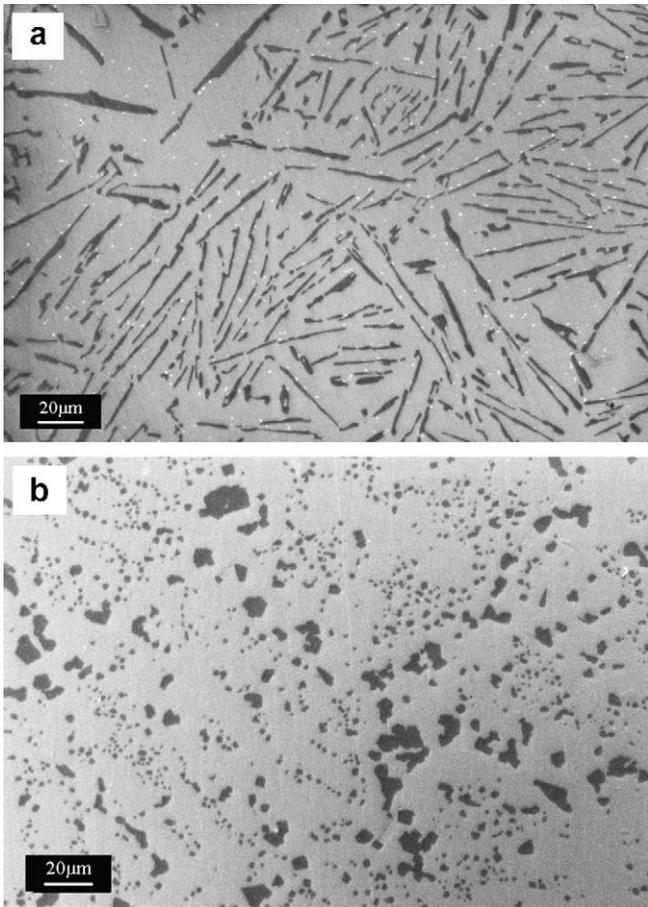


Fig. 2. Microstructures of *ds*-Al-Si and *ds*-Al-Si-(Sr) eutectic alloys.

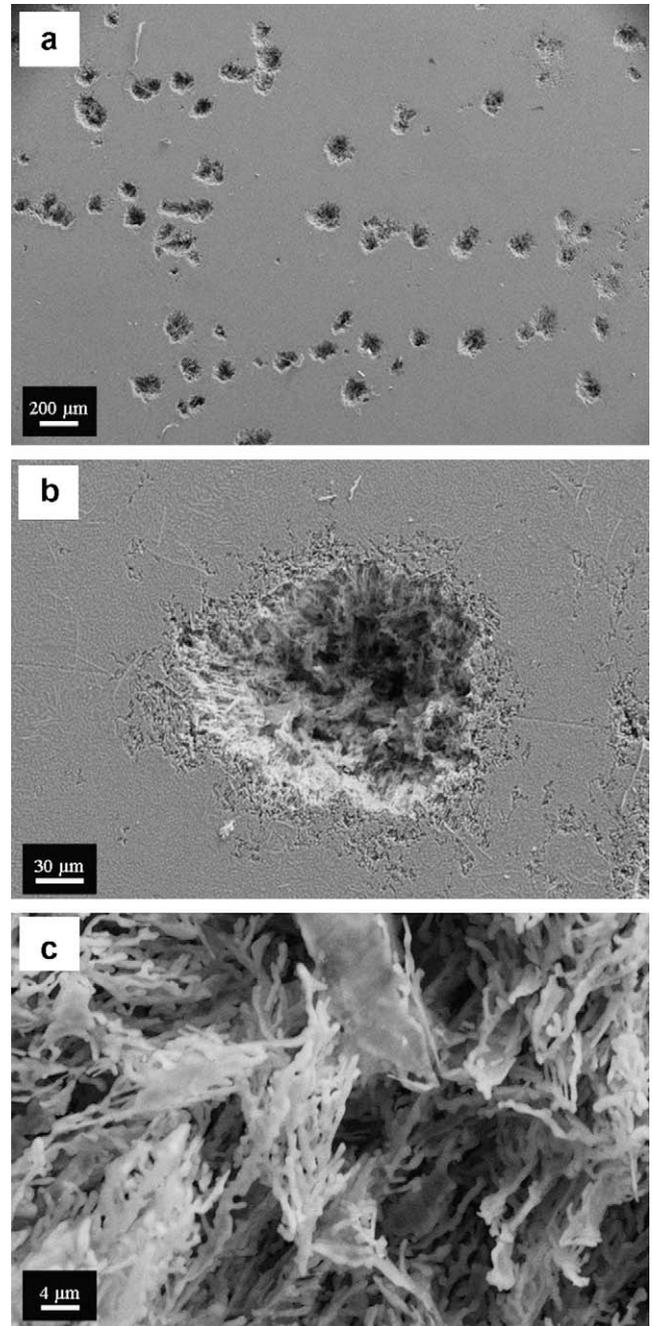


Fig. 4. Microstructures of *ds*-Al-Si-(Sr) alloy treated for 4 h at 0.3 V (SHE) 1 M HCl (pH 0).

Si eutectic is much finer and the silicon assumes fibrous morphology. The silicon particles appear as isolated spherical crystals. Despite the huge efforts that have been spent to reveal the mechanism and the kinetics of chemical modification, no unifying theory has been reached. Two different approaches have been considered with its distinct ideas regarding the genesis of the Al-Si eutectic and the modification of its morphology via chemical additives. According to the first one the mechanism underlying the nucleation of eutectic silicon in Al-Si alloys determines the eutectic silicon morphology [19–22], whereas the other attributes the morphology of the silicon eutectic to the kinetics of its growth [2,15,23,24].

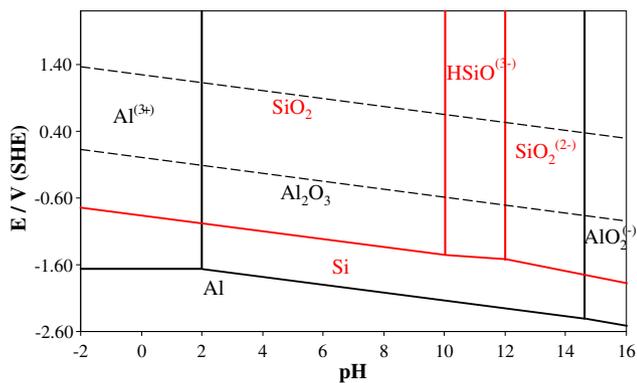


Fig. 3. Combined Pourbaix diagram for Al and Si.

### 3.2. Electrochemical dissolution

Initially, an electrochemical approach which proved successful in previous studies was chosen [25–28]. It is based on deriving optimum conditions for selective dissolution of the matrix by using superimposed thermodynamic stability diagrams [29] of the constituent elements, the so-called Pourbaix diagrams. Simplified Pourbaix diagrams of Al and Si in aqueous solutions were combined in Fig. 3 (adapted from Ref. [29]) for a molar concentration of the soluble species. The lines in the diagram depict the areas of relative predominance of the different species involved. It can be seen that Si can form oxide over a wider range of pH (–2 to 10) and may therefore passivate better. Aluminium, on the other hand, is in a pH range from 2 to 15 considered to be

in equilibrium with the oxide. From a practical point of view the stability range is much narrower if computing the reactions with millimolar or even micromolar concentrations. One would find the minimum solubility at around pH 6.0. Moreover the stability depends considerably on the nature of the ionic species. Chloride containing electrolytes for example tend to pit the aluminium even at pH 6.0 [30,31]. Once again it should be emphasized that these diagrams are purely thermodynamic but anyhow they are quite useful for directing into a pH potential region for studying selective dissolution of either phases. For the dissolution of the Al matrix acidic conditions of pH slightly above 0 (1 M HCl) and a potential of 0.3 V (SHE) within the electrochemical window were chosen. Fig. 4 shows the microstructure after 4 h treatment.

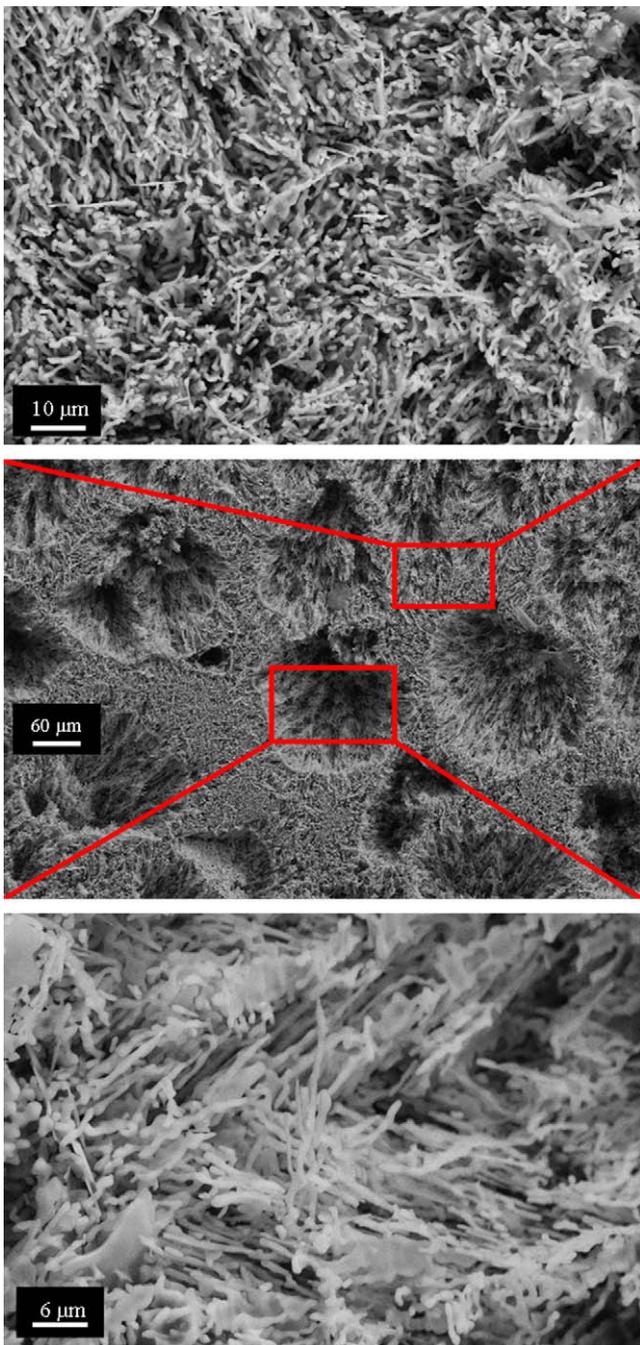


Fig. 5. Microstructures of *ds*-Al-Si-(Sr) alloy treated for 20 h at 0.3 V (SHE) 1 M HCl (pH 0).

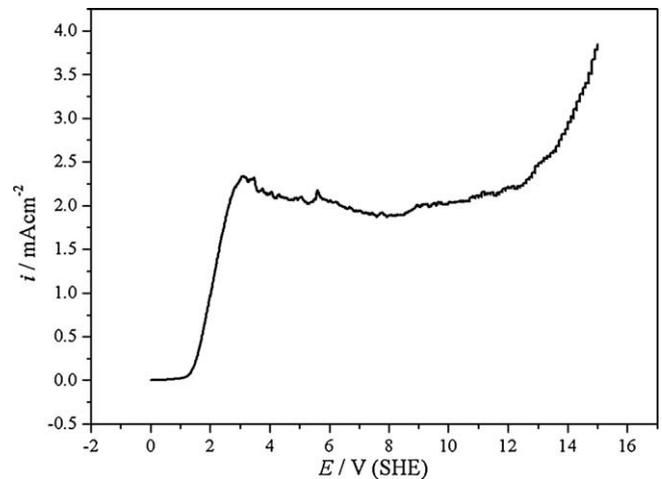


Fig. 6. Polarisation curve of *ds*-Al-Si-(Sr) in a mixture of HClO<sub>4</sub> and H<sub>3</sub>COH (10:90) at 0 °C at the scan rate of 10 mV s<sup>-1</sup>.

Only few corrosion pits were found, while most of the sample remained intact. The material shows a surprising stability despite the pH is rather low, chloride ions are quite aggressive against Al and the potential should be sufficiently high to foster dissolution of the matrix. However, the approach was partially successful as Al is dissolved in the pits while Si is not (Fig. 4c). Next, the samples were treated for a longer time (20 h) under the same conditions, to see if the initially forming pits would grow in size and

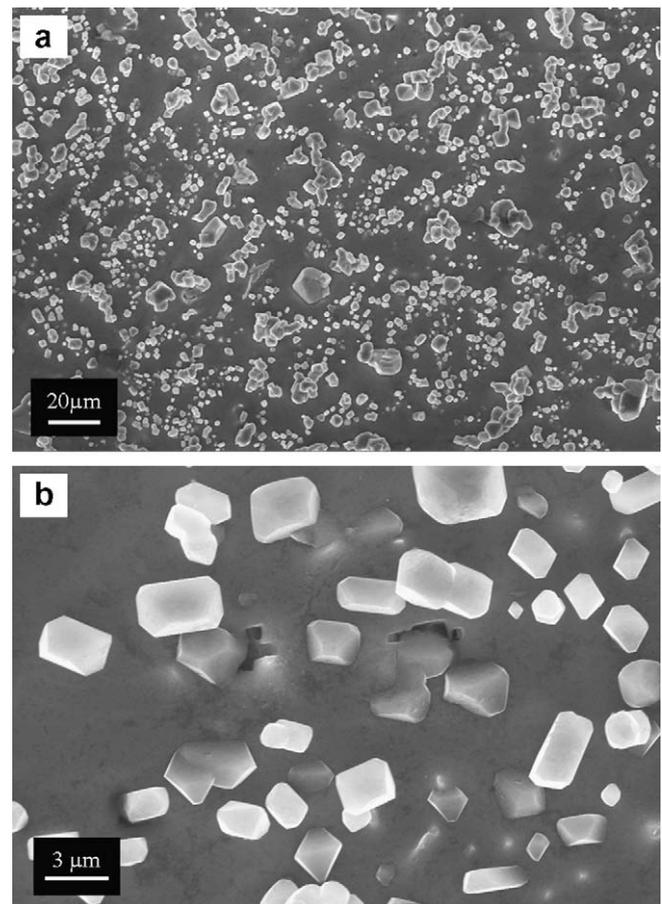
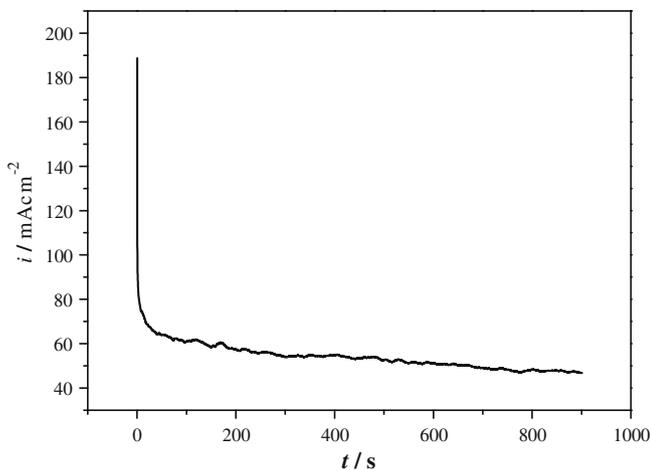
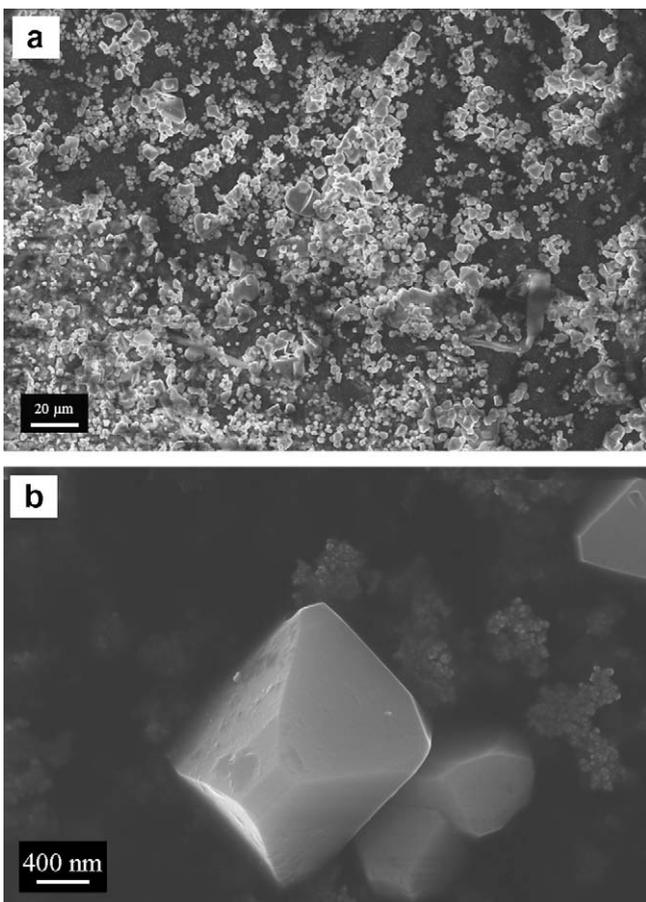


Fig. 7. Microstructure of *ds*-Al-Si-(Sr) alloy after partial electrodisolution of the Al matrix.

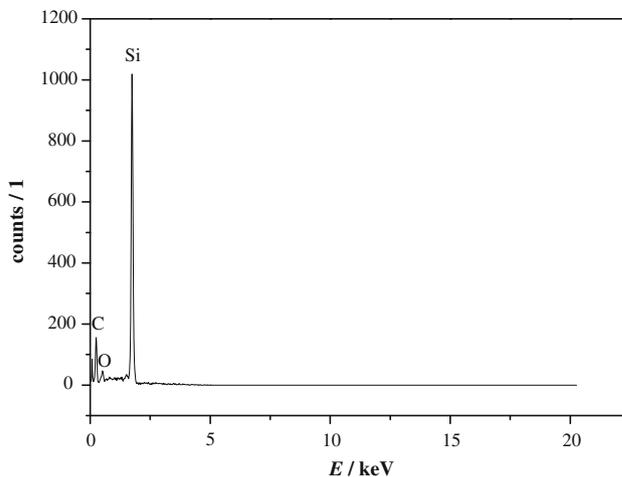


**Fig. 8.** Current transient recorded for the potentiostatic anodisation of Al-Si-(Sr) samples at 7 V (SHE) in a mixture of HClO<sub>4</sub> and H<sub>3</sub>COH (10:90) at 0 °C.

number, eventually leading to the desired dissolution. The result is displayed in Fig. 5. In this case, although pits are still present (Fig. 5a), in the regions between the pits only Si phase can be observed (Fig. 5b), indicating that the Al is dissolved. In the pits, similarly, only Si could be observed, as depicted in Fig. 5c. Albeit under these conditions it was possible to remove Al from the whole surface, the long periods suggested that the applied procedure is still not optimal, especially in cases when complete removal of the matrix is desired.



**Fig. 9.** Eutectic Si after complete electro dissolution of the Al matrix.



**Fig. 10.** EDX spectrum of extracted Si particles.

### 3.3. Electropolishing of selected phase

For quite a number of applications a well controlled homogeneous removal of the matrix would be desirable. For other systems such as NiAl-Re it was demonstrated that the length of the released nanostructures can be nicely controlled electrochemically [28,32]. Thus, electrolytic polishing was employed as an alternative route. Although electropolishing is mostly used for attaining deformation-free shiny surfaces for metallographic examination, it shall be demonstrated that it may be applied to selective phase dissolution as well. With the aim to define the optimum conditions, a potential scan was carried out. The electrolyte was a mixture of perchloric acid and methanol (10:90) which was held at 0 °C. The obtained polarisation curve is shown in Fig. 6. It can be seen that the polishing region, i.e. limiting current density is in the range from 2 to 9 V (SHE). Hence, a potential of 7 V (SHE) was chosen. Fig. 7 shows the microstructure after 15 min of electropolishing. This procedure yielded Si particles protruding from the Al matrix forming an array. It can be seen that a large number of fibers are released from the matrix and are standing upright and parallel. In addition, the selective etching of the matrix provided a closer insight into the Si morphology and enabled examinations of the microstructures in all three dimensions. In fact, the large depth of focus of the scanning electron microscope makes it possible to view both, the longitudinal and the transverse sections simultaneously, as depicted in Fig. 7. No pits could be spotted. Fig. 8 shows the current transient recorded during the matrix dissolution. After an initial equilibration period the transient shows a steady decrease in current. This decrease is attributed to the transport hindrance for the aluminium through the protruding silicon structures. By continuing this process for an hour the matrix was completely digested so that subsequent filtration yielded free Si particles on a filter paper (Fig. 9). It clearly shows, that the Si is unaffected by the process. Also, the composition of the extracted structures was confirmed by energy-dispersive X-ray (EDX) spectroscopy and found to be exclusively Si (Fig. 10), showing that no residual Al is present.

## 4. Summary

Al-Si is an example of a faceted/non-faceted type of eutectic exhibiting an irregular structure. It can be chemically modified by adding small amount of Sr (300 ppm), obtaining a fine fibrous morphology, which is preferable from technological point of view. Further, the selective phase dissolution has been investigated using two different electrochemical approaches. Applying conditions de-

rived from superimposed Pourbaix diagrams (0.3 V SHE in 1 M HCl) lead to pitting corrosion in HCl solution and was partially successful only after an extended period of time (20 h). Conversely, electropolishing in a mixture of perchloric acid and methanol (10:90) at 0 °C proved successful in both the partial and the complete matrix dissolution, without affecting Si particles. Thus, a well controlled procedure for selective phase dissolution in the Al–Si eutectic is established. It may be applied in studying nucleation, growth mechanism and kinetics of the transformation in this commercially important eutectic alloy. Moreover, the same method is applicable to the extraction of Si particles for investigating their properties and potential further application in semiconductor industry or, with its low density, excellent electron/mass ratio and large surface in a novel air silicon battery which is presently under development.

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