XAFS studies on a modified Al-Si hypoeutectic alloy

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Abstract. To understand the role of Sr in doped aluminium-silicon alloys, we have conducted for the first time, Sr-K edge XAFS measurements on Al-3%Si-0.04%Sr. Aluminium-Silicon alloys are widely used in automobile and aerospace applications. Modification of these alloys with addition of trace levels of Sr (200-400 ppm) results in changing the morphology of Si eutectic from “plate” like structure to “fibrous” structure. Several theories have been proposed to understand the mechanism of modification of eutectic phases with Sr addition in these alloys, but there is no conclusive evidence in support of these theories. From our XAFS analysis, we suggest Sr-Si bonds and Sr-Sr correlations may be responsible for the morphological transformation observed in the alloy.

1. Introduction
Aluminium Silicon alloys are widely used in automobile, aerospace and domestic casting applications [1]. These alloys became prominent as structural materials ever since Pacz [2] discovered the modification of eutectic phases with trace level additions of Na. The modification treatment with Na or Sr results in transforming the eutectic silicon morphology from a coarse plate-like (flake) to a fine fibrous (coral) morphology, thereby improving their mechanical and performance properties [2-6]. Figure 1 represents the morphology of eutectic silicon in unmodified and modified Al-Si alloys. Several hypotheses have been proposed on the modification of eutectic phases by Sr or Na additions [7-9]. However, there is no conclusive evidence supporting any one of the hypotheses and the mechanism still remains unclear.

Recently, Shankar et al. proposed a theory on modification of eutectic phases by addition of Sr [7]. Based on extensive study of TEM, SEM and thermal analysis, they found that the Sr addition changes the rheological properties of the melt thereby changing the interfacial energies for the nucleation. Srirangam and Shankar conducted high energy x-ray diffraction experiments to determine the effect of Sr on liquid structure of Al-Si alloys [10]. They observed that the addition of Sr decreases the coordination number of the alloy melt at any given superheat temperature and changes the Si-Si pair correlations as compared to Al-Si and Al-Al pair correlations. However, no attempts were made to understand the correlations of Sr-Al, Sr-Si and Sr-Sr in Al-Si alloys modified with Sr. Since Sr is only 200-400 parts per million (ppm)
in the melt, advanced characterization techniques are required to study the Sr correlations and its neighboring environment in Al-Si alloy.

Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy is a characterization technique that can be used for obtaining element specific information and local structure around a particular element which is present even in ppm levels. In order to study the effect of Sr addition on Al-Si alloys, the Sr K-edge was investigated using EXAFS. In this publication, we present the results of EXAFS analysis of a Sr doped Al-Si eutectic alloy with composition Al-3wt%Si-0.04wt%Sr. (Alloy compositions are in weight %).

2. Experimental Procedure
Alloy samples were prepared from 99.999% pure Al and electronic grade (99.9999% pure) elemental Si. Each alloy sample was placed in a clean alumina crucible, melted in an electric furnace and poured into a cylindrical copper mold of 15 mm diameter and 70 mm height to form a cast specimen. The alloy chemistry was evaluated with Inductively Coupled Plasma (ICP) and confirmed with Glow Discharge Optical Emission Spectroscopy (GDOES).

Sr K-edge (16,105 eV) x-ray absorption measurements were carried out at the MRCAT 10-ID beamline [11] at the Advanced Photon Source, Argonne National Laboratory, Argonne, IL-USA. EXAFS data was collected in fluorescence mode for the Al-3%Si-0.04%Sr alloy sample using an ion chamber with Stern-Heald geometry filled with argon gas. Measurements were taken with continuous monochromator scanning mode and energy calibration was performed with Zr foil at an energy of 17,998 eV. The size of the incident x-ray beam on the sample was 0.8 mm by 0.8 mm.
Figure 3. Plots representing the EXAFS results for Al-3% Si-0.04%Sr: (a) magnitude and (b) real part of the data and fit along with each of the paths contributing to the model.

The alloy sample was loaded into the beam in the form of a very thin sheet and 30 scans were recorded and averaged. EXAFS spectra were collected from -250 eV below the Sr K-edge to 1000 eV above with 0.4 eV step size. The data was processed using Athena [12] by extracting the XAFS oscillations $\chi(k)$ as a function of photoelectron wave number $k$ using standard procedures. The theoretical paths were generated using FEFF6 [13] and the fits were performed in R-space using the Artemis fitting program [12]. During fitting, the $S_0^2$ (amplitude) value for the Sr edge was set to 1.03 as determined from a SrO spectrum. Data sets were simultaneously fitted in R-space with k-weights of 1, 2 and 3.

3. Results

Normalized x-ray absorption data above the Sr-K edge for Al-3%Si-0.04%Sr alloy is shown in Figure 2(a). The background subtracted k-weighted $\chi(k)$ data is shown in Figure 2(b).

To model the EXAFS data for Al-3%Si-0.04%Sr, theoretical paths were generated from the following compounds using FEFF: (a) Sr-Al paths were generated from the compound Al$_4$Sr which is the composition of the starting material used to incorporate Sr into AlSi alloys; (b) Sr-Sr path was generated from Sr metal; and (c) Sr-Si paths were generated using SrSi. The model for Al-3%Si-0.04%Sr includes 2 Sr-Al paths with path lengths of 3.58Å and 5.72Å and coordination numbers (CN) of 16 and 16 respectively from Al$_4$Sr; a Sr-Sr path with path length 4.32Å and CN = 12 from Sr metal; and the Sr-Si paths with path lengths 3.33Å and 5.25Å and CN = 7 and 8 respectively from strontium silicide. Figure 3 shows the experimental data and the model fit for the Al-3%Si-0.04%Sr alloy. Figure 3(a) represents the magnitude of the data and the fit, while Figure 3(b) shows the data and the fit in real space. The 14 (compared to 17 degrees of freedom available) variable fit parameters are listed in Table 1 and the values compare well with those of the parent compounds. Figure 3(b) shows the real part of the fit along with the individual paths that contribute to the fit. Inspection of Figure 3(b) indicates that the main contribution to the highest amplitude peak is from Sr-Si and Sr-Al paths. Sr seems to have Si as its nearest neighbor at 3.17Å. The peak around 4.2Å can be fitted with a Sr-Sr path of length 4.32Å, which is between the Sr-Sr second shell distances in SrSi (3.74Å) and Al$_4$Sr (4.46Å). In order to rule out other sources for this peak, we attempted a fit with generated Sr-Si and Sr-Al paths at around 4.32Å. In both cases, the reduced chi square and R-factor values increased substantially (more than 50%), indicating that the Sr-Sr path is responsible for the peak. The
Table 1. Fit parameters for the Sr edge of the Al-3%Si-0.04%Sr sample. $S_0^2$ (amplitude) was held fixed at 1.03±0.04. The k-range for used is from 2.5-9.8 Å$^{-1}$ while the R-range is from 1.8-5.6 Å. For comparison, the coordination numbers for the starting compounds from which the paths have been chosen are given in parentheses.

| Path          | N   | R(Å)   | $\sigma^2$ | $\Delta E$ |
|---------------|-----|--------|------------|------------|
| **Al$_4$Sr paths** |     |        |            |            |
| Sr-Al1        | 9.3 ± 2.8 (16) | 3.70 ± 0.01 | 0.019 ± 0.005 |          |
| Sr-Al2        | 16 | 5.90 ± 0.3 | 0.022 ± 0.005 |          |
| **SrSi paths** |     |        |            | 1.17 ± 0.65 |
| Sr-Si1        | 6.4 ± 0.8 (7) | 3.17 ± 0.01 | 0.009 ± 0.002 |          |
| Sr-Si2        | 7.3 ± 1.5 (8) | 5.24 ± 0.02 | 0.010 ± 0.003 |          |
| **Sr metal path** |     |        |            |            |
| Sr-Sr         | 4.0 ± 1.1 (12) | 4.18 ± 0.01 | 0.010 ± 0.003 |          |

relatively high CN (4.0) for this path, given the low concentration of Sr (0.012 at%), points to a non-random distribution of the Sr dopant in the Si-rich regions of the alloy.

4. Summary
EXAFS measurements have been carried out for the first time on an Al-Si hypoeutectic alloy chemically modified with 0.04% Sr, to understand the local atomic environment around Sr in these alloys. It is observed that the Sr shows a favorable tendency to bond with Si. The bond lengths of Sr-Si are shorter as compared to the bond lengths of Sr-Al. Further, we observe the presence of Sr-Sr bonds in the alloy. The presence of Sr-Sr bonds along with Sr-Si bonds could play a role in the nucleation and morphological changes of eutectic phases, which occur with incorporation of tiny amounts of Sr in the eutectic. Further studies are underway on various Al-Si alloy compositions as well as on Al-10%Sr master alloy to understand the morphological changes occurring with addition of small amounts of Sr.

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