μ-XRF による共晶改良亜共晶 Al-Si 合金中の Sr 偏析同定
Determination of strontium segregation in modified hypoeutectic Al-Si alloy by μ-XRF analysis

野北和宏[a]、安田秀幸[b]、吉田健太郎[b]、上杉健太朗[c]、竹内晃久[c]、鈴木芳生[c]、アーニ・ダール[a]

K. Nogita[a], H. Yasuda[b], K. Yoshida[b], K. Uesugi[c], A. Takeuchi[c], Y. Suzuki[c] and A. K. Dahle[a]

[a] The ARC Centre of Excellence for Design in Light Metals, Materials Engineering, The University of Queensland Brisbane, Qld 4072 - Australia

[b] Department of Adaptive Machine Systems, Osaka University, Suita, Osaka, 565-0871 - Japan

[c] Japan Synchrotron Radiation Research Institute, SPring-8, Sayo, Hyogo, 679-5198 - Japan

This research utilises a μ-XRF (X-ray fluorescence) technique at the SPring-8 synchrotron radiation facility X-ray source and reveals that the modifying element strontium segregates exclusively to the eutectic silicon phase and the distribution of strontium within this phase is relatively homogeneous. This has important implications for the fundamental mechanisms of eutectic modification in hypoeutectic aluminium-silicon alloys.

Introduction

Modification of the eutectic silicon phase in hypoeutectic Al-Si alloys is carried out extensively in industry to improve mechanical properties. Modification results in a structural transformation of the silicon phase from a needle-like to a fibrous morphology. This fine fibrous eutectic modification of hypoeutectic Al-Si alloys by elements such as strontium and sodium has been explained based on the theory of impurity-induced twinning (IIT) of twin plane re-entrant edge (TPRE) growth of silicon [1]. The impurity-induced twinning theory suggests that a high density of twinning occurs in silicon in modified alloys because atoms of the modifier are absorbed onto the growth steps of the silicon solid-liquid interface[1], thus poisoning the regular TPRE growth. However, the IIT mechanism is somewhat controversial as there are published examples illustrating well-modified silicon fibres without a high density of twins[2], suggesting that, at least, other mechanisms are also important such as e.g. altered nucleation frequency of eutectic grains or surface tension.

Hampering efforts to confirm and expand on the IIT theory for silicon modification are the fundamental difficulties involved in analysing the inter- and intraphase concentrations and distributions of typical modifying elements. For instance, strontium, the most common commercial modifier is often present in concentrations ranging from only 20ppm to 600ppm. While at high concentrations (>300ppm) coarse strontium-rich intermetallics (most commonly Al2Si2Sr) are often present and visible, at lower and more typical concentrations there is no microscopic evidence of the strontium distribution. The low concentrations used are below the limits of many, more conventional, techniques such as EDS and WDS (energy and wavelength dispersive spectroscopy). In fact, the only successful study examining the interphase distribution of strontium was performed by selectively dissolving the aluminium and silicon eutectic phases and performing atomic absorption spectroscopy on the solutions[3]. In this research it was shown that strontium is strongly partitioned to the eutectic silicon phase, however it was not possible to comment on the distribution of strontium within the silicon phase.

Recently, a method for elemental mapping using X-ray fluorescence microscope technique (μ-XRF) has been developed at the synchrotron radiation light source, SPring-8 Japan [4, 5]. The spatial resolution is sub-100 nm order, which is comparable to the current FE-SEM/EDX resolution. This research uses this new technique to investigate the strontium distribution in an Al-10wt%Si-1wt%Cu alloy modified by 250ppm strontium.

Experimental

The samples used in the experiments were Al-10wt%Si-1wt%Cu alloys with and without 250ppm addition of strontium. Also Ni in Sn-0.7wt%Cu, Na, K and other impurity elements in Al-10wt%Si alloys have been measured. For this report, the result of Sr is described.

The μ-XRF experiment was performed at an undulator beamline 47XU of SPring-8, Japan. A schematic diagram of the experimental set-up is shown elsewhere[4, 5]. The undulator radiation was monochromatized at 17.9keV by passing through a liquid-nitrogen-cooled Si 111 double-crystal monochromator. A Fresnel zone plate was used as an X-ray focusing device to produce a fine probe. The FZP was fabricated by the electron-beam lithography technique at NTT Advanced Technology Co. Ltd. A zone structure with 1-mm-thick tantalum is deposited onto a 2-mm-thick SiC membrane. The diameter is 155 mm and the focal length at the X-ray energy of 17.9 keV is 223.75 mm. The outermost zone width is 100 nm. In this setup, the beam size was 180 nm (vertical) x 150 nm (horizontal) and the total flux of the focused probe was ~2 x 10^9 photons/sec. The focused X-ray beam was used as the probe. The samples were mounted on a translation scanning stage with a motion accuracy of better than 10 nm. The XRF spectra were measured with a Si drift diode detector (Rontec Xflash D301).

Results and Discussion

The XRF spectra corresponding to the samples without and with strontium are shown in Figure 1. Both spectra are taken from a region of approximately 50x50mm incorporating aluminium dendrites, eutectic aluminium and eutectic silicon, and clearly indicate the presence of aluminium, silicon, and copper. Strontium Kα1 and Kα2 (14.17 and 14.10 keV) are present only in the sample containing 250ppm Sr. Therefore, the elemental mapping of Sr for the analysis that follows has been taken from this region. The use of the strontium

Kα avoids any confusion that may occur from the overlap of the strontium Lα1 and silicon Lα1 peaks.

A μ-XRF elemental map of a eutectic region (containing eutectic aluminium and silicon) taken (scan pitch: 0.25 mm, signal integration time for each point: 0.3 sec) are shown in Figure 2 (a-d). It is clear from the mapping results that strontium is present in the eutectic silicon, and is of negligible concentration in the eutectic aluminium phase. The map confirm that strontium is relatively homogeneously distributed throughout the eutectic silicon fibres. Surprisingly, it is noted that there is an intermetallic containing Al, Si and Sr at the periphery of the Si particle, and morphologically this intermetallic appears to be part of the adjacent Si crystal. This intermetallic is likely to be Al2Si2Sr and would not be expected to form in this alloy at this Sr-level. In contrast to strontium, copper can be observed both as a precipitate on the grain boundaries (most likely as CuAl2) and also in solution in primary and eutectic aluminium.

Future Works

It would be interesting to determine whether other known modifier elements in Al-Si alloys, such as Na and Ca, segregate in the same manner and also relate this behaviour to the latent heat of the eutectic silicon.

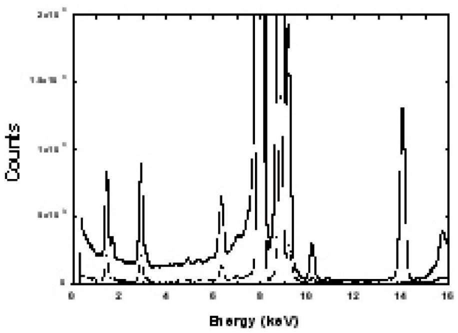

Fig. 1 XRF spectra of Sr modified and unmodified samples.

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Status of publications and patents

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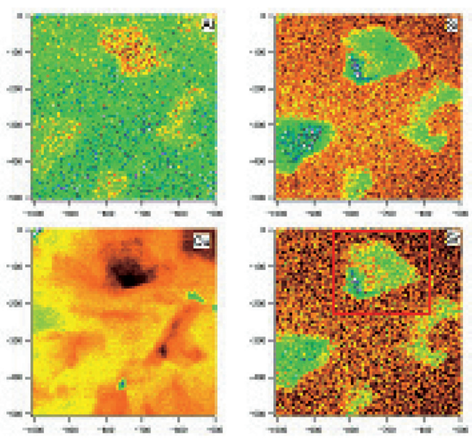

Fig. 2 μ-XRF images taken by roughly scan of (a) Al, (b) Si, (c) Cu, and (d) Sr. (scan pitch: 0.25 mm, integration time: 0.3 sec)

Keywords

aluminium alloys, X-ray fluorescence