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Metallographic techniques for the characterization of quasicrystalline phases in aluminium alloys

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Abstract. Several Al-alloys strengthened by quasicrystalline phases have been developed over the last few years showing the considerable potential for practical application. Therefore there is a strong need for developing new metallographic methods or adapting the traditional ones in order to identify and characterize quasicrystalline phases in a reliable, quick and economical way. This paper describes different techniques: the classical metallographic method, deep etching, particle extraction technique and cross-sectioning using focused ion beam (FIB), and discusses their advantages and disadvantages when identifying quasicrystalline particles. It was discovered that particle extraction techniques are very powerful methods for the identification of phases according to their morphology, and preparation of quality samples for X-ray diffraction (XRD). Transmission electron microscopy (TEM) analyses are also possible provided the extracted particles are thin enough.

Introduction

Quasicrystal-strengthened aluminium alloys can be produced either by rapid solidification [1, 2] or conventional casting techniques [2–4]. After the rapid solidification of many alloys, a two-phase microstructure can be obtained consisting of a dispersed quasicrystalline phase in an Al-rich matrix. The sizes of the quasicrystalline particles can vary from a few nm to 500 nm, and the particles usually possess the form of pentagonal dodecahedron. Moderate cooling rates attainable by conventional casting often produce multiphase microstructures. In addition to the quasicrystalline phase and the Al-rich matrix, several other crystalline phases (very often quasicrystalline approximants) can also be present in the microstructure [2–4]. Moreover, quasicrystalline phases can have very different shapes and sizes due to variable local cooling conditions in the conventionally cast parts. All these make the identification of quasicrystalline phases more difficult. Quasicrystalline phases are the most frequently characterised using TEM because of their unique diffraction patterns. However, access to TEM facilities is not always easily available, the preparation of TEM-samples is difficult and requires special equipment and, finally, only a relatively small region of initial casting is investigated. Because of the further development of alloys containing quasicrystals and their practical application it is necessary to find new metallographic techniques and/or adapt the traditional ones in order to recognize quasicrystalline phases in a reliable, quick, and economical way [5]. One such technique is particle extraction. The particles are isolated by dissolving the matrix using chemical and electrochemical methods, and characterized by the application of scanning electron microscopy (SEM). Some convenient methods for the extraction of crystalline phases are described in Ref. [5]; however, the particle extraction in Al-alloy is rather difficult since most of the particles dissolve more readily than the aluminium matrix.

In this paper we describe different techniques for the preparation of samples: the classical metallographic method, deep etching, particle extraction technique and cross-sectioning using a focused ion beam (FIB), which are applied for the characterisation of quasicrystals in Al–Mn–Be, Al–Mn–Be–Cu and Al–Mn–Be–B alloys. The applications of these SEM-based methods are discussed together with their advantages and also disadvantages. In addition, attention is given to the use of deep etching and powder extraction techniques for sample preparation regarding analytical TEM, and X-ray diffraction (XRD).

Experimental

The investigated alloys were synthesised from pure Al and Mn, and AlBe5, AlCu10 and AlB3 master alloys using vacuum induction melting and casting. The nominal compositions of the alloys were: $Al_{86}Mn_3Be_{11}$, $Al_{94}Mn_2Be_2Cu_2$ and $Al_{89}Mn_2Be_2B_7$ (numbers indicate at%). Afterwards the alloys were cast into a copper mould with the following dimensions: 100 mm × 10 mm × 1 mm.

Standard mechanical metallographic procedures (grinding and polishing) were used for the SEM preparation of

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the samples. For deep-etching and particle extraction various chemical dissolution procedures were used. The most effective solution for both techniques was the mixture of 1 g iodine and 3 g acetic acid in methanol [6]. By deep etching the dissolution was carried out at room temperature for several hours. Filtering was done with care in order to avoid damage of the particles; the aim of filtering was also to remove the reaction products formed during the dissolution. By deep etching the samples were first mechanically polished and thereafter rinsed into the solution held at room temperature. The process lasted from several minutes up to 1 hour, depending on the particle sizes.

The samples were investigated using two scanning electron microscopes: a dual beam (ion and electron) Quanta 200 3D and a FEG-SEM Sirion 400 NC (both FEI Company). Energy dispersive analysis (EDS) was performed using an INCA 350 system (Oxford Analytical). Focussed ion beam (FIB) was used for ion microscopy (ion current 10 pA), and milling (1 nA and 3 nA) and polishing (0.1–0.5 nA). The X-ray diffraction (XRD) was carried-out at XRD1-beamline (Elettra, Sinchrotrone Trieste, Italy) using synchrotron X-rays with a wavelength of 0.1 nm in the transmission mode.

Results and discussion

Quasicrystals normally have 5-, 8-, 10- and 12-fold rotational symmetries which also reflect themselves in the morphology of the quasicrystalline phases, and are absent in the periodic crystals [7]. In this way, the quasicrystalline phases can be reliably identified on the basis of their morphology. Examination of the polished surface is very important in order to obtain a general overview of the microstructural constituents, and also allows for the most reliable EDS analysis. Figure 1 shows a typical cast microstructure of Al–Mn–Be alloy consisting of several phases.

In the case of the investigated alloys, the best contrast was usually obtained using a backscattered electron detector since the electron backscattering coefficients of several phases were quite different. The predominant phase, the Al-rich solid solution, had the darkest appearance. The particles of the Be_4AlMn phase were slightly brighter. All other phases were bright and had a variety of shapes and sizes, such as faceted equiaxed particles (i-phase), dendritic particles (i-phase) and plate-like particles (a hexagonal phase).

The icosahedral quasicrystalline particles on the polished surface very rarely exhibited a pentagonal symmetry; consequently it was almost impossible to clearly identify quasicrystalline particles only from those 2D-sections prepared by traditional metallographic techniques. In addition, it is also very difficult to determine the 3D-shapes of microstructural constituents based on 2D-sections only. This is why Kral *et al*. [8] obtained 3D-shapes of phases in steels by using computer-aided visualization of 3D reconstructions from serial section images. They gradually removed approximately 0.2 μm of material in a step-wise manner and took photos of the section after each step. Nowadays, sequential cross-sectioning is done using FIB (usually dual beam SEM/FIB systems are used). In the systems equipped with EDS, 3D-elemental distribution can be obtained along with the particle shapes [9]. Nonetheless, such approach is feasible, but is very time consuming, and is unlikely to be used for regular routine investigations. In the case of the studied alloys it has to be stressed that distinction between quasicrystals and their approximants is very difficult, when using both backscattering images, and EDS. Namely, the compositions of phases of interest are very similar or almost alike.

As mentioned earlier, the shape of a crystal as well as a quasicrystal depends on its point group symmetry [7]. For example, icosahedral quasicrystals often exhibit the shape of pentagonal dodecahedron [7]. In this way a well-faceted quasicrystal can also be unambiguously identified by its shape. Moreover, also non-faceted quasicrystalline dendrites can be undoubtedly recognized by their "non-crystallographic" symmetry. Therefore, it is extremely important that during particle extraction a reagent does not dissolve quasicrystalline phases, and that they still exhibit their original shape after removing the matrix. There were some early attempts to apply these techniques for the identification of quasicrystals, but only with limited success [10]. Yet, considerable progress has been achieved recently, exemplified by Fig. 2. Some particles have the shape of a pentagonal dodecahedron confirming the presence of an icosahedral quasicrystalline phase. It was also discovered that branch structures (eutectic i-phase) grew most often from the vertices of pentagonal dodecahedra indicating that it also has an icosahedral structure. It was

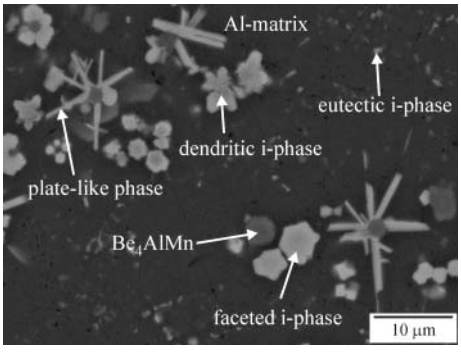

Fig. 1. SEM microcgraph of the multiphase as-cast microstructure of Al–Mn–Be alloy prepared by classical metallographic techniques (backscattered electron image).

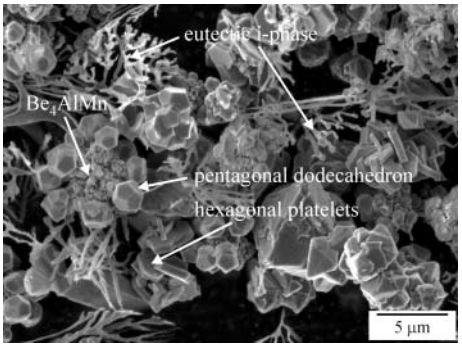

Fig. 2. SEM micrograph of the extracted particles placed on the carbon adhesive tape; as-cast Al–Mn–Be alloy (secondary electron image)

impossible, however, to identify their structure according to their shape since they were non-faceted. Even in this case, the i-phase can be identified unambiguously by measuring the angles between the branches, which are typical for icosahedral symmetry. In addition, during short annealing at temperatures between 450 °C and 550 °C eutectic i-phase become faceted showing typical pentagonal dodecahedron form. For definite confirmation of the icosahedral structure of the eutectic phase, TEM can be performed. Afterwards eutectic i-phase can be identified according to its specific morphology even in cases when it is not faceted.

An important disadvantage of particle extraction technique is that all particles are mixed together, so no information can be obtained about their spatial distribution in the microstructure. The particle extraction also takes more time than deep etching offering more possibilities for particles to be attacked by the etchant. Less material has to be removed during deep etching. Satisfactory results have already been obtained when the etching depth approaches the typical particle sizes. This also implies longer etching times when the particles are larger. Figure 3a shows the distribution and morphology of the eutectic icosahedral quasicrystalline phase in the as-cast Al−Mn−Be alloy. In addition, in Fig. 3b it can be observed that, in an Al−Mn−Be−Cu alloy after annealing at 500 °C for 3 hours, the quasicrystalline particles are covered by smaller particles, and rod-like particles are present in the matrix. Such small particles can often be lost, at least partially during filtering after particle extraction, but after deep etching some of them remain in their original positions. We can also improve the performance of EDS analysis, predominantly with smaller particles, since the matrix is removed. The removal of the matrix qualitative analysis is more beneficial, but it is not necessarily true for quantitative analysis since the surface is rough and not as smooth, as required for the most reliable results.

Figure 4a shows an extracted quasicrystalline dendrite covered with small particles. Its shape can be recognized at a glance, indicating particle extraction is a very powerful method. But a drawback is also obvious. The particles on the quasicrystal's surface can be seen, but there are no indications how far they extend inside the particle. This information can be gathered from standard metallographic sections. Nevertheless, a combination of particle extraction techniques (and deep etching) with FIB cross-sectioning can be an extremely powerful tool. The main advantage is that we can simultaneously see the morphology of phases and their internal structure, and the process is much faster than making cross-sections in bulk material, since much less material has to be removed. This can also be upgraded by 3D-reconstruction and 3D-mapping. According to our knowledge, no one has attempted to do this yet.

Particle extraction can also provide some advantages by the application of some characterisation techniques other than those related to SEM. For instance, the extracted particles can be reliably examined with TEM. Particles thin enough are placed on a holy carbon grid, which also allows HRTEM and EELS examination without any other preparation steps. Another possibility is to perform XRD analysis, where peaks belonging to the matrix are absent, allowing

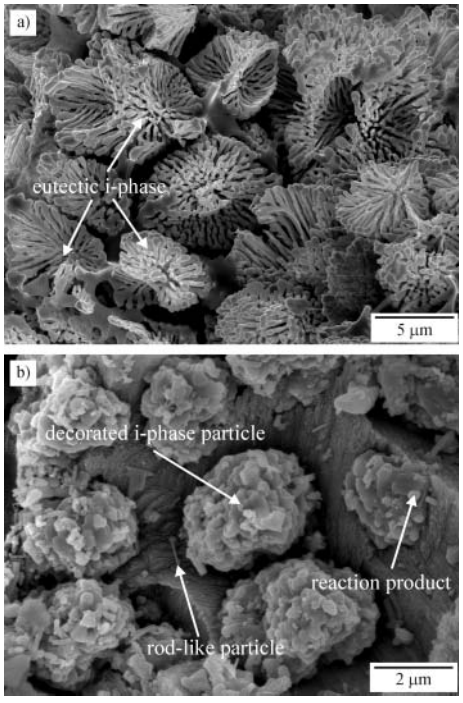

Fig. 3. SEM micrographs of deep-etched samples (methanol-iodine solution). (**a**) The morphology of the eutectic icosahedral quasicrystalline phase in the as-cast condition. (**b**) Distribution of quasicrystalline particles covered with reaction products after annealing at 500 °C for 3 hours (Al−Mn−Be−Cu alloy). Note rodlike particles in the matrix.

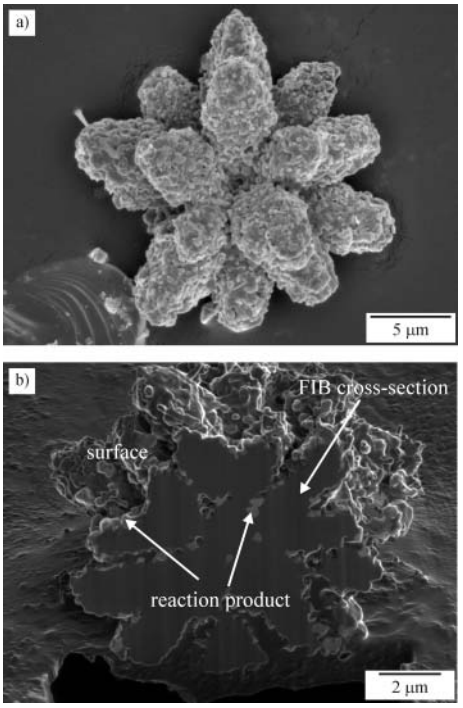

Fig. 4. (**a**) SEM micrograph of an extracted quasicrystalline particle (alloy Al−Mn−Be−Cu after annealing at 500 °C for 5 hours) covered by the reaction products, and, in (**b**) extracted quasicrystalline particle after FIB cross-sectioning. Internal structure is revealed, with the particles of a new phase appearing on the surface of the quasicrystalline particle, and some entrapped inside it because of coarsening.

Fig. 5. Diffraction patterns of a multiphase Al−Mn−Be alloy in the as-cast condition. (**a**) Bulk specimen, powder pattern shows incomplete Al-rings, indication presence of a small number of Al-grains, rings of other phases are rather weak. (**b**) Extracted particles. Al-rich matrix is dissolved, lines of minor phases became more pronounced. Only the most important rings of the i-phase are indicated.

weaker peaks belonging to the investigated phases to be clearly seen (Fig. 5). It was also confirmed that with the application of the iodine-methanol solution all reaction products formed during dissolution were completely removed.

The particle extraction method could be used for all Al-alloys containing i-phase in Al-rich alloys with the same solution and with similar process parameters. It was also proved to be a very powerful technique for revealing several phases in other Al-alloys, such as Al_3Ti, TiB_2, AlB_2 [11] with the same solution, but with applications of different solutions it could be used for identification of phases in other alloys [12].

Conclusions

This contribution exposes the strengths and weaknesses of different SEM sample preparation techniques for identifying and characterizing quasicrystalline phases embedded in Al-rich matrix. The results obtaining using the classical metallographic method, the deep etching, particle extraction technique, and cross-sectioning extracted particles using a focused ion beam (FIB), are presented and discussed.

The faceted quasicrystalline particles can be the most reliably identified by their shape, since the quasicrystalline phases normally have different point group symmetries than periodic crystals. In this regard, the classical 2D metallographic sections only offer limited possibilities for the identification of quasicrystals. Deep etching and particle extractions using chemical reagents that preserve the quasicrystalline and other phases intact during dissolution of the matrix have proved to be very powerful methods for fast and simple identification of quasicrystals. Both deep-etching and particle extraction could be also used in an industrial environment. The strength of these two methods for scientific investigations can be augmented by FIB cross-sectioning to reveal particle interiors and, in addition, by 3D-morphology and chemical reconstruction. Deep etching preserves spatial distribution of phases, whereas particle extraction techniques may provide samples for analytical TEM investigations and X-ray diffraction (XRD) experiments.

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