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Epitaxial growth of a metastable icosahedral quasicrystal on a stable icosahedral quasicrystal substrate

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ABSTRACT

This study confirms that the stable icosahedral quasicrystal (iQc) phase $Al_{65}Cu_{20}Fe_{15}$ (iQc–AlCuFe) can serve as a substrate for the nucleation of the metastable iQc–AlMnSi phase formed in rapidly solidified Al–Mn–Si alloys. The results reveal that a continuous, thin layer of the metastable iQc–AlMnSi phase can be formed on a stable iQc–AlCuFe particle. Electron backscatter diffraction patterns and selected-area electron diffraction patterns confirmed that epitaxy exists between the stable and the metastable iQc phases.

Metastable quasicrystals (Qcs) were first discovered in the rapidly solidified Al–Mn alloy system [1]. These Qcs are thermodynamically metastable, which means that they decompose upon heating into a crystalline compound or an approximant [2–4]. Stable Qcs were discovered several years later [5]. Their stability ensures that the Qc phase is an equilibrium phase and can be grown at slow cooling rates [6]. During the decades that followed these discoveries, a large number of metastable and stable Qcs were discovered [7–13].

Qcs possess long-range atomic order without translational symmetry and, therefore, their diffraction patterns show a non-periodic array of diffraction peaks. They are classified as icosahedral (i-), octagonal (o-), decagonal (d-) or dodecagonal (dd-) phases based on their rotational symmetries (5-fold in iQcs, 8-fold in oQcs, 10-fold in dQcs and 12-fold in ddQcs), which are not found in periodic crystals. IQcs are the only type that are non-periodic in all three spatial directions [14,15]. Their structure consists of six intersecting 5-fold axes, ten 3-fold axes and fifteen 2-fold axes [1]. Three types of Bravais lattice are theoretically consistent with the icosahedral symmetry in three dimensions. They correspond to the primitive (P-type), body-centered (I-type) and face-centered (F-type) hypercubes in six dimensions. The P- and the F-type have been verified in several alloys [8,10].

The structures of the stable (F-type) iQc phase $Al_{65}Cu_{20}Fe_{15}$ (iQc–AlCuFe) and the metastable (P-type) iQc phase $Al_{73}Mn_{21}Si_6$ (iQc–AlMnSi) are very similar [8,10,16]. In addition, their quasilattice constants are also very similar, being 0.445 nm for the stable iQc–AlCuFe phase and 0.460 nm for the metastable iQc–AlMnSi phase [16]. The difference between the quasilattice constants, in other words, the misfit [17], expected between planes with the same indices is only 3.4%. Due to such a small difference and the similarity in the structure the stable iQc–AlCuFe phase could represent an effective substrate for the nucleation of the metastable iQc–AlMnSi phase, although there is no report about this in the literature. In the future this could enable control of the size and the distribution of in-situ-formed iQc phases in different alloy systems like with conventional alloys that contain crystalline phases.

Therefore, the aim of this investigation was to evaluate the possibility that a stable iQc–AlCuFe phase could serve as a substrate for the nucleation of the metastable iQc–AlMnSi phase in a rapidly solidified Al–Mn–Si alloy.

A bulk piece of stable iQc–AlCuFe phase was prepared in a chamber furnace by melting pure aluminum (99.99 wt%), copper (99.9 wt%) and iron (99.9 wt%) at 1100 °C. It was then cast and subsequently annealed at 800 °C for 24 h. The Al–Mn–Si alloy was prepared in the same chamber furnace at 880 °C using pure aluminum (99.8 wt%), manganese (99.9 wt%) and silicon (99.99 wt%). The chemical compositions of these alloys were determined by EDS and are given in Table 1. A small particle of stable iQc–AlCuFe phase with a diameter between 2 and 3 mm was placed on the bottom of the mould cavity. The Al–Mn–Si alloy melt was then cast into the mould, completely engulfing the iQc–AlCuFe particle at the bottom. The mould itself was made of a pure copper block with dimensions of 100 × 100 × 120 mm and a cylindrical casting cavity with a 5-mm diameter.

The Al–Mn–Si alloy was chosen because of its ability to form metastable iQcs throughout the whole volume of the casting at cooling rates of approximately 500 °C/s [9]. The casting was cut in the region with the 5-mm diameter where the particle of stable iQc–AlCuFe

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Table 1
Chemical compositions of the alloys in at.% with corresponding experimental uncertainties.

Alloy	Al	Cu	Fe	Mn	Si
iQc–AlCuFe	62.6 ± 0.4	24.6 ± 0.3	12.8 ± 0.2	–	–
Al–Mn–Si	95.1 ± 0.3	–	–	3.9 ± 0.1	1.0 ± 0.1

phase was located. The samples for the electron microscopy and micro-analyses were prepared by grinding and final polishing with 0.05-μm grade colloidal silica.

A PANalytical X'Pert PRO X-ray diffractometer was used for the characterization of the phases. Non-monochromated X-rays, produced by the Cu-target tube (0.15418 nm), were used in the XRD experiments. A JEOL JSM-7600F field-emission-gun scanning electron microscope was used for the microstructural characterization. The elemental and micro-crystallographic analyses were performed using the Oxford Instruments INCA Microanalysis Suite, by energy-dispersive X-ray spectroscopy (EDS) with an X-Max 20 SDD detector and by electron backscatter diffraction (EBSD) with a Nordlys detector and CHANNEL5 software. The crystallinity and orientation of the phases were studied with the EBSD technique performed at 20 kV, while the composition of the alloys and the phases were determined with the EDS at 20 and 5 kV. An FEI HeliosNanolab 650 focused ion beam (FIB) was used to prepare the transmission electron microscopy (TEM) sample. Gallium ions were used in the preparation processes, which started with high-energy milling (30 keV) and ended with low-energy final polishing (2 keV) of the sample. A Jeol JEM-2100 transmission electron microscope equipped with a Gatan CCD camera ORIUS was used for the microstructure and the electron-diffraction characterization.

The phases present in the investigated materials were first determined by XRD, with the XRD patterns shown in Fig. 1.

The Al–Mn–Si alloy in the as-cast state contains the α–Al [18], α–AlMnSi [19] and iQc–AlMnSi [12,20] phases. The iQc–AlCuFe [10,21] bulk material contains only traces of β–AlCuFe [18].

Fig. 2a shows a back-scattered electron (BE) image of several iQc–AlCuFe particles scattered in the matrix of the Al–Mn–Si alloy casting. The large white iQc–AlCuFe particle is partly covered with a continuous layer of a grey phase that formed during the solidification. The composition of the layer determined by EDS at a 5-kV accelerating voltage revealed that it contains 79.7 ± 0.3 at.% Al, 16.5 ± 0.2 at.% Mn and 3.3 ± 0.2 at.% Si. This composition corresponds to the composition of the primary metastable iQc–AlMnSi phase in the Al–Mn–Si alloy [20,22].

Fig. 2b shows an EBSD pattern acquired from the iQc–AlCuFe particle, while EBSD pattern acquired from the thin continuous layer,

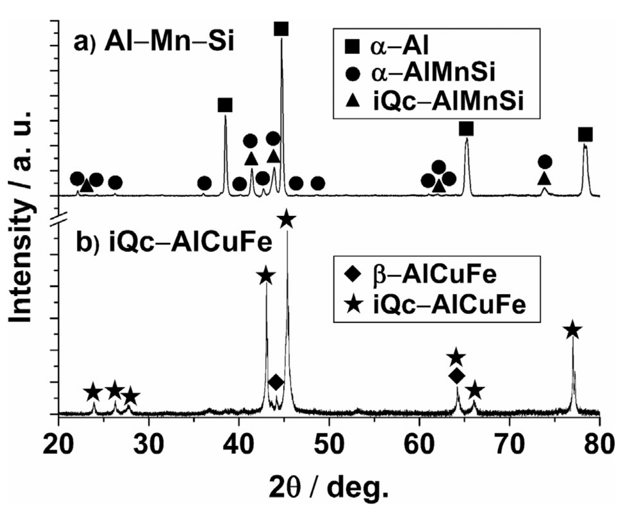

Fig. 1. a) XRD patterns of the as-cast Al–Mn–Si alloy (bulk sample) and b) iQc–AlCuFe powder after heat treatment at 800 °C for 24 h.

which formed on the iQc–AlCuFe particle during solidification of the Al–Mn–Si alloy is shown in Fig. 2c. Both EBSD patterns reveal the presence of 5-fold (white five-pointed star), 3-fold (white triangle) and 2-fold (white ellipse) symmetry axes characteristic for iQcs [23]. The EBSD patterns indicate that the 5-fold, 3-fold and 2-fold symmetry axes of both, the iQc–AlCuFe particle and the metastable iQc–AlMnSi layered phase, are parallel, indicating a coherent interface.

Detailed analysis of the interface region between the iQc–AlCuFe particle and a thin continuous layer of metastable iQc–AlMnSi phase was further investigated by means of TEM (Fig. 3).

Fig. 3a shows the bright-field TEM image of the iQc–AlCuFe particle covered with the layer of the iQc–AlMnSi in contact with α–Al matrix. The interface between both iQc phases (iQc–AlCuFe and iQc–AlMnSi), is free of any other phase, and reveals that the interface is indeed coherent. The iQc–AlMnSi phase has nucleated on the surface of the iQc–AlCuFe particle and grew into the surrounding melt. The interface between the iQc–AlMnSi phase and the α–Al matrix clearly indicates that the initially planar solidification front for iQc–AlMnSi phase broke down and first cells and dendritic branches started to form. Fig. 3b and c show the selected-area electron diffraction (SAED) patterns of the iQc–AlCuFe particle and the layer of iQc–AlMnSi phase, both acquired at the same orientation of the sample. The SAED patterns indicate that the direction of the incident beam is, in both cases, parallel to the 5-fold symmetry axis. It can be concluded that the 5-fold symmetry axes and the (110000) planes are parallel in both the iQc phases. This orientation relationship agrees with the one established using the EBSD technique.

The interplanar spacings for the (110000) planes in both the metastable iQc–AlMnSi and the stable iQc–AlCuFe phases were also measured using SAED patterns. The measured interplanar spacings were 0.2065 ± 0.01 nm for the iQc–AlMnSi phase and 0.2000 ± 0.01 nm for the iQc–AlCuFe phase. The measured values are in good agreement with the reported (110000) interplanar spacings, which are 0.2064 nm for the metastable $Al_{73}Mn_{14}Si$ iQc phase [20] and 0.2001 nm for the stable $Al_{65}Cu_{20}Fe_{15}$ iQc phase [5]. The misfit calculated from the measured interplanar spacings for the (110000) planes in the iQc–AlMnSi and iQc–AlCuFe phases is 3.3%, which agrees very well with the misfit calculated from the published interplanar spacings, i.e., 3.2% [5,20]. The results presented here support the hypothesis that the stable iQc–AlCuFe phase can serve as a substrate for the nucleation of metastable iQc–AlMnSi.

The main shortcoming associated with the stable iQc–AlCuFe phase to be used as a substrate for the nucleation of the metastable iQc–AlMnSi phase is that it is soluble in the Al-based melt. Fig. 2a indicates that the stable iQc–AlCuFe particle already started to dissolve with the formation of an uneven, curved surface (top right-hand surface of the iQc–AlCuFe in Fig. 2a) where Cu-rich structures formed. On the other hand, the composition of the iQc–AlMnSi thin layer (left-hand faceted surface of the iQc–AlCuFe in Fig. 2a) indicates that the dissolution of the stable iQc–AlCuFe particle in this region never took place, as no copper and iron were detected within this layer. The dissolution of the stable iQc–AlCuFe phase in an Al-alloy melt was already reported by Fleury et al. and Lee et al. [24,25].

As discussed in the ref. [5,26,27], 2-, 3- and 5-fold planes, differ in stability with the 5-fold plane being the most stable one. This has been shown by the studies of the dissolution rate of different planes in the Al–Cu–Fe iQc alloy [26]. We used geometry data acquired during the FIB preparation of the lamellae in Fig. 3a and a computer generated iQc model to create dissections. We then related those to our EBSD and SAED patterns in order to determine the nature of the surface where the iQc–AlMnSi grew. It has been established thus that the faceted surface that served as a substrate for the iQc–AlMnSi phase to grow on was the 5-fold plane. Regarding the uneven, curved surface in Fig. 2a and taking both, the Refs. [5,26,27] and the stereographic projection for iQc into account, we can conclude that the dissolved surface is less stable, and should represent 2- or 3-fold planes of the stable iQc–AlCuFe.