J Mater Sci (2010) 45:1438–1442
DOI 10.1007/s10853-009-4150-z

Interfacial reaction between $Al_{72}Ni_{12}Co_{16}$ decagonal quasicrystalline particles and liquid aluminium

Suling Cheng · Gencang Yang · Jincheng Wang ·
Feng Liu · Man Zhu · Yaohe Zhou

Received: 2 September 2009 / Accepted: 18 December 2009 / Published online: 5 January 2010

Abstract The interfacial reaction between $Al_{72}Ni_{12}Co_{16}$ quasicrystalline particles and pure Al melt at 670 °C was investigated. For all the studied samples, only one interfacial reaction product was detected at the interface by scanning electron microscopy. The product was identified to be the $Al_9(Co, Ni)_2$ crystalline phase, which show an rod-like morphology. The growth rate of the $Al_9(Co, Ni)_2$ phase layer is very fast. Based on the microstructure analysis results, it is proposed that the layer growth is initially towards the liquid phase, but changes direction towards the quasicrystalline phase by the solid state reaction of diffusional Al with the quasicrystalline phase at the $Al_{72}Ni_{12}Co_{16}/Al_9(Co, Ni)_2$ interface. A grain boundary grooving effect is deduced to have been involved during the reaction process.

Introduction

To explore the practical applications of quasicrystal (QC) in structural materials, some efforts were recently initiated by several research groups to use QC (Al–Cu–Fe) as the particle reinforcement for Al matrix composites (AMCs) [1–4]. As the coexistence of quasicrystalline phase with Al phase in the corresponding equilibrium phase diagram has not been found yet, the QC was introduced to Al matrix mainly by mechanical alloying and powder metallurgy methods. Effort was also initiated by Lee et al. [2] to develop Al–Cu–Fe quasicrystalline particle (QCP)-reinforced AMC using conventional casting method. Unfortunately, the volume fractions of the quasicrystalline phase in the Al–Cu–Fe particles decreased accompanied with the dissolution of small particles [2]. Actually, diffusion reactions between the QCPs and Al matrix are inevitable even in a solid/solid state at high temperatures [1, 4].

In Ref. [5], we have reported an Al–Ni–Co intermetallic-reinforced AMC fabricated by adding $Al_{72}Ni_{12}Co_{16}$ QCPs into a pure Al matrix using a stir-casting method. It was found that the $Al_{72}Ni_{12}Co_{16}$ quasicrystalline phase transformed completely to the $Al_9(Co, Ni)_2$ crystalline phase in a very short time during the casting process. The particle size of the $Al_9(Co, Ni)_2$ phase is much smaller than that of the original QCPs. However, the detailed interfacial reaction process between the particles and the Al melt, and the formation process of the composite microstructure have not been presented in that article. Also, the study of the interfacial reaction between single-phase QCPs and molten metal has not been found in a survey of the literature.

Therefore, the present study aims to study the interfacial reaction between the $Al_{72}Ni_{12}Co_{16}$ single-phase QCPs and pure Al melt concerning the morphology and growth of the interfacial reaction product. Based on the experimental results, the microstructure formation mechanism of the Al–Ni–Co intermetallic-reinforced AMC reported in Ref. [5] was also explained. The study may provide additional information of the mechanism of intermetallics/molten metal interfacial reactions and interfacial compound growth.

Experimental procedure

The quasicrystalline alloy with the nominal composition of $Al_{72}Ni_{12}Co_{16}$ was prepared by melting industrial pure elements in an induction furnace under the protection of Ar

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S. Cheng (✉) · G. Yang · J. Wang · F. Liu · M. Zhu · Y. Zhou
State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, 710072 Xi'an, China
e-mail: chengsuling@163.com

atmosphere [5]. Scanning electron microscopy (SEM), X-ray diffraction, and selected area diffraction analysis showed that the as-cast ingot consists of a single decagonal quasicrystalline phase. The ingot was then crushed and sieved. To prepare an infinite reaction system, big size particles (1–3 mm) were selected. Commercial pure Al (99.8%) was used as the matrix. The particles were added to the Al melt at 670 °C (a temperature slightly higher than the melting point of pure Al), stirred to promote wetting and dispersing, and poured immediately in a copper mould to avoid excessive reaction (the whole process does not exceed 10 s). The microstructures and phase compositions of the interfacial zone were analysed by SEM and energy dispersive spectroscopy (EDS), respectively.

Results and discussion

Interfacial morphology

Figures 1a–c show backscattered electron images of three types of interfacial characteristics found along each individual QCP embedded in the Al matrix. They are wetted interface without interfacial reaction product (Fig. 1a), wetted interface with scattered interfacial reaction product (Fig. 1b) and a relatively continuous interfacial layer composed of rod-like grains with Al phase in the grain boundaries (Fig. 1c). The interfacial layer in Fig. 1c has a thickness up to 20 μm. The different amounts of the product should be due to the surface situation differences of the QCPs, such as surface contaminant, which can affect the wetting and interfacial reaction process. For all the samples, only one interfacial reaction product was detected using SEM, and it was determined to be the $Al_9(Co, Ni)_2$ phase by EDS analysis combined with the Al–Ni–Co phase diagram analysis [5]. There is also eutectic phase formed in the Al matrix, which is due to the dissolution of the QCPs or the $Al_9(Co, Ni)_2$ phase and formed during the solidification process of the matrix according to the Al-rich Al–Ni–Co phase diagram [6].

To review the three-dimensional morphology of the $Al_9(Co, Ni)_2$ phase, Al matrix was eliminated by a deep etching method. A typical appearance of the $Al_9(Co, Ni)_2$ phase is shown in Fig. 2. It can be seen that the $Al_9(Co, Ni)_2$ phase seems to grow from the QCP's surface with a rod-like morphology. There are many coarse rods due to

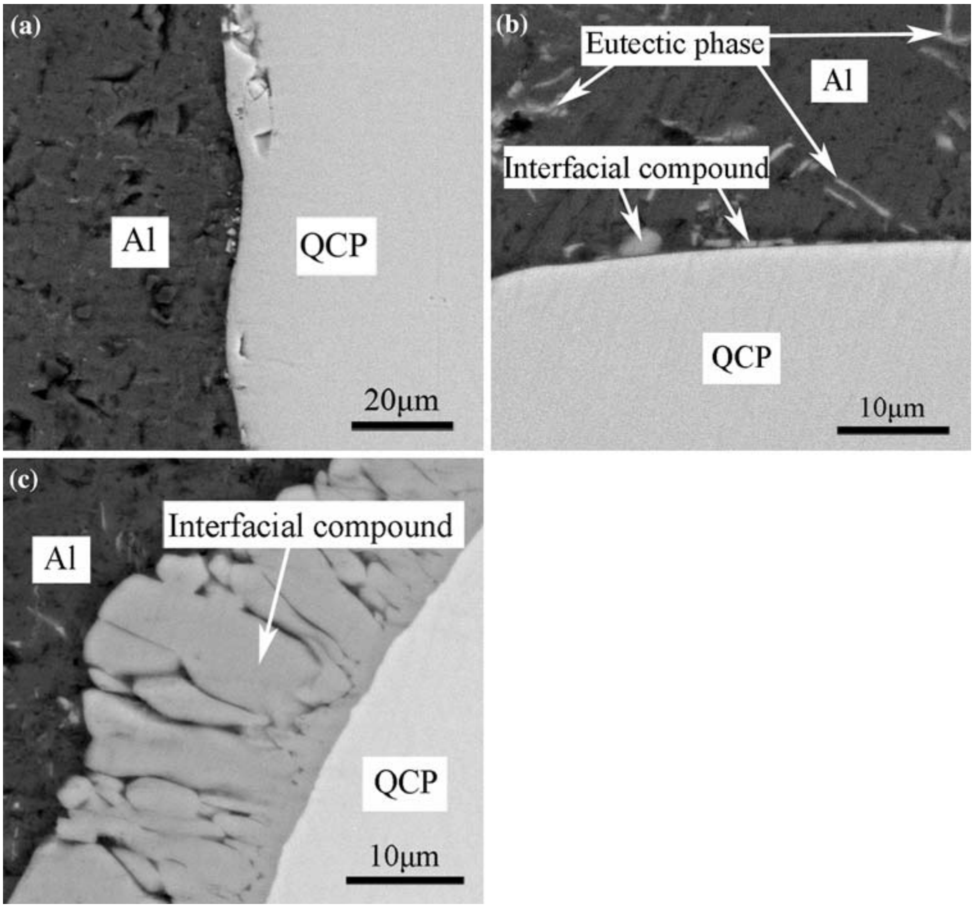

Fig. 1 Backscattered electron (BSE) images of the interfacial zone of $Al/Al_{72}Ni_{12}Co_{16}$ QCP formed by reacted at 670 °C for 10 s: **a** wetted interface without interfacial reaction; **b** wetted interface with scattered interfacial reaction product; **c** a relatively continuous interfacial layer composed of rod-like grains with Al phase in the grain boundaries

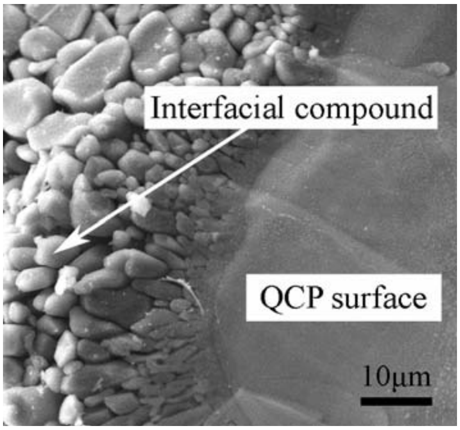

Fig. 2 Scanning electron microscope image showing three-dimensional morphology of the $Al_9(Co, Ni)_2$ compound on the QCP's surface

growth and ripening effect and also slim rods, which are newly growing from the QCP's surface.

Reaction rate

The thickening of the interfacial layer with reaction time at 670 °C was studied. The average thicknesses of the layer with standard deviations as a function of reaction time are plotted in Fig. 3. It can be seen from the figure that the reaction rate between the QCPs and Al melt is very fast. In a very short reaction time (30 s) at 670 °C, the thickness of the interfacial layer reached to an average value of 90 μm. In other words, particles with a size less than 180 μm can hardly preserve its decagonal quasicrystalline structure, when it is dispersed into Al matrix using conventional casting method with the operation time exceeds 30 s due to the rapid reaction rate. As a result, the $Al_{72}Ni_{12}Co_{16}$ QCPs with a size range of 100–150 μm have reacted completely with the Al melt as reported in Ref. [5], since the reaction time was longer than 30 s and the processing temperature was higher than 670 °C. In addition, the stirring operation during the fabrication process should also have accelerated the reaction process.

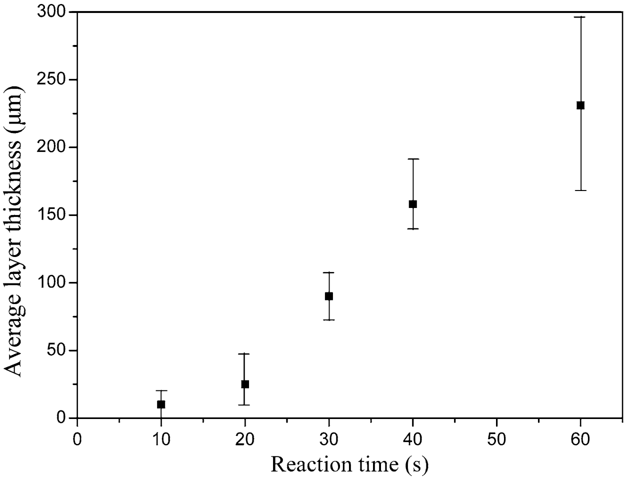

Fig. 3 Interfacial compound layer thickness of $Al/Al_{72}Ni_{12}Co_{16}$ QCP reacted at 670 °C versus reaction time

The reaction rate of $Al/Al_{72}Ni_{12}Co_{16}$ QCPs system is considerably fast when compared with other Al/metal or Al/intermetallic compound reaction systems in liquid/solid state, such as Al/Ni [7] and $Al/Ni_{73}Al_{23}B_1Zr_1$ [8]. In the Al/Ni reaction system, it was reported that the interfacial layer thickness is below 30 μm after annealed at 750 °C for 25 min [7]. It was found by Varin et al. [8] that several layers has formed at the $Al/Ni_{73}Al_{23}B_1Zr_1$ interface and their overall thickness are only about 20, 24 and 57 μm, when casting temperatures are 700, 715 and 730 °C (the stirring time was about 2–3 min), respectively. The reason for the rapid growth of the interfacial layer in the present study is unclear. The distinct atomic structure of the $Al_{72}Ni_{12}Co_{16}$ quasicrystalline phase should be the main reason because it may result in rapid dissolution into Al melt and rapid reaction with Al to form the $Al_9(Co, Ni)_2$ phase. Gähler and Hocker [9] has studied the atomic dynamics of Al–Ni–Co decagonal QCs by molecular dynamics simulations. They found that above about $0.6T_m$ (T_m is the melting temperature), a large fraction of the Al atoms become very mobile, which leads to a high Al diffusivity, comparable to that of vacancy diffusion in fcc Al. It has been pointed out that this must be due to the particular (local) structure of the QC. We have measured the melting temperature of $Al_{72}Ni_{12}Co_{16}$ QC by differential thermal analysis as 1,098 °C, so $0.6T_m = 660$ °C, which is below the experimental temperature used in the present study. In other words, in the experimental temperature (670 °C), the diffusivity of the Al atoms in $Al_{72}Ni_{12}Co_{16}$ QC is very fast, which may have led to the fast interfacial reaction.

Reaction mechanism

Figure 4 shows a reaction zone formed after reacted at 670 °C for 30 s. Some coarse rods look broken off from the substrate (see white arrows in Fig. 4). The root of some rods are slim (see black arrow in Fig. 4), which may be due to the grooving effect as detailedly described in Ref. [10].

Adopting the EDS point analysis, the composition gradients in the reaction layer and inside the QCP were analysed. The locations of the electron beam during the EDS analysis and the corresponding point composition (Al–Co–Ni at.%) are shown in Fig. 5. It is found that there is no composition gradient exists inside the $Al_{72}Ni_{12}Co_{16}$ QCPs. While in the reaction layer, the Co:Ni ratio slightly increases with increasing distance from $Al_{72}Ni_{12}Co_{16}/Al_9(Co, Ni)_2$ interface, while the Al content is relatively

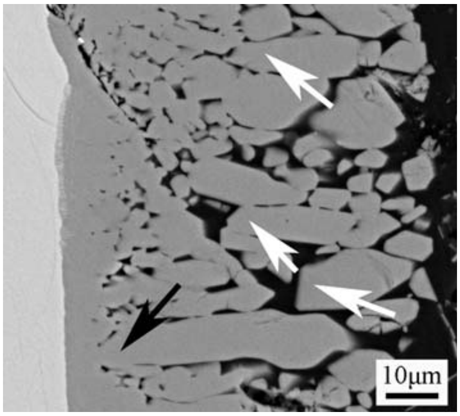

Fig. 4 BSE images of the reaction zone of Al/$Al_{72}Ni_{12}Co_{16}$ QCP formed at 670 °C for 30 s

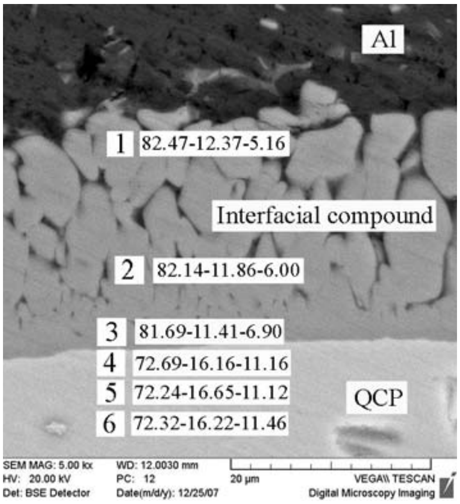

Fig. 5 The locations of the electron beam during the EDS analysis and the corresponding point composition (Al–Co–Ni at.%)

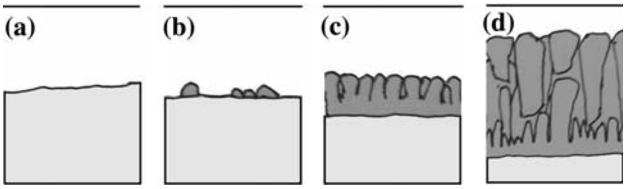

Fig. 6 Schematic illustration of the reaction process of Al/$Al_{72}Ni_{12}Co_{16}$ QCP

constant. According to Ref. [6], the solubility of Ni in the Al_9Co_2 phase is extensive and the replacement of Co by Ni proceeds atom for atom up to about 13 at.%. In the present experiment, the content of Ni in the $Al_9(Co, Ni)_2$ phase is in the range of 4–6.90 at.%. The composition analysis results indicate that there is no element diffusion inside the inner QCP. Al atoms diffuse mainly through the channels between the $Al_9(Co, Ni)_2$ grains, while Ni atoms through both $Al_9(Co, Ni)_2$ grains and the channels.

From the results of the microstructural analysis described above, the reaction process of Al/$Al_{72}Ni_{12}Co_{16}$ QCPs system is proposed as follows, and the process is schematically shown in Fig. 6. First, the QCPs dissolve into the liquid Al rapidly after the wetting process (Fig. 6a). A Co, Ni-enrichment zone around each QCP is thus produced, from which $Al_9(Co, Ni)_2$ particles precipitate by nucleate on the QCPs' surface (Fig. 6b). The particles continuously form and growth and produce a continuous reaction layer, which grows into the Al solution (Fig. 6c). Maybe due to the grooving effect [10] or reaction stress [11], the roots of some coarse rods are dissolved or fractured and the rods departed from the substrate. The departed rods are forced away by newly formed rods or swept away by the liquid (Fig. 6d). After the continuous reaction layer was formed, if the interfacial layer keeps on growing into the liquid phase, the element Ni and Co should diffuse through the interfacial layer to feed the growth and Kirkendall voids should present at QCP/$Al_9(Co, Ni)_2$ interface. However, we cannot find any voids at the interface. Besides, we found that during the reaction process the QCP cores was becoming smaller and smaller. So, the layer growth after the formation of a continuous interfacial layer is manly by the diffusion of Al across the interfacial layer and react with the QCP at QCP/$Al_9(Co, Ni)_2$ interface:

$$Al_{72}Ni_{12}Co_{16} + Al_{\text{diffusing}} \rightarrow Al_9(Co, Ni)_2 + Ni. \qquad (1)$$

The excessive Ni atoms diffuse through the interfacial layer or the grooves between the rod-like grains to dissolve into the liquid Al.

It is reasonable to expect that the interfacial layer formed by the reaction between diffusional Al and the QCPs at QCP/$Al_9(Co, Ni)_2$ interface should be a dense layer. However, the interfacial compound keeps its rod-like morphology as shown in Fig. 4. This can be attributed to the grain boundary grooving effect. Ma et al. [12] has made an effort to elucidate the mechanism of non-planar interfacial layer formation at solder/Cu interface in liquid/solid state. They found that an initially planar interfacial layer formed during solid/solid reaction transformed to a non-planar morphology when the reaction system was heated to an elevated temperature (in which the solder was melted) and explained it as owing to a thermal grooving process. In the present study, the inner layer formed by reaction of diffusional Al with QCP does not exhibit a planar and dense layer structure may also be explained by the grooving effect.

During the growth and ripening process of the $Al_9(Co, Ni)_2$ rods, if a stirring process is imposed, the $Al_9(Co, Ni)_2$ rods should be broken and the fragment dispersed uniformly into the Al matrix by the stirring effect. This can explain the formation process of the microstructure of the Al–Ni–Co intermetallic-reinforced AMC reported in Ref. [5].

Conclusions

The interfacial reaction between the $Al_{72}Ni_{12}Co_{16}$ QCPs and liquid Al are experimentally investigated and the following conclusions can be drawn.

1. In all the studied samples, only one interfacial reaction product was detected at $Al/Al_{72}Ni_{12}Co_{16}$ interface by SEM. The reaction product was identified to be the crystalline phase $Al_9(Co, Ni)_2$ and showed an rod-like morphology. The growth rate of the $Al_9(Co, Ni)_2$ phase at $Al/Al_{72}Ni_{12}Co_{16}$ interface is very fast when compared to that of other interfacial compound at Al/metal or Al/intermetallic compound interfacial reaction systems reported by other researchers.
2. Based on the microstructure analysis results, the reaction can be described as: after the wetting process, the QCPs dissolve into the liquid Al. The $Al_9(Co, Ni)_2$ phase nucleate on the QCPs' surface and grow. After a continuous interfacial layer is formed, the layer growth changes direction towards the QCP phase. The interfacial layer keeps its rod-like morphology by a grain boundary grooving process.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant No. 50571081) and the Aviation Foundation of China (Grant No. 04G53024).

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