Development of an Al–Mn–Be–Cu alloy with improved quasicrystalline forming ability

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Abstract. An Al₉₄Mn₂Be₂Cu₂ cast alloy was developed displaying increased quasicrystalline formation ability at moderate cooling rates. The as-cast microstructure consisted of a mainly icosahedral phase in the Al-matrix. The microstructure remained stable during uniform heating to 580 °C and isothermal annealing at 400 °C. Most of the icosahedral phase was preserved even after 24 h annealing at 500 °C. For that reason, this alloy presents a promising basis for further development of cast Al-alloys containing quasicrystals.

Introduction

Quasicrystals form an additional state of matter to those of crystalline and glassy. The atoms positions are ordered but with non-crystallographic rotational symmetry and without three-dimensional periodicity [1]. The first icosahedral quasicrystal (*i*-phase) was identified in the melt-spun Al–Mn alloys [2]. It was discovered to be metastable since *i*-phase transformed to crystalline *o*-Al₆Mn at temperatures above 400 °C [3]. Furthermore, it was not formed by casting into metallic dies, but instead formed thermodynamically stable *o*-Al₆Mn [4]. However, by using different methods of conventional casting, *i*-phase was found in some ternary and quaternary alloys based on the Al–Mn system, as well as in some other systems. Yet, considerable amounts of crystalline intermetallic phases were also observed [4–12] (Table 1).

The aim of our study was to develop alloys consisting of *i*-phase in Al-rich solid solution matrix (α -Al). The *i*-phase should form at those moderate cooling rates typical for conventional die casting, should have an appropriate volume fraction and be uniformly distributed in α -Al. In addition, the volume fraction of crystalline intermetallic compounds should be as small as possible. In principle,

alloying additions should increase quasicrystalline forming ability and prevent the formation and growth of crystalline intermetallic compounds.

Selection of alloying elements

For this purpose we selected an Al–Mn icosahedral forming system as a starting point. It is known [13] that *i*-phase may form at a Mn content as low as 2.5 at%. We decided to even decrease the Mn content to 2 at% in order to further lower the liquidus temperature and as a consequence also reduce the potential for forming the stable *o*-Al₆Mn-phase. The Be was selected as a third element, since it proved to considerably increase the quasicrystalline forming ability [4, 8–12] when added to Al–Mn alloys. In all investigated alloys Be-content has been rather high, therefore it was not only present in the *i*-phase, but always formed stable ternary compounds with Al and Mn. In order to reduce the potential for forming these ternary compounds, the content of Be was reduced to 2 at%, which is slightly below the eutectic point in the binary Al–Be system (2.4 at% Be at 644 °C, [14]). The criteria for selecting the fourth element were:

- low tendency for the formation of stable intermetallic compounds with Al, Mn and Be
- possibility of incorporating into the *i*-phase to increase its stability
- appropriate solubility in Al in order to enable tuning of the strength-to-ductility ratio by subsequent heat treatment
- possibility for enhancing the thermal stability of the *i*-phase

Amongst several elements taken into account, Cu was selected because it definitely fulfils criteria 1 and 3. It is also known to be present in several quasicrystalline phases in Al-alloys (*e.g.* Al–Cu–Fe), and Cu was an alloying element in high ductility nanoquasicrystalline alloys [15]. The content of Cu was chosen to be 2 at%, just below the maximum equilibrium solubility of Cu in Al (2.4 at% Cu at 548.2 °C [14]).

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Table 1. Phase composition of cast Al-alloys in which *i*-phase was observed.

Alloy	Casting method	Phase composition	Reference
Al ₉₁ Mn ₇ Fe ₂ Al ₉₂ Mn ₆ Ce ₂	centrifugal casting	α -Al, <i>i</i> -phase, Al ₆ Mn Al ₁₀ Mn ₇ Ce ₂ , Al ₆ Mn, Al ₄ Ce, α -Al, <i>i</i> -phase	[5]
Al ₈₀ Pd ₁₅ Mn ₅ , Al ₉₀ Pd ₈ Mn ₂		α -Al, <i>i</i> -phase, Al ₃ Pd	
Al ₉₂ Fe ₃ Cr ₂ Mn ₃	wedge casting	Al _{75.7} Cr _{8.2} Mn _{8.4} Fe _{7.7} Al _{75.7} Cr _{8.2} Mn _{8.4} Fe _{7.7}	[6]
	centrifugal casting	α -Al, Al ₆ Mn, Al ₁₂ (Cr,Mn)	
Al ₉₃ Fe ₃ Cr ₂ Ti ₂	suction casting	α -Al, Al ₁₃ (Fe, Cr), Al ₃ Ti, <i>i</i> -phase	[7]
Al ₉₀ Mn _{2.5} Be _{7.5} , Al _{79.9} Mn _{13.5} Be _{6.6} , Al ₉₃ Mn _{2.5} Be _{4.5} , Al ₈₀ Mn _{13.5} Be _{6.5} Al ₈₃ Mn ₆ Be ₁₁	conventional casting injection moulding cone shape die	α , <i>i</i> -phase, hexagonal approximants	[4], [8], [9], [10], [11]
Al _{79.9} Mn ₁₃ SiBe ₆	conventional casting	α -Al, <i>i</i> -phase, α -Al-Mn-Si 1/1 cubic approximant	[12]

Table 2. Chemical composition of the investigated alloy after die casting (ICP).

	Al	Mn	Be	Cu
mass%	90.64	4.24	0.68	4.44
at%	93.78	2.15	2.11	1.95

Experimental

As a result of the selection process, the designed alloy Al₉₄Mn₂Be₂Cu₂ was prepared from pure Cu (99.99%), Mn (99%), Al (99.89%) and master alloy AlBe₅ (AFM Affilips) by vacuum induction melting and casting into bars with 50 mm diameter. The bars were sectioned, remelted and cast into rectangular copper die (100 mm × 10 mm × 1 mm). The chemical composition of the alloy after the casting was determined by ICP–AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy), and is given in Table 2.

The specimens for the SEM (FEI, Sirion 400 NC) were prepared using conventional metallographic techniques. In addition, methods were used for deep etching and particle extraction. Specimens for TEM were prepared by focussed ion beam (FIB), extraction of particles and ion milling. Transmission electron microscopy (TEM) was carried-out on a Philips CM20 and a FEI Titan 80–300. Energy dispersive spectroscopy (EDS) was carried-out both in SEM and TEM. Electron energy-loss spectroscopy (EELS), energy-filtering TEM (EFTEM) and high-resolution transmission electron microscopy (HRTEM) was done on an FEI Technai F20. X-ray diffraction (XRD) was carried out at XRD1-beamline (Elettra, Sinchrotrone Trieste, Italy) using X-rays with a wavelength of 0.1 nm in the transmission mode.

Results and discussion

Figure 1a shows the microstructure of Al₉₄Mn₂Be₂Cu₂ alloy after casting into the copper die. It consisted mainly of three phases: α -Al, *i*-phase and Al₂Cu. The primary *i*-phase was present mainly in the form of well developed dendrites (Fig. 1). The symmetry of the primary *i*-phase

already inferred their icosahedral structure, whereas their twofold diffraction patterns indicated that their structure corresponded to the primitive one. The EDS-analysis confirmed that it contained Al, Mn, and only around 2.5 at% Cu, which is slightly more than the average Cu content in the alloy. The *i*-phase was also part of two-phase eutectic cells (α -Al plus *i*-phase). Extraction of particles clearly revealed the rodlike structure of the eutectic *i*-phase (Fig. 2). The rods evolved from a common centre and, as the distance from the centre increased, frequent branching occurred in order to keep the distance between branches as constant as possible. Detailed TEM analysis of the eutectic *i*-phase showed that the whole rodlike structure is

Fig. 1. Microstructure of the alloy Al₉₄Mn₂Be₂Cu₂ in the as-cast condition. (a) Backscattered electron micrograph showing primary *i*-phase, two-phase (*i*-phase + α -Al) and (α -Al + Al₂Cu) eutectics. (b) Secondary electron micrograph of extracted primary *i*-phase, rod-like eutectic *i*-phase and eutectic Al₂Cu phase.

Fig. 2. Micrographs of (a) extracted eutectic *i*-phase, (b) selected area diffraction patterns taken along a fivefold axis, at position 1 indicated in (a). Arrows indicate the rotation direction of the diffraction patterns, when moving from point 1 to 2.

a monoquasicrystal because no sharp orientation changes were observed, not even at positions where branching took place. This indicated that branching did not occur by *e.g.* twinning, which is typical for the Si phase in the Al–Si eutectic, but growth direction can be quickly changed to one of the other preferred directions due to the very high symmetry of the icosahedral phase. Furthermore, it was observed that orientation was changing uniformly along each rod. A rotation of 2.7° around a fivefold zone axis took place when moving from position 1 to position 2. This kind of lattice rotation might indicate the presence of quasilattice defects, such as phason strains [16]. This was confirmed by peer examination of the diffraction patterns since many diffraction spots were deflected from their ideal positions (especially weaker ones), and the shapes of some spots showed strong anisotropy. EDS in TEM and SEM, and EFTEM showed the *i*-phase contained Al, Mn, Be and Cu, similar to the primary *i*-phase's composition. Al/Mn ratio was ≈ 3.5 , which is almost the same as in the ternary Al–Mn–Be alloys [11]. On the other hand, the ratio Al/Cu was approximately 30 indicating an important content of Cu in the *i*-phase. Al_2Cu was present mainly between (*i*-phase + α -Al) cells.

Fig. 3. Microstructure of the alloy $\text{Al}_{94}\text{Mn}_2\text{Be}_2\text{Cu}_2$ after annealing for 3 h at 500°C . (a) Secondary electron micrograph showing spheroidal primary *i*-phase covered with a new phase, (b) secondary electron micrograph of the region between primary *i*-phase, showing eutectic *i*-phase particles and needle-like precipitates in α -Al.

The low tendency to form intermetallic compounds reflected itself in as low liquidus temperature as $\approx 650^\circ\text{C}$ (DSC analysis with 10°C/s heating and cooling rates). For example, the typical quasicrystalline alloy $\text{Al}_{86}\text{Mn}_{14}$ has liquidus temperature of $\approx 900^\circ\text{C}$ and the alloy $\text{Al}_{98}\text{Mn}_2$ of 690°C . Alloying with Be and Cu additionally lowers the liquidus temperature. It was suggested [8] that Be atoms stabilize icosahedral configuration in the liquid state. This leads, combined with the decreasing driving force for the formation and perhaps also growth of competitive crystalline compounds by the addition of Cu, to adequate melt undercooling favouring the formation and growth of the *i*-phase. The as-cast microstructure indicated that solidification took place in a similar manner as in a binary eutectic system with hypereutectic composition. In this case, primary solidification starts with the formation and growth of the *i*-phase, followed by the eutectic solidification: coupled growth of the *i*-phase and α -Al. As a result of low partition coefficient of Cu (much less Cu in α -Al than in the liquid phase) and non-equilibrium solidification, the remaining melt becomes enriched with Cu. Therefore the solidification of the last liquid takes place in a similar way as in the binary Al–Cu system with the eutectic reaction ($\text{L} \rightarrow \text{Al}_2\text{Cu} + \alpha\text{-Al}$). Taking into account that the investigated system is not a binary one but quaternary, solubility product for the formation of some other compounds may be exceeded, leading to their formation in the remaining melt pool.

Neither isothermal annealing of the alloy at 300°C and 400°C for 1 hour nor the uniform heating up to 580°C and cooling at rate of temperature decrease 10°C/min resulted in any visible microstructural changes. Most of

i-phase was preserved even after 24 h annealing at 500 °C. During annealing coarsening of the primary *i*-phase dendrite branches took place and *i*-phase obtained more spherical shape (Fig. 3a). EDS in SEM showed that the content of Cu in the *i*-phase increased (ratios Al/Mn and Al/Cu was 3.6 and 8, respectively). Darker phase appeared within the primary *i*-phase and at the interface of the primary *i*-phase with α -Al. It contained much higher amount of Cu than the *i*-phase, and its darker appearance in the backscattered electron image strongly indicated that it contained substantial amount of Be. XRD results pointed-out the presence of CuBe-phase, however additional research is needed to confirm this completely. The morphology of the eutectic *i*-phase changed completely; branched rods transformed to faceted particles with diameters of 500–1000 nm (Fig. 3a) probably due to Rayleigh instability and Ostwald coarsening. Al₂Cu phase present in the as-cast condition dissolved completely. Within α -Al needle-like precipitates appeared with lengths from 1 to 2 μ m and a diameter of 100 nm (Fig. 3b).

Conclusions

By the appropriate selection of alloying elements and their contents it was possible to reduce the tendency of forming crystalline intermetallic compounds and to increase the quasicrystalline forming ability. The icosahedral phase (*i*-phase) was present in the form of dendritic particles and as part of eutectic (rodlike *i*-phase and α -Al). It contained all alloying elements. During annealing at 500 °C there was a morphology change of the rod-like eutectic *i*-phase to individual particles, whilst on the other hand the primary dendritic *i*-phase obtained a more spherical shape. The content of Cu in the *i*-phase increased and a small amount of phase rich in Cu and Be formed within the *i*-phase and at *i*-phase/ α -Al interface. The θ -Al₂Cu phase dissolved completely during annealing and Cu in α -Al presented the possibility for tuning strength-to-ductility ratio by further heat treatment. The alloy Al₉₄Mn₂Be₂Cu₂ represents a promising platform for the further development of cast Al-alloys containing quasicrystals and, therefore, new materials with interesting combinations of properties.

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References

- [1] Divinski, S.V.: On the possible types of quasicrystal structures. *Scripta mater.* **34** (1996) 1351–1355.
- [2] Shechtman, D.; Blech, I.; Gratias, D.; Cahn, J. W.: A Metallic Phase with Long-Range Orientation Order and No Translation Symmetry. *Phys. Rev. Lett.* **53** (1984) 1951–1953.
- [3] Vojtech, D.; Saksl, K.; Werner, J.; Bartova, B.: Structural evolution of rapidly solidified Al–Mn and Al–Mn–Sr alloys. *Materials Science and Engineering A* **428** (2006) 188–195.
- [4] Song, G. S.; Fleury, E.; Kim, S. H.; Kim, W. T.; Kim, D. H.: Enhancement of the quasicrystal-forming ability in Al-based alloys by Be-addition. *Journal of Alloys and Compounds* **342** (2002) 251–255.
- [5] Schurack, F.; Eckert, J.; Schultz, L.: Synthesis and mechanical properties of cast quasicrystal-reinforced Al-alloys. *Acta mater.* **49** (2001) 1351–1361.
- [6] Triveno Rios, C.; Bolfarini, C.; Botta, F. W. J.; Kiminami, C. S.: Rapidly solidified Al₉₂Fe₃Cr₂Mn₃ alloy. *Materials Science and Engineering A* **449–451** (2007) 1057–1061.
- [7] Kim, C. B.; Xu, W.; Fornut, M.; Stoica, M.; Calin, M.; Yi, S.; Lee, W. H.; Eckert, J.: Formation of icosahedral phase in an Al₉₃Fe₃Cr₂Ti₂ bulk alloy. *Journal of Alloys and Compounds* **436** (2007) L1–L4.
- [8] Kim, S. H.; Song, G. S.; Fleury, E.; Chattopadhyay, K.; Kim, W. T.; Kim, D. H.: Icosahedral quasicrystalline and hexagonal approximant phases in the Al–Mn–Be alloy system. *Philosophical Magazine A* **82** (2002) 1495–1508.
- [9] Chang, H. J.; Fleury, E.; Song, G. S.; Kim, W. T.; Kim, D. H.: Formation of quasicrystalline phases in Al-rich Al–Mn–Be alloys. *J Non-cryst solids* **334** (2004) 12–16.
- [10] Song, G. S.; Fleury, E.; Kim, S. H.; Kim, W. T.; Kim, D. H.: Formation and stability of quasicrystalline and hexagonal approximant phases in an Al–Mn–Be alloy. *J. Mater. Res.* **17** (2002) 1671–1677.
- [11] Bončina, T.: Master Degree Thesis, University of Ljubljana, Slovenia 2006.
- [12] Chang, H. J.; Fleury, E.; Song, G. S.; Lee, M. H.; Kim, W. T.; Kim, D. H.: Microstructure modification and quasicrystalline phase formation in Al–Mn–Si–Be cast alloys. *Materials Science and Engineering A* **375–377** (2004) 992–997.
- [13] Saksl, K.; Vojtech, D.; Franz, H.: Quasicrystal-crystal structural transformation in Al-5 wt% Mn alloy. *J Mater Sci* **42** (2007) 7198–7201.
- [14] Massalski, T. B. (Ed.): *Binary Alloy Phase Diagrams*, Second Edition, ASM International, 1990.
- [15] Inoue, A.; Kimura, H.: Fabrication and mechanical properties of bulk amorphous, nanocrystalline, nanoquasicrystalline alloys in aluminium based system. *Journal of Light Metals* **1** (2001) 31–41.
- [16] Tsai, A.-P.; Inoue, A.; Masumoto, T.: Phason strains on growth, stability and structure of icosahedral phases. *Prog. Crystal Growth and Charact.* **34** (1997) 221–236.