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THERMAL STABILITY OF Al-Mn-Be MELT-SPUN RIBBONS

TEMPERATURNA OBSTOJNOST HITRO STRJENIH TRAKOV Al-Mn-Be

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As with other kinds of finely dispersed, small particles, icosahedral quasicrystals (IQCs) also have a distinct strengthening effect, which can be utilised to enhance the mechanical properties of aluminium alloys. In Al–Mn–Be alloys, IQCs already form at moderate cooling rates, which can be utilised when using some conventional casting processes, like mould or injection casting. In this case, however, crystalline intermetallic phases are also present and the mechanical properties are inferior to those of two-phase α_{Al}-IQC alloys. Two-phase microstructures are feasible using rapid solidification techniques, e.g., melt spinning. Further processing often involves technologies (consolidation, extrusion etc.), which include the influence of heat. The alloy must not be overheated in order to preserve the strengthening effect of the metastable IQC-particles.

In this investigation the Al-Mn-Be alloy was melt-spun using a free-jet melt spinner. Subsequently, the thermal stability of the IQCs was explored by annealing the ribbons for 24 h at different temperatures. The samples were examined in the as-cast and heat-treated conditions using a dual-beam, scanning electron microscope (SEM-FIB), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). It was discovered that in the as-cast condition, the ribbons had a two-phase microstructure, consisting of an α_{Al} matrix and finely dispersed IQCs. During annealing at temperatures up to 400 °C, the IQCs did not decompose and the phase composition remained unchanged. Annealing at 500 °C and at higher temperatures caused a decomposition of the IQCs, and only the crystalline intermetallic phases Al_6Mn and Be_4AlMn could be found in the α_{Al} matrix.

Keywords: quasicrystal, Al-Mn-Be alloy, thermal stability

Ikozaedrični kvazikristali (IQC) imajo kakor druge vrste fino razpršenih drobnih delcev utrjevalni učinek, ki ga lahko izkoristimo za povečanje trdnosti aluminijevih zlitin. V zlitinah Al-Mn-Be kvazikristali nastajajo že pri zmernih ohlajevalnih hitrostih, kakršne dosežemo pri postopkih litja, kot sta npr. kokilno litje in tlačno litje. Toda mikrostruktura, ki nastane pri teh postopkih litja, vsebuje tudi kristalne intermetalne faze in trdnostne lastnosti so slabše kot pri zlitinah z dvofazno mikrostrukturo (α_{Al}-IQC). Dvofazno mikrostrukturo pa lahko dosežemo le z velikimi ohlajevalnimi hitrostmi, tj. s postopki hitrega strjevanja. Nadaljnja predelava hitro strjenih materialov pogosto poteka s postopki (kompaktiranje, iztiskovanje itd.), ki zahtevajo segrevanje. Pri tem materiala ne smemo pregreti, če želimo ohraniti utrjevalni učinek kvazikristalov.

V okviru te raziskave so bili uliti hitro strjeni trakovi Al-Mn-Be s postopkom prostega litja na vrteče se kolo (angl.: melt spinning). Temperaturno obstojnost trakov hitro strjene zlitine smo ugotavljali z žarjenjem 24 h pri različnih temperaturah. Mikrostrukture trakov smo analizirali v litem stanju in po toplotni obdelavi z vrstičnim elektronskim mikroskopom z elektronskim in ionskim curkom (SEM-FIB), rentgensko difrakcijo (XRD) in z diferenčno dinamično kalorimetrijo (DSC). Trakovi so imeli v litem stanju dvofazno mikrostrukturo, sestavljeno iz matice α_{Al} in fino dispergiranih kvazikristalov. Žarjenje pri temperaturah do 400 °C ni povzročilo razpada kvazikristalov in fazna sestava je ostala nespremenjena. Po žarjenju pri 500 °C ali višjih temperaturah pa je bila mikrostruktura sestavljena iz matice α_{Al} in kristalnih intermetalnih faz Al_6Mn ter Be_4AlMn.

Ključne besede: kvazikristal, zlitina Al-Mn-Be, temperaturna obstojnost

1 INTRODUCTION

The existence of icosahedral quasicrystals (IQCs or i-phase) was discovered by Schechtman et al. in melt-spun Al-Mn alloys[1]. Later, the possibility of IQC formation was proven for dozens of others alloys[2,3].

Some elements, beryllium being one of them, strongly increase the quasicrystalline-forming ability in Al–Mn alloys[4–6]. IQCs had already been observed in different conventionally cast ternary and quaternary alloys based on the Al-Mn system, and also in several Al-Mn-Be alloys. In conventionally cast alloys, however, other crystalline phases are also present[4–8] in addition to the IQCs.

One of the most promising potential applications for quasicrystals is their utilisation as a strengthening phase in lightweight aluminium alloys. As early as 1992 Inoue[9] reported on Al–Mn–Ce melt-spun ribbons achieving tensile strengths above 1 GPa. Recently, a hardness of over 290 HV was reported[10] for Al-Mn-Be melt-spun ribbons, which, based on the well-known empirical relationship between hardness and tensile strength, also allows us to expect tensile strengths in the range of 1 GPa. However, extraordinarily high strengths were only reported for alloys having two-phase (α_{Al} + IQCs) microstructures, consisting of a fine dispersion of quasicrystalline particles in an Al-rich solid solution matrix, as yet unattained by conventional casting.

Melt-spun ribbons are rarely directly applicable, because of their dimensions. Consequently, for the vast majority of applications the ribbons must be compacted into much larger pieces of material. The compacting processes mostly involve heating, so rapidly solidified materials must exhibit sufficient thermal stability in order to preserve their advantages.

Unfortunately, IQCs in Al–Mn-based alloys have been discovered to be metastable. The thermal stability of the IQCs in a rapidly solidified binary Al-5 wt.% Mn alloy was reported to be below 1 hour of isothermal annealing at 500 °C [11], and by means of DSC analysis with a high heating rate of 40 K min^{-1}, the onset temperature of thermal decomposition was estimated to be 472 °C for the mole fraction Al-14 % Mn alloy[8]. The thermal stabilities of the conventionally cast ternary alloys Al-2.5Mn-7.5Be (in mole fractons, x/%) and Al-5Be-1.5Mn (in mass fractions, w/%) were investigated by Song et al.[4] and Chang et al.[7], respectively. In both studies the ingots, initially consisting of ICQs and hexagonal approximants dispersed in an α_{Al} matrix, were annealed for 100 h at 540 °C. According to Song et al.[4] the annealing caused no phase transformations, and in addition the DSC did not reveal any transformations below 600 °C. In contrast, Chang et al.[7] reported that upon annealing the IQC-phase dissolved and only hexagonal approximants remained in the matrix. Although these results appear to be contradictory, the differences could possibly be attributed to different chemical compositions and different cooling rates during the solidification of the ingots and, in addition, because in both cases no shorter and no longer annealing times than 100 h were applied, the actual thermal stabilities did not necessarily need to be significantly different at all.

In any case, due to much lower cooling-rates, conventionally cast ingots as well as IQCs also contain crystalline intermetallics, and the microstructure is much coarser than in rapidly solidified alloys. As a result, the conventionally cast material is, already in an as-cast condition, much closer to the thermodynamic equilibrium than the rapidly solidified one, which in an as-cast condition exhibits an extremely fine, two-phase (α_{Al} + IQCs) microstructure. Therefore, the driving force for changes during annealing is higher in rapidly solidified materials and, consequently, a lower thermal stability can be expected. On the other hand, due to the stabilising effect of Be, the thermal stability of the IQC phase could be improved in rapidly solidified, ternary, Al-Mn-Be alloys.

The aim of this work was to evaluate the thermal stability of IQCs in a rapidly solidified, ternary, Al-Mn-Be alloy, which has yet to be determined.

2 EXPERIMENTAL

Although with beryllium the critical content of Mn to produce IQCs is reduced to no more than x = 2.5 % [4], a higher Mn content was chosen in order to achieve a higher volume fraction of quasicrystals. The nominal composition of the alloy was (in mole fractions x) 89 % Al, 6 % Mn and 5 % Be, **Table 1**. It was prepared from Al 99.99, and master alloys of Al–Mn and Al–Be containing (in mass fractions) 30 % Mn and 5.5 % Be, respectively. The precursors were vacuum induction melted and cast into 50-mm round bars. The bars were cut into appropriate lengths and melt-spun in a 30 M-type Melt Spinner, Marko Materials Inc, USA. The melt-spinning conditions were as follows: a BN-protected graphite crucible with a 1-mm orifice, a wheel speed of 25 m min^{-1}, a casting temperature of 900–950 °C.

Table 1: Nominal and analysed chemical compositions of the melt-spun ribbons (ICP-AES)
Tabela 1: Imenske in analizirane kemične sestave hitro strjenih trakov, ulitih s postopkom litja na vrteče se kolo (ICP-AES)

element	x(Al)/%	x(Mn)/%	x(Be)/%
nominal	89	6	5
analysed	88.6	5.6	5.8

x/% – mole fraction; x/% – molski delež

The chemical composition of the melt-spun ribbons was verified using ICP-AES (inductively coupled plasma-atomic emission spectroscopy), see **Table 1**.

The microstructures were investigated in the as-cast condition and after annealing under a protective atmosphere of Ar. The annealing temperatures were (200, 300, 400, 500 and 550) °C, where the annealing time was always 24 h, regardless of the temperature. Different techniques were applied for the metallographic characterisation. The scanning electron microscopy was performed using a dual-beam FEI Quanta 200-3D microscope (SEM-FIB). The X-ray diffraction was carried out at the XRD1 beam-line (Elettra, Sinchrotrone Trieste, Italy) using synchrotron X-rays with a wavelength of 0.1 nm in the transmission mode. The phase compositions were identified using Powder Diffraction File-2[12]. The DSC analyses were performed with a STA 449 Jupiter, from room temperature to 640°C, with heating and cooling rates of 10 °C min^{-1} in nitrogen.

3 RESULTS AND DISCUSSION

3.1 As-cast ribbons

The analysed composition is given in **Table 1**, along with the nominal composition. The actual composition only slightly deviated from the nominal one; therefore, the ribbons were evaluated as being appropriate for the intended purpose.

The microstructural analysis of the as-cast ribbons revealed a two-phase microstructure, consisting of fine IQCs dispersed throughout the α_{Al} matrix. **Figure 1** shows a backscattered-electron SEM image. The backscattered-electron imaging provided the best phase contrast. The α_{Al}-matrix appears dark. The coarser quasicrystals could be identified by their characteristic dendritic morphology and the finer ones, most of them being too small to be distinguishable in a SEM micrograph, by their shapes as pentagonal dodecahedrons[13]. Beside IQCs, no other phase could be found in the matrix of the as-cast ribbons when using scanning

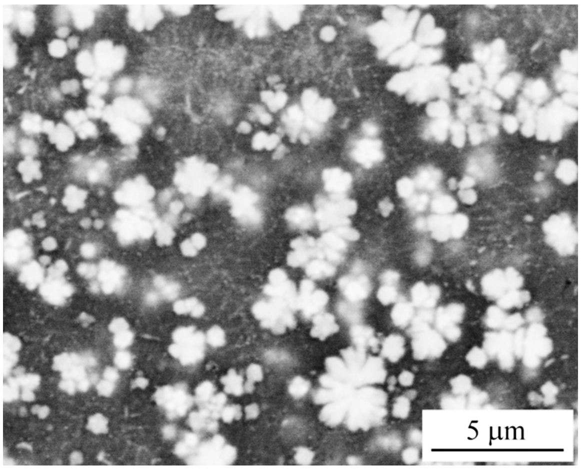

Figure 1: Microstructure of the as-cast ribbon, SEM-image. The coarser quasicrystals exhibit a characteristic dendritic morphology.

Slika 1: Mikrostruktura traku v litem stanju, SEM-slika. Grobi kvazikristali imajo značilno dendritno morfologijo.

electron microscopy. In addition, the XRD analysis (the lowest curve in **Figure 2**) only confirmed the presence of the IQC and the α_{Al}. Therefore, the as-cast ribbons were considered to have a two-phase α_{Al} + IQC microstructure.

Upon heating, **Figure 3**, the DSC analysis of as the as-cast ribbons showed a phase transformation that started at approximately 530 °C, reached its peak at approximately 570 °C and ended at approximately 600 °C. The thermal decomposition of the metastable ICQs started at 530 °C, as indicated by the absence of a reverse transformation upon cooling. As is quite common for DSC, the heating rate was relatively fast. Therefore, the influence of the transformation kinetics

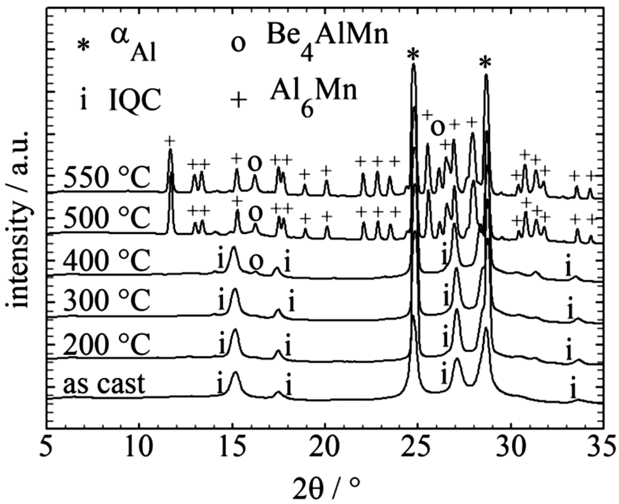

Figure 2: X-ray diffractograms. From bottom to top: as-cast ribbon, ribbons annealed for 24 h at 200 °C, 300 °C, 400 °C, 500 °C and 550 °C.

Slika 2: Rentgenski difraktogrami. Od spodaj navzgor: trak v litem stanju, trakovi, žarjeni 24 h pri 200 °C, 300 °C, 400 °C, 500 °C in 550 °C.

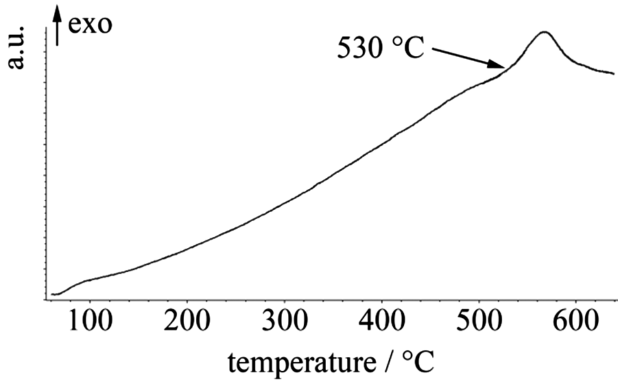

Figure 3: DSC curve of as-cast sample upon heating; heating rate 10 K min^{-1}

Slika 3: DSC-krivulja traku v litem stanju; hitrost segrevanja 10 K min^{-1}

was unavoidable and the determined transformation temperatures were shifted to higher values. The influence of the transformation kinetics reduced with the prolongation of the annealing time, so it was expected that during the 24-hours of isothermal annealing, decomposition would take place at a lower temperature. Therefore, only one of the temperatures for the 24 h annealing was selected above the DSC-estimated start of the decomposition, 550 °C, and one of the lower temperatures only slightly below, i.e., 500 °C.

3.2 Annealed ribbons

The X-ray diffractograms of the samples annealed at 200 °C, 300 °C, and 400 °C were very similar to the diffractograms of the as-cast sample, **Figure 2**. No distinguishable peaks for the crystalline intermetallic phases could be recognised and, only those peaks for IQCs and α_{Al} could be observed. The absence of peaks of the crystalline intermetallics indicates that at temperatures up to 400 °C over 24 h the decomposition did not start or at least did not advance enough to be detected by XRD. Also, in the SEM micrographs of those samples annealed at temperatures up to 400 °C, **Figure 4**, no distinct changes in the average size and morphology of the larger IQCs could be observed. Compared to the as-cast condition (**Figure 1**), the number of smaller particles slightly diminished, indicating that annealing at 400 °C caused a certain degree of Ostwald ripening.

In the XRD diffractograms of the samples annealed at 500 °C and 550 °C an absence of IQC peaks could be observed at first sight. In their place, distinct peaks for the intermetallic phases Be_4AlMn and Al_6Mn were present. The pronounced equality of both XRD diffractograms indicated that at 500 °C the decomposition of the IQCs had already been completed within the 24 h. The SEM micrograph of the sample annealed at 550 °C, **Figure 5a**, at first sight appeared similar to the micrographs of samples annealed at temperatures up to 400 °C. The average size of the large particles remained almost unchanged. However, their morphology changed

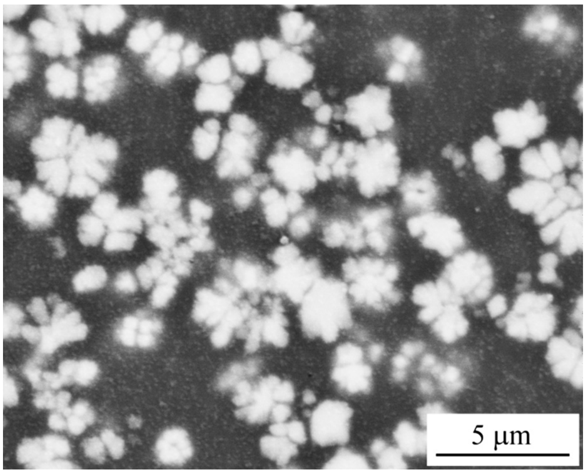

Figure 4: SEM micrograph of a sample after 24-h annealing at 400 °C: compared to the as-cast sample, no distinct changes can be observed.

Slika 4: SEM-slika vzorca po 24-urnem žarjenju pri 400 °C: v primerjavi z vzorcem v litem stanju ni opaziti večjih sprememb.

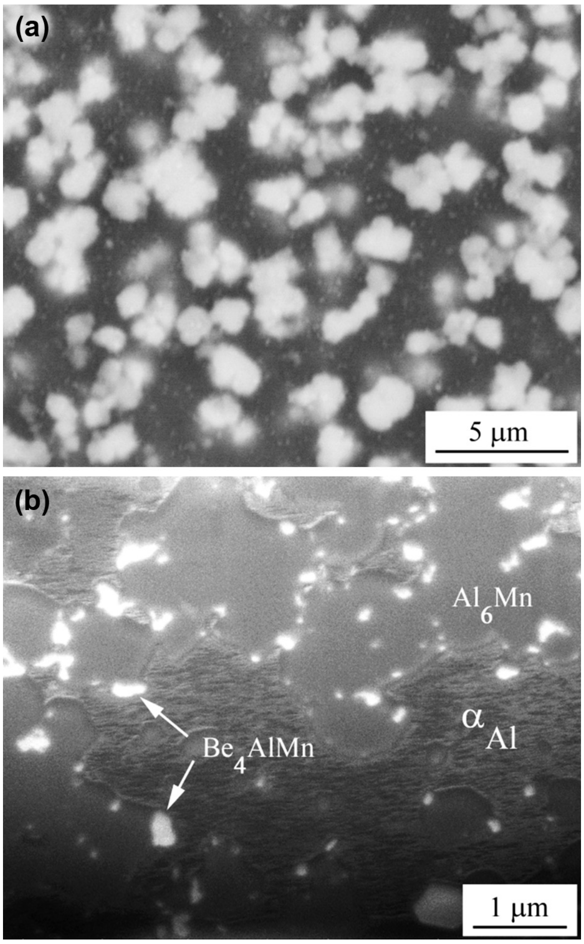

Figure 5: Ribbon annealed for 24 h at 550 °C: a) SEM backscattered-electron image: Be_4AlMn and Al_6Mn can practically not be distinguished; b) FIB secondary-electron image of an in-situ prepared cross-section: all phases identified by XRD can be recognised

Slika 5: Trak, žarjen 24 h pri 550 °C: a) SEM-slika z odbitimi elektroni: Be_4AlMn in Al_6Mn praktično ni mogoče razlikovati; b) FIB-slika in situ pripravljenega prereza: prepoznavne so vse faze, odkrite z XRD

to a more compact shape. According to the XRD analysis, Be_4AlMn and Al_6Mn were present in the α_{Al} matrix. As can be seen from the micrographs in **Figures 4** and **5a**, through the thermal decomposition of the IQCs, neither the size nor the distribution of the dispersed particles changed significantly. Obviously, the sizes and the distribution of the crystalline intermetallic particles, grown through the thermal decomposition of the IQCs, were determined by the sizes and distribution of the IQCs. However, as reported by Bončina et al.[14], in the SEM backscattered-electron images the Be_4AlMn appears only slightly brighter than the Al_6Mn and, consequently, cannot be unerringly recognised. Therefore, cross-sections were cut by the focused ion beam in-situ in the dual-beam SEM-FIB microscope. In the FIB secondary-electron image in **Figure 5b**, both phases could be clearly distinguished. The Be_4AlMn appeared as very bright, almost white, and the surface of the Al_6Mn appeared as smoothly grey. Consistent with the peak heights in the XRD diagrams in **Figure 5b**, it can be observed that the volume fraction of Be_4AlMn was significantly lower than the fraction of Al_6Mn.

4 CONCLUSIONS

The metallographic investigations of the rapidly solidified (melt-spun) Al-Mn-Be alloy led to the following conclusions:

1. The microstructure of the as-cast melt-spun (in mole fractions) 89 % Al-6 % Mn-5 % Be ribbons consisted of IQCs dispersed in an α_{Al} matrix. No quasicrystal approximants or equilibrium intermetallics could be detected.
2. The thermal stability of the rapidly solidified 89 % Al-6 % Mn-5 % Be alloy lasted at least 24 h at temperatures up to 400 °C. After 24 h annealing at 400 °C, only insignificant coarsening of the IQCs was perceivable, whilst the phase composition was preserved.
3. Upon annealing at 500 °C the thermal decomposition of the IQCs into Al_6Mn and Be_4AlMn was completed after no later than 24 h. The sizes and dispersion of the newly formed Al_6Mn–Be_4AlMn clusters were very similar to the sizes and dispersion of the dendritic IQCs. As a result, due to the thermal decomposition of the IQCs, the mechanical properties may not drastically decrease.
4. The rapidly solidified 89 % Al-6 % Mn-5 % Be alloy can be processed using techniques that involve elevated temperatures.

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