THE INFLUENCE OF COOLING RATE ON THE MICROSTRUCTURE OF AN Al-Mn-Be ALLOY

VPLIV OHLAJEVALNE HITROSTI NA MIKROSTRUKTURO ZLITINE Al-Mn-Be

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In ternary Al-Mn-Be alloys a metastable quasicrystalline phase can form at relatively low cooling rates ($\approx$ 100 K/s); however, besides the quasicrystalline phase other phases can also be present. We found that the investigated alloy is very prone to the formation of metastable phases, which are also quasicrystalline. Using different investigation methods we determined the type of phases, their shape, morphology, chemical composition and distribution. Special attention was given to the micro- and nano-sized quasicrystalline particles. When using slow cooling, $Al_{10}Mn_3$ and Be_4AlMn were present; however, with a faster cooling rate a quasicrystal approximant and a quasicrystalline phase were formed.

Key words: aluminium, quasicrystals, cooling rate, microstructure

V ternarnem zlitinskem sistemu Al-Mn-Be lahko nastane metastabilna kvazikristalna faza pri relativno majhni ohlajevalni hitrosti ($\approx$ 100 K/s), vendar lahko poleg nje nastanejo še druge kristalne faze (predvsem intermetalne faze). Z uporabo različnih raziskovalnih metod smo ugotovili vrsto nastalih faz, kemijsko sestavo in porazdelitev. Ugotovili smo, da je zlitina nagnjena k nastanku metastabilnih faz (tudi kvazikristalnih). Predvsem so zanimivi kvazikristalni delci, ki se pojavljajo v mikro- in nanometrskih velikostih. S počasnim ohlajanjem so nastale faze $Al_{10}Mn_3$ in Be_4AlMn, pri hitrem ohlajanju pa so se namesto njih pojavili kvazikristalni aproksimanti in kvazikristalne faze.

Ključne besede: aluminij, kvazikristali, ohlajevalna hitrost, mikrostruktura

1 INTRODUCTION

The production and application of aluminium alloys has increased considerably in the past few decades because of their good strength-to-weight ratios. Their use is justified in a variety of processes where a light and corrosion-resistant material is needed. The progress of aluminium alloys is leading to better mechanical properties and to improvements in the relatively poor strength and heat resistance of classical aluminium alloys [1].

The properties of an alloy depend on its chemical composition, structure and microstructure, which in turn depends on a variety of production conditions. Thermal treatment (quenching in our case) is one of the influences that affects the microstructure. In this research the effect of the solidification and cooling rates on the microstructure is investigated.

The alloy investigated was an Al-Mn-Be alloy, one of less-investigated alloys so far. Al-Mn alloys are suited for the manufacturing of metastable quasicrystalline materials with rapid solidification. In the past few years it was discovered by Song et al. [2] that the addition of beryllium to an Al-Mn alloy reduces the solubility of manganese in an aluminium solid solution and leads to the formation of quasicrystals and quasicrystal approximants at lower cooling rates. In practice, for the production of quasicrystals other aluminium based alloys are also used, for example, Al-Cu-Fe, Al-Cu-Cr, Al-Mn-B, Al-Cr-B, and Al-Si-Mn [2–5].

A quasicrystal is an intermediate state between a crystalline and an amorphous material. Quasicrystals normally have a non-characteristic symmetry and are not periodic; however, they do have long-range order (quasi-periodicity). It is usually more difficult to obtain the quasicrystalline state rather than the crystalline state, hence we do not know the conditions for quasicrystalline growth. We only have predictions based on their diffraction patterns. Quasicrystals can be stable or metastable. The metastable phases usually form from the melt with rapid cooling or large undercooling. Upon heating, these phases transform into stable crystalline phases. A survey of quasicrystals and their approximants can be found in reference [6].

In this study an Al-Mn-Be alloy was solidified with different cooling rates using melt spinning and casting into a special copper mould and cooling in a controlled manner (DSC analysis). The main aim of this work was to explore the influence of solidification and cooling rate on the microstructure.

2 EXPERIMENTAL

The Al-Mn-Be (M5) alloy was manufactured using the master alloys AlMn30 and AlBe5.5 and pure aluminium (Al 99.99 %). A charge was melted in a

LEYBOLD-HEREAUS IS vacuum furnace. The chemical composition of the M5 alloy is shown in **Table 1**. The relatively high content of Mn was selected in order to attain an appropriate volume fraction of quasicrystalline phase in the rapidly solidified ribbons, whereas the large content of Be ensured the formation of the quasicrystalline phase with casting in a copper mould. Since it was a new alloy and therefore its properties were not known, we conducted a differential scanning calorimetry (DSC) analysis in order to determine the liquidus, solidus and other transformation temperatures. The DSC analysis was performed on apparatus from Bähr Thermoanalyse GmbH with heating and cooling rates of 10 °C/min. Since beryllium is highly reactive with air at high temperatures the DSC analysis was performed in an inert atmosphere.

Table 1: Chemical composition of the investigated alloy
Tabela 1: Kemijska sestava preiskovane zlitine

Alloy	Al $w/\%/x/\%$	Mn $w/\%/x/\%$	Be $w/\%/x/\%$
M5	90.6/86.1	5.4/2.5	4.0/11.4

$w/\%$ (mass fractions), $x/\%$ (mole fractions)

A specimen cooled at ≈ 1 °C/s was obtained by vacuum melting and casting into a 50 mm × 20 mm × 300 mm steel mould. It was then used as a reference material for determining the influence of quenching on the formation of the microstructure of the investigated alloy. A quenching rate of above 100 K/s was attained by casting into a special 10 mm × 1 mm × 100 mm copper mould. The largest cooling rate of between 10^5 K/s and 10^6 K/s was obtained by casting on a model M10 melt spinner (Marko Materials).

The metallographic investigation of alloys was carried out using light microscopy (LM) and scanning electron microscopy (SEM). The micro-chemical analysis was performed with energy-dispersive spectroscopy (EDS) and with Auger electron spectroscopy (AES); since beryllium could not be reliably detected with EDS most of the analyses were performed with AES. The AES analysis was performed with a high-resolution spectrometer with a field-emission MICROLAB 310F. The general characterisation of the phases was made with x-ray diffraction (XRD), and for the characterisation of very small particles, that could not be reliably analysed with XRD, transmission electron microscopy (TEM) was used.

3 RESULTS AND DISCUSSION

To investigate the formation of phases in the investigated alloy in conditions close to the equilibrium condition a DSC analysis was performed with a heating and cooling rate of 10 K/min, assuming that the temperature gradient was sufficiently small to achieve the transformations close to the thermodynamic equilibrium.

The DSC analysis showed the temperature of formation of the individual phase and the amount of energy absorbed or released in the process. Several transformations occurred during heating and cooling, and they are indicated in **Figure 1** (a and b). **Figure 1a** shows that the melting is completed at 945 °C, so it is obvious that we had to heat the alloy above this temperature before casting to achieve the melting of all the constituents of the alloy. On the cooling curve (**Figure 1b**) the peak 4 at 934 °C is probably connected with the formation of an oxide (BeO·AlO$_2$) and does not indicate a solidus temperature of an alloy phase. Oxide particles may act as heterogeneous nucleation sites during the subsequent alloy solidification. The liquidus temperature at a cooling rate of 10 K/min was 870 °C and the solidus temperature of ≈ 640 °C depends on how the cooling rate affects the undercooling interval, which then affects the transformation temperatures. As shown in the **Figure 1c** applying XRD, SEM and EDS the
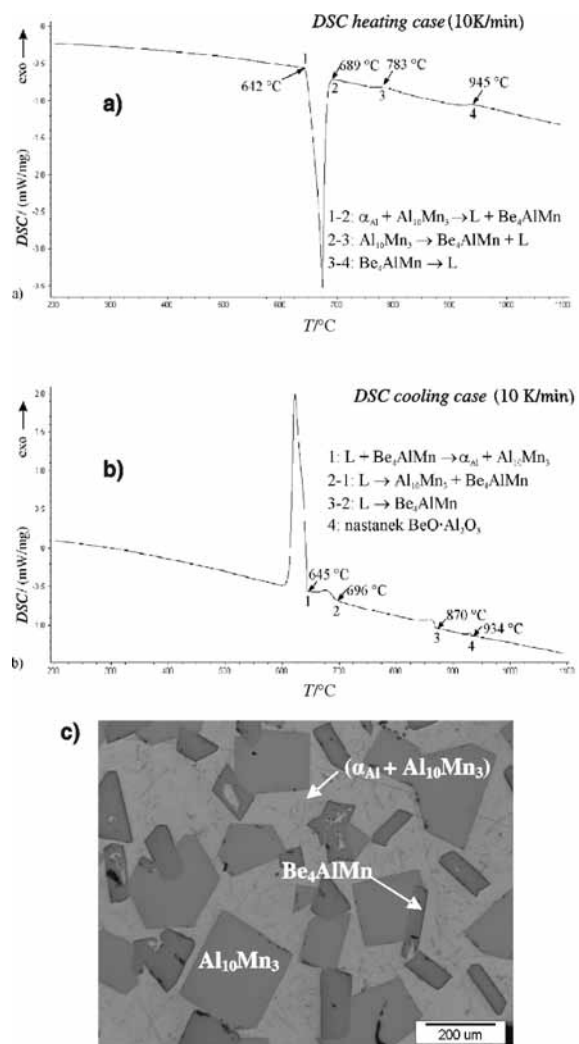

Figure 1: a) DSC analysis of heating, b) DSC analysis of cooling, c) microstructure after DSC cooling
Slika 1: a) DSC-analiza segrevanja, b) DSC-analiza ohlajanja, c) mikrostruktura

Table 2: Characteristics of the phases in the investigated Al-Mn-Be alloy
Tabela 2: Značilnosti faz v preiskani zlitini Al-Mn-Be

Casting Litje	Phases Faze	Size of phases Velikost faz	Chemical composition (x/%) Kemijska sestava (x/%)
Casting into steel mould Litje v jekleno kokilo	α_{AL} $Al_{10}Mn_3$ Be_4AlMn	up to 100 μm 10-20 μm	66 % Be, 7 % Mn, 20 % Al
Casting into copper mould Litje v bakreno kokilo	Rod-like eutectic (paličast evtektik)	–	–
	Hexagonal approximant (heksagonalni aproksimant)	1–2 μm	73 % Be, 7 % Mn, 20 % Al
	Quasicrystals (kvazikristali)	0.2–1 μm	30 % Be, 15 % Mn, 55 % Al
Melt spinning (wheel-side) Ohlajanje na vrtečem se kolesu (ob kolesu)	Quasicrystals (kvazikristali) α_{AL}	up to 50 nm	35 % Be, 15 % Mn, 50 % Al
Melt spinning (air-side) Ohlajanje na vrtečem se kolesu (na zunanji strani)	Quasicrystals (kvazikristali) α_{AL}	up to 500 nm	35 % Be, 15 % Mn, 50 % Al

phases $Al_{10}Mn_3$ and Be_4AlMn were identified in the eutectic ($\alpha + Al_{10}Mn_3$) matrix. The sizes of the phases are given in **Table 2**. It is interesting to note that stable phases from the ternary phase diagram like $Al_{15}Mn_3Be_2$ and Al_6Mn were not found [7]. This is not very unusual since in the binary Al-Mn system, as well as in the higher component systems based on this system, meta-stable phases very often form [7].

In **Figure 2** the microstructure obtained at an increasing cooling rate is shown. During relatively slow cooling with solidification in the steel mould (**Figure 2a**) the microstructure consists of $Al_{10}Mn_3$ phases, smaller faceted B_4AlMn phases and a eutectic matrix. These phases were of the same type as the phases formed during the DSC cooling. The size of the phases was smaller because of the greater cooling rate and the greater undercooling. After casting into the 1-mm copper mould the melt temperature was decreased faster and a larger undercooling was achieved. **Figure 2b** shows the corresponding microstructure with small, bright
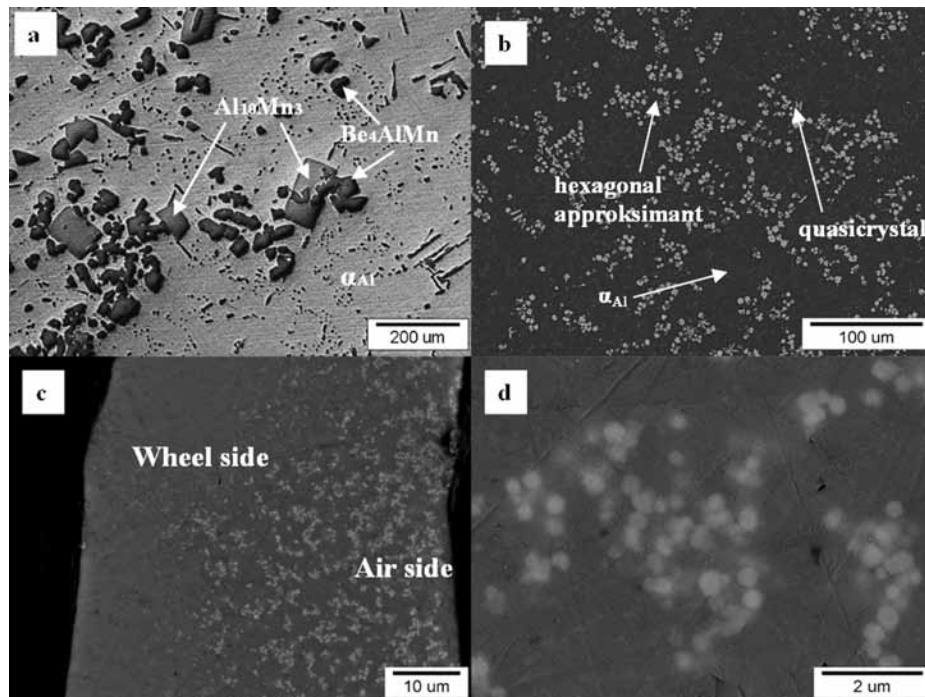

Figure 2: Microstructure of a) reference sample, b) sample casted in copper mould, c) melt-spun ribbon, d) microstructure of the air side of the ribbon
Slika 2: Mikrostruktura: a) referenčni vzorec, b) lit v bakreno kokilo, c) lit na vrteči se boben, d) leva stran traku

quasicrystal particles uniformly distributed in the Al-rich matrix. The size of these particles was significantly smaller than the size of the phases formed at a slower cooling rate (**Table 2**). With deep etching, scanning electron microscopy, x-ray diffraction and TEM we proved that these small particles did not belong to the same phases as those obtained with the slower cooling rates and were identified as hexagonal approximants and quasicrystals, as reported in reference [8]. The matrix consisted of a eutectic of a quasicrystalline phase (with a rod-like morphology) and the Al-rich solid solution α-Al.

The microstructure of a melt-spun ribbon with a thickness between 40 μm and 60 μm is shown in **Figure 2c**. Rapid solidification ($\approx 10^6$ K/s) produced a large undercooling, allowing the formation of only the quasicrystalline phase, present in the form of dispersed particles in an Al-rich matrix. The left-hand side of the ribbon was in contact with the wheel and the right-hand side with the atmosphere. With optical microscopy no particular phase was detected in the microstructure, while high-resolution SEM and TEM showed that the microstructure consisted of relatively uniformly distributed quasicrystalline particles of sizes around 50 nm. The cross-section of the ribbon shows the influence of the cooling rate on the particles and their size. Using a smaller cooling rate, i.e., at a larger distance from the wheel side of the ribbon the particle size was greater. According to the morphology, the quasicrystals were presumably formed in the melt before the solidification of the Al-rich matrix. On the wheel side, where the solid interface propagated with a faster rate, the quasi-crystalline particles were often entrapped in the matrix. On the air-side of the ribbon the solidification was slower. The morphology of α_{Al} was dendritic and the quasicrystalline particles were entrapped in the interdendritic space.

The chemical composition of the phases shown in **Table 2** was determined with EDS and AES. Under equilibrium conditions, according to the ternary phase diagram, the alloy M5 should contain many intermetallic phases. Intermetallic particles were present in the microstructure obtained with a slow solidification rate; however, they were not the same as those in the Al-Mn-Be equilibrium ternary phase diagram. Inter-metallic phases have a different crystallographic structure than the solid solutions and represent an independent sort of crystal with high hardness and low ductility [9].

Table 2 clearly shows that with an increasing cooling rate, not only does the size of the particles become smaller, but the type of phases changes also. According to the chemical composition the intermetallic phase $Be_{10}MnAl_3$ could be a hexagonal approximant.

4 CONCLUSIONS

The formation of phases in the investigated alloy depends on the cooling rate. It was confirmed that the investigated Al-Mn-Be alloy is prone to the formation of metastable phases. Using DSC the $Al_{10}Mn_3$ and Be_4AlMn phases were found to be present in the Al-rich matrix. A small increase in the cooling rate by casting into a steel mould did not lead to the formation of new phases, but only to smaller sized particles, apparently because of the reduction of coarsening in the faster-solidifying undercooled melt. The additional increase of cooling rate by casting into a small copper mould resulted in the creation of a hexagonal quasicrystalline approximant (a crystalline phase that closely resembles the quasicrystalline phase in terms of structure and properties). Finally, with the fastest cooling, produced by melt spinning, only quasicrystals formed in the α-Al solid solution.

Uniformly distributed quasicrystals and their approximants could act as dispersion-strengthening elements and improve the strength-to-weight ratio of the alloy.

5 REFERENCES

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