Effect of cooling rate on the constitution of Al-Mn-Be-Cu

Vpliv ohlajevalne hitrosti na konstitucijo Al-Mn-Be-Cu

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Abstract: In this article the constitution of the Al-Mn-Be-Cu alloys and the influence of the cooling rate on the constitution was studied. Cooling rates were determined through the measurements of the dendrite arm spacing and the heat calculations. By the use of computer program which is part of the light microscopy technique, individual fractions of i-phase were determined. It was found that at cooling rates between 500 K s^{-1} and 1 350 K s^{-1} the preferred phase formed was a quasicrystalline phase – especially in the form of the quasicrystalline eutectic (α_{Al} + i-phase). In addition to the quasicrystalline i-phase within eutectic, it is also formed as the primary phase. The fraction of the i-phase varied depending on the diameter of the castings (2 mm and 4 mm) and in most cases it increased with the decreasing diameter. Fractions of the i-phase in the individual castings were higher in the alloy with a higher content of manganese. Morphology of the i-phase depended on the content of the alloying elements and the cooling rate. Thus in the alloy with a higher mole content of the manganese (4.5 at. % Mn) i-phase possessed the dendritic form, while in the alloy with lower manganese content (1.8 at. % Mn) it was in form of needles, which were thicker at the tips. With the distance from the edge of the sample (with decreasing cooling rate) the dendrites grew, the primary branches were thicker and the secondary branches started to grow also. In the case of the needle morphology, the length and the thickness of needles grew with increasing distance from the sample edge.

Izvleček: V članku je obravnavana konstitucija dveh zlitin Al-Mn-Be-Cu in vpliv ohlajevalne hitrosti nanjo. Opravljene so bile ocene

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ohlajevalnih hitrosti z merjenjem sekundarnih dendritnih razdalj in izračunov toplotne bilance strjevanja. Z računalniškim programom, ki je del svetlobnomikroskopske opreme, so bili določeni površinski deleži faze i v ulitkih. Ugotovljeno je bilo, da je pri ohlajevalnih hitrostih med 500 K s^{-1} in 1350 K s^{-1} prednostna tvorba kvazikristalne faze (zlasti v obliki kvazikristalnega evtektika (α_{Al} + faza i)). Poleg kvazikristalne faze i v okviru heterogenega zloga se le-ta pojavlja tudi kot primarna faza. Delež faze i se spreminja glede na premer ulitih valjčkov (2 mm in 4 mm) in v povprečju raste s padajočim premerom. Deleži faze i v posameznih ulitkih so višji pri zlitini z višjim deležem mangana. Morfologija faze i se spreminja v odvisnosti od vsebnosti zlitinskih elementov in hitrosti ohlajanja. Tako je v zlitini z višjim deležem mangana (4,5 at. % Mn) faza i prisotna večinoma v dendritni obliki, medtem ko je v zlitini z nižjo vsebnostjo mangana (1,8 at. % Mn) v obliki iglic, ki so na koncu odebeljene. Z oddaljenostjo od roba vzorca, torej v odvisnosti od ohlajevalne hitrosti, pa dendriti rastejo, primarne veje se debelijo, sekundarne začno rasti. Pri igličasti morfologiji pa dolžina in debelina iglic z oddaljenostjo od roba vzorca rasteta.

Key words: quasicrystals, microstructure, aluminum alloys
Ključne besede: kvazikristali, mikrostruktura, aluminijeve zlitine

Introduction

Quasicrystals were first discovered by D. Shechtman in the year 1984 in an $Al_{86}Mn_{14}$ alloy.[1] They are considered to be the third state of matter in addition to the crystal and amorphous state. The atoms are ordered but with non-crystallographic rotational symmetry and without three-dimensional periodicity.[2] Quasicrystals have until now been found in more than a hundred binary and ternary metallic systems. About half of them are metastable and can only be obtained by rapid solidification techniques, such as melt spinning.[3] In binary Al-Mn alloys the metastable quasicrystalline phases form only at higher cooling rates. In some cases the addition of the third element (e.g. Be) causes the formation of quasicrystalline phases in Al-Mn alloys already at lower cooling rates,[4] that is why it was added in our case. Copper was selected since it has a good solubility in aluminum.

In this paper the constitution of two Al-Mn-Be-Cu alloys was investigated (in as-cast state) mostly to establish the influence of the addition of beryllium and copper during casting with lower cooling rates. The emphasis was on the effect of cooling rate on the constitution of the Al-Mn-Be-Cu alloys.

Materials and methods

Materials

Two different alloys were prepared (Table 1) using master alloys AlBe5.5, AlCu50 and AlMn20 and pure aluminum (Al 99.9). Major difference between the two Al-Mn-Be-Cu alloys was the content of manganese (4.5 at. % Mn and 1.8 at. % Mn). Synthesis and casting were performed in vacuum. Casting was done in water chilled copper mould at around 750 °C. Castings were cylindrical in shape with different diameters ((2, 4, 6 and 10) mm). By that it was possible to estimate the influence of the cooling rate and chemical composition on the formation, fraction and morphology of the quasicrystalline phase, which in our case was i-phase. In this article only the smaller diameters (2 mm and 4 mm) of the two alloys are discussed, since the cooling rates were sufficient for the formation of more significant amounts of the i-phase.

Methods for estimating the cooling rates

Cooling rate was not monitored during the casting procedure. Instead we performed measuring of DAS (dendrite arm spacing) using LOM and SEM images. Measurements were performed with the Axio Vision software from the edge to the middle of the sample. According to reference[5] the cooling rates were evaluated through DAS measurements. Measurements were performed for the 62MCuKO alloy, while that was not possible for the 22MCuKO alloy because the morphology of the microconstituents was not dendritic. Additionaly to DAS measurements heat calculations were carried out, where the unsteady transport of the heat was taken into account. For the calculations the approximate method – Lumped-System analysis – was used.

Microstructural characterization

Microstructural characterization of the two alloys was performed by light optical microscopy (LOM – ZEISS Axio Imager.A1m) and scanning electron microscopy (SEM - JEOL JSM-5610, JEOL JSM-5800 and JEOL JSM-7600F) in combination with the energy dispersive X-ray spectroscopy (SIRI-

Table 1. Chemical composition of alloys in atomic fractions, *x*/%

Alloy	*x*(Al)	*x*(Mn)	*x*(Be)	*x*(Cu)
62MCuKO	92.4	4.5	1.6	1.6
22MCuKO	95.4	1.8	1.2	1.5

US 10/SUTW (Gresham Scientific Instruments) and Oxford Isis 300). The specimens were prepared and etched using a solution of the distilled water and NaOH for both analytical methods, LOM and SEM. By the EDS analysis we determined only the amounts of the aluminum, manganese and copper within the individual phases, while for the beryllium that was not possible. Beryllium cannot be analyzed using EDS because it is a lightweight chemical element.

Estimating the fraction of the i-phase in individual castings

Determination of the fraction of the i-phase was carried out by a computer software Axio Vision and imported SEM images, which were captured from the sample edge towards the center of the sample. Selection of the SEM images was due to the good contrast between the different phases when using backscattered electrons. Principle of determining fraction of the i-phase with Axio Vision software is the separation of the phases by different colors.

Results and discussion

Alloy 62MCuKO

Casting of diameter* 2 mm *(alloy 62MCuKO)

In addition to the α_{Al} matrix, phases present in the microstructure were: dendritic i-phase within the quasicrystalline eutectic and the θ-Al_2Cu phase as part of the (α_{Al} + θ-Al_2Cu) eutectic (Figure 1). From the edge to the center of the sample the dendrites of the i-phase grew and were more branched. In some places i-phase occured as a primary phase. In some cases the i-phase within the quasicrystalline eutectic was very fine (Figure 2). Phase α_{Al} in average contained atomic fractions 98.0 % Al, 1.0 % Mn and 0.9 % Cu (Table 2), where the copper meant a high probability of θ-Al_2Cu precipitates. Average composition of i-phase was (Table 2): 82.7 % Al, 15.6 % Mn and 1.7 % Cu, which is quite similar to the results in reference.[6]

It was found that the i-phase was also present in the center of the sample which indicated that the cooling rate was sufficient for its formation (reference[7] states, that the critical cooling rate for the formation of the i-phase is 500–520 K s^{-1}). Therefore an assessment of the cooling rate on the edge and the centre of the sample was carried out through DAS measurements and the heat calculations (Table 3). Assessed cooling rate via DAS measurements was: on the edge of the sample 1 350 K s^{-1} and in the middle of the sample 1 000 K s^{-1}. Heat calculations of the edge of the sample (1 296 K s^{-1}) well confirm value of 1 350 K s^{-1}, while the heat calculations for the middle of the sample (1 036 K s^{-1}) are decisive only when the average dT/dt is taken into account. Both methods for determining the cooling rate are suitable in the case of the sample of 2 mm in diameter because all SEM and LOM images confirm the existence of the i-phase in the middle of the sample (in addition to the presence on the edge of the sample). The cooling rate was the highest on the edge of the sample, therefore it was expected that there will be the highest fraction of the i-phase. Measurements of the fraction showed that the average fraction on the edge of the sample was 26.7 % and in the middle of the

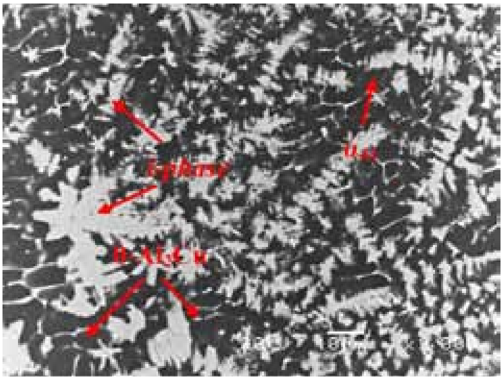

Figure 1. Microstructure of casting with 2 mm diameter (62MCuKO alloy) – SEM (BSE)

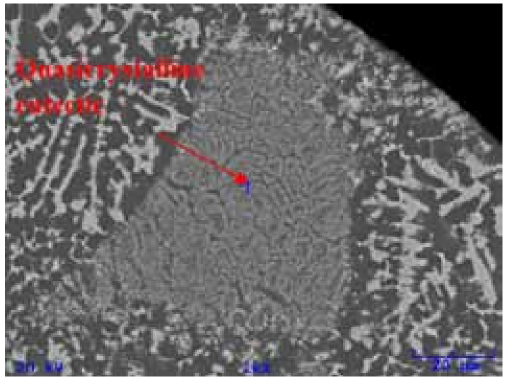

Figure 2. Very fine i-phase within the quasicrystalline eutectic – SEM (BSE)

Table 2. EDS analysis of the phases in the casting with 2 mm diameter (62MCuKO alloy); mass fractions w/% and atomic fractions x/%

	w(Al)	w(Mn)	w(Cu)	x(Al)	x(Mn)	x(Cu)	Phase
1	96.23	1.69	2.08	98.25	0.85	0.90	α_{Al}
2	96.51	2.15	1.34	98.34	1.08	0.85	α_{Al}
3	69.19	27.63	3.17	82.26	16.13	1.60	i-phase
4	71.74	24.92	3.61	83.85	14.36	1.80	i-phase
5	68.83	27.71	3.47	82.03	16.22	1.76	i-phase

Table 3. Results of the heat calculations for the casting with 2 mm diameter (62MCuKO alloy)

	Solidification start t/s	Solidification finish t/s	Solidification time t/s	Max. dT/dt K s^{-1}	Average dT/dt K s^{-1}
D = 2 mm (α_{max} = 2 500–1 700 W m^{-2} K^{-1})	0.16	0.76	0.6	1 296	1 036

sample it was 26 %. The difference is small probably due to the short size of the casting and due to the very small difference in time when the edge and the middle of the sample solidified.

Casting of diameter* 4 mm *(alloy 62MCuKO)

The microstructure consisted of the α_{Al} matrix, small amount of θ-Al_2Cu phase and dendritic i-phase (Figure 3). Dendrites had thick primary branches but they already grew the secondary ones. In the middle of the sample all dendrite branches were thicker, larger and longer and it was difficult to distinguish primary branches from the secondary. The i-phase in average contained atomic fractions 83.9 % Al, 13.2 % Mn and 1.2 % Cu (Table 4). Average composition of α_{Al} phase was (Table 4): 97.8 % Al, 1.0 % Mn and 1.2 % Cu. Again the content of copper in the matrix indicated presence of the θ-Al_2Cu precipitates.

In addition to the microstructural characterization the estimations of the cooling rate on the edge and in the middle of the sample were made. The cooling rate on the edge of the sample was approximately 800 K s^{-1} according to DAS measurements and about 650 K s^{-1} according to the heat calculations (Table 5). In the middle of the sample this estimations were 600 K s^{-1} and 520 K s^{-1}, respectively. It should be noted that the estimated values of cooling rates through DAS measurements are approximate, since dendritic morphology in some places was not representative. But from the SEM images it was obvious that the i-phase was present in the middle of the sample so the cooling rate should be at least 500 K s^{-1} in the middle of the sample (according to reference [7]). The calculated values were slightly lower that the cooling rates obtained from measurements of the DAS but in the same order of magnitude. The problem was that it is virtually impossible to determinate the accurate heat transfer coefficient which strongly depends on the given conditions of the casting. Furthermore, the model predicts the cooling of the sample without a temperature gradient in its cross-section.

Influence of the cooling rate on the formation of the i-phase is crucial. Fraction of the i-phase is also dependent on the cooling rate, so the measurements

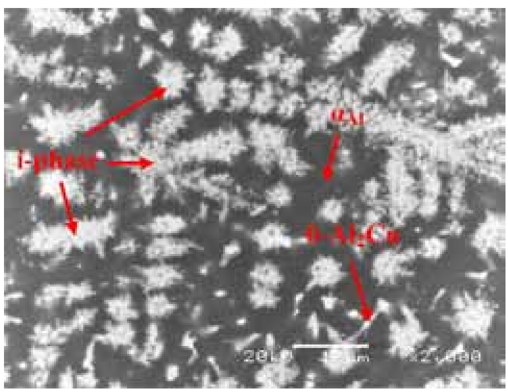

Figure 3. Microstructure of casting with 4 mm diameter (62MCuKO alloy) – SEM (BSE)

Table 4. EDS analysis of the phases in the casting with 4 mm diameter (62MCuKO alloy)

	w(Al)	w(Mn)	w(Cu)	x(Al)	x(Mn)	x(Cu)	Phase
1	95.68	1.99	2.33	97.98	1.00	1.01	α_{Al}
2	94.71	2.10	3.19	97.54	1.06	1.40	α_{Al}
3	72.98	19.75	7.27	85.09	11.31	3.60	i-phase
4	72.44	22.33	5.24	84.60	12.81	2.60	i-phase
5	68.87	26.91	4.94	82.15	15.34	2.50	i-phase

Table 5. Results of the heat calculation for the casting with 4 mm diameter (62MCuKO alloy)

	Solidification start t/s	Solidification finish t/s	Solidification time t/s	Max. dT/dt K s^{-1}	Average dT/dt K s^{-1}
D = 4 mm (α_{max} = 2500–1700 W m^{-2} K^{-1})	0.202	1.349	1.147	648	516

of the fraction of the i-phase on the edge and in the middle of the sample were carried out. From the edge of the sample towards the center values decreased from 28.6 % to 26.5 %, which is consistant with the decreasing cooling rate.

Alloy 22MCuKO

Casting of diameter **2 mm** *(alloy 22MCuKO)*

In addition to the α_{Al} matrix. the primary i-phase was present (Figure 4) along with the i-phase within the quasicrystalline eutectic. There were traces of the θ-Al_2Cu phase as well. The primary i-phase formed a 0.5 mm thick rim which extended from the surface into the specimen. The references[6, 7] also report the existence of only those phases. Quasicrystalline eutectic (α_{Al} + i-phase) had a typical skeletal form, made of thin needles which were thicker at the end. From the edge of the sample to the center the skeletons of i-phase and θ-Al_2Cu grew and interspaces were getting smaller. The matrix α_{Al} in average contained atomic fractions 96.5 % Al, 2.3 % Mn and 1.3 % Cu. The EDS measurements were not performed for the i-phase, while the particles were too fine and small.

Since the morphology of the i-phase was not dendritic, the DAS measurements were not possible. Cooling rates were estimated on the basis of the previous measurements and estimations (62MCuKO alloy), since the diameter was the same. It was assessed that the cooling rate on the edge of the sample was about 1 300 K s^{-1} and in the middle of the sample around 1 000 K s^{-1}. That is quite possible considering the presence of the i-phase in the whole cross-section of the sample.

The 22MCuKO alloy contained considerably less manganese, therefore it was expected that the fraction of the i-phase in these castings will be lower than in the previously discussed castings (62MCuKO alloy). Fraction of the i-phase was on the edge of the sample 8.7 % and in the middle 8.4 %. Once again the difference in the fractions between the edge and the middle of the sample was small, but it was large in comparison with the casting of the same diameter but different chemical composition.

Casting of diameter* 4 mm *(alloy 22MCuKO)

Casting of 4 mm diameter had microstructure composed of matrix α_{Al} and two binary eutectics (α_{Al}+ i-phase) and (α_{Al} + θ-Al_2Cu) (Figure 5). Primary i-phase was not detected like in the previous sample. Towards the center of the sample dendrite networks grew. Considering the typical morphology of the quasicrystalline eutectic and due to the smallness of i-phase only EDS measurements of the matrix α_{Al} were carried out. In average the α_{Al} phase contained atomic fractions 96.4 % Al, 1.5 % Mn and 2.1 % Cu.

Because of the absence of the dendrite morphology of the i-phase it was impossible to estimate cooling rate via DAS measurements. The estimates of the casting of the same diameter (4 mm) were taken; on the edge of the sample around 800 K s^{-1} and in the center 600 K s^{-1}. In addition to the value of 800 K s^{-1}, value of 600 K s^{-1} in the middle of the sample is reasonable, since the i-phase was present also in the entire area of the sample's center.

Differences in cooling rate at the edge and the center of the sample should be

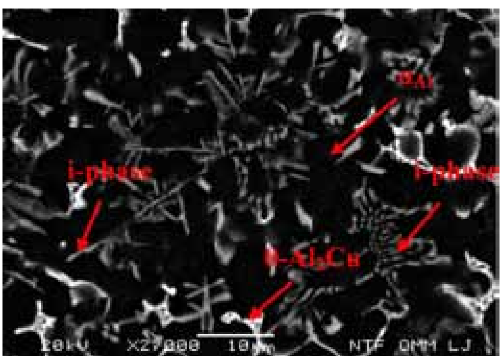

Figure 4. Microstructure of casting with 2 mm diameter (22MCuKO alloy) – SEM (BSE)

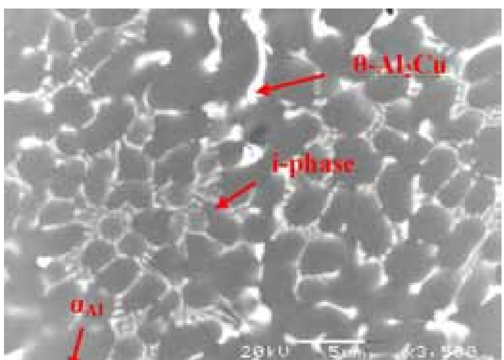

Figure 5. Microstructure of casting with 4 mm diameter (22MCuKO alloy) – SEM (BSE)

evident from measurements of fraction of the i-phase on the edge and in the middle of the sample. Average fraction of the i-phase on the edge of the sample was 6.1 % and then it increased (to 10.1 %), but at some point it started to decrease. In the middle of the sample fraction was 8.5 %. Obviously the points of measurements were not selected appropriately.

Conclusions

Based on the results of the constitution research, estimated cooling rates and fraction measurements of the i-phase, the following can be concluded:

- the addition of the beryllium and copper enables the formation of the quasicrystalls at lower cooling rates than that of the casting processed via melt spinning (where the cooling rates are of the order of 10^6 K s^{-1})
- in addition to the appropriate chemical composition the main influence on the fraction (shape, size distribution and size) of the i-phase is due to the cooling rate
- with increasing cooling rate the fraction of the i-phase increase in general, but the additional further studies and measurements are necessary
- i-phase dendrites in the case of the dendrite morphology with decreasing cooling rate grow, the primary branches are thicker and in some places already the second start to grow. At the highest cooling rate (edges of the castings with diameter of 2 mm) the i-phase is very small and fine, therefore it is difficult to distinguish its morphology
- i-phase occurs both in primary form such as the part of the quasicrystalline eutectic
- method used for the heat calculations is appropriate for estimating the cooling rate in case of the smaller samples (diameters of 2 mm and 4 mm), as the values agree well with the reference[7] and measurements DAS
- in all the samples inevitable θ-Al_2Cu phase occurs. The desire is to eliminate and dissolve it all, which would additionaly contribute to the hardening when heat-treated.

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