

## INFLUENCE OF COOLING RATE AND ALLOYING ELEMENTS ON THE MICROSTRUCTURE OF THE Al-Mn-BASED ALLOY

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**Abstract:** Aluminum-based alloys have been used extensively for the past five decades primarily due to their good strength vs. specific weight ratio. Numerous methods and techniques have been devised to further improve mechanical properties of these alloys as they are often used in the transport applications. Influence of the cooling rate and chemical composition on the constitution of Al-Mn-based alloy has been investigated. Elements such as B, Be, C, Ca, Cu, Fe, Mg, Si, Sr and Ti have been introduced to Al-Mn alloys in order to study their influence. Changes in cooling rates during casting using permanent copper molds with different sized troughs have also been monitored. Combined influence of changes in chemical composition and cooling rates was followed using LOM, SEM, EDS, DAS measurement and mathematic modeling. It has been established that Al-Mn-based alloys form a lot of different phases during synthesis and solidification, mostly crystalline intermetallics, but also in some cases quasicrystalline (QC) ones, especially when cooling rates exceed  $500 \text{ Ks}^{-1}$ . QCs are currently also considered as an alternative for reinforcement of Al-Mn-based alloys. It was found that in the case of alloy system Al-Mn-Cu-Be and cooling rates between 500 and  $1350 \text{ Ks}^{-1}$  the preferred phase formed was an icosahedral QC phase or iQC. Icosahedral QC phase formed as the primary phase and in some cases also in the form of the quasicrystalline eutectic ( $\alpha_{\text{Al}} + \text{iQC}$ ). Additions of B, C, Ca, Ti and Sr have not proven to be effective in promoting formation of quasicrystals in cast Al-Mn alloys whilst Fe, Cu, Mg and Si proved to be highly efficient.

**Keywords:** Al-Mn alloys, cooling rate, chemical composition, quasicrystals.

### 1. INTRODUCTION

Lightweight and high-strength alloys which have a high strength and density ratio are desirable since such properties enable reduction of weight of constructions made from such materials. Reduction of weight in transportation for example is one of the main motives as it allows reduction of energy consumption, of harmful emissions as well as improved performance. Aluminum alloys have been used in transportation industry for at least half a century. Such alloys should, besides desired properties, also allow for large scale production which ought to be as simple as possible. The strength of aluminum alloys can be increased via various mechanisms among which e.g. strengthening by grain size reduction, solid-solution strengthening, precipitation and strain hardening. Quasicrystalline state is the third state of matter and as such has special physical and metal-

lurgical properties [1,2]. Quasicrystals (QCs) are deformable but still relatively hard materials and could as such serve as a reinforcing phase of in-situ produced aluminum-based composite materials [3-6]. Such primary formed QC phases for instance can deform together with aluminum matrix while they still harden the alloy due to higher hardness in comparison to aluminum matrix.

QCs were found in numerous aluminum-based alloy systems as equilibrium or metastable phases [7]. In an Al-Mn system, where they were first reported, primary icosahedral QCs (iQCs) were formed only at high cooling rates which are not achievable by existing conventional large scale casting technologies [8]. Adding elements like beryllium enabled the formation of iQCs also at moderate cooling rates (around  $500 \text{ Ks}^{-1}$ ) which can be achieved using conventional casting technologies [9-20]. Recent results indicate that primary iQCs can

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also form at such cooling rates in Al-Mn system with an addition of elements such as Cu, Si, and Mg without a need to add beryllium.

These iQC phases can be used as strengthening phases in these alloys. Therefore, a series of Al-Mn alloys were produced by melting and chill casting into round molds with diameters of 2.5, 4, 5, 6, 10 and 16 mm. This allowed us to establish the influence of the cooling rate in the first place and after that we also studied the influence of chemical composition on the formation, fraction and morphology of phases in synthesized alloys. The influence of alloying elements was studied through additions of B, Be, C, Ca, Cu, Fe, Mg, Si, Sr and Ti. Elements were added individually or as a combination of two or more. For our analyses LOM (light microscopy), SEM (scanning electron microscopy) and EDS (energy-dispersive x-ray spectroscopy) were used. Cooling rates were estimated by heat calculations and measurement of DAS (dendrite arm spacing).

## 2. MATERIALS AND METHODS

All alloys were synthesized using pure (99,9%) Al, Be, Cu, Fe, Si in an electric heated furnace. Cu, Fe, Mg, Mn and Si were added as pure elements, while B, Be, C, Ca, Ti and Sr were added to aluminum as master alloys. After synthesis all alloys were cast into permanent copper molds which had curved-in troughs of different diameters ranging from 2.5, 4, 5, 6, 8, 10 to 16 mm. In this way we could achieve different cooling rates and compare that to the microstructure evolved when exact cooling rate of 10 K/min typical for DTA or DSC analyses was employed.

Samples for LOM and SEM were prepared via routine metallographic method starting with grinding, polishing and finishing with deep etching in some cases. The chemical composition of all alloys is shown in Table 1.

Table 1. Chemical composition of synthesized alloys in at. %

El.	Al	Mn	Be	B	C	Ca	Cu	Fe	Mg	Si	Sr	Ti
Designation												
AM-1	96	4	–	–	–	–	–	–	–	–	–	–
AMC-2	94	4	–	–	–	–	2	–	–	–	–	–
AMM-1	94	4	–	–	–	–	–	–	2	–	–	–
AMCBF	94	1,6	2	–	–	–	2	0,4	–	–	–	–
AMCB-TBC	93,9	2	2	0,018	0,004	–	2	–	–	–	–	0,042
AMC-M1	85,5	2,5	–	–	–	–	2	–	10	–	–	–
AMC-M2	84	4	–	–	–	–	2	–	10	–	–	–
AMC-M3	92	4	–	–	–	–	2	–	2	–	–	–
AMC-M4	88	4	–	–	–	–	2	–	6	–	–	–
AMC-MS1	85	4	–	–	–	–	2	–	6	3	–	–
AMC-CP	94	2	–	–	–	2	2	–	–	–	–	–
AMC-S	95,5	1,8	–	–	–	–	1,5	–	–	–	1,2	–

## 3. RESULTS AND DISCUSSION

By studying the microstructures of alloys in Al-Mn-Cu-Be system we could establish that the lowest cooling rate needed for QCs to form is approx.  $500 \text{ Ks}^{-1}$  achievable in the case of 5 mm diameter troughs. In the case of cooling rates lower than needed for the formation of iQC, competitive, the so-called approximants appeared, such as the H-phase. Our results also suggest that the cooling rate necessary for formation of iQC phase depends on the alloying elements present in the alloy as well as on their quantity. We therefore decided to cast all our experimental alloys into 5 mm copper mold which ensured cooling rates around and above  $500 \text{ Ks}^{-1}$ . In order to verify the cooling rates in our al-

loys we employed DAS measurements and mathematical model based on lump-sum analysis. Calculations were carried out using following equations:

Heat balance on the mould/casting interface is:

$$\alpha \cdot A \cdot (T^n - T^k) \cdot dt = \rho \cdot c \cdot V \cdot (T^{n+1} - T^n) + \rho \cdot L \cdot V \cdot \frac{dfs}{dT}$$

Now, if the amount of the already solidified alloy is considered to be linear dependent upon temperature, i.e.  $\frac{dfs}{dT} = \frac{(T^n - T^{n+1})}{\Delta T_o}$ , we get:

$$\alpha \cdot A \cdot (T^n - T^k) \cdot dt = -\rho \cdot c \cdot V \cdot (T^{n+1} - T^n) + \rho \cdot L \cdot V \cdot \frac{(T^n - T^{n+1})}{\Delta T_o}$$

The cooling rate is defined as:

$$\frac{dT}{dt} = -\frac{\alpha \cdot A \cdot (T^n - T^k)}{V \cdot \rho \cdot c} \cdot \left(1 - \frac{L \cdot df_s}{c \cdot dT}\right)^{-1}$$

If the linearity between the amount of solidified alloy and the temperature is assumed as  $\frac{df_s}{dT} = \frac{(T^n - T^{n+1})}{\Delta T_o}$ , then the cooling rate within the solidification interval, becomes:

$$\frac{dT}{dt} = -\frac{\alpha \cdot A \cdot (T^n - T^k)}{V \cdot \rho \cdot c \cdot \left(1 - \frac{L \cdot (T^n - T^k)}{c \cdot \Delta T_o}\right)}$$

while outside the solidification interval the cooling rate is:

$$\frac{dT}{dt} = -\frac{\alpha \cdot A \cdot (T^n - T^k)}{V \cdot \rho \cdot c}$$

–The following assumptions were made for the calculation purposes:

– Heat transfer coefficient is constant prior to solidification with  $\alpha_{\max} = 2500 \text{ Wm}^{-2}\text{K}^{-1}$ ;

– Heat transfer coefficient within the solidification interval is dropping linearly from  $2500 \text{ Wm}^{-2}\text{K}^{-1}$  to  $1700 \text{ Wm}^{-2}\text{K}^{-1}$ ;

– Heat transfer coefficient after the solidification ended was close to  $400 \text{ Wm}^{-2}\text{K}^{-1}$ ;

– Density of the melt, specific heat and the crystallization latent heat are constant with:

- $\rho = 2750 \text{ kgm}^{-3}$
- $c = 875 \text{ Jkg}^{-1}\text{K}^{-1}$
- $L = 390 \text{ kJkg}^{-1}$

– Liquidus temperature was assumed to be  $654 \text{ }^\circ\text{C}$  and solidus temperature  $543 \text{ }^\circ\text{C}$ , yielding the solidification interval of  $111 \text{ }^\circ\text{C}$ .

It is evident from the Table 2 that the calculated and measured cooling rates correlate better in some cases than in others.

Table 2. Comparison of average calculated and measured cooling rates for synthesized alloys

Diameter [mm]	Solidification start [s]	Solidification end [s]	Solidification duration [s]	Max. dT/dt [ $\text{Ks}^{-1}$ ]	Average dT/dt [ $\text{Ks}^{-1}$ ]	DAS [ $\text{Ks}^{-1}$ ]	
						edge	central
2,5	0,16	0,76	0,6	1296	1036	1350	1000
4	0,202	1,349	1,147	648	516	750	600
6	0,303	2,023	1,72	432	343	–	–
10	0,505	3,370	2,680	259	205	280	180
16*	–	–	–	90	70	–	–

Nevertheless, it is obvious that the cooling rates needed for QCs to form were readily achieved with 6 mm diameter being a border line.

The presence of the primary iQC was in alloy systems other than Al-Mn-Cu-Be confirmed through their typical morphology using LOM. As iQCs have characteristic high symmetry structure, the morphology which develops in the process of growth usually adopts characteristic pentagonal- or trigonal-like shape.

Microstructures of all alloys listed in Table 1, show that iQC appeared in cases where Cu, Fe, Mg, Si were added and no QCs could be identified when B, C, Ca, Sr and Ti were added as presented in Figures 1 and 2.

We have also established that the morphology of iQC phase itself depends on the cooling rate as well as on the kind of alloying elements. Morphology tends to change from polygonal to heavily branched dendritic form. With the growing distance

from the edge of the samples and with a cooling rate decreasing in such a way the dendrites grow in size. The primary branches can get thicker and in some cases the secondary branches appeared as well, Figure 2.

LOM of synthesized alloys in the following set of micrographs in Figures 1 and 2 shows the influence of alloying elements on the constitution of Al-Mn-based alloy when the cooling rate was constant opposed to pure binary Al-Mn alloy.

Addition of B, C and Ti obviously did not promote the formation of typical QCs at approximately  $500 \text{ Ks}^{-1}$  as it was the case with the additions of Be, Cu and Fe presented in Fig. 1c. Addition of only Cu to Al-Mn system seems to enable the formation of QCs at these cooling rates as it can be seen from comparison of Fig. 1a and 1b. Similarly as Cu, Mg also seems to promote the formation of primary iQCs but less effectively than Cu as it is presented in Figures 1a and 1e.

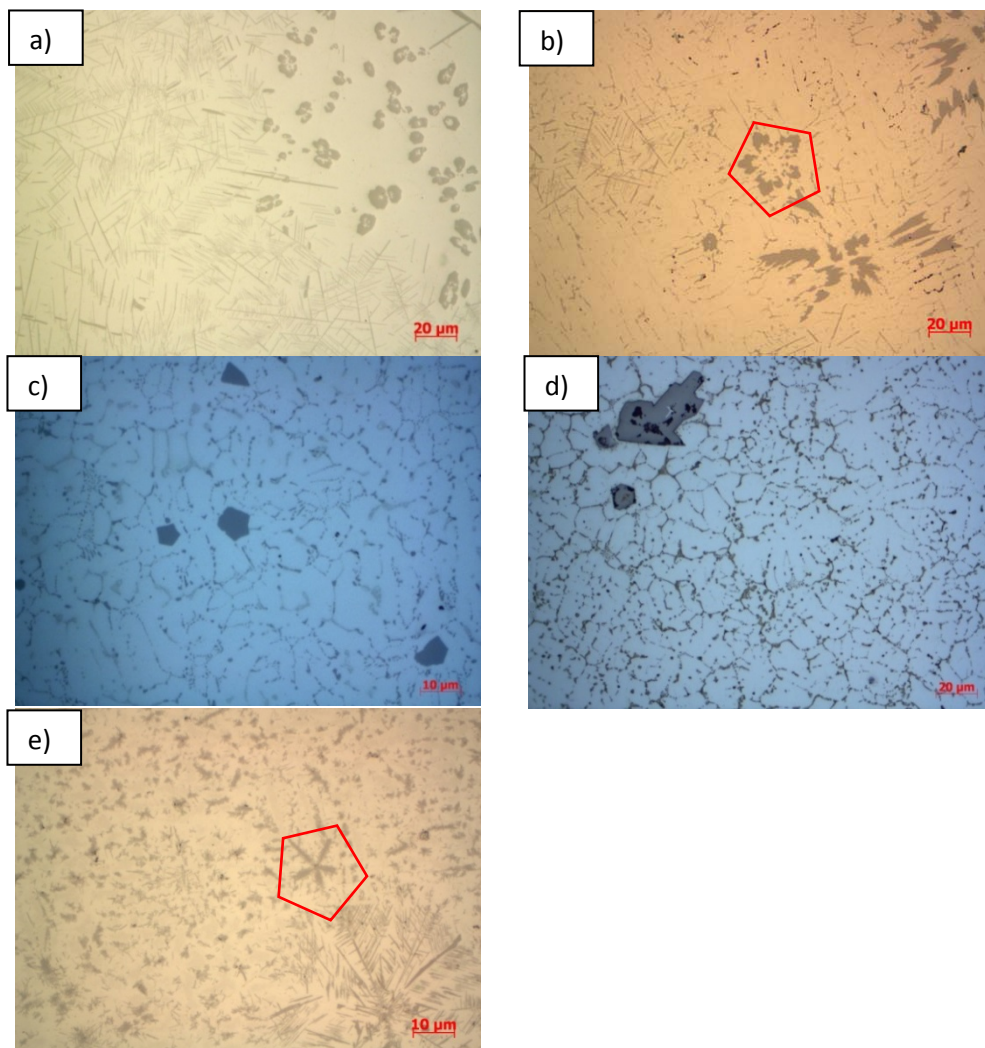


Figure 1. As-cast microstructure (LOM) of Al-Mn-based alloys: AM-1 (a), AMC-2 (b), AMCBF (c), AMCB-TBC (d) and AMM-1 (e)

Adding different concentrations of only Mg along with Cu and Mg and Si along with Cu sparked the formation of QCs throughout the volume of investigated alloys presented in Figure 2. Simultaneous presence of more elements, which promotes the formation of primary iQCs, seems much more effective. Presence of both Mg and Si in these alloys represents additional opportunity for possible precipitation hardening of these alloys.

Microchemical analysis using EDS on AMC-M4 alloy in as-cast condition offered evidence suggesting that besides Cu, Mg also incorporates into iQCs which obviously means that Mg promotes

formation of iQCs in Al-Mn-based alloys, Figure 3 and Table 3.

Table 3. Microchemical composition determined at point 2 in Figure 3 by EDS at 15 KV

	Al	Mn	Cu	Mg
at. %	76.57	18.17	3.31	1.95
wt. %	62.19	30.06	6.33	1.43

Furthermore, the amount of iQC phase in AMC-M4 alloy increased compared to AMC-2 alloy and seems more evenly distributed over the whole volume of the casting.



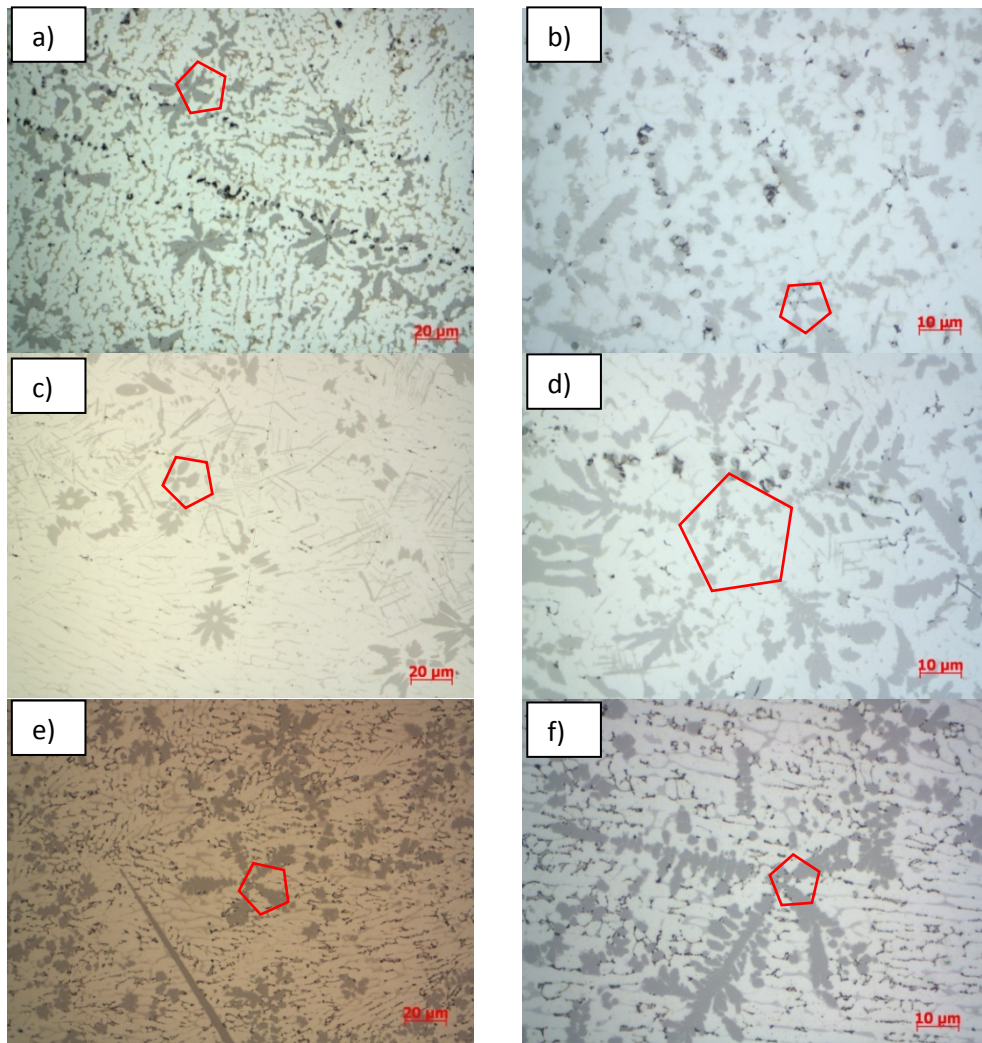


Figure 2. As-cast microstructure (LOM) of Al-Mn-based alloys: AMC-M1 (a), AMC-M2 (b), AMC-M3 (c), AMC-M4 (d) and AMC-MS1 (e) and (f)

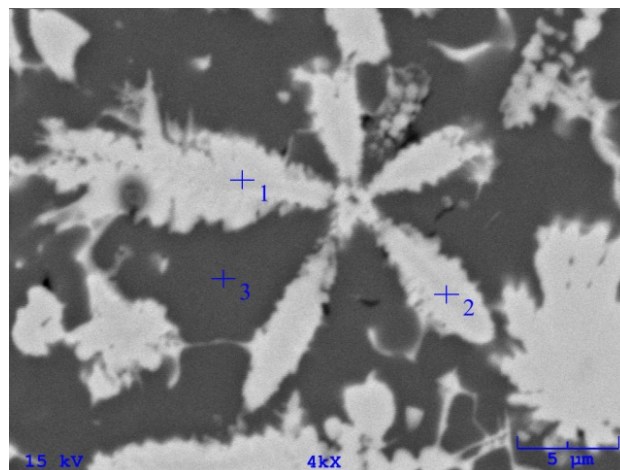


Figure 3. Backscattered electron image of AMC-M4 alloy with indicated spots for microchemical EDS analysis

#### 4. CONCLUSIONS

Based on the microstructural analysis of Al-Mn-based alloys in as-cast condition with the addition of several elements we can conclude that:

- Addition of B, C, Ca, Ti, and Sr was not effective in promoting the formation of the iQCs at cooling rates of approximately  $500 \text{ Ks}^{-1}$ .
- On the other hand, the addition of Be, Cu, Fe, Mg and Si has a positive effect on the ability of

iQCs formation at cooling rates of approximately  $500 \text{ K s}^{-1}$ . Simultaneous presence of more elements seems to be even more effective.

– Microchemical EDS analysis suggests that both Cu and Mg incorporates in primary iQCs phase in Al-Mn-Mg-Cu alloys.

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## УТИЦАЈ БРЗИНЕ ХЛАЂЕЊА И САДРЖАЈА ЛЕГИРАЈУЋИХ ЕЛЕМЕНАТА НА МИКРОСТРУКТУРУ Al–Mn ЛЕГУРА

**Сажетак:** Алуминијумске легуре се већ пет деценија интензивно користе, прије свега захваљујући свом повољном односу чврстоће и специфичне тежине. Због њихове масовне употребе у индустрији транспорта, осмишљене су бројне методе и

технике побољшања механичких особина ових легура. У раду је представљен утицај брзине хлађења и хемијског састава легура на бази Al-Mn система. Елементи као што су В, Ве, С, Са, Cu, Fe, Mg, Si, Sr и Ti додавани су у основну Al-Mn легуру и испитиван је њихов утицај. Утицај промјене брзине хлађења праћен је коришћењем ливења у бакарну кокилу са цилиндричним каналима различитих димензија. Комбиновани утицај промјена хемијског састава и брзина хлађења праћен је уз коришћење LOM, SEM, EDS, DTA експерименталних техника, као и математичког моделирања. Утврђено је да се у добијеним легурама на бази система Al-Mn формира већи број различитих фаза током процеса формирања и очвршћавања легура и то, углавном, кристални интерметалиди, али у неким случајевима и квазикристалне фазе (QC), нарочито када брзине хлађења прелазе  $500 \text{ Ks}^{-1}$ . Квазикристалне фазе се тренутно сматрају алтернативом за ојачавање Al-Mn легура. Утврђено је да се код легура система Al-Mn-Cu-Be, при брзинама хлађења између 500 и  $1350 \text{ Ks}^{-1}$ , формира икосаедрална QC фаза (iQC). Икосаедрална QC фаза се формира као примарна фаза, а у неким случајевима и у облику квазикристалног еутектикума ( $\alpha\text{Al} + \text{iQC}$ ). Додатак В, С, Са, Ti и Sr основној Al-Mn легури нкије изазивао формирање квазикристала у ливеној Al-Mn легури, док су се Fe, Cu, Mg и Si показали врло ефикасним у овом смислу.

**Кључне ријечи:** Al-Mn легуре, брзина хлађења, хемијски састав, квазикристали.

