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POLSKA AKADEMIA NAUK

A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S

Volume 60 2015 Issue 2

DOI: 10.1515/amm-2015-0204

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ESTIMATION OF COOLING RATES IN SUCTION CASTING AND COPPER-MOULD CASTING PROCESSES

OSZACOWANIE SZYBKOŚCI CHŁODZENIA STOPÓW W METODACH *SUCTION CASTING* I *COPPER-MOULD CASTING*

The cooling rates associated with suction and copper-mould casting of ø2, ø3 and ø5 mm rods made in Fe-25wt%Ni and Al-33wt%Cu alloys were determined based on their cellular and lamellar spacings, respectively. The work showed that the temperature profile in cylindrical samples can not be determined merely by microstructural examination of eutectic sample alloys. A concave solidification front, as a result of eutectic transformation, caused decrease of a lamellar spacing while approaching to the rod centre. The minimum axial cooling rates, estimated based on the cellular spacing in the Fe-25wt%Ni alloy, were evaluated to be about 200 K/s for both ø2 and ø3 mm and only 30 K/s for the ø5 mm suction cast rods. The corresponding values were slightly lower for the copper-mould cast rods.

Keywords: suction casting, copper mould casting, cooling rate, cellular solidification; eutectic solidification

Na podstawie analizy wielkości dendrytów komórkowych w stopie Fe-25Ni i odległości międzypłytkowych w stopie Al-33Cu zostały oszacowane szybkości chłodzenia w trakcie odlewania stopów metodami suction casting i copper-mould casting. Badania wykazały, że rozkład szybkości chłodzenia w cylindrycznych próbkach nie może być oszacowany w stopach z krystalizacją eutektyczną. W tym przypadku bowiem dochodzi do zmniejszania odległości międzypłytkowej w miarę zbliżania się do osi pręta, ze względu na wklęsły charakter frontu krystalizacji.

Minimalna szybkość chłodzenia w osi prętów odlanych za pomocą metody *suction casting*, wyznaczona w oparciu o pomiary wielkości dendrytów komórkowych w stopie Fe-25wt%Ni, wyniosła ok. 200 K/s dla stopów o średnicy ø2 i ø3 mm, i tylko 30 K/s dla stopów o średnicy ø5 mm. W przypadku stopów odlanych metodą *copper-mould casting* oszacowane wartości były nieznacznie mniejsze.

1. Introduction

The critical cooling rate R_c, required to hinder the crystallization process, depends mostly on the alloy composition. The first metallic glass, reported in 1960, was made of Au-Si binary system with a cooling rate in the range of 10^6 to 10^7 K/s [1]. High cooling rates limited the thickness of the first synthesized metallic glasses to several microns. Since then, amorphous materials in larger sizes were made by improving glass forming ability (GFA) at lower cooling rates and this led to the development of bulk metallic glasses (BMG's), with thicknesses greater than 1 mm. The best glass former reported up to date is the Pd-Cu-Ni-P system, with critical cooling rate below 1 K/s [2,3]. BMG's exhibit superior properties such as a high elastic limit and strength or excellent soft magnetic properties in the Fe-based systems [4,5]. However until development of relatively low-cost CuZr-based alloys [6-8] the widespread commercialization of BMGs was not possible.

R_c is effective indicator of GFA, but it is very difficult to be measured accurately. Therefore several different parameters, based on the thermal analysis at constant heating rate of the glassy alloy, has been proposed in order to infer the relative GFA among BMG's [9]. Formation of the amorphous phase requires application of a casting technique that allows reaching cooling rates above critical cooling rate.

Bulk metallic glasses can be fabricated with different forms and shapes using various rapid solidification techniques, *e.g.* suction casting, copper-mould casting and die pressure casting [10-12]. Most of these processes utilize copper moulds as a heat sink. In the suction casting method, an arc-melted alloy is sucked into a copper mould, due to a negative pressure in the mould relative to the main chamber. Moreover cooling rate of suction-cast alloys depends on the casting temperature, interfacial heat transfer, mould temperature and mould geometry or configuration [13].

The copper-mould casting process relies on induction melting of the alloy in quartz crucible with small orifice in the bottom, and using pressurised gas to eject the melt into the cavity of a copper block.

In order to obtain a homogeneous glassy structure, the cooling rate should be higher than R_c on the entire cross section of the as-cast alloy. Thermocouples can only measure moderate cooling rates on the surface of a cast [12]. Pyromet-

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ric measurements are also excluded if the melt is poured into a casting form.

Alternatively, indirect methods based on the microstructural features of the as-cast alloys, can be used to estimate cooling rates during solidification. However, the results obtained from microstructural features of the suction-cast Fe-25Ni [14] and Al-33Cu [12] alloys were completely different. In case of the suction-cast 2 and 4 mm rods, the cooling rate was about of $5 \cdot 10^3$ K/s close to the rod surface which was sharply decreased to ~10^2 K/s in the centre due to a radial cooling [14]. On the other hand in the Al-33Cu eutectic alloy, no evidence for the radial cooling was noticed. The cooling rate near the bottom of the 3 mm thick rod was in the range of 50 to 220 K/s and decreased along the axis towards the 40 to 125 K/s [12]. Such discrepancies may result from different types of equipment and/or different suction parameters (pressure difference, suction force etc.).

In this work the cooling rates were estimated by examining the microstructure of the suction cast and copper-mould cast Fe-25wt%Ni and Al-33wt%Cu rods.

2. Experimental procedure

The Fe-25wt%Ni (hereinafter referred to as Fe-25Ni) and Al-33wt%Cu (Al-33Cu) alloy ingots were synthesized by arc melting of a mixture of elements (with 99.9% or higher purity) under Ti-gettered argon atmosphere. The ingots were re-melted four times in order to ensure its homogeneity. The Arc Melter AM (Edmund Bühler GmbH) with a special water-cooled suction casting unit was used. This unit is adjusted to the copper plate, with hole in its central part, enabling formation of rods by suction of the liquid alloy into the two-parts copper form.

The chamber was evacuated to $6 \cdot 10^{-5}$ mbar and then filled with high purity argon up to 800 mbar. Two vacuum tanks were evacuated to $1 \cdot 10^{-4}$ mbar and used to produce required suction force. Three rods with 2, 3 and 5 mm diameter and an identical length of 55 mm were produced.

The copper-mould cast rods (ø2 and ø5×55 mm) were synthesized using Melt Spinner HV (Edmund Bühler GmbH) in which the 2-part copper form was mounted just below the quartz crucible orifice, instead of the spinning wheel. The chamber was evacuated to the pressure of about 10^{-4} mbar and then filled with argon to the pressure of 200 mbar. After melting, the alloy was ejected through a round nozzle into the cavity of the copper block, by applying a gas pressure of 1000 mbar into the quartz tube.

The Fe-25Ni and Al-33Cu microsections were ground, polished and then etched in 2% Nital and Keller's reagents, respectively. Light microscopy (Leica DM LM) enabled observations up to a magnification of 1000x. More detailed investigations were conducted in the Al-33Cu alloy, using scanning electron microscope (FEI Nova NanoSEM 450).

In order to evaluate the superficial and axial cooling rates, the microstructure analysis was carried on the near-to-surface (<100 um depth) and in central part of rods at three position from the rod bottom end, namely at x=5 mm (5 mm from the end – "foot"), x=27.5 mm (middle) and x=50 mm (5 mm from the top end – "head"), as shown in Figure 1.

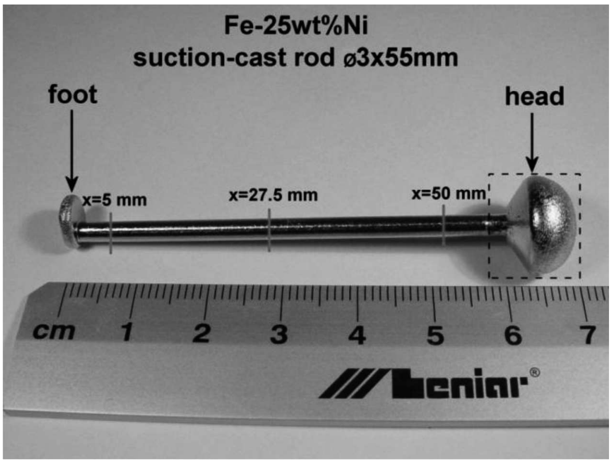

Fig. 1. A suction-cast ø3×55 mm Fe-25Ni rod

For the Fe-25Ni alloy, the cooling rate ε was estimated based on relationship between measured dendrite arm spacing λ [14,15]:

$$\varepsilon = \left(\frac{\lambda}{B_6}\right)^{-\frac{1}{n}} \tag{1}$$

where:

B_6 – constant equal 60 μm(K/s)^n for the Fe-25wt%Ni alloy [14,15],

n – constant equal 0.32 for the Fe-25Ni alloy [14,15].

In case of the eutectic Al-33wt%Cu alloy, the cooling rate was estimated by measuring the interlamellar spacing. The relationship between solidification front velocity v and interlamellar spacing λ was determined from [12]:

$$v = \frac{K}{\lambda^2} \tag{2}$$

where:

K – the constant equals $27.5 \cdot 10^{-12}$ cm^3s^{-1} obtained from unidirectional solidification

experiments for the Al-Al_2Cu eutectic system [12].

Cooling rate (ε) was estimated from the following equation [12]:

$$\varepsilon = \left(\lambda h_f / c_p\right)(2v/R) \tag{3}$$

where:

Δh_f – latent heat,

c_p – specific heat,

R – radius of cylinder.

3. Results and discussion

The Fe-25Ni alloy

Typical micrographs of the 3 mm diameter suction cast and copper-mould cast rods, are shown in Figs. 2 and 3, respectively. The cellular morphology, with most cells oriented perpendicular to the rod surface, indicates, that radial heat flux during solidification was dominant, independently of the casting process. The observed cellular-dendritic structure in the centre of the rods was due to high constitutional supercooling. The X-ray diffraction studies (not shown) revealed the presence of two-phase structure; BCC martensite and FCC austenite. Martensitic transformation takes place at concentrations below 40 at% Ni and at high cooling rates [16].

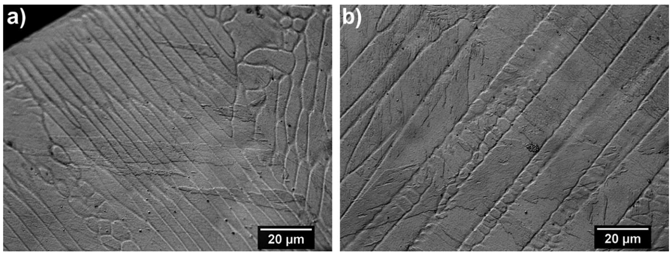

Fig. 2. Cross-sectional microstructure of the **suction cast** ø3 mm Fe-25Ni alloy at x=5 mm: a) near the rod surface, b) in the rod axis (light microscopy, 1000x)

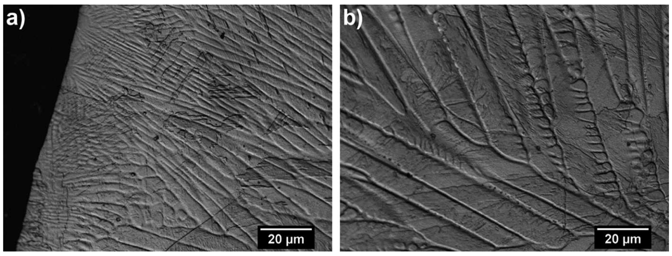

Fig. 3. Cross-sectional microstructure of the **copper-mould cast** ø3 mm Fe-25Ni alloy at x=5 mm: a) near the rod surface, b) in the rod axis (light microscopy, 1000x)

The results of microstructure investigations are summarized in Tables 1-2 and in Fig. 4. The cell widths close to the rod surface (<100 μm depth), are about 3-4 μm. The corresponding superficial cooling rates are higher than 1000 K/s (Fig. 4a). In this range, the cooling rate strongly depends on the cell width. The increase in interlamellar spacing λ from 2,7 to 3.9 μm indicated a reduction in the cooling rate from 15710 K/s to 1380 K/s.

However, in synthesising BMGs, lowest cooling rate across profile is most important factor. A mean cellular spacing, measured in the rod axis in the suction cast Fe-25Ni rods of diameter 2 and 3 mm, are of about 10 μm with no significant change along the rod (Table 1). These values represent a cooling rate of about 200 K/s. On the other hand, for the 5 mm diameter suction cast rod significant increase of mean cell width led to much lower cooling rates in the range of 30-50 K/s (Fig. 4b).

TABLE 1

Results of cellular spacing measurements in Fe-25wt%Ni suction cast rods

Distance from the foot (x), mm	Suction cast Fe-25Ni - cellular spacing (λ), μm					
	ø2 mm		ø3 mm		ø5 mm	
	Surface	Axis	Surface	Axis	Surface	Axis
5	2.9±1.5	9.4±3.4	4.3±1.6	10.8±3.9	4.8±1.7	17.1±5.6
27.5	3.3±1.4	10.9±4.5	4.2±1.4	10.6±3.3	4.3±2.3	16.5±5.7
50	2.8±1.3	10.7±4.6	4.7±1.8	11.1±3.3	5.5±2.2	19.8±7.3

In case of the copper-mould casting process, the mould was not fully filled with molten alloy and shrinking-induced holes close to the rod head were formed. The axial cooling rates of the copper-mould alloys are lower than those of the suction cast. In case of the 5 mm rods, at distance x = 5 mm, the lowest estimated cooling rate was 11 K/s (Fig. 4b). However, close to the rod surface the cooling rates was higher compared to the suction casting process (Fig. 4a).

TABLE 2

Results of cellular spacing measurements in Fe-25wt%Ni copper-mould cast rods

Distance from the foot (x), mm	Copper-mould cast Fe-25Ni - cellular spacing (λ), μm			
	ø2 mm		ø5 mm	
	Surface	Axis	Surface	Axis
5	3.9±1.8	13.3±4.5	3.8±2.0	27.4±7.6
27.5	3.4±1.8	10.4±4.2	5.9±2.9	20.4±7.2
50	2.7±1.6	hole	5.9±2.8	hole

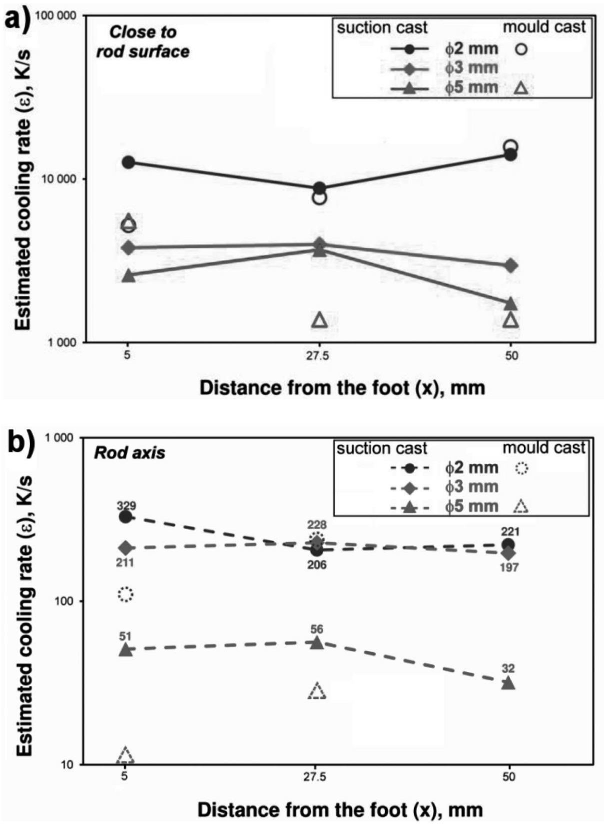

Fig. 4. Estimated a) superficial and b) axial cooling rates based on observed cellular spacing in Fe-25Ni alloy

The Al-33Cu alloy

Microstructures of the 3 mm diameter suction cast Al-33Cu rod, close to the surface and at axis, are shown in Fig. 5 in which typical lamellar eutectic morphologies, composed of the α-Al and $CuAl_2$ phases, can be seen. The mean values of interlamellar spacing λ close to the rod axis at positions x=5 mm, 27.5 mm and 50 mm were 111.9 nm, 122.3 nm and 102.4 nm, respectively. Based on the Eq. (3) the corresponding cooling rate should be about 643.3 K/s, 539.1 K/s and 770.0 K/s. Unexpectedly, in the rod axis the lamellar spacing was smaller compared to those observed on the surface. For 3 mm diameter suction cast rod, the λ was estimated to be about

90.0 nm, 105.5 nm and 85.1 nm at x=5, 275 and 50 mm, respectively.

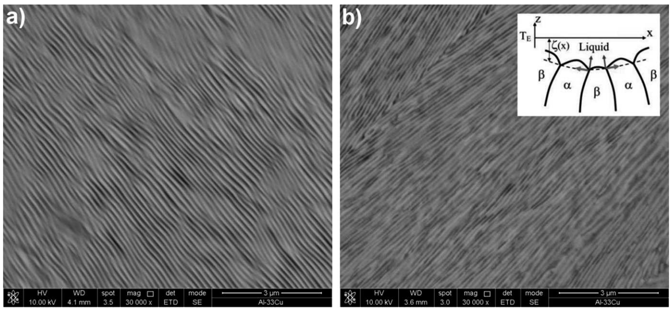

Fig. 5. Microstructures of ø3 mm Al-33Cu rod suction-cast at x = 27.5 mm: a) close to the rod surface, b) in the rod axis (SEM, 30000x). Inset shows a schematic illustration of lamellar elimination caused by a concave perturbation of the eutectic front [17]

Corresponding superficial and axial cooling rates in the 3 mm diameter suction cast Al-33Cu alloy are presented in Fig. 6. These results indicate than the axial cooling rate is higher than cooling rate on the surface, hence radial heat transfer could not be the dominant mechanism of heat removal.

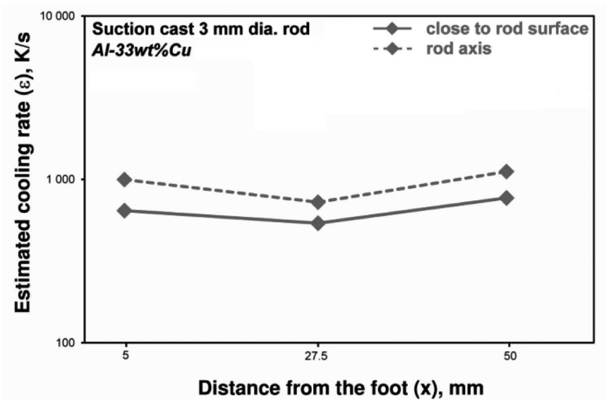

Fig. 6. Estimated superficial and axial cooling rates in Al-33wt%Cu (ø3×55 mm) suction cast alloy

Estimation of cooling rates based on the microstructural features in Fe-25Ni and Al-33Cu alloys led to inconsistent results, despite using the same casting process. Results obtained for the Al-Cu alloy indicated that the interlamellar spacing, controlled by the magnitude of undercooling, was also influenced by other factors. Karma and Plapp [17] have explained a lamellar elimination due to a concave perturbation of the eutectic front, as shown in Fig. 5b (inset). The envelope of the composite interface is shown as a dashed line that passes through trijunctions. The arrows denote a motion of the trijunctions of the central β lamella normal to this envelope and lateral motion of the junctions in the direction of increasing spacing, respectively. For the lamellae growing locally perpendicular to the envelope of the eutectic front, lateral displacement of the trijunctions to the local slope of the envelope of the eutectic front occurs. This means that the lamellar spacing decreases in the concave region of the envelope. The smaller lamellar spacing cause the front temperature to drop further and hence finer lamellar structure is formed [17].

The main outcome of this work is that the eutectic alloys should not be used to estimate the cooling rate or temperature profile across cylindrical samples. In the Ref. [12], the authors have estimated the cooling rate along the axis of samples, but did not consider the radial cooling rates.

The Fe-25Ni alloy exhibited cellular solidification, with most cells oriented perpendicular to the rod surface. Estimated superficial cooling rates are much higher than those in the rod axis, which confirms that the radial cooling is dominant during suction casting process. The cooling rate estimated in this work is consistent with the published values [14].

In order to compare suction casting and copper-mould casting processes, some factors must be taken in account. Firstly, in the former the sample was arc melted, while in the latter induction heating was used. Thus, the casting temperature and heat content are higher in the suction casting method than in the copper cast samples. On the other hand, the heat removal strongly depends on the equipment setup. Secondly, in case of the copper-mould casting the heat was removed from the alloy only through the copper, while in the suction casting, a water-cooled system was used. Estimated axial cooling rates obtained for the suction cast Fe-25Ni alloys are slightly higher than those of the copper-mould cast, but the results have the same order of magnitude.

It is expected that the cooling rate for the glass-forming systems to be higher compared to those obtained from the conventional solidification due to absence of the latent heat during glass formation. Other factors that should be considered are (1) much lower thermal conductivity of BMG's, and (2) heat flow affected by the interfacial resistance at the mould-metal interface. Finally, it should be noted that the cooling rates were calculated using the equations adopted from unidirectional solidification experiments, which was not the process used in this work.

4. Conclusions

Having measured the cellular spacing in Fe-25wt%Ni alloy, superficial and axial cooling rates were evaluated. Cooling rate estimated for the suction cast and copper-mould cast alloys were comparable, although the former had a slightly higher cooling rates due using a water cooled system. Estimated minimum axial cooling rates, as the most important parameter in synthesising BMGs, were about 200 K/s for the ø2 and ø3 mm, and about 30 K/s for the ø5 mm suction cast rods. The outcome of this work clearly showed that the eutectic alloys should not be used to estimate temperature profile (*e.g.* cooling rates) in cylindrical samples, since the interlamellar spacing is affected by the concave perturbation of the solidification front.

Acknowledgements

This work was financially supported by the National Science Centre (NCN) under contract No. 2011/03/D/ST8/04131. Valuable contribution of Dr. Jerzy Latuch (Warsaw University of Technology) to the experimental work is also acknowledged.

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Received: 20 April 2014.