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ESTIMATION OF THE COOLING RATE IN 3 mm SUCTION-CAST RODS BASED ON THE MICROSTRUCTURAL FEATURES

OSZACOWANIE SZYBKOŚCI CHŁODZENIA PRĘTÓW O ŚREDNICY 3 mm ODLANYCH METODĄ SUCTION-CASTING NA PODSTAWIE CECH MIKROSTRUKTURY

Abstract

One of the factors influencing possibility of bulk metallic glass formation is cooling rate attainable in the casting process. The evaluation of the cooling rate of the suction-cast 3 mm rods is presented based on the measurements of the cellular spacing in the Fe-25Ni and lamellar spacing in the Cu-33Al alloys. The estimated cooling rates are higher close to the rod surface (2952–3817 $K \cdot s^{-1}$) than in the rod axis (228–328 $K \cdot s^{-1}$), which indicates the dominant radial heat flow. In contrast, for the Al-33Cu alloy higher cooling rates were evaluated in the rod axis than close to the surface due to the concave perturbation of the solidification front during eutectic transformation. Based on the results obtained for the Fe-25Ni alloy, it is concluded, that the cooling rate for the suction-cast 3 mm rod is not lower than 228 $K \cdot s^{-1}$.
Keywords: rate, cellular solidification, eutectic, lamellar spacing

Streszczenie

Jednym z czynników determinujących możliwość uzyskania masywnych szkieł metalicznych jest szybkość chłodzenia osiągana w danej metodzie odlewania. Przedstawiono wyniki jej oszacowania dla prętów o średnicy 3 mm odlanych metodą *suction-casting* na podstawie pomiaru odległości międzykomórkowych w stopie Fe-25Ni i odległości międzypłytkowych w stopie Cu-33Al. Oszacowane szybkości chłodzenia są znacznie wyższe przy powierzchni pręta (2952–3817 $K \cdot s^{-1}$) niż w osi (228–328 $K \cdot s^{-1}$), co wskazuje na dominującą rolę radialnego odprowadzania ciepła. Odwrotną zależność uzyskano dla stopu Al-33Cu ze względu na wpływ kształtu krzywizny frontu przemiany podczas krzepnięcia. Bazując na wynikach otrzymanych dla stopu Fe-25Ni stwierdzono, że szybkość chłodzenia prętów o średnicy 3 mm, odlanych za pomocą metody *suction-casting*, jest nie mniejsza niż 228 $K \cdot s^{-1}$.
Słowa kluczowe: szybkość chłodzenia, krzepnięcie komórkowe, eutektyka, odległość międzypłytkowa

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1. Introduction

Metallic glasses possess unique physical and mechanical properties, such as superior magnetic properties, excellent corrosion resistance, high strength and high elastic limit [1]. During the cooling process of a liquid alloy at cooling rates high enough to suppress the nucleation and growth of thermodynamically stable crystalline phases, the undercooled melt solidifies into an amorphous phase at glass transition temperature. Metallic glasses can be considered as solids with a frozen-in liquid structure, absence of translational periodicity and macroscopic compositional homogeneity [2].

There are many techniques commonly used for the fabrication of bulk metallic glasses (BMG's) in the form of rods, tubes, plates, etc. In the suction casting method, the arc-melted alloy is sucked into a copper mold by a pressure difference between the melting chamber and the casting unit connected to the pre-evacuated vacuum tanks. The suction force depends on the pressure difference and can be regulated by means of the throttle valve. Moreover, the possibility of glass formation is determined by interfacial heat transfer, casting temperature, mold temperature and mold geometry [3].

In order to obtain a homogeneous glassy structure it would be useful to know a cooling rate in an applied casting method. Although it is possible to measure this parameter using thermocouples, it is limited only to outer surface and for moderate cooling rates [4]. The cooling rate can be estimated indirectly from microstructural features. However, results of such investigations obtained for the Fe-25Ni [5] and Al-33Cu [4] alloys are dissimilar. In the case of the Fe-25Ni suction-cast 2 and 4 mm rods, the cooling rate close to the rod surface was in the range of $5 \cdot 10^3$ K/s and exponentially decreased to ~10^2 K/s in the area close to the rod center due to a radial cooling [5]. On the other hand, in the Al-33Cu eutectic alloy, no evidence of radial cooling within a cross-section is reported, but a decrease of the cooling rate along the axial coordinate is noticed. For 3 mm rods, produced by different casting methods including suction casting, a maximum cooling rate was in the range of 50 to 220 K/s close to the bottom part of the rod and decreased along the axis towards the 40 to 125 K/s. Moreover, authors pointed out that suction casting provides a much lower cooling rate compared to the centrifugal and copper-mould casting [4].

The goal of this paper is the estimation of cooling rates during the suction casting of 3 mm rods, based on the microstructural features of the Fe-25Ni and Al-33Cu alloys, at fixed suction casting parameters.

2. The experimental procedure

The master alloys of Fe-25wt%Ni (referred to as Fe-25Ni) and Al-33wt%Cu (Al-33Cu) were prepared by arc the melting of a mixture of high purity (99.9% or higher) elements under titanium gettered argon atmosphere. The ingots were remelted four times in order to ensure its homogeneity. The Arc Melter AM (Edmund Bühler GmbH) used in this experiment can work in a melting or suction casting mode. In the latter, a special water-cooled suction casting unit is adjusted to the copper plate with a hole in the central part, enabling the formation of rods by the suction of the liquid alloy into the two-parts copper form. Prior to the arc melting process, nevertheless before synthesis or suction casting, the chamber was evacuated to the level of $6 \cdot 10^{-5}$ mbar using rotary and turbomolecular pumps, and then filled with high purity (5N) argon to the pressure of 800 mbar. While pumping down prior to the suction-casting process, two vacuum tanks were also evacuated to the pressure of $1 \cdot 10^{-4}$ mbar.

In this paper results for the suction-cast cylindrical samples of diameter 3 mm and length of 55 mm are presented. Figure 1 shows images of as-cast alloys. The microstructure analysis was carried on the cross-sections of the rods near the bottom part (5 mm from the "foot"), in the central part (half crosswise) and near the top (5 mm from the "head").

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 of up to a magnification of 1000x. In the latter alloy, because of fine lamellar spacing, more detailed investigations were carried out by means of scanning electron microscopy (FEI Nova NanoSEM 450).

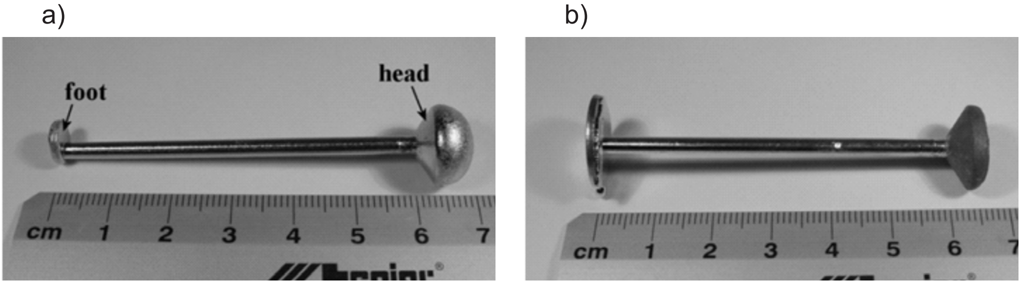

Fig. 1. Images of the suction-cast rods: a) Fe-25Ni, b) Al-33Cu alloys

The relationship between measured dendrite arm spacing λ and cooling rate ε [5] is given by:

$$\lambda = B_6\ \varepsilon^{-n} \tag{1}$$

where:

B_6 – constant equal 60 μm $(K/s)^n$ for the Fe-25Ni alloy [5, 6],
n – constant equal 0.32 for the Fe-25Ni alloy [5, 6].

Thus the cooling rate ε in the Fe-25Ni alloys can be estimated from the formula:

$$\varepsilon = \left(\frac{\lambda}{B_6}\right)^{\frac{-1}{n}} \tag{2}$$

The measurements of cellular spacing (width of the cell) were carried out perpendicular to its length. If a cellular-dendritic morphology was observed, a total width of the cell was considered, as shown in Figure 2c (line).

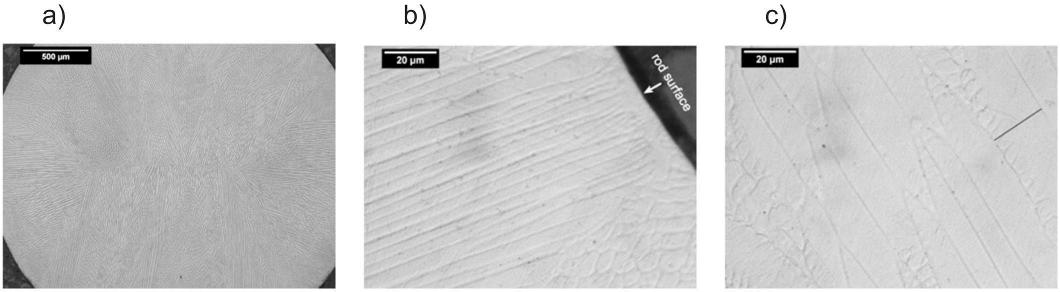

Fig. 2. Microstructures of the suction-cast Fe-25Ni alloy: a) cross-sectional image of the rod cut in half crosswise (light microscopy, 50x), b) magnified area close to the rod surface and c) in the rod axis (light microscopy, 1000x)

On the other hand, Srivastava et al. [4] have estimated the cooling rate based on the lamellar spacing measurements in the suction-cast eutectic Al-33Cu model alloy. By comparing the heat balance between solidification at fixed temperature TE and temperature change during the cooling of a cylindrical disk, the cooling rate can be estimated from (3) [4].

$$T = \left(\frac{\Delta h_f}{c_p}\right)\cdot\left(\frac{2\cdot v}{R}\right) \tag{3}$$

where:

Δh_f – latent heat,

c_p – specific heat,

v – solidification front velocity,

R – radius of cylinder (in this paper 1.5 mm).

The ratio $\Delta h_f/c_p$ for the Al-33Cu is 440 K [4, 6], while the solidification front velocity can be determined from [4]:

$$v = \frac{K}{\lambda^2} \tag{4}$$

where:

K – the constant equals $27.5\cdot10^{-12}$ $cm^3\cdot s^{-1}$ obtained from unidirectional solidification experiments for the Al-$CuAl_2$ eutectic system [4],

λ– interlamellar spacing.

A final formula, via eq. (4), for the estimation of the cooling rate in the Al-33Cu eutectic alloy is:

$$T = \left(\frac{\Delta h_f}{c_p}\right)\cdot\left(\frac{2\cdot K}{R\cdot \lambda^2}\right) \tag{5}$$

Random secants were projected over the lamellar microstructure. On each secant the numbers of intersections with plates of α-Al and $CuAl_2$ phases were counted. The estimation of true interlamellar spacing has been performed according to the method presented in references [7, 8].

3. Results

3.1. Fe-25Ni alloy

Cross-sectional images of the suction-cast Fe-25Ni alloy rod, cut in half crosswise, are presented in Figures 2 and 3. The cellular and cellular-dendritic morphologies were observed. The latter results from an increasing degree of constitutional supercooling when approaching to the rod axis (Figs 2c, 3). Much smaller cellular spacing was observed close to the rod surface (in max. distance of 100 µm from the surface) in comparison to the rod axis, as shown in Figures 2b and 2c.

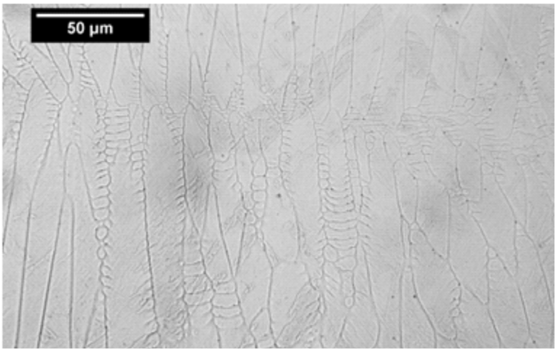

Fig. 3. Example of cellular-dendritic morphology observed in the Fe-25Ni alloy (light microscopy, 500x)

The results of the microstructure investigations and estimated cooling rates in the Fe-25Ni alloy are presented in Figure 4. The cellular spacing was measured close to the rod surface (in max. distance of 100 μm) and in the rod axis for three positions: 5, 27.5 (half crosswise) and 50 mm from the bottom of the rod. The mean value spacing close to the rod surface was in the range of 4.2–4.7 μm and no significant change was noticed along axial coordinate.

On the other hand, the cellular spacing in the rod axis was in the range of 9.3–10.5 μm. These results indicate that radial heat flux is dominant in the suction casting process. Accordingly the estimated cooling rates are much higher close to the rod surface (2952–3817 K·s^{-1}) than in the rod axis (228–328 K·s^{-1}), as shown in Figure 4b.

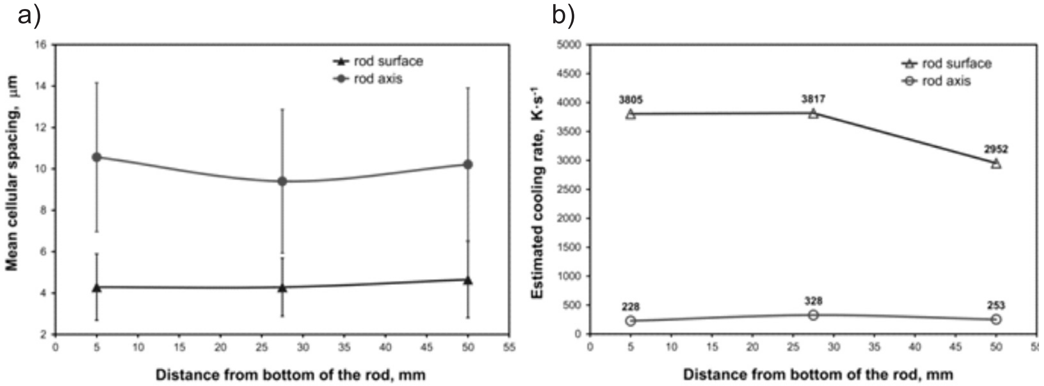

Fig. 4. Results of microstructure investigation in the Fe-25Ni alloy close to the rod surface and in the rod axis: a) mean cellular spacing with standard deviations, b) estimated cooling rates

3.2. Al-33Cu alloy

Figure 5 presents cross-sectional images of the Al-33Cu suction-cast alloy, cut in half crosswise. Light microscopy (Fig. 5a) did not allow to observe lamellar structure, but one may observe colonies of different contrast, indicating local differences in lamellar spacing. Scanning electron microscopy (SEM) images showing structure of the eutectic, composed of the λ-Al and CuAl$_2$ phases, are presented in Figures 5b and 5c.

Based on the measurements of the lamellar spacing, the cooling rate was estimated, according to equation (5). The measured values are in the range of 0.085 to 0.122 μm, but a mean lamellar spacing, for each position from bottom to top, is clearly smaller in the rod axis (Fig. 6a). Hence, the cooling rate close to the rod surface is smaller (539–770 K·s^{-1}) than in the rod axis (725–1115 K·s^{-1}).

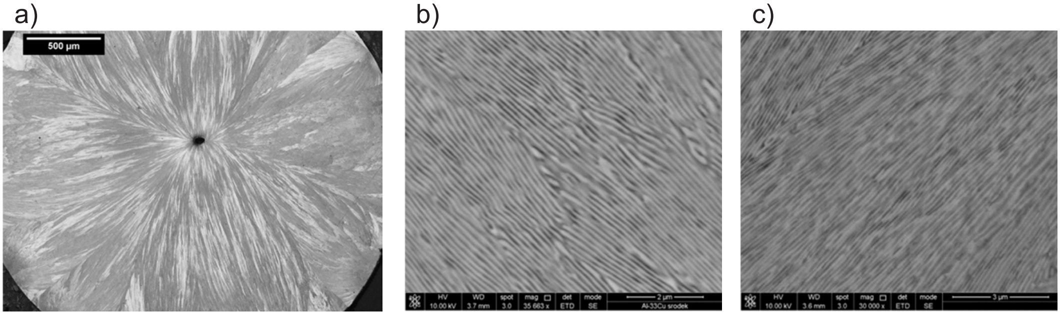

Fig. 5. Microstructures of the suction-cast Al-33Cu alloy: a) cross-sectional image of the rod cut in half crosswise (light microscopy, 50x), b) magnified area close to the rod surface and c) in the rod axis (scanning electron microscopy, 30000x)

4. Discussion

Microstructure investigations of the Fe-25Ni and Al-33Cu suction-cast alloys enabled an estimation of the cooling rates. In the case of the first alloy, the cooling rate is much higher close to the rod surface than in the rod axis. It indicates that radial cooling is dominant during the suction casting process. Similar results were presented by Pawlik et al. [5]. In the present studies the estimated cooling rate would be even higher, if we measured the distance between secondary dendrite arms spacing in the case of the presence of cellular-dendritic morphology, like in reference [5].

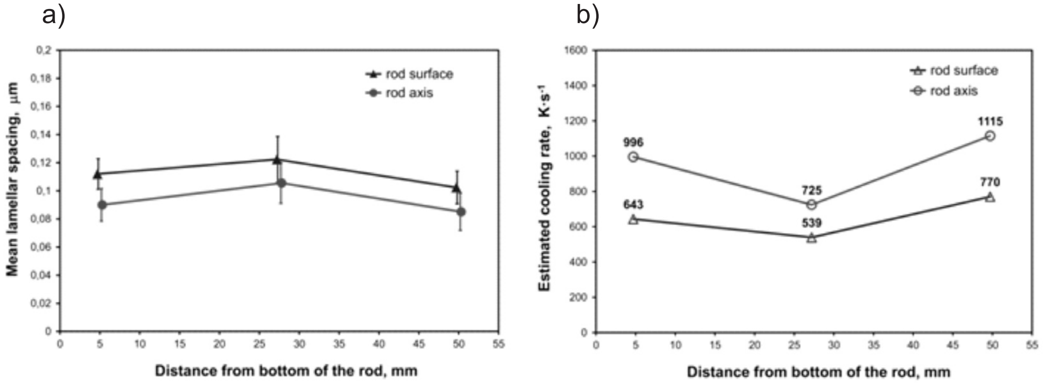

Fig. 6. Results of microstructure investigation in the Al-33Cu alloy close to the rod surface and in the rod axis: a) mean lamellar spacing with standard deviations, b) estimated cooling rates

In contrast, the results obtained for the Al-33Cu eutectic alloy were quite surprising. A smaller lamellar spacing was noticed in the rod axis. It is interesting to note that in the Srivastava et al. [4] did not compare surface and axial lamellar spacing, but were focused only on the measurements with the length coordinate parallel to the rod axis.

The eutectic solidification involves the extraction of heat from the liquid and the motion of the interface. A cooperative growth of two solid phases from a liquid was described by Jackson–Hunt [9]. However, in this theory a steady-state growth is considered for lamellar spacing much smaller than a diffusion distance and for sufficiently small interface undercooling. Accordingly the lamellar structures can exist for a continuous range of spacing, but there is some range of stable spacing, which, for eutectic growth, is located at the minimum undercooling (maximum temperature) spacing λ_m [10]. Figure 7 shows a schematic of the lamellar elimination caused by a concave perturbation of the eutectic front. The envelope of the composite interface is shown as a dashed line that passes through trijunctions. The blue arrows indicate a motion of the trijunctions of the central β lamella normal to this envelope, while the red ones depict a lateral motion of the junctions in the direction of the increasing spacing. If we assume that the lamellae grow locally perpendicular to the envelope of the eutectic front, it leads to the lateral displacement of the trijunctions to the local slope of the envelope of the eutectic front. It means that the lamellar spacing decreases in the concave region of the envelope. The smaller lamellar spacing causes the front temperature to decrease and the lamella to become even narrower [11].

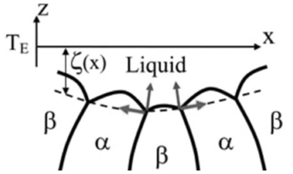

Fig. 7. A schematic illustration of lamellar elimination caused by a concave perturbation of the eutectic front [11]

It is concluded that formation of a concave solid/liquid interface, with curvature radius decreasing while approaching to the central part of the solidifying rod, leads to decrease of the lamellar spacing. Thus the cooling rate evaluated for the Al-33Cu eutectic alloy in its central part is overestimated.

Nevertheless the cooling rates in bottom (foot) and top (head) parts of the rod are substantially higher compared to the half crosswise (Fig. 6b). A reason of increased cooling rate in a top part of the rod (5 mm from the head) is probably due to a design of the suction-casting unit used in these experiments. A top part of the casting form, besides radial cooling through a water-cooled casting unit, has huge contact with a copper crucible plate, leading to increase of the cooling rate.

Direct transfer of the results obtained for the solidified crystalline alloys to the glass formation should be considered with care because of:

– use of the equations adopted from the unidirectional solidification experiments, which can not be fulfilled in a suction casting process,
– heat flow affected by the interfacial resistance at the mold-metal interface and the thermal conductivity of the casting and mold,
– much lower thermal conductivity of BMG's with respect to the possible generation of thermal gradients and (iv) absence of latent heat during glass formation which was considered during typical crystallization.

5. Conclusions

An investigation of the microstructural features of suction-cast alloys provides useful information about cooling rates during casting and makes easier selection of potential alloys for synthesis of BMG's. However based on the empirical equations, given for the Fe-25Ni and Al-33Cu model alloys, significant discrepancies were noticed. In the latter, the estimated cooling rate is not reliable, because lamellar spacing, besides undercooling, is additionally affected by a concave perturbation of the solidification front. Thus, based on the microstructural investigation of the Fe-25Ni alloy, it is assumed that cooling rate for the 3 mm suction-cast alloy is not lower than 228 K/s.

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