Cooling Rate Evaluation for Bulk Amorphous Alloys from Eutectic Microstructures in Casting Processes

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The structural features of metallic glasses depend on the cooling rate of the melt. The cooling rates for casting processes which are typically employed for preparation of bulk metallic glasses are suggested from microstructures of an eutectic Al–33 mass%Cu model alloy. The interlamellar spacing \( \lambda \) of eutectic Al–CuAl₂ rod-shaped specimens of 50 mm in length and 2 to 5 mm in diameter has been determined by optical microscopy and scanning electron microscopy. From the measured interlamellar spacings ranging from \( \lambda = 0.18 \) to 0.5 \( \mu \)m, the solidification front velocities and the cooling rates at different positions in the as-cast samples are derived. The decisive effect of the diameter of cast rods is confirmed. For a centrifugal casting technique, the maximum cooling rate decreases from 730 to 95 K/s when the diameter increases from 2 to 5 mm. Moreover, it is revealed that the local cooling rates decrease significantly from the bottom towards the top of the rods. From the estimated cooling rates at a fixed rod diameter the centrifugal casting technique is assessed as superior to other methods applied, namely copper-mould casting and suction casting. The estimated cooling rates are compared with literature data for glass-forming alloys.

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1. Introduction

Amorphous materials have long been known as promising materials due to their favourable magnetic and mechanical properties or high corrosion resistance which are superior to those of their conventional crystalline counterparts.1,2) Since metallic melts usually crystallize when cooled at rates for which non-metallic liquids form glassy, high cooling rates of about \( 10^4 – 10^6 \) K/s are necessary to circumvent crystallization. For a long time multicomponent metallic systems that form glasses at cooling rates as low as 1–100 K/s were scarce and restricted to some Pd-based alloys.3,4) However, the discovery of the Mg–RE–TM5 glass forming system (TM=transition metal, and RE=rare earth elements) in 1988 opened a new door for bulk metallic glasses. Since then new systems exhibiting large glass-forming ability (GFA) have been explored.5) Among these alloys Zh–Ti–Cu–Ni–Be bulk metallic glasses5) have achieved technical importance because of their outstanding mechanical properties6) and the high degree of processability.

A full exploitation of the technical potential of the various bulk amorphous alloys requires good control of the casting processes used for their synthesis. Now it seems rather evident that the structure and the properties of these materials are greatly affected by the method and the conditions of preparation. In order to get a detailed knowledge of the process, the temperatures as function of time during mould casting of bulk metallic glasses at various coordinates within a wedge-shaped mould have been determined by thermocouples.6) One particular outcome of the studies was the critical cooling rate for glass formation (inferred from the absence of recalcitrance events) for representative alloys, e.g., \( T_C \approx 110 \) K/s for Zh₂₀Al₁₀Ni₁₀Cu₁₂Pd₁₀5 and \( T_C < 1.58 \) K/s for Pd₂₀Cu₁₅₀Ni₁₀P₂₀.10) Though measurements with thermocouples supply important information on the casting and solidification process they are limited to moderate cooling rates and the resolution of spatial variation in cooling processes is given by the distance between thermocouples (typically several millimetres). That is, for small specimen dimensions differences in cooling processes, e.g., between outer shell and central part or along the axis are not accessible. However, this information is highly desirable for quality control of castings and assessment of process parameters.

On the other hand, cooling rates (or alternatively the growth velocity) can be estimated indirectly from microstructural features. In bulk metallic glasses crystalline precipitates are formed if the cooling rate falls below \( T_C \). These crystals in a glassy sample can easily be detected by optical microscopy but quantitative information is rather poor.6) Crystalline model alloys have been successfully applied to characterize rapid solidification process parameters by distinct microstructural features such as grain size, dendrite arm spacing, eutectic interlamellar spacing.11) The power law relationship between the eutectic interlamellar spacing and the solidification front velocity is of particular value, since it holds over several orders of magnitude. Heat transfer coefficients, cooling rate and melt undercooling in rapid solidification processes were estimated from the interlamellar spacing of splat-quenched12) and melt spun13,14) eutectic Al–Cu alloys. However, so far no such investigations are known for casting methods and process parameters of bulk metallic glasses.

Consequently, the purpose of this paper is an assessment of various methods namely copper-mould casting, centrifugal mould casting and suction casting, by detailed microstructure investigations of an Al–33 mass%Cu eutectic model alloy. Characteristic cooling rates are evaluated from the eutectic interlamellar spacing for various process parameters and for different positions in the as-cast bulk rods. The transfer of the results from crystallization to glass-forming alloys must be considered with care because of (i) latent heat release on crys-
tallization which is absent in glass formation, (ii) different melting temperatures of the studied eutectic alloy and glass-forming alloys, and (iii) differences in metal-mould interfacial heat transfer caused by the specific features of melt wetting and shrinking processes during solidification. Notwithstanding these objections the method can provide useful information about the assessment of different casting methods for bulk metallic glasses and variation of process parameters within the as-cast specimen, too.

2. Experimental

Master alloys of Al–33 mass%Cu were prepared by induction melting from 99.999% pure aluminium and copper under argon atmosphere. For casting of rods with diameters of 1 to 5 mm and 50 mm in length, dimensions which are typical for bulk amorphous samples, six different methods were employed.

In mould casting crushed ingots were re-melted within a quartz crucible by an induction coil. Cylindrical rods were cast by ejecting the melt with argon gas pressure through a small orifice at the bottom of the quartz tube into the cavity of the copper block. The whole process proceeds in an argon atmosphere within a vacuum chamber.

The centrifugal mould casting unit consists of a vacuum chamber, which contains a horizontal beam mounted on a vertical rod. At one end of the beam a vacuum box containing both the graphite crucible surrounded by quartz tube and the water cooled copper-mould are mounted. The nozzle of the graphite crucible is aligned onto the cavity of the copper-mould. Melting by an induction coil surrounding the quartz tube is performed under observation through a glass window. Immediately after melting the rod is rotated with 500 rpm, which applies the centrifugal force to the melt. The crucible design is such that the vertical component of the centrifugal force transports the molten metal to the nozzle whereas the horizontal component drives the melt into the mould cavity.

In suction casting the alloy is arc-melted in a zirconium-gettered argon atmosphere with \( \sim 50 \) kPa. The melt is sucked into a copper-mould through a hole at the bottom of the water cooled copper hearth by opening the valve between the mould and a vacuum chamber with \( 10^{-1} \) Pa.

For microstructure investigations, the as-cast rods were cut into 1 mm thick disks. The polished transverse cross-sections of samples were investigated in a ‘Jenapol’ polarized light optical microscope up to a magnification of 1000×. For more detailed investigations, micrographs were prepared up to magnifications of 5000× by using a ‘Zeiss DSM 962’ scanning electron microscope (SEM).

3. Methods of Data Evaluation

The interlamellar spacing \( \lambda \) of eutectic alloys (in this study the half-cell spacing was used as interlamellar spacing \( \lambda \) throughout the paper) is often given as function of the solidification front velocity \( v \) according to the Jackson-Hunt relation\(^{5}\)

\[
v \cdot \lambda^2 = K.
\]  

The constant \( K = 27.5 \times 10^{-12} \) cm\(^3\)s\(^{-1}\) is determined from unidirectional solidification experiments for the Al–Al\(_2\)Cu eutectic system.\(^{16}\) Unsteady growth by variation of the velocity \( v \) can lead to discontinuous adjustment and local deviation of lamellar spacings \( \lambda \) from the steady state value given in eq. (1).\(^{17}\) However, the effect is more pronounced for slow growth rates (\( v \approx 5 \times 10^{-5} \) ms\(^{-1}\)) but expected to be small for velocities considered in this paper. The relationship given by eq. (1) has been first employed by Burden and Jones\(^{12}\) to evaluate the effective velocity \( v \) from lamellar spacings of Al–Cu eutectic alloy gun splats. The same authors have also estimated the effective cooling rate of splats, which seems to be a more appropriate parameter for glass formation than the eutectic solidification front velocity at a fixed temperature \( T_E \).

We can transfer their procedure to the cylindrical geometry by considering the heat balance of a solidifying cylindrical disk cooled from the outer surface

\[
q_s(A/V) = -c_p(dT/dt) + \Delta h_t \cdot (df_s/dt).
\]  

Here, \( q_s \) is the external heat flux density at the sample surface, \( A/V = 2/R \) is the surface to volume ratio of a cylinder of radius \( R \), and \( c_p \) and \( \Delta h_t \) are the specific heat (assumed to be equal for melt and solid) and the latent heat of fusion per unit volume, respectively. In general, heat extraction can lead to both a decrease of temperature \( T \) with cooling rate \( \dot{T} = dT/dt \) or, alternatively, a rise of the solidified fraction \( f_s \). With radial heat flux for solidification of the disk from the surface \( R_s = R \) (where \( R_s \) is the position of the solid-liquid interface) towards the centre a relation

\[
df_s/dt = -(2R_s/R^2) \cdot (dR_s/dt)
\]  

between the freezing rate \( df_s/dt \) and the solidification front velocity \( dR_s/dt = v \) holds. By comparing the heat balance between solidification at a fixed temperature \( T_E \) and temperature change during cooling of a cylindrical disk a relationship between the effective cooling rate \( \dot{T} \) (at \( T_E \)) and the solidification front velocity can be established:

\[
\dot{T} = \left( \Delta h_t/c_p \right) \cdot \left( 2v/R \right).
\]  

Except for a factor of two because of the cylindrical geometry the equation is similar to the planar case.\(^{12}\) If the solidification front velocity \( v \) in eq. (4) is replaced by the interlamellar spacing \( \lambda \) via eq. (1), we finally arrive at a direct relationship between the experimentally determined interlamellar spacing and the cooling rate, where \( \Delta h_t/c_p = 440 \) K is valid for Al–Cu.

4. Results

4.1 Microstructure of copper mould cast rods

Cross sectional images showing the lamellar eutectic microstructure at different positions of copper-mould cast 3 mm diameter rods of the eutectic Al–Cu alloy are presented in Fig. 1. Micrographs obtained from optical microscopy at 1000× magnification near the bottom and near the top of the rod are shown in Figs. 1(a) and (b), respectively. The main part of the section consists of a lamellar eutectic microstructure. Apart from that a small volume fraction of circular shaped Al-dendrites (bright dots) can be seen, which means that the eutectic alloy composition was not precisely
obtained. The lamellae are not entirely ideally aligned but form cells. Moreover, the lamellae are not completely uniform in thickness, and even areas with irregular microstructure are present with lamellar sheets running into different directions. Such microstructures have been previously described by Cooksey et al.\textsuperscript{18) Reasons for irregular morphology are: (i) non-uniform orientation of a set of lamellae with respect to the plane of section, (ii) occurrence of localized cooling at junctions of cells that enhances the freezing rate. The volume fraction of irregular structures was larger at the beginning of the solidification (bottom of the rods), most likely due to the non-radial heat flow conditions. In the centre of the rods we generally found irregular morphologies because of the heat flow conditions. Only regions of regular lamellar microstructure were evaluated. Since the lamellar spacings varied within a certain range, the average of 10 to 30 readings for each sample has been taken into account. The lamellar spacing was determined for various cross-sections at different axial positions of the rods. It gradually increases along the rod axis (from bottom to top), which indicates a reduced cooling rate along the length co-ordinate of the rod. The difference becomes apparent from the comparison of Figs. 1(a) and (b), which show the microstructure near the bottom and the coarser one near the top of the rod, respectively. By SEM investigation with higher resolution up to a magnification of 5000×, areas of fine lamellae have been detected, which could not be resolved in the optical microscope. Scanning electron micrographs of fine-lamellar areas at cross-sections near the bottom and the top of the 3 mm diameter copper-mould cast rod are shown in Figs. 1(c) and (d). Again the coarser microstructure near the top (Fig. 1(d)) becomes apparent.

The results show that the observed lamellar spacing increases with the magnification employed. That is because the fine lamellae are not detected and not accounted for when using small magnifications. This effect is more prominent at positions near the rod surface where higher cooling rates are realized. Here, the discrepancy between the lamellar spacing determined using different magnifications amounts up to a factor of two. Therefore, in this work the variation of the average interlamellar spacings determined by optical microscopy at a magnification 1000× and by SEM at a magnification of 5000× are compared. No significant change has been observed for magnifications larger than 5000×.

4.2 Microstructure data evaluation for copper mould casting

The average lamellar spacing $\lambda$ determined at different cross-sections has been evaluated to derive important features of the solidification process, namely the solidification front velocity $v$ (as per eq. (1)) and the effective cooling rate $\dot{T}$ (as per eq. (4)). Apart from a considerable local scatter of $\lambda$ between different cells we have not detected a clear radial dependence in lamellar spacing within a cross-section. The
variation of $\lambda$, $v$, and $\dot{T}$ as function of the axis co-ordinate (from bottom to top) is shown in Fig. 2 for a copper mould cast 3 mm diameter rod. The lamellar spacings were derived from SEM images at 5000× magnification. Apparently, the average lamellar spacing increases from 0.27 $\mu$m at the bottom to 0.36 $\mu$m at the top of the rod. Accordingly, the solidification front velocity decreases from 0.37 mm/s to 0.21 mm/s and the effective cooling rate from 220 to 125 K/s. The lamellar spacing ($\lambda \approx 0.27 \mu$m) observed is one order of magnitude larger than in 30 $\mu$m thick splats (2 $\cdot$ $\lambda = 50$ nm, for grit blast substrate surface finish), revealing that the cooling rate for copper-mould casting process is nearly 3 orders of magnitude smaller than for rapid solidification processing ($10^5$ K/s).

The change of the interlamellar spacing $\lambda$ of cast rods for different conditions will give important information about the features of the solidification process. Therefore, Fig. 3 compares the variation of the interlamellar spacing with the length coordinate parallel to the rod axis (from bottom to top) of the copper mould cast rods of 3 and 5 mm diameter, respectively. The data are derived from SEM images at 5000× magnification. The lamellar spacings of the 5 mm thick rod are about 0.1 $\mu$m bigger than for the 3 mm rod. This is due to the lower solidification velocity. The effective cooling rate for the two rods of different thickness is shown in Fig. 4. A range of cooling rates rather than a single value is presented taking into account the large scatter of the local lamellar spacing. The upper and lower limit of the cooling rate is determined from the average lamellar spacing derived at 5000× and 1000× magnification, respectively. The cooling rate near the bottom of the 3 mm thick rod ranges from 50 to 220 K/s and decreases towards 40 to 125 K/s near the top. For the 5 mm thick rod, the ranges of cooling rates of 25 to 80 K/s at the bottom and of 17 to 50 K/s at the top are reduced by more than a factor of two compared to the 3 mm diameter rod.

4.3 Comparison of different casting methods

The microstructure data can also be used for a quantitative assessment of the efficiency of the different casting techniques. The variation of the interlamellar spacing $\lambda$ with the length coordinate parallel to the rod axis (from bottom to top) is given in Fig. 5 for centrifugally cast rods of 2, 3 and 5 mm diameter, respectively. The data are derived from SEM images at 5000× magnification. For comparison, the results for a suction cast rod of 3.8 mm diameter are also shown. Similar to the case of copper mould casting, here also the average lamellar spacing increases with the axis co-ordinate from bottom to top and eventually the increasing rod diameter leads to microstructure coarsening. The difference in lamellar spacings between the 2 and 3 mm diameter rods is relatively small, but becomes more obvious for rod diameters between 3 and 5 mm. The suction cast rod displays a much coarser lamellar spacing ($\lambda \approx 0.40 \mu$m (bottom) to 0.50 $\mu$m (top)) despite the smaller diameter (3.8 m) compared to the 5 mm diameter rod prepared by centrifugal casting ($\lambda \approx 0.32 \mu$m (bottom))
The aim of the present work was the evaluation of cooling rates and other features like solidification front velocity for different casting processes and rod diameters typical for the preparation of bulk metallic glasses: copper-mould casting, centrifugal casting and suction casting. One serious deficiency of the method is the irregularity of the microstructure, which exhibits a cellular morphology which is clearly distinct from the aligned lamellae known from controlled directional solidification. This leads to a random scatter of the local lamellar spacing of different cells within a given cross-section without an obvious change of the global solidification conditions, as it is known from earlier studies. The reason for the irregularities can originate from the radial solidification, which does not allow undisturbed growth of lamella but can lead to selection or abrupt termination during the growth of the cells if the solidification front proceeds from the surface towards the centre. Moreover, axial heat flux components, vigorous melt flow during casting, and non-homogeneous interfacial heat transfer are sources of microstructure inhomogeneities. Because of the scatter, average lamellar spacings have been derived from microstructure images with different magnifications, and ranges of cooling rates of a certain process are presented rather than single values.

In all samples studied an increase of the average lamellar spacing was detected from bottom to top. Accordingly, the cooling rate decreases along the axial coordinate. This is a proof for an axial heat flux component for these cylindrical casting methods. From TEM investigation we have got some evidence of cooling rate differences within as-cast Zr54.5Ti5.5Cu26.7Ni11Al10 bulk metallic glass cylinders. The number density of crystalline nuclei and the fraction crystallized increased from bottom to top. These facts confirm the importance of the present analysis for casting of bulk metallic glasses. However, the axial gradient in lamellar spacing does not necessarily mean a dominance of the axial heat flow in the casting. It may be caused by a variation of the metal-mould interfacial heat transfer along the axis co-ordinate from bottom to top and the according change in the radial heat flow in the considered rod section. Obviously, the solidification of the rods starts at the bottom. The freezing of the upper part of the rods proceeds with a time lag due to excess heat transfer at the bottom and the finite filling time and, moreover, it is affected by the already solidified lower part of the rods. Accordingly, one must expect a difference in structure and properties between different parts of as-cast bulk metallic glass samples, too. So far we do not know any useful two-dimensional heat flow model for an assessment of the complex experimental situation, which must take into account spatial and time dependence of metal-mould interfacial heat transfer coefficient as well as the finite mould filling time in the casting process.

The dominant influence of the rod diameter on the local cooling rate is reflected by the coarser lamellar spacing of thick rods. The difference of cooling rates seems to be more prominent for the increase of diameter from 2 to 3 mm than from 3 to 5 mm. One other interesting point are the different cooling rates achieved by various casting methods. For a fixed
rod diameter (e.g. 3 mm) the cooling rate achievable by centrifugal casting considerably exceeds that of copper-mould casting, whereas unexpectedly suction casting provided rather poor results. This may be attributed to some shortcomings of the casting equipment (e.g. insufficient quality of vacuum) used for the present experiments.

The cooling rates derived from the features of the microstructure may be compared with those from direct measurements of Inoue et al. for injection mould casting of Zr_{60}Al_{10}Ni_{10}Cu_{15}Pd_5 metallic glass. There, the critical cooling rate of 110 K/s achieved for a distance of 30 mm from the bottom edge of the wedge-shaped mould with an angle of 12.5° corresponds to a thickness of ≈ 6 mm. Hence, the cooling rate is superior (but of the same order of magnitude) compared to our cooling rates of 35–90 K/s near the bottom of 5 mm diameter rods for centrifugal casting. However, because of the higher liquidus temperature $T_l \approx 1120$ K (and the higher temperature difference between melt and mould) of the glass-forming alloy prepared by Inoue et al. (compared to $T_g = 821$ K for Al–Cu) one expects enhanced interfacial heat transfer in that case. A direct transfer of the results must be considered with caution because of the different solidification processes, i.e. eutectic crystallization at a fixed temperature and glass formation of a viscous melt over a wide temperature range, respectively.

The crucial quantity which governs the solidification behaviour achieved by different process parameters is the melt-mould interfacial heat transfer coefficient $h$. It can be estimated from the boundary condition at the solidification front via $h = \Delta h_t \cdot v/(T_g - T_0)$, where $T_0 = 293$ K is the initial mould temperature. From the growth velocity $v = 0.15$ to 0.58 mm/s near the bottom of the 3 mm diameter rod and with $\Delta h_t = 1.31 \cdot 10^3$ Wm$^{-3}$ we derive $h = 3.7 \cdot 10^5$ to $1.4 \cdot 10^3$ Wm$^{-1}$K$^{-1}$ for centrifugal casting. The Nusselt number $Nu = h \cdot R/k$ is the relation between the melt-mould interfacial heat flux and conductive heat flux. For the cylindrical sample with radius $R = 1.5$ mm and heat conductivity $k = 88.8$ Wm$^{-1}$K$^{-1}$, a range of $Nu = 0.006$ to 0.024 is obtained. These small Nusselt numbers ($Nu \ll 1$) inferred are near to Newtonian heat transfer. Therefore, the present analysis allows to conclude that interfacial heat flux and cooling rates can be further improved if ideal heat transfer is approached by optimised process parameters. Such optimisation may comprise the melt flow on pouring and the melt temperature as well as the ambient gas and the surface finish of the mould cavity.

6. Conclusions

The cooling rates for casting processes typically applied for preparation of bulk metallic glasses have been revealed from the analysis of interlamellar spacings $\lambda$ in cast rods of an eutectic Al–33 mass%Cu model alloy. It is shown that the rod diameter is the decisive parameter which determines the cooling rate. The cooling rate steeply decreases if the rod diameter increases. A considerable reduction of the cooling rate within the cast rod from the bottom to the top is inferred. Among the different casting techniques employed centrifugal casting is found to be superior compared to copper-mould casting and suction casting. Although the conditions between the freezing processes for a crystalline material and the solidification of metallic glass may differ in certain aspects the microstructure analysis of crystalline alloys can be utilized to improve casting processes and properties of bulk metallic alloys.

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