PLATINUM-BASED BULK METALLIC GLASSES FOR JEWELRY APPLICATIONS

Dr. Ulrich Klotz

Precious based bulk metallic glasses (BMG) are interesting materials for jewelry and watch making applications due to their properties such as high as-cast hardness, corrosion resistance, and outstanding surface quality. However, high critical cooling rates are required to achieve amorphous solidification which implies challenges for their manufacturing. Thus, they are cast in metallic molds which strongly limits the geometric complexity of cast parts. The present work focuses on the process development for investment-based casting of Pt-P-Cu based BMGs in order to allow for jewelry casting on an industrial scale. The results of centrifugal and vacuum-die casting applied for two different alloys are presented. One of the alloys contains 74wt% Platinum and shows a high glass forming ability, whereas the other alloy has 85wt% Platinum with a significantly lower glass forming ability. Cast filigree jewelry parts with an outstanding surface quality have been demonstrated.

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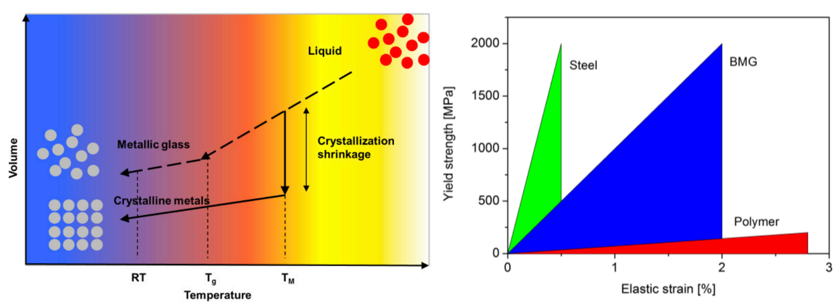
INTRODUCTION

The group of platinum-phosphorus-based bulk metallic glasses (Pt-P-based BMG) was developed in 2005 by Schroers and Johnson for jewelry applications.[1,2] Pt-BMG exhibit exceptional properties compared to conventional platinum alloys with a Pt content of 850 or 950 ‰ platinum and a crystalline microstructure. Bulk metallic glasses do not exhibit crystallization during solidification (Figure 1a). This is referred to as a frozen melt in which the atoms are disordered or amorphous. This ability to solidify amorphously, for which conditions such as a sufficient cooling rate of the melt and a high purity of the alloy must be fulfilled, is referred to as glass forming ability (GFA) and is alloy-dependent. To meet these requirements, metallic glasses are cast in metallic molds or in thin-walled investment molds which have to be subsequently quenched after casting.[3] The glass forming ability is higher in alloys with at least three alloying elements with large differences in their atom size and in the immediate vicinity of the eutectic composition.[4]

The melting or casting temperatures are in the range of 600-1000°C (1112-1832°F), which is about 50% lower than for conventional platinum alloys. This circumstance inevitably leads to less wear or reaction of the consumables (e.g. crucibles) with the melt and thus proves to be more resource-saving. A further property of amorphous BMG is the virtual absence of volume shrinkage during solidification. This circumstance is highly desirable in view of the near-net-shape production of jewelry parts in investment casting. The third unique characteristic of Pt-BMG are the superior mechanical properties of the components in the as-cast state such as a hardness of approximately 450HV1 and an elastic elongation of > 2% (Figure 1b). These properties cannot be achieved with conventional decorative alloys, or only after complex strain hardening or heat treatment. The platinum-phosphorus-based metallic solid glasses, like many other glass-forming systems, exhibit exceptional properties upon fully amorphous solidification. As already mentioned, these include the high hardness (400-500HV1) in the as-cast state, the low melting and casting temperature with a low volume change during solidification, the high elastic or thermoplastic deformability and the high surface quality due to the absence of microstructural constituents or a homogeneous microstructure at the atomic level. In addition, the high chemical resistance and the noble character of platinum pave the way for an application in the jewelry and watchmaking sector.



a) *b)*

Figure 1: Special properties of bulk metallic glasses.
a) Volume change during solidification for a metallic glass and for a conventional crystalline alloy,
b) mechanical properties and stored elastic energy.[5]

Although Pt-P-based BMG have been known for several years, there is still a lack of widespread applications in the jewelry and watchmaking industry. It is evident that the transfer of the process technology for the production and processing of these alloys is a major obstacle for many users. Bridging the gap from laboratory to industrial application requires well-founded process knowledge and, last but not least, industry-standard demonstrators and samples in order to be convincing.

The material class of BMG is a comparatively young one. Traditionally, metallic materials are considered crystalline and have a lattice structure with a corresponding long-range atomic order, i.e., the atoms are present in a repeating, three-dimensional lattice. If the shape and size of the unit cell are known, the overall structure can be inferred. Based on the lattice structure, material properties can often be predicted or understood. This is in contrast to metallic glasses, in which no long-range order can be found at the atomic level. This is referred to as an amorphous structure that can be equated with a super cooled liquid or melt in which only a certain short-range order can be observed. This short-range order can be reflected in the form of a fractal structure, which can be compared with a cluster-like accumulation (so-called percolation clusters). These can already form in the melt and are the explanation for the unusual properties of the metallic glasses in the solidified state.[6]

Natural findings of metallic glass are not known so far, only isolated particles in meteorites are an exception.[7] The first artificially produced metallic glass was described in 1960 by Duwez.[8] Very thin ribbons (10μm) were realized with a binary, eutectic Au-Si alloy at extremely high cooling rates (critical cooling rate $r_c \approx 10^5$-10^6K/s) by the melt spinning method. The low temperature of the eutectic (363°C/685°F) is responsible for the stabilization of the melt against crystallization, since only a small temperature range has to be overcome during cooling to a solid room temperature state. Later, the development to multicomponent systems around deep melting eutectic compositions allowed lower critical cooling rates and paved the way for bulk metallic glasses. The maximum thickness of an amorphous sample that can be created with a given alloy is called critical thickness dc. The term bulk metallic glass is used for alloys that can be produced with a thickness of at least 5-10 mm or more in all dimensions.[9,10]

The disordered structure of an amorphously solidified sample is derived from the structure of a metallic alloy in the molten state. For the production of a metallic glass, it is therefore necessary to cool the melt correspondingly fast in order to slow down the diffusion processes and to obtain a structure without long-range order.[11] This relationship is illustrated by a time-temperature transformation (TTT) diagram with a comparison between an amorphous and a crystalline solidification (Figure 2).

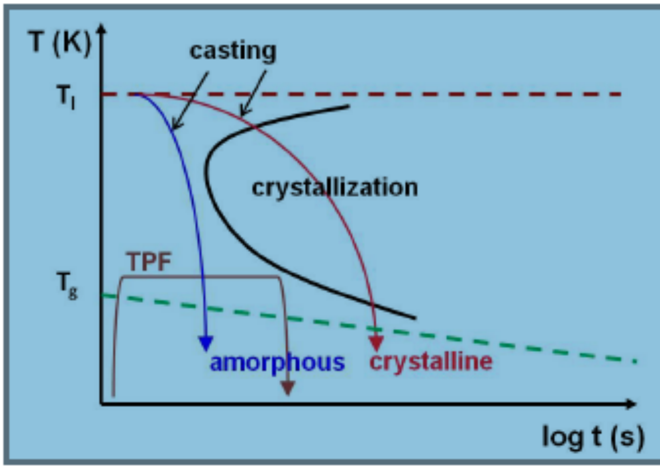


Figure 2: Schematic representation of a TTT diagram with crystallization nose and typical temperature profiles for crystalline casting conditions vs. amorphous casting and thermoplastic forming (TPF) conditions.[5]

The two cooling curves start in the molten state and initially intersect the liquidus temperature Tl. Due to the low cooling rate r, one of the curves intersects the crystalline phase, also referred to as the nose, and forms at least one crystalline component. The other curve, however, with a higher cooling rate, reaches the glass transition temperature Tg without first intersecting the crystalline phase and thus solidifies amorphously. When the glass transition temperature Tg is reached, there is a sudden decrease in viscosity, and the mobility of the atoms is severely restricted. Although the glass state can be regarded as a metastable one, it is assumed to be stable at temperatures $<$ Tg.

Recently, precious metals based bulk metallic glasses have gained increasing interest as the manufacturing methods are developing.[12,13] However, there still are two main challenges in the production of bulk metallic glasses in larger quantity, (i) the melting from pure elements including phosphorus and (ii) achieving an amorphous structure after casting into refractory molds. These challenges were addressed in the present work.

1. EXPERIMENT

In the present work, two compositions of platinum-phosphorus-based metallic glasses are the focus of the investigations. These are a ternary Pt-Cu-P (alloy A) and a quaternary Pt-Cu-Ni-P alloy (alloy B). The chemical composition of the alloys is given in atomic-% and mass-% Table 1. Due to the very high amount of P, the preparation of such alloys is challenging. In most research works only very small quantities (few grams) of alloys are produced, which is sufficient for the study of the basic properties. The aim of this work was to prepare larger amounts and to produce them by typical machines that are available in the jewelry industry in order to transfer the technology.

The alloys A and B that are listed in Table 2 are very similar in their chemical composition. The main difference lies in the alloy component nickel, but both alloys contain the same percentage of phosphorus. The lower platinum content in the quaternary alloy is compensated by the nickel content and a higher copper content. Alloy B has a critical thickness dc of 20 mm, which is almost three times greater than alloy A. The critical thickness dc is a measure to quantify the glass-forming ability of an alloy. Directly related to the critical thickness dc is the critical cooling rate rc. The critical cooling rate rc describes the minimum cooling rate requirements to realize amorphous solidification. The critical cooling rate rc is temperature-dependent. Depending on the alloy, there are critical temperature ranges in which the system shows an increased tendency to crystallize.

Table 1: Alloy composition and basic properties of the used Pt-P-based BMG.[2,14]

	Alloy A		Alloy B	
	Atom%	Mass%	Atom%	Mass%
Pt	58	85,1	42,5	73,9
Cu	21	10	27	15,3
Ni	-	-	9,5	5
P	21	1,9	21	5,8
Liquidus temperature [°C]	575		598	
Hardness [HV5]	430		480	
Critical thickness [mm]	7		20	
Density [g/cm³]	15,2		13,6	
Hallmark	850Pt		–	

2. ALLOY MELTING

The melting of the alloys from pure elements is described in further detail in.[15] After initial alloying the evaporation of phosphorus is very strongly reduced and further melting can be done in a conventional way. However, if larger quantities of the alloys should be melted, laboratory conditions and equipment are too limited and a need for upscaling arises. Therefore, a melting technique was developed were both alloys were melted in a conventional vacuum pressure casting machine (Indutherm VC500D), starting with pure components and master alloys. Three criteria are crucial for the evaluation of a melting of Pt-P based alloys:

- the handling of the phosphorus and aspects of work safety
- the sensitivity of the glass-forming ability to impurities
- the material and procurement costs

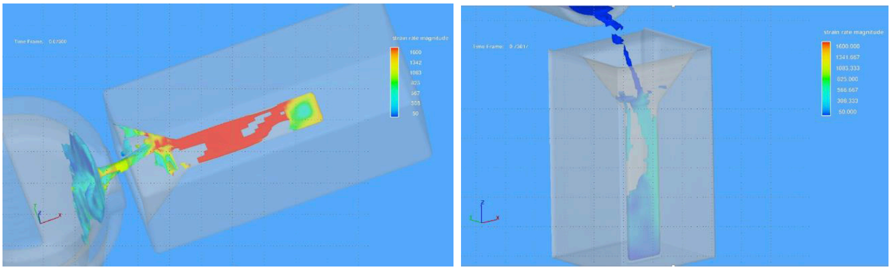
The safe handling of the red phosphorus is the main focus of the investigation. The phase transition of red phosphorus from the solid to the gaseous state (sublimation) already occurs at 431°C (807°F). For this reason, the concept of a pre-alloying process in which the reactant phosphorus is provided with a carrier can pay off. This reduces the evaporation of phosphorus significantly. Impurities can significantly reduce the glass forming ability, because they act as heterogeneous nucleation sites. However, high purity materials or melt cleaning processes (so-called fluxing) are expensive and time consuming, which might significantly increase the manufacturing costs. The optimum melting and casting conditions were evaluated in several casting trials. The amount of melt was increased from batch sizes of several 10g to about 200g. Careful monitoring of the melt temperature is required and excessive overheating has to be avoided. In this case, such batches could be handled safely, without evaporation of phosphorus or contamination of the casting machine. Larger batch sizes are possible and only limited by the crucible dimension.

3. INVESTMENT CASTING PROCESS

3.1 Basic considerations

Bulk metallic glasses are usually not suitable for investment casting. The main reason for that is the insufficient cooling rate in a refractory mold with low thermal conductivity. Metallic molds are the only possibility to guarantee the required high cooling rates. However, the Pt-P bulk metallic glasses show a very low melting temperature and a very high critical thickness. If the possibility of investment casting is considered, then these alloys would be the best suited candidates.

The investment casting process was studied for centrifugal casting and gravity casting. Centrifugal casting provides high form filling ability for filigree items, which would be ideal for thin-walled jewelry parts that require high cooling rate to form an amorphous structure. However, previous studies with gold-based BMG showed that the high shear rate might be critical.[16] Figure 3 shows the computational fluid dynamics simulation result for the casting of a simple plate geometry. Red values indicate a high shear rate in the centrifugal casting process while the shear rate during tilt casting is much lower. Shearing of the melt promotes crystallization and therefore reduces the critical thickness. Because the critical thickness of Pt-P based BMG is much higher than for Au-based BMG, both casting methods - centrifugal casting and gravity pouring were tested.



a) b)

Figure 3: Shear rate in a) centrifugal and b) tilt casting determined by CFD simulation as described in.[5]

Some near-application castings are produced and evaluated in the following. The primary objective remains to obtain completely amorphous castings. The requirements are extended with regard to a user-related assessment. These include visual and economic criteria. After this section, it should be possible to make statements on the applicability of Pt-P-based bulk metallic glasses in investment casting as a manufacturing solution for jewelry production. Details about the investment casting process can be found here.[17]

The first casting test of this work with demonstrator jewelry parts can be seen in Figure 4. This is a centrifugal casting of the alloy B. The structure of the side gates is based on the casting trees for platinum casting, it is a 90° angular 2x2 arrangement.[18,19] Two fine retention meshes and two simple rings (1x closed and 1x open) are used as models. All models originate from the additive manufacturing system and are made of PVB plastic. As shown in Fig. b, feeding is omitted to reduce the total amount and bring less total thermal energy into the system. The casting temperature was approximately 990°C (1814°F). The retention nets are not utility models, rather they are used to evaluate the mold filling.

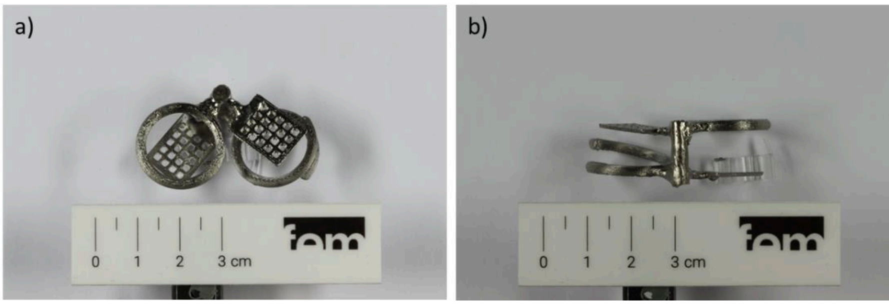


Figure 4: Overview images of the casting test ring (open/ closed) + fine retention grid in centrifugal casting with the alloy Pt42.5Cu27Ni9.5P21 (a: top view, b: side view).

The casting shows outstanding mold filling. Although the material savings mean that no postfeeding is provided, there are no disadvantages in terms of reproducibility of the model. A metallographic inspection of the cast ring was made in transverse and longitudinal direction. Primarily, this micrograph is used to assess the maximum defect size, which should be below 30µm.[20] Figure 5 shows the findings of the optical microscope images. Figure 5a gives an overview of the porosity distribution in the ring sample, which increases towards the gate. Figure 5b and d show the ring in transverse section (position marked in Figure 5a). Here, too, the porosity is found to increase in the vicinity of the sprue. The maximum defect size is < 30µm (see image c). It can be observed that the porosity is increasingly located in the center of the cross-section. The pores have the shape of perfect spheres, which indicates gas porosity. Furthermore, the microstructure shows no significant features, which is an indication for at least partial amorphous structure. The step-wise structure on the ring surface is a result of the 3D printing process of the wax model. Due to the printing method (FDM printer) the layer thickness is quite high and not suitable for actual jewelry parts, but the ability for high form filling can be demonstrated nonetheless.

The second ring was broken to document the fracture surface. Most of the fracture surface showed a typical fracture pattern for amorphous solidification with characteristic features. An SEM observation of the crack origin revealed a crystalline phase as the presumed starting point of the material failure.

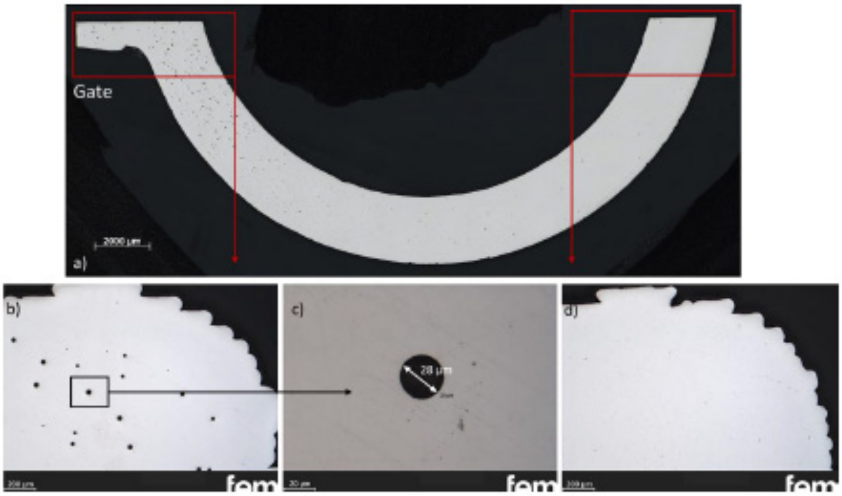


Figure 5: Optical light microscopy image of the cast ring.
a) longitudinal section of one half of the ring from tip to sprue,
b) overview of the transverse section,
c) detailed image from picture c with defect size determination,
d) cross-section on the tip side

3.2 Investment casting of filigree jewelry items with stones

These promising results allowed to cast more filigree jewelry items. Some resin models with very high surface quality were provided by Formlabs GmbH (Figure 6). Three different alloys or alloy batches were compared. The detailed surface structure of the pattern allowed to assess the mold-filling capability of the Pt-P bulk metallic glasses. Furthermore, statements can be made about the sprue system used and its influence on the mold filling of the cavity. Figure 6a - c shows the resin model. The lost model has a very high surface quality, which is also used in industry. The ring possesses a completely hollow ring rail (see picture a) in combination with the very detailed prong setting (picture b). There is only one sprue on the ring shank. Therefore, this model places high demands on the mold filling.

All casting trials were realized by centrifugal casting. The casting temperature was approx. 1000°C (1832°F). The model was positioned at 90° to the main sprue. Initial tests with the original sprue showed an issue with the form filling in the very thin sections at the side of the ring shank. With alloy A (ternary Pt-Cu-P alloy) a few segments of the filigree ring shank could not be completely filled by the melt. Above that, during devesting the ring broke at the transition from the ring shank to the sprue.

No cracking or failure occurred for the same casting with the quaternary Pt-Cu-Ni-P alloy B under identical conditions. The ring shows nearly complete form filling with only a small defect. This indicated that the sprue should be optimized. Although alloy B showed the better casting result, a third casting test was conducted with the ternary alloy A, because alloy A can be hallmarked as 850Pt and is free of allergenic nickel.

Based on the results from the previous casting trials 1 and 2, the following modifications of the casting process were made: the sprue system was adapted (Figure 6d - f). The original sprue was replaced by two thinner sprues on the ring shank. The pattern was rotated by 90° and mounted at a 45° angle to the main sprue. The casting temperature was reduced to approx. 850°C (1562°F). The result is a perfect part without defects. In the overview image (Figure 6d), the casting is shown immediately after devesting; no defects or deformations are apparent. No discrepancies can be seen when looking at the detailed image at the prongs either. The casting defect on the lateral surface of the ring shank, which was critical in the first two casting trial, is no longer to be found in the third test.

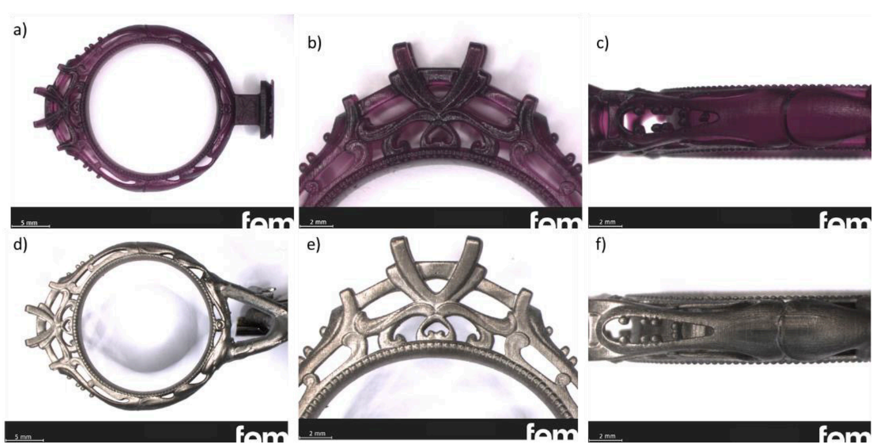


Figure 6: Image documentation of the ring with a prong setting. a-c: resin model made of castable Wax Resin provided by Formlabs GmbH with original sprue, d-f: as-cast ring (alloy A) with optimized sprues.

The filigree ring model was ideal for testing the form filling ability of the Pt-P bulk metallic glass alloy. However, the conventional stone setting with prongs that are plastically deformed requires new setting techniques with these alloys. Instead, a spring-loaded setting would be ideal, due to the extremely high elasticity of the alloys (Figure 7).

Figure 7: Finished jewelry produced by amorphous investment casting of alloy B with a spring-loaded zirconia stone.

A second jewelry item that combines the unique properties of bulk metallic glasses with investment casting technique is a filigree lattice sphere (Figure 8). The model of the lattice sphere is not necessarily a utility model from the jewelry sector, but it reflects many features of one. Due to the one-sided sprue, the melt has to travel a long distance with very narrow cavities to achieve complete filling. The grid sphere has an outer diameter of 15 mm and a volume of 125.3 mm^3 (without the sprue system). The bars in the model have a cross-section of 0.5 mm at the narrowest point. The master cast and the lost mold (wax pattern) are shown in Figure 8. The aim of this investigation is to exhaust the mold filling capacity of the available alloys. Furthermore, the use of the produced lattice spheres as demonstrators for the mechanical performance of the Pt-P based BMG is in the scope of the study with this item.

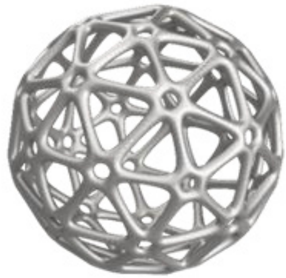


Figure 8: Master pattern and lost pattern of the filigree lattice sphere with annular side sprue. Master pattern (STL file).

The item represents a geometry with a particularly high surface/ volume ratio. The total initial weight of the test cast was 5.31g. It was investment cast in both alloys. No fractures or defects were detected on the casting. Different casting trials with one or two spheres were conducted. The lattice structure was always completely filled and no fractures occurred, independent of the alloy. Testing by x-ray diffraction proofed a nearly fully amorphous structure even for alloy A with the lower glass forming ability.

Figure 9 shows the three production stages of the filigree lattice sphere. Figure 9 a and b show the lost model with the lateral sprue immediately after fabrication in the wax printer. Picture c shows the sphere after investment casting. The sprue system has already been completely removed. No casting defects or other critical features can be seen on the surface. Fig. d shows the lattice sphere in the manually reconditioned state. The freely accessible surface of the sphere is first smoothed with fine sandpaper. The holes are then drilled out with a ball cutter (1 mm). The polish is applied in two separate steps. The material shows very good workability in terms of surface finishing.

Due to the low mass, the spherical shape and the high elasticity of the material used, the castings of the filigree lattice sphere exhibit a high springy effect.[17] After many repeated, manually conducted drop tests, no damage to the casting can be seen.

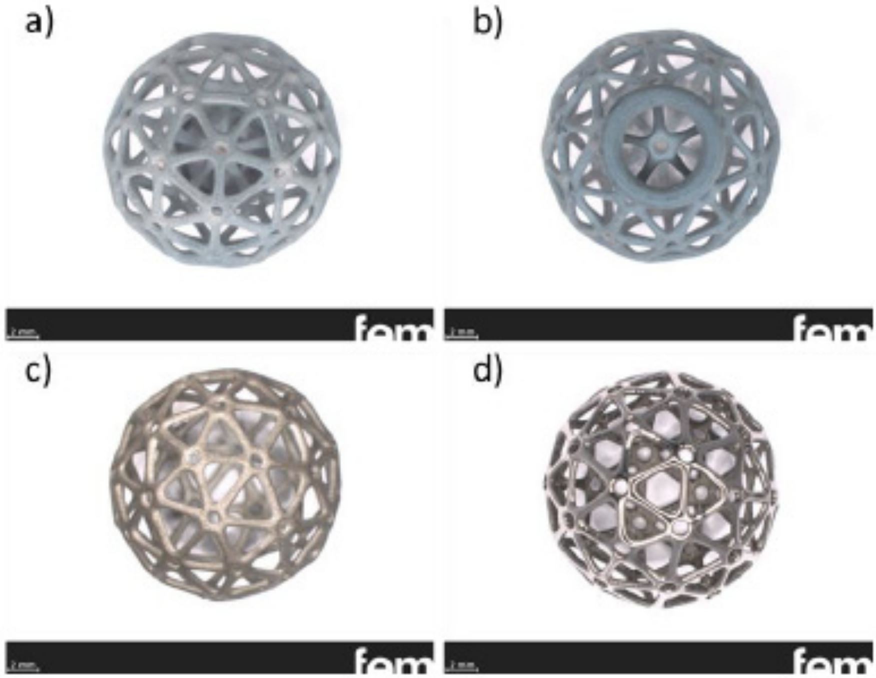


Figure 9: Investment cast filigree lattice sphere.
a) top side wax pattern, b) bottom side wax pattern with gating system, c) as-cast surface in alloy B without sprues, d) finished part.

SUMMARY AND OUTLOOK

The present work demonstrated that platinum-phosphorus-based bulk metallic glasses can be processed by investment casting with conventional equipment that is available in many casting companies. The two critical steps of alloy preparation by induction melting the investment casting in refractory mold were mastered successfully. Very filigree jewelry objects of high quality could be produced and the transfer to standard industry production is conceivable.

In order to prevent crystallization, bulk metallic glasses require very high purity of the alloy and are hence usually produced under special laboratory production process conditions. In the upscaling to investment casting of larger amounts of material, the purity level of the alloy products is inferior to that of alloy production under laboratory conditions. However, there is sufficient process stability, which means that an acceptable glass formation capability was achieved. This can be demonstrated not only by a realized amorphous solidification in a critical thickness dc of 6 mm, but also in a further use in investment casting of patterns custom to the jewelry industry. Furthermore, the developed alloying concept shows a way to scale up the process and thus solves one of the major drawbacks of the previous manufacturing process. By increasing the quantity, the production of the hallmarkable and nickel-free alloy A becomes more cost-effective and far more profitable in terms of commercial use. Up to now, the lack of such upscaling possibilities has been a decisive reason why Pt-P-based bulk metallic glasses have rarely been found in jewelry production.

A second reason for the limited availability of glass-based jewelry products in the portfolios of established manufacturers are the severely limiting processing options available to date. In addition to thermoplastic molding, castings into metallic molds are established processes for the near-net-shape production of metallic solid glass. However, these processes are very limited in terms of geometrical freedom and short-term adaptations and require costly metallic molds. With the opening of the investment casting process on the basis of refractory-based investment as a shaping process for bulk metallic glasses, completely new applications are made possible for the user. In combination with 3D printing of the lost models, detailed individual and small series productions can be carried out comparatively resource-saving. Detailed and filigree geometries in particular suit the glass-forming alloys in centrifugal investment casting. Due to the small-scale structure of such models, the high surface/volume ratio to the surrounding investment material during the casting process leads to a sufficient cooling rate to realize amorphous solidification. The mold filling capacity of the bulk metallic glass alloys was very high. The generally very low volume shrinkage during solidification of glass-forming systems is also very helpful. Therefore, there is no need for backfeeding of the melt, which significantly reduces the volume of the casting tree and cone. This not only offers a financial advantage due to material savings, but also prevents heat buildup, which would be associated with an increased risk of crystalline solidification.

In the case of the two alloys investigated, the quaternary composition (alloy B) with higher glass forming ability was more process-stable with regard to use in investment casting. Various application profiles have been tested in the form of jewelry samples. Geometries with a material thickness of up to 2.5 mm solidify amorphously with the quaternary alloy. The ternary alloy (alloy A) can be hallmarked as 850Pt and is free of allergenic nickel. However, it shows only limited applicability in investment casting due to its fundamentally lower glass-forming ability. The maximum critical thickness of alloy A that solidifies amorphously in investment casting is 1 mm. Thus, the application of this alloy is limited to very fine structures at the current state of research. Nevertheless, a qualitative comparison of the material batches from the experimental alloy production and the conventionally produced ternary alloy has so far not revealed any differences. This confirms the suitability of the material from the alloy concept developed for use in investment casting without the additional need for a melting metallurgical purification process.

Irrespective of the alloy used, the castings produced by investment casting show a susceptibility to fracture when subjected to a high mechanical load in subsequent use. Very sporadic crystalline solidification on the immediate casting surface, which cannot be avoided so far, has a notch effect and leads to premature failure. This locally random solidification behavior also influences the quality in terms of mechanical surface refinement. Thus, this phenomenon in the production of Pt-P based metallic solid glasses in investment casting will require further work in future.

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