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Bulk metallic glasses, also called amorphous metals, are a new fascinating class of materials with special properties such as a low melting temperature, high hardness and scratch resistance and very high elasticity. Although their appearance is like that of/similar to that of conventional metallic alloys they show some very special properties due to their different atomic structure. They can be thermoplastically formed like plastics at very low temperature and pressed into complex shapes. Compared with their crystalline counterparts, they usually show a higher strength, hardness and a higher elastic strain while the Young's modulus is lower, which makes them excellent spring materials.

Amorphous alloys have been developed based on many different metals, including gold and platinum. To enable their way into industrial applications their properties relevant for jewelry were investigated in a publicly funded research project together with several partners from industry. A new casting method similar to lost wax investment casting was developed in order to exploit their near net-shape formability. Hardness, wear resistance and tarnishing in different atmospheres were investigated. With an as cast hardness of around 360 HV1, a liquidus temperature below 400°C and an as cast color which ranks it among the best premium white gold alloys, the 18 carat gold based bulk metallic glass alloy has attractive qualities regarding jewelry applications. This article is an updated version of [26].

Gold based bulk metallic glasses - hard like steel, moldable like plastics

1.1 What is a bulk metallic glass?

The three classes of materials (metals, ceramics and polymers) exist in two principle types: crystalline and amorphous structure. However, for metals, the amorphous structure, a so called “metallic glass” or “amorphous metal”, does not form under conventional processing conditions, but only after very rapid quenching. A metallic glass is formed, if the crystallization during cooling from the melt can be avoided. This is the case as soon as the cooling rate R during solidification is sufficiently high to bypass crystallization. A cooling rate which results in a fully amorphous metal is shown in the schematic TTT diagram (Time-temperature-Transition) in Figure 1. The lowest cooling rate, which is still sufficient to avoid crystallization in a distinct alloy system, is called the critical cooling rate R_c . A bulk metallic glass (BMG) is formed, if the critical cooling rate is sufficiently high to cast geometries of at least several millimeters and up to several centimeters in thickness. The maximum thickness, which can be achieved for a certain bulk metallic glass is called the critical casting thickness d_c (see for example reference [5]).

Back when the first metallic glass was introduced in 1960 [6], relatively high critical cooling rates of about 106 to 108 K/s were necessary to form an amorphous solid. Due to this high R_c only very thin (20-30 μm) samples could be produced by splat cooling or melt spinning [7]. Years of research have led to complex and viscous alloy compositions, with the crystallization retarded to a degree, in which cooling rates of less than 1 K/s can be applied and still amorphous products can be cast. Cooling rates of that order are typically achieved by casting in cooled copper molds. Today, the bulk metallic glass with the highest d_c known so far is a Pd-based bulk metallic glass. It can be cast fully amorphous in diameters up to 80mm [8]. Now, that the amorphous metals are available in bulk form, applications in industry are possible, and, regarding their extraordinary properties, very desirable. The most widely used BMG are Zr-based and are currently used for example in sporting equipment and luxurious watches.

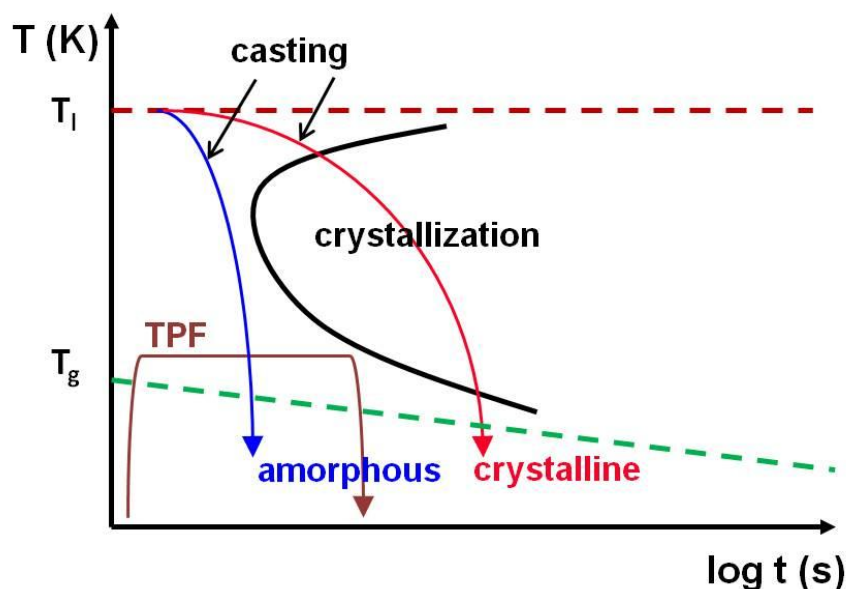


Figure 1: Schematic TTT diagram with crystallization nose and typical temperature profiles for casting and thermoplastic forming (TPF)

1.2 Properties of bulk metallic glasses

Most bulk metallic glasses are found at eutectic or near eutectic compositions [9, 10], e.g. the first metallic glass ($\text{Au}_{75}\text{Si}_{25}$ eutectic) was found in the Au-Si system, which shows a very deep eutectic. In eutectic compositions, the melt is very stable against crystallization, which is reflected in their low liquidus temperature T_{liq} compared with the T_{liq} of the constituents. The low liquidus temperature leads to a very good castability of otherwise high temperature melts. A very good example is the platinum based bulk metallic glass $\text{Pt}_{85.24}\text{Cu}_{7.1}\text{Ni}_{2.36}\text{P}_{5.3}$ (all compositions in this article are given in wt.%), which can be cast at 600-800°C compared to more than 1800°C for conventional Pt alloys [2]. Another effect of the low liquidus temperature is the low Young's modulus E , as the Young's modulus is proportional to the liquidus temperature.

Having a eutectic or near eutectic composition is not the only criterion for finding good glass forming alloys. Despite the absence of a precise theory for the rules of finding good glass formers, some empirical rules seem to apply [11]. The more complex an alloy is and the more different atoms with different sizes are arranged in the melt, the more densely the atoms are packed and the more difficult the movement of a single atom becomes. This helps to slow down the crystallization but it also means that a metallic glass melt usually has a higher viscosity than a conventional metal melt [12]. E.g. for the well-known Zr-based BMG Vit1, the equilibrium melt viscosity is reported to be in the order of 1 Pa·s, which is three orders of magnitude higher than the viscosity values usually found in pure metal melts [13]. Pure metal melts have a similar viscosity as water has at room temperature. This has to be kept in mind, because together with the need for fast quenching, these properties can be detrimental for a good form filling during casting and they have to be considered during design for casting.

When a metallic glass is cooled down from its melt to room temperature, the disordered structure of the liquid is preserved while the supercooling causes the viscosity to rise significantly. The temperature at which the viscosity has a value of 10^{12} Pa·s is defined as the glass transition temperature T_g [14]. Below T_g the viscosity reaches values in the order of 10^{14} Pa·s and is high enough for the material to behave like a usual/crystalline solid. When the metallic glass passes T_g during reheating, the viscosity drops again and the glass relaxes into a so called super cooled liquid state until during further heating it finally passes the crystallization temperature T_x at which it instantly crystallizes. The temperature range $T_x - T_g$ is often referred to as ΔT . The width of the ΔT -range is of practical importance because the bulk metallic glass can be thermoplastically formed and strained within this temperature range up to several hundred percent by thermoplastic forming. The metallic glass can within T_g be handled similar to a thermoplast and even blown like a conventional silicate glass [2, 15]. The limitation for this process is crystallization; the time limits for the onset of crystallization depend on the applied processing temperature according to the TTT diagram. Once the supercooled liquid crystallizes, it can no longer be thermoplastically formed. A typical processing route for thermoplastic forming is shown in the schematic TTT-diagram in Figure 2 (left).

Bypassing crystallization during quenching of the melt not only means, that an amorphous phase is formed, it also means, that crystallization shrinkage is not taking place (Figure 2, right). The lack of crystallization shrinkage leads to a significant reduction of shrinkage related casting defects like shrinkage porosity. This also means that only minor dimensional discrepancies between casting products and mold geometries are present and filigree surface patterns are accurately reproduced on the surface of the cast product. Near net-shape casting can be applied.

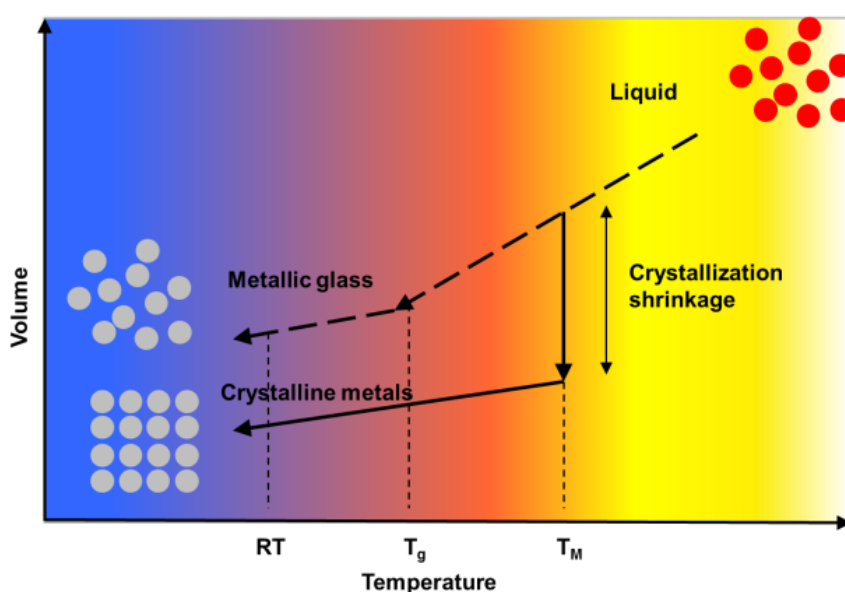


Figure 2: Volume change during solidification for a metallic glass and for a conventional crystalline alloy

Amorphous metals lack the classic mechanisms for plastic deformation of crystals like the movement of dislocations and can therefore withstand higher mechanical stresses without yielding. They show elastic strains of up to 2%. In combination with the relatively low Young's modulus, this results in a high resilience $E_e=0,5\sigma^2/E$ [16]. In Figure 3 the resilience, which is resembled by the area beneath the Hooke's line for elastic deformation, is shown for high strength steel, polymers and bulk metallic glasses in comparison. These typically high resilience values make the bulk metallic glasses excellent spring materials [16]. This combination of high strength and high elasticity is usually not found in other engineering materials.

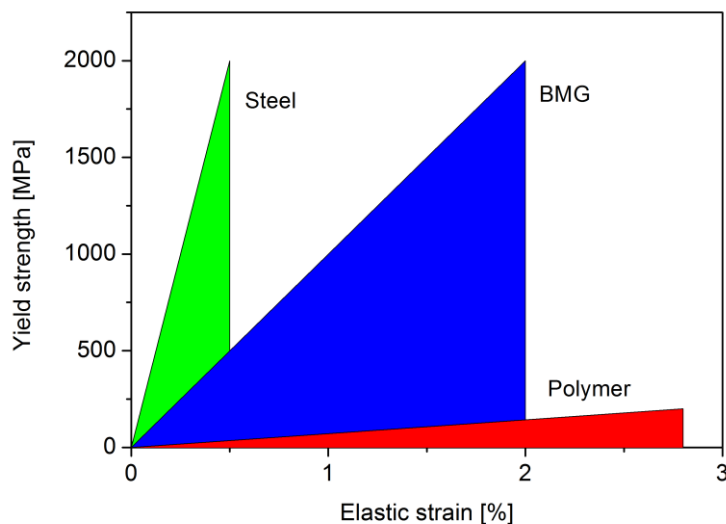


Figure 3: Schematic resilience of different Material groups classes in comparison

Due to their amorphous structure, the bulk metallic glasses possess unique properties, which make them more than attractive for applications in jewelry technology. They cannot, however, be processed like crystalline alloys. The lack of classic deformation mechanisms leads to a completely different failure behavior. Under tensile loading, instead of yielding by plastic deformation, the bulk metallic glasses almost reach the theoretical strength, before they abruptly fail under the evolution of shear bands. As all the plastic deformation in most glasses is concentrated in one or few shear bands, those metallic glasses macroscopically fail brittle. They are therefore not fit to be plastically deformed below the glass transition temperature like it would be the case during cold working.

1.3 Gold based bulk metallic glasses and their properties regarding jewelry technology

In 2005, gold based bulk metallic glasses were introduced for the first time [17]. With a gold content of 76 wt.% Au, they can be hallmarked as 18k gold alloys. The Au-based bulk metallic glasses, which are known today, are all based on the Au-Si eutectic. The critical casting thickness was enhanced by alloying palladium, copper and silver and is today as high as 5mm when cast in copper molds. In 2007, one of those alloys, $Au_{76.26}Ag_{4.69}Pd_{1.93}Cu_{13.5}Si_{3.62}$, was introduced at the Santa Fe Symposium together with a Pt-based alloy with the composition $Pt_{85.24}Cu_{7.1}Ni_{2.36}P_{5.3}$ [2]. As those bulk metallic glasses have an as cast hardness of 360HV1 and 400HV1, respectively, their hardness and strength are superior to classic crystalline alloys, without the need for thermo mechanical treatment. For simplification, the alloy $Au_{76.26}Ag_{4.69}Pd_{1.93}Cu_{13.5}Si_{3.62}$ will be referred to as Au-BMG1 in this article. With a glass transition T_g of 128°C and a crystallization temperature T_x of 186°C, Au-BMG1 can be thermoplastically formed within a temperature region ΔT of 58°C. Its critical casting thickness is 5mm [17]. It is reported to have a tensile strength of 1200 MPa, a Young's module E of 66,38 GPa and an elastic strain limit of 1.5% [18]. This results in a resilience of about 7.5 MPa. All these properties are already present in the as cast state.

Conventional crystalline precious metals based alloys, on the other hand, are usually comparatively soft in as cast condition and are therefore prone to be scratched in use and appear dull already after short periods of wearing. The hardness of gold can be improved by alloying with other metals and by thermo mechanical treatment such as cold working and ageing. With these measures, hardness values almost similar to that of Au-BMG1 can be achieved [19]. Typical hardness values of Au-Cu-Ag alloys are plotted for annealed and hardened state depending in Ag content in Figure 4. One has to keep in mind that those values were measured after preparation at laboratory scales. During actual industrial production, those values are difficult to achieve and values between 160 and 250 HV1 are more common.

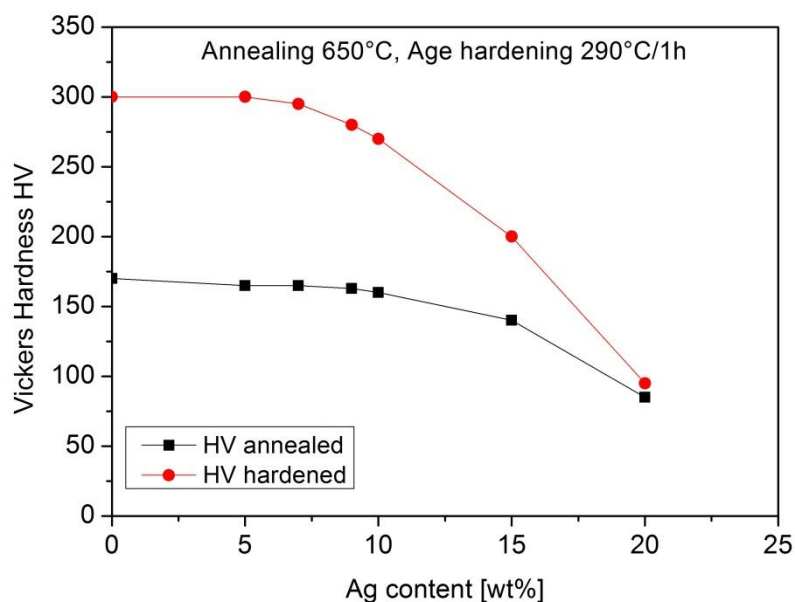


Figure 4: Effect of alloying and hardening in 18k AuAgCu alloys [19].

With this background in mind, a widespread use of gold based bulk metallic glasses in jewelry production within few years after their development was anticipated [3] and bulk glass forming alloy compositions in the Au-Pd-Cu-Ag-Si system were patented [20]. To test the prospects of applying bulk metallic glasses as jewelry alloys, a research project was brought to life and has been carried out at fem from 2011 to 2013. The processing of Au-BMG1 was investigated and studies on the tarnishing behavior were carried out.

1. Processing of gold based bulk metallic glasses

For an easy handling as a jewelry alloy, the production of a semi-finished granule product with the final composition of Au-BMG1 was developed. In a first step, alloying of the pure elements was tested in a boron nitride crucible and in a graphite crucible. Subsequently, the carbon contamination of both samples was analyzed but in both cases, no carbon could be detected. Thus it was concluded, that the alloy can be processed in graphite crucibles.

For the granulation process, the compounds were alloyed in a graphite crucible, which was designed with a small nozzle at the bottom. Forcing the melt through the nozzle by applying an Ar pressure on the melt surface led to the formation of small spherical droplets which were quenched in a mixture of water and ethanol to guarantee an amorphous structure. Figure 5a) shows a test installation with small melt droplets. After investigation of the parameters for droplet formation in this test setup, the process was transferred to an industrial casting device (Indutherm VC500D), because processing in pure air, as is the case in this setup, caused a massive SiO₂ layer to form on the surface. To prevent the silicon from forming a massive SiO₂ layer on the surface, the atmosphere in the quenching tank was fluxed by Ar. (Some optimization of the process was necessary to produce homogeneous spheres, because the high viscous melt tends to solidify as wires instead of spheres.) With this optimized process, spheres with a very smooth surface and diameters mostly between 0.7 and 2 mm were obtained (Figure 5 b) and c)).

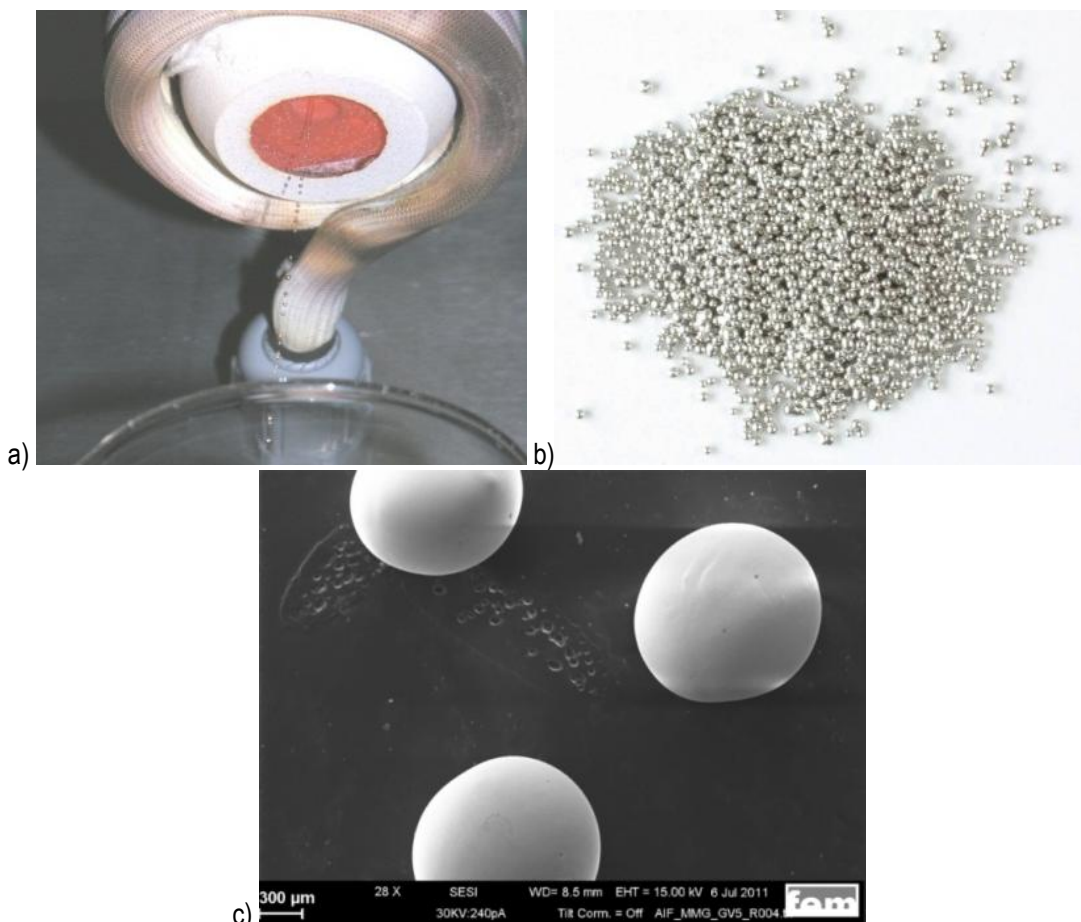


Figure 5: Production of granules as semi-finished products

The semi-finished product of Au-BMG1 was then used as feedstock material for thermoplastic forming (not published here) and for casting. To investigate the behavior of bulk metallic glass forming alloys in casting processes, at first simple shapes were cast in massive copper molds like for example 2mm thick plates (Figure 6). Temperature measurements of the copper mold near the sample showed, that a temperature rise in the range of 3-5°C from room temperature occurred during casting, which granted at any time a sufficiently low temperature to provide an ample cooling rate for casting of amorphous products. Both tilt casting in an Indutherm MC50 and centrifugal casting in a Topcast TCE10 casting machine were applied to form amorphous samples of Au-BMG1, thereby casting directly after inductively melting the pure elements as well as using the semi-finished product as feedstock material. In all cases, a good reproducibility of amorphous samples was observed with Au-BMG1. The alloy showed a high tolerance towards the handling in industrial casting machines. Figure 6 a) shows X-ray diffractograms of polished plates, which were centrifugal

cast and tilt cast, respectively, both times using the amorphous granules as feedstock material. It shows the typical two broad maxima of amorphous samples. In crystalline metals, the long ranged ordered atomic structure gives distinct peaks for each crystalline phase in the diffractogram of the metal, while the only medium range ordered bulk metallic glass results in two broad maxima.

Investigating the downsizing of the sample geometry, an interesting behavior was observed. For these small granules, a critical minimum mass seems to exist, below which the amorphous granules can no longer be inductively melted. This is probably due to the low electric conductivity, which is typical for amorphous metals [21]. In our casting device, this critical mass was found to be 8 g below which we no longer were able to inductively melt the granules. Small geometries can still be cast from those granules, using indirect heating for example in graphite crucibles or by simply crystallizing the granules prior to casting in an annealing procedure.

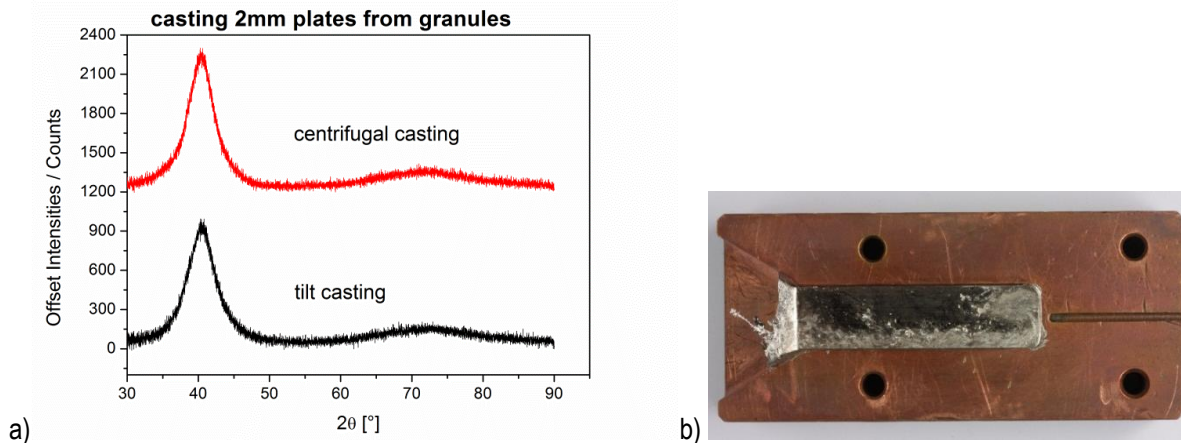


Figure 6: a) Xray diffractogram of cast plates after centrifugal casting and after tilt casting; b) 2mm thick plate

During casting of other compositions some problems occurred, though. Figure 7 shows an etched cross section of a 2mm plate of the alloy $\text{Au}_{83.88}\text{Ag}_{5.74}\text{Cu}_{6.99}\text{Si}_{3.39}$ which was introduced by Zhang et. al. in 2009 [22]. This alloy, centrifugal cast under the same conditions as alloy 18kt Au-BMG1, showed partly crystallization in some tests. Crystals are distributed inhomogeneous over the entire cross section (Figure 7), but somewhat concentrated towards the surface and in the center of the sample. This is probably on the one hand due to heterogeneous nucleation in contact to the copper molds surface and on the other hand to lower cooling rates in the center of the sample.

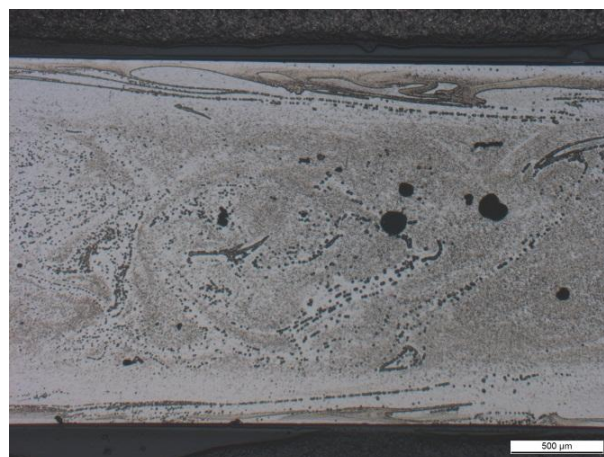


Figure 7: cross section of 2mm plate of alloy $\text{Au}_{83.88}\text{Ag}_{5.74}\text{Cu}_{6.99}\text{Si}_{3.39}$

This alloy, despite having the same critical casting thickness of 5mm, proved to be much more susceptible to crystallization than 18kt Au-BMG1. As the critical casting thickness is reported to be 5 mm for this alloy, and the sample in this case has only a thickness of 2mm, the casting procedure probably has an influence on the crystallization kinetics. To investigate how the casting procedure may be able to trigger crystallization, a simulation of tilt casting and centrifugal casting was carried out and the strain rate of the melt was plotted during form filling. While form filling during tilt casting is happening in a rather laminar manner (Figure 8), a lot of turbulences are present during form filling in the centrifugal casting process (Figure 9). The turbulences and the velocity gradient in the melt caused by the dynamics of the

centrifugal casting process result in significantly higher (up to three times higher) strain rates than in tilt casting. This is a probable explanation for the reduced critical casting thickness in this case, as strain rate induced crystallization was observed to take place in Au-based bulk metallic glasses before [23]. Nevertheless, after learning how to successfully cast fully amorphous samples of 18kt Au-BMG1 in simple shapes, the process was further refined and developed to cast actual jewelry products with more complex shapes.

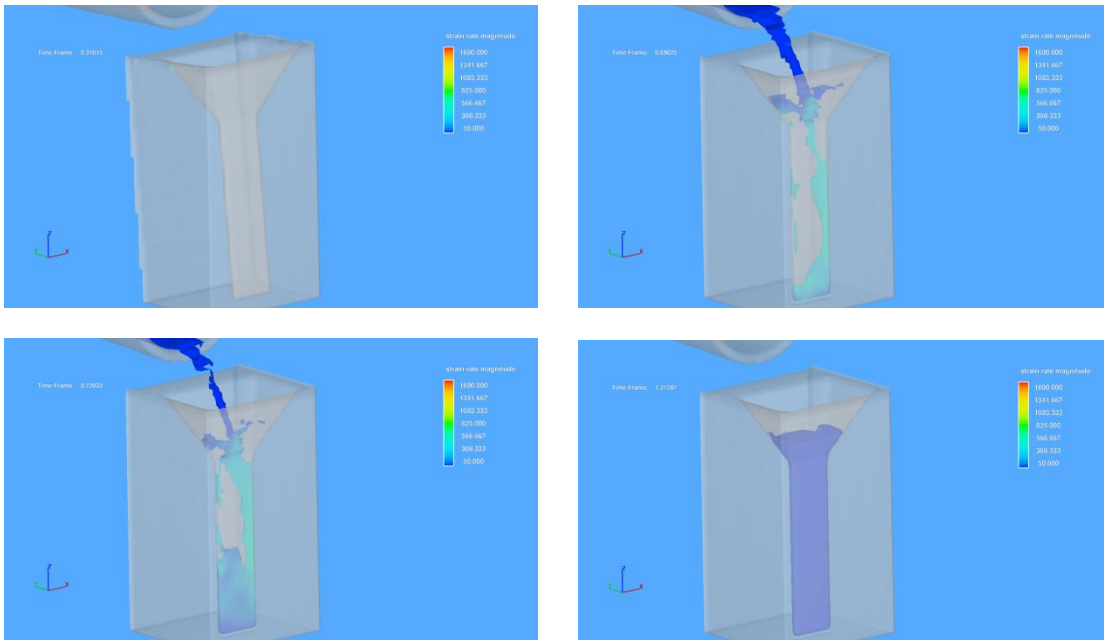


Figure 8: Simulation of the strain rate during tilt casting process

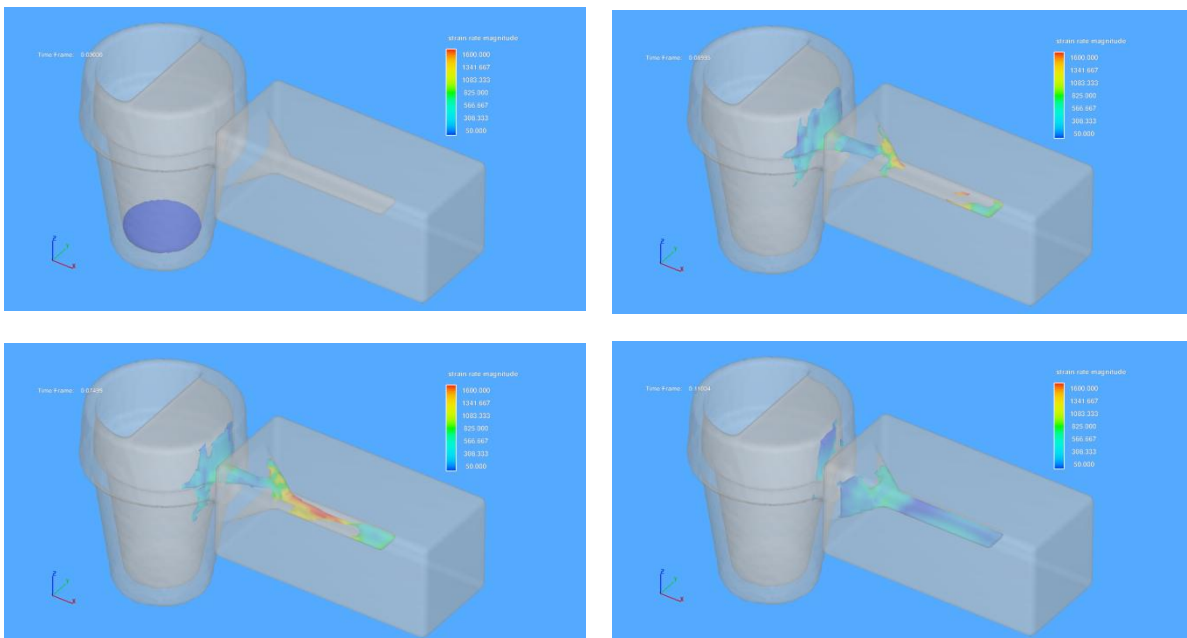


Figure 9: Simulation of the strain rate during centrifugal casting process, blue and red color indicate low and high strain rates, respectively

Investment casting is a widespread processing routine in jewelry production. For the casting of amorphous products the cooling rate provided by the investment is unfortunately not sufficient to guarantee an amorphous solidification. The classic investment casting process was therefore modified by replacing the investment with a copper mold. The copper mold was grown directly on the actual wax surface of the jewelry model by galvano-forming (Figure 10). The galvano-formed copper mold can easily be grown to a thickness of several millimeters, until a copper mass is build up that is sufficient to guarantee a fast enough cooling beneath T_g . Figure 10 shows an example of a copper mold directly electroformed on a wax surface. The wax can be removed by a melting procedure similar to the melting procedure that is applied in conventional investment casting. The now empty copper mold can be used like any other metal mold in the desired casting process. After the bulk metallic glass is solidified inside the mold, the copper is removed for example by immersion in nitric acid. The acid does not affect the noble jewelry product. A patent for this processing routine is filed under number DE 10 2013 009 975.7

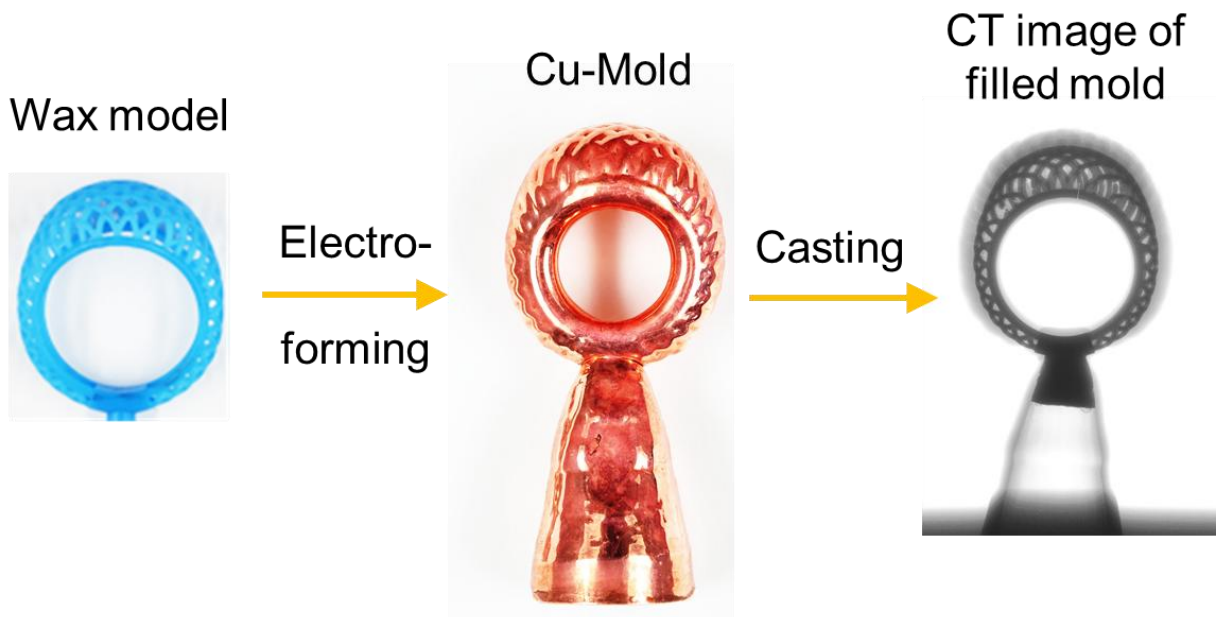


Figure 10: New casting technique with lost metal molds: wax model (left), galvano-formed copper mold (center) and CT image of a filled copper mold (right)

Despite the need for high cooling rates and the higher viscosity of the bulk metallic glass melt, a surprisingly high form filling was achieved. Figure 11 shows some jewelry items cast with the new casting process.



Figure 11: Jewelry products cast at Fem

2. Investigation of the tarnishing behavior

The properties of Au-BMG1 relevant for jewelry products as analyzed at **fem** were partly published in 2010 [24]. The color of the alloy was then reported to be standard white or off-white with an average yellowness index of 25.3. New tests revealed, that those values were affected by the samples storage conditions. Testing the yellowness index on several freshly polished samples according to standard test DIN 6174 produced an average Yellowness Index of 17.7, which corresponds to a premium white gold color [25].

To evaluate how the high hardness and other properties of bulk metallic glasses influence abrasion during wearing, polished samples of Au-BMG1 and an 18k white gold alloy were subjected to a 10 h nutshell abrasive test according to standard method DIN EN 12472 to simulate the wear behavior of a typical jewelry product. The bulk metallic glass samples experienced much less change in roughness.

Table 1: Roughness values before and after 10h nutshell test

Sample	polished		10 h nutshell test	
	Hardness HV1	R _z [μm]	R _z [μm]	Δ R _z [μm]
18k WG alloy	221	0.13	0.37	0.24
Au-BMG1_a	361	0.27	0.31	0.04
Au-BMG1_b	358	0.14	0.19	0.05
Au-BMG1_c	353	0.13	0.24	0.11

The success in casting of actual jewelry products gives rise to the expectation that bulk metallic glasses are to be applied in jewelry industry within a foreseeable future. There is only one disadvantage of the alloy Au-BMG1. The alloy happens to show significant color changes at rather short time scales if worn on skin or after longer storage at room temperature (Figure 17). As this is usually the case for jewelry products, this tarnishing effect is detrimental to widespread applications in jewelry production.



Figure 12: Bulk metallic glass ring as polish (left) and after wearing test of 52 days (right)

In order to understand the underlying mechanisms behind the tarnishing behavior, studies on the tarnishing effects were carried out under several different environmental conditions, including standard tests in artificial sweat and saliva and ageing of a set of samples in air, Ar and vacuum at different temperatures. However, this test program is not finished at this point and will require further work in future to understand the underlying mechanism of this tarnishing effect.

The test in artificial sweat and artificial saliva was carried out according to the standard DIN EN ISO 10271 and DIN EN 1811. The samples surface was sanded prior to the test in order to remove possible oxide residues of the casting process. Some minor parts were not sanded, though, as some pores were present on the samples surfaces, as can be seen in Figure 13. The samples were then kept in test solutions, which are designed to represent body fluids (artificial sweat and artificial saliva), at 37°C for 7 days and the metal release into the test solution was analyzed after that period.

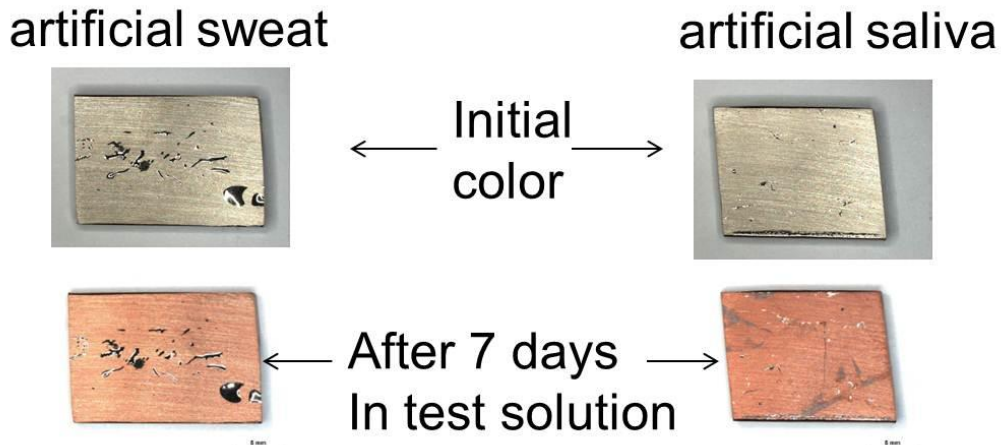


Figure 13: Sanded samples of Au-BMG1 before and after the test in artificial sweat and artificial saliva (left), distribution of element concentration in test solution (right)

After the test, the test solution is analyzed in order to quantify which alloy constituents are soluble in body fluids. This test was originally established to investigate whether or not elements, which are detrimental for human health (e.g. nickel), dissolve during wearing. In this case, the alloy contains no hazardous elements, but the solubility of the non-precious elements copper (Cu) and silicon (Si) can be detected nonetheless. Two samples each were independently tested in artificial sweat and artificial saliva. The test solution for artificial sweat had a copper concentration of 0,017 and 0.026 mg/cm², respectively, after the test. For the artificial saliva test solution, an even higher concentration of 0.058 and 0.062 mg/cm², respectively, was detected. A comparatively small amount of silicon between 0.0012 - 0.0024 mg/cm² was also found, the noble elements were not dissolved.

The samples show a uniform reddish coloring of the sanded surface area after the test. The surface of the pores, though, retained their initial white color, as can be seen in Figure 14. The pore surface is only compromised and discolored, where it was damaged by scratches from the initial grinding procedure. These scratches, show a reddish color as well.

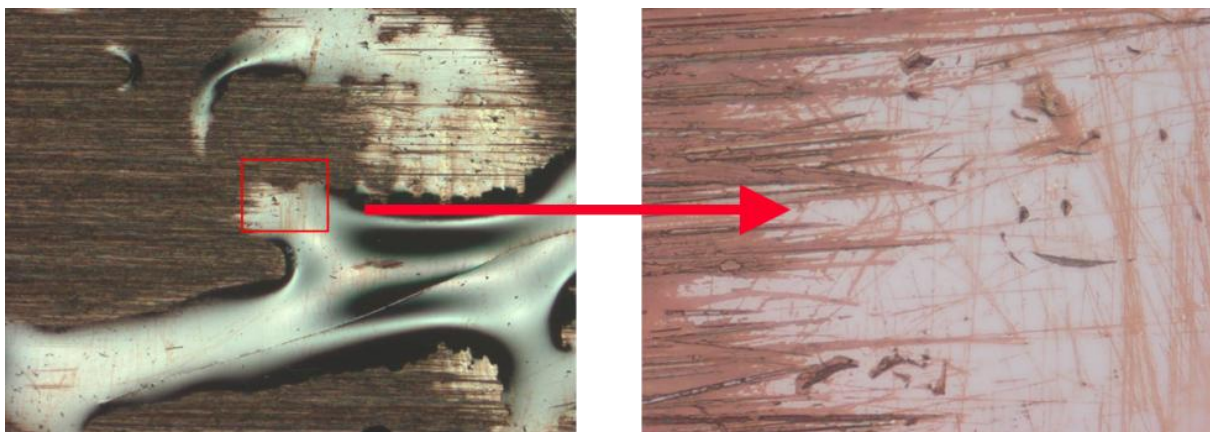


Figure 14: magnified images of the samples surface after the test in artificial sweat

An energy dispersive X-Ray mapping (EDX) of the copper and the oxygen distribution at the interface between sanded surface and pore surface revealed a depletion of copper at the sanded surface, whereas in the pore, copper was clearly detected (Figure 15 a). For the oxygen, the distribution was found to be exactly reverted (Figure 15 b). In the silicon distribution, no relation to the surface condition (sanded or pore) could be found (Figure 15 c), as was the case for the noble alloy constituents, Au, Pd and Ag (not shown here). From this observation an oxidation reaction was concluded to have taken place in the sanded surface region. A transparent protective SiO₂ surface layer on the as cast pore surface is supposedly preventing the pore surface from tarnishing.

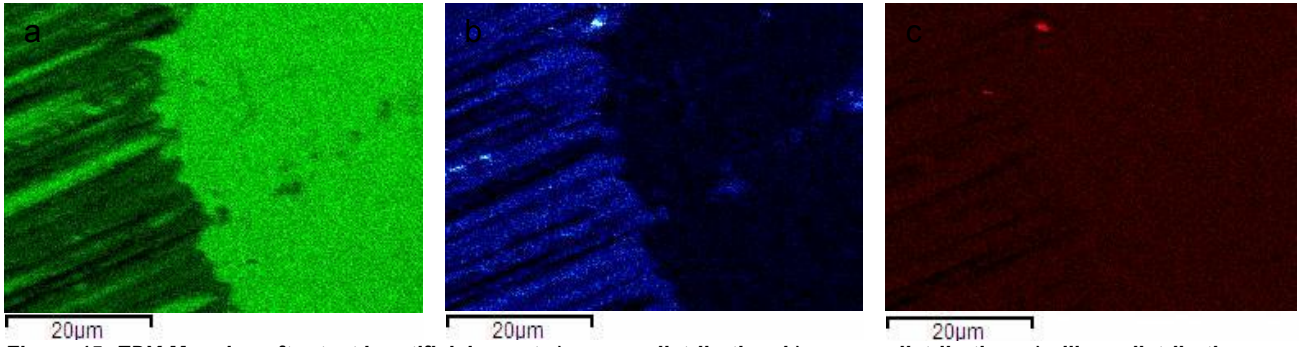


Figure 15: EDX-Mapping after test in artificial sweat a) copper distribution, b) oxygen distribution, c) silicon distribution

A similar surface layer is suspected to be present on the granules. The granules were observed to maintain their premium white color over long periods of time at room temperature (in air) and tarnish remarkably slow when kept at 75°C in air. Figure 16 shows granules in as produced condition next to granules, which were kept at 75°C (in air) for 7 days. The color did not change. When etched with hydrofluoric acid (HF) prior to ageing for 7 days at 75°C, the granules tarnish significantly within 7 days. This can be explained by the removal of the supposed SiO₂ layer by the HF treatment. Silicon oxide is known to be removed very efficiently by HF etching, in this case leaving the granules without protection. Although it could be proven, that the SiO₂ layer effectively improves tarnishing, this does not help to avoid tarnishing of jewelry items as the protective cast layer is removed during polishing.

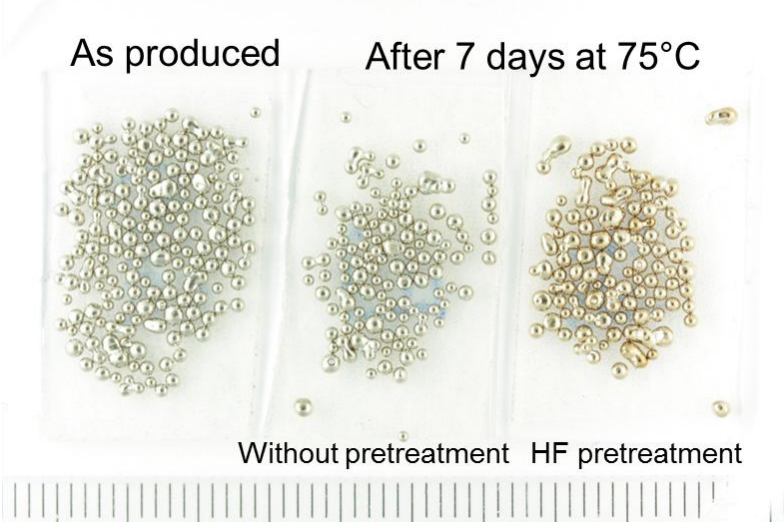


Figure 16: granules as produced, and after 7 days at 75°C with and without HF etching prior to ageing

To quantify the tarnishing behavior at different temperatures, another experiment was set up. Rectangular samples were cut from 2mm plates and polished to obtain a smooth and clean surface without residual oxides. The samples were then subjected to different environmental conditions i.e. different atmospheres at different temperatures and the Yellowness Index was monitored. Not surprisingly, the higher the temperature, the faster the tarnishing occurred. The color was first measured according to standard test DIN 6174 in freshly polished condition and several times during ageing. Figure 17 shows the development of the YI of Au-BMG1 at room temperature.

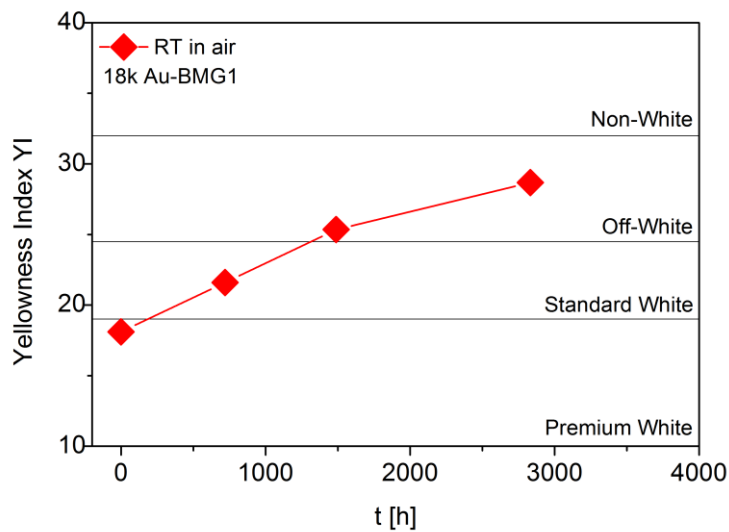


Figure 17: Yellowness Index (YI) development of Au-BMG1 at room temperature

Microstructural investigation of tarnished surfaces revealed, that the interaction between Cu and Si causes the unusual fast tarnishing of Au-BMG1. As was already reported in [26-29], silicon has been observed to oxidize at room temperature in the presence of copper and oxygen. When the cast SiO₂ surface layer is removed from the cast item, the silicon in the bulk metallic glass matrix is oxidized, thereby releasing Cu from the amorphous matrix [30]. The copper can diffuse to the surface where it itself can react with oxygen from the surrounding air to form Cu₂O or Cu₂S, depending on the environmental conditions under which the item is kept [31]. Figure 18 shows a distinctly large corrosion pit on Au-BMG1 which was formed during a long exposure to air at 75°C for 327 days. The growth of SiO₂ into the matrix and Cu₂O on the surface was detected by EDX and XPS analysis and can clearly be seen in Figure 18.

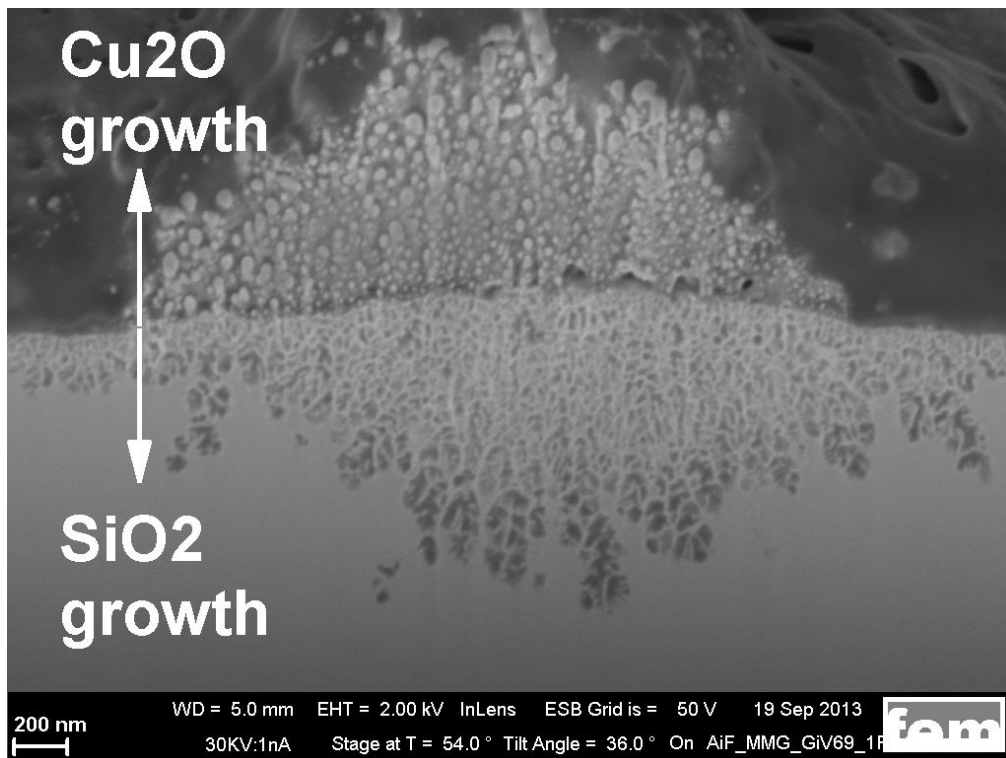


Figure 18: Corrosion pit on the surface of Au-BMG1. SiO₂ grows into the matrix, Cu₂O is formed on the surface

3. Summary and outlook

The process ability of Au-BMG1 exceeded the expectations. Even complex shaped jewelry products could be cast, despite the restrictions concerning fast quenching of the comparatively high viscous melt. The alloy proved to have a high tolerance towards handling in different processing techniques and was found to have a premium white color, which is highly desirable for applications in the jewelry sector. Nutshell tests in comparison to conventional white gold showed a better resistance to scratching. The overall impression has been that bulk metallic glass alloys can easily be applied in jewelry casting, if the special properties of bulk metallic glass melts are kept in mind.

The alloy composition of Au-BMG1, though, tarnishes massively during wearing already within short time scales. The key to prevent the tarnishing of Au based bulk metallic glasses lies in the detrimental Cu-Si ratio. The systematic development of new, tarnish resistant alloy compositions on Au base is planned to be carried out, basing on the results concerning the underlying mechanism behind the tarnishing.

4. Acknowledgement

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