WILL THEY WORK? A PROOF-OF-CONCEPT STUDY COMPARING A 500 Pd BMG AND CRYSTALLINE ALLOYS FOR WATCH PIECES AND JEWELRY

Owain Houghton

Bulk metallic glasses based on precious metals offer exceptional hardness compared to conventional crystalline alloys. They can be processed like plastics via routes analogous to injection molding, with excellent as-cast surface finish and far shorter cycle times compared to conventional investment casting of crystalline alloys. The properties of these alloys were presented and discussed at the 34th Santa Fe Symposium. Amongst many potential applications are hallmark-compliant watch casings and jewelry. For the former, current hallmarked alloys are generally too soft. Results of accelerated lab tests for a Pd500 BMG in comparison with comparable crystalline alloys are presented, to assess the suitability of BMGs for watch and jewelry. The outcomes are discussed and critically evaluated to understand the suitability of these alloys now and in the future.

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WILL THEY WORK? A PROOF-OF-CONCEPT STUDY COMPARING A 500Pd BMG AND CRYSTALLINE ALLOYS FOR WATCH PIECES AND JEWELRY

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INTRODUCTION

As manufacturers search for harder and more scratch resistant alloys, interest has turned to bulk metallic glasses.[1] A metallic glass has the structure of a liquid, but the resistance to deformation of a solid. Consequently, atoms are arranged without any regular lattice structure (that repeats throughout space), as would be seen in a crystalline material.

The term “glass” is more familiar in reference to oxide glasses, and polymers, which have had a long-standing technological importance. Metallic glasses were first reported in 1960 in a Au-Si alloy ($Au_{75}Si_{25}$ – at.%).[3] These partially glassy samples were unstable at room temperature (crystallizing) and were formed via splat cooling – a technique that achieves cooling rates of up to 10^6 Ks^{-1} forming samples less than 30 µm thick.

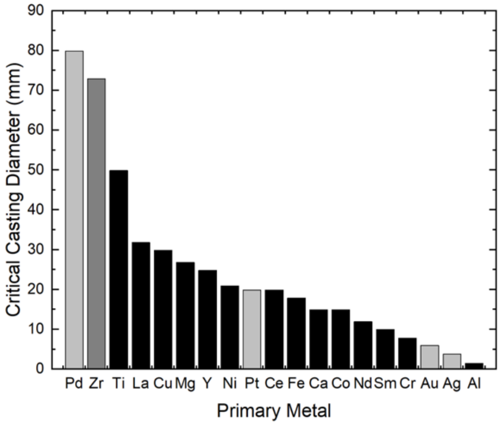
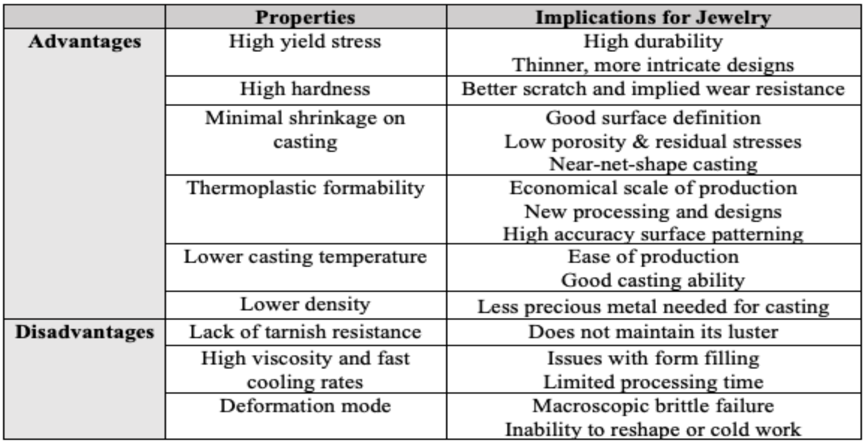


Figure 1: A summary of critical casting diameter dc in different alloy systems grouped by the primary metal in the alloy. BMGs based on precious metals are highlighted in light grey, while commercially available Zr-based BMGs are highlighted in dark grey. Reproduced from reference 2.

In subsequent work, careful alloying led to fully glassy samples that could be formed at lower cooling rates, and therefore in thicker sections. With the development of such glasses, the term bulk metallic glass (BMG) was defined: a metal alloy that is fully glassy when cooled from the liquid melt and can be cast with this glassy structure in sections thicker than 1 mm[4,5,6,7] The critical thickness or diameter in which an alloy can be cast fully glassy is denoted as dc. A wide range of compositions for BMGs have been reported with good glass-forming ability, as summarized previously (Fig. 1).[8]

Table 1: A summary of the advantages and disadvantages of BMGs and their implications for jewelry.



	Properties	**Implications for Jewelry**
Advantages	High yield stress	High durability Thinner, more intricate designs
	High hardness	Better scratch and implied wear resistance
	Minimal shrinkage on casting	Good surface definition Low porosity & residual stresses Near-net-shape casting
	Thermoplastic formability	Economical scale of production New processing and designs High accuracy surface patterning
	Lower casting temperature	Ease of production Good casting ability
	Lower density	Less precious metal needed for casting
Disadvantages	Lack of tarnish resistance	Does not maintain its luster
	High viscosity and fast cooling rates	Issues with form filling Limited processing time
	Deformation mode	Macroscopic brittle failure Inability to reshape or cold work

There is already use of zirconium-based BMGs in the bezel or lunette of some high-end watches, originally under the tradename LiquidMetal®[9] but now their use is more widespread. In this study, we consider the current suitability of precious-metal bulk metallic glasses for industrial applications, with a specific focus on one of the two most promising alloy series – 500Pd BMGs. With the mechanical behavior of metallic glasses being very different to crystalline metals, this paper presents some results but also serves as a complementary guide to the presentation.

BMGs FOR JEWELRY: NEW POSSIBILITIES

BMGs based on precious metals (specifically 18K gold-based BMG[10]) immediately attracted interest for jewelry,[10,11] where high hardness (exceeding 300 HV in the as-cast state) and associated wear and scratch resistance are desirable.[12] The different structure of BMGs also brings many other advantages (Table 1).

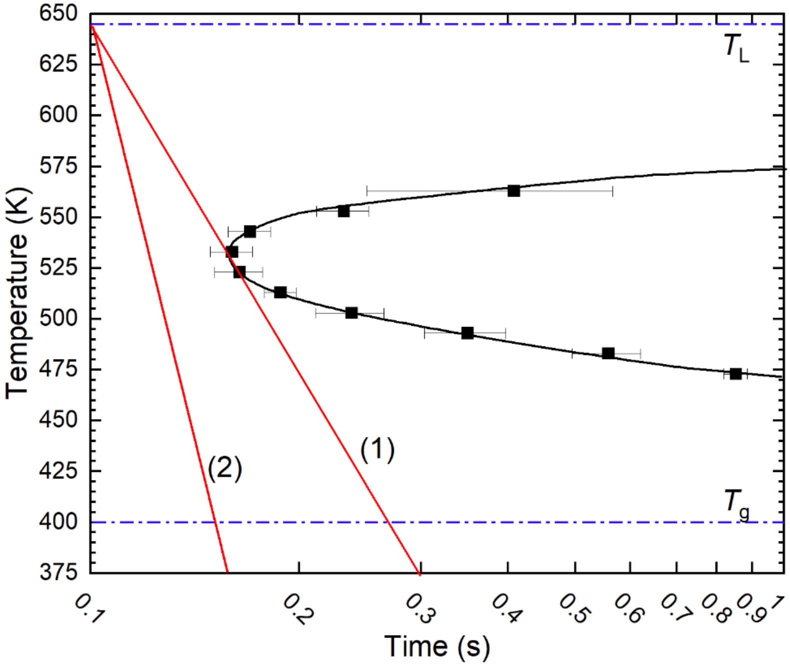


Figure 2: The conditions for glass formation considered using a TTT (time-temperature-transformation) curve for crystallization in the melt measured for a composition that can form a gold-based metallic glass. Fast cooling (2) gives a fully glassy sample. Critical cooling rates, Rc, (1) for metallic glasses are higher than for conventional oxide glasses due to the non-directional nature of metallic bonding. Lines are guides to the eye. Reproduced from reference 2.

The alloy melt must be cooled fast enough to avoid crystallization (Fig. 2). As it cools, the liquid melt becomes more viscous which prevents atoms from rearranging themselves to form a crystal. At the glass-transition temperature (Tg), the viscosity reaches 1012 Pa s (1013 poise). Atoms in the liquid become thermally arrested; crystallization cannot occur with atoms "frozen" into a liquid-like arrangement.

The absence of a crystalline structure means plastic flow by dislocation motion cannot occur, and so mechanical failure must occur at a much higher stresses – these approach the theoretical stress limit of a metal (the perfect sliding of atomic layers). This is accompanied by an elastic strain limit, typically six times that of a typical crystalline jewelry alloy. BMGs are extremely elastic and can behave much like a rubber ball.[13]

But not all compositions can form a glass at a cooling rate suitable for industry (<100 K s^{-1}). To avoid crystallization, alloys are designed so that the liquid is as stable as possible relative to the crystal.[14] Eutectic compositions are ideal as there is a narrow region between the glass-transition temperature and the liquidus temperature (T_L). This is characterized by a high reduced glass-transition temperature $T_{rg} = T_g/T_L$.[15]

The result is that these alloys have far lower melting and working temperatures compared to their crystalline counterparts. This lower temperature and an absence of crystallization means there is minimal shrinkage upon casting (below 1%), accompanied by a new level of "mirror finish";[11] near atomically smooth surface finishes are possible (due to the absence of a grain structure). In addition to conventional casting, there is also the opportunity for thermoplastic forming, processing them like plastics, which takes the total casting time down from days to minutes for simple geometries (e.g. rings).[16]

BMGs' unique array of intrinsic properties offer the potential for many new design possibilities and fast mass production that rivals metal injection molding. These high-hardness alloys can be processed like plastics, with near-net-shape casting and the accurate reproduction of intricate surface patterns and details. The successful application of Zr-based BMGs for jewelry paves the way for their precious-metal equivalents.[1,9]

BMGs FOR JEWELRY: THEY HAVE THEIR LIMITS

Still, BMGs aren't without their disadvantages. While some are resolvable, others are not and present a new set of concerns for the bench-top jeweler. Perhaps the biggest (and unique) challenge for jewelry-specific BMGs is hallmarking and stamping regulations.

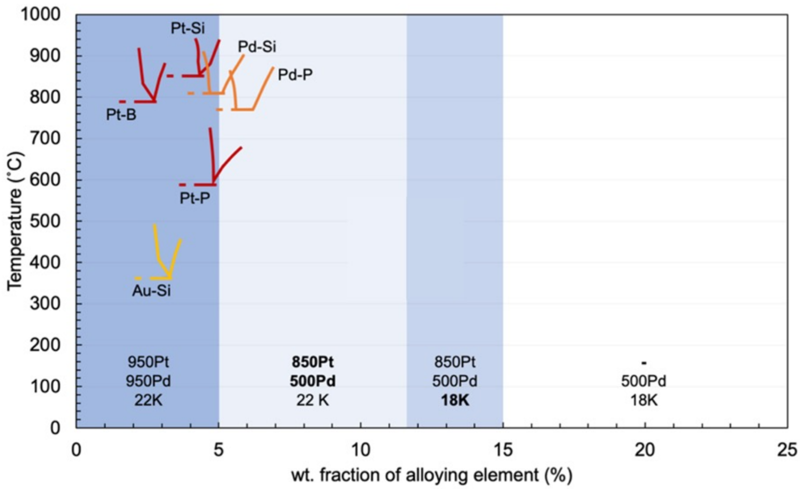


Figure 3: Compositions and temperatures of all near-eutectic compositions used in BMGs that are, or are near being, commercially available. The restriction to near-eutectic compositions means that high-fineness BMGs are not currently obtainable. Even for non-eutectic BMGs, a large degree of alloying is necessary to achieve the variety in atomic radius required for GFA and glass stability. Reproduced from reference 2.

BMG compositions are carefully designed to ensure that the liquid is as stable as possible relative to the crystal (eutectic alloys are typically the starting point). Four or more elements are usually required to "confuse" and thus to "frustrate" crystallization,[17] and ensure a densely packed and highly viscous liquid.[14] High glass-forming ability can be achieved in only very few compositions, and substantial alloying is required. It is difficult to reach high fineness[2,8] (Fig. 3). For jewelry-specific BMGs, alloy design is a trade-off between reaching precious metal contents that meet stamping regulations and ensuring that glass-forming ability is high enough to avoid crystallization.[18]

While their different atomic structure leads to high hardness, it means BMGs cannot be cold-worked. A crystal deforms via the motion of dislocations while metallic glasses deform via the formation of shear bands.[19] Under an applied stress, small, localized regions of atoms in the BMG rearrange themselves, known as "shear-transformation" zones (STZs).

Under sustained load, these STZs join together and form a shear band. In tension, most BMGs form a single dominant shear band, resulting in macroscopic brittle failure (<1% ductility). If multiple shear bands form, there is some plasticity, but deformation still leads to unsightly surface marks. BMG components should be cast in, or near to, their final shape.

Ultimately the final shape casting is limited in size, due to the critical cooling rate (R_c) required to form a glass. Below R_c, the melt crystallizes since the crystalline structure remains the most stable state below TL (Fig. 2). If the critical cooling rate to form a fully glassy sample is higher, the maximum thickness or size of piece that can be cast is smaller (Fig 1).

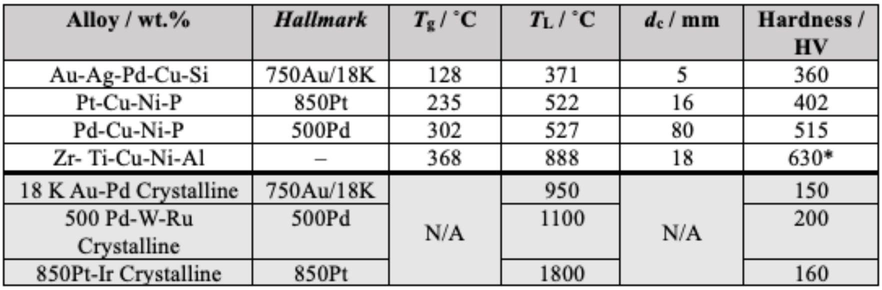
Techniques such as thermoplastic forming and additive manufacturing are attractive as they mitigate the cooling rate concerns, allowing larger parts or worse glass-formers to be made. Yet, they bring many of their own challenges. Thermoplastic forming leads to difficult-to-eliminate inclusions and pores,[16,20] while additive manufacturing (specifically SLM) must overcome the high reflectivity of precious metals and the trade-off between the overall glassy fraction and the porosity.[21] With BMGs performing so poorly in tension, the mechanical properties are sensitive to both the degree of crystallinity and porosity. Working with BMGs requires careful bespoke design of the piece as well as its processing route.

BMGs FOR JEWELRY: ALLOYS AVAILABLE TO THE INDUSTRY

Outside of the precious-metal composition space, Zr-based BMGs have already found great interest in luxury watches.[1] Their high hardness has made them a useful material for watch bezels (lunettes).[9] This technology has become increasingly widespread, with some companies now processing over 100 kgs of precious-metal material each year.[1]

Platinum-, palladium- and gold-based BMGs have all been reported in hallmark-able and high-fineness regions (Table 2). For the reasons outlined above, achieving a combination of high fineness and glass-forming ability is a challenge due to the intrinsic requirements to form a glass.[8] Table 2 gives a summary of the highest-fineness alloys with a critical glass-forming diameter above 3 mm (often considered a critical value for industrial application[20]).

*Table 2: Key bulk metallic glasses and their values for glass-forming ability and hardness. Comparative crystalline alloys are also listed. Data collected from references 10, 11, 22, 23, 24, 25. *denotes an estimate from tensile yield strength.*



Alloy / wt.%	*Hallmark*	T_g / °C	T_L / °C	d_c / mm	Hardness / HV
Au-Ag-Pd-Cu-Si	750Au/18K	128	371	5	360
Pt-Cu-Ni-P	850Pt	235	522	16	402
Pd-Cu-Ni-P	500Pd	302	527	80	515
Zr- Ti-Cu-Ni-Al	–	368	888	18	630*
18 K Au-Pd Crystalline	750Au/18K	N/A	950	N/A	150
500 Pd-W-Ru Crystalline	500Pd		1100		200
850Pt-Ir Crystalline	850Pt		1800		160

For 18K Au BMGs, there is an extensive problem of tarnishing.[26, 27] The interplay between copper and silicon in these alloys leads to a rapid discoloration (in a matter of weeks at room temperature). Efforts to produce a tarnish-resistant alloy have so far been ultimately unsuccessful.[28,29] While colored gold BMGs are available with careful metallurgy, $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ (at.%) is a white-gold alloy due to the high silicon content.[10]

For 950Pt, 950Pd, 925Ag BMGs, there is a substantial issue with glass-forming ability.[8] There is generally low glass-forming ability in currently known Ag-based BMGs.[30] While some 950Pt/Pd BMGs exist, they show marginal glass-forming ability.[23] There is good reason why this is not expected to change dramatically.

The reason for the drop in glass-forming ability is two-fold. First, as we move to finer alloys, the liquid viscosity decreases faster as the temperature is raised (it becomes more “fragile”), and so it can crystallize faster. Secondly, as we deviate from eutectic compositions, the liquid becomes less stable relative to the crystal, so there is a larger (thermodynamic) driving force for crystallization.[18]

For these reasons, BMGs in the less popular 850Pt and 500Pd hallmarks are the only alloys available that may currently be suitable for market. For the 850Pt BMGs, separate work at fem has begun to characterize their suitability for jewelry.[31] However, 850Pt BMGs do not form a patina and this may challenge customer perception and desires; as will be discussed, BMGs wear quite differently and do not work-harden. Even so, they remain of great interest. This review aims to study 500Pd BMGs and compare both 500Pd and 850Pt BMGs with Zr-based BMGs and conventional crystalline alloys.

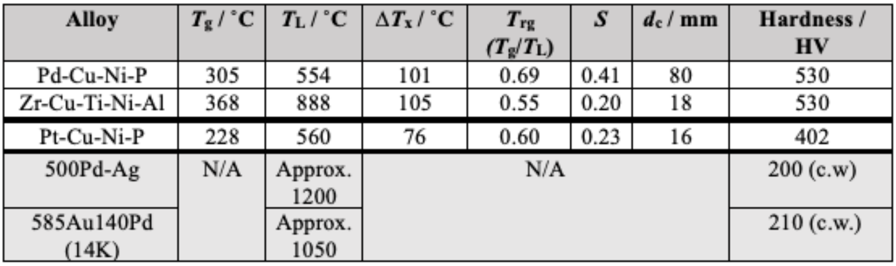
A CAREFULLY CHOSEN SET OF ALLOYS AND TESTS

In Pt-based BMGs, the Pt-(Cu,Ni)-P quaternary system is the base for almost all BMGs. While containing nickel is generally undesirable, the release rates are below the required legal limits.[31] For 500Pd, there are both Pd-Cu-Si and Pd-(Cu,Ni)-P based BMGs. Alongside the presence of nickel, phosphorus-containing alloys are often fluxed to remove impurities and heterogeneities that can assist crystallization. In some cases, glass-forming ability is high enough in the alloys to not require fluxing – these are the alloys most desirable for industry.

In Pd-Si-based BMGs, the presence of both copper and silicon leads to a tarnishing phenomenon, very similar to that in 18K Au BMGs though slower.[31,32] For this reason, these alloys were not a priority for inclusion in this study.

For appropriate comparison, we take Vitreloy 105, the commercially available and widely used Zr-based BMG.[1,20] Two crystalline alloys are also compared – a 500Pd-Ag alloy and a 14K Pd-white Au alloy.

*Table 3: Bulk metallic glasses studied here and their values for glass-forming ability and hardness. Comparative crystalline alloys and the best performing 850Pt BMG are also listed. Higher Trg, *Tx and S indicate higher glass-forming ability, thermal stability, and thermoplastic formability. Data except hardness collected from references 10, 11, 22, 23, 24, 25, 31. C.W. denotes cold-worked to approximately 10–20% reduction.*



Alloy	T_g / °C	T_L / °C	ΔT_x / °C	T_{rg} (T_g/T_L)	S	d_c / mm	Hardness / HV
Pd-Cu-Ni-P	305	554	101	0.69	0.41	80	530
Zr-Cu-Ti-Ni-Al	368	888	105	0.55	0.20	18	530
Pt-Cu-Ni-P	228	560	76	0.60	0.23	16	402
500Pd-Ag	N/A	Approx. 1200	N/A				200 (c.w)
585Au140Pd (14K)		Approx. 1050					210 (c.w.)

To understand the performance of these alloys, and to give meaningful values to assess suitability, a series of tests were conducted to characterize both wear resistance and tarnish resistance, arguably the two key factors in material performance for jewelry.

Wear resistance was assessed using a pin-on-disk machine from CSEM, with each sample in contact with a 6 mm diameter Al2O3 pin applying a light pressure of approximately 75 kPa. Wear depth and volume were assessed and imaged by profilometry, confocal microscopy and scanning electron microscopy. A scratch test was also performed to show the deformation features characteristic of a single wear cycle.

Tarnish resistance was assessed using ion-release tests and colorimetric assessment (before and after) while immersed in simulated body fluids (artificial saliva) in accordance with DIN EN ISO 1811, DIN EN 10271, and DIN 5033. Color change, ΔE, and yellowness index YI can be determined according to DIN 6174 and ASTM D1925, respectively.

The comparative hardness, thermal parameters (T_g, temperature of crystallization onset T_X, and T_L) and key metrics of glass-forming ability are included (Table 3). Pd-based BMGs are some of the very best glass formers.

A DEEP-DIVE INTO TRIBOLOGY: UNDERSTANDING WEAR

Compared with mechanical measurements like hardness, studies of wear (tribology) are much more diverse. There are many types of wear with forces of different magnitude acting in different directions. With wear and scratch resistance among the primary attractions of BMGs for jewelry, a wide-ranging understanding is important and necessary.

There are generally two main types of wear – sliding and abrasive wear. Sliding wear involves sliding of two smooth surfaces in contact over one another, either dry or lubricated. Abrasive wear involves harder than the material particles (embedded in either material or free between them) being abraded. The particles indent, plough and groove the surface. The different types of wear have different mechanisms and lead to different features.[33]

A ‘rule of thumb’ is that wear resistance scales with hardness. This result is taken from Archard’s law,[34] which gives the volume of material removed by wear V_w as:

$$V_W = K\frac{LN}{H}$$

where L is the total relative sliding distance and N is the normal load applied, H is the material hardness and K is the wear coefficient. Wear resistance is inversely proportional to V_w.

With many parameters affecting the overall wear, it is difficult to make a reliable comparison of results from different set-ups. For example, wear resistance scales well with hardness in three-body abrasive wear tests but it does not in pin-on-disc tests.[33] Even when the same set-up is used, wear resistance remains difficult to analyze. For example, when a pure metal is work-hardened, its hardness increases but its wear resistance does not.[33] Wear is also a combination of both mechanical and chemical effects.[35]

In crystalline alloys, whether wear is "severe" or "mild" often depends on whether a film of oxide and oxidized debris form on the surfaces. Direct metal-on-metal contact leads to severe wear. Oxidation has a lubricating effect that results in milder wear.[33] Oxidation does not need to be observable by eye or even by scanning electron microscopy to have a substantial effect. Of course, oxidation is not common (or expected) for precious-metal alloys because of their noble behavior, which would be consistent with their generally poor wear resistance.

For conventional crystalline ductile metals, a ploughing-like behavior is often seen as a result of work hardening.[33] In the case of BMGs, there is no work hardening, but the character of the wear debris and the wear scar on the surface remain the main indicators of performance.

In the Pt-based BMGs, where hardness is typically more than twice that of work-hardened crystalline alloys of similar fineness, wear marks show a great scatter in depth across the different compositions[31] (Fig. 4). A greater wear depth indicates inferior wear resistance. Images of the worn regions indicate a wide range of features: some show extreme brittleness (cracking and loose particles); others show daubed regions of deformed and flattened material. In some cases, the BMGs are inferior to the crystalline alloys in wear resistance.

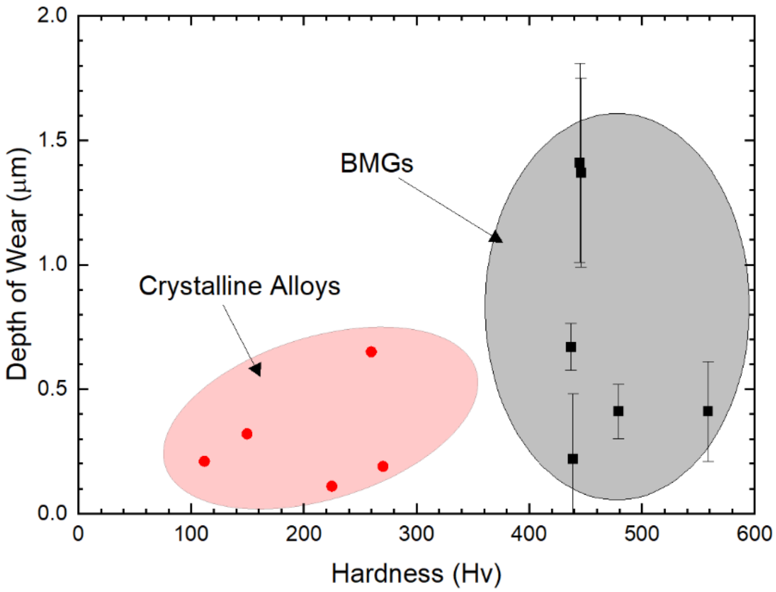


Figure 4: For fixed test conditions, the depth of wear mark as a function of measured hardness for Pt-based amorphous and conventional crystalline alloys. A higher depth of wear corresponds to an inferior wear resistance. Results show a high degree of scatter in the performance of Pt-based BMGs, contrary to the expected behaviour (wear depth decreases with increasing hardness). Reproduced from references 2, 31.

The results for the least wear-resistant BMGs (those that crack) suggest a transition from sliding to abrasive wear.[36] Debris particles are likely crystallized or oxidized and consequently embrittle and harden.[33] Once loose, these particles to abrade the surface, and consequently there is a transition to the more aggressive abrasive-wear regime. A transition to abrasive wear resulting from oxidation can also occur in crystalline metals.[37] The wear scar surface on BMGs is also known to crystallize, which can lead to high wear rates (once crystallized, these materials are very brittle).[38]

In precious-metal BMGs, crystallization of debris seems more likely, and is common for other BMGs,[39] but detailed characterization of the wear debris (the loosened particles) is necessary. The crystallization may be mechanically induced without temperature rise but may also be thermally induced as frictional forces are considered to generate sufficient heat.[35,40] However, the wear resistance of BMGs does not relate simply to crystallization temperature, the thermal stability of the glass ($\Delta T_x = T_x\text{-}T_g$) or glass-forming ability parameters (e.g. $T_{rg}=T_g/T_L$), weakening support for an analysis based on temperature rise. However, the worst performing alloys studied in ref. 31were not Pt-P-based alloys, with different compositions they are therefore likely to show a different atomic structure; resulting in different mechanical and corrosion properties.

Schmitt et al. suggest that wear resistance improves with nickel content.[31] Many reports on Ni-containing BMGs suggest that oxidation occurs during wear.[41,42] The oxide layer need not need be visible, nor increase hardness, to have a dramatic effect on wear behavior.[43] In crystalline alloys, an oxide layer would not readily form at room temperature. The atomic-level structure in a BMG has intrinsically higher energy and is more reactive, making BMGs attractive as catalysts.[44] Consequently, oxidation may be accelerated, an effect that is particularly significant at lower temperatures.[42] This may help to explain the higher normalized copper-release rates seen in the 850Pt BMGs.

At least in some tests, Zr-based BMGs show some of the best wear resistance amongst BMGs.[33] Alongside jewelry, they are attractive for space applications where they are self-lubricating, perform well at low temperatures and under vacuum.[45] In fact, these alloys tend to perform better in vacuum as the worn surface can oxidize in air (Zr is often used as an oxygen getter in alloying) leading to accelerated wear.[46] The environmental conditions in space are very different from those relevant for jewelry!

While these specific details of wear mechanism are not important to the application or to a benchtop jeweler or consumer, they illustrate this remains an interesting area of academic research. Wear mechanisms and rates depend not only on mechanical and chemical factors intrinsic to the material, but also on the test conditions (type of wear, temperature, air/vacuum/protective atmosphere etc.).

In general, there are few trends in behavior across the different alloys due to the combination of both chemical and mechanical effects. Only in three-body adhesive wear tests does the wear resistance correlate well with hardness[47]; the loading conditions on the sample by the free particles are predominantly normal rather than shear.

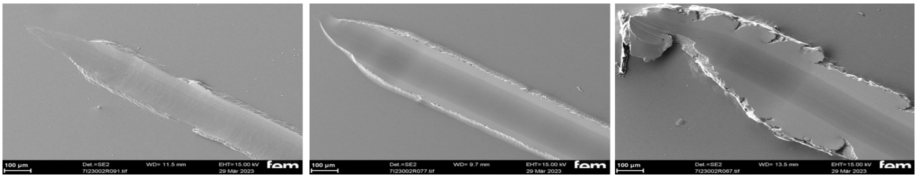


Figure 5: Scanning electron microscopy (SEM) images of a scratch test performed on the crystalline 500Pd alloy (right), the 500Pd BMG (center) and the Zr-based BMG. The crystalline alloy shows classical features of a ductile metal, which are absent in the BMG, largely due to a lack of work-hardening.

It is difficult to separate the many ongoing effects during wear, a problem exacerbated by the aggressive nature of accelerated wear tests. Changing the sliding rate of the pin, or similar, to accelerate wear can often change the mode of wear. It is important to consider the relative rates of surface removal (faster sliding means more wear) and thermally induced oxidation (faster sliding means more friction, so more heating and faster oxidation).[41] This highlights the important of “real-life” tests, where the wear conditions are less aggressive.

THE COMPARATIVE PERFORMANCE OF PALLADIUM-BASED BMGs

Given the similarities in the chemistry of platinum and palladium, and in the compositions of their BMGs, (Pt/Pd)-(Cu,Ni)-P, we would expect their wear and tarnishing behavior to be similar. But the behavior of these superficially similar systems can be quite different: mechanical tests suggest that the Pd-BMGs are comparatively brittle.[48] Structural studies suggest that the packings of atoms in Pd-Cu-Ni-P and Pt-Cu-Ni-P are distinct.[49] Such findings are discussed in more detail elsewhere.[18] We conclude that while both alloy series may be macroscopically brittle, they can have different local plastic behaviors.

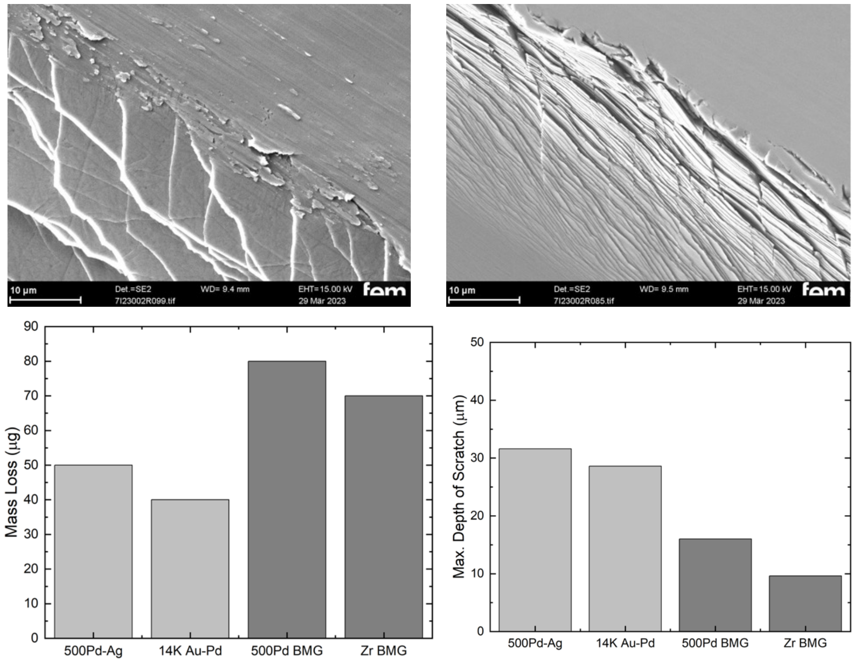


Figure 6: SEM images of the edge of the scratch in the Zr-based BMG (top left) and the 500Pd BMG (top right). The Pd BMG shows a far higher density of shear bands, indicative of higher fracture toughness and more microscopically ductile behavior. The depth of scratch (bottom right) and mass loss during the test (bottom left) suggest that the 500Pd BMG and Zr-based BMG have similar resistance to abrasive wear.[50]

Scratch tests provide indications of abrasive wear resistance and of fracture toughness.[50] The benchmark 14K Pd-white gold and 500Pd alloys show features characteristic of ductile metals (Fig. 5). In contrast, the Zr- and Pd-based BMGs show signs of shear bands. Scratch depths show damage in the crystalline alloys that is much more severe than in BMGs. The high hardness of the BMGs should indeed resist normal loads and inhibit scratching. However, the difference in deformation mechanism ultimately leads to a higher mass loss (Fig. 6). An absence of work hardening means the ploughing-like behavior cannot occur. Such results suggest that the BMGs may indeed be more scratch resistant, where the force applied is predominantly normal.

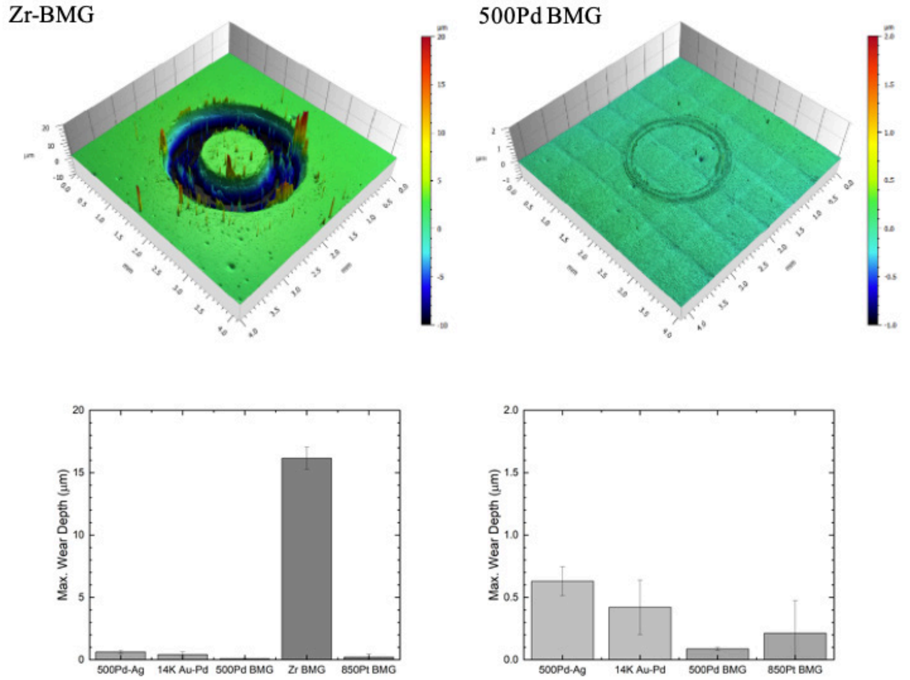


Figure 7: Pin-on-disc wear depth for the various alloys and confocal images of the wear for Zr (top left) and Pd BMGs (top right). An 850Pt BMG, $Pt_{57.3}Cu_{14.6}P_{22.8}Ni_{5.3}$ (at.%) was used for comparison from reference 31 measured under identical conditions. The 500Pd BMG shows the highest resistance to sliding wear of any alloy.

Pin-on-disc tests, performed at fem, give a preliminary indication that, in sliding wear, 500Pd BMGs perform much better than Zr-based BMGs, or benchmark crystalline alloys (Fig. 7). When imaging each scratch, the key difference between the Zr-based and the 500Pd BMG is the apparent density of shear bands around the scratch. The 500Pd BMG shows a far higher density of shear bands; this is to be expected since some Pd-based BMG compositions show “liquid-like” behavior with the formation of multiple shear bands.[23,51] But the difference in behavior during sliding wear cannot be explained by these subtle changes in deformation, especially given comparable performance in a scratch test. There is no evidence of cracking in the surface, as can be seen in some 850Pt BMGs[31] indicating a more advanced stage of wear. Further characterization of the wear scar and debris is necessary, but a plausible explanation is the oxidation of the wear scar surface.[46]

Further results will assist further understanding of the differences and similarities between Zr-based BMGs, precious-metal BMGs and crystalline alloys. Advanced techniques such as nanoindentation and transmission electron microscopy may help to understand the underlying physics of difference in behavior, by imaging and mechanically probing the atomic structure on the smallest possible length scales.

Alongside further study of mechanical wear, tarnishing results will be presented in full at the symposium. As seen in the gold-based glasses containing copper and silicon, Pt-Cu-Si and Pd-Cu-Si glasses both show evidence of tarnishing. Copper and silicon-free 850Pt and 500Pd alloys contain nickel, although its release rates are far below the industrial standard limit.[31,32]

In Pt-based BMGs absolute copper release rates can appear far higher than conventional Pt alloys, due to the higher copper content of Pt-based BMGs; when normalized, the differences are far smaller.[31] Diffusive processes in metallic glasses are complicated and remain under active research.[52]

Given that nickel-ion release rates are low and that other elements are not associated with skin sensitization (although the industry view is under review[53]), the colorimetric change after exposure to various corrosive environments is the greatest concern in jewelry applications. After incubation in artificial saliva, Pt-based BMGs show comparable tarnish resistance to conventional alloys.[31] In air there is a more pronounced color change, although $Pt_{57.3}Cu_{14.9}Ni_{5.3}P_{20}$ (at.%) shows a color change in one month that is not easily discernible by eye ($\Delta E \leq 5$). It would be plausible to expect Pd-based BMGs to show a similar level of resistance to tarnishing as Pt-(Cu/Ni)-P BMGs.

The initial color of BMGs is often different to that of comparable crystalline alloys. Given their dramatically different compositions, such a difference is not surprising, but this remains an important consideration for any jeweler or watchmaker.

DISCUSSION AND OUTLOOK

BMGs offer an exciting opportunity for use in jewelry, watchmaking, and luxury goods. Early results for 500Pd BMGs suggest that these materials wear at far lower rates than Zr-based BMGs that are already used in the watchmaking industry. Their wear mechanisms and behavior are very different to those of conventional crystalline alloys of comparable fineness. These results warrant further study. There is a clear case for further investigation with “real-life” tests, that assess performance under actual wear conditions. Furthermore, 500Pd BMGs show excellent glass-forming ability, even superior to Zr-based BMGs.

The 500Pd and 850Pt BMGs based on the Pt/Pd-P system do not appear to succumb to the tarnishing problem seen in 18K Au BMGs. Testing for 500Pd BMGs is ongoing, but 850Pt BMGs tend to tarnish (as measured by discoloration) at a similar rate to crystalline Pt alloys in saliva tests.[31] Pt-Cu-P based alloys tend to show a small discoloration in air during laboratory testing, but the relative rate of wear and tarnishing need to be carefully considered. The performance in real-life use is difficult to assess in a laboratory.

Comparative laboratory tests are only one step towards commercial realization. For alloys currently available, in-person wear tests are an important next step. As has been shown in similar studies, laboratory testing is a useful indicator but not equivalent to in-person wear tests.[54] Laboratory testing can show certain phenomena in isolation, rather than combined; synergetic effects are difficult to account for and may dramatically affect behavior.

For subsequent work and development, there is a need to better assess the mechanical wear in precious-metal BMGs, in combination with tarnishing behavior. Real-life testing is arguably the easiest and most reliable method but is expensive. While deeper understanding of wear in precious-metal BMGs (and BMGs more generally) is desirable to assist further alloy development, this is no trivial task. High-fineness precious-metal and Zr-based BMGs are a special subset within the BMG field owing to their high fragility (highly temperature-dependent viscosity).[23] Even so, the difference in their wear behavior suggests there are many important factors affecting wear resistance.

In summary, precious-metal BMGs continue to be of great interest and promise as future jewelry materials. They bring new-found hardness and many novel design opportunities, as is demonstrated by Dr Ulrich Klotz in another presentation at this Symposium. In some cases, there are alloys on the cusp of commercialization, and for these alloys larger in-person “real life” studies, as is seen for the development of new crystalline alloys, is an important next step. For precious-metal BMGs to make it to the consumer, however, industry involvement in conducting and guiding further research is necessary.

500Pd and 850 Pt BMGs appear the most promising. When density is accounted for, both alloys currently cost a similar amount. 850Pt BMGs strike a higher fineness, but in the absence of work-hardening, they do not form a patina, and that lack may prove undesirable to consumers. 500Pd BMGs appear to be most resistant to wear. Realistic expectations should be set about what is and what is not possible. While 950Pt/950Pd/925Ag BMGs are desirable, there are fundamental challenges to their development. 18K gold BMGs do not suffer from the same alloying constraints, but the currently available alloys show highly undesirable tarnishing. Precious-metal BMGs may be on the wrist soon and provide many exciting opportunities but bring their own set of challenges to the benchtop jeweler and watchmakers alike.

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