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Bulk metallic glass coating of polymer substrates

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Abstract. Bulk Metallic Glass (BMG) alloy with the composition of $Zr_{55}Cu_{30}Al_{10}Ni_5$ was deposited by sputtering as thin films on several different engineering polymers and polymer composites. Polycarbonate, polymethyl methacrylate, polyamide 12, polyarylamide (50GF=50 % glass fibers), polyphenylene sulfide (30GF) and polybutylene terephthalate (30GF) were used as substrates. The microstructure of the deposited BMG coatings was studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results of XRD and SEM studies were consistent with amorphous microstructure. Elemental compositions of the coatings were verified by energy dispersive spectroscopy (EDS). Mechanical properties of the coatings were compared to copper mould cast BMG using nano-indentation tests with similar results. According to the cross-cut tape tests good adhesion was achieved between the studied BMG alloy and all other polymer substrates except polycarbonate. Nano-indentation results showed similar mechanical properties for coating and cast BMG. The results of this study look promising as they open new opportunities for BMG-polymer composite applications.

1. Introduction

Bulk metallic glasses (BMG) are amorphous metals that can be cast into a copper mould with a diameter larger than 1 mm before detectable crystallization appears [1]. In heating these alloys often have a glass transition temperature (T_g), followed by a super-cooled liquid region (SLR) before crystallizing. Enhanced stability against crystallization is usually achieved by alloying multiple elements with significant size difference in atomic radius above 12 % and negative heats of mixing among the constituent elements. Typically the obtainable critical casting diameters of known BMG alloys range from 1 to ~100 mm depending on the alloy composition and process conditions. BMG alloys have been found in many different alloy groups and new alloys have been discovered and reported with a variety of different properties. The known alloy groups include Mg-, La-, Zr-, Ti-, Fe-, Co-, Pd-Cu-, Ni- and Cu-based systems. Because of the large number of possible alloy compositions and the atomic level structures, adjusting mechanical properties, electrical resistance, corrosion resistance and magnetic properties can be done in large degree with relatively minor alloying changes.

With BMG alloys it is possible to achieve different combinations of strength, stiffness and ductility. Properties reported in the literature include very high strength in the as-cast state, typically ranging from 1500 to more than 5500 MPa, and Young's modulus ranging from 70 to 275 GPa with unusually large elastic strain of almost 2 % compared to crystalline alloys [2]. The lack of grain boundaries produces very accurate surface finishes and enhances corrosion resistance.

The methods to produce BMG alloys are combinations of high-vacuum melting of the elements for alloying and various ways to solidify the end-product in the desired shape. The most used methods to produce relatively large components are copper mould casting, quench casting and sintering from atomized powder [7, 8]. The most studied methods to produce coatings include high velocity oxygen fuel (HVOF) and physical vapour deposition such as magnetron sputtering [5, 6]. BMG alloys can be very accurately deformed in the SLR region without causing crystallization, either during cooling from the molten state or with a separate reheating from the quenched state.

The wider industrial use of BMG alloys suffers from the costly high purity requirements of the materials and the manufacturing processes. Here we study the possibility of minimizing the amount of high strength BMG and the possibility to use the known processability of polymers to produce hybrid material parts with high contact strength surface and high specific strength interior. To evaluate the feasibility of these BMG-polymer composites it is necessary to determine if it is possible to create sufficient adhesion between the two and what the properties of the deposited BMG alloy are.

Although many results of BMG coating of various substrates have been published and made, so far we have not found any published studies of BMG coating of polymer substrates. We have studied here the possibility to deposit one BMG alloy on selected engineering polymer substrates using magnetron sputtering. The coating micro-structure, composition, hardness, Young's modulus and adhesion to the substrate were evaluated.

2. Experimental

Target alloy of composition $Zr_{55}Cu_{30}Al_{10}Ni_5$ (at-%) was weighed from the elements of Zr (+Hf) 99.99 mass-%, Cu 99.999 mass-%, Ni 99.99 mass-% and Al 99.99 mass-% purity. The cut and weighed pieces were melted in a titanium gettered laboratory arc-melter under reduced pressure in argon atmosphere. The vacuum-chamber was evacuated to a vacuum of higher than 1E-3 Pa before filling the chamber with argon. The ingot was melted and flipped over five times to ensure even distribution of alloying elements.

The target was machined with a lathe from the ingot to the final dimensions for use in the magnetron sputtering. The cast bulk specimens were manufactured in a casting furnace where they were remelted with induction heater inside a quartz crucible and cast with Ar pressure into a copper mould under vacuum atmosphere better than 1E-3 Pa. The glassy nature of the copper mould cast BMG was verified with X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The compression tests were performed with strain rates 5×10^{-6}, 1×10^{-5}, 5×10^{-5} and 1×10^{-4} s^{-1} with an Instron-type machine. The Young's moduli were obtained from recorded strain-gage data. Magnetron sputtering under reduced Ar pressure was used to deposit the target alloy to various substrates without heating them too much. The base pressure of the industrial purity deposition chamber was 1E-3 Pa. These tests are compared to the results from a high purity deposition chamber with base pressure <1E-5 Pa. The details of this equipment are listed in ref. [5].

Polycarbonate (PC), polymethyl methacrylate (PMMA), polyamide 12 (PA12), polyarylamide (PAA+50GF), polyphenylene sulfide (PPS+30GF), polybutylene terephthalate (PBT+30GF) were used as substrates. The numbers in the last three codes refer to the content of glass fibre filler (GF) in weight %. Thin films of about 400 nm were deposited on each polymer substrate.

The microstructures of the deposited alloys were studied with Zeiss Ultra 55 field emission gun scanning electron microscope (FEG-SEM) and the elemental composition was analyzed with Bruker AXS energy dispersive spectrum (EDS) analyzer connected to the SEM. The X-ray diffraction (XRD) patterns of the samples were analyzed with Siemens Kristalloflex 710H X-ray generator and Inel CPS 120 position sensitive detector. Transmission electron microscopy (TEM) samples were prepared with Leica UC6 ultramicrotome using a diamond knife and studied with FEI 120 kV LaB6 electron gun and Gatan UltraScan CCD 2048*2048 pix detector for pictures and CCD 1392*1040 pix for transmission electron microscopy selected area electron diffraction (TEM-SAED) pattern. Adhesion of the BMG coating to the polymer substrates was studied with tape tests and cross-cut tape tests. The nano-indentation results were measured with a CSM Ultra Nanoindentation Tester.

3. Results and Discussion

Elemental compositions of the coatings were characterized by FEG-SEM and EDS and they were compared to the target composition. Coatings made by both industrial purity process ($Zr_{54,7}Cu_{32,0}Al_{6,8}Ni_{6,6}$) as well as the high purity process ($Zr_{49,2}Cu_{27,4}Al_{14,9}Ni_{8,5}$) were rather close to the intended composition $Zr_{55}Cu_{30}Al_{10}Ni_5$ (at%). Composition of deposit varied slightly with different sputtering parameters. Ni and Cu contents were measured to be slightly higher than the composition of the target alloy. The exceptionally large 30 mm critical casting diameter of the target alloy ensures that the deposited alloy is in the high glass forming region.

X-ray diffraction patterns shown in figure 1 were obtained to determine the structure of the deposited coating. The selected area diffraction pattern in figure 2 does not show any indication of crystallization, but does show the diffuse ring characteristic of an amorphous structure. According to Chen and Spaepen, amorphous structure can be difficult to distinguish from ultra-fine-grained polycrystals without DSC-measurements [3]. The cross-section in figure 2 shows a section of characteristic smooth BMG coating on the polyamide substrate. The TEM sample was prepared by cutting the hard BMG coating on top of a very soft polyamide substrate with an ultramicrotome having Ø1 nm diamond edge. Based on the XRD, TEM and TEM-SAED results, it can be stated that the studied coating material is amorphous. This is in good accordance with the DSC studies of the same alloy reported in literature in sputtered[5] and cast[4] form.

The adhesion test results indicate that the studied BMG alloy can be coated on various polymer substrates by magnetron sputtering. The coating was successfully attached to all studied polymers except polycarbonate. The mechanical test results in table 1 and the similarity of the load-displacement patterns of figures 3 and 4 show that the mechanical properties of the coatings are similar to copper mould cast BMG when tested with the same method.

Table 1. Mechanical property test results.

	Coating	Cast BMG	Coating (literature) [5]
Hardness (nano-indentation)[1]	9.1 ± 0.2 GPa	8.0 ± 0.1 GPa	10.3 GPa
Young's modulus (nano-indentation)	130 ± 5.6 GPa	118 ± 2.3 GPa	128 GPa
Hardness HV_1	-	489 ± 16 HV_1 (3.45x0.489=1.7 GPa)	-
Young's modulus [2] (compression test)	-	93 ± 2.3 GPa	-

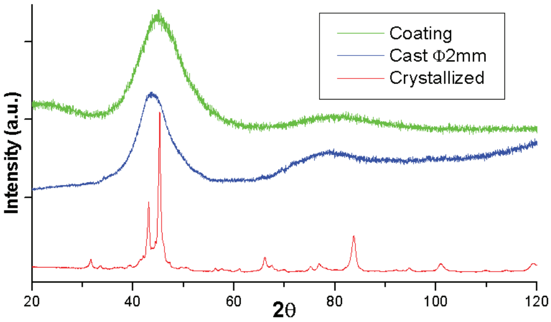

Figure 1. X-ray diffraction (Co K_α) patterns of deposited coating(top), cast bulk sample (middle) and arc-melted ingot (bottom)

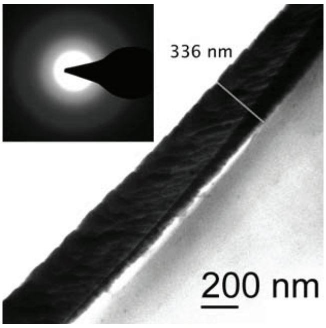

Figure 2. Selected Area Electron Diffraction and ultramicrotomy of the cross-section of the coating.

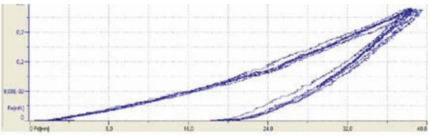

Figure 3. Nano-indentation load-displacement of the industrial purity coating.

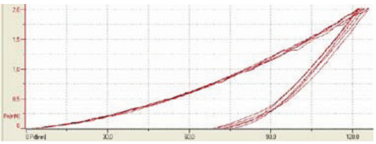

Figure 4. Nano-indentation load-displacement of the cast BMG.

4. Conclusions

BMG alloy $Zr_{55}Cu_{30}Al_{10}Ni_5$ (at-%) was successfully deposited on various engineering polymer substrates by magnetron sputtering as thin homogeneous layers of about 400 nm. The deposited alloys were shown to have amorphous structure and elemental composition close to the target alloy. According to the cross-cut tape tests good adhesion was achieved between the studied BMG alloy and all other polymer substrates with the exception of polycarbonate. The mechanical properties of coating and cast BMG appear similar when tested with the same method. These results with the novel BMG-polymer hybrid structures look promising and may open new opportunities for BMG alloy applications.

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