Biomedical Potential of a Zirconium-Based Bulk Metallic Glass

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ABSTRACT

Due to their unique mechanical properties, bulk metallic glasses (BMG) have potential for biomedical applications. Biocompatibility and corrosion tests of a zirconium-based BMG showed comparable behavior to current implant alloys. Mechanical properties, such as an elastic limit of 2% and a yield strength of 1700 MPa, are significantly higher than current implant alloys. In addition, it was found that medical MRI images of BMG, possibly due to the amorphous structure, are significantly better than other alloys even though the reference alloy contains 14.6 at.% Ni. Nickel-free compositions also retained similar glass forming characteristics and showed even better MRI images. Edge holding for cutting tool applications was demonstrated. Fatigue tests were performed in simulated body conditions and directly compared to Ti-6 Al-4 V. While one specimen failed at more than 3,000,000 cycles at 500 MPa, there was much scatter in the data. Further concentration on processing issues to produce pore free material is needed to produce reliable material for prototype development. Potential uses, especially associated with an interventional MRI for MRI guided surgeries, will be discussed.

INTRODUCTION

Bulk metallic glasses (BMGs) constitute a new class of metallic materials in which the amorphous liquid state is frozen in with thicknesses as high as 2 cm [1,2]. These materials have high hardness, tensile strength, and toughness. The unique properties of BMG alloys make them extremely attractive for biomedical implant applications. The BMG alloys also have a lower modulus and most uniquely an extremely high elastic limit of 2% as compared to that of a typical metal, namely ~0.2%. Bone has an elastic limit of ~1%. BMGs would be unique in their ability to flex elastically with the natural bending of the bones and so distribute stresses more uniformly. Faster healing rates will result from reduced stress shielding effects while minimizing stress concentrators. Because of the unique mechanical properties of the BMGs, screws could have a thinner shank and deeper threads yielding greater holding power. Compared to stainless steel, a BMG would require only 1/3 of the cross section and would have more than 5 times the deflection. Potential applications include fracture fixation screws, rods, pins, hip joint wear surfaces and shafts, aneurysm clips, endodontic files, and orthodontic arch wires.

For example, our reference alloy, BAM-11, with a composition of Zr-10 at.% Al-5 Ti-17.9 Cu-14.6 Ni, has a yield strength of 1700 MPa, an elastic limit of 2 to 2.2%, Young's Modulus of 90 GPa, Vickers hardness of 590 kg/mm^2, and a toughness of 55 to 60 MPa√m [3]. Table 1 presents these properties compared to Co-Cr-Mo, Ti-6 wt.% Al-4 V, 316L-CW, bone, and an experimental low modulus alloy with a composition of Ti-35 wt.% Nb-5 Ta-7 Zr [4].

Results of initial screening tests on biocompatibility and corrosion on BAM-11 performed at the Biomaterials and Orthopedic Research Department at the University of

Table 1- Property comparison between a BMG and leading implant materials

Property	BMG, BAM-11 [3]	Co-Cr	Ti-6Al-4V	316CW	Bone, cortical	Ti-35Nb-5Ta-7Zr* [4]
Tensile Yield Strength, MPa	1700	450	830	690	Compressive 130-150	547
Elastic Strain Limit, %	2-2.2	0.18	0.67	0.34	1	0.9
Plastic Strain to failure, %	0	8	10	12		19
Young's Modulus, GPa	90	248	124	200	15	55
Hardness, Vickers, kg/mm^2	590	350-390	320	365		
Toughness, MPa√m	55-60		57	100		
Density, g/cc	5.9	8.5	4.4	8.0	1.7	
Corrosion rate I_{corr}, nA/cm^2	56±32		8±3	14±7		
Magnetic Susceptibility	109×10^{-6}	Ferro-magnetic	190×10^{-6}	CW is ferromagnetic, austenitic is 3 to 6×10^{-3}	-11 to -7×10^{-6}	
Fatigue limit at 10^7 cycles, MPa		310	520	240		265

*experimental alloy
^contains Ni to which some people become sensitive

Mississippi Medical Center are presented. Results on initial tests on fatigue, edge holding, and magnetic susceptibility are also presented.

EXPERIMENTAL DETAILS

Ingots of a BMG with a composition of Zr-10 Al-5 Ti-17.9 Cu-14.6 Ni (all compositions are in at.%) and the designation BAM-11 were prepared by arc melting in inert gas and drop casting into 7 mm diam by 72 mm long copper molds [3]. For the corrosion tests, all specimens were wet ground with SiC paper, 80, 240, 320, 600, and 1500 grit, followed by ultrasonic cleaning in distilled water for 5 min. Titanium, used as one of the controls, was additionally passivated in 40% HNO_3 for 30 min according to an ASTM standard. Cyclic polarization tests were conducted on triplicate samples of the alloys in Ringer's solution (9.0 g/L-NaCl, 0.42g/L-KCl, 0.25 g/L-$CaCl_2$). Specimens were allowed to reach an open-circuit potential (E_{corr}) for a period of one hour. A potential scan increasing at a rate of 0.1667 mV/s (ASTM G5) was then initiated at 100 mV below E_{corr} and continued until a current threshold of 1×10^2 nA/cm^2 was reached. At this point the scan was reversed and decreased at the same rate until E_{corr} was reached. E_{br} is the broken voltage at which point passivation is disrupted.

MRI imaging was performed in an interventional MRI which is large enough to use for MRI guided surgeries. Univ. of Mississippi has one of the first five interventional MRI built by GE and sited at hospitals. Magnetic susceptibility measurements were made in a SQUID magnetometer at 300K in fields up to 65 kOe.

Fatigue tests were performed on bars, $4 \times 4 \times 38$ mm in a 4-point bend arrangement in Ringer's solution at 37˚C at 5 Hz. Unnotched bend bars finished to 600 grit were selected as the most representative of actual use conditions and therefore would produce the most convincing data to present to industrial contacts. Tension-tension fatigue was used with R=0.1. Scanning electron microscope, SEM, images were used to determine the fracture mode.

Table 2 Biocompatibility

	BAM-11	Ti, commercially pure	Polyethelyne
Macrophage Viability, %	85	90	91
Macrophage/Catalase Activity, standardized activity/protein quantity	18	22	12
Macrophage/Lactate Dehydrogenase, standardized activity/protein quantity	6	8	6
Macrophage/Cytokine, picograms/protein quantity	19	18	11
Fibroblast Viability, % survival	95	90	92
Fibroblast/Catalase Activity, standardized activity/protein quantity	9	5	5.5
Fibroblast/Lactate Dehydrogenase, standardized activity/protein quantity	6.5	4	5

RESULTS AND DISCUSSION

Biocompatibility

Biocompatibility measurements, Table 2, were made on BAM-11 and compared to two control specimens: commercially pure Ti and polyethylene. For this initial biocompatibility screening, two cell lines were selected: macrophage and fibroblast. Because these cell types are a key in inflammation and encapsulation processes they are generally predictive of soft tissue biocompatibility. Four analyses of biocompatibility were conducted for each cell type: 1) cellular viability, 2) catalase activity, 3) TNF beta cytokine concentration and 4) lactate dehydrogenase concentration. These biocompatibility results show similar behavior to the titanium and polyethylene comparison specimens. Corrosion measurements, Table 3, were directly compared to 316 stainless steel specimens and to commercially pure titanium specimens and showed that the BAM-11 material has adequate corrosion rates for biomedical applications.

MRI Imaging

Any new implant material needs to have a low MRI signature to allow later imaging. Current implant materials produce a distortion or blooming in the MRI image. Figure 1 shows comparison MRI images of 7 mm diameter rods of a) a copper alloy, b) BAM-11 alloy (Zr-17.9 Cu-14.6 Ni-5.0 Ti-10.0 Al) and C) a nickel free BMG (Zr-32.5 Cu-5 Ti-10 Al, in a 75 mm flask of salt water showing that the BMG specimens exhibit the correct diameter and the Ni-free rod shows better end definition.
Copper has a magnetic susceptibility near that of body tissue. This is a surprising result since the 14.6% Ni in BAM-11 is ferromagnetic and should make MRI imaging difficult. Apparently the amorphous

Table 3 Corrosion under simulated body conditions

Alloy	E_{corr}(mV)	E_{br}(mV)	I_{corr}(na/cm^2)
Titanium	-51±61.5	None recorded	8.2±3.4
316LSS	-72.7±20	323±66.4	14.1±6.7
BAM11	-228.3±38.6	-65.3±53.0	56.1±32.8

structure significantly alters the magnetic properties. For these reasons, BMG's unique mechanical and magnetic properties yield the ability to fabricate MRI-friendly implant devices as well as a new class of surgical instruments for use within the interventional MRI environment. Minimally invasive procedures not possible via conventional surgical techniques can be successfully performed through interventional MRI. The need for tools to facilitate these procedures will be critical as this technology advances.

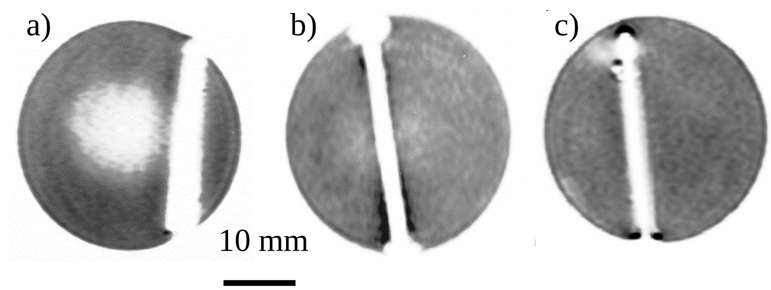

Figure 1. MRI images of 7 mm diam rods in a 75 mm diam dish of salt water of a) Cu-4 Cr-2 Nb, b) BAM-11, and c) Ni-free BAM, Zr-32.5 Cu-5 Ti-10 Al.

Susceptibility Measurements

Actual susceptibility measurements resulted in a value of 109×10^{-6} for BAM-11 which is very close to that of its major constituent element, zirconium [5]. Comparison measurements on a control specimen of Ti-6 Al-4 V alloy yielded 190×10^{-6}. While susceptibility is an obvious indicator for the amount of distortion, a medical MRI image is more complicated due to varying fields. Schenk [6] simply categorized materials into 3 classes based on the relative amount of distortion caused in actual MRI images.

Fatigue

Fatigue tests were alternately run with a BMG specimen followed by Ti-6Al-4V specimens made from a biomedically certified rod. Table 4 presents the results. A few specimens showed pores on the fracture surfaces. In addition, there was scatter in data from specimens that had no obvious defect on the fracture surfaces. Because of this scatter, the experiments were suspended while we investigated different casting processes to produce more uniformly pore-free material. However, one specimen did survive 3,300,000 cycles at 500 MPa. Figure 2 shows the fracture surface after fatigue failure. Only the bottom 1/3 is catastrophic failure with the molten-appearing fracture surface. In the top of the photo where the fatigue crack initiated, striations are clearly seen. Although this material is completely brittle and with a notch present from the beginnings of a fatigue crack, the specimen did not catastrophically fail but continued to carry the same load.

Table 4 Fatigue Tests -Cycles to Failure*

Stress, MPa	BAM-11	Ti-6Al-4V
450	3,170 (10Hz)	
	1,449,110 (10 Hz)	
	32,960 (10Hz)	
	12,720	
	26,000 (10 Hz)	
500	3,300,000	
550	15,980	
	9,380	
600	40,040	
700	5,790	3,000,000
750		126,180
800	5,460	44,650
		57,470
850	4,050	29,780
900	3,240	24,780
	1,950	28,230

*at 5 Hz unless otherwise indicated, in Ringer's solution at 37˚C, 600 grit finish on 4 pt bend bars, $4 \times 4 \times 38$ mm.

Edge Holding

Edge holding is important for cutting tools. The hardness of BMG alloys suggests that the material should produce a fine cutting edge. The high elastic limit may result in elastic bending of the sharp edge instead of chipping. The quality of our hand-sharpened edges was close to that of a new surgical blade, see Fig. 3. Our best edge came not from using the special grinding and polishing compounds and wheels in our laboratory but came from a black Arkansas stone with oil as a lubricant. Also interesting was to learn that an edge that felt sharp did so because of small nicks, tears and curls at the edge. Unfortunately, processing difficulties prevented us from casting thin slabs to make real blades to do actual usage tests.

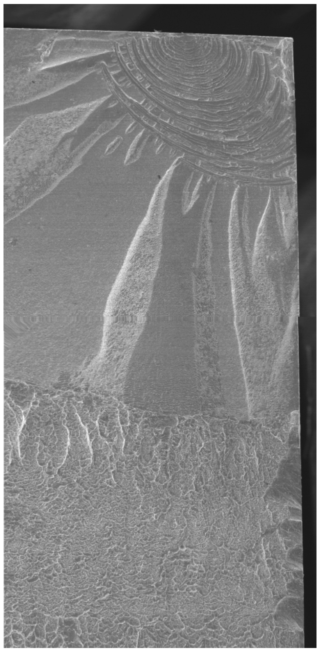

Figure 2. SEM images of fatigue fracture surface across the entire 4 mm specimen; only the lower part is catastrophic failure.

Alloy Development

Nickel is an element that is currently contained in alloys that do pass the biocompatibility tests. However, since some people develop a sensitivity to nickel, future implant alloys will probably be nickel-free. Nickel also is ferromagnetic and so degrades the MRI image. A series of alloys with low or no nickel was tried. Selection of the substituted elements was based on atomic size, biocompatibility, glass forming tendencies and deep eutectic phase diagram information, and following the early transition metal-late transition metal-metalloid recipe. The trial alloys included Pd, Mn, Hf, Nb, Ag, Mn, La, Sn, and P substitutions. The best non-nickel alloy that was cast simply had more copper substituted for the nickel and had a composition of Zr-5 Ti-32.5 Cu-10 Al. The amount of amorphous phase present in this alloy was comparable to BAM-11 and is barely detectable optically and not detectable by x-ray.

Processing

Processing is the key to further development of these materials. Many opportunities for prototype tool development are available. For example, sometimes in hip joints the bone support structure weakens and then the dense surface layer collapses due to a weak substrate. The physicians would like to be able to scoop out the weakened bone in a MRI guided procedure and replace it with cement. A BMG tool would give an excellent MRI and a sharp cutting edge. For this application, we attempted to supply a BMG piece with an L shaped scoop approximately 10 cm long with a 1 cm L on the end. With this scoop inserted in an off center hole in a 1 cm carrier piece and by rotating both items, a 3 cm diameter area could be scooped out.

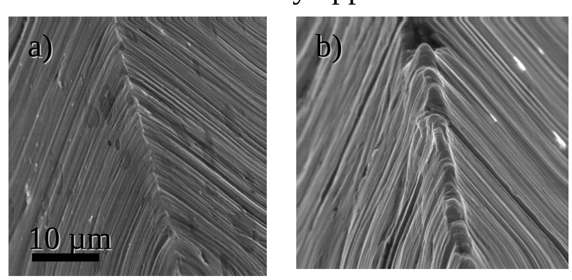

Figure 3. SEM micrographs of a) new surgical blade and b) BAM-11 hand sharpened on black Arkansas stone.

We made a number of tries in two different labs to suction cast this geometry but unfortunately failed so far to produce pore free material.

CONCLUSIONS

A bulk metallic glass with a composition of Zr-10 Al-5 Ti-17.9 Cu-14.6 Ni was evaluated for biomedical applications. Biocompatibility and corrosion resistance were comparable to current implant materials. MRI images were excellent compared to current implant alloys. A nickel-free composition that retained similar glass forming characteristics to our reference BMG alloy was produced. Edge holding for cutting tool applications was demonstrated. Fatigue tests were performed in simulated body conditions and directly compared to Ti-6Al-4V. While one specimen did go more than 3,000,000 cycles at 500 MPa, there was much scatter in the data. Suction casting processing efforts made in two different labs failed to produce pore-free material in some special geometries for prototype tools for use in an interventional MRI. Further concentration on processing issues is needed to produce reliable material for prototype development.

ACKNOWLEDGMENTS

The authors wish to thank C. A. Carmichael and J. L. Wright for technical support. Research sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (ORNL), and by the Division of Materials Sciences and Engineering at ORNL, managed by UT-Battelle, LLC for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

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