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Sulfur-bearing metallic glasses: A new family of bulk glass-forming alloys

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ABSTRACT

Metallic glasses constitute a class of engineering materials having an enormous potential for many fields of application due to their superior properties. Here, we report on a new family of sulfur-bearing bulk metallic glasses. So far, sulfur was not considered as alloying element for the synthesis of bulk metallic glasses. We observe bulk glass formation in a variety of sulfur-containing systems, including titanium-based bulk glass-forming systems with an extremely high titanium content of 70 at.%. These findings allow the development of a whole new class of amorphous metals, having good processability and consisting of alloying elements suitable for industrial applications.

Efforts of Duwez and co-workers on supersaturating a solid solution resulted in the discovery of metallic glasses [1], which are metallic solids existing in a microscopically disordered, thermodynamically unstable state. The development of metallic glass formers with a high glass-forming ability (GFA), so-called bulk metallic glasses (BMGs), was achieved in the following decades. Raising the number of alloying components and carefully adjusting their composition resulted in highly viscous melts (~3 orders of magnitude higher than pure metals [2,3]). The high viscosity leads to sluggish crystallization kinetics and at moderate cooling rates a sufficient undercooling can be reached to entirely frustrate and bypass the crystallization process. The amorphous structure of the liquid is frozen-in, the system falls out of equilibrium [4] and a metallic glass (MG) is formed. Even though the prediction of bulk glass-forming compositions is hardly possible by simulation, extensive research has led to a variety of BMG forming systems [5], including Cu- [6], Fe- [7], Ni- [8], Pd- [9], Ti- [10], and Zr-based alloys [11]. Among these systems the best glass formers e.g. Zr-Ti-Cu-Ni-Be [11] and Pd-Cu-Ni-P [12] show high contents of beryllium or phosphorous, limiting their industrial applicability because of the toxicity of beryllium and the unfavorable processability of phosphorous. Other bulk glass-forming systems like Zr-Cu-Ni-Al-Ti [13] show a good glass-forming ability and processability in combination with outstanding properties e.g. for the production of electronical and medical devices. The particular interest in BMGs is justified by their high yield strength (typically above 2 GPa) and elastic limit. However, the high raw material price and poor availability of Zr as main constituent is limiting their widespread industrial application. Exploring alternative alloy systems is therefore considered to be the main task in order to facilitate the commercialization of metallic glasses.

The present study reveals that sulfur, which was never before considered as main constituent in BMGs, can be used to design new metallic glass-forming compositions, making a whole new family of metallic glass-forming alloys accessible. Sulfur is widely used in industry, e.g. for the vulcanization of natural rubber or in chalcogenide glasses and is commonly known in materials science. Hence, it is easily available and the discovered sulfur-bearing glass-forming alloys may have significant impact on the metallic glass community as well as other scientific and industrial fields due to new possibilities for their application.

Since sulfur is cheaper, shows a better processability and has no toxic modifications, it might have a high relevance as a substitute for phosphorous for the industrial application of amorphous metals. Especially the stability of the liquid phase of sulfur ($T_{liq}^{sulfur} = 388.36$ K, $T_{boil}^{sulfur} = 717.85$ K) entails benefits for the preparation of pre-alloys in comparison to the fabrication of alloys that contain phosphorous (sublimation at $T_{sub}^{phosphorous} = 689.15$ K).

In this study, amorphous samples were produced in a four-step process. Sulfur-bearing pre-alloys with Ni (99.98 mass%), Pd (99.99 mass%), Cu (99.999 mass%), and S (99.9995 mass%) were produced by inductively melting the raw elements in a silica tube under a high purity argon atmosphere. Subsequently, the pre-alloys were treated in B_2O_3 at 1473 K for at least 4 h. These pre-alloys were alloyed with the high purity raw elements Ti (99.99 mass%), Zr (99.99 mass%), Ni (99.98 mass%), Pd (99.99 mass%), Cu (99.999 mass%), and Al (99.999 mass%) according to the desired composition in an electric arc furnace under a high purity argon atmosphere. The resulting master-alloys were cast into water-cooled copper molds in a suction casting apparatus to produce glassy samples.

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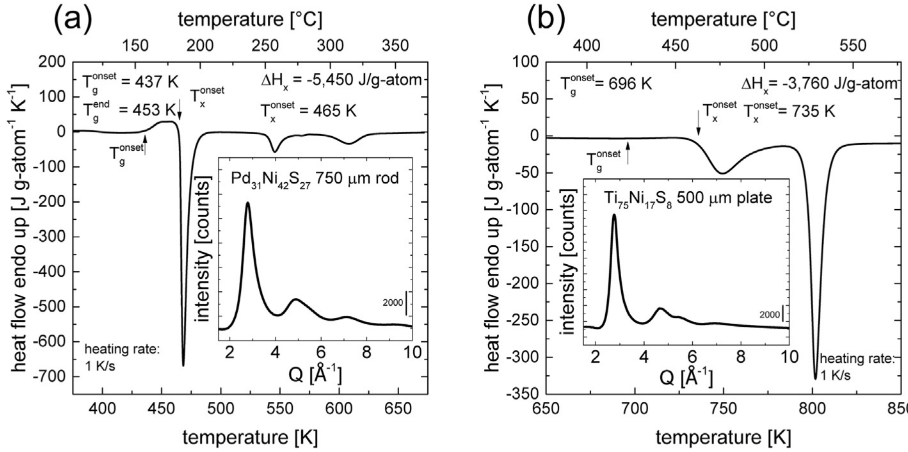

Fig. 1. (a) DSC scan at 1 K/s of a novel $Pd_{31}Ni_{42}S_{27}$ bulk glass-forming alloy. The inset shows a high energy synchrotron X-ray diffraction pattern (I_q raw) verifying the amorphous character of a sample with a diameter of 750 μm. (b) DSC scan at 1 K/s of a 500 μm plate of $Ti_{75}Ni_{17}S_8$. The inset shows the corresponding high energy synchrotron X-ray pattern (I_q raw).

Differential scanning calorimetry was conducted using a power-compensated Perkin-Elmer Hyper DSC 8500 at a heating rate of 1 K/s to determine characteristic temperatures and enthalpies of the produced amorphous samples. The amorphous structure of the samples was verified by high-energy synchrotron X-ray (60 keV) in transmission at the DESY (German Electron Synchrotron) in Hamburg and by using X-ray diffraction in a PANalytical Empyrean XRD with monochromatic Cu Kα radiation. 3-point flexural bending tests were carried out with a Shimadzu testing machine to measure Young's modulus and fracture strength at a deflection rate of 0.3 mm/min on samples with a cross section of 0.9 ± 0.05 mm × 1.1 ± 0.05 mm and a support span of 15 mm. In addition, hardness measurements were carried out using a Wolpert Wilson 930 N universal hardness tester with a Vickers indenter and a loading force of 49.03 N.

In this study, we observe bulk glass formation in several alloying systems with sulfur, including Pd-, Ni-, Cu-, Zr- and Ti-based alloys. Fig. 1(a) shows a DSC scan performed at a heating rate of 1 K/s of the fully amorphous Pd-Ni-based bulk glass-forming alloy $Pd_{31}Ni_{42}S_{27}$. High energy synchrotron X-ray diffraction, as shown in the inset in Fig. 1(a), was used to confirm the amorphous structure of the 750 μm thick rod. The short glass transition region ($T_g^{end} - T_g^{onset} = 16$ K) upon heating, the high jump of the heat flow at T_g ($\Delta H^{glass\text{-}SCL} \approx 30$ J g-atom^{-1} K^{-1}), and the high entropy of fusion ($\Delta S_f \approx 15$ J g-atom^{-1}) suggest a kinetically very fragile behavior [14–16] according to Angell's classification of liquids [17]. Using the slope of T_g-scaled DSC scans according to the method proposed by Wei et al. [14] we can estimate the fragility parameter of the liquid to be $D^* \approx 7$, indicating a very high temperature sensitivity of viscosity or structural relaxation time in comparison to other bulk glass-forming alloys.

Due to the compositional similarity to one of the best metallic glass formers in the ternary Pd-Ni-P system ($Pd_{40}Ni_{40}P_{20}$) [9], the investigation of the different effects of phosphorous and sulfur on the glassy structure and the connected macroscopic properties, like mechanical behavior and kinetic fragility, is possible. Moreover, the high tendency of sulfur to form covalent bonds plays a key role for the understanding of the amorphous structure. With sulfur contents of up to 30 at.%, this new class of metallic glasses is at the compositional edge to the so-called sulfide glasses. These belong to the group of chalcogenide glasses which are covalently bonded network glasses, being of special interest for electrical and optical applications [18,19]. Thus, it might be possible to study the transition between these two different groups of glasses with respect to their properties as a function of the sulfur content.

Sulfur-containing bulk metallic glass-forming systems are also found in Ti-rich alloy compositions. The novel ternary alloy $Ti_{75}Ni_{17}S_8$ forms a glass up to a critical thickness of 500 μm. So far, a critical casting thickness of 500 μm has not been reported for MGs with such an exceptionally high Ti-content. A DSC scan as well as the corresponding high energy XRD pattern are shown in Fig. 1(b), confirming the amorphous structure of the sample.

In general, Ti-based bulk glass-forming alloys are of special interest for an industrial application due to their low densities, high strengths and good corrosion resistance. To this day, beryllium-free Ti-based glass-forming alloys with high Ti-contents (≥60 at.%) show very low casting diameters for fully amorphous samples. The limitations of the critical casting thickness of Ti-based glass-forming alloys are visualized in Fig. 2, with Be-bearing alloys shown as red squares, Be-free alloys shown as black dots, and S-bearing Be-free alloys shown as blue triangles. The dashed-lines are trend lines to reflect the state of the art and are not predictive. So far, bulk metallic glasses with diameters > 1 mm and Ti-contents higher than 60 at.% could only be formed in Be-bearing

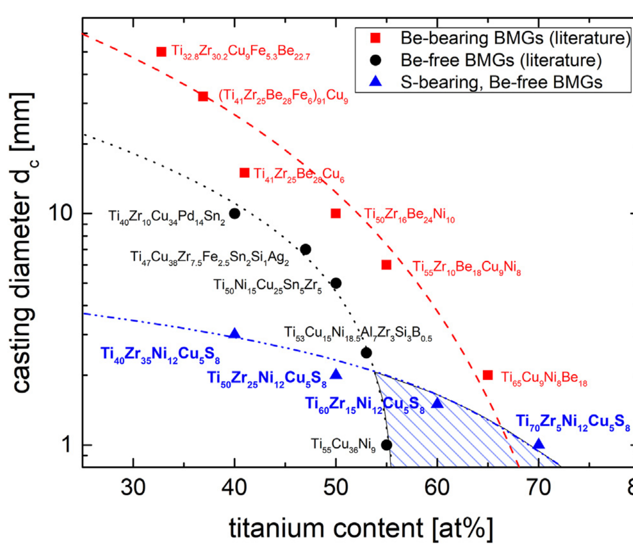

Fig. 2. Critical casting diameters of Ti-based bulk glass formers as a function of their Ti-content. The dashed lines are trend-lines only used to guide the eye. Be-containing BMGs [28–32] (red squares, dashed line) generally show a higher GFA than Be-free alloys [33–37] (black circles, dotted line). No bulk glass formation is observed for Be-free alloys with a Ti-content higher than 55 at.%. The sulfur-bearing glass-forming alloys in this study (blue triangles, dash-dotted line) show bulk glass formation for Ti-contents up to 70 at.% for the first time. The shaded area highlights the newly opened compositional range of bulk glass formation for Be-free titanium alloys containing sulfur. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)