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Revealing the relationships between chemistry, topology and stiffness of ultrastrong Co-based metallic glass thin films: A combinatorial approach

Volker Schnabel [a, *], Mathias Köhler [b], Simon Evertz [a], Jana Gamcova [c, d], Jozef Bednarcik [c], Denis Music [a], Dierk Raabe [b], Jochen M. Schneider [a]

[a] Materials Chemistry, RWTH Aachen University, Kopernikusstr. 10, D-52074 Aachen, Germany
[b] Max-Planck-Institut für Eisenforschung, Max-Planck-Straße 1, D-40237 Düsseldorf, Germany
[c] Deutsches Elektronen Synchrotron DESY, FS-PE Group, Notkestrasse 85, D-22607 Hamburg, Germany
[d] Pavol Jozef Šafárik University, Department of Condensed Matter Physics, Park Angelinum 9, Košice, Slovakia

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ABSTRACT

An efficient way to study the relationship between chemical composition and mechanical properties of thin films is to utilize the combinatorial approach, where spatially resolved mechanical property measurements are conducted along a concentration gradient. However, for thin film glasses many properties including the mechanical response are affected by chemical topology. Here a novel method is introduced which enables spatially resolved short range order analysis along concentration gradients of combinatorially synthesized metallic glass thin films. For this purpose a CoZrTaB metallic glass film of 3 μm thickness is deposited on a polyimide foil, which is investigated by high energy X-ray diffraction in transmission mode. Through the correlative chemistry-topology-stiffness investigation, we observe that an increase in metalloid concentration from 26.4 to 32.7 at% and the associated formation of localized (hybridized) metal – metalloid bonds induce a 10% increase in stiffness. Concomitantly, along the same composition gradient, a metalloid-concentration-induced increase in first order metal - metal bond distances of 1% is observed, which infers itinerant (metallic) bond weakening. Hence, the metalloid concentration induced increase in hybridized bonding dominates the corresponding weakening of metallic bonds.

1. Introduction and motivation

Chemistry-topology-property relationships of metallic glasses have been a topic of intense discussion [1–5]. Metallic glasses fall into two groups, namely those with [6] and those without metalloids [7]. The most common synthesis techniques for metallic glasses are bulk casting [8–10] and melt spinning [11]. In these studies, chemical composition is varied through multiple synthesis experiments. By employing conventional bulk synthesis techniques, metallic glasses are developed as a result of multiple, sequential bulk synthesis experiments, often based on trial-and-error approaches [1,2,12–15]. In contrast, combinatorial thin film synthesis has been used to systematically study the chemistry-topology-property relationship of various materials systems [16,17]. Recently, combinatorial metallic glass synthesis by physical vapor deposition has been employed to study the chemistry – mechanical property relationship of metallic glass thin films [18]. Furthermore, literature has shown clear agreement between bulk and thin film properties of Co-based metal-metalloid metallic glasses regarding elasticity, density and magnetism [19,20]. Ergo, combinatorial thin film synthesis can be an efficient tool to investigate the chemistry-topology-property relationship of metallic glasses in general. However, up to now there is no high throughput method present in literature to study the chemically induced topological evolution along a defined compositional gradient of metallic glass thin films [18]. The short range order of metallic glasses is usually studied by sequential synthesis of homogeneous specimen and analysis employing high energy diffraction experiments [1,5,19,20], which is an inefficient way of investigating the chemistry-topology-mechanical properties relationship.

* Corresponding author.
E-mail address: schnabel@mch.rwth-aachen.de (V. Schnabel).

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The topology of metallic glasses without metalloids is strongly determined by dense packing [7,21], whereas the topology of metal-metalloid metallic glasses is additionally influenced by strong covalent bonding [5,6,19,22]. Due to the complex chemistry-topology-property relationships the design of metal-metalloid metallic glasses is challenging [6,13,23]. The metal-metalloid Co-based metallic glasses discussed here possess a unique local atomic configuration [5,22,24], which leads to the combination of extraordinary high fracture strength of above 5000 MPa and high Young's modulus of 268 GPa [13]. It is inferred in the literature that through chemically induced topology changes, properties such as glass formability [1,3,6], magnetic properties [2] and mechanical properties [3,4,19,25] can be enhanced. The Young's modulus [19,22] as well as the elastic limit [5] have also been reported to exhibit a strong topological dependence. In the case of Co-based metallic glasses it has been observed that the metal-metalloid short range order is strongly affecting the mechanical properties [5,19,20,22]. Furthermore, it has been reported for Fe–Cr–Mo–P–C–B metallic glasses that an increase in metalloid concentration increases the number of strongly bound metal-metalloid clusters, which on the other hand weakens the metal-to-metal bonds [26]. These chemical-induced topology changes have implications on how shear stress may be accommodated [26]. Hence, an influence on the Young's modulus, shear modulus and plasticity of these type of metal-metalloid metallic glasses has been observed [6]. The discussion above suggests that understanding the chemistry-topology-property relationship is an essential prerequisite to the knowledge-based design of strong metallic glasses.

The objective of this work is to describe the chemically induced topology and stiffness changes of Co–Zr–Ta–B metallic glass thin films. A novel method is introduced, where the chemically induced topology and stiffness changes are measured along a composition gradient of Co–Zr–Ta–B metallic glass thin films. For this purpose a combinatorial metal-metalloid Co–Zr–Ta–B metallic glass thin film is deposited by physical vapor deposition [19,27] on low X-ray scattering and radiation damage tolerant thin polyimide foil [28]. The topological analysis of the combinatorial thin film is performed in transmission, using high energy X-ray diffraction [29].

2. Experimental procedure

Combinatorial Co–Zr–Ta–B metallic glass thin films were magnetron sputtered onto Si and polyimide substrates. The film deposited onto the 50.8 mm Si (100) substrate was used for chemical and mechanical characterization, while the films on 50 μm thick radiation damage tolerant polyimide foil [28] were employed for structural analysis. The base pressure of the system was $6 \cdot 10^{-5}$ Pa [30]. The films were synthesized from circular elemental targets with a diameter of 50 mm and a purity of 99.95% for Co, Zr and Ta and 99.5% for B. The applied power densities were 2.0, 1.6, 0.3 and 8.4 W/cm^2 for Co, Zr, Ta and B targets, respectively. The three metals were sputtered using separate direct current (DC) power supplies, whereas B was sputtered with a radio frequency power supply. As a sputtering gas Ar with a pressure of 0.4 Pa was employed. The targets were tilted by 19° normal to the substrate as described in Fig. 1 and the target to substrate distance was 10 cm. The deposition time was 3 h resulting in a film thickness of 3 μm.

The chemical composition was analyzed by three dimensional atom probe tomography (3D-APT). The APT samples were prepared according to a standard lift-out procedure [31] using focused-ion-beam (FIB) cutting. The measurements were performed in a commercial local electrode atom probe (LEAP 3000X HR, CAMECA Instruments) in voltage mode.

The APT result was used for a standard calibration of the energy dispersive X-ray analysis (EDX). The chemical composition was measured along the concentration gradients as indicated in Fig. 1. A spacing between the individual measuring points of 4 mm was chosen, corresponding to a gradient of 0.2 at% B per mm along the Ta–B gradient.

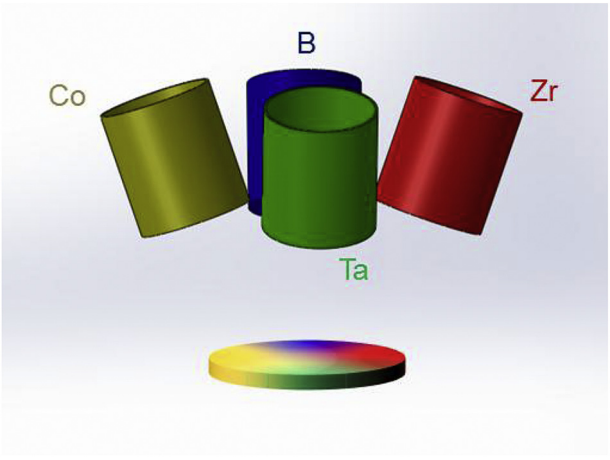

Fig. 1. Schematic drawing of the combinatorial deposition setup. The chemical symbols denote the direction of the elemental sputtering sources, which results in the schematic compositional gradient depicted. The measurements were performed along the B – Ta and the Co – Zr gradient with a spacing of 4 mm between the individual measurement points.

The topology analysis was performed by applying high energy X-ray diffraction at the P02.1 beamline of the PETRA III electron storage ring at DESY (Hamburg, Germany). A monochromatic photon beam with a wavelength of $\lambda = 0.02071$ nm and a beam size of 0.7 mm × 0.7 mm was used. The diffraction was recorded in transmission using the thin film sample deposited on polyimide foil. Each measuring point was illuminated for 30 s and the diffracted photons were recorded as 2D patterns with a fast image plate detector Perkin Elmer 1621. The sample to detector distance was set to be 246 mm, whereas the q vector ($q = 4\pi \sin\theta/\lambda$) up to 14 Å^{-1} was used [29].

The 2D diffraction patterns were integrated into q-space using the FIT2D software package [32]. The background was directly subtracted from the 2D diffraction patterns. The data sets were corrected for polarization, sample absorption, fluorescence contribution and inelastic scattering using the PDFgetX2 software [33]. The total structural factor was obtained from the normalized elastically scattered intensity according to the Faber-Ziman equation [34]. The pair distribution functions (PDFs) were obtained by a sine Fourier transform using standard procedure described elsewhere [12,19].

After chemical and structural analysis, the reduced Young's modulus was measured along the concentration gradient using a depth-sensing nanoindenter (Hysitron TriboIndenterTM). A Berkovich indenter with a tip radius of 100 nm was used. A maximum indentation load of 1000 μN was employed, which corresponded to a contact depth of less than 10% of the film thickness. 24 indentations were performed for each film composition. The Oliver and Pharr method [30] was applied to extract the reduced Young's modulus.

3. Results and discussion

3.1. Chemical analysis

Due to the geometrical arrangement of the magnetrons with respect to the substrate normal (Fig. 1) and the chosen 10 cm target