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Oxidation of glassy Ni–Nb–Sn alloys and its influence on the thermodynamics and kinetics of crystallization

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ABSTRACT

The best bulk metallic glass (BMG) forming systems are very viscous multi-component liquids, whose sluggish kinetics is the most important factor that impedes the nucleation and growth of crystals. However, it is usually the case that these BMG systems are a mixture of elements with very different nobility, where preferential oxidation and partitioning are common processes observed upon reaction with oxygen. The atomic partitioning induces a change in composition that thermodynamically destabilizes the amorphous phase and promotes crystallization. In this work, we show that adding a third element can suppress this oxidation-induced crystallization if it has a large size mismatch with respect to the base elements. The Ni–Nb-based BMG system is taken as a case study system to elucidate the thermodynamic and the kinetic reasons for the improved thermal stability of the amorphous phase upon addition of Sn. Due to the selective oxidation of Nb, atomic partitioning of Ni and Sn takes place underneath the oxide scale, and favors the nucleation of Ni_3Sn instead of the otherwise thermodynamically stable Ni_2NbSn ternary phase. Due to the sluggish diffusivity of the large Sn atoms ahead of the internal oxidation reaction front, the nucleation process is slow and the overall oxidation kinetics that are parabolic for the binary glass assume passive logarithmic behavior for the ternary glass counterpart. Microscopy experimental techniques include electron backscattering diffraction (EBSD) mapping and atom probe tomography (APT).

1. Introduction

Bulk metallic glass (BMG) forming liquids are typically developed by starting from a binary alloy with a pronounced eutectic that shows glass formation upon moderately fast cooling. Judicious addition of further elements can lower the melt temperature and reduce the critical cooling rate for glass formation further. Classic examples for binary eutectic alloys being the base for BMG, are Au–Si [1], Zr–Cu [2] or Nb–Ni [3], of which the latter two eutectic alloys combine an early with a late transition metal. This leads to the fact, that there is a pronounced difference in electronegativity between the two species. In an oxidizing environment this results in preferential oxidation of one of the species, partitioning and early crystallization. Since these thermodynamic facts cannot be overcome, it must be the goal to slow down kinetics in the vicinity of the glass transition, to improve resistance against oxidation and crystallization.

In general, good bulk metallic glass forming systems are very viscous, highly dense random-packed, multi-component liquids, in which the sluggish kinetics is the most important factor that impedes the nucleation and growth of crystals [4]. Sluggish kinetics controls the thermal stability of the BMG not only in terms of resistance to crystallization, but also in terms of resistance to oxidation. In fact, the fast oxidation kinetics of binary Zr-based metallic glasses, like $Zr_{70}Pd_{30}$ or $Zr_{70}Au_{30}$, have been drastically slowed down by alloying with the less noble Cu and Ni compared to Pd and Au [5], which indicates that the oxidation kinetics are strongly influenced by the atomic mismatch and by the mobility of the alloying elements rather than the reactivity of the elements.

In the present work, the Ni–Nb system is selected as an example to investigate the role of the addition of atoms with large size mismatch to a metallic glass. This system was chosen because the binary Ni–Nb system has shown to form BMG glasses at around the

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eutectic composition of $Ni_{62}Nb_{38}$ [6]. In addition, the glass forming ability of the binary system was improved by adding Sn which has a larger atomic size [7,8], and by tailoring the composition near the ternary eutectic composition. The ternary eutectic is located within the three-phase region defined by the three intermetallic phases, $NbNi_3$ (orthorhombic, β-Cu_3Ti type), Nb_7Ni_6 (hexagonal, W_6Fe_7 type), and $NbNi_2Sn$ (BiF_3-type). Previous studies on the thermal stability of Nb–Ni–Sn glass formers were conducted on the $Ni_{60}Nb_{35}Sn_5$ composition [9]. This composition was found to have an-exceptionally high glass transition temperature and a large supercooled liquid region. These properties are common to the Ni–Nb-based glassy system and they are of great practical importance, making it a technology relevant refractory alloy glass material. The calorimetric glass transition temperature, T_g, of $Ni_{60}Nb_{35}Sn_5$ is 883 K, which is approximately 200 K higher than the T_g of Zr-based BMGs. The performance as a refractory alloy glass depends, however, greatly on its ability to passivate and to retard crystallization during aging at high temperatures. In the presence of oxygen, an oxidation-induced crystallization of $Ni_{60}Nb_{35}Sn_5$ consisting of Ni-rich intermetallic phases was previously observed to occur [9]. It was suggested to be the result of local compositional changes in the amorphous sub-matrix due to preferential oxidation of Nb and partitioning of elemental Ni at the reaction front.

The present work examines both the thermodynamic and kinetic roles played by the slow diffuser Sn during the crystallization of the supercooled liquid phase under argon and during the oxidation-induced crystallization of the glass. Several experimental techniques are combined in this investigation, including atom probe tomography (APT). Due to the recent developments in laser-pulsed APT instrumentation [10,11] the technique becomes highly reliable for 3D analysis with sub-nm resolution for a wide range of materials such as semiconductors, oxides, and insulators [12–14].

2. Materials and methods

The master alloys with the composition of $Ni_{62}Nb_{38}$, $Ni_{59.35}Nb_{34.45}Sn_{6.2}$ and $Ni_{58.85}Nb_{34.45}Sn_{6.2}Si_{0.5}$ were produced by alloying the pure elements (purity > 99.95 at. %) under a high purity argon flux in a custom-built arc melting furnace. The quaternary composition was developed aiming for an improvement of the mold-filling properties of $Ni_{59.35}Nb_{34.45}Sn_{6.5}$ due to the ability of Si to lower the surface tension. The glassy specimens were prepared by suction casting the master alloys in a Buehler MAM 1 arc melting furnace. The binary and the quaternary compositions were produced with casting dimensions of 10 × 5 × 0.5 mm. The ternary alloy was cast into dimensions of 10 × 10 × 1 mm. A heat treatment to relax the amorphous structure was performed at 831 K for 2.5 h with the $Ni_{59.35}Nb_{34.45}Sn_{6.2}$ alloy in a horizontal quartz tube furnace under vacuum with a pressure of 10^{-4} hPa.

Prior to all thermal treatments the cross sections of the specimens were shown to be X-ray amorphous using X-ray diffraction (XRD), conducted with Cu-Kα radiation in a PANalytical X'Pert Pro diffractometer. After the heat treatments, the XRD analyses were conducted on the top-surfaces of the specimens unless specified differently.

The calorimetric scans and the isothermal thermogravimetric investigations were performed with a Netzsch STA 449C Jupiter Differential Thermal Analyzer (DTA/TGA) in the differential scanning calorimetry (DSC) mode, and in the thermogravimetric analyzing (TGA) mode, respectively. DSC scans were performed with a heating rate of 0.33 K/s under a constant flow of high purity argon in graphite crucibles. The isothermal oxidation treatments were performed under a constant flow of 50 ml/min of dry O_2, at the temperature of 50 K below T_g in an Al_2O_3 sample holder. The time for the isothermal experiments performed with the ternary alloy was chosen to be 25% shorter than the time to reach the onset of crystallization. The times were selected according to the experimentally determined time–temperature-transformation diagram reported in Ref. [9]. Prior to the oxidation study, the TGA samples were mechanically ground with SiC sand paper down to 600 grit. The baseline of the TGA was measured with the empty alumina sample holder under conditions identical to the isothermal sample run and subtracted from this sample run in each case. A reliability test based on five identical runs determined that the measurements have an experimental error that is smaller than 0.1 mg/cm^2.

The microstructures were investigated in cross section with a JEOL JSM-7000F Field Emission Microscope in scanning microscopy mode (SEM) using an EDAX Genesis 2000 Energy Dispersive X-Ray Spectrometer (EDX) and EDAX-TSL Digiview 3 Electron Backscatter Diffraction (EBSD) Detector. The EBSD maps were measured under a 70° specimen-tilt to the electron beam with a 30 nm step size. Atom probe specimens were prepared by focused-ion beam (FIB) implementing the in-situ lift-out technique [15], using a Helios Nanolab 600 (FEI) dual beam workstation. APT measurements were performed in a CAMECA™ LEAP 3000X HR system in the laser pulsing mode. A green light laser with a wavelength of 532 nm was used with 0.55 nJ laser energy and 50 kHz repetition rate. The chosen target evaporation rate was one ion per 200 pulses and the specimen base temperature was around 70 K. The data were reconstructed using the standard algorithm of Bas et al. [16], and analyzed by CAMECA™ IVAS 3.6.6 software.

The Gibbs free energy diagrams were constructed using the interaction parameters for the binary Ni–Nb alloy system, obtained with the CALPHAD method [17].

3. Results

Fig. 1a shows the DSC scans of the glassy ternary alloy in as-cast conditions in comparison to the relaxed counterpart, which resulted from an isothermal treatment at a temperature of 831 K for 9000 s. In Fig. 1b the calorimetric up-scan of the as-cast ternary is compared to that of the as-cast binary glass. On heating, the ternary alloy shows the onset of the glass transition, T_g, at 881 K, followed by four exothermic events, that mark the stepwise crystallization of the supercooled liquid phase. The T_g of the ternary alloy is lower than that of the binary, which is due to the depression of the *liquidus* temperature of the ternary composition compared to the binary. Because of the low melting point of Sn, the *liquidus* temperature of the ternary alloy is 1469 K versus 1522 K for the binary. The supercooled liquid region, defined as the temperature range between the end of the glass transition and the onset of crystallization, increases by five degrees compared to the binary at the applied heating rate.

During the isothermal treatment at 831 K the glassy structure of the ternary alloy relaxes towards the supercooled liquid structure. The as-cast ternary specimen shows the evidence of exothermic heat release characteristic for enthalpy relaxation before the onset of the glass transition. The relaxed specimen, in contrast, shows an endothermic enthalpy overshoot effect (enthalpy recovery) at the completion of the glass transition. The calorimetric detection of the crystallization is not significantly affected by the relaxation treatment prior to the DSC up-scan. To identify each crystallization event of the ternary $Ni_{59.35}Nb_{34.45}Sn_{6.2}$ alloy, various calorimetric up-scans under Argon are stopped at the temperatures labelled *a* through *d* in the inset of Fig. 1b. Fig. 2 shows the XRD patterns detected after these treatments. Prior to the XRD measurements, the surfaces of the specimens are ground-off to expose the bulk matrix. The primary crystallization consists of the formation of Ni_2NbSn. The second exothermic DSC peak is due to the formation of the Ni_3Nb compound. The reaction continues with the