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Characterization of bulk metallic glasses via fast differential scanning calorimetry

S. Pogatscher *, D. Leutenegger, A. Hagmann, P.J. Uggowitzer, J.F. Löffler

Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich, 8093 Zurich, Switzerland

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ABSTRACT

This study explores the thermophysical properties of Au-based bulk metallic glasses (BMGs) via fast differential scanning calorimetry (FDSC). Using this technique, the glass formation of the alloys $Au_{60+x}Cu_{15.5-x}Ag_{7.5}Si_{17}$ ($x = 0$, 5 and 10) was investigated in situ. The critical cooling rate (Φ_c) and heating rate (Φ_h) required to avoid crystallization were analyzed for various sample masses and chip sensor surface materials. The results show that the alloy with the highest Au-content exhibits the lowest resistance against crystallization. Silicon nitride, silicon oxide and graphite used as chip sensor surface material were proven not to influence the measurements. In general, a dependence of crystallization on sample mass was observed for all compositions. Both the critical cooling and critical heating rates increase until a certain mass is reached. This phenomenon is explained via a size-dependent nucleation effect.

1. Introduction

Bulk metallic glasses are non-crystalline metallic solids which can be produced by rapid cooling of metallic melts to temperatures below their glass transition [1]. Compared to all other classes of materials BMGs possess unique properties such as high strength and elastic strain limit, good soft-magnetic properties, excellent corrosion resistance and high hardness [2–5]. Their good viscous flow workability in the supercooled liquid and homogeneity and isotropy on a small scale are great advantages, especially in the production of small-scale devices (e.g. micro-electro-mechanical systems, micro-robotics and micro-manipulators) via imprinting, embossing, micro-replication or micro-molding [6–8]. Au-based BMGs [9–12] in particular have been shown to be suitable materials for this emerging field [8].

For metallic systems, BMGs demonstrate extraordinary stability against crystallization, i.e. they exhibit a low critical cooling rate for reaching the glass transition without crystallization during cooling from the equilibrium liquid. Nevertheless, crystallization still occurs rapidly and thus limits many experimental studies in the supercooled liquid region [3–5]. Using conventional thermo-analytical methods (e.g. differential scanning calorimetry, DSC) it is not possible to reach constant cooling rates higher than a few $K\,s^{-1}$, and in situ probing of the glass formation from an equilibrium metallic melt is not feasible. Recent chip-based fast differential scanning calorimeters [13,14] enable thermo-analytical measurements at orders of magnitude higher rates. Heating and cooling with several $10^4\,K\,s^{-1}$ and $10^3\,K\,s^{-1}$, respectively, can be realized with a recently available commercial instrument (Mettler Toledo Flash DSC 1 [15]). This instrument has generally been used to study polymers [15] and phase-change materials [16,17], but in recent studies it has also been successfully applied to a $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ BMG [18]. Au-based BMGs are ideal candidates for investigation via FDSC because here in situ exploration of the glass formation and crystallization behavior in the whole supercooled liquid region is possible [18]. Compared to most other known BMGs, Au-based BMGs have a low liquidus temperature, which is accessible by FDSC, and are not sensitive to oxidation. However the characterization of BMGs via FDSC is still a new procedure and no work on the measurement conditions and the influence of measurement parameters has so far been published. In this study we explore the crystallization and glass formation of $Au_{60+x}Cu_{15.5-x}Ag_{7.5}Si_{17}$ ($x = 0$, 5 and 10) in situ and focus also on the effects of sensor surface material and sample mass.

2. Material and methods

2.1. Alloy production

To obtain thin and chemically homogenous samples Au-based glassy ribbons were produced by melt spinning. The elements Au

* Corresponding author. Present address: Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 4, 8093 Zurich, Switzerland. Tel.: +41 44 633 64 65; fax: +41 44 633 14 21.
E-mail addresses: stefan.pogatscher@mat.ethz.ch (S. Pogatscher), danieleu@student.ethz.ch (D. Leutenegger), hagmanna@student.ethz.ch (A. Hagmann), peter.uggowitzer@mat.ethz.ch (P.J. Uggowitzer), joerg.loeffler@mat.ethz.ch (J.F. Löffler).

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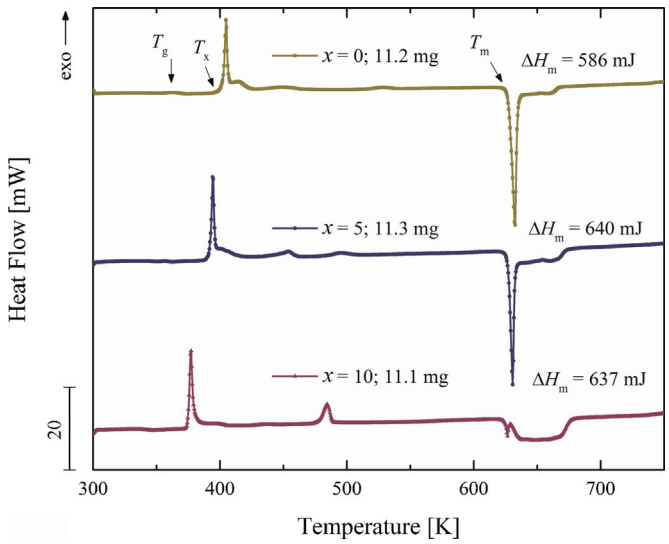

Fig. 1. DSC traces of $Au_{60+x}Cu_{15.5-x}Ag_{7.5}Si_{17}$ ($x = 0$, 5 and 10) metallic glasses measured with a heating rate of 0.33 K s^{-1} and corresponding ΔH_m values.

(purity 99.99 wt.%), Ag (99.99 wt.%), Si (99.999 wt.%) and Cu (99.995 wt.%) were weighed according to the atomic compositions $Au_{60}Cu_{15.5}Ag_{7.5}Si_{17}$, $Au_{65}Cu_{10.5}Ag_{7.5}Si_{17}$ and $Au_{70}Cu_{5.5}Ag_{7.5}Si_{17}$ and inserted into quartz glass tubes with a diameter of 5 mm. The tubes were purged several times with Ar (5 N purity) and closed under 200 mbar Ar pressure by melting the tube ends. To produce homogenous pre-alloys the elements were mixed well in the tube, subjected to induction melting at 1273 K [19], and finally quenched in water. The pre-alloys were polished and broken up into small, manageable parts for ribbon production via melt spinning under a 500 mbar He atmosphere (5 N purity). The rotating frequency of the copper wheel used for melt spinning was 25 Hz and its distance from the hole of the graphite crucible containing the melt was 0.2 mm. About 1 g of the pre-alloy was heated to 923 K within 7 min and held for 2 min at this temperature before the ribbons were produced. The overpressure applied to push the melt out of the crucible onto the rotating copper wheel was 150 mbar. The thickness of the ribbons produced ranged from 20 to 30 μm; 20 μm thick ribbons were deployed for the FDSC investigations.

2.2. Thermo-analytical measurements

Conventional thermal analysis was performed in a differential scanning calorimeter (Mettler-Toledo DSC1) to determine the mass of the small-scale FDSC samples. The DSC measurements were conducted at a heating rate of 0.33 K s^{-1} under Ar atmosphere (5 N purity) at a flow rate of 30 ml min^{-1} and using aluminum pans on the sample and reference platforms. The enthalpy of fusion (ΔH_m) measured by conventional DSC was used as a reference value according to Eq. (1) [20]:

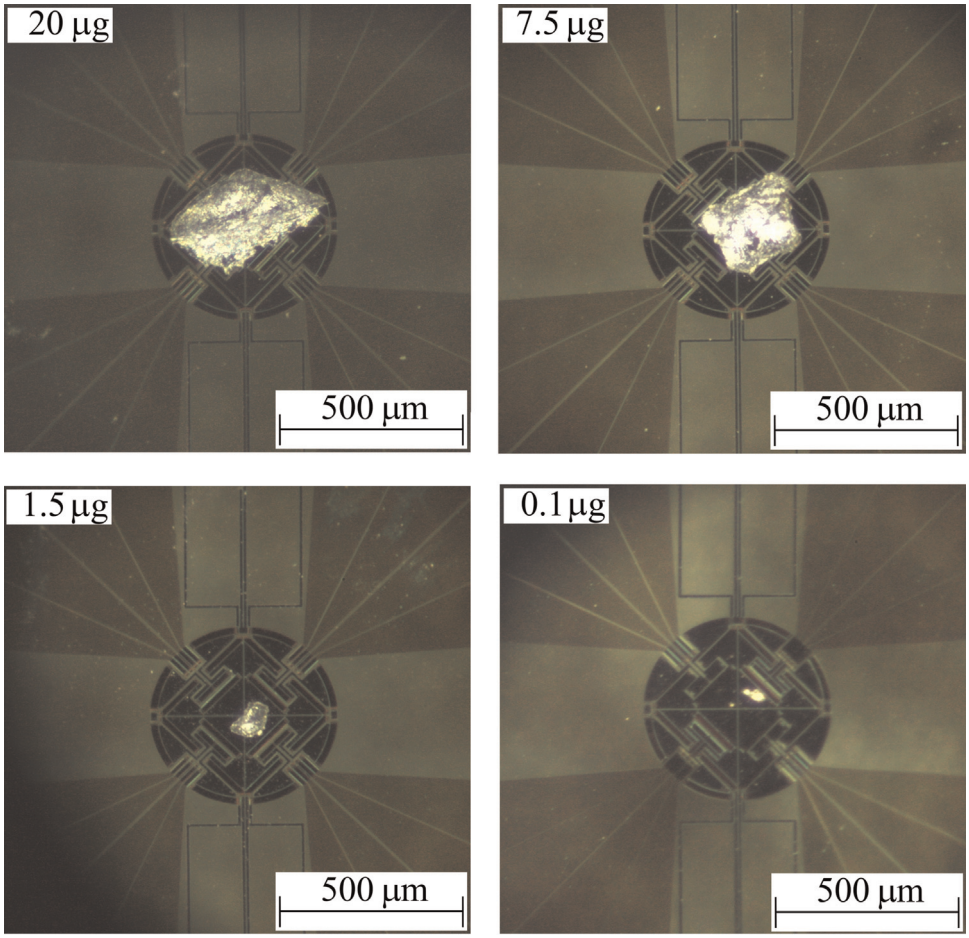

Fig. 2. Micrographs of pre-molten samples with various masses on the sample platform of the sensor. For large sample masses (>10 μg) and samples larger than the small square of the chip sensor (a, b), technical artifacts may occur and can reduce the maximum rates accessible.