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Reprint of: Characterization of bulk metallic glasses via fast differential scanning calorimetry☆

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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 (F_c) and heating rate (F_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.

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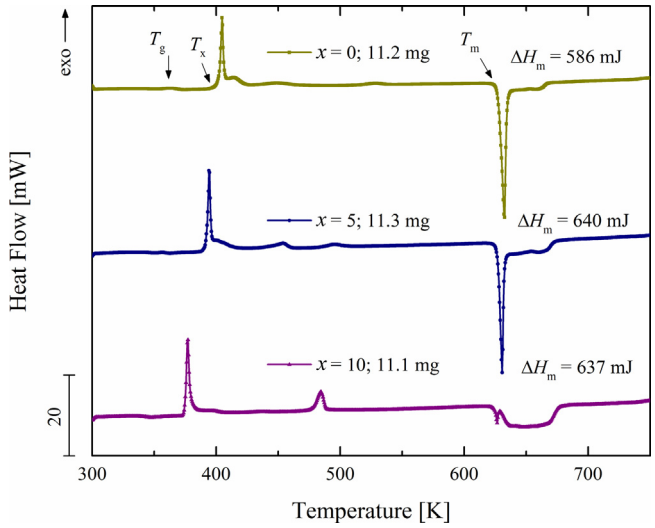

Fig. 1. DSC traces of $Au_{60+x}Cu_{15.5-x}Ag_{7.5}Si_{17}$ ($x = 0$, 5 and 10) metallic glasses measured with a heating rate of 0.33 K s^{-1} and corresponding ΔH_m values.

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 (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 over-pressure 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]:

$$m_{\mathrm{FDSC}} = \frac{\Delta H_{m,\mathrm{FDSC}}}{\Delta H_{m,\mathrm{DSC}}} \times m_{\mathrm{DSC}} \quad (1)$$

Fig. 1 shows DSC traces of the alloys investigated and the corresponding ΔH_m values. The glass transition (T_g), onset of crystallization (T_x) and onset of melting (T_m) are indicated as examples for $Au_{60}Cu_{15.5}Ag_{7.5}Si_{17}$. Note that more than one crystallization peak is visible for all BMGs investigated in Fig. 1.

FDSC was performed in power compensation mode using the Mettler-Toledo Flash-DSC 1. The sample support temperature of the FDSC was set at 183 K using a Huber intracooler TC90. The furnace was purged with Ar of 5 N purity at a flow rate of 10 ml min^{-1}. FDSC samples were prepared by cutting the melt-spun ribbons under a stereomicroscope to small pieces with weights of 30 ng to 20 μg and then transferred by an electrostatic manipulator hair onto a conditioned and temperature-corrected MultiSTAR UFS1 sensor (according to the instrument provider's specification). Fig. 2 illustrates samples of various masses on the sensor.

To protect the samples from bouncing due to strains in the material they were pre-melted with a heating rate of 1 K s^{-1} from room temperature to 748 K, which is a temperature accessible for most sensors. For all experiments the samples were heated or cooled between 298 K and 748 K. The exact time–temperature regimes used are displayed in the corresponding heat-flow figures. Reproducibility was always found to be very high, as was judged from comparing the same thermal cycles at the start and end of each measurement series.

To explore sensor materials other than the silicon nitride surface provided, the reverse side of the sensors made of silicon oxide was used, and the silicon nitride surface was also coated with a graphite layer of approximately 10 nm thickness.

3. Results

3.1. Sensor surface material

Fig. 3 shows FDSC scans at a heating rate of 100 K s^{-1} for $Au_{60+x}Cu_{15.5-x}Ag_{7.5}Si_{17}$ ($x = 0$, 5 and 10) on a standard silicon nitride sensor surface, on the reverse silicon oxide side of the sensor, and on a graphite-coated sensor membrane. The samples were amorphized in situ by quenching from 748 K to RT with a cooling rate of 5000 K s^{-1} prior to the measurements. The inserts to Fig. 3 illustrate the time–temperature regime. Clear glass transitions followed by exothermic crystallization peaks and melting of the samples can be observed for all Au-based glasses, and the sensor surface material does not influence the measurements. The curves are not normalized to the mass, which introduces some differences in the size of the peaks only.

3.2. Critical cooling rate

Fig. 4 shows typical FDSC scans of $Au_{60+x}Cu_{15.5-x}Ag_{7.5}Si_{17}$ BMGs with $x = 0$, 5 and 10 when cooling the equilibrium liquid at different rates. The inserts illustrate the applied temperature–time programs. The exothermic crystallization peaks (400–500 K) shift to lower temperatures and their enthalpy of crystallization decreases with increasing cooling rate until the crystallization peak vanishes. This means that for this and higher cooling rates no crystallization occurs and the critical cooling rate F_c is reached. All alloys also demonstrate a clear glass transition which depends on the cooling rate. Fig. 4(a) shows the curves of the heat flow measured during cooling of a $Au_{60}Cu_{15.5}Ag_{7.5}Si_{17}$ melt at rates of 425 K s^{-1} up to 675 K s^{-1} and a sample mass of 1.5 μg on the standard silicon nitride sensor membrane. The transition from crystallization in the supercooled liquid region to in situ amorphization is observed at $\Phi_c \approx 575$ K s^{-1}. Fig. 4(b) shows the cooling curves of a $Au_{65}Cu_{10.5}Ag_{7.5}Si_{17}$ melt (sample mass 3.3 μg) at rates of 200–375 K s^{-1}. The critical cooling rate is observed at around 350 K s^{-1}. $Au_{70}Cu_{5.5}Ag_{7.5}Si_{17}$ (sample mass 1.3 μg) was investigated between 500 K s^{-1} and 1200 K s^{-1} and exhibits a higher F_c value of around 1200 K s^{-1} (Fig. 4(c)). Note that Fig. 4 is also a good example