Thermochimica Acta 522 (2011) 20–27

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Development of static and dynamic structures in glass-forming metallic alloys

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ARTICLE INFO

Article history:
Available online 21 December 2010

Keywords:
Bulk metallic glass
Nanocrystallization
Dynamic glass transition
Modulation calorimetry
Quenched-in cluster
Phase separation

ABSTRACT

Glass-forming metallic systems are either simple and show a marginal glass-formation tendency with high transformation rates towards the crystalline state or the systems offer a high stability of the undercooled liquid state against crystallization, but are chemically complex. However, metallic systems can be utilized as model systems if the variations in kinetic stability are used as a tool to select appropriate alloy systems for a limited range of problems to be investigated. Here, marginal glass-forming Al-based metallic glasses were used to study the early stages of crystal formation. A bulk glass-forming Pd-based system provided sufficient kinetic stability against crystallization to allow analyzing the relaxation spectrum near the glass transition by modulation calorimetry. These measurements were analyzed in the framework of a fluctuation model of the glass transition. Finally, possible interrelations between the length scale of dynamic heterogeneities and structural heterogeneities in the deeply undercooled liquid are discussed.

1. Introduction

With the discovery of glass formation in metallic alloy systems by Duwez and co-workers in 1960 [1], research on phase formation kinetics in the undercooled melt and on the nature of the liquid state including the glass transition experienced increased attention since these systems were thought of as easy describable, molecular liquids. Yet, experimental experience has shown that metallic systems with sufficient stability against crystallization that allow for bulk-glass formation require rather complex stoichiometries and considerable covalent contributions to the binding energy of the constituents [2]. As a result, strong tendencies towards short-range ordering into complex associations develop that are discussed with respect to either quasi-crystalline structures or crystalline aggregates with low symmetry that evolve and dissolve in a temperature-dependent dynamic equilibrium [3–6]. More recent attempts for structural descriptions even postulate non-crystalline aggregates with fixed structures that are forming the basic structural units in glass-forming metallic melts [7]. Chemically simple systems, e.g. binary glass-forming alloys, on the other hand are kinetically unstable and do not allow experimental access to the undercooled liquid state. Consequently, no glass-forming alloy exists, except in computer simulations [8,9], that provides the opportunity to study the entire spectrum of questions that are concerned with the glass transition, the structure of the liquid state and the early stages of crystalline phase formation. Either metallic systems are simple and show a marginal glass-formation tendency with high transformation rates towards the crystalline state or the systems offer a high stability of the undercooled liquid state against crystallization but are chemically complex. However, metallic systems can be utilized as model systems if the variations in kinetic stability are used as a tool to select appropriate alloy systems for a limited range of problems to be investigated.

Recently, two types of structure development in metallic systems have attracted increased attention that are related to the occurrence of nano-scaled crystalline phases at low temperatures [10–14] and to the underlying processes that lead to the occurrence of the glass transition, respectively. Two alloys, $Al_{92}Sm_8$ and $Al_{88}Y_7Fe_5$, were chosen as representatives of the class of marginal glass formers to study the nanocrystallization process in detail. At the same time, these materials provide the opportunities to study the early stage of the formation of a crystalline structure since crystallization proceeds sluggishly at temperatures very close to T_g.

The second type of structure development that has received increased attention recently is concerned with the temperature-dependent evolution of a dynamic structure in the undercooled liquid state of glass-forming material. Such structures are not necessarily related to the corresponding crystalline state of the material, but to associations of atoms within the fluctuating arrangement of the melt that have a higher degree of correlation [15,16]. These correlated regions exist only temporarily in a given configuration, i.e. they do not form permanent clusters in

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doi:10.1016/j.tca.2010.12.011

the melt. However, the presence of an average fraction of more strongly correlated atoms in the liquid state leads to a higher effective degree of cooperativity for atomic motion. Thus, stochastic density fluctuations do not decay in the long-time limit as they would for an ideal molecular liquid. With decreasing temperature, the amount of correlation increases and the associated correlation length in the liquid state finally diverges. Recent investigations, e.g. by inelastic neutron scattering on glass-forming liquid metals near their melting temperatures indicate the presence of cooperative dynamic structures also in metallic systems [17]. At high temperatures, this cooperative dynamic behavior is explained by mode-coupling theories (MCT) [18,19]. Yet, below a critical temperature T_c, which is well above the glass transition observed as a kink in the second derivatives of thermodynamic potentials, MCT describe the dynamics of the material as arrested (or glassy) in contrast to the liquid-like behavior above T_c. However, with respect to the appearance of the glass transition that is observed on macroscopic properties and that is marked by the transition from viscous flow to rigidity, the temperature dependence of the correlation length at temperatures below T_c is of utmost importance. Yet, any contribution to investigate these dynamic structures and consequently the dynamics of the undercooled liquid state requires a high kinetic stability that must be sufficient to achieve metastable equilibrium during the measurements, i.e. the time for structural relaxation needs to be shorter than the time necessary for a significant crystalline fraction to occur. Therefore, glass-forming Pd-based alloys have been chosen here to investigate the thermodynamic properties and the dynamics of deeply undercooled glass forming metallic alloys. In particular, $Pd_{40}Ni_{40}P_{20}$ – one of the first bulk glass-forming alloys – was investigated in detail since this alloy does not show any detrimental effects related to crystallization or chemical decomposition in a wide temperature interval above the glass transition [20,21]. Innovations in alloy design have produced Pd-based alloys that allow for vitrification at even lower rates [22] and that have higher values of the reduced glass temperature.

2. Marginal glass-formers

Solid-state amorphization as an alternative vitrification route is often viewed as a non-equilibrium process resulting from the destabilization of crystalline phases when the maximum metastable solubility is exceeded. This perspective is also consistent with the general rules based upon a large negative heat of mixing and a large atomic size difference for the components that have been effective in identifying bulk glass forming compositions [23]. Within this framework, amorphization is depicted by a generalized phase diagram for partition less transformations [24,25] as also indicated in Fig. 1, i.e. the T_0-curves of a terminal solid solution phase of a eutectic system that represent the limiting curves for partitionless reactions where the Gibbs free enthalpy of the liquid and the solid solution of equal composition are equal and the composition-dependent glass temperature. According to this perspective, equivalent glassy states are obtained, which, during heating should follow identical transformation routes towards thermodynamic equilibrium. However, amorphization by strain-induced mixing proceeds at low temperatures (i.e. low mobilities) while melt quenching from high temperatures involves rather fast diffusing atomic species in a homogeneous liquid phase that have to bypass the kinetic competition between vitrification and crystallization in order to form a glass. Therefore, in the case of nanocrystallization in marginally glass-forming alloys, the variation of the processing pathway can lead to drastic modifications of the structure formation sequence if vitrification by rapid quenching is growth controlled [26].

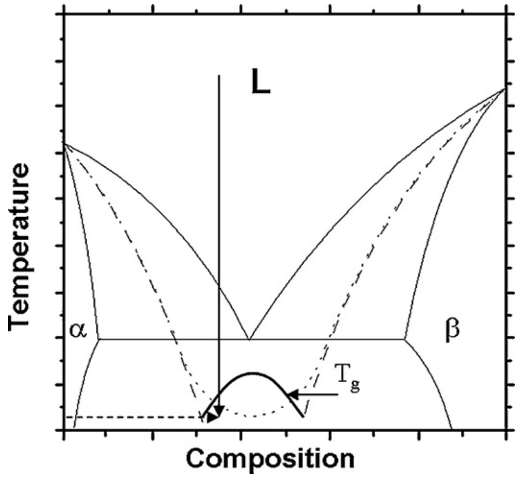

Fig. 1. The extensions of the T_0 curves to temperatures below a (metastable) eutectic are indicated as dashed curves. If the primary phases have different crystal structures and low mutual solubility, then the T_0 curves might not intersect. Such a situation favors glass formation in the composition range where the T_g curve lies above the T_0 curves. The dashed arrow represents an isothermal solid-state amorphization process.

Experimentally, both types of amorphization routes were applied to $Al_{92}Sm_8$—one of the chemically simplest glass-forming metallic alloys. Melt spinning was used as rapid-quenching technique. Mechanical intermixing at ambient temperatures was achieved by cold rolling stacked arrays of elemental foils of Al and Sm. The rolling procedure was used to avoid the detrimental temperature spikes that occur in high strain-rate processes such as ball milling. TEM and XRD studies have shown that $A1_{92}Sm_8$ melt-spun ribbon (MSR) samples reveal a completely amorphous structure (Fig. 2a). Similar investigations on cold-rolled samples have yielded the same results: amorphous regions are free from crystalline fractions (Fig. 2b) [27]. However, on heating in a DSC, the samples prepared by melt spinning always showed a non-symmetrical exothermic signal in the temperature range between 170 °C and 220 °C, i.e. well below the crystallization of the eutectic Al–Al_3Sm phases at the crystallization temperature, $T_x = 260\,°C$ (Fig. 2c). The glass transition of the melt-spun sample could not be observed. In fact, even after annealing at a temperature of only 150 °C for 10 min a high number density of $3.5 \times 10^{22}\,m^{-3}$ Al-nanocrystals was observed within the amorphous matrix as indicated in Fig. 2e.

The DSC signal on heating an $A1_{92}Sm_8$ sample at 20 K/min that was partially vitrified by cold rolling is given in Fig. 2d. The sample was annealed at 150 °C before the actual measurement in order to allow for relaxation of the vitreous state and to promote the development of any Al-nanocrystals. Two important characteristics can be observed on the heating curve in Fig. 2d: first, the calorimetric glass transition signal is clearly revealed at about $T_g = 172\,°C$. This signal and the characteristic hysteresis, which is associated with the glass transition, could be observed reversibly on carefully heating and cooling through the transition region. Secondly, no exothermic signal occurs before the onset of the solid state reaction at about 230 °C at which the eutectic phases are formed. Moreover, TEM experiments on cold rolled and annealed samples confirmed that Al nanocrystals do not develop within the amorphous phase at temperatures at or below the glass transition. The TEM micrograph (Fig. 2f) taken on a sample directly after annealing for 60 min at 150 °C does not reveal any signs of crystallinity within the amorphous regions even after tilting the foil. Thus, calorimetry and microstructural analysis confirm that amorphous $A1_{92}Sm_8$ samples, which have not been exposed to high temperatures in the liquid state before vitrification, exhibit a clear T_g signal and do not show formation of a high number density of Al-nanocrystals.