Journal of Alloys and Compounds 707 (2017) 3–11

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Al-based amorphous alloys: Glass-forming ability, crystallization behavior and effects of minor alloying additions

Y. Shen, J.H. Perepezko*

University of Wisconsin-Madison, Department of Materials Science and Engineering, 1509 University Ave., Madison, WI, 53706, USA

ARTICLE INFO

Article history:
Received 30 August 2016
Received in revised form
4 November 2016
Accepted 6 November 2016
Available online 8 November 2016

Keywords:
Primary crystallization
Glass forming ability
Metallic glasses

ABSTRACT

The main recent advances in Al-based amorphous alloys are discussed in three areas: crystallization behavior, glass-forming ability and minor alloying effects. First, as a brief introduction, the special features and structure-property relationships are presented for the Al-based amorphous alloys. The different models for the nucleation behaviors, such as phase separation model and the quenched-in nuclei model, are compared and evaluated. In addition, an overview is given for the effects of minor alloying additions on glass-forming ability (GFA) and the crystallization behavior in terms of the reported structural, thermodynamic, kinetic factors.

1. Introduction

Al-based metallic glasses (Al>80 at.%) with the rare-earth metals (RE) and transition metals (TM) additions were first discovered in the 1980s [1,2]. There are several special features for Al-based metallic glass. First, most of the Al-based metallic glasses are marginal glass formers, which are different from the bulk metallic glasses due to the requirement for higher critical cooling rates (10^5–10^6 K/s) to avoid crystallization. Therefore, rapid solidification techniques such as melt spinning have been mainly used to prepare Al-based metallic glasses. Other synthesizing methods include cold rolling [3] and ball milling [4]. Secondly, most of the Al-based metallic glasses exhibit no obvious glass transition signal T_g nor the supercooled liquid region in the differential scanning calorimetry (DSC) continuous heating trace because the onset of the primary crystallization peak T_x nearly coincides with the glass transition [5]. Other approaches such as the temperature-modulated DSC (TMDSC) and dynamic mechanical analysis (DMA) can be applied to measure T_g more precisely [5–8] and a hold below T_x can reveal the T_g signal [9,10]. Thirdly, a typical continuous DSC trace for most of the Al-based metallic glass shows a shallow primary crystallization peak for Al_{fcc} followed by sharp secondary crystallization peaks of intermetallic phases (Fig. 1(a)). The separation between the primary and secondary crystallization of more than 50 °C signifies a metastable Al and glass equilibrium. This is somewhat unexpected because within the hypereutectic glass forming composition range, the thermodynamic driving free energy for crystallization favors the Al rich intermetallic phase over the Al_{fcc} (Fig. 1(b)) [11]. Thus, the kinetic selection of Al as the primary crystallization phase must be promoted by a nucleation catalyst. A change in composition may lead to a change of the crystallization pathway [12–14]. Tsai et al. conclude that only when the values of the atomic size ratio λ and the Al content fall into the range of 0.04–0.07 and 82–90 at.% respectively, a dispersion of nanoscale fcc-Al in the amorphous matrix could be obtained in Al-Ni-Ce amorphous alloys [15]. Moreover, a high number density of primary crystallized Al_{fcc} nano-particles (10^{21}–10^{24} m^{-3}, 5–50 in diameter) dispersed in the amorphous matrix. (Fig. 1(c)) can be generated by either annealing the as-quenched amorphous Al alloys under suitable experimental conditions [5] or by the direct solidification of the molten alloy at a cooling rate lower than the critical cooling rate [16,17]. In addition, the Williamson and Hall analysis on XRD (X-ray diffraction) traces indicates that the Al nanocrystals are under an elastic compressive stress [18].

The Al-based metallic glasses show great potential in applications requiring high corrosion resistance, high wear resistance, high strength, and relatively low density. The specific strength can be further increased to levels beyond that of many common steels through partial devitrification [19–21]. For example, Kan et al. have obtained a novel Al-based composite material with an ultrahigh strength of about 1.34 GPa through the controlled annealing treatment of an Al-Ni-Y-Co-La amorphous alloy [22]. Inoue et al.

* Corresponding author.
E-mail address: perepezk@engr.wisc.edu (J.H. Perepezko).

http://dx.doi.org/10.1016/j.jallcom.2016.11.079
0925-8388/

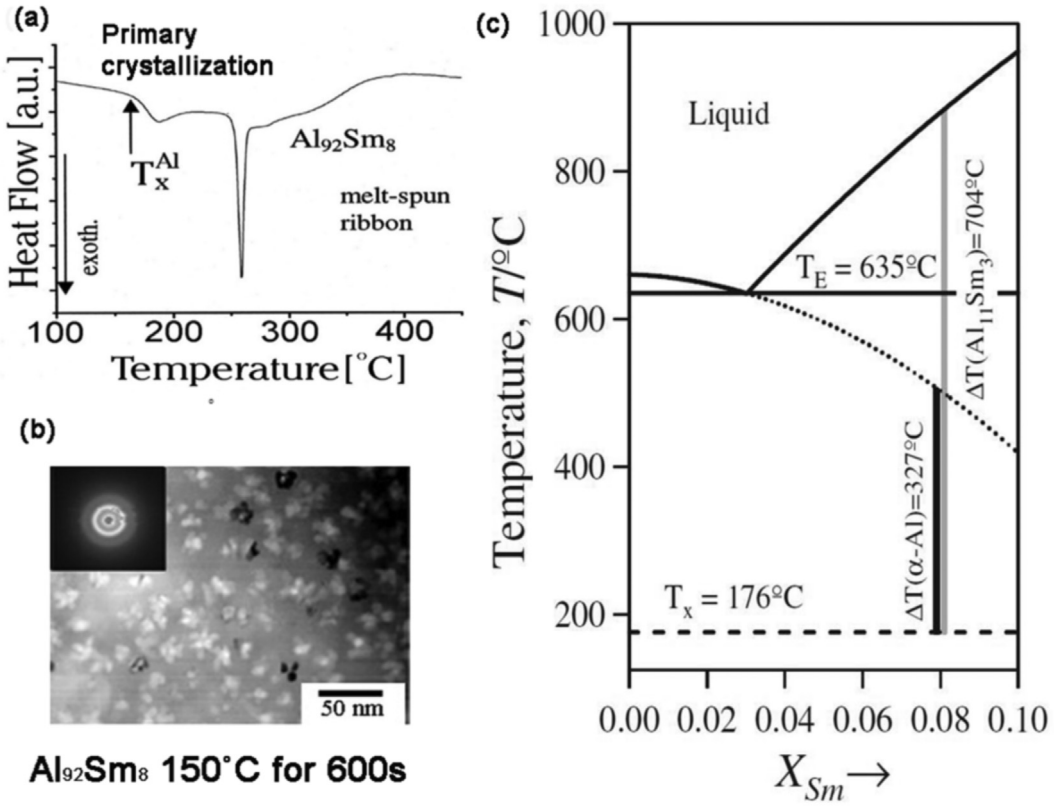

Fig. 1. (a) Continuous DSC heating trace for $Al_{92}Sm_8$ at 20 K/min. (b) TEM bright field image for $Al_{92}Sm_8$ annealed at 150 °C for 600s. (c) Al-Sm phase diagram on the Al rich side.

have prepared novel Al-based alloys with the high rotating beam fatigue strength above 400 MPa at 10^7 cycles and high corrosion resistance below 20 mm/year in 0.25 M NaOH aqueous solution at 293 K [23]. Also, both the mechanical and corrosion properties of the partially crystallized Al-based metallic glass are closely related with the microstructure. In the $Al_{86}Ni_6Y_6Ce_2$ alloy, the formation of nano-sized α-Al and fine hard Al_3Ni intermetallic compounds at the first and second crystallization stages is favored in the hardening effect because the residual amorphous matrix is hardened from solute enrichment and there is a precipitation hardening effect. However, the coarsening of the particles and formation of a weak intermetallic compound $Al_{11}Y_3$ at the final stage lowers the hardness [24] For the Al-Ni-Ce alloy, the high pitting corrosion resistance of the amorphous alloy was not deteriorated by the nanocrystalline α-Al precipitation, whereas the pitting potential was decreased due to the formation of the intermetallic phases Al_3Ni and $Al_{11}Ce_3$ [25].

The unique features of the Al-based metallic glasses, such as the high critical cooling rate, the unclear T_g and the high number density of Al_{fcc} nanoparticles, suggest a high nucleation rate and a sluggish growth. The understanding of the crystallization behavior of the Al-based metallic glasses is important in order to control the microstructure for optimizing the material properties and is considered in the initial part of the review. The poor glass forming ability is a big challenge and has limited the applications of the Al based amorphous alloys. As a result, there has been a focused effort that aims to overcome this bottleneck problem of the relatively low glass forming ability (GFA). Both the crystallization behaviors and the GFA of the Al-based metallic glasses are very sensitive to minor element doping and the underlying mechanism has been considered in terms of the structural, thermodynamic and kinetic factors. Within the available coverage, the discussion of recent advances will focus on the main highlights for GFA, crystallization and minor alloying effects.

2. Crystallization behavior

In most cases, crystallization in Al-based amorphous alloys is induced by thermal treatment. However, severe plastic deformation (SPD), such as rolling, tension and torsion, is an alternative approach to stimulate crystallization. From in-situ tensile straining in the TEM on amorphous $Al_{88}Y_7Fe_5$ [26] and the multiple rolling on Al-Ni-Co-Gd-Si [27], nanocrystals were observed to form preferentially in shear bands presumably due to the enhanced atomic mobility from the marked increase in the excess volume inside the shear bands. However, observations following the high pressure torsion applied to an $Al_{90}Y_{10}$ amorphous alloy indicated that there was no correlation between the location of nanocrystals and the position of shear bands [28] and Jiang et al. reported that in the tensile region of the amorphous Al-Fe-Gd sample under bending, nanocrystals formed only at the fracture surface, which was likely to be due to the adiabatic heating [29]. Lastly, other examples including the corrosion induced [30] and ion irradiation induced crystallizations [31] have been reported for Al based metallic glasses.

For thermally activated crystallization, the Johnson-Mehl-Avrami (JMA) relation (Eq. (1)) and the Kissinger analysis (Eq. (2)) are two convenient and widely used approaches to describe the crystallization kinetics.

$$\alpha(t) = 1 - \exp\{-[k(t-\tau)]^n\} \tag{1}$$

$$\ln\left(\frac{T^2}{\Phi}\right) = \left(\frac{E}{RT}\right) + constant \tag{2}$$