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Glass-forming ability and crystallization behavior of some binary and ternary Ni-based glassy alloys

Dmitri V. Louzguine-Luzgin [a,*], Larissa V. Louzguina-Luzgina [b], Guoqiang Xie [a], Song Li [a], Wei Zhang [a], Akihisa Inoue [a]

[a] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[b] Research and Development Project, SORST, Japan Science and Technology Agency, Sendai 985-8577, Japan

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Abstract

The purpose of the current paper is to study the influence of Ti, V, Nb, Al, Sn and Pd additions on the glass-forming ability, formation of a supercooled liquid region and a devitrification process of some Ni–Zr glassy alloys as well as to compare the results with those obtained for similar Cu-based alloys studied earlier. The Ni-based glassy alloys were investigated by using X-ray diffraction, differential scanning and isothermal calorimetries. Although the studied Ni-based alloys showed high values of the reduced glass-transition temperature of about 0.6, their glass-forming ability is quite low. This fact may be explained by low stability of the supercooled liquid against crystallization and formation of the equilibrium intermetallic compounds with a high growth rate compared to those observed in similar Cu-based alloys studied earlier. Relatively low thermal conductivity of Ni-based alloys is also found to be another factor limiting their glass-forming ability.

Keywords: Glassy alloy; Glass-forming ability; Supercooled liquid; Devitrification

1. Introduction

At present bulk glassy alloys (bulk metallic glasses) attract significant attention of the scientists working in the filed of materials science [1] due to their promising physical [2] and functional [1–3] properties. Recently, bulk glass formation was achieved in Ni–Nb–Ti–Zr [4], Ni–Nb–Ti [5] and a number of similar alloys, which belong to LTM–ETM (LTM-late transition metals, ETM-early transition metals) group of alloys. Ni-based glassy alloys were also formed in Ni–Zr–Ti–(Si,Sn) [6,7], Ni–Nb–Ti–Hf [8,9], Ni–Nb–Sn [10] and some other systems. $Ni_{59}Zr_{16}Ti_{13}Si_3Sn_2Nb_7$ bulk glassy alloy showed a significant plastic deformation of 6.5% to failure [11]. However, it may contain nanoparticles embedded in the glassy matrix which are not detectable by an X-ray diffraction (XRD) technique. The devitrification behavior of Ni–Nb–Ti [12], Ni–Nb–Ti–Zr and Ni–Nb–Ti–Zr–Pt [13] glassy alloys has been studied recently.

An addition of Ni to Cu-based alloys stabilized oC68 $(Ni,Cu)_{10}Zr_7$ phase [14,15] while the isomorphous $Ni_{10}Zr_7$ phase formed primarily in the Ni–Zr–Ti alloy on devitrification [16].

In the current paper, we study the influence of Al, Ti, V, Sn and Nb additions on the glass-forming ability, the supercooled liquid region and the devitrification behavior of Ni–Zr glassy alloys. Slightly off-eutectic $Ni_{65}Zr_{35}$ alloy has been chosen by analogy with recently studied Cu–Zr bulk glassy alloys [17–20] due to close similarity of Ni–Zr and Cu–Zr phase diagrams [21]. Al, V, Sn, Ti and Nb have a negative mixing enthalpy in liquid with Ni [22]. They also form intermediate compounds. These factors favor glass-formation. Compositions of $Ni_{60}Zr_{30}Ti_{10}$ and $Ni_{60}Zr_{30}V_{10}$ alloys were chosen by analogy with the recently studied $Cu_{60}Zr_{30}Ti_{10}$ alloy [17] while $Ni_{64}Zr_{26}Nb_{10}$ was created by analogy with Ni–Nb–Ti and Ni–Nb–Zr alloys [5].

2. Experimental procedure

The ingots of Ni-based alloys (all alloy compositions are given in nominal at.%) were prepared by arc-melting mixtures of pure elements with 99.9 mass% purity, except for Zr and Ti, which had 99.8 mass% purity, in an argon atmosphere. From these ingots, ribbon samples of about 20–25 μm in thickness and

* Corresponding author. Tel.: +81 22 215 2592; fax: +81 22 215 2381.
E-mail address: dml@imr.tohoku.ac.jp (D.V. Louzguine-Luzgin).

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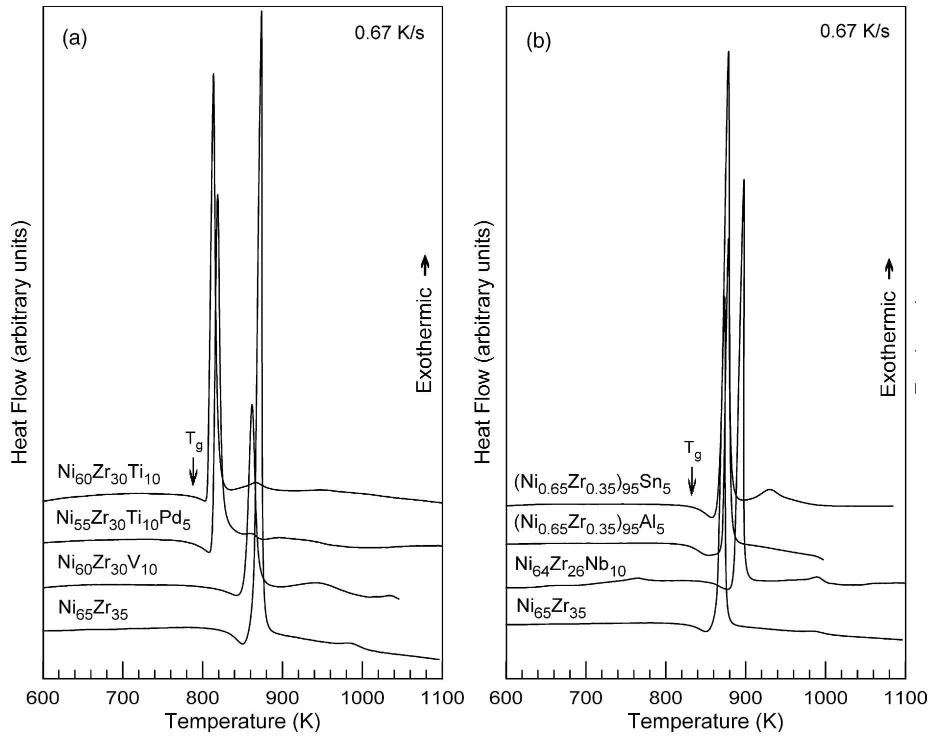

Fig. 1. DSC traces of the studied alloys.

1 mm in width were prepared by rapid solidification of the melt on a single copper roller at a tangential velocity of 42 m/s. The structure of the samples was examined by X-ray diffractometry with monochromatic Cu Kα radiation. The phase transformations were studied by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s and differential isothermal calorimetry. During isothermal calorimetry the samples were heated up to the testing temperature at the highest possible heating rate of 1.67 K/s. The temperature and enthalpy for the DSC were calibrated within ±0.2 K and ±0.1 J/g using the melting of In as a standard. Differential thermal analysis (DTA) has been carried out on cooling at 0.067 K/s from the melt.

3. Results and discussion

Compositions of the studied Ni-based alloys are listed in Table 1. DSC traces of the studied alloys are shown in Fig. 1. The data on glass transition temperature (T_g) (which actually corresponds to the onset of the glass-transition region), temperature of crystallization (T_x), supercooled liquid region (ΔT_x) and enthalpy of phase transformation ΔH_1 and ΔH_2 are presented in Table 1.

Thus, most of the studied alloys show double-stage transformation first of which is related to the primary formation of the equilibrium oC68 $Ni_{10}Zr_7$ compound or its-based solid solutions observed in the hypereutectic $Ni_{60}Zr_{30}Ti_{10}$ and $Ni_{55}Zr_{30}Ti_{10}Pd_5$ alloys (Fig. 2) (FCC phase is formed in $Ni_{60}Zr_{30}V_{10}$ alloy (Fig. 2)) or eutectic-type crystallization of the glassy phase observed in nearly eutectic $Ni_{65}Zr_{35}$ (Fig. 3), $(Ni_{0.65}Zr_{0.35})_{95}Al_5$ (Fig. 4) and $(Ni_{0.65}Zr_{0.35})_{95}Sn_5$ alloys. The second stage in the nearly eutectic alloys is rather related to subsequent crystal growth (Figs. 3 and 4). FCC phase in the $Ni_{60}Zr_{30}V_{10}$ alloy exhibits a steady-state nucleation and diffusion-controlled growth [23] as follows from the Avrami analysis (Fig. 5).

From the binary Ni–Zr phase diagram one can see that $Ni_{65}Zr_{35}$ alloy has a liquidus temperature of about 1100 C (1373 K) which gives quite a high so-called reduced glass-transition T_g/T_l temperature [24] of 0.60. This value is usually considered as high enough to enable bulk glass formation as observed in Cu- and Zr-based alloys [22]. Nevertheless,

Table 1
Thermal analysis data for the studied alloys

Alloy	T_g (K)	T_x (K)	ΔT_x (K)	ΔH_1 (J/g)	ΔH_2 (J/g)
$Ni_{65}Zr_{35}$	827	863	36	59.9	1.3
$Ni_{60}Zr_{30}Ti_{10}$	793	806	13	45.8	2.2
$Ni_{60}Zr_{30}V_{10}$	811	851	40	28.4	6.0
$Ni_{64}Zr_{26}Nb_{10}$	856	886	30	68.4	3.1
$Ni_{55}Zr_{30}Ti_{10}Pd_5$	781	811	30	42.8	6.1
$(Ni_{0.65}Zr_{0.35})_{95}Al_5$	829	871	42	51.3	–
$(Ni_{0.65}Zr_{0.35})_{95}Sn_5$	837	867	30	88.6	7.9

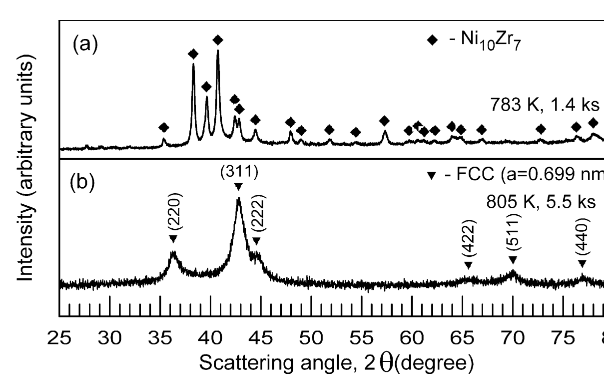

Fig. 2. XRD patterns of (a) $Ni_{60}Zr_{30}Ti_{10}$ and (b) $Ni_{60}Zr_{30}V_{10}$ alloys in the annealed state.