Glass formation in mechanical milled Ni-Ti-Zr-Sn pre-alloy powders

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Abstract. Glass formation by mechanical milling was achieved in a multicomponent Ni-based alloy system. It was found that the milling time required for forming a fully glassy phase decreased with the increase in Zr content. The enhanced atomic size mismatch of constituents was responsible for the increase of glass forming ability of these alloys. The transformation from crystalline to glassy phase might be due to the destabilization of crystalline phase, induced by a combination of factors involving refinement of grain size, high pressure exerted to powders during repeated collision, and elastic mismatch energy.

1. Introduction
A number of bulk glassy alloys with extremely high glass-forming ability have been developed by conventional casting techniques in various multicomponent alloy systems [1-3]. Among these alloy systems, Ni-based bulk glassy alloys have attracted increasing interest due to their high strength, good corrosion resistance and lower material cost compared to noble metal (NM)-based bulk glassy alloys [4]. However, glass formation by rapid quenching from the melt often requires a high cooling rate to prevent the nucleation and/or growth of crystalline phases. In particular, changes in composition strongly affect their glass forming abilities.

In view of these facts, solid-state techniques, such as mechanical alloying of elemental powder mixtures or ball milling of crystalline pre-alloys, have been alternative processing methods for fabricating metallic glassy alloys due to their advantages over liquid quenching, such as glass formation in a wide composition range, low processing temperature and simple processing route [5-8]. This enables the preparation of bulk glassy alloys through the consolidation of glassy powders by extrusion, spark plasma sintering and microwave sintering using low viscous flow of glassy powders at temperatures close to the glass transition temperature ($T_g$) [9-12].

In the present work, glass formation by mechanical milling in a quaternary Ni$_{59}$Ti$_{36-x}$Zr$_x$Sn$_5$ (16≤x≤28 at.%) alloy system was investigated. Due to the chemical similarity of Ti and Zr, the influence of the substitution of Ti by Zr on glass formation of mechanical milled Ni$_{59}$Ti$_{36-x}$Zr$_x$Sn$_5$ alloys was also studied by measuring the milling time required to form a glassy state.

2. Experimental details
The alloy ingots with the nominal composition Ni$_{59}$Ti$_{36-x}$Zr$_x$Sn$_5$ (x= 16, 20, 24 and 28 at.%) were prepared by arc melting a mixture of pure elemental metals Ni (99.99 wt.%), Ti (99.95 wt.%), Zr (99.99 wt.%) and Sn (99.99 wt.%) in a Ti-gettered pure argon atmosphere and re-melted four times to ensure their chemical composition homogeneity. These ingots were crushed into small particles with dimensions of smaller than 125 μm and sealed in a stainless vial together with some stainless balls.
The initial ball-to-powder mass ratio was about 5:1. The ball milling processes were carried out in a Retsch PM100 planetary mill under purified argon atmosphere at a rotating velocity of 400 rpm. After some selected milling time, the milling process was interrupted to cool down the jar and small amounts of powders were withdrawn to examine the progress of the amorphization reaction. Structural evolution during the milling process was studied by X-ray diffraction (XRD) with a Cu-Kα radiation (\(\lambda=0.154\) nm). Thermal analysis was performed using a differential thermal analysis (DTA) at a heating rate of 20 K/min.

3. Results and discussion

Figures 1(a)-1(d) shows the XRD patterns of Ni_{59}Ti_{36-x}Zr_{x}Sn_{5} alloys after various milling times for x=16, 20, 24 and 28 at.% Zr, respectively. The diffraction patterns of the initial powders consist of sharp peaks from the different crystalline intermetallic compounds. Whatever the Zr content, some diffraction peaks with weak intensity disappear firstly and a halo pattern occurs at low 2θ position after 2 h of milling, indicating the formation of an amorphous phase. Besides this, the intensities of the crystalline diffraction peaks decrease strongly compared to those of the initial powder. The halo pattern becomes wider and its intensity also increases distinctly with the increase in milling time. This means that the amounts of the amorphous phase increase whereas the amounts of the crystalline phase decrease. Due to the difference of the composition, the time required for glass formation is also different for Ni_{59}Ti_{36-x}Zr_{x}Sn_{5} alloys. For Ni_{59}Ti_{20}Zr_{16}Sn_{5} alloy, after 20 h of milling the diffraction peaks of the crystalline phases were vanished, and only the typical broad diffraction pattern for a glassy phase is visible. While for Ni_{59}Ti_{16}Zr_{20}Sn_{5} alloy, glass formation was achieved after 24 h of milling. With the increase of Zr content the time required for glass forming of Ni_{59}Ti_{36-x}Zr_{x}Sn_{5} alloys decreases. For Ni_{59}Ti_{12}Zr_{24}Sn_{5} and Ni_{59}Ti_{8}Zr_{28}Sn_{5} alloys, glass formation could be achieved earlier after 8 h of milling. This means that glass forming ability of Ni_{59}Ti_{36-x}Zr_{x}Sn_{5} alloys has been improved. However, further milling beyond the formation of a fully glassy phase leads to crystallization of the

![Figure 1](image-url). XRD patterns of ball milled Ni_{59}Ti_{36-x}Zr_{x}Sn_{5} alloys with (a) x=16, (b) x=20, (c) x=24, (d) x=28 at different milling times.
glassy phase. Compared to Ni$_{59}$Ti$_{12}$Zr$_{24}$Sn$_5$ alloy, Ni$_{59}$Ti$_8$Zr$_{28}$Sn$_5$ alloy shows higher structural stability. Fully glass formation occurs after 12 h of milling, again a time longer than for Ni$_{59}$Ti$_{12}$Zr$_{24}$Sn$_5$ alloy.

Figure 2 presents DTA curves of Ni$_{59}$Ti$_6$Zr$_{32}$Sn$_5$ alloy samples after different milling times at a heating rate of 20 K/min. Two exothermic peaks were observed for all specimens after ball milling. This can be attributed to crystallization of the amorphous phase. With the increase of milling time, the exothermic peaks become sharpened. The local structural fluctuations for the amorphous phase have been homogenized by extensive mechanical milling, which have induced a sharpened exothermic peak. Simultaneously, the crystallization onset temperature also shifts to higher temperature with the increase of milling time from 2 h to 8 h. It is clear that after 8 h of milling the DTA trace of Ni$_{59}$Ti$_6$Zr$_{32}$Sn$_5$ alloy powder shows an extended supercooled liquid region, which is limited by two exothermic events corresponding to crystallization. Subsequent milling results in the decrease of crystallization onset temperature and the broadening of crystallization peak. This means that the crystallization of the fully amorphous phase occurs. DTA curves from the other alloys (with x= 16, 20 and 24) also show a similar behavior except for the times required for glass transition.

Figure 3 shows the milling time required for glass formation as a function of Zr content in Ni$_{59}$Ti$_{36-x}$Zr$_x$Sn$_5$ alloy system. It can be seen that the time for glass formation increases up to a point and then decreases with the increase of Zr content, indicating the improvement of glass forming ability of Ni$_{59}$Ti$_{36-x}$Zr$_x$Sn$_5$ alloys. Considering the chemical similarity of Ti and Zr, the improved glass-forming ability for Ni-based alloy may be more linked with its enhanced atomic size mismatch. Since Zr has an atomic diameter of 0.3186 nm, substantially larger than that of Ti (0.2896 nm), the substitution of Ti by Zr leads to the increase of strain in the crystal lattice due to the large difference in the atomic sizes of the constituent elements and the improvement of the atomic packing density. The increase of Zr content enhances topological disorder in Ni$_{59}$Ti$_{36-x}$Zr$_x$Sn$_5$ alloy system. This can be also reflected by nearest-neighbor atomic distance. The diffraction angle for the first maximum in the XRD pattern is known to be related to the largest interatomic distance $d_m$. The value of $d_m$ can be estimated using the formula $1.23\hat{\lambda}=2d_m\sin\theta$, where $\hat{\lambda}$ is the wavelength of the X-radiation.
used, \(d_m\) is the distance between neighboring atoms, \(\theta\) is the peak position and 1.23 is the correction factor used for liquid and amorphous solids [13]. Since Ni\(_{59}\)Ti\(_{36-x}\)Zr\(_x\)Sn\(_5\) alloys consist of only metallic atoms, the value of \(d_m\) obtained from the above formula can be considered as the average nearest-neighbor atomic distance. Figure 4 presents the variation of the \(d_m\) values as a function of Zr content in Ni\(_{59}\)Ti\(_{36-x}\)Zr\(_x\)Sn\(_5\) alloy system. It is clear that the addition of Zr leads to the increase of the nearest-neighbor atomic distance, which results in the increase of topological disorder.

The mechanism responsible for glass formation of mechanical milling of Ni\(_{59}\)Ti\(_{36-x}\)Zr\(_x\)Sn\(_5\) pre-alloyed powders should be different from those of mechanical alloying of elemental mixed powders. The destabilization of crystalline phase and chemical disordering of the system induced by shear deformation is likely to be responsible for the transformation from crystalline to glassy phase in this Ni-based multicomponent alloy system [14]. It has been found that the accumulation of structure defects, such as vacancies, dislocations, grain boundaries and distortion of lattice and the refinement of grain lead to the increase of the Gibbs free energy of crystalline phase [15]. If the free energy of crystalline phase is higher than the glassy phase, the transformation to the glassy state can be expected.

4. Conclusions
Glass formation of Ni-Ti-Zr-Sn alloy system was achieved by mechanical milling of crystalline pre-alloy powders in a wide composition range. It was found that the milling time required for forming a fully glassy phase decreased with the increase of Zr content in Ni\(_{59}\)Ti\(_{36-x}\)Zr\(_x\)Sn\(_5\) alloy system. The transformation from crystalline to glassy phase was due to the destabilization of crystalline phase, induced by a combination of factors involving refinement of grain size, high pressure exerted to powders during repeated collision, and elastic mismatch energy.

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