Thermal Stability of Amorphous Ti–Cu–Ni–Sn Prepared by Mechanical Alloying

N. T. H. Oanh[a], P. P. Choi[b], J. S. Kim[c], J. C. Kim[d], Y. S. Kwon[e]

Research Center for Machine Parts and Materials Processing, School of Materials Science and Engineering, University of Ulsan, Namgu Mugeo 2-Dong, Ulsan 680-749, Korea
[a]oanh_chem2@yahoo.com, [b] ppchoi@mail.ulsan.ac.kr,[c] jskim@mail.ulsan.ac.kr, [d]jckimpml@ulsan.ac.kr, [e] yskwon@ulsan.ac.kr

Abstract

Ti-Cu-Ni-Sn quaternary amorphous alloys of $Ti_{50}Cu_{32}Ni_{15}Sn_3$, $Ti_{50}Cu_{25}Ni_{20}Sn_5$, and $Ti_{50}Cu_{23}Ni_{20}Sn_7$ composition were prepared by mechanical alloying in a planetary high-energy ball-mill (AGO-2). The amorphization of all three alloys was found to set in after milling at 300rpm speed for 2h. A complete amorphization was observed for $Ti_{50}Cu_{32}Ni_{15}Sn_3$ and $Ti_{50}Cu_{25}Ni_{20}Sn_5$ after 30h and 20h of milling, respectively. Differential scanning calorimetry analyses revealed that the thermal stability increased in the order of $Ti_{50}Cu_{32}Ni_{15}Sn_3$, $Ti_{50}Cu_{25}Ni_{20}Sn_5$, and $Ti_{50}Cu_{23}Ni_{20}Sn_7$.

Keywords : Ti-based alloys, amorphous, mechanical alloying

1. Introduction

Bulk metallic glasses (BMGs), developed for numerous alloy systems, possess unique properties that can be rarely found in crystalline materials such as high strength, unusual corrosion resistance and good wear resistance, etc. [1,2]. Among these systems, Ti-Cu based BMG alloys have shown potential as structural materials due to their high strength (2.2 GPa compressive strength for $Ti_{50}Cu_{23}Ni_{20}Sn_7$ alloy [3]), good corrosion resistance and a relatively low density of the main alloying element Ti (4.5 g/cm^3). However, it has been difficult to prepare the Ti-Cu-based BMGs of large size. The maximum critical diameter of an as-cast bulk sample with a single amorphous phase obtained for the Ti-Cu-Ni-Sn system was only 5mm [3]. To overcome the size and shape limitations of BMGs, powder metallurgical methods of BMGs have been recently explored. Mechanical alloying (MA) has been employed for preparing homogenous amorphous alloy powders with good reproducibility [4]. In this work, Ti-Cu-Ni-Sn alloy powders of different compositions ($Ti_{50}Cu_{32}Ni_{15}Sn_3$, $Ti_{50}Cu_{25}Ni_{20}Sn_5$, and $Ti_{50}Cu_{23}Ni_{20}Sn_7$) were produced by ball-milling and their structure and thermal stability were investigated.

2. Experimental and Results

Elemental powders of Ti, Cu, Ni and Sn (purity $\geq 99.9\%$) were accurately mixed to compositions of $Ti_{50}Cu_{32}Ni_{15}Sn_3$, $Ti_{50}Cu_{25}Ni_{20}Sn_5$ and $Ti_{50}Cu_{23}Ni_{20}Sn_7$. MA was performed at a rotational velocity of 300rpm using an AGO-2 planetary ball mill. Hardened steel vials and balls, and a ball to powder weight ratio of 20:1 were used. The vials were evacuated and filled with protective Ar gas (5×10^3 Pa). X-ray diffraction (XRD) was performed for structural characterization of the samples. Differential scanning calorimetry (DSC) analyses of amorphous samples were done at a heating rate of 20 K/min under Ar atmosphere. The chemical composition of alloy powders obtained after 20h of milling was determined using inductively coupled plasma (ICP) spectroscopy.

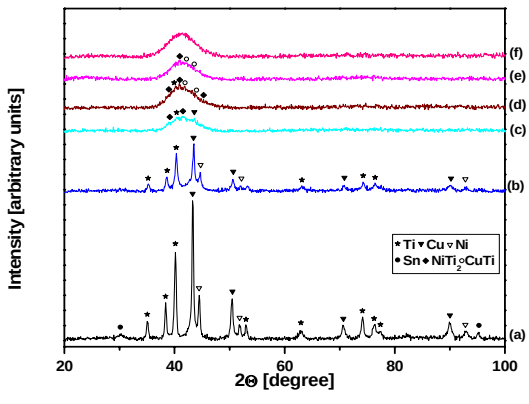

Fig. 1. XRD pattern of $Ti_{50}Cu_{32}Ni_{15}Sn_3$ milled for (a) 1h, (b) 2h, (c) 5h, (d) 10h, (e) 20h and (f) 30h.

Figs. 1(a)-(f) show the XRD patterns of $Ti_{50}Cu_{32}Ni_{15}Sn_3$ powders as a function of milling time. After milling for 1h, the main peaks of pure Ti, Cu, Ni and Sn phase can be seen in the XRD patterns. After milling for 2h, Sn peaks disappear and a broad halo peak corresponding to the

© Korean Powder Metallurgy Institute

amorphous phase starts appearing. After 5h of milling, the Ni peaks vanish, and at the same time, the $NiTi_2$ intermetallic phases occur. An intermetallic phase, γCuTi, appears after 10h of milling. When the milling time was extended to 30h, only the halo peak remained. This means that milling has the effect of enhancing the chemical homogeneity until a steady state of the structural evolution is reached and a fully amorphous structure is formed.

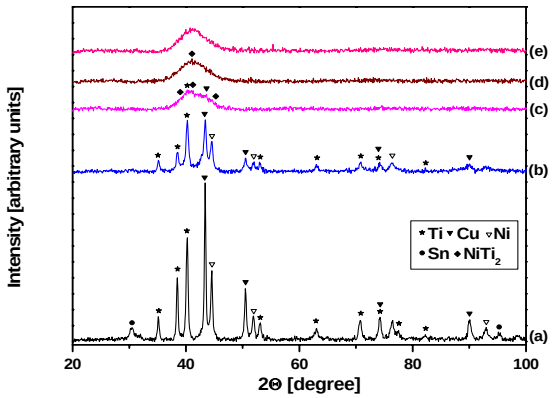

Fig. 2. XRD pattern of $Ti_{50}Cu_{25}Ni_{20}Sn_5$ milled for (a) 1h, (b) 2h, (c) 5h, (d) 10h and (e) 20h.

Figs. 2 (a)-(e) show selected XRD patterns of the $Ti_{50}Cu_{25}Ni_{20}Sn_5$ alloy after different milling time. As observed for $Ti_{50}Cu_{32}Ni_{15}Sn_3$, a halo peak appears after 2h of milling. After milling 10h, only peaks of $NiTi_2$ intermetallic phase detected in amorphous matrix. A fully amorphous $Ti_{50}Cu_{25}Ni_{20}Sn_5$ alloy can be obtained after 20 h milling.

For $Ti_{50}Cu_{23}Ni_{20}Sn_7$ alloy we could not obtain a fully amorphous alloy even after 30h of milling. $NiTi_2$ and γCuTi intermetallic phases could be detected together with the amorphous phase.

Fig. 3 illustrates the DSC scans for the amorphous $Ti_{50}Cu_{32}Ni_{15}Sn_3$, $Ti_{50}Cu_{25}Ni_{20}Sn_5$ and $Ti_{50}Cu_{23}Ni_{20}Sn_7$ alloy samples after 20h of milling. The DSC curves exhibit an endothermic event characteristic of the glass transition, followed by a supercooled liquid region (SLR) $\Delta T_x=T_x-T_g$ and a peak resulting from primary crystallization. The glass transition temperature, T_g, the onset temperature of primary crystallization, T_x and crystallization enthalpy values for all three alloys are given in Fig. 3.

The $Ti_{50}Cu_{23}Ni_{20}Sn_7$ alloy exhibited a relatively better thermal stability than other alloys.

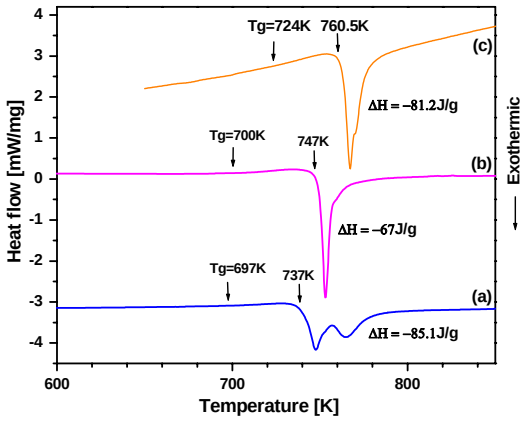

Fig. 3. DSC scans of 20h MA (a)$Ti_{50}Cu_{32}Ni_{15}Sn_3$, (b) $Ti_{50}Cu_{25}Ni_{20}Sn_5$ and (c) $Ti_{50}Cu_{23}Ni_{20}Sn_7$

The chemical composition of the as-milled samples after 20h of milling as measured by ICP shows the measured compositions does not exactly correspond to the nominal compositions, most likely due to some sticking of powder to the milling tools during milling process.

3. Summary

Amorphous $Ti_{50}Cu_{32}Ni_{15}Sn_3$, $Ti_{50}Cu_{25}Ni_{20}Sn_5$ and $Ti_{50}Cu_{23}Ni_{20}Sn_7$ powders were produced by MA. Fully amorphous structure could be obtained within the resolution of XRD patterns for $Ti_{50}Cu_{32}Ni_{15}Sn_3$ and $Ti_{50}Cu_{25}Ni_{20}Sn_5$ after 30h and 20h milling respectively, while $Ti_{50}Cu_{23}Ni_{20}Sn_7$ showed nearly full amorphization after 30h of milling. The $Ti_{50}Cu_{23}Ni_{20}Sn_7$ alloy also somewhat exhibited better thermal stability than other alloys. The small changing in the actual composition of the amorphous phase may be the reason for the differences in thermal stability between mechanically alloyed powders and melt-spun ribbons.

4. References

1. G.J. Hao, Y. Zhang, J.P. Lin, Y.L. Wang, Z. Lin, G.L. Chen, Materials Letters, **60** (2006) 1256–1260
2. J.M. Park, H.J. Chang, K.H. Han, W.T. Kim, D.H. Kim: Scripta Mater., **53** (2005), p. 1
3. D.V. Louzguine and A. Inoue: Scripta mater., **43** (2000), p. 371
4. R. Sundaresan, A.G. Jackson, S. Krishnamurthy, F.H. Froes: Mater. Sci. Eng., **97** (1988), p.115.

© Korean Powder Metallurgy Institute