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# Composition optimization of the NiZrYAl glass forming alloys

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#### Abstract

A NiZrYAl eutectic point was located by means of DTA method, and near the eutectic point, an alloy Ni<sub>56</sub>Zr<sub>16</sub>Y<sub>18.5</sub>Al<sub>9.5</sub> was found to exhibit a better GFA than the previously reported similar alloy Ni<sub>55</sub>Zr<sub>17</sub>Y<sub>17</sub>Al<sub>11</sub>, which was confirmed by the results of DSC, XRD and SEM. Both the alloys exhibit a same melting temperature ( $T_m$ ), which indicates that they belong to the same quarternary eutectic system. © 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

Since early 1990s great progress has been made in research on bulk metallic glasses (BMGs). Many bulk metallic glass systems have been developed, which offers great potential for commercial applications [1]. Of these systems Ni based bulk metallic glasses exhibit excellent mechanical properties and corrosion resistance, its strength can be as high as 3000 MPa [2,3]. Due to the small critical size [4–7] compared with other based alloys, developing a new Ni based bulk metallic glass system is more challenge. Despite the remarkable mechanical properties of these bulk metallic glasses, there is still a need to develop a material with even higher strength. These materials included some Ni based alloys. It was reported that alloy Ni<sub>55</sub>Zr<sub>17</sub>Y<sub>17</sub>Al<sub>11</sub> exhibit a wide supercooled liquid region and a good glass forming ability (GFA) [5]. In this paper the melting and solidification behaviors of the alloys near Ni<sub>55</sub>Zr<sub>17</sub>Y<sub>17</sub>Al<sub>11</sub> composition were studied, and the alloys with better GFA were found.

## 2. Experimental

NiZrYAl alloy ingots were prepared by arc melting pure metals of Ni, Zr, Y and Al together in Ti-gettered argon atmosphere. Before melting, the vacuum level in the furnace reached  $10^{-2}$  Pa. Each of ingots was melted six times to

0925-8388/\$ - see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2005.12.020 ensure uniformity in composition. DTA and DSC experiments were carried out using the TA instrument at a heating and cooling rates of 20 K/min. During the DTA experiments the alloy samples were sealed in quartz tubes to prevent the samples from oxidized. XRD experiments were also carried out with a Philip X'Pert X-ray diffraction instrument to verify the amorphous and crystalline states of the samples.

#### 3. Results and discussion

The curve 1 shown in Fig. 1 is the DTA result of the previously reported alloy Ni<sub>55</sub>Zr<sub>17</sub>Y<sub>17</sub>Al<sub>11</sub>, which exhibit a good GFA [5]. It is obvious that the alloy is not a eutectic alloy. Its onset melting temperature  $(T_m)$  is at 1134 K, but its liquidous temperature  $(T_1)$  is as high as 1401 K. The difference between  $T_1$  and  $T_m$ is 267 K. In order to study the correlation between the GFA of the NiZrYAl alloys and the eutectic transition, the eutectic point nearby should be located. More than 30 alloys were tried and finally it was found that the eutectic composition is at or very near Ni<sub>56</sub>Zr<sub>15</sub>Y<sub>23</sub>Al<sub>5</sub>. The  $T_m$  and  $T_1$  of some NiZrYAl alloys at 57 at.% Ni and 5 at.% Al are shown in Fig. 2. The curve 3 shown in Fig. 1 is the DTA result of the alloy Ni<sub>56</sub>Zr<sub>15</sub>Y<sub>23</sub>Al<sub>5</sub>, and only one eutectic transformation peak can be found either when heating or cooling the specimen. All the alloys in Figs. 1 and 2 exhibit the same  $T_{\rm m}$  (eutectic temperature), thus they are in the same eutectic system.

According to the DSC and XRD results of the rod 1.5 mm in diameter cast from the eutectic alloy  $Ni_{56}Zr_{15}Y_{23}Al_5$ ,

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Fig. 1. DTA results of the alloys studies: (a) heating; (b) cooling.



Fig. 2.  $T_1$  and  $T_m$  of the NiZrYAl alloys at 57 at.% Ni and 5 at.% Al.



Fig. 3. DSC results of the rods 1.5 mm in diameter and the ribbons.

no amorphous phase was found, which indicates that alloy Ni<sub>56</sub>Zr<sub>15</sub>Y<sub>23</sub>Al<sub>5</sub> exhibit a poor GFA. Thus we tried to look for NiZrYAl alloys which would exhibit a good GFA from the offeutectic alloys. As Ni55Zr17Y27Al11 has good GFA, the alloys  $Ni_{56}Zr_{16}Y_{20}Al_8$ ,  $Ni_{56}Zr_{16}Y_{19}Al_9$ , and  $Ni_{56}Zr_{16}Y_{18,5}Al_{9,5}$ , which are between the eutectic alloy Ni<sub>56</sub>Zr<sub>15</sub>Y<sub>23</sub>Al<sub>5</sub> and the previously reported alloy Ni<sub>55</sub>Zr<sub>17</sub>Y<sub>27</sub>Al<sub>11</sub> in composition, were tried. The rods 1.5 mm in diameter were cast from these alloys. From the DSC results shown in Fig. 3 it can be found that Alloy  $Ni_{56}Zr_{16}Y_{18.5}Al_{9.5}$  exhibits the best GFA of these alloys. The DSC results of the ribbons from alloys Ni<sub>55</sub>Zr<sub>17</sub>Y1<sub>7</sub>Al<sub>11</sub> and Ni<sub>56</sub>Zr<sub>16</sub>Y<sub>18.5</sub>Al<sub>9.5</sub> were also shown in Fig. 3, and their heat flows released during crystallization are 69 and 74 J/g, respectively. The heat flows of the rods 1.5 mm in diameter cast from the alloys Ni<sub>55</sub>Zr<sub>17</sub>Y1<sub>7</sub>Al<sub>11</sub> and Ni<sub>56</sub>Zr<sub>16</sub>Y<sub>18.5</sub>Al<sub>9.5</sub> are 34 and 69 J/g, respectively. Thus the amount of the glass phases in the rods of the alloys  $Ni_{55}Zr_{17}Y_{17}Al_{11}$  and  $Ni_{56}Zr_{16}Y_{18.5}Al_{9.5}$  are 34/69 = 49.3%and 69/74=93.2%, respectively. The XRD results of rods 1.5 mm in diameter cast from alloys Ni<sub>55</sub>Zr<sub>17</sub>Y<sub>17</sub>Al<sub>11</sub> and Ni<sub>56</sub>Zr<sub>16</sub>Y<sub>18.5</sub>Al<sub>9.5</sub> shown in Fig. 4, further confirm that the amount of crystalline phases in Ni<sub>56</sub>Zr<sub>16</sub>Y<sub>18.5</sub>Al<sub>9.5</sub> is less than that in  $Ni_{55}Zr_{17}Y_{17}Al_{11}$ . Though fully amorphous rod has not been obtained under our condition it still could be found that alloy Ni<sub>56</sub>Zr<sub>16</sub>Y<sub>18.5</sub>Al<sub>9.5</sub> exhibits a better GFA than that of the previously reported alloy Ni<sub>55</sub>Zr<sub>17</sub>Y<sub>17</sub>Al<sub>11</sub>. The micrographs of the etched cross-section of the rods 1.5 mm in diameter cast from both the alloys were shown in Fig. 5. In the rod of the alloy Ni<sub>55</sub>Zr<sub>17</sub>Y<sub>17</sub>Al<sub>11</sub> the amorphous phase is found only in the rim, and much crystalline phase dendrites is found in the center where the cooling rate is lower. In the rod of the alloy Ni<sub>56</sub>Zr<sub>16</sub>Y<sub>18.5</sub>Al<sub>9.5</sub> there is only very little isolated crystal crystalline phase in the amorphous matrix in the center.

Eutectic transformation is very important to GFA of alloys [8,9]. In fact most BMGs alloys are around the eutectic compositions. In equilibrium phase transformations entirely eutectic growth can occur only at exact eutectic composition and eutectic

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