The Structural Characterization of Ni–Ti–Zr Metallic Glass

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Metallic glasses, in contrast to its crystalline counterparts, exhibit unique mechanical and structural properties, which make them attractive for practical applications. Especially Ni–Ti–Zr metallic glass is a promising alloy for micromechanical systems because of its known shape memory properties. Shape memory effect is connected with structural phase transformation. In this paper, the ambient-temperature-structure of Ni–Ti–Zr metallic glass is investigated using transmission electron microscopy and synchrotron X-ray diffraction, the surface and chemical analysis is documented using scanning electron microscopy. Thermal stability of the alloy has been determined using differential scanning calorimetry.

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1. Introduction

Shape memory alloys (SMA) belong to smart materials with capability of recovery its original shape by heating after high degree of deformation. Ni–Ti–Zr is seen as one of the most promising high-temperature SMAs. This alloy has many positive characteristics of the binary system and also significantly increases martensite-to-austenite transformation temperature, which can be controlled with the Zr content [1–3]. Ni–Ti is well known SMA and has suitable mechanical properties, corrosion resistance and biocompatibility [4]. Since the shape memory effect is manifested only in crystalline materials, our goal was to produce and investigate amorphous precursor material, from which reliable shape memory material with interesting mechanical properties will be prepared later.

2. Material preparation

For preparation of the master alloy, elements of high purity are needed in order to avoid formation of unwanted phases, e.g. oxides, and/or intermetallic. For preparation of the master alloy, elements of purity 99.9% were used. The powder material was compressed by press machine to the tablet form, which suppresses material losses during subsequent arc-melting. For master alloy preparation, Mini Arc Melting System MAM-1 was used. The sample has been re-melted 3 times in order to ensure homogeneous elements distribution within the entire volume of alloy. The resulting master alloy had lens-like shape. For the preparation of ribbon with composition of Ni\textsubscript{60}Ti\textsubscript{25}Zr\textsubscript{15} at.% alloy Melt Spinner SC was used. The final ribbon has thickness of 60 µm and width of 4 mm. The melting point of Ni\textsubscript{60}Ti\textsubscript{25}Zr\textsubscript{15} has been estimated to be 1657 K.

Differential scanning calorimetry (DSC) is a method commonly used for determining the thermal stability characteristics of amorphous alloys. DSC measurements were performed using the Perkin Elmer DSC 8000 under argon atmosphere with heating rate 10 K/min.

3. Experimental part

Figure 1 shows DSC curve of the as-quenched alloy measured at heating rate 10 K/min. It exhibits one endothermic event and three exothermic peaks as a characteristic feature for amorphous materials.

Fig. 1. DSC curve obtained at constant heating rate of 10 K/min.

The glass transition temperature ($T_g$) represented by endothermic event is at 790 K. The first observable crystallization starts at temperature $T_{x1onset} = 807$ K. The second crystallization starts at temperature $T_{x2onset} = 875$ K. The third crystallisation starts at $T_{x3onset} = 1003$ K. The super-cooled liquid region calculated as $\Delta T = T_{x1onset} - T_g$ is 17 K wide for the applied heating rate.
By heating the as-quenched alloy to crystallisation temperatures, the sample becomes crystalline having significantly different properties. In the associated paper [5] the structural and magnetic properties were investigated. Based on DSC results the as-quenched state as well as samples heated to \( T_{x1}, T_{x1\text{out}}, T_{x2}, T_{x2\text{out}} \) and \( T_{x3} \) were chosen (Table I).

<table>
<thead>
<tr>
<th>( T_g ) [K]</th>
<th>( T_{x2} ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>790</td>
<td>890</td>
</tr>
<tr>
<td>( T_{x1\text{onset}} ) [K]</td>
<td>( T_{x2\text{onset}} ) [K]</td>
</tr>
<tr>
<td>807</td>
<td>914</td>
</tr>
<tr>
<td>( T_{x1\text{onset}} ) [K]</td>
<td>( T_{x3} ) [K]</td>
</tr>
<tr>
<td>837</td>
<td>1023</td>
</tr>
<tr>
<td>( T_{x2\text{onset}} ) [K]</td>
<td>( \Delta T ) [K]</td>
</tr>
<tr>
<td>875</td>
<td>17</td>
</tr>
</tbody>
</table>

For the study of ribbon surfaces, the scanning electron microscope (SEM) Tescan Vega-3 XMU was used. Accelerating voltage was set on 20 kV with respect to detected elements in regime of secondary electrons. Imaging in secondary electrons and energy-dispersive X-ray spectroscopy (EDS) spectrum of the alloy free surface (Fig. 2a), wheel surface (Fig. 2b) and cross-section (Fig. 3a) were done.

![Fig. 2. (a) SEM image of Ni\(_{60}\)Ti\(_{25}\)Zr\(_{15}\) free surface. (b) SEM image of Ni\(_{60}\)Ti\(_{25}\)Zr\(_{15}\) wheel surface.](image)

From the EDS analysis, it is evident that prepared sample is consistent with the intended composition (Table II).

<table>
<thead>
<tr>
<th>Area</th>
<th>Ti</th>
<th>Ni</th>
<th>Zr</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>free (Fig. 2a)</td>
<td>27.31</td>
<td>58.04</td>
<td>14.66</td>
<td>100.00</td>
</tr>
<tr>
<td>wheel (Fig. 2b)</td>
<td>27.42</td>
<td>57.39</td>
<td>15.19</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Chemical composition across the sample was verified by line EDS analysis, and it can be concluded that the sample is completely homogeneous over the sample thickness (Fig. 4). From the images, we can also estimate that the thickness of the ribbon is \( \approx 60 \mu\text{m} \) (Fig. 3b).

The structural state of the prepared as-quenched alloy has been examined also by transmission electron microscopy (TEM) JEOL JEM 2100F UHR equipped by Schottky FEG cathode. Applied accelerating voltage was 200 kV. Both, the image and the selected area diffraction pattern were taken in order to determine the amorphous/crystalline nature of as-quenched Ni\(_{60}\)Ti\(_{25}\)Zr\(_{15}\) alloy (Fig. 5). The imaged structure does not reveal presence of any nanocrystals and confirms fully amorphous phase. Embedded electron diffraction pattern taken from the selected area shows typical diffuse rings and also confirms amorphous nature of the investigated sample. Even on diffraction pattern there is no indication of any crystalline phase present.

![Fig. 3. (a) SEM image of Ni\(_{60}\)Ti\(_{25}\)Zr\(_{15}\) cross-section, (b) depicted line for EDS line profiles acquisition of Ni\(_{60}\)Ti\(_{25}\)Zr\(_{15}\) ribbon in cross-section.](image)

![Fig. 4. Line profiles of measured EDS spectra of Ni\(_{60}\)Ti\(_{25}\)Zr\(_{15}\) cross-section.](image)

Experimental measurements of the phase composition of the alloy were examined using X-ray diffraction at the synchrotron radiation sources in Deutsches Elektronen Synchrotron — DESY (Germany, Hamburg). The results of processed synchrotron XRD data are shown in Fig. 6. Obtained diffraction profile also confirms fully amorphous nature of Ni\(_{60}\)Ti\(_{25}\)Zr\(_{15}\) alloy.

### 4. Conclusions

1. The DSC curve of the alloy shows three distinctive exothermic peaks corresponding to different phase transi-
Fig. 5. Bright-field TEM image and diffraction pattern of Ni$_{60}$Ti$_{25}$Zr$_{15}$ melt-spun ribbons.

Fig. 6. XRD patterns of Ni$_{60}$Ti$_{25}$Zr$_{15}$.

tions of the alloy. The DSC curve shows one-endothermic three exothermic events. The endothermic event corresponds to glass transition temperature ($T_g$) and it was determined at 790 K. The first, the second, and the third observable crystallizations start at the temperatures 807, 875, and 1073 K, respectively. Super cooled liquid region width is 17 K.

2. TEM, DSC, and XRD analyses proved that as-quenched sample Ni$_{60}$Ti$_{25}$Zr$_{15}$ is fully amorphous.

3. Examined chemical composition was confirmed by point EDS analysis and by line EDS analysis across the edge. The sample exhibits acceptable grade of homogeneity.

4. In the related paper [5] saturation magnetization measurements of the sample depending on temperature was performed, during which segregation of pure nickel from solid structure was noticed. The most appropriate explanation of this peculiar phenomenon is the superposition of several effects. The first one is the decomposition of structure well-known from Ni-Ti shape memory alloy [6] via precipitation of Ni-rich particles. The second, with the decrease of mixing enthalpy $\Delta H^\text{mix}$, the tendency towards formation of intermetallic phase is increasing, and if we consider negative $\Delta H^\text{mix}$ of Ni-Ti and Ni-Zr pairs, the precipitation of Ni-rich particles should be more understandable. However, pure nickel separation may be caused by the third effect. $\Delta H^\text{mix}$ for Ti–Zr pair is equal to 0 kJ/mol, which means that Ti–Zr has great potential to create simple solid solution with complete mutual solubility in solid state. The formation of the Ti–Zr solid solution is also encouraged by the same hexagonal lattice of both elements and small difference in electronegativity. According to all that, we assume the Ni–Ti–Zr alloy decreases its overall volume energy by separation of Ti–Zr atoms from the structure, forming its solid solution and changing nickel paramagnetic state into ferromagnetic.

Acknowledgments

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References