Martensitic transformation and microstructure in Nb–Ru–Fe shape memory alloys

Xin Gao, Wei Cai∗, Y.F. Zheng, L.C. Zhao

School of Materials Science and Engineering, Harbin Institute of Technology, P.O. Box 405, Harbin 150001, China

Received 22 April 2005; received in revised form 31 January 2006; accepted 9 February 2006

Abstract

The martensitic transformation behavior and microstructure in Nb–Ru–Fe alloys have been investigated by means of differential scanning calorimetry, X-ray diffraction, optical microscopy and transmission electron microscopy. It is shown that two-step phase transformation of \( \beta \rightarrow \beta' \rightarrow \beta'' \) occurs during cooling from high temperature to room temperature. The monoclinic crystal structure remains unchanged with the addition of Fe, but all lattice parameters of the martensite unit cell decrease with increasing Fe content. The crystal symmetry of martensite is \( \text{Cmmm} \). The \( \beta'' \) martensite variants exhibit self-accommodation morphology and the substructure is determined to be \( (1\,0\,1) \) type I twin.

Keywords: Nb–Ru–Fe alloy; High-temperature shape memory alloy; Microstructure; Martensitic transformation

1. Introduction

High-temperature shape memory alloys (HTSMA) are attractive in the field of shape memory and superelastic applications. Extensive research has been carried out on these alloys, e.g. on Ti–Ni–Hf, Cu–Zn–Al, Ti–Pd–Ni, etc. [1–5], but their martensitic transformation temperatures are usually lower than 600 °C. Nb–Ru alloy is one of the potential high-temperature shape memory alloys since its martensitic transformation temperature is as high as about 1100 °C. Clearly, this kind of shape memory alloy is the promising for use in high-temperature environment, such as aerospace. Thus, some research including shape memory characteristics, martensitic transformations and mechanical behavior of the alloys has been done in recent years [6–8]. However, it is found that Nb–Ru alloy shows poor toughness at room temperature which limits its applications [9]. Previous work indicated that the addition of third elements such as Fe, Co commonly improve the mechanical properties of Ti–Pd and Ti–Ni binary alloys [10]. In the present work, the effect of Fe content on the martensitic transformation and microstructure of Nb–Ru–Fe alloys is studied.

2. Experimental

Nominal compositions (numbers indicate at.%) of the experimental material used in this study are \( \text{Nb}_{50}\text{Ru}_{43}\text{Fe}_7 \) and \( \text{Nb}_{50}\text{Ru}_{36}\text{Fe}_{14} \). Button-shape samples with several grams weight are melted in arc-melting furnace under argon atmosphere using 99.95% Nb thread, 99.95% Ru powders and 99.9% Fe thread. The low mass loss during sample fabrication assures that the composition remelting several times are within 1 at.% of the composition.

Foil specimens of a thickness of 50 μm and a diameter of 3 mm are prepared by mechanical polishing, followed by etching in a mixture of \( \text{H}_2\text{SO}_4 \) and \( \text{CH}_3\text{OH} \) with the volume ratio of 1:4. Transmission electron microscopy (TEM) is performed on a Philips CM20 microscope operating at 200 kV.

3. Results and discussion

3.1. Martensitic transformation

Fig. 1 shows the DSC curves of the as-cast Nb–Ru–Fe alloys. It is shown that the as-cast Nb–Ru–Fe alloys exhibit a two-step martensitic transformation behavior both in heating and cooling. Nb–Ru–Fe alloys. According to work of Fonda et al. [7], the lattice types of high-temperature phase, mid-temperature
Fig. 1. DSC curves of Nb–Ru–Fe alloys specimen: (a) Nb50Ru36Fe14 and (b) Nb50Ru43Fe7.

Fig. 2. X-ray diffraction patterns of Nb–Ru–Fe alloys at room temperature.

Table 1
Transformation temperatures of Nb–Ru–Fe alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Ms1 (°C)</th>
<th>Ms2 (°C)</th>
<th>As1 (°C)</th>
<th>As2 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb50Ru50</td>
<td>887</td>
<td>741</td>
<td>890</td>
<td>725</td>
</tr>
<tr>
<td>Nb50Ru43Fe7</td>
<td>841</td>
<td>689</td>
<td>830</td>
<td>680</td>
</tr>
<tr>
<td>Nb50Ru36Fe14</td>
<td>795</td>
<td>637</td>
<td>797</td>
<td>606</td>
</tr>
</tbody>
</table>

phase and low temperature phase are identified to be CsCl (B) type, face-centered tetragonal (B’) type, monoclinic (B’’) type, respectively. The transformation temperatures of Nb50Ru43Fe7 and Nb50Ru36Fe14 alloys are determined by differential scanning calorimetry (DSC) shown in Table 1. It is obvious that the transformation temperatures decrease with increasing Fe content.

In order to study the effects of Fe addition on the crystal structure and lattice parameters of Nb–Ru binary alloys, X-ray diffraction experiments have been made. The results obtained are shown in Fig. 2. The exact lattice parameters of the as-cast Nb50Ru50, Nb50Ru43Fe7 and Nb50Ru36Fe14 are listed in Table 2, calculated with the help of high angle reflections of X-ray diffraction spectra. The monoclinic crystal remains unchanged with the addition of Fe but all lattice parameters of the martensite unit cell decrease with increasing Fe content. The crystal symmetry of martensite is Cm m m. That means only β” martensite exists at room temperature. The X-ray peaks of Nb–Ru–Fe alloys are wider and weaker with the addition of Fe than that of Nb–Ru binary alloy.

Table 2
Lattice parameters of martensite of Nb–Ru–Fe alloys at room temperature

<table>
<thead>
<tr>
<th>Alloys</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
<th>β (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb50Ru50</td>
<td>0.834</td>
<td>0.446</td>
<td>0.545</td>
<td>98.9</td>
</tr>
<tr>
<td>Nb50Ru43Fe7</td>
<td>0.816</td>
<td>0.421</td>
<td>0.523</td>
<td>96.3</td>
</tr>
<tr>
<td>Nb50Ru36Fe14</td>
<td>0.804</td>
<td>0.407</td>
<td>0.507</td>
<td>95.6</td>
</tr>
</tbody>
</table>

3.2. Microstructure

Fig. 3 shows the microstructure of the as-cast Nb50Ru43Fe7 alloy at room temperature. It is a typical dendritic structure with the grain size uniformly distributed. After long time annealing and furnace cooling, typical regularly alternated bands can be found inside each grain without any secondary phase been found, that means the microstructure is only the solid solution of Nb50Ru43Fe7 alloy. It can also be found that the average grain size of Nb–Ru–Fe alloy is refined than that of Nb–Ru alloy, which means Fe addition can reduces the grain size.
The room-temperature crystal structure of the as-cast Nb–Ru–Fe alloys is analyzed with electron diffraction. Fig. 4(a) shows the typical TEM bright field image of the Nb50Ru50 alloy. It can be described as the shape accommodation microstructure, the dominant morphology is the alternating regular fine bands inside each martensite variant. This is similar to the feature of the martensite variants in TiNi shape memory alloy. The intervariant orientation relationship is difficult to be identified since the opportunity to observe the intervariant boundary due to the big grain size.

The typical morphologies of martensite variant in Nb50Ru43Fe7 and Nb50Ru36Fe14 alloys are similar to that of Nb50Ru50 alloy, while the width of martensite variant bands increases with increasing Fe content. Some stacking faults can be observed in these bands in Nb50Ru43Fe7 and Nb50Ru36Fe14 specimens too. Further investigation would be undertaken to explain the factors which affects the microstructure of Nb–Ru–Fe alloys, Fig. 4(d) is the corresponding electron diffraction pattern of the neighboring bands inside one martensite variant taken from [010] zone orientation, indicating the substructure of the single variant is (101) type I twinning.

4. Conclusions

1. Two-step phase transformation of $\beta \rightarrow \beta' \rightarrow \beta''$ occurs during cooling from high temperature to room temperature in Nb–Ru–Fe alloys.
2. The monoclinic crystal structure remains unchanged with the addition of Fe, but all lattice parameters of the martensite unit cell decrease with increasing Fe content. The crystal symmetry of martensite is $Cmmm$.
3. The $\beta''$ martensite variants exhibit self-accommodation morphology and the substructure is determined to be (101) type I twin.

Acknowledgement

This research is supported by the National Natural Science Foundation of the People’s Republic of China, Grant No. 50531020.

References