Microstructure and martensitic transformation of Ti$_{49}$Ni$_{51}$ – $x$Hf$_x$ high temperature shape memory alloys

Yunxiang Tong$^{a,*}$, Feng Chen$^a$, Bing Tian$^a$, Li Li$^a$, Yufeng Zheng$^{a,b}$

$^a$ Center for Biomedical Materials and Engineering, Harbin Engineering University, Harbin 150001, China
$^b$ Department of Advanced Materials and Nanotechnology, College of Engineering, Peking University, Beijing, China

**Abstract**

In present work, the microstructure and martensitic transformation of Ti$_{49}$Ni$_{51}$ – $x$Hf$_x$ ($x = 3$–$15$) alloys were studied. The microstructure of Ti$_{49}$Ni$_{51}$ – $x$Hf$_x$ alloys consists of B19' martensite and (Ti,Hf)$_2$Ni phase at room temperature. The martensitic transformation behavior is characterized by a single-stage transformation. With increasing Hf content, the transformation temperature increases from 75 to 279 °C resulting from the reduced valence electron concentration, indicating that the replacement of Hf for Ni is effective in increasing the transformation temperatures. The results suggest that the Ti$_{49}$Ni$_{51}$ – $x$Hf$_x$ shape memory alloy is one of potential candidates for high temperature applications.

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**1. Introduction**

TiNi-based high temperature shape memory alloys (SMAs) have attracted much attention because of their potential applications for high temperature conditions (higher than 100 °C), including NiTiX ($X = Hf, Zr$, thereafter, NiTiX refers to the alloys in which the $X$ is in replacement of Ti) [1], TiNiX ($X = Pt, Pd, Au$, thereafter, TiNiX refers to the alloys in which the $X$ is in replacement of Ni) [2] alloys. Among them, the NiTiHf alloys resulting from the replacement of Hf for Ti seem more practical for engineering applications due to their high transformation temperature, superior shape recovery properties and lower cost as compared to TiNiX ($X = Pt, Pd, Au$) alloys [3]. On the other hand, the ductility of NiTiHf alloys has been greatly reduced as compared to that of NiTi binary alloys [4]. To date, several important aspects of the NiTiHf alloys have been reported, including processing [5,6], martensitic transformation [7,8], precipitation behavior during ageing [9,10], mechanical property and shape memory effect (SME) [11–13], effect of ternary alloying elements [5,14], effort to improve the ductility [5] etc. Very recently, the results reported by Zarinejad et al, show that the replacement of Hf for Ni is effective in increasing the martensitic transformation temperature, which may provide an opportunity to develop the new high temperature SMAs [15]. They further reported that for TiNiHf alloys, Hf occupies the Ni sites [16]. However, so far, no further reports on the effect of Hf content on the microstructure and martensitic transformation behavior of the TiNiHf alloy are available.

* Corresponding author. Center for Biomedical Materials and Engineering, College of Materials Science and Chemical Engineering, Harbin Engineering University, 145 Nantong Da Street, 150001 Harbin, China. Tel.: +86 451 8251 8173; fax: +86 451 8251 8644.

**E-mail address:** tongyx@hrbeu.edu.cn (Y. Tong).

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**2. Experimental**

A series of Ti$_{49}$Ni$_{51}$ – $x$Hf$_x$ ($x = 3, 5, 7, 10, 15$ at.%) ingots were prepared by arc-melting of 99.99% Ti plate, 99.9% Ni plate, 99.95% Hf wire in a water cooled copper crucible under an argon atmosphere. The ingots were remelted at least six times, being flipped over after each melting step in order to ensure homogeneity in composition. A pure Ti button was also melted and used as a getter. After melting, the ingots were homogenized at 900 °C for 5 h in a vacuum-sealed quartz tube following by quenching into water. The samples were spark-cut from the ingots with the thickness of 2 mm and polished for the subsequent measurements. The transformation temperatures were determined by differential scanning calorimetry (DSC) using a Perkin Elmer diamond DSC calorimeter. The heating and cooling rate was 20 °C/min. Microstructure was observed on a Quanta 200 scanning electron microscope (SEM) operated at 20 kV equipped with energy dispersive X-ray spectrometry (EDS). Before measurement, the EDS system was carefully calibrated. The X-ray diffraction (XRD) was carried out on a PANalytical Xpert pro diffractometer using Cu Kα radiation by step-scanning in the 20 range of 10–100°.

**3. Results and discussion**

Fig. 1 shows the XRD patterns of the Ti$_{49}$Ni$_{51}$ – $x$Hf$_x$ alloys with different Hf contents. All patterns can be indexed as a mixture of B19'

In the present work, several Ti$_{49}$Ni$_{51}$ – $x$Hf$_x$ alloys with different Hf contents were studied by X-ray diffraction (XRD) and differential scanning calorimetry (DSC) method. On the basis of experimental results, the effect of Hf on the martensitic transformation of the Ti$_{49}$Ni$_{51}$ – $x$Hf$_x$ alloys was discussed.

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type martensite and a fcc structure (Ti,Hf)2Ni phase, which is similar to the solution-treated Ni49Ti41Hf10 alloy [3]. Table 1 shows the effect of Hf content on lattice parameters of B19' martensite and (Ti,Hf)2Ni phase. The lattice parameters of B19' martensite and (Ti,Hf)2Ni phase are close to the reported values [12]. With increasing the Hf content, the lattice parameter of (Ti,Hf)2Ni phase continuously increases.

Fig. 2 shows the typical back-scattering electron image of the Ti49Ni41Hf10 alloy. Other alloys show the quite similar results. The microstructure of the Ti49Ni41Hf10 alloys consists of two different phases, being consistent with the XRD results. The compositions of the two phases determined by the EDS analysis are listed in Table 2 with an estimated error of ±2 at.%. It is seen that for the two different phases, the Ni content remains almost constant, irrespective of the Hf content. The composition of the dark area can be generally expressed as (Ti,Hf)2Ni in atomic %, that of the bright area is (Ti,Hf)-rich Ni50(Ti,Hf)50. This means that the bright phase is Ni-rich Ni50Ti29.4Hf20 alloy [10]. With increasing Hf content, the continuous (Ti,Hf)2Ni phase.

Fig. 3(a) plots the DSC curves of the Ti49Ni51Hf10 alloy. For all alloys with different Hf contents, the Ni content remains almost constant, irrespective of the Hf content. The microstructure is characterized by the irregular morphology of martensite surrounding by the continuous (Ti,Hf)2Ni phase, suggesting that the formation of (Ti,Hf)2Ni phase in the solidification is prior to that of Ni50(Ti,Hf)50 parent phase. Fig. 3(a) plots the DSC curves of the Ti49Ni51Hf10 alloys with different Hf contents. It is seen that both forward and reverse transformation curves of all alloys are characterized by one stage transformation, same as the solution-treated Ti49.8Ni50.2Hf10 alloy [3]. No R-phase can be identified, which is different from the results in the aged Ni-rich Ni50.6Ti29.4Hf20 alloy [10]. With increasing Hf content, the transformations shift to high temperature side, same as the trend in the Ni49.8Ti50.2−xHf x alloys [17]. When more than 10 at.% Hf was added, the transformation temperature is higher than 100 °C, indicating the potential as high temperature SMAs. The enthalpy changes associated with the forward and reverse transformation are determined to be about −9 to −4.5 and 5−8.5 J/g, respectively. Fig. 3(b) shows the transformation temperatures of the present Ti49Ni51Hf10 alloys and the reported solution-treated Ni49.8Ti50.2−xHf x alloys as a function of Hf content, in which Mf denotes martensitic transformation start temperature, Mr martensitic transformation finish temperature, A f reverse transformation start temperature, A r reverse transformation finish temperature. It is seen that the present Ti49Ni51−xHf x alloys have overall higher values than the reported Ni49.8Ti50.2−xHf x alloys with the identical Hf content, indicating that the replacement of Hf for Ni is more effective in increasing the transformation temperatures than that for Ti. The dependence of martensitic transformation temperature of Ni-Ti-based SMAs on composition could be correlated with the variations of valence electron concentration (Cv) which is defined as the ratio of the number of valence electrons to the total number of electrons of the alloy [15]. Following Ref. [15], the Cv was calculated and its relationship with Mf temperature is shown in Fig. 3(c). It is evident that with increasing the Cv resulting from the decrease of Hf content, the Mf temperature decreases. The difference of transformation temperatures between the present alloys and the Ni49.8Ti50.2−xHf x alloys agrees well with the results reported by Zarinejad et al. in which the transformation temperature of Ti50Ni30Hf20 alloy is higher than that of Ni50Ti30Hf20 alloy since the former has the lower Cv [16]. It seems that the present case can be rationalized by the same mechanism.

4. Conclusions

The microstructure of Ti49Ni51−xHf x (x = 3−15) alloys consists of the B19' martensite and the (Ti,Hf)2Ni (x = 3−15) alloys. The martensite with an irregular morphology is surrounded by the continuous (Ti,Hf)2Ni phase.

### Table 1

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Lattice parameters (nm)</th>
<th>B19' martensite</th>
<th>(Ti,Hf)2Ni</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
<th>β (°)</th>
<th>Volume (10−3 nm3)</th>
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<tr>
<td>Ti49Ni41Hf5</td>
<td>1.1382</td>
<td>0.2923</td>
<td>0.4097</td>
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<td>100.04</td>
<td>57.0268</td>
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<td>1.1389</td>
<td>0.2918</td>
<td>0.4099</td>
<td>0.4852</td>
<td>100.40</td>
<td>57.0811</td>
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<td>1.1437</td>
<td>0.2951</td>
<td>0.4136</td>
<td>0.4850</td>
<td>99.66</td>
<td>58.0600</td>
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</tr>
<tr>
<td>Ti49Ni36Hf15</td>
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<td>0.2976</td>
<td>0.4117</td>
<td>0.4865</td>
<td>99.32</td>
<td>58.8047</td>
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### Table 2

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Composition (at%)</th>
<th>Bright phase</th>
<th>Dark phase</th>
</tr>
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<tr>
<td>Ti49Ni44Hf5</td>
<td>49 47 4</td>
<td>34 62 4</td>
<td></td>
</tr>
<tr>
<td>Ti49Ni41Hf5</td>
<td>50 45 5</td>
<td>33 60 7</td>
<td></td>
</tr>
<tr>
<td>Ti49Ni36Hf15</td>
<td>49 38 13</td>
<td>34 54 12</td>
<td></td>
</tr>
<tr>
<td>Ti49Ni36Hf15</td>
<td>49 33 18</td>
<td>32 51 17</td>
<td></td>
</tr>
</tbody>
</table>
The martensitic transformation is characterized by the single-stage transformation. With increasing the Hf content, the transformation temperatures elevate due to the reduced $C_v$. The replacement of Hf for Ni is more effective in increasing the transformation temperatures than that of Hf for Ti.

References


Fig. 3. (a) DSC curves (solid line: cooling; dash line: heating) for the samples with different Hf contents showing the martensitic transformation behavior. (b) Effect of Hf content on the transformation temperatures of Ti$_{48}$Ni$_{38}$Hf$_x$ and Ni$_{49.8}$Ti$_{50.2}$Hf$_x$ alloys. (c) Effect of the valence electron concentration ($C_v$) on the $M_s$ temperature of Ti$_{48}$Ni$_{38}$Hf$_x$ alloys. The corresponding Hf contents are also shown.