Martensitic Transformation of Ti_{50}Ni_{25−x}Pd_{25−y}Cu_{x+y} Quaternary Shape Memory Alloys with \( X, Y \leq 10 \) at\% 

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1. Introduction 

It is well known that equiatomic TiNi shape memory alloy (SMA) exhibits martensitic transformation of B2 parent phase to B19\(^*\) monoclinic martensite with its martensitic transformation starting temperature, Ms, below 373 K.\(^1\) Ti\(_{50}\)Ni\(_{50}\) ternary alloy has a Ms of about 20 at\% has been found in Ti\(_{50}\)Ni\(_{50}\) as a high temperature SMA (HTSMA) in the temperature range from about 373 to 773 K.\(^2\)\(^-\)\(^4\) Khachin et al.\(^2\) reported that, from XRD studies, the transformation sequence of Ti\(_{50}\)Ni\(_{50}\) ternary SMAs with X \( \geq 20 \) at\% has been found to remain almost constant and is not strongly dependent on Cu addition.\(^5\) From the periodic table, Cu is also neighboring to Pd. Meanwhile, Cu is much cheaper than Ni and Pd. Therefore, it is worthy to study the martensitic transformation of Cu added Ti-Ni-Pd quaternary HTSMAs. In this study, Ti\(_{50}\)Ni\(_{50}\)Pd\(_{25}\) is chosen as the alloy to replace some of its Ni and/or Pd by Cu due to its moderate Ms temperature (Ms = 416.8 K)\(^6\) and its typical B2 ↔ B19 transformation.\(^7\) The effects of Cu addition on Ms temperature, transformation enthalpy, hardness, cold-rolling workability and lattice constants of Ti\(_{50}\)Ni\(_{25−x}\)Pd\(_{25−y}\)Cu\(_{x+y}\) HTSMAs with X, Y \( \leq 10 \) at\% are studied. Meanwhile, the effects of annealing and thermal cycling on the transformation behavior and the precipitates formation of Ti\(_{50}\)Ni\(_{15}\)Pd\(_{25}\)Cu\(_{10}\) HTSMA are also discussed. 

2. Experimental Procedure 

Eight Ti\(_{50}\)Ni\(_{25−x}\)Pd\(_{25−y}\)Cu\(_{x+y}\) ternary or quaternary HTSMA with X, Y \( \leq 10 \) at\% listed in Table 1 were prepared by vacuum arc-remelter (VAR) in which high purity Ti (99.8 mass\%), Ni (99.9 mass\%), Cu (99.9 mass\%) and Pd (99.95 mass\%) were remelted six times in a high purity argon atmosphere. The weight of the VAR ingot for each alloy is about 20 g. These ingots were hot-rolled at 1173 K to plates of 1.3 mm thickness by STANAT TA-515-5-5X8 rolling machine at a constant rolling speed of 10 m/min. These hot-rolled plates were then solution-treated at 1173 K for 1 h and subsequently quenched into water. The oxidation layer of the plate was chemically etched by a solution composed of HF : HNO\(_3\) : H\(_2\)O = 1 : 5 : 20 in volume. After removing the oxidation layer, the thickness of these plates became about 1.2 mm. 

Ms temperature and transformation enthalpy were determined by TA Q10 DSC equipment with 10 K/min cooling/ heating rate. For DSC tests, specimens about 20 mg were cut from the hot-rolled strips, sealed in evacuated quartz tubes and then annealed at 523 K~1073 K for different time intervals. In order to study the effect of Cu addition on workability, the hot-rolled plates were further cut into strips of 60 mm × 15 mm with the longitudinal along the hot-rolling direction. Then, they were cold-rolled along the hot-rolling direction at room temperature by the same rolling machine and rolling speed with the thickness reduction about 3~5% for each pass. Microvickers hardness (HV) was measured by Mitutoyo HM micro-Vickers hardness tester with the applied load and time being 500 g and 15 s, respectively. Specimens for hardness tests were polished by up to #2000 sandpapers. The Hv hardness values were determined from the average of at least 5 measurements for each specimen. Lattice constants of B19 martensite were measured from the XRD results conducted by Philip PW1830 instrument equipped with CuK\(_\alpha\) radiation at room temperature. The applied voltage, applied current, scanning range, scanning speed and

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3.1.1 The change of Ms temperature and transformation enthalpy during cooling (ΔHc) were set at 30 kV, 30 mA, 3°/min and 0.02°/step, respectively. The specimens for XRD tests were mechanically ground by up to #2000 emery paper and then polished with 0.3 μm Al2O3 powder. A FEI Tecnai G2200 TEM equipped with EDS at 200 kV was used to observe the alloy microstructures and identify the formed precipitates. TEM specimens were prepared by double-jet electropolishing using an electrolyte solution of 20 vol% sulfuric acid and 80 vol% methanol under 273 K. The applied voltage and current for electropolishing were 15 V and 30 mA, respectively. The chemical composition analyses of the matrix and precipitates were determined from the average of at least 5 EDS measurements for each TEM specimen. The EDS composition was calibrated by pure Ti, Ni, Pd and Cu as the standards. The thermal cycling test was conducted in between 573 K salt bath and room temperature water.

3. Results and Discussion

3.1 The effects of Cu additions on Ti50Ni25−xPdx−yCuX+Y HTSMAs

3.1.1 The change of Ms temperature and transformation enthalpy

Figure 1 shows the DSC result of as solution-treated Ti50Ni15Pd25Cu10 specimen in which only B2 ↔ B19 martensitic transformation peak appears. From Fig. 1, Ms temperature and transformation enthalpy during cooling (ΔHc) are 453.8 K and 20.1 J/g, respectively. The DSC results of the other as solution-treated Ti50Ni25−xPdx−y−CuX+Y specimens are similar to Fig. 1 with different Ms and ΔHc. Table 1 lists the data of Ms and ΔHc of all as solution-treated Ti50Ni25−xPdx−y−CuX+Y specimens. From Table 1, the effects of composition on Ms and ΔHc can be formulated by the linear regression method as follows:

\[
\text{Ms (°C)} = 424.2 + 2.7X - 9.7Y \quad (1)
\]

\[
\Delta Hc (J/g) = 17.1 + 0.2X - 0.6Y \quad (2)
\]

The correlation coefficients, R-factors, of eqs. (1) and (2) are 0.99 and 0.97, respectively. From eq. (1), the substitution of Ni by Cu in Ti50Ni25−xPdx−yCuX+Y specimens increases both Ms and ΔHc but that of Pd by Cu decreases both with the former is more significant than the latter. According to Table 1, the linear regression results of ΔHc vs. Ms can be plotted in Fig. 2. From Fig. 2, the linear relationship between Ms and ΔHc means that the transformation behavior of these Ti50Ni25−xPdx−y−CuX+Y HTSMAs follows Clausius-Clapeyron equation and exhibits the thermoelastic martensitic transformation characteristics.

3.1.2 Hardness and cold-rolling workability

The experimental results of Hv hardness and cold-rolling workability are also listed in Table 1. Here, the cold-rolling workability is defined as the maximum reducible thickness of the strip during cold-rolling with no crack occurring at the strip rims. From Table 1, the effect of composition on Hv hardness and cold-rolling workability can be formulated by the linear regression method as follows:

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Ti50Ni25−xPdx−y−CuX+Y (at%)</th>
<th>Ms/K</th>
<th>ΔHc/J·g−1</th>
<th>Hv</th>
<th>Cold-rolling workability, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti50Ni25Pd25</td>
<td>0</td>
<td>0</td>
<td>416.8</td>
<td>16.3</td>
<td>205.2</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu</td>
<td>5</td>
<td>0</td>
<td>442.4</td>
<td>19.5</td>
<td>217.6</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu10</td>
<td>10</td>
<td>0</td>
<td>453.8</td>
<td>20.1</td>
<td>220.1</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu10</td>
<td>5</td>
<td>5</td>
<td>380.7</td>
<td>13.8</td>
<td>219.8</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu10</td>
<td>5</td>
<td>5</td>
<td>384.1</td>
<td>14.9</td>
<td>237.7</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu15</td>
<td>10</td>
<td>5</td>
<td>400.1</td>
<td>15.4</td>
<td>243.9</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu10</td>
<td>0</td>
<td>10</td>
<td>333.0</td>
<td>11.4</td>
<td>239.7</td>
</tr>
<tr>
<td>Ti50Ni20Pd25Cu15</td>
<td>5</td>
<td>10</td>
<td>337.5</td>
<td>12.5</td>
<td>262.1</td>
</tr>
</tbody>
</table>

Fig. 1 DSC result of as solution-treated Ti50Ni15Pd25Cu10 specimen.

Fig. 2 The linear regression results of ΔHc value vs. Ms temperature.
The correlation coefficients, R-factors, of eqs. (3) and (4) are 0.97 and 0.93, respectively. From eqs. (3) and (4), it indicates that the more the Ni/Pd is substituted by Cu, the higher the Ms temperature and thus increase the values of Ms and ΔHc; while that of Pd by Cu shows in reverse behavior. Besides, for the effect of Ni substituted by Cu on lattice constants of B19 martensite is opposite to that of Pd by Cu, the different atomic radii of Ni (0.125 nm), Cu (0.128 nm) and Pd (0.137 nm)\(^{13}\) can explain this feature. The atomic radius of Ni is smaller than that of Cu but the atomic radius of Pd is larger than that of Cu. Moreover, the substitution of Ni and Pd by Cu both can increase hardness but decrease cold-rolling workability. This feature also results from the different atomic radii of Ni, Cu and Pd, i.e., the substitution of Pd by Cu has higher solid-solution strengthening effect than that of Ni by Cu.

### Table 2 XRD results and their corresponding lattice constants of B19 martensite of the HTSMAs shown in Table 1.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>XRD peak, 2θ°</th>
<th>Lattice constant, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(002)(_{B19})</td>
<td>(020)(_{B19})</td>
</tr>
<tr>
<td>Ti50Ni25Pd25</td>
<td>38.27</td>
<td>40.55</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu</td>
<td>38.18</td>
<td>40.39</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu10</td>
<td>38.24</td>
<td>40.37</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu15</td>
<td>38.51</td>
<td>40.91</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu20</td>
<td>38.42</td>
<td>40.58</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu25</td>
<td>38.48</td>
<td>40.67</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu30</td>
<td>38.99</td>
<td>41.51</td>
</tr>
<tr>
<td>Ti50Ni25Pd25Cu35</td>
<td>39.08</td>
<td>41.30</td>
</tr>
</tbody>
</table>

\[ Hv = 202.8 + 2.2X + 4.2Y \]  
\[ \text{Workability (\%)} = 35.1 - 0.6X - 1.4Y \]

The correlation coefficients, R-factors, of eqs. (3) and (4) are 0.97 and 0.93, respectively. From eqs. (3) and (4), it indicates that the more the Ni/Pd is substituted by Cu, the higher the alloy’s hardness value is and, at the same time, the lower the alloy’s cold-rolling workability has. Besides, on the increase of hardness and the decrease of cold-rolling workability, the effect of Pd substituted by Cu is more significant than that of Ni by Cu. At the effect of Pd substituted by Cu is equivalent to increase the Pd content and thus increase the Pd content can increase Ms temperature\(^{12}\) and the decrease of cold-rolling workability. This effect also results from the different atomic radii of Ni, Cu and Pd, i.e., the substitution of Pd by Cu has higher solid-solution strengthening effect than that of Ni by Cu.

#### 3.1.3 The lattice constants of B19 martensite

In order to understand the structure of B19 martensite, Ti50Ni25-Pd25-Cu15\(_{x+y}\) specimens were conducted by XRD at room temperature. The XRD 2θ peak values of (002)\(_{B19}\), (020)\(_{B19}\) and (111)\(_{B19}\) of B19 orthorhombic martensite\(^{11}\) and the calculated lattice constants \(a\), \(b\) and \(c\) of B19 martensite of Ti50Ni25-Pd25-Cu15\(_{x+y}\) specimens are shown in Table 2. From Table 2, the effect of composition on lattice constants \(a\), \(b\) and \(c\) can be formulated by the linear regression method as follows:

\[ a (\text{Å}) = 2.7932 - 0.0027X + 0.0041Y \]  
\[ b (\text{Å}) = 4.4537 + 0.0025X - 0.0091Y \]  
\[ c (\text{Å}) = 4.7124 + 0.0002X - 0.0090Y \]

The correlation coefficients, R-factors, of eqs. (5), (6) and (7) are 0.94, 0.96 and 0.97, respectively. From eqs. (5)–(7), the effect of Pd substituted by Cu on the lattice constants of B19 martensite is more significant than that of Ni by Cu. At the same time, the substitution of Ni by Cu can decrease \(a\) but increase \(b\) and \(c\); while that of Pd by Cu shows in reverse effect.

#### 3.1.4 The effect of Cu addition on martensitic transformation of Ti50Ni25-Pd25-Cu15\(_{x+y}\) HTSMAS

According to the above experimental results, the substitution of Ni by Cu can increase the values of Ms and ΔHc; while that of Pd by Cu shows in reverse effect. Since the Cu content does not affect Ms obviously,\(^{5}\) the change of Ms and ΔHc is mainly due to the change of Ni/Pd content. The reported study has indicated that, from TiNi-TiPd pseudobinary phase diagram, the decrease of Ni content and the increase of Pd content can increase Ms temperature\(^{12}\) and thus increase ΔHc according to Clausius-Clapeyron eq.\(^{10}\). For Ti50Ni25-Pd25-Cu15\(_{x+y}\) HTSMAS, the substitution of Ni by Cu is equivalent to increase the Pd content and thus increase the values of Ms and ΔHc; while that of Pd by Cu shows in reverse behavior. Besides, for the effect of Ni substituted by Cu on lattice constants of B19 martensite is opposite to that of Pd by Cu, the different atomic radii of Ni (0.125 nm), Cu (0.128 nm) and Pd (0.137 nm)\(^{13}\) can explain this feature. The atomic radius of Ni is smaller than that of Cu but the atomic radius of Pd is larger than that of Cu. Moreover, the substitution of Ni and Pd by Cu both can increase hardness but decrease cold-rolling workability. This feature also results from the different atomic radii of Ni, Cu and Pd, i.e., the substitution of Pd by Cu has higher solid-solution strengthening effect than that of Ni by Cu.

### 3.2 The annealing and thermal cycling effects on Ti50Ni15Pd25Cu10 HTSMA

In order to understand the annealing and thermal cycling effects on Ti50Ni25-Pd25-Cu15\(_{x+y}\) HTSMAS, Ti50Ni15Pd25-Cu10 HTSMA was chosen to do the intensive studies. Ti50Ni15Pd25Cu10 specimens were annealed at 523 K up to 9 weeks for the study of thermal stability, annealed at 623 K–1073 K \(× 6\) h for the study of annealing precipitates and thermal-cycled in between 573 K salt bath and room temperature water up to 100 times for the study of thermal-cycling stability. The reason to choose Ti50Ni15Pd25Cu10 HTSMA from all the eight Ti50Ni25-Pd25-Cu\(_{x+y}\) HTSMAS is that the as solution-treated Ti50Ni15Pd25Cu10 specimen has the highest Ms temperature (453.8 K) with the largest ΔHc value (20.1 J/g).

#### 3.2.1 Annealing effect on Ti50Ni15Pd25Cu10 HTSMA

Figure 3(a) shows DSC cooling curves of Ti50Ni15Pd25-Cu10 specimens annealed at 623 K, 723 K, 823 K, 923 K and 1073 K for 6h. Figure 3(b) plots the relationship of Ms temperature and ΔHc value vs. annealing temperature of Ti50Ni15Pd25Cu10 specimens annealed at 623 K–1073 K \(× 6\) h for every 50 K interval. For the reference, Ms temperature and ΔHc value of as solution-treated Ti50Ni15Pd25Cu10 specimen has the highest Ms temperature (453.8 K) with the largest ΔHc value (20.1 J/g).
Martensitic Transformation of Ti$_{50}$Ni$_{25-\chi}$Pd$_{25-\chi}$Cu$_{\chi+1}$ Quaternary Shape Memory Alloys with $X, Y \leq 10\text{ at}\%$

broad. Ti$_{50}$Ni$_{15}$Pd$_{25}$Cu$_{10}$ specimen annealed at 823 K × 6 h has the lowest Ms temperature (418.4 K) and smallest $\Delta Hc$ value (8.8 J/g) with the broadest transformation peak, as shown in Fig. 3(a). The suppression of Ms temperature and $\Delta Hc$ value is resulted from the formation of precipitates during annealing and will be discussed in Section 3.2.2. For high annealing temperature (higher than 973 K), both Ms temperature and $\Delta Hc$ value increase with increasing the annealing temperature and the transformation peak also becomes sharp. Here, the annealing temperature is higher than the recrystallization temperature which is around 873 K$^{15}$ the increase of Ms temperature and $\Delta Hc$ value is due to the grain growth. From Fig. 3, Ti$_{50}$Ni$_{15}$Pd$_{25}$Cu$_{10}$ specimens annealed below 673 K and above 973 K for 6 h are not affected by the precipitates and exhibit the same transformation behavior as solution-treated specimen of Fig. 1.

Figure 4(a) shows the DSC cooling curves of Ti$_{50}$Ni$_{15}$Pd$_{25}$Cu$_{10}$ specimens annealed at 523 K for 1~9 weeks and (b) Plot of Ms temperature and $\Delta Hc$ value vs. annealing time of Fig. 4(a).

Table 3 The chemical composition analysis results of the matrix and precipitates in as solution-treated and 923 K × 6 h annealed Ti$_{50}$Ni$_{15}$Pd$_{25}$Cu$_{10}$ specimens by EDS.

<table>
<thead>
<tr>
<th>Content, at%</th>
<th>Ti</th>
<th>Ni</th>
<th>Pd</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>As solution-treated</td>
<td>matrix</td>
<td>49.8</td>
<td>15.8</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>Ti$_2$Ni</td>
<td>66.9</td>
<td>16.6</td>
<td>10.8</td>
</tr>
<tr>
<td>923 K × 6 h annealed</td>
<td>matrix</td>
<td>50.1</td>
<td>16.6</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td>Ti$_2$Pd</td>
<td>68.4</td>
<td>2.7</td>
<td>24.4</td>
</tr>
<tr>
<td></td>
<td>Ti(Cu,Pd)$_2$</td>
<td>34.5</td>
<td>7.3</td>
<td>25.0</td>
</tr>
</tbody>
</table>

3.2.2 Precipitates formed in annealed Ti$_{50}$Ni$_{15}$Pd$_{25}$Cu$_{10}$ HTSMA

Figure 5(a) shows the bright field (BF) image of as solution-treated Ti$_{50}$Ni$_{15}$Pd$_{25}$Cu$_{10}$ specimen. Figures 5(b) and 5(c) show the selected area diffraction patterns (SADPs) of precipitates and matrix of Fig. 5(a), respectively. From Fig. 5(a), chemical compositions of matrix and precipitates are detected by EDS and the results are listed in Table 3. From Fig. 5(b) and Table 1, the SADP can be identified as Ti$_2$Ni precipitate with [211]$_{Ti_2Ni}$ zone axis which is formed during solidification process due to its melting point lower than the matrix.$^{16}$ From Fig. 5(c), the SADP can be identified as B19 martensite with [321]$_{B19}$ zone axis.

Figures 6(a)~6(c) show the BF images of 723 K, 823 K and 923 K × 6 h annealed Ti$_{50}$Ni$_{15}$Pd$_{25}$Cu$_{10}$ specimens, respectively. From Figs. 6(a)~6(c), two kinds of precipitates can be found, as indicated by single arrows (Ti$_2$Pd) and double arrows (Ti(Cu,Pd)$_2$) with the former size about 0.2 μm, 0.2 μm and 1 μm, respectively; and the latter one
about 0.2 μm, 0.15 μm and 0.5 μm, respectively. At the same time, the quantity of precipitates in 823 K annealed specimen is higher than that in 723 K and the lowest quantity of precipitates is in 923 K. From Fig. 3, the annealing treatment has the maximum effect in 823 K × 6 h annealed specimen which is consistent with the microstructure observation shown in Fig. 6.

At 723 K and 823 K × 6 h annealed specimens of Figs. 6(b) and 6(c), respectively, the precipitates are too small to identify their structure and composition. Therefore, 923 K × 6 h annealed specimen which has the largest size of precipitates is selected to study. Figures 6(d) and 6(e) show the SADPs of precipitates indicated by the single arrows and double arrows, respectively. The chemical compositions of the matrix and precipitates are also detected by EDS and the results are listed in Table 3. From Figs. 6(d) and 6(e), the orientation relationships of precipitates and matrix can be identified as \(1\over 2\{110\}\text{Ti}_2\text{Ni}_2 \approx \{100\}\text{Ti}(\text{Ni},\text{Cu})_2\) and \(\{100\}\text{Ti}(\text{Ni},\text{Cu})_2 \approx \{001\}\text{B}19\), respectively. Fukuda et al.\(^\text{(17)}\) investigated the transformation behavior of 873 K annealed \(\text{Ti}_{49.5}\text{Ni}_{40.5}\text{Cu}_{10}\) SMA which is affected by \(\text{Ti}(\text{Ni},\text{Cu})_2\) precipitates. They pointed out that the lattice mismatch of cubic B2 parent phase and tetragonal \(\text{Ti}(\text{Ni},\text{Cu})_2\) precipitates causes the orientation relationships of \(\{100\}\text{B}2 \approx \{100\}\text{Ti}(\text{Ni},\text{Cu})_2\) and \(\{001\}\text{B}2 \approx \{001\}\text{Ti}(\text{Ni},\text{Cu})_2\). From Figs. 6(d) and 6(e), both \(\text{Ti}_2\text{Pd}\) and \(\text{Ti}(\text{Cu},\text{Pd})_2\) precipitates show good orientation relationships with the matrix which may also result from the lattice mismatch in between the matrix and precipitates. This lattice mismatch can induce coherent stresses at the precipitate/matrix interface and provide the complex BF image, as shown Fig. 6(b).

### 3.2.3 Thermal cycling effect of \(\text{Ti}_{50}\text{Ni}_{15}\text{Pd}_{25}\text{Cu}_{10}\) HTSMA

Figure 7(a) shows the DSC cooling curves of \(\text{Ti}_{50}\text{Ni}_{15}\text{Pd}_{25}\text{Cu}_{10}\) specimen thermal-cycled for 5, 20, 50 and 100 times in between 573 K and room temperature. Figure 7(b) plots the Ms temperature and \(\Delta H_c\) value vs. the number of thermal cycle (N) from Fig. 7(a). The Ms temperature and \(\Delta H_c\) value of as solution-treated \(\text{Ti}_{50}\text{Ni}_{15}\text{Pd}_{25}\text{Cu}_{10}\) are also indicated by the parallel dot lines in Fig. 7(b). From Fig. 7, Ms temperature and \(\Delta H_c\) value of \(\text{Ti}_{50}\text{Ni}_{15}\text{Pd}_{25}\text{Cu}_{10}\) specimen thermal-cycled up to N = 100 show no obvious change. Thus, from the viewpoint of thermal cycling application,
Ti₅₀Ni₁₅Pd₂₅Cu₁₀ HTSMA exhibits quite good thermal stability.

4. Conclusions

Ti₅₀Ni₂₅₋ₓPd₃₀₋ₓCuₓ₊₁₉ HTSMAs with X, Y ≤ 10 at% have been studied by DSC, XRD, TEM/EDS, hardness and cold-rolling workability tests. Experimental results show that all these HTSMAs exhibit B2 ↔ B19 martensitic transformation with Ms temperature in the range of 330 K~453 K. The substitution of Ni by Cu can increase both the values of Ms and ΔHc; while that of Pd by Cu shows in reverse effect. Ms temperature of these HTSMAs can be predicted by linear regression as: Ms (K) = 424.2 + 2.7X − 9.7Y. The
substitution of Ni by Cu on lattice constants of B19 martensite is also opposite to that of Pd by Cu. This feature can be explained by the different atomic radii of Ni, Cu and Pd with the atomic radius of Ni being smaller than that of Cu but that of Pd being larger than that of Cu. The substitution of Ni and Pd by Cu both can increase the hardness but decrease the cold-rolling workability. This characteristic results from solid-solution strengthening effect which is also related to the effect of different atomic radii of Ni, Cu and Pd. Ti$_{50}$Ni$_{15}$Pd$_{25}$Cu$_{10}$ specimens annealed at 523 K up to 9 weeks and thermal-cycled in between 573 K and room temperature up to 100 times show no obvious change in both Ms temperature and $\Delta H_c$ value which indicates that Ti$_{50}$Ni$_{15}$Pd$_{25}$Cu$_{10}$ HTSMA has quite good thermal stability. However, Ti$_{50}$Ni$_{15}$Pd$_{25}$Cu$_{10}$ HTSMA annealed in between 723 K~923 K shows significant decrease of Ms temperature and $\Delta H_c$ value, in which the decrease reaches the maximum at 823 K. This is due to the formation of tetragonal Ti$_2$Pd and orthorhombic Ti(Cu,Pd)$_2$ precipitates which have [110]$_{Ti_2Pd} // [110]_{B19}$ and [100]$_{Ti(Cu,Pd)_2} // [100]_{B19}$ orientation relationships and coherent stresses can be induced at the precipitate/matrix interface.

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