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Martensitic transformation and shape memory effect in B2 intermetallic compounds of titanium

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Résumé. — Nous avons étudié les aspects cristallographiques et cinétiques de la transformation martensitique et les paramètres de l’effet mémoire de forme dans les alliages Ti$_{50}$Ni$_{50-x}$X$_x$ (X = Fe, Co, Pd, Pt, Au, Cu) et Ti$_{50}$Pd$_{50-x}$Y$_x$ (Y = Fe, Co, Cu), 0 ≤ x ≤ 50. Nous avons mesuré la température, l’hystérésis, la grandeur de la déformation et la contrainte du cisaillement martensitique pour la transformation martensitique et pour l’effet mémoire de forme. Nous avons déterminé les compositions d’alliage donnant des conditions excellentes pour l’effet mémoire de forme.

Abstract. — Crystallographic and kinetic characteristics of martensitic transformations and parameters of shape memory effect in B2 compounds of titanium Ti$_{50}$Ni$_{50-x}$X$_x$ (X = Fe, Co, Pd, Pt, Au, Cu) and Ti$_{50}$Pd$_{50-x}$Y$_x$ (Y = Fe, Co, Cu), where 0 ≤ x ≤ 50 are investigated. Temperature, hysteresis, value of reversible deformation and stress of martensitic shear for martensitic transformations and shape memory effect are defined. Compositions of alloys with optimum conditions for shape memory effect were determined.

Titanium exists in BCC and HCP modifications (T$_{^n_0}^n_1$ = 1 115 K) and forms binary and multicomponent B2 compounds with Ni, Fe, Co, Pd, Pt, Au, Cu and other metals, many of them being unstable and undergoing various martensitic transformations (MT) at different temperatures [1-4]. The most famous among them are TiNi and alloys on its base where monoclinic martensitic phase B19' is formed either directly by B2 → B19' or by rhombohedral R structure B2 → R → B19' [5]. Shape memory effect (SME) is vividly expressed in these alloys. At present new B2 compounds of titanium of the type Ti(Ni, Cu), Ti(Ni, Pd), Ti(Ni, Pt), Ti(Ni, Au), Ti(Pd, Fe) with different MT and SME characteristics are intensively investigated [2-4, 6, 7]. Some of the alloys have rare and SME characteristics observed neither in TiNi, nor in other SME alloys. However the results of the researches are not well known. The present paper sums the results of the author’s latest publications and presents new data on MT and SME in a series of triple compounds Ti$_{50}$Ni$_{50-x}$X$_x$ (X = Fe, Co, Pd, Pt, Au, Cu) and Ti$_{50}$Pd$_{50-x}$Y$_x$ (Y = Fe, Co), where 0 ≤ x ≤ 50. The present alloys cover the main compounds of titanium with unstable B2 lattice. The methods of making alloys and specimens as well as methods of structure and SME studies are described in [2-4].

Martensitic transformations.

1. SYSTEMS Ti$_{50}$Ni$_{50-x}$Fe$_x$ AND Ti$_{50}$Ni$_{50-x}$Co$_x$. — MT in Ti$_{50}$Ni$_{50-x}$Fe$_x$ (0 ≤ x ≤ 3) are studied in detail in [5, 8]. However a total (0 ≤ x ≤ 50) MT diagram with cooling up to 4.2 K is designed only in [9]. At the same time genetically related alloys system Ti$_{50}$Ni$_{50-x}$Co$_x$ was studied much less. Figure 1 presents the resultant MT diagram which agrees qualitatively with MT diagram in Ti$_{50}$Ni$_{50-x}$Fe$_x$. In the both systems B2 → R → B19' is the basic MT accurately fixed against the temperature dependence of resistivity (Fig. 1a). The parameters of B19' martensitic phase (a = 0.288 nm, b = 0.412 nm, c = 0.465 nm, β = 97.6° for Ti$_{50}$Ni$_{50}$Co$_7$) vary slightly with the change of alloy composition and they are close to the parameters of B19' martensite in TiNi (a = 0.289 nm, b = 0.412 nm, c = 0.464 nm, β = 97.3°).

With the increasing of Co(Fe) content at first MT R → B19' and then MT B2 → R are under suppression. The stabilization of initial B2 structure in its
transition from TiNi to TiCo (TiFe) is accompanied by a qualitative variation of elastic properties of crystal lattice. It should be stressed here that data on single crystals Ti$_{50}$Ni$_{50-x}$Fe$_x$ ($0 \leq x \leq 50$) obtained in [10, 11] are of particular interest. The effect of premartensitic softening of lattice ($dC_{44}/dT > 0$, $dC'/dT > 0$, $A = C_{44}/C' \approx 2$) in alloys on TiNi basis gradually disappears in the process of transition to alloys undergoing no MT therefore the temperature dependence of elastic constants goes to normal ($dC_{44}/dT < 0$, $dC'/dT < 0$, $A < 1$).

2. SYSTEMS Ti$_{50}$Ni$_{50-x}$X$_x$ ($X = $ Pd, Pt, Au, Cu). — For all alloys of these systems MT evolution is the same in quality at increasing $x$. Figure 2 presents the typical MT diagram. Similar diagram was observed in Ti$_{50}$Ni$_{50-x}$Pd$_x$ [3], Ti$_{50}$Ni$_{50-x}$Au$_x$ [4] and Ti$_{50}$Ni$_{50-x}$Cu$_x$ [2]. The characteristic feature of these diagrams is the change of MT $B2 \rightarrow R \rightarrow B19'$ ($x < 7$) into $B2 \rightarrow B19 \rightarrow B19'$ ($7 < x < 14$) and then into $B2 \rightarrow B19$ ($x > 14$) sequence, where B19 is orthorhombic phase. B19 and B19' martensitic phases have two different space groups, where B19' is $P2_1/m$ with a distortion of the angle $\beta$ (Fig. 3, curve 1) and B19 is $P2_1/m2/m2/a$. So the parameters of B19 and B19' martensitic phases undergo significant variations with the change of alloy composition. Figure 3 presents the evolution of parameters B19 and B19' in Ti$_{50}$Ni$_{50-x}$Pt$_x$. Similar complete evolution is observed in Ti$_{50}$Ni$_{50-x}$Pd$_x$ [3], Ti$_{50}$Ni$_{50-x}$Au$_x$ [4] and close one in Ti$_{50}$Ni$_{50-x}$Cu$_x$ [2].

The uncommon crystallogeometric peculiarity observed during MT $B2 \rightarrow B19 \rightarrow B19'$ is of great interest. As is seen in figure 3, crystal lattice undergoes no deformation in the direction of parameter $b$ at both MT. The results of Bain's homogeneous deformation calculations for all MT sequences in Ti$_{50}$Ni$_{50-x}$Pt$_x$ are given in table I. Analogous results are observed for other three systems of alloys as well. The scheme of calculation with the application of tensor strain is presented in [12]. As is seen from the table I, the value and direction of lattice strain are change essentially after the removing of alloy composition from TiNi and the change of MT sequence. The main peculiarity of these changes is as follows: one of eigenvalues of tensor strain in transformed into zero (or near zero) at each out of two MT $B2 \rightarrow B19 \rightarrow B19'$, what implies an invariant plane to be present. It should be stressed in this connection that the above mentioned plane is the invariant one at microscopic level, that is, it belongs to both crystal lattices simultaneously. Naturally the plane of maximum lattice correspondence is to pass the interface plane (habit plane). In fact, habit plane $\{334\}$ observed experimentally in Ti$_{50.3}$Ni$_{99.5}$Cu$_{10}$ [13] is in good agreement with a theoretically calculated $\{19, 29, 25\}$, which is equivalent to $\{3, 3, 3.95\}$. The table presents orientation and the
Table 1. — Calculation of lattice strain for martensitic transformations in the Ti$_{50}$Ni$_{50-x}$Pd$_x$ alloys.

<table>
<thead>
<tr>
<th>Pd, at. %</th>
<th>Transformation type and temperature of phases parameters measurements, K</th>
<th>Eigenvalue of tensor strain, $\times 10^2$</th>
<th>Coordinates of eigenvectors</th>
<th>Symbols of invariant plane</th>
<th>Rotation angle of invariant plane, grad.</th>
<th>The axis of rotation is (110) B2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>B2 $\rightarrow$ B19</td>
<td>$-6.51$</td>
<td>0.93 0.37</td>
<td></td>
<td></td>
<td>$37^{37} 50_{B2}$</td>
</tr>
<tr>
<td></td>
<td>373 293</td>
<td>$-3.29$</td>
<td>0 1 0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>B2 $\rightarrow$ B19</td>
<td>$-6.76$</td>
<td>0.92 0.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>293 273</td>
<td>$-3.16$</td>
<td>0 1 0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$11.75$</td>
<td>$-0.38$ 0.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>B2 $\rightarrow$ B19</td>
<td>$-7.02$</td>
<td>0.93 0.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>293 293</td>
<td>$-2.64$</td>
<td>0 1 0</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>$11.21$</td>
<td>$-0.38$ 0.93</td>
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<tr>
<td>8.5</td>
<td>B2 $\rightarrow$ B19</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>273 253</td>
<td>$-0.04$</td>
<td>0 1 0</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>$6.94$</td>
<td>0 0 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-3.91$</td>
<td>0.64 0.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>173 173</td>
<td>$-2.26$</td>
<td>0 1 0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$8.22$</td>
<td>$-0.77$ 0.64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.5</td>
<td>B19 $\rightarrow$ B19$'$</td>
<td>$-3.91$</td>
<td>0.64 0.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>173 173</td>
<td>$-2.26$</td>
<td>0 1 0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$8.22$</td>
<td>$-0.77$ 0.64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>B2 $\rightarrow$ B19</td>
<td>$-6.50$</td>
<td>0 1 0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>273 273</td>
<td>$0.13$</td>
<td>0 1 0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$6.90$</td>
<td>0 0 1</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>$-2.05$</td>
<td>0.69 0.72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>113 113</td>
<td>$0$</td>
<td>0 1 0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.42$</td>
<td>$-0.72$ 0.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>B2 $\rightarrow$ B19</td>
<td>$-9.54$</td>
<td>0 1 0</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>573 293</td>
<td>$1.86$</td>
<td>0 1 0</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

angle of rotation of habit planes calculated in other alloys which unfortunately have not been observed experimentally as yet.

One more interesting peculiarity of MT B2 $\rightarrow$ B19 $\rightarrow$ B19$'$ should be noted here. In the case of the second MT B19 $\rightarrow$ B19$'$ the maximum lattice deformation lies in a plane which was an invariant one at the first transformation. On the contrary, in the case of the first MT B2 $\rightarrow$ B19 the maximum lattice deformation is in the plane which will be invariant one at the second transformation. That is to say, directions of the maximum and zero crystal lattice deformations are interchangeable at the first and second MT. In other words, the formation of complicated monoclinic lattice at MT B2 $\rightarrow$ B19 $\rightarrow$ B19$'$ is done through two simple « elongation-compression » operations in the two interchangeable directions with the planes undistorted in each case.

One can say that marked crystallographic peculiarities of MT B2 $\rightarrow$ B19 $\rightarrow$ B19$'$ are rare in general not only for MT but also for MT in alloys with SME they are not observed in TiNi. As it will be said later these features will play exceptionally important role in provision of optimum conditions for SME manifestation.

Pay your attention to MT B2 $\rightarrow$ B19 realization at high temperatures with small hysteresis that provides real conditions for high-temperature SME display.

3. SYSTEM Ti$_{50}$Pd$_{50-x}$Y$_x$ (Y = Fe, Co, Cu). — The compound Ti$_{50}$Pd$_{50}$ undergoes one MT B2 $\rightarrow$ B19 at 783 K [3, 14]. The substitution of palladium for iron or cobalt makes B2 structure stabilized: the temperature of MT B2 $\rightarrow$ B19 falls down (Fig. 4), the effect of premartensitic softening is decreased [15], the lattice strain is suppressed significantly (Fig. 5, curve 1). The present system is suitable for studying distabilization process of B2 compounds (TiFe and TiCo) with respect to one simple MT B2 $\rightarrow$ B19.

First in the case of alloying TiPd with copper ($<5$ at % Cu) the temperature of MT B2 $\rightarrow$ B19 falls down and then with ($>10$ at % Cu) the
Fig. 3. — The effect of composition of Ti(Ni, Pt) on parameters initial \((a_0)\) and martensitic B19 \((a, b, c)\), B19' \((a', b', c', \beta)\) phases and hysteresis MT.

Fig. 4. — Diagram MT of composition Ti_{30}Pd_{30-x}Co_x (left) and Ti_{30}Pd_{30-x}Fe_x (right) and temperature dependences of resistivity Ti_{30}Pd_{40}Co_{10} (a) and Ti_{30}Pd_{40}Fe_{10} (b), Ti_{30}Pd_{30}Fe_{15} (c).

Fig. 5. — The effect of composition of Ti(Pd, Fe) on parameters initial \((a_0)\) and martensitic B19 \((a, b, c)\) phases and value deformation of lattice (1).

Fig. 6. — Temperature dependences of resistivity Ti_{30}Pd_{30}Co_{15} (a) and Ti_{30}Pd_{30}Fe_{10} (b), Ti_{30}Pd_{30}Fe_{15} (c).

Intensive B2 structure desintegration into two tetragonal phases with the ratio \(c/a < 1\) and \(c/a > 1\) occurs. The results of investigations of these alloys will be published separately [16], therefore they are not considered here in detail. In connection with these investigations, work [17] should be noted.

Thus spectrum of MT B2 \(\rightarrow\) B19, B2 \(\rightarrow\) R, B2 \(\rightarrow\) R \(\rightarrow\) B19' and B2 \(\rightarrow\) B19 \(\rightarrow\) B19' are realized in B2 compounds on the basis of titanium. The most interesting crystallographic peculiarities are observed at MT B2 \(\rightarrow\) B19 \(\rightarrow\) B19'.

Shape Memory Effect. — Shape memory effect is observed in all alloys during MT with particular temperature, magnitude and hysteresis of reversible strain which are connected with each transformation (Figs. 6, 7).

It should be pointed out that the essential feature of SME at MT B2 \(\rightarrow\) B19 is its realization at high temperatures up to 800 K (Fig. 6, curve 1). However, the magnitude of macroscopic reversible deformation (as a lattice strain — see Tab. 1) is relatively not high — 7-8\%, but \(\sigma_M\) is rather high — 150-200 MPa even within the interval Ms-Mf. That is, conditions for realizing anelastic (reversible) deformation at MT B2 \(\rightarrow\) R are far from optimum ones.

Narrow hysteresis (3-5 K) and small value (~1\%) of reversible strain due to closeness of given transformations to transitions of the second order (Fig. 6, curve 2) is the peculiarity of SME at MT B2 \(\rightarrow\) R. This SME type has been studied well enough earlier, see for example [18].

Undoubtedly, the first and the most evident SME peculiarity at B2 \(\rightarrow\) R \(\rightarrow\) B19' and B2 \(\rightarrow\) B19 \(\rightarrow\) B19' is its two-stage character of accumulation and recovery of deformation (Fig. 7), with the resultant revers-
Fig. 6. — SME at $B2 \rightarrow B19$ MT in $\text{Ti}_{50}\text{Pt}_{36}\text{Ni}_{14}$ (1), and reversible SME at $B2 \rightarrow R$ MT in $\text{Ti}_{50}\text{Ni}_{45}\text{Fe}_{5}$ (2) after prior plastic deformation 7.3 % at 353 K. Stress 200 MPa for (1) suppressed during the heating.

Fig. 7. — Reversible SME at $B2 \rightarrow R \rightarrow B19'$ MT in $\text{Ti}_{49}\text{Ni}_{51}$ (1) and at $B2 \rightarrow B19 \rightarrow B19'$ in $\text{Ti}_{50}\text{Ni}_{40}\text{Pd}_{10}$ (2) after prior plastic deformation 6.0 % at 453 K (1) and 0.3 % at 323 K (2).

Fig. 8. — Temperature dependence of $\sigma_M$ and diagram of $\sigma(\varepsilon)$ in $\text{Ti}_{80}\text{Ni}_{15}\text{Pd}_{10}$ (1) and $\text{Ti}_{80}\text{Ni}_{15}\text{Au}_{10}$ (2).

Fig. 9. — The effect of composition of Ti(Ni, Pd) (1) and Ti(Ni, Cu) (2) on reversible deformation accumulated at cooling alloy with stress 100 MPa.

Ms-Mf (Fig. 8). Such MT sequence is characterized by more narrow hysteresis (Fig. 3, curve 2). That is MT $B2 \rightarrow B19'$ is more optimal for SME manifestation what is graphically seen in figure 9, where the reversible deformation value accumulated under the same stress at the cooling of alloy is at its maximum.

Discussion.

The MT spectrum is realized in B2 compounds of titanium. Nevertheless only two basic martensitic reactions $B2 \rightarrow B19$ and $B2 \rightarrow R$ should be chosen.
from the variety of structural transformations and all the rest chains of transformations $B2 \rightarrow R \rightarrow B19'$ and $B2 \rightarrow B19 \rightarrow B19'$ should be regarded as the result of successive realization of these two MT. This is really the case.

As was shown, the formation of MT chains and monoclinic structure of B19' occurs gradually at the change of composition of alloy from TiPd (Ti Pt, TiAu) to TiNi and further to TiFe (TiCo). So MT $B2 \rightarrow B19$ are complicated gradually in $B2 \rightarrow B19 \rightarrow B19'$ and through $B2 \rightarrow R \rightarrow B19'$. Such MT $B2 \rightarrow B19$ evolution testifies to gradual destabilization of initial B2 structure to a new MT forming R phase. The destabilization of B2 structure occurs gradually and initially $T_R$ ($B2 \rightarrow R$) $M_S$ ($B2 \rightarrow B19$). In this case the formation « R-martensite » in B19 phase gives the results in monoclinic distortion of the latter, that is $B19 \rightarrow B19'$. It is easy to demonstrate it because the direction of [111]$_{B2}$ is equivalent to [101]$_{B19}$ and rhombohedral deformation of B2 lattice is equivalent to monoclinic B19 distortion relatively. And so, the value of monoclinic distortion depends on intensity of the second (R) MT canal development. Originally, when $T_R < M_S$ and « R-canal » starts formation, monoclinic angle is small (Fig. 3, curve 1). As far as the second « R-canal » is developing the temperature of its realization rises and approaches $T_R = M_S$ or even exceeds ($T_R > M_S$) temperature of the first MT ($M_S$). The monoclinic angle of B19 structure reaches its maximum and R-phase is formed evidently. It should be pointed out that the monoclinic distortion of B19 phase and the scheme of Bain's deformation are changed simultaneously with the development of the second MT canal. Tension is changed by compression along b axis. Such change is the result of crystallography of MT B19 $\rightarrow B19'$. The tension of orthohombic lattice along [101] direction, which provides monoclinic distortion should be accompanied by compression of lattice in perpendicular [010] direction which is b axis. In short, both the monoclinic distortion and the compression along b axis are the consequence of only one reason: realization of the second « R-canal » MT.

Thus, the main peculiarities of the MT developing in B2 compounds of titanium can be given as the following scheme

$$B2 \xrightarrow{[B19]} + \xrightarrow{R} \rightarrow B19'. $$

The concrete MT sequence is defined by composition of alloy.

The most striking peculiarity of anelastic behavior of B2 compounds of titanium are anomalously low values of $\sigma_M$ and narrow hysteresis at MT $B2 \rightarrow B19 \rightarrow B19'$. Such conditions of developing anelastic deformation are associated first of all with crystallography of MT sequence. A total (or near total) lack of the displacements of atoms and internal stress in habit planes {334}$_{B2}$ (for $B2 \rightarrow B19$) and {100} (for $B19 \rightarrow B19'$), that is practically ideal coherence of the interfaces provides a low resistance of material against their motion (low $\sigma_M$ and narrow hysteresis).

Low values of elastic modules at the moment MT [10, 11] and stage by stage deformation of lattice promotes lowering accomodational strains too and effective development of anelastic deformation. That is to say, the optimum for SME manifestation at MT $B2 \rightarrow B19 \rightarrow B19'$ is connected with combination of several favourable factors with the presence of total coherence of the interface being determinant among them.

One more peculiarity of anelastic behavior of B2 compounds of titanium is the SME realization at high temperatures in the process of MT $B2 \rightarrow B19$. It was for the first time that by direct nickel titanium alloying the temperature MT and mechanical properties could be increased simultaneously, this enabled one to preserve thermoelastic property of MT and practically the total SME up to 800 K. It should be noted that SME is not higher than 400-420 K in alloys on TiNi basis. Naturally, alloy production with high temperature SME broadens the region of its technical application. The scientific value of this result is obvious for the principal possibility of realization of thermoelastic MT SME at higher temperatures than it was believed before. Thus different MT and total SME are realized in B2 compounds of titanium. In this connection B2 compounds of titanium occupy chief position among other alloys with SME and will be a perspective base for the subsequent working out of new alloys of this class.

References
