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Effect of the Be and Y on the martensite transformation parameters in TiNi compound

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Abstract: To our knowledge, the effect of Be and Y on the martensite transformation parameters in TiNi-based shape memory alloys was studied occasionally and mainly on a level of the technological additions. Recently, due to the development of non-conventional production technologies applied to the shape memory materials, both metals are found to be the appropriate canditates for production of the potential TiNi-based shape memory alloys in an initially amorphous structural state by means of the melt-spinning and injection casting techniques. First of all, the Be and Y attract attention due to satisfaction of the so-called "golden rules" known for the bulk amorphous alloy systems. We present the result of the experimental study regarding the systematic substitution of the main constituent elements Ti and Ni by Be and Y up to (2-10) at.%. In as-cast condition, all the Ti-Ni-Be and Ti-Ni-Y alloys undergo the dual B2⇐⇒R⇐⇒B19′ martensite transformation sequence, well resolved on the cooling run and often overlapping on the heating run. Both the T_R and M_S transformation temperatures smoothly decrease with the Be or Y content, the slope to be higher for substitution of the Ti than the Ni. The ternary TiNiBe and TiNiY melt-spun ribbons produced in the standard technological condition are rather brittle and don't show a good metallic aspect. They are in the crystalline structural state and undergo the martensite transformation sequence similar to the bulk material but in the lower temperature range. The contribution of the chemical composition, microstructure and strain/stress field (caused by the difference in the atomic radii) to the martensite transformation temperatures is considered.

1. INTRODUCTION

The development of non-conventional techniques for the production of Shape Memory Alloys is desirable in order to have a near-net shape forming with a high level set of the functional properties. We have attempted to develop new multicomponent alloys in the amorphous state by mean of rapid solidification technique. Since the bulk amorphous materials demonstrate an extremely large capacity for deformation (above 15000%) in the supercooled liquid region [1], they can be considered as precursors for production of crystalline materials with the shape memory property. The TiNi- and Cu-base alloys constitute two main groups of shape memory materials for which the non-conventional technologies have been developed. It was widely stated, to reach the required level of the shape memory parameters (namely, transformation temperatures, hysteresis, recoverable strain, recovery stress, etc.) to find the optimum combination of the chemical composition, production technique and heat treatment regimes. In this paper, we focus our attention to the TiNi-base alloys. It is well known that the introduction of a small quantity of the third and fourth transition metal elements on a TiNi alloy acts additionally on the martensite transformation temperatures, which can be increased in a large proportion. Moreover there is a need for shape memory alloys with high transformation temperatures for many industrial applications. Excluding the betha-phase stabilizers elements, the elements from the very beginning (V, Zr, Y, Nb, Hf, Ta) or from the end (Cu, Pd, (Ag), Pt, (Au)) of each transition metal series often result in the increase of the martensite transformation temperatures. The direct production of amorphous alloys drastically depends on the chemical composition. The selection of such a composition is helped by three « golden rules » which are supposed to favor the glass forming ability of the material submitted to a rapid solidification process. These rules help to choose elements of multicomponent alloys with large differences between atomic radii and large negative mixing energy of the different atomic pairs but with high transformation temperatures. This alloys selection is developed in this paper.

2. ALLOYS SELECTION AND EXPERIMENTAL PROCEDURE

Starting from a binary A:B alloy, Ti50Ni50, which undergoes the dual B2 <=> R <=> B19′ martensite transformation sequence, the substitution of the A-element, Ti, by Hf and B-element, Ni by Cu and increases the transformation temperatures [2, 3]. With the binary, other three basic alloys A:B have been selected for this study, the ternary $Ti_{50}Ni_{25}Cu_{25}$ alloy which undergoes the B2<=>B19 martensite transformation sequence and is known to have good amorphization ability and quaternary $Ti_{32}Hf_{18}Ni_{(50-X)}Cu_X$ alloys with x = 0, 5, 10, 15. These last alloy undergo the B2<=>(B19)<=>B19′ martensite transformation sequence. On the other hand, the effect of Be and Y on the martensite transformation parameters in TiNi-based shape memory alloys have been studied occasionally and mainly on a level of the technological additions [4] [5]. Here, we have systematically examined the introduction of Be and Y elements into A:B alloys since it allows to satisfy from the very beginning simultaneously at least two "golden rules" (multicomponent alloys and atomic radii criteria) and consequently, supposed to increase the glass forming ability of TiNi-based alloys.

We present here the results of the experimental study regarding the effect of systematic substitutions of the main constituent elements Ti and Ni of the binary alloy, by Be and Y up to 5 at.% (asymetric alloys) and simultaneous introduction of the same atomic quantity of Be and Y up to 10 at.% (symetric alloys) into the ternary and quarternary alloys, on the parameters of the martensite transformation.

The alloys ingots (25 and 10 g weight) were prepared by induction melting in an inductive cooled copper crucible under a Helium atmosphere. Rapidly solidified ribbons (of thickness varied from 30 up to 60 microns) were prepared by the planar-flow casting technique. The simple {25°C → (570-600°C), 1'} heating step has been used to transform the amorphous ribbon into the crystalline state and restore the martensite transformation. Very often such a procedure is not enough to observe the martensite transformation and subsequent various heat treatment regimes were used in the (400°C÷900°C) temperature range. Thermal stability and thermodynamic properties were studied by the differential scanning calorimetry (DSC) in temperature range (-150°C, +600°C). The material structure and phase analysis were examined by the XRD technique.

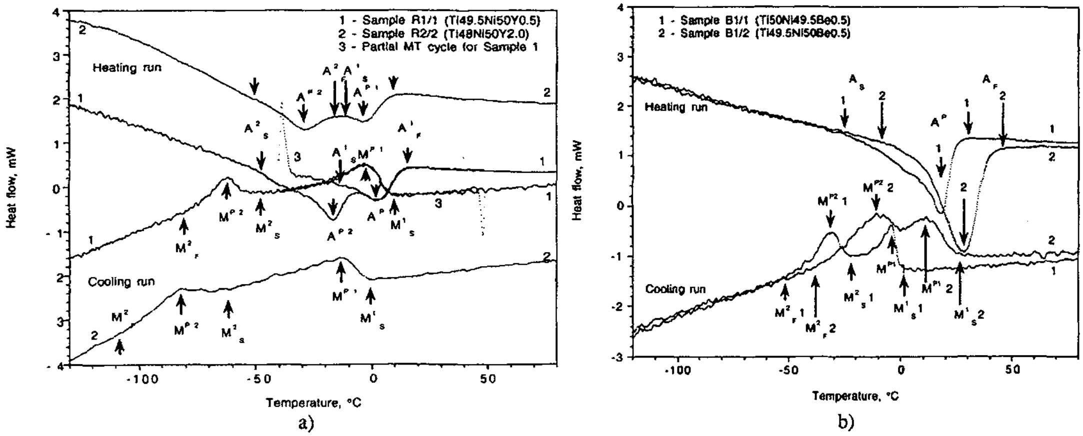
3. RESULTS AND DISCUSSION

The typical representative DSC curves obtained in the continuous heating/cooling runs through the martensite transformation onset are drawn in figure 1 for the binary alloy with the substitution of Ti by Y and of Ni by Be. Usually two or three cycles have been done in order to be sure that measurements are done for material in a "steady" condition. For simplicity, an heat flow peak will be characterized later by the temperature of its maximum.

In as-cast condition, starting from a reference binary TiNi alloy, usually we observed in practically all the Ti-Ni-Be, Ti-Ni-Y and Be-(AB)-Y alloys, two heat-flow peaks M_{P1} and M_{P2} on cooling and often an overlapping A_{P1}/A_{P2} on heating. (i.e. figure 1, 2). The partial cooling/heating cycle (see figure 1a) cycle 3 and 2b) cycles 2' and 3) has been used to differentiate a correspondence of two peaks observed in full martensite transformation cycles. The hysteresis of both transformations has been defined by difference in the peak position on cooling and heating steps, $\Delta T = (A_{Pi} - M_{Pi})$. The hysteresis of the first transformation varies below 10-12°C and the correspondent transformation heat does not exceed 5,0 J/g. Both values are close to those observed for the B2 ⇔ R transition in the binary TiNi alloys. The hysteresis of the second transformation exceeds 30°C and the value of the transformation heat is higher 6-8 J/g. These values are typical for the R ⇔ B19' transformation in binary TiNi.

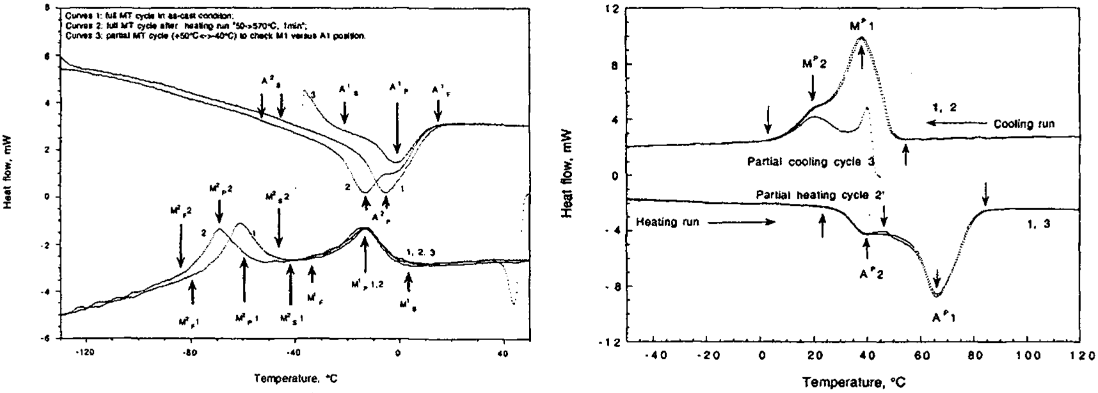
So, taking into account the fact that a small quantity of the third and fourth elements does not change considerably the transformation sequence of the TiNi-master alloy, the conclusion may be as follows: all the Ti-Ni-Be, Ti-Ni-Y and Be-TiNi-Y alloys undergo the dual B2<=>R<=>B19′ martensite transformation sequence. Most of the alloys are homogeneous both in the chemical composition and microstructure.

Their homogeneity was checked by the position of the martensite transformation temperature intervals which are known to be strongly dependent on the alloy chemical composition and microstructure. Only slight variations in the $M_S/M_P/M_F$ and $A_S/A_P/A_F$ temperature intervals are observed between the as-cast condition and after homogenization at 900-950°C,1hour.



a) b)

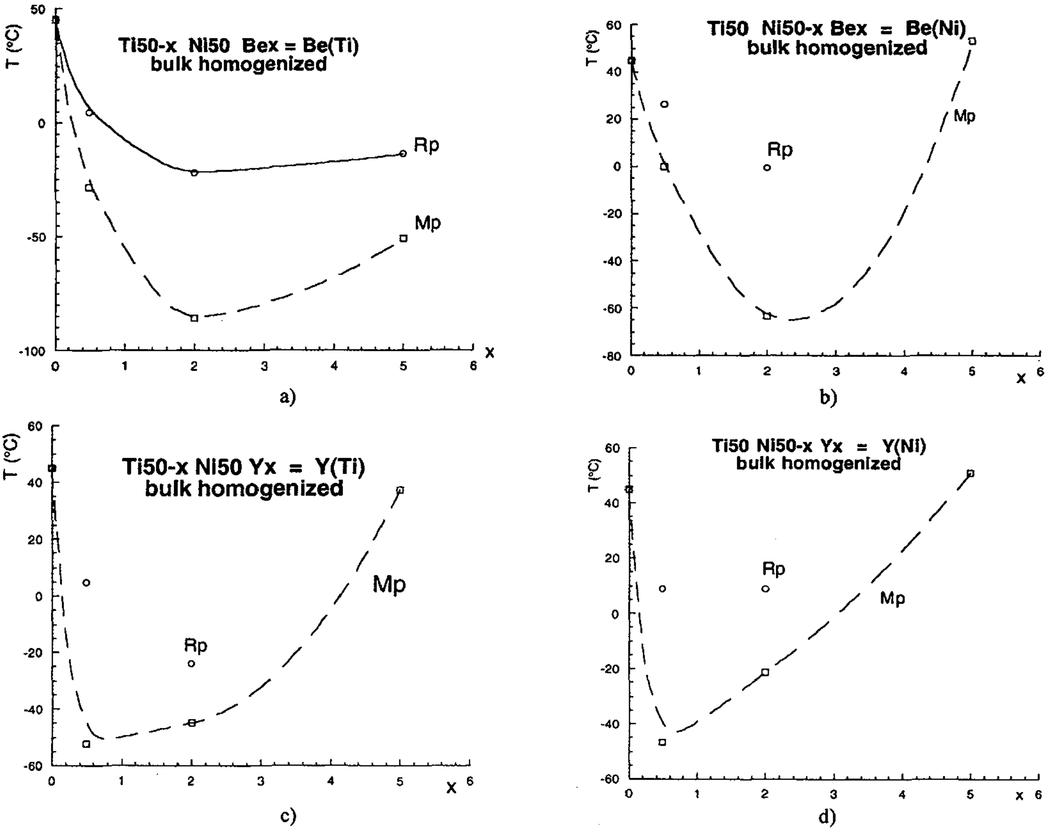
Fig. 1 : DSC heat flow for as received bulk alloys for a) Y(Ti) alloys Ti49.5 Ni50 Y0.5 and Ti48 Ni50 Y2 ; b) Be(Ni) alloys Ti50 Ni49.5 Be0.5 and Ti49.5 Ni50 Be2



a) b)

Fig. 2 : DSC heat flow for as received bulk alloys for a) Be1 Y1 (Ti50 Ni50)98 ; b) Be10 Y10 (Ti50 Ni50)80

That means that both alloying components, Be and Y, are really substitutional (both for Ti and Ni) and that there is no sensible evolution of the microstructure with this annealing treatment. Another interesting support of this conclusion comes from the comparison of the XRD spectra for equal quantity of the substituing element for the same substituing species. Despite the large difference in the initially atomic radii of the Be and Y elements, the final B2 structure of the Be-AB-Y alloys has approximately the same lattice parameter up to 10at.%. The difference is mainly in a type of preferential texture formed by Be or Y. The experimental data obtained from the DSC measurements are summarized in a form of the metastable phase diagrams for homogenized bulk material (figure 3a,b, c, d). We can observe that the effect of both elements is different from the effect of the betha-phase stabilizers. There is a "return point " around 2-3 at.% where the effect reverses from decreasing martensite transformation temperatures to a stable increasing.



a) b) c) d)

d)

Fig. 3: metastable phase diagrams showing the effect on R_p (temperature of the maximum of the heat flow of the B2 → R transformation) and M_p (temperature of the maximum of the heat flow of the R → B19' transformation) for the substitution by Be and by Y as follow, a) Ti50 – x Ni50 Bex, b) Ti50 Ni50 – x Bex, c) Ti50 – x Ni50 Yx, d) Ti50 Ni50 – x Yx.

The additive rule known for the transition metals is probably not also valid for Be and Y additions. For the symmetrically substituted alloys, BexYx (Ti50Ni50)100-x, with x = 1, 2, 5, 10, the behavior is similar to the previous results till x = 2 at % for each element (Fig. 4).

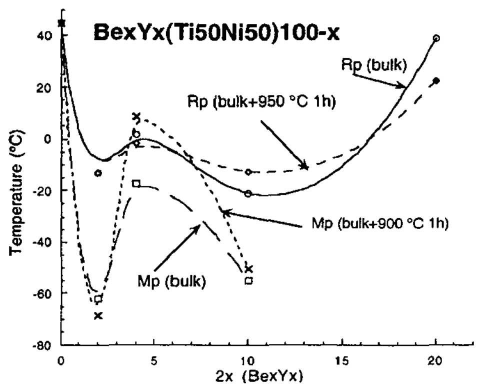


Fig. 4 : Metastable phase diagram showing the effect on Rp and Mp of the double substitution (Be,Y) for BexYx(Ti50Ni50)x as-cast bulk and annealed 1h at 950°C

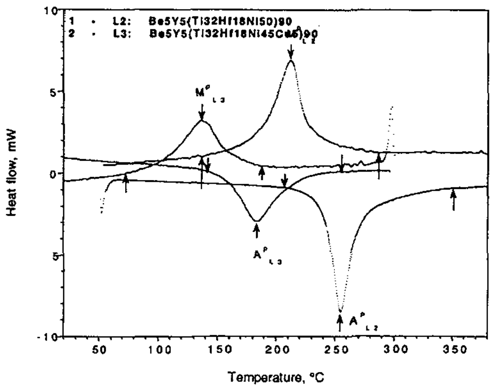


Fig. 5 : DSC Plot of high temperature bulk alloys(annealing 1hour at 900 °C) Be5Y5(Ti32Hf18Ni50)90 and Be5Y5 (Ti32Hf18Ni45Cu5)90

For x = 25, the martensite transformation is not observed any more. The fact that introduction of Be and/or Y does not supress the martensite transformation in binary TiNi, ternaries TiNiCu and TiHfNi, quaternary TiHfNiCu alloys in bulk material (fig. 5) allows us to produce the multicomponent melt-spun ribbons according to the "golden rules". These ribbons are fully amorphous (fig. 6) or amorphous with B2 and sometime B19' (table 1).

Table 1: *Some thermodynamic and structural characteristics of multicomponent alloys with substitution of Hf:Ti, Cu:Ni and* (Be, Y) on the overall composition.

Alloy composition	Quenching T °C	condition	Mp °C	Ap °C	Structures
Ti32Hf18Ni50		bulk	212	253	B19'
		Homogenized	212.4	258	B19'
	1300	Ribbon as-cast	140	212	A+B2+B19'
		Ribbon, 570°C, 1 mn	138	210	Two B2↔B19'
			25	105	
Be5Y5(Ti32Hf18Ni50)90		bulk	226	270	
		Homogenized 950°C	212.3	252.5	
		Bulk 570°C, 1 mn	219	263	
	1300	Ribbon as-cast			A
Ti32Hf18Ni35Cu15		bulk	-8		B2↔B19
			-46	2.1	B19↔B19'
		Homogenized 950°C, 1 h	130		B2↔B19
			30	70	B2↔B19'
	1285	Ribbon as-cast			A
		Ribbon 570°C, 1 mn			B2+ precipitates
Ti32Hf18Ni45Cu5		bulk	122.2	178	B2→(B19+B19')?
		Homogenized	130.2	191.8	B2→(B19+B19')?
	1296	Ribbon as-cast	-18	59.5	A+(B2↔B19')
		600°C, 1 mn:	68.8	115	B2↔B19
		dT/dt=10°C/mn	-10.5	74	B19↔B19'
Be5Y5(Ti32Hf18Ni45Cu5)90		bulk	147	195	
				158	
		Homogenized 950°C	134.3	181.7	
	1250	Ribbon as-cast	No MT		A

It is interesting to mention from the very beginning that introduction of only Be or Y atoms (in other words partially satisfiying the "golden rules" principle), usually results in flakes (up to 5at.% of the substituting matter). Nevertheless, flakes undergo the reversible martensite transformation (heat flow anomaly in DSC scans and recoverable shape change in the bending tests). So, even for this case, the appropriate parameters of the solidification process should be established.

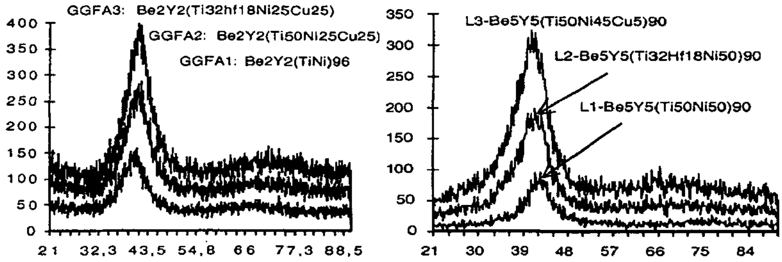


Fig. 6 : Xray diffraction patterns of amorphous multicomponent rapidly solidified alloys

Totally amorphous ribbon can be easily crystallized in a simple{25°C->(570°C-600°C), 1'} crystallization step or during subsequent heat treatments in the (400÷900)°C temperature range. They may undergo the reversible martensite transformation in the (-150°C-+300°C) temperature range as a function of the alloy composition and microstructure condition.

4. CONCLUSIONS

Alloying by Be or Y at least up to 5at.% both instead of Ti or Ni species, leads to the formation of the substitutional B2-type structure. All the Ti-Ni-Be, Ti-Ni-Y and Be-TiNi-Y alloys undergo the dual B2<=>R<=>B19′ martensite transformation sequence. Both elements Be and Y may be recommended to be a main constituent element for production of amorphous materials with potential ability to demonstrate the reversible martensite transformation and the shape memory phenomena after appropriate primary crystallization and heat treatment regimes.

New multicomponent shape memory alloys of the Be-"A:B"-Y type general series ("A"=(Ti, Hf) and "B"=(Ni, Cu,) in initially amorphous state have been systematically produced by means of the planar flow casting technique. Despite the amorphous state, the ribbons obtained are very brittle. Practically all developed amorphous alloys can be easily crystallized into the b.c.c. phase in the simple {25°C->(570°C-600°C), 1'} crystallization step or during subsequent heat treatments in the (400÷900)°C temperature range. They may undergo the reversible martensite transformation in the (-150°C-+300°C) temperature range as a function of the alloy composition and microstructure condition.

Absence of substantial amount of secondary phases detected in the Be and Y ribbons after homogenization at T=950°C for 1hour means that both alloying elements should be treated as the really substituing species and not to be treated as additions oriented on grain refinement or grain boundary cleaning.

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