Ruthenium Effect on the Transformation in Equiatomic Titanium-Nickel Alloy

PHASE STABILISATION AND MARTENSITIC TRANSFORMATION

By E. L. Semenova, N. Yu. Rusetskaya, V. M. Petyukh and V. Ye. Listovnichiy

I. N. Frantsevich Institute for Problems of Materials Science, Kiev, Ukraine

Martensitic transformations in equiatomic titanium-nickel and titanium-nickel based alloys are of interest because they are associated with the shape memory effect. Equiatomic titanium-nickel, which possesses such superior mechanical properties as high strength, elevated ductility and corrosion resistance, is the most important of several shape memory alloys. Here, the character of the martensitic transformation in equiatomic titanium-nickel alloy with some of the nickel replaced by ruthenium is discussed. Data are presented on the temperature of the transformation upon heating and cooling, the transformation sequence and the stabilisation of the high temperature phase in TiNi-TiRu alloys, using electrical resistance, thermal expansivity and differential thermal analysis between ~300°C and liquid nitrogen temperatures. Alloys which contained 0.5 to 2 atomic per cent ruthenium were found to undergo a two stage transformation, while the high temperature phase in titanium-nickel-ruthenium, which has B2-type crystal structure, was stabilised by the addition of 2 atomic per cent ruthenium.

For the past twenty-five years we have been working on interactions occurring in binary and ternary systems containing platinum group metals. Among the systems we have studied are those of the binary alloys of zirconium and the platinum group metals. We have constructed phase diagrams for these systems and shape memory effects have been found for the equiatomic zirconium-rhodium compound, as well as for the equiatomic titanium-rhodium compound. Shape restoration is assumed to occur at about 1000°C for zirconium-iridium (1, 2). The crystal structures for the high- and low-temperature modifications to equiatomic zirconium-rhodium and zirconium-iridium compounds have been determined for the first time (2).

Later work has dealt with the ternary system: titanium-nickel-platinum group metal. The interactions in the systems of titanium-nickel-rhodium and titanium-nickel-iridium along the section with 50 atomic per cent titanium have been investigated and melting diagrams have been constructed. The effects of substituting rhodium and iridium for nickel in the equiatomic titanium-nickel compound and of nickel for rhodium in equiatomic titanium-rhodium systems, together with shape memory effects, have also been studied (3, 4).

We are now studying interactions in the titanium-cobalt-rhodium and titanium-nickel-ruthenium systems, and as a continuation of our work on the phase diagram of the latter system and on the effects to the martensitic transformation in equiatomic titanium-nickel compound caused by additions of the platinum group metals, we discuss here the effect caused by ruthenium. Alloys of the titanium-nickel-ruthenium system lying along the section through equiatomic phases of the titanium-nickel and titanium-ruthenium binary systems were investigated.

Rhodium and iridium additions are known to

TiNi-TiRu Transformation Temperature Data

Composition, ruthenium, atomic per cent	Solid Transformation Temperature									
	Electrical resistance					Thermal expansion				
	M_s	M_f	A_s	A_f	T_R	M_s	M_f	A_s	A_f	T_R
0	76	40	78	109	-	-	-	-	-	-
0.5	37	17	-	-	49	22	17	-	-	37
1	9	–23	2	22	32	8	–28	17	32	32
2	–73	–113	– 65	– 43	20	–73	–113	– 68	– 43	22
5	—	-	-	-	–25	-	-	-	-	-

lower the martensitic transformation temperature of equiatomic titanium-nickel compound when 6 atomic per cent is added along the isopleth of 50 atomic per cent titanium; the B2 crystal structure phase being stabilised down to room temperature (3, 4). Taking other data into consideration, it can be concluded that the high temperature B2-phase stabilisation down to room temperature in TiNi-TiPt and TiNi-TiPd alloys does not occur (although a contrary interpretation has been given by others (5)).

In all the systems mentioned above the transformation in TiNi-based alloys with nickel partially substituted by rhodium, palladium or platinum occurs in two stages:

High temperature B2-phase → intermediate R-phase (rhombohedral structure) → low temperature monoclinic B19′-phase.

The latter phase is preserved down to liquid nitrogen temperatures. Such a two-stage transition in TiNi-based alloys is also typical of systems containing other Group VIII metals, such as cobalt and iron (7–9).

Experimental Method

The purities of the ruthenium powder and the nickel from which the alloys were prepared were 99.95 and 99.99 per cent, respectively; iodised titanium was also used. In order to avoid sputtering and losses during alloying, the ruthenium powder was sintered in vacuum at 1200°C and then melted in an arc furnace. Titanium-nickel-ruthenium alloys containing 0.5, 1, 2 and 5 atomic per cent ruthenium along the TiNi-TiRu section were prepared from melts of their component parts in an arc furnace under an argon gas atmosphere. In order to ensure a complete melt, the ingots were remelted four times. The weight losses which occurred on melting amounted to only 0.05 weight per cent, so the final compositions were considered to be identical to the initial ones. Investigations were carried out on both as-cast and annealed specimens.

Measurements of microhardness were carried out by a standard method at a load of 50 g. Other determinations of the temperature dependence of the electrical resistance and thermal expansivity were performed using custom designed equipment (6). A modified differential thermal analysis method was used to record the solid state transformations in the alloys, from liquid nitrogen temperatures up to room temperature.

Experimental Results and Discussion

The constitution of the TiNi-TiRu section of the titanium-nickel-ruthenium ternary system is important for the present work. It is necessary to know the state of the parent phase which then transforms upon cooling. During our investigations we found that the titanium-nickel equiatomic alloy formed a pseudo-binary continuous solid solution with the titanium-ruthenium equiatomic alloy, TiNi-TiRu.

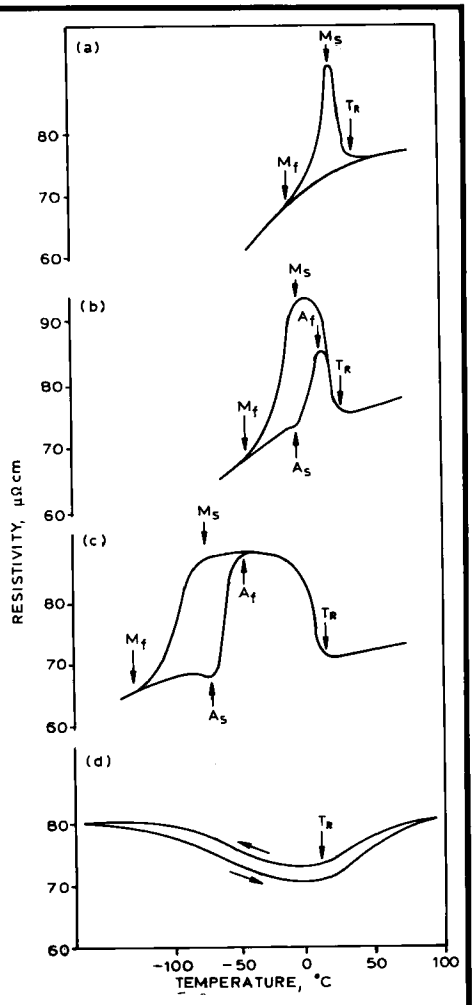

Fig. 1 Resistivity-temperature variations in:
(a) Ti50Ni49.5Ru0.5
(b) Ti50Ni49Ru1
(c) Ti50Ni48Ru2, and
(d) Ti50Ni45Ru5 alloys
Changes which occur at various temperatures are as follows:
At T_R the B2-phase begins to transform to the R-phase
At M_s the martensitic transformation starts
At M_f the martensitic transformation finishes
At A_s the B19′ transformation to R starts
At A_f the B19′ transformation to R finishes

Data showing the dependence of the electrical resistance upon temperature for alloys which contain 0.5, 1, 2 and 5 atomic per cent ruthenium, and measurements of thermal expansion with temperature for alloys containing 0.5, 1 and 2 atomic per cent ruthenium between room temperature and liquid nitrogen temperatures, are shown in Figures 1 and 2, and also in the Table.

Transformations in the TiNi-TiRu system occur in two stages, in a similar way to the transformations in titanium-nickel based alloys containing additives of iridium, rhodium and iron (1, 3, 4, 7). This can be clearly seen from the shapes of the electrical resistance curves for alloys containing 1 and 2 atomic per cent ruthenium. The sequence B2 → R → B19′ is the same as for the alloys mentioned above, see Figures 1(b) and 1(c). The stages are associated with rhombohedral (R) and monoclinic (B19′) lattice distortions. T_R is the temperature at which the parent B2-phase starts to transform into the intermediate R-phase and at which the electrical resistance sharply increases. At M_s the martensitic transformation from the R-phase starts, causing a decrease in the resistance. M_f is the temperature at which the martensitic transformation is complete. On heating the alloys from liquid nitrogen temperatures the reverse transitions take place. A_s and A_f are the temperatures at the start and finish of the B19′ → R transformation, respectively, for alloys containing 0.5 and 1, and 2 atomic per cent ruthenium.

One of the characteristics of the electrical resistance/temperature curves is that they reveal a pronounced hysteresis for R ↔ B19′ transformation, while the R-phase transformation, R → B2, does not. Thus the cooling and heating curves for alloys containing 1 and 2 atomic per cent ruthenium almost coincide at temperatures above A_f, see Figures 1(b) and 1(c).

The B2 → R transformation causes a decrease in the volume of the sample, that is, the alloy is observed to shrink, while the R → B19′ transformation results in an increase in the volume of the sample, that is, thermal expansion occurs, see Figures 2(b) and 2(c).

The observed variations in electrical resistance and thermal expansion with temperature show that the R → B19′ transformation appears to represent a first order transition. This correlates

well with the DTA data, which demonstrate the corresponding thermal effects on heating and cooling (the thermal curves in Figure 3 show only the effects caused by heating, because the data on cooling obtained in our experiments reveal the same transition temperature regardless of composition).

The B2 → R transformation is a reversible process, according to the electrical resistance data shown in Figure 1, and almost reversible, as shown by the thermal expansion data in Figure 2, and therefore can be considered as a transformation close to a second order transition. However the DTA data shown in Figure 3 illustrate that the B2 → R transformation is accompanied by thermal effects, as is the R → B19′ transformation.

It is worth noting that the intermediate phase formed during the B2 → R transformation in titanium-nickel based alloys with added iron (as well as in titanium-palladium based alloys with added nickel) is divided into ranges of incommensurate and commensurate phases with different crystal structures (10, 11). The first range (incommensurate phase) corresponds to the second order transition and the next range (commensurate phase) corresponds to the first order transition. This could explain the thermal effect which was observed in the B2 → R stage for the TiNi-TiRu alloys.

The solid state transformation in titanium-nickel-ruthenium alloy containing 5 atomic per

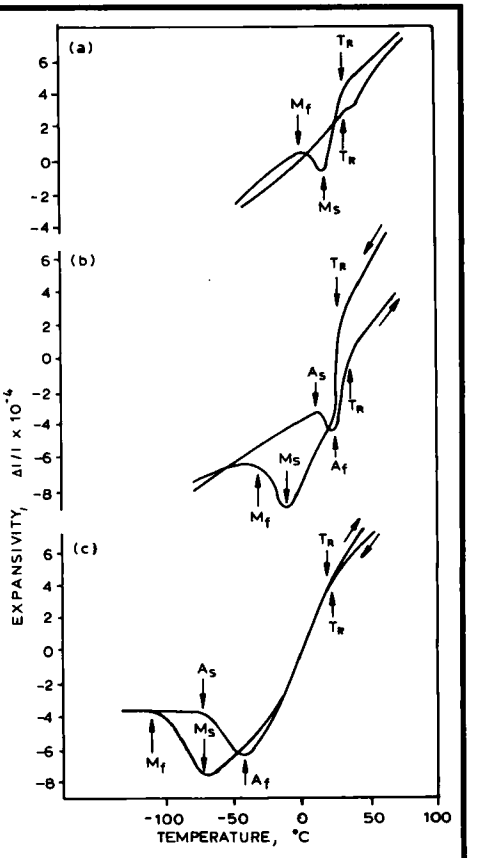

Fig. 2 Variation of thermal expansion with temperature for the alloys:
(a) Ti50Ni49.5Ru0.5
(b) Ti50Ni49Ru1
(c) Ti50Ni48Ru2

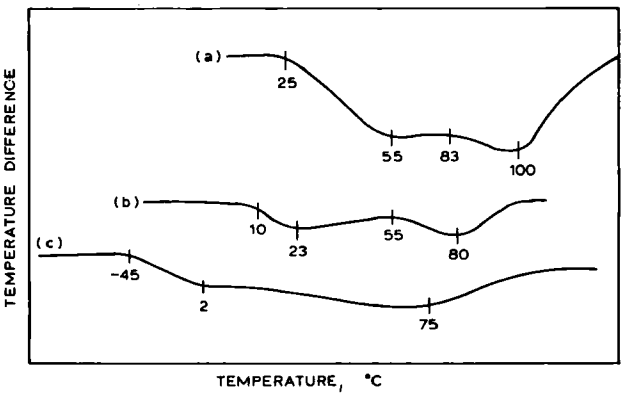

Fig. 3 Differential thermal analysis data on the solid state transformations on heating for the alloys:
(a) Ti50Ni49.5Ru0.5
(b) Ti50Ni49Ru1 and
(c) Ti50Ni48Ru2

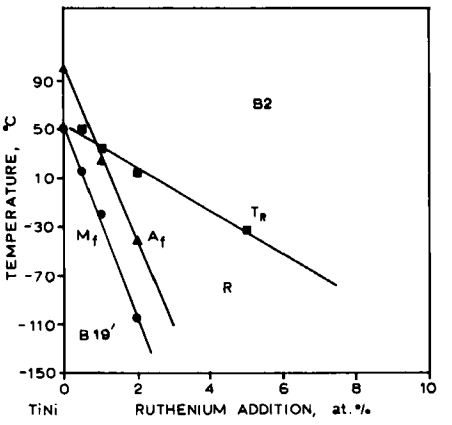

Fig. 4 Phase structure transformations with temperature in TiNi-TiRu alloys for ruthenium additions from 0 to about 8 per cent

cent ruthenium, see Figure 1(d), starts at –20°C. The R-phase exists over a wide temperature range, down to liquid nitrogen temperatures.

The martensitic transformation scheme, Figure 4, shows that the B2-phase is approximately stabilised at room temperature in alloy containing 2 atomic per cent ruthenium. The substitution of ruthenium for nickel results in a lowering of all critical transformation temperatures, but the decrease in the T_R temperature occurs less acutely than the decrease in the temperatures which indicate the transformation range

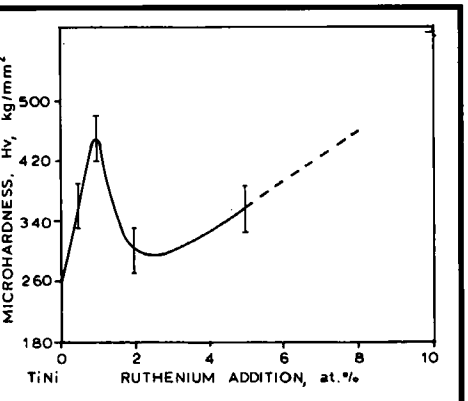

Fig. 5 Variation of the microhardness with composition for the TiNi-TiRu alloys, based on titanium-nickel alloy

of the phase having the B19′ crystal structure.

The microhardness of the titanium-nickel-ruthenium alloys varies with composition and is at a minimum for an alloy containing about 2 atomic per cent ruthenium, and at a maximum for an alloy containing about 1 atomic per cent ruthenium, see Figure 5. A comparison of these findings with those obtained from the electrical resistance and thermal expansion analyses indicates that the minimum is in accordance with the absence of a martensitic transformation in the alloys, and that the maximum is associated with accumulation of the R-phase.

Comparison of the results of the present investigation with data from the literature on the influence of platinum metals on the martensitic transformation in titanium-nickel based alloys enables the following observations to be made:

[a] Additions of ruthenium are very effective in reducing the martensitic transformation temperatures of titanium-nickel based ternary alloys. The B2-phase can be stabilised by the addition of approximately 2 atomic per cent ruthenium. (The same results can also be expected from additions of osmium.)

[b] Higher concentrations of rhodium and iridium (6 atomic per cent) are required to stabilise the B2-phase.

[c] Platinum and palladium do not appear to stabilise the B2-phase at room temperature.

Conclusions

The substitution of ruthenium for nickel in titanium-nickel-ruthenium ternary alloys along the TiNi-TiRu section, as examined by physical and chemical analyses, results in the stabilisation of the high temperature B2-type phase at room temperature for alloys containing at least 2 atomic per cent ruthenium. Alloys containing 0.5 to 2 atomic per cent ruthenium undergo a two stage transformation.

In continuation of our work with the platinum group metals, we intend to study phase equilibria in the titanium-nickel-ruthenium system both experimentally and by calculation, and following that calculate the effect of ruthenium on the martensitic transformation in equiatomic titanium-nickel compound. Data obtained from

the titanium-nickel-ruthenium alloys will make it possible to forecast the effect of osmium on martensitic transformations in TiNi-based alloys; we expect that it will sharply decrease the transformation temperatures in a way similar to that of ruthenium.

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