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Phase transformation and shape memory effect in Ru-based high temperature shape memory alloys

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Abstract. Among the different systems for high temperature shape memory alloys (SMA's), equiatomic RuNb and RuTa alloys demonstrate both shape memory effect (SME) and MT temperatures above 800°C.
For both systems, it is interesting to find a way to control the transformation temperatures while keeping the shape memory effect. One way to change the transformation temperatures is to change the composition in the binary alloys; another is to add a ternary element like Fe. The eight investigated alloys show two different space groups at room temperature. The monoclinic alloys undergo two successive displacive transformations on cooling, starting from the high temperature β phase field: β (B2) → β' (tetragonal) → β'' (monoclinic). The tetragonal alloys exhibit a single transition from cubic to tetragonal. A multiple twinned microstructure can be found in all alloys. Transformation temperatures decrease with lower Ru content and with the addition of Fe.
The β' → β transformation seems to be the main responsible for the SME. Compression tests performed in the martensitic phase give a quantitative result of the shape memory effect. In the binary alloys, the SME decreases with decreasing Ru content, which is in accordance with the evolution of the lattice parameters of martensites. A lower SME in the ternary alloys can also be linked to the lattice parameters and seems to be quite reliable to predict the evolution of the shape memory effect.

Introduction

Shape memory alloys (SMAs) have the ability to perform both sensing and actuating functions and have consequently been identified as potential materials for various functions within turbo-engines components. The introduction of this category of materials in aerospace gas turbines however requires SMAs with martensitic transformation (MT) temperature above 250°C, which is well over MT temperatures of commercially available materials. Among the different SMAs, only a few can be used as high temperature SMAs, i.e. Ti-Ni(Pt, Pd), NiAl, RuTa and RuNb alloys [1]. Ti-Ni(Pd-Pt) systems demonstrate high MT temperature but are reported to present a poor shape memory effect (SME), which may be due to a decrease of the critical stress for slip towards a level that is characteristic for the martensite detwinning process [2]. NiAl alloys transformation temperatures may be raised up to 900°C depending on the composition but the brittle room temperature martensite is not an equilibrium phase and decomposes into NiAl+Ni_5Al_3 upon aging [3]. Equiatomic RuTa and RuNb alloys demonstrate both MT temperatures above 800 °C and SME [4–6], which makes them a very promising option.
This study aims at finding a way to control the shape memory effect by changing the transformation temperature. As it is known for multiple shape memory materials, mechanical characteristics are better when the transformation temperature M_s is less than half of the melting temperature T_m.

There are two ways of decreasing the high transformation temperature we find in the equiatomic alloys: (1) by changing the composition of the binary alloys or (2) by adding a third element like Fe, which will partially substitute the Ru.
These alloys may undergo two successive displacive equilibrium transformations [7]. The high-temperature transition takes place on cooling from the cubic B2 β-phase to a tetragonal β'-phase. The second transformation gives rise to a monoclinic β'' phase. Alloys with a Nb or Ta content higher than approximately 54 at.% undergo a single cubic→tetragonal transformation [4, 8]. Shape memory behaviour in these systems has been observed either from the β' or β'' phase, whereas only the high temperature MT is considered to be responsible for the SME [9, 10].

Experimental procedures

All alloys have been prepared from high purity elements by vacuum arc melting technique. The alloys have been re-melted several times to ensure homogeneity. Final compositions were determined by atomic absorption spectrometry within an experimental precision of 0.5 at. % and proved to be very close to the intended compositions.
Ingots have been homogenised in a vacuum furnace at 1600 °C for 168 h. All specimens were cut by an electro-discharge machine.
Microstructural observations were performed by scanning electron microscopy (SEM) using a Zeiss DSM962 system operating at 15 kV and transmission electron microscopy (TEM) on a Philips CM20 microscope operating at 200 kV. Transformation temperatures have been determined on homogenised specimens by differential scanning calorimetry (DSC) from RT to 700°C on a Mettler Toledo DSC 822e and from RT to 1200°C on a Netzsch DSC404 apparatus with a heating/cooling rate of 10 K/min. Compression tests curves were carried out in a vacuum furnace at a strain rate of 10^{-4} s^{-1} on 3×3×6mm^3 samples. Reheating of the deformed samples was performed in a vacuum furnace.
In order to quantify the SME for each alloy, compression tests were performed in the martensitic phase at 55°C below the transformation temperature and stopped at various total strains. The length of the specimen was measured at room temperature before testing and after compression. The remaining length was measured at room temperature after heating up the specimen to A_p'+150°C in the B2 phase.

Results and discussion

Martensitic transformation. The crystallographic structure of both alloys at room temperature was determined from X-ray diffraction experiments and from TEM analysis. $Ru_{50}Nb_{50}$, $Ru_{50}Ta_{50}$ and $Ru_{40}Ta_{50}Fe_{10}$ exhibit a monoclinic structure (P2/m), whereas $Ru_{45}Nb_{55}$, $Ru_{45}Ta_{55}$, $Ru_{43}Nb_{57}$, $Ru_{43}Ta_{57}$ and $Ru_{40}Nb_{50}Fe_{10}$ prove to be tetragonal (P4/mmm).
According to these results, $Ru_{45}Nb_{55}$, $Ru_{45}Ta_{55}$, $Ru_{43}Nb_{57}$, $Ru_{43}Nb_{57}$ and $Ru_{40}Nb_{50}Fe_{10}$ are expected to undergo a single cubic-to-tetragonal martensitic transformation whereas a second transformation from this β'-tetragonal structure to the β''-monoclinic phase occurs in $Ru_{50}Nb_{50}$, in $Ru_{50}Ta_{50}$ and in $Ru_{40}Ta_{50}Fe_{10}$. DSC measurements confirm these assumptions (table 1). One can notice the low hysteresis (Ap'-Mp' and Ap''-Mp'') associated to both transformations.
It can be seen very clearly that the decrease of Ru-content decreases the transformation temperatures. The binary monoclinic alloys show clear and well pronounced peaks, as does $Ru_{45}Nb_{55}$. The peaks in the other alloys are very small and rather widely spread. A possible explanation may be the loss of energy associated to the transformation with the Ru-content.
The addition of iron to the binary alloys affects widely the transformation temperature. Both ternary alloys show transformation temperatures that are rather in the order of the 43% Ru containing alloys than that of their binary correspondents. The addition of iron seems to be a reliable way to decrease the transformation temperatures.

Table 1. Transformation temperatures (°C) and corresponding hysteresis determined from DSC experiments

High temperature transformation β → β'							
	Ms'[°C]	*Mp'[°C]*	*Mf'[°C]*	*As'[°C]*	*Ap'[°C]*	*Af'[°C]*	*Hyst*
$Ru_{50}Ta_{50}$	1038	1033	1028	1041	1045	1050	12
$Ru_{50}Nb_{50}$	887	886	884	898	899	900	13
$Ru_{45}Ta_{55}$	548	538	520	529	543	554	7
$Ru_{45}Nb_{55}$	492	491	489	493	496	496	5
$Ru_{43}Ta_{57}$	366	347	302	308	350	369	3
$Ru_{43}Nb_{57}$	327	321	314	318	322	330	1
$Ru_{40}Ta_{50}Fe_{10}$	447	419	395	398	422	451	3
$Ru_{40}Nb_{50}Fe_{10}$	342	336	331	336	340	347	4
Low temperature transformation β' → β''							
	Ms''[°C]	*Mp''[°C]*	*Mf''[°C]*	*As''[°C]*	*Ap''[°C]*	*Af''[°C]*	*Hyst*
$Ru_{50}Ta_{50}$	787	780	771	781	793	799	13
$Ru_{50}Nb_{50}$	751	746	742	751	760	762	14
$Ru_{40}Ta_{50}Fe_{10}$	320	284	264	273	293	326	9

Microstructure. Details of the microstructure have been reported previously [11-13]. The microstructural characteristics and their evolution with composition are very similar for RuNb, RuTa and ternary systems. Every alloy is characterized by a microstructure consisting of lamellar grains with an average diameter of 300 microns. The lamellae (average width of 10 microns) also exhibit an internal twinning, particularly pronounced in the case of monoclinic alloys. TEM observations confirm the presence of microtwins, with an average width of 50-100 nm.

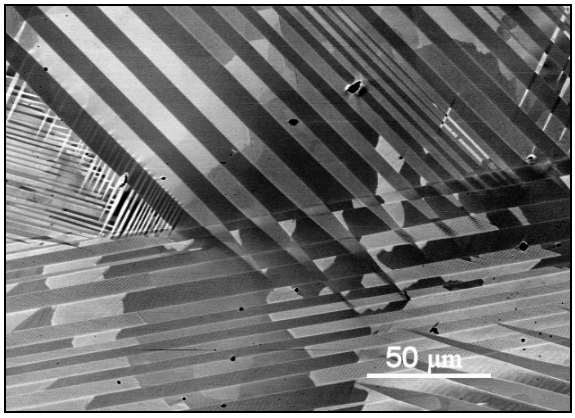

Fig. 1: SEM image of the microstructure of $Ru_{43}Ta_{57}$

The shape memory effect.

The shape memory effect is reported in table 2.

Table 2. Recovered strains for the eight alloys deformed 55°C below the transformation temperature.

	Maximum SME	Maximum 100% recovery
$Ru_{50}Ta_{50}$	3	1.8
$Ru_{50}Nb_{50}$	2.9	1.5
$Ru_{45}Ta_{55}$	0.2	-
$Ru_{45}Nb_{55}$	2.3	0.5
$Ru_{43}Ta_{57}$	0.3	-
$Ru_{43}Nb_{57}$	0.2	-
$Ru_{40}Ta_{50}Fe_{10}$	1.3	1
$Ru_{40}Nb_{50}Fe_{10}$	0.8	-

The highest shape recoveries can be observed for the equiatomic alloys, $Ru_{45}Nb_{55}$ and, to some extend, $Ru_{40}Ta_{50}Fe_{10}$. However, when observing the limit of 100% recovery for these four alloys, it can be seen that this value is very low for $Ru_{45}Nb_{55}$. The most interesting alloys remain therefore the equiatomic alloys, to which the ternary $Ru_{40}Ta_{50}Fe_{10}$ can be added. The shape memory effect of the other alloys is too low to be of any interest, and their 100% recovery is too small to be measured.

The general tendency is a lowering of the SME with the lower Ru concentration and therefore the decrease of the transformation temperatures. Decreasing transformation temperatures cannot explain a higher shape memory effect, which we could have expected by the initial assumption of $M_s<0.5\ T_m$. This result is a bit surprising if we consider that a decrease of the temperatures should be associated to a lower mobility of the dislocations. Another possibility is that this decrease of shape memory properties with Ms can be related to the evolution of crystallographic characteristics of the resulting martensite with composition.

The maximum compression strain for an ideal martensitic reorganisation under stress is associated to the transformation stress of the unit cell. In this case, the stress is caused by shearing. The shearing amplitude can be calculated from the c/a ratio, measured by x-ray diffraction, by a simple geometrical consideration in the tetragonal cell. The amplitude s is directly related to the angle θ between (0-11) of both variants (equation 1), the twinning plane being (011). This angle θ can also be measured directly in diffraction patterns (equation 2).

$$s = 2\tan\left(\frac{\theta}{2}\right) \quad (1)$$

$$\theta = 180° - 4\arctan\left(\frac{a}{c}\right) \quad (2)$$

It can then be interesting to consider the evolution of the c/a ratio of the tetragonal unit cell with the composition.

The monoclinic alloys having a different crystallographic structure, their c/a cannot be directly compared to the others. However, as a first approximation, parameters of the corresponding tetragonal cell have been determined from the monoclinic cell. A theoretical ratio between interplanar distances can be calculated by using the correspondence between the monoclinic and the tetragonal structures [11, 12] as follows:

$c_T/a_T = d_{001T}/d_{100T} \rightarrow d_{20\text{-}1M}/d_{1\text{-}11M}$.

The evolution of the c/a ratio of RuNb, RuTa and the ternary alloys is reported in table 3. The c/a ratio tends to 1:1 with decreasing Ru content. The ternary alloys can be fitted in this figure and it can be seen that their c/a is lower than that of their corresponding binary alloy.

Table 3. The evolution of the c/a ratio in the tetragonal alloys and its equivalent for the monoclinic alloys.

	c/a ratio
$Ru_{50}Ta_{50}$	1.12
$Ru_{45}Ta_{55}$	1.07
$Ru_{43}Ta_{57}$	1.05
$Ru_{40}Ta_{50}Fe_{10}$	1.10
$Ru_{50}Nb_{50}$	1.14
$Ru_{45}Nb_{55}$	1.06
$Ru_{43}Nb_{57}$	1.04
$Ru_{40}Nb_{50}Fe_{10}$	1.08

Conclusion

Transformation temperatures decrease with lower Ru content and with the addition of Fe. X-ray diffraction shows that $Ru_{40}Ta_{50}Fe_{10}$ is monoclinic at room temperature, as are the equiatomic alloys, while $Ru_{40}Nb_{50}Fe_{10}$ is tetragonal, just as the binary non-equiatomic alloys.

After compression tests in the martensitic phase, a maximum shape recovery of 3% has been obtained for the equiatomic binary alloys and at transformation temperatures over 900°C. Shape recovery decreases with decreasing Ru content and decreasing transformation temperatures and it is linked to the c/a ratio of the tetragonal structure. A decreasing c/a ration decreases the shape memory effect.

The consideration of the c/a ratio seems to be a more reliable way to explain the shape memory effect evolution than the transformation temperature. Apparently, the transformation shearing is a more powerful mechanism than the dislocation movement.

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