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Influence of Rapid Solidification on $Ni_{50-x}Ti_{50}Co_x$ Shape Memory Alloys

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Abstract. Rapidly solidified (R.S.) $Ni_{50-x}Ti_{50}Co_x$ ribbons have been produced by a single roller melt spinning technique. The influence of rapid solidification experimental parameters on the structure and transition behaviour were investigated by DSC, by X-ray diffraction and by TEM. The DSC curves are stable from the first cycle and a preferred orientation exists in the rapidly solidified NiTiCo alloys. An experimental parameter such as quenching temperature increasing is followed by the precipitate growth. These precipitates of Ti_2Ni, may be responsible for the martensitic and R transition temperature decreasing. Annealings enlarge the precipitate size and the transition temperatures decrease again.

1. INTRODUCTION

The NiTi based Shape Memory Alloys, made by the conventional melting method have a difficult and expensive metal forming : hot and cold rollings, metal cutting, thermal treatments are laborious and need a long time. Moreover, they can introduce defaults and others elements like oxygen.
The melt spinning method produces thin fine grained ribbons [1] directly from the melting condition, reducing fabrication tests and costs.
In this paper, we report on the properties of R.S. $Ni_{50-x}Ti_{50}Co_x$ (x = 0, 2, 3 at.%) in either the as-spun or the heat-treated conditions.

2. EXPERIMENTAL

Three compositions have been studied : $Ni_{50}Ti_{50}$, $Ni_{48}Ti_{50}Co_2$ and $Ni_{47}Ti_{50}Co_3$.
After conventional elaboration of alloy ingots, the ribbons of R.S. $Ni_{50-x}Ti_{50}Co_x$ were prepared by a single roller melt spinning technique in a helium atmosphere. The melt was spread out on the surface of a wheel.
Two wheels have been experimented : steel, and copper-berillium-cobalt. The thermal conductivities and the surface conditions of the wheels are different and affect the rapid solidification conditions.
The quenching temperature of the molten alloys in the nozzle varies within the range of 1390 to 1560°C.
The characteristics of ribbons : width, thickness are reported in table 1.

Table 1. The experimental parameters of the rapidly solidified alloys studied in the present investigation

Alloy (at. %)	Specimen	Wheel velocity ($m\ s^{-1}$)	Wheel materials	Quenching temperature (°C)	Ribbon width (mm)	Ribbon thickness (μm)	Quality
$Ni_{50}Ti_{50}$	a	19	steel	1500	8	50	brittle
$Ni_{50}Ti_{50}$	b	19	steel	1490	8	50	brittle
$Ni_{50}Ti_{50}$	c	19	steel	1430	2 to 4	50	good aspect
$Ni_{48}Ti_{50}Co_2$	d	19	CuBeCo	1560	9	100	good aspect
$Ni_{48}Ti_{50}Co_2$	e	19	steel	1530	5	70	brittle
$Ni_{47}Ti_{50}Co_3$	f	19	steel	1390	8	50	good aspect

The ribbons were examined by X-ray diffraction using Cu Kα radiation, by transmission electron microscopy (TEM) and by differential scanning calorimetry (DSC).

3. RESULTS AND DISCUSSION

3.1. Ribbon aspects

The size of the matrix B2 grains and precipitates decreases when the wheel surface velocity increases [2]. This experimental parameter has been fixed at 19 m s^{-1}.
The ribbon aspect depends on both the wheel materials and the quenching temperature. On a steel wheel, the rapidly solidified specimens have a better aspect when the quenching temperature is lower than 1430°C. For a Cu-Be-Co wheel, an high quenching temperature is consistent with a good quality (Table 1).

3.2. DSC results

3.2.1. DSC on massive $Ni_{50-x}Ti_{50}Co_x$ specimens

We have studied the evolution of transition temperatures with the cobalt content by DSC (Fig. 1).
Thermal cycling is necessary to obtain the separation between R and martensite phases in equiatomic NiTi (5 cycles). For the three alloys, 20 cycles are necessary to have reproductive transition temperatures [3].
After thermal cycling, the equiatomic NiTi alloy is in the martensitic state at room temperature. The $Ni_{48}Ti_{50}Co_2$ and $Ni_{47}Ti_{50}Co_3$ alloys are in a mixed parent and R phase at room temperature.

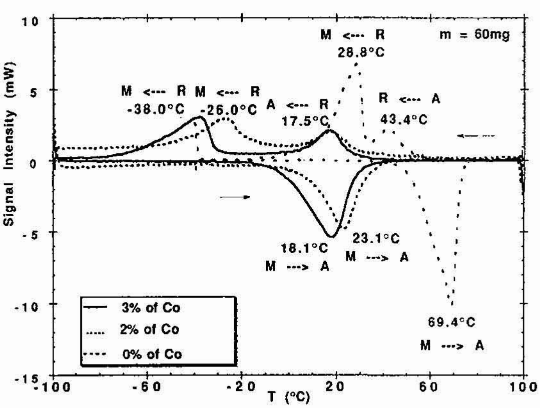

Figure 1 : DSC curves of $Ni_{50-x}Ti_{50}Co_x$ (x = 0, 2 and 3 %) after 20 cycles

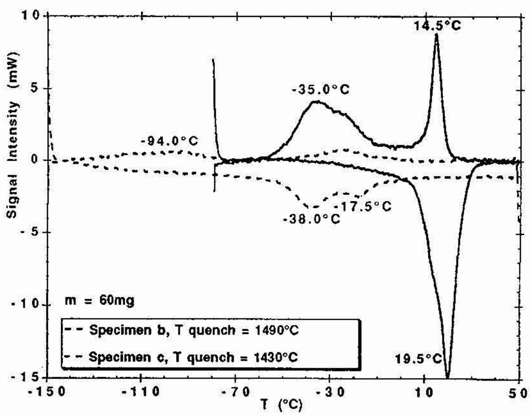

Figure 2 : Influence of the quenching temperature on the R.S. equiatomic NiTi transition behaviour (specimen b and c)

3.2.2. DSC on rapidly solidified equiatomic NiTi specimens

The transition points of the R.S. specimens of NiTi are lower than those found in alloys produced by conventional methods. The martensite phase appears below room temperature. R and martensite phases are distinct on the DSC curves from the first cycle.
The Ms decreasing is related to a microstructural change induced by rapid solidification. The formation of precipitates may modify the matrix local composition and so lower the transition temperatures.
On DSC curves, it can be noticed that the martensitic and R transformation temperatures decrease when the quenching temperatures increase (Fig. 2). The NiTi samples a and b have neighbour quenching temperatures and their DSC spectrums are similar.

The NiTi specimen c has been annealed under vacuum at 800°C, for 10h. The spectrum is stable from the first cycle. A -> R transformation is quite spread out and the martensitic transformation temperatures are decreased (Fig. 3).

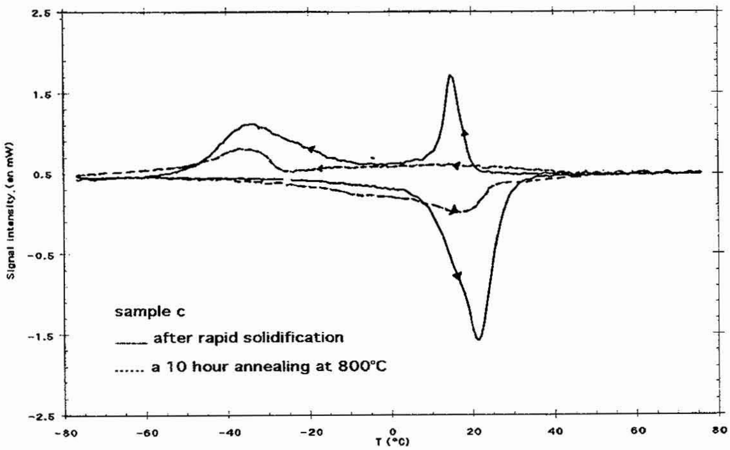

Figure 3 : DSC for the R.S. and annealed NiTi specimen c

3.2.3. DSC on rapidly solidified $Ni_{48}Ti_{50}Co_2$ specimens

The two spectrums of $Ni_{48}Ti_{50}Co_2$ specimens d and e are comparable (Fig. 4). The R and martensitic transformations cannot be distinguished. The transition is extended in temperature and there is a lot of stored elastic energy. Consequently, on heating, for specimen d, the reverse transformation starts very abruptly.
Short annealings (5 min) in air at 400°C and 500°C relax stresses and the martensitic and R phase transformation temperatures are distinct (Fig. 5).

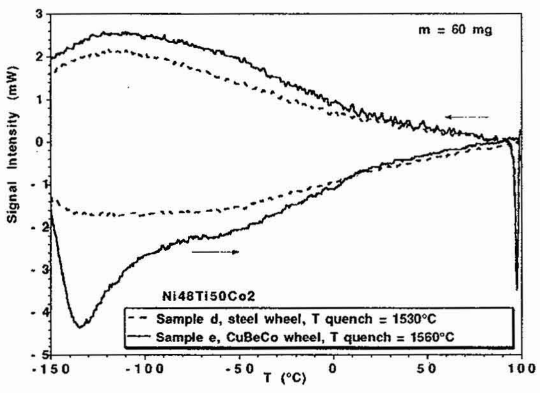

Figure 4 : Influence of wheel materials and quenching temperature on the DSC curves of the R.S. $Ni_{48}Ti_{50}Co_2$ specimens d and e

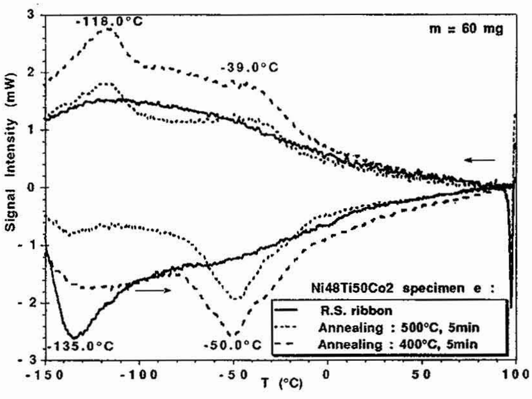

Figure 5 : Influence of short annealings on the R.S. $Ni_{48}Ti_{50}Co_2$ specimen e

3.2.4. DSC on rapidly solidified $Ni_{47}Ti_{50}Co_3$ specimen

The martensitic and R transition temperatures are clearly distinct. On heating, we observed two peaks. The second peak corresponds to the R -> A transition. This transition shows an offset of 6 degrees with respect to the A -> R transition on cooling (Fig. 6 and Fig. 7).

This R.S. $Ni_{47}Ti_{50}Co_3$ alloy, specimen f, is annealed 2, 4 and 10h at 800°C under vacuum. It can be noticed that the transition temperatures decrease with the annealing time (Fig. 6 and Fig. 7). After 10 hours the specimen is fragile and no peak is noticed.

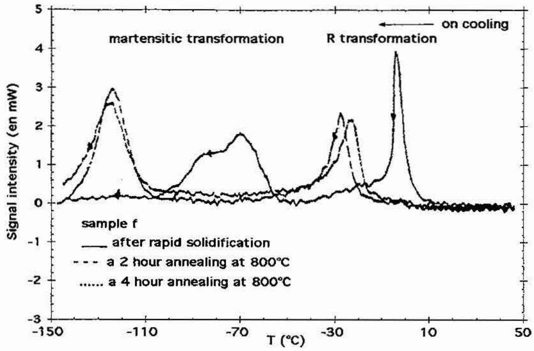

Figure 6 : DSC cooling curve for the $Ni_{47}Ti_{50}Co_3$ R.S. and annealed sample f. Annealing 800°C, 10h

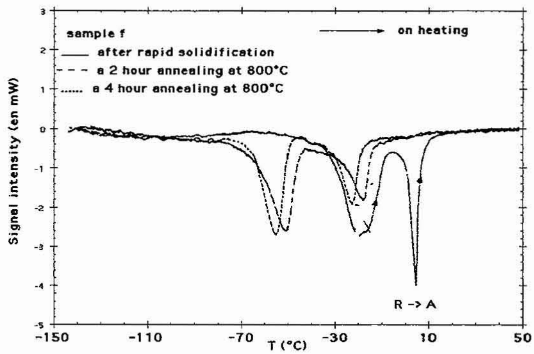

Figure 7 : DSC heating curve for the $Ni_{47}Ti_{50}Co_3$ R.S. and annealed sample f. Annealing 800°C, 10h

3.3. X-ray diffraction

3.3.1. Crystallinity and texture

All the specimens studied have a good crystallinity at room temperature. The diffraction lines are very sharp and no diffuse scattering is noticed.
No difference is observed between the two faces of the ribbons.
In the X-ray diffraction of a perfect B2 NiTi, the most important peak is 110. The preferred 200 orientation is noticed in the R.S. alloys $Ni_{50-x}Ti_{50}Co_x$, but also in the $Ni_{50-x}Ti_{50}Y_x$ with y = Cu, Pd... [4], [5].
In Table 2, we compare the X-Ray intensities of the austenite maximum peak values measured in the R.S. specimens d and e of $Ni_{48}Ti_{50}Co_2$ composition with the same alloy elaborated classically by induction and after annealing under vacuum at 800°C for 10h. The R.S. specimen e has been annealed at 800°C for 10h too.
The annealing process modifies the peak intensities but not the preferred orientation. The 200 texture is specific to rapidly solidified alloys and influences their properties (Fig 8 and 9).

Table 2. The relative intensities of the austenite maximum peak values of two R.S. ribbons (d and e) with $Ni_{48}Ti_{50}Co_2$ composition are compared with ASTM and with classical and annealed alloys.

hkl B2	$Ni_{48}Ti_{50}Co_2$ R.S. specimen d	$Ni_{48}Ti_{50}Co_2$ R.S. specimen e	$Ni_{48}Ti_{50}Co_2$ R.S. specimen e 800°C, 10h	Reference ASTM B2	$Ni_{48}Ti_{50}Co_2$ after conventional elaboration	$Ni_{48}Ti_{50}Co_2$ conventional elaboration 800°C, 10h
(100)	22	24	27		17	2
(110)	30	2	48	100	100	100
(200)	100	100	100	40	100	2
(211)	0.63	0.25	9	60	6	22

3.3.2. The influence of precipitates

In the R.S. $Ni_{48}Ti_{50}Co_2$ alloy, specimen d (fig. 8), the Ti_2Ni X-ray intensities are extremely weak (about 0.2 to 0.3% of relative intensity). After annealing, the Ti_2Ni lines are more intense (Fig. 9).
In specimen f, after annealing, Ti_3Ni_4 peaks are detected.

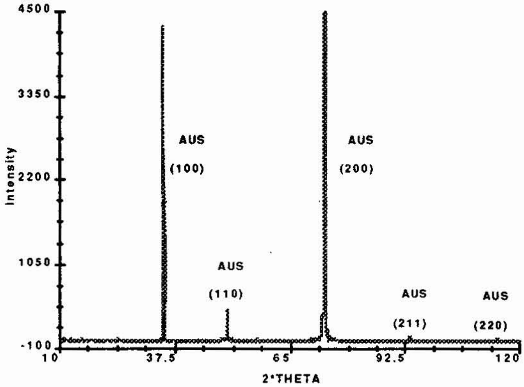

Figure 8 : X-ray spectrum of R.S. $Ni_{48}Ti_{50}Co_2$ sample (e)

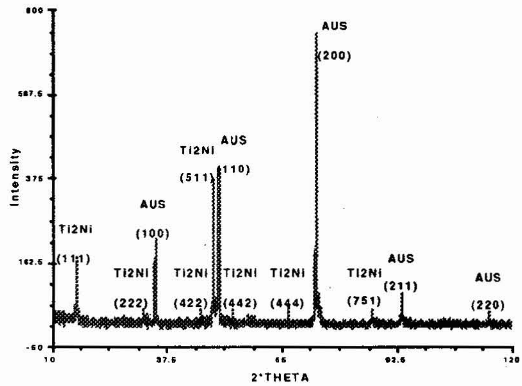

Figure 9 : X-ray spectrum of R.S. and annealed $Ni_{48}Ti_{50}Co_2$ sample (e) Annealing : 800°C, 10h

3.4. TEM study

This study corroborates the DSC and X-ray investigations.

3.4.1. Rapidly solidified equiatomic NiTi specimens

For the R.S. NiTi specimens a and b , fine precipitates are detected in the matrix. Their size varies from 30 to 45 nm (Fig. 10).
Such precipitates are not observed in the specimen c.
After annealing, the sample c has Ti_2Ni precipitates at grain boundaries and within the grains.

3.4.2. Rapidly solidified $Ni_{48}Ti_{50}Co_2$ specimens

For the R.S. $Ni_{48}Ti_{50}Co_2$ specimen e : small round precipitates (40 nm) and few oxyde diffraction patterns are recognized.
For the R.S. $Ni_{48}Ti_{50}Co_2$ specimens d and e : Ti_2Ni precipitates from 120 to 150 nm are scattered in the matrix as well as lenticular shape precipitates Ti_3Ni_4.

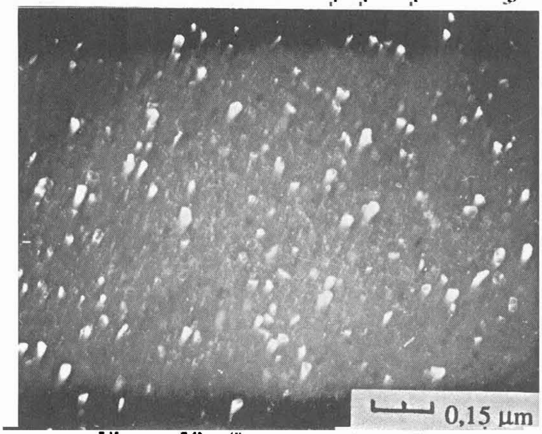

Figure 10 : fine precipitation in R.S. NiTi specimen b

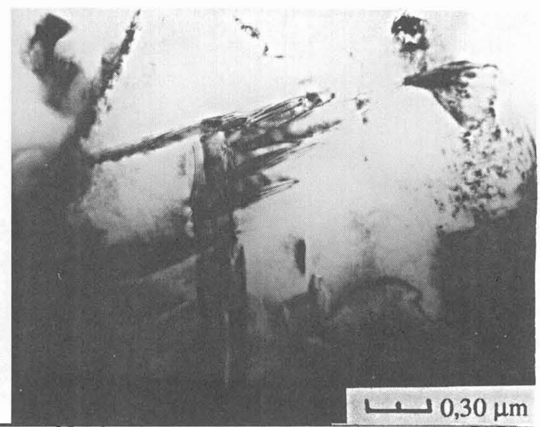

Figure 11 : lenticular shape precipitates in the R.S. and 10 hour annealed $Ni_{47}Ti_{50}Co_3$ specimen (f)

3.4.3. Rapidly solidified $Ni_{47}Ti_{50}Co_3$ specimen

Specimen f : grains have tortuous shapes. Oxyde diffraction patterns and fine precipitation are present.
A 2 hour annealing shows an increasing of the precipitate size (from 35 to 80 nm).
For a 4 hour annealing, the precipitate size is about 150 nm.
For a 10 hour annealing, the precipitation is very important and varied. Ti_2Ni and Ti_3Ni_4 precipitates have been recognized (Fig. 11). This result confirms the X-ray informations. The Ti_2Ni precipitates lower the composition of titane in the matrix and the precipitation of Ti_3Ni_4 may compensate it.

4. CONCLUSION

The rapid solidification permits a modification of the NiTi properties. In DSC, the transition temperatures of the R.S. and annealed alloys are stable from the first cycle. The experimental conditions of melt spinning are very important because they influence the precipitation and the grain size. By the use of wheels of different materials, the thermal conductivity is changed and then the cooling velocity. The precipitation varies proportionally to the quenching temperature and the annealing time increases the precipitate size. Consequently, precipitates hamper martensite and R phase formation and the transition temperatures decrease.

Acknowledgments

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