

# Influence of manganese on the transformation temperatures of Ni<sub>50</sub>Ti<sub>50</sub> shape memory alloys

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The transformation temperatures of NiTi-based alloys strongly depend on the number of (valence) electrons. It has been argued that the  $M_s$  of Ni<sub>0.50-x</sub>Ti<sub>0.50-x</sub>Mn<sub>2x</sub> is independent of  $x$ , because  $e/a=7.00$ , unchanged relative to Ni<sub>0.50</sub>Ti<sub>0.50</sub>, for any  $x$ . In this work, a model is presented, in which it is argued that not only changes in the number of electrons, but also band-structure changes should be considered. The calculations, made with this model, are confirmed by experimental results.

## 1. Introduction

In the literature, the martensitic transformation is traditionally thought to have an electronic origin (see, e.g., refs. [1-4]). Wang [1] and Honma et al. [2] show a clear dependence of  $M_s$  on  $e/a$ , i.e. the number  $4s+3d$  electrons per atom. Honma et al. [2] argued that the  $M_s$  of Ni<sub>0.50-x</sub>Ti<sub>0.50-x</sub>Mn<sub>2x</sub> is independent of  $x$  because in these alloys  $e/a=7.00$ , as in NiTi. They confirmed this by (unpublished) measurements. To our knowledge, Ni<sub>0.50-x</sub>Ti<sub>0.50-x</sub>Mn<sub>2x</sub> is not further investigated. Only Chernov [5] performed some investigations on Ni<sub>0.50-x</sub>Ti<sub>0.50-x</sub>Mn<sub>2x</sub>, but he did not consider Mn as an addition. All additions investigated by Chernov cause a lowering of the transformation temperatures in such types of alloys.

Substitution of either Ni or Ti by Mn lowers the transformation temperatures. In Ni<sub>0.50-x</sub>Ti<sub>0.50</sub>Mn<sub>x</sub>,  $A_s$  is lowered by more than 53 K per atomic percent Mn and  $M_s$  by 70 K per percent [6]. Eckelmeyer [7] found a lowering of  $A_s$  by 37 K per percent Mn when Mn substituted Ti, while Honma [2] finds a lowering of  $M_s$  by 62 K per percent in the same alloy system.

In the further development of a recently described

model, which considers the martensitic transformation itself and predicts the influence of ternary additions on the transformation temperature  $M_s$  [8,9], it is found that apart from a change in the number of electrons, a change in band structure is required to explain the  $M_s$  temperature of ternary NiTi-based alloys. According to this line of reasoning, it is expected that the  $M_s$  temperature of Ni<sub>0.50-x</sub>Ti<sub>0.50-x</sub>Mn<sub>2x</sub> is not independent of  $x$ .

In this work, the present model is applied to this alloy system in order to predict  $M_s$  as a function of  $x$ .  $M_s$  is experimentally determined for a range of alloys for verification.

## 2. Experimental

Alloys of Ni<sub>0.50-x</sub>Ti<sub>0.50-x</sub>Mn<sub>2x</sub> are arc melted (six times for homogeneity), annealed at 1223 K for 72 h, 10% deformed at 1073 K (0.1 mm/min). (More detailed description is given in refs. [10,11].) The composition is checked by electron microprobe analysis (see table 1 and fig. 1). The Ti content is somewhat higher than intended, but this will not be of much influence, since it is known that the transformation temperatures in Ti-rich non-stoichiometric NiTi alloys are fairly composition independent.

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Table 1  
Alloy composition,  $M_s$  and  $A_s$  (third cycle)

Alloy code	Composition (at.%)			Transformation temperature (K)	
	Ti	Ni	Mn	$M_s$	$A_s$
01	50.6	49.4	0.01	325	345
15	50.6	48.5	0.91	266	291
02	49.9	48.7	1.34	238	269
2-1	49.7	49.0	1.36	220	235
2-2	48.9	48.6	2.51	< 148	
2-3	48.4	48.6	2.93	< 148	
04	48.4	47.0	4.54	< 148	
06	45.7	44.9	9.39	< 148	
10	42.1	40.0	17.91	< 148	

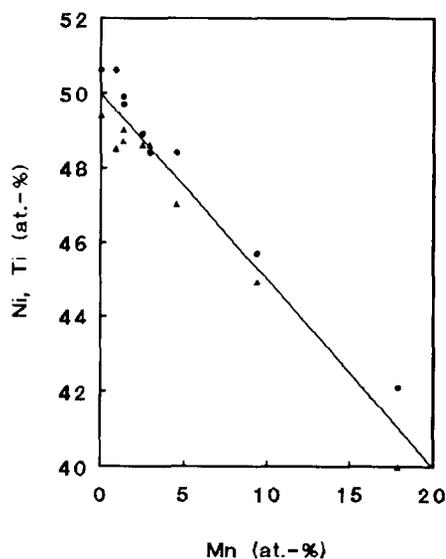


Fig. 1. Composition of the NiTiMn alloys.  $\blacktriangle$ , Ni;  $\bullet$ , Ti.

### 3. A short description of the present model

In the literature, the martensitic transformation is usually thought to have an electronic origin. Samsonov [12] argues that in pure or diluted Ti, the bcc to hcp transformation takes place as the degree of localization of the electrons is about 60%. In a new model, which is described extensively elsewhere [8], this hypothesis is reformulated in order to include the temperature in the model: instead of considering

the relative amount of electrons that is localized, the occupation of d states is considered.

As transformation takes place, electron states are shifted along the energy axis. In order to gain structural energy, which is a condition for transformation to take place, states that are shifted to higher energies should be sufficiently emptied while states that are shifted to lower energies should preferably be filled. So, in order for transformation to take place, a number of states has to be emptied by lowering the temperature.

The present model [8] describes the influence of ternary additions on the martensitic transformation temperatures. It starts with the introduction of a (composition-dependent) electron state, called state A, with energy  $E_A$ , which is the last state to be sufficiently emptied (to a critical occupation probability  $\rho^*$ ) before transformation takes place. The model is based on the hypothesis that state A has always the same occupation probability  $\rho^*$  at the  $M_s$  temperature. The temperature dependence of the occupation probability is described by Fermi-Dirac statistics. This hypothesis corresponds, implicitly or explicitly, to a number of models existing in the literature (see ref. [8]). However, in the literature, no simple quantitative model in the influence of ternary additions is available yet.

For ternary NiTi-based alloys, the foregoing leads to an equation that describes the  $M_s$  temperature as a function of the concentration  $x$  of  $Mx$  (substituting Ni, Ti or both). The parameters in this equation are

the Fermi energy, the number of d electrons and the  $M_s$  temperature of NiTi and the alloy that results when the concentration of the addition is maximum (which will be called the "final alloy"). This alloy can be TiMx (when Ni is substituted), NiMx (Ti is substituted) or the pure element Mx (both Ni and Ti are substituted). The equation is generally written as [8]

$$M_s = C(E_F - E_A), \quad (1)$$

in which

$$C = \frac{1}{k_B \ln(1/\rho^* - 1)}. \quad (2)$$

For ternary alloys, this is developed to:

$$\begin{aligned} M_{s, \text{NiTiMx}} &= C\{(1-2x)[E_{\text{B, NiTi}}(n(x)) - E_{\text{A, NiTi}}] \\ &+ 2x[E_{\text{B, f.a.}}(n(x)) - E_{\text{A, f.a.}}]\} \\ &= (1-2x)\{M_{s, \text{NiTi}} + C[E_{\text{B, NiTi}}(n(x)) - E_{\text{F, NiTi}}]\} \\ &+ 2x\{M_{s, \text{f.a.}} + C[E_{\text{B, f.a.}}(n(x)) - E_{\text{F, f.a.}}]\}, \quad (3) \end{aligned}$$

with f.a. the final alloy TiMx, NiMx or Mx and  $E_A$  of NiTi and f.a. from (1):

$$E_{\text{A, NiTi}} = E_{\text{F, NiTi}} - M_{s, \text{NiTi}}/C, \quad (4)$$

$$E_{\text{A, MxTi}} = E_{\text{F, MxTi}} - M_{s, \text{MxTi}}/C. \quad (5)$$

$E_B(n(x))$  is the energy of the state that would have been the Fermi level of NiTi or f.a., provided that this alloy had the number of d electrons,  $n(x)$ , corresponding to the ternary composition under consideration, i.e.

$$\int_0^{E_B(n(x))} D(E) dE = n(x). \quad (6)$$

When the final alloy does not show a martensitic transformation, similar to B2→B19, but other lattice structures instead (as is the case for pure Mn), these other structures have a lower structural energy. Band-structure calculations for the B2 and B19 structure can, however, be performed in principle. For Mn, density of states calculations of bcc Mn are performed by Snow and Waber [13]. When energy calculations are performed on both the austenite and martensite structures, a transformation temperature can be calculated in principle, too. When a state A, that should be sufficiently emptied, has an energy

below  $E_F$ , a virtual negative transformation temperature  $M_s = C(E_F - E_A)$  should be assigned.

The occurrence of an R-phase, which is thought to be independent of the martensitic transformation (see, e.g., ref. [14]), is not taken into consideration. Because of the minor structural differences between the B2 and the R-phase, only minor differences are expected in the aspects of the band structure that are important for the model. Adaptations to the model that are required in some cases are described elsewhere [8].

#### 4. Results and discussion

In the case of  $\text{Ni}_{0.50-x}\text{Ti}_{0.50-x}\text{Mn}_{2x}$ , eq. (3) is written as

$$\begin{aligned} M_{s, \text{NiTiMn}} &= (1-2x)M_{s, \text{NiTi}} + 2xM_{s, \text{Mn}} \\ &+ C\{(1-2x)[E_{\text{B, NiTi}}(n(x)) - E_{\text{F, NiTi}}] \\ &+ 2x[E_{\text{B, Mn}}(n(x)) - E_{\text{F, Mn}}]\}. \quad (7) \end{aligned}$$

The number of d electrons in NiTi is 5.15 [15], in Mn it is 5.14 [13] (both values are calculated using the APW formalism). Therefore, the term  $C\{\dots\}$  will be negligible, because for any  $x$ ,  $E_B \approx E_F$ . This corresponds to the statement of Honma et al. [2] that in case the number of electrons does not change,  $M_s$  is not changed. In eq. (7), however, extra band-structure-dependent terms are introduced. These cause a linear change of  $M_s$ . The tangent of this linear  $M_s$  versus at.% Mn curve cannot be calculated with (7), because  $M_{s, \text{Mn}}$  is not known. In order to calculate this tangent, (7) will be written in an alternative way.

Eq. (7) is based on a substitution of both Ni and Ti by Mn. An alternative way to achieve the same alloy system is to substitute part of the NiTi by NiMn and an equal part by TiMn. The disadvantage of this approach is that the final alloy is  $\text{Ni}_{0.25}\text{Ti}_{0.25}\text{Mn}_{0.50}$ , so not all Ni and Ti is substituted. A large advantage is, however, that this approach gives the possibility to use the known influence of Mn when substituting Ni or Ti only. Taking  $n(x) = 5.15$  for any  $x$ , which accounts at least for small values of  $x$ , eq. (3) is now written as (with  $E_{\text{B, NiTi}}(n(x)) - E_{\text{F, NiTi}} = 0$ ):

$$M_{s,\text{NiTiMn}} = (1-4x)M_{s,\text{NiTi}} + 2x\{M_{s,\text{TiMn}} + C[E_{\text{B,TiMn}}(5.15) - E_{\text{F,TiMn}}]\} + 2x\{M_{s,\text{NiMn}} + C[E_{\text{B,NiMn}}(5.15) - E_{\text{F,NiMn}}]\}. \quad (8)$$

In order to calculate the terms concerning TiMn and NiMn, the alloys  $\text{Ni}_{0.50-2x}\text{Ti}_{0.50}\text{Mn}_x$  and  $\text{Ni}_{0.50-2x}\text{Ti}_{0.50-2x}\text{Mn}_x$  are considered. For these alloys, the number of d electrons  $n(x)$  is  $\leq 5.15$  and  $\geq 5.15$  respectively. For  $\text{Ni}_{0.50-2x}\text{Ti}_{0.50}\text{Mn}_x$  (indicated with superscript  $x0$ ), eq. (3) is then written as:

$$M_{s,\text{NiTiMn}}^{x0} = (1-2x)\{M_{s,\text{NiTi}} + C[E_{\text{B,NiTi}}(\leq 5.15) - E_{\text{F,NiTi}}]\} + 2x\{M_{s,\text{TiMn}} + C[E_{\text{B,TiMn}}(\leq 5.15) - E_{\text{F,TiMn}}]\}. \quad (9)$$

A similar equation accounts for  $\text{Ni}_{0.50}\text{Ti}_{0.50-2x}\text{Mn}_x$  (indicated with superscript  $0x$ ).  $M_{s,\text{TiMn}} + C[E_{\text{B,TiMn}}(5.15) - E_{\text{F,TiMn}}]$  follows from the derivative of (9) in  $x=0$ , which is given by

$$\left[\frac{dM_{s,\text{NiTiMn}}^{x0}}{dx}\right]_{x=0} = 2C\left[\frac{n_{\text{TiMn}} - n_{\text{NiTi}}}{D_{\text{NiTi}}(E_{\text{F,NiTi}})}\right] - 2M_{s,\text{NiTi}} + 2\{M_{s,\text{TiMn}} + C[E_{\text{B,TiMn}}(5.15) - E_{\text{F,TiMn}}]\}. \quad (10)$$

A similar equation can be derived concerning NiMn. Substituting into eq. (8) gives

$$M_{s,\text{NiTiMn}} = M_{s,\text{NiTi}} + 2x\left\{\frac{1}{2}\left[\frac{dM_{s,\text{NiTiMn}}^{x0}}{dx}\right]_{x=0} - C\left[\frac{n_{\text{TiMn}} - n_{\text{NiTi}}}{D_{\text{NiTi}}(E_{\text{F,NiTi}})}\right]\right\} + 2x\left\{\frac{1}{2}\left[\frac{dM_{s,\text{NiTiMn}}^{0x}}{dx}\right]_{x=0} - C\left[\frac{n_{\text{NiMn}} - n_{\text{NiTi}}}{D_{\text{NiTi}}(E_{\text{F,NiTi}})}\right]\right\}. \quad (11)$$

Taking  $n_{\text{XY}}$  as a linear interpolation between  $n_{\text{X}}$  and  $n_{\text{Y}}$  of the bcc structures of the elements X and Y gives, with  $n_{\text{Mn}} \approx n_{\text{NiTi}}$ ,

$$n_{\text{TiMn}} + n_{\text{NiMn}} = 2n_{\text{NiTi}}. \quad (12)$$

With [6,2]

$$M_{s,\text{NiTiMn}}^{x0} = M_{s,\text{NiTi}} - 70 \times 10^2 x, \quad (13)$$

$$M_{s,\text{NiTiMn}}^{0x} = M_{s,\text{NiTi}} - 62 \times 10^2 x, \quad (14)$$

it follows

$$M_{s,\text{NiTiMn}} = M_{s,\text{NiTi}} - 66 \times 10^2 \times 2x, \quad (15)$$

in which  $2x$  is the atomic percentage of Mn. This dependence of  $M_s$  on  $x$  is a linear dependence, as concluded from eq. (7). A virtual  $M_{s,\text{Mn}}$  has to be taken  $M_{s,\text{NiTi}} - 66 \times 10^2$  K.

Although the model is developed with special attention for  $M_s$ , it is assumed to be valid for  $A_s$ , too. Using the measurements of refs. [6,7] calculation of  $A_s$  gives

$$A_{s,\text{NiTiMn}} = A_{s,\text{NiTi}} - 45 \times 10^2 x. \quad (16)$$

The transformation temperatures of the third transformation cycle, as measured by differential scanning calorimetry, are given in table 1 and fig. 2. No martensitic transformation is found above 148 K in alloys with a Mn content of 2.5 at.% and higher. The lowering of  $M_s$  is found to be 66 K per at.% Mn.  $A_s$  is lowered by 58 K per at.% Mn. An R-phase is also observed above  $M_s$  (see fig. 3). As stated before, this is not influencing the results of the model.

The dependence of  $M_s$  on the Mn content in  $\text{Ni}_{0.50-2x}\text{Ti}_{0.50-2x}\text{Mn}_{2x}$ , as predicted on the basis of the new model, is in good agreement with the experimental data, which is strong support for the new model. It also indicates that the numbers of d elec-

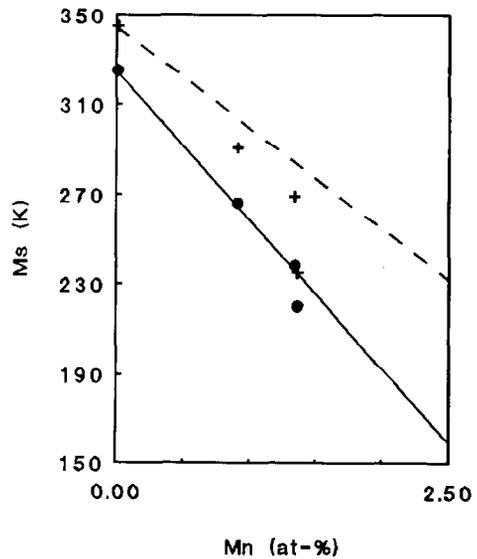


Fig. 2.  $M_s$  and  $A_s$  of NiTiMn: measurements and calculations. ●,  $M_s$  (DSC), third cycle; +,  $A_s$  (DSC), third cycle; —,  $M_s$  calculation; ---,  $A_s$  calculation.

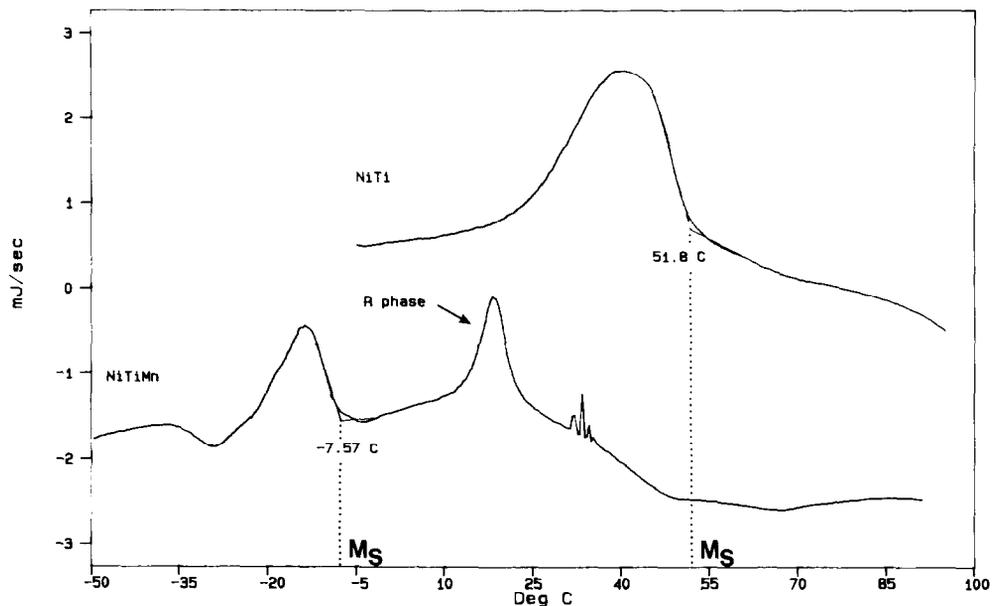


Fig. 3. DSC measurements of  $M_s$  of NiTi and NiTiMn (code 15).

trons of NiTi and Mn, as given in refs. [13,15], are indeed comparable. Although this model is not developed for  $A_s$ , it also describes the dependence of  $A_s$  on the Mn content fairly well. The deviation between theory and experiment may be explained by the use of the results of Eckelmeyer [7].  $A_s$  temperatures are generally related to recrystallized samples, whereas Eckelmeyer determined his recovery temperatures on thermomechanically treated material, which is known to shift the transformation temperatures. This may also be the explanation for differences of Eckelmeyer's measurements on NiTiAu with those of Khachin [16] and of NiTiZr with those performed in our own laboratory [17,18]. The satisfying description of  $A_s$  indicates that the reverse transformation can be described with a similar model as the martensitic transformation.

Apart from the support for the model as a whole, some aspects of it deserve special attention. It is shown that it is not sufficient to take  $e/a$  as the only quantity to describe the transformation temperature  $M_s$ . Changes in band structure significantly influence  $M_s$ . One of the quantities that influences the band structure (through the lattice parameter) is the atomic size. Honma et al. [2] only take the atomic size in account for fifth (and higher) period ele-

ments. Another important aspect of the above calculation is that it is possible to calculate with virtual negative temperatures and structures that do not occur in reality in an alloy. It is also shown that quantitative predictions can be made with the present model in some cases in which not all parameters are given.

Manganese lowers the  $M_s$  of NiTi to about the same extent in  $\text{Ni}_{0.50-x}\text{Ti}_{0.50-x}\text{Mn}_{2x}$  as it does when either Ni or Ti is substituted by Mn [2,6,7]. An advantage of the  $\text{Ni}_{0.50-x}\text{Ti}_{0.50-x}\text{Mn}_{2x}$  type of alloy is, however, that a range of alloys with different Mn contents can be easily produced when NiTi is available as a binary alloy, by simply adding different amounts of manganese. This advantage makes the  $\text{Ni}_{0.50-x}\text{Ti}_{0.50-x}\text{Mn}_{2x}$  alloys very interesting for industry, for which these alloy systems deserve more attention.

## 5. Conclusions

The present model very well describes the  $M_s$  and  $A_s$  temperatures of the  $\text{Ni}_{0.50-x}\text{Ti}_{0.50-x}\text{Mn}_{2x}$  system. It shows that not only changes in the number of valence electrons, but also changes in the band structure should be taken into account in a calculation of

the influence of ternary additions on the transformation temperatures. The use of negative temperatures and unrealistic lattice structures does not influence the validity of the model.

The  $\text{Ni}_{0.50-x}\text{Ti}_{0.50-x}\text{Mn}_{2x}$  alloy system is easy to prepare, and therefore interesting for large-scale production.

### Acknowledgement

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