

Control of the transformation temperatures of TiNi shape memory alloys by ternary additions

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Introduction

TiNi can successfully be used as a shape memory alloy in various applications. In specific cases, special demands are made on the transformation temperatures. In medical sciences, very well defined transformation temperatures are required. Branches like automobile industry require high transformation temperatures, i.e. 160°C or higher.

To meet with those requirements, many investigations need still to be done. Since the transformation temperatures are extremely sensitive to thermomechanical treatment and variations in concentrations of the constituting elements and of impurities, it is difficult to control these temperatures without the basic understanding of the mechanisms involved.

The purpose of the current investigation is to understand the influence of ternary additions to the TiNi alloy. A model will be proposed, on basis of which it will be possible to make TiNi shape memory alloys with pre-established transformation temperatures by choosing the right combinations of elements, thereby taking into account the price, shape memory properties and the workability of the resulting alloys.

It may also be possible that this understanding leads to alloys that are less sensitive to thermomechanical treatment and concentration variations, so that alloys with well defined transformation temperatures are easier to prepare.

Experimental techniques

In order to eliminate the influence of thermomechanical treatment, all alloys were prepared in the same way. The alloys were melted from pure elements by arc melting under Argon. To ensure homogeneity, the buttons, of approximately 25 grams each, were turned and remelted several times. Then they were vacuum annealed, 50 to 200 hours at 950°C, for homogenization. For further homogenization and in order to get workable dimensions they were hot worked in vacuum, at 860°C, in order to remove the casting structure. Then they were cold rolled to a diameter of 3.7 mm. After every rolling step the alloys were annealed at 800°C. Before every rolling step the alloys were cooled in liquid nitrogen to ensure the martensitic structure. When the above dimensions are reached, the alloys were annealed during 1 hour at 900°C to define the starting material.

All specimens were checked for homogeneity by optical inspection and by microprobe measurements. The composition of all alloys was also determined by microprobe. Although the elements were very accurately weighted before melting, it always turned out that the nickel content of the alloy appeared to be lower than it was meant to. It is not yet clear if this is caused by the standards in the microprobe or by the melting process itself. However, in all alloys the Ni content is less than 50 at.%, so the influence of this composition difference on the transformation temperatures is expected to be negligible. Transformation temperatures are determined by Differential Scanning Calorimetry (DSC) measurements. M_s and A_s are defined as the points where the DSC curve leaves the baseline (1). These points are considered to represent the start of the transformation from a physical point of view, i.e. the nucleation. A_s is the transformation temperature that is considered in this paper, because the shape memory is related to the reverse transformation

and because As is less sensitive to very little variations in element concentrations and thermomechanical treatment. Lattice structures are determined by Transmission Electron Microscopy (TEM).

Theory on transformation

In the past two decades many descriptive work has been done on the martensitic transformation in TiNi alloys. In order to develop a model on the influence of ternary additions on this transformation, however, an understanding of the physical origin of the transformation is required. In literature, there is no complete physical model of the transformation available, although some attempts have been made. Most of these attempts are focused on an electronic origin of the transformation. Mitchell et. al. (2) calculate a shift of the 4s state through the 3d state during transformation, which, in their opinion, drives the transition. Egorushkin et. al. (3) find a relation between T_a (onset temperature of the transformation to the rhombohedral phase) and the chemical potential μ . Related to ternary alloys, Samsonov (4) and Ossi et. al. (5) developed a model based on the acceptor and donor concept. As a ternary element is acting to TiNi as an acceptor, the transformation temperatures are lowered, while they are raised as the ternary element acts as a donor. Since it is known that the lattice structure is related to the number of valence electrons per atom (e/a) (6,7), this approach, i.e. to base a model on the electronic structure, seems to be reliable.

Neither of the models named above exactly describes what directly causes the transformation, and, what is more important, neither of them are supported by measurements. Recently Shabalovskaya et. al. (8) performed some XPS measurements on TiNi and several TiNi-based ternary alloys. They see some major changes in the state of the valence band due to the ternary elements. According to them, the change of M_s in different ternary alloys is connected to the statistical weight of the Ti-3d states at E_F . The place of the Ti-3d states with respect to the Fermi level is then determined by the ternary element and its concentration. However, the mechanism of transformation can never be fully understood if the temperature is not taken into account in the considerations. Related to this, the occupation of the Fermi level is important. Although the authors of (8) see a change in occupation of the Fermi level, no attention is paid to this.

In our present opinion, the occupation of the Fermi level and electronic Ti- and Ni- states within $3kT$ from it (e.g. the Ti-3d state (8)) is of major importance, because it is the only variable that changes due to a change in temperature. We suggest that at the start of transformation a certain Ti- or Ni- state always has the same occupation. It can also be said that this state needs a certain occupation in order to make transformation possible. The occupation of the Fermi level and the states within $3kT$ from the Fermi level can be changed by a temperature change, but also by a change in composition, because substitutional atoms of a third element and/or structural vacancies cause a shift of the Fermi level with respect to the electronic structure (or, alternatively, a change of the electronic structure with respect to the Fermi level). The occupation of that particular state, needed for transformation, can now be reached through a combination of composition change and temperature change, so that the transformation temperature is different for different compositions. This can only be possible when this particular state lies within $3kT$ (≈ 0.076 eV) from E_F . To show that alloying causes shifts of the same order of magnitude, we can refer to Eibler et. al. (9) who show that the shift of the Fermi level with respect to the band structure is 1.36 eV when going from NiTi to FeTi. Assuming a linear shift, addition of 3 percent of iron (a concentration that is often used) leads to a shift of E_F of 0.041 eV.

To support this hypothesis, we would like to do very sensitive and temperature

dependent measurements on the occupation of the states near Er. However, most analysis equipment can not reach the required sensitivity. In order to get more insight in the mechanism of transformation we first investigate if the relative position of the Fermi level to the electronic structure is the major factor in the determination of the transformation temperatures. If this is so, it must be possible to control the transformation temperatures by tuning the Fermi level. When the martensitic and reverse transformation are determined only by the occupation of a certain electronic Ti- or Ni- state near Er, it must be possible to make quaternary TiNi-based alloys with the same transformation temperatures as the binary TiNi alloy. This can be explained as follows. The occupation of the states near Er can easily be influenced by a shift of Er, due to a change in composition. When we can induce to equal shifts of opposite sign, these shifts should cancel. So, when a ternary element lowers the transformation temperature, as e.g. Fe, this can be seen as a shift of Er with respect to the bandstructure. An element that raises the transformation temperature, e.g. Zr, should then cause a shift of Er in the opposite direction. When however both these elements are added to TiNi (in proper concentrations), the shift of Er caused by the one added element should be eliminated by the shift of Er due to the other added element. And when Er is not shifted (at least not with respect to that specific state that needs a specific occupation level), the transformation temperatures should not be shifted either. So when Fe and Zr are added in proper concentrations the transformation temperatures of the resulting TiNiZrFe alloy should almost be the same as that of the corresponding TiNi alloy.

Results and Discussion

Because of the large influence of the preparation method on the transformation temperatures, TiNi, TiNiFe and TiNiZr alloys are prepared in order to measure the shift of the transformation temperatures in alloys that are prepared following the method we described in paragraph 2. From these transformation temperatures the composition of the quaternary alloy TiNiFeZr can be calculated.

The transformation temperatures, as measured by DSC, are tabulated in table 1. As can be seen in the table, two TiNiZr alloys are made. This is because the first alloy made did not meet the expectations we had from literature. Instead of raising these temperatures, as it is expected from literature (9), the ternary element Zr lowers them. However, both alloys, made from completely separate melts show the same result.

Table 1: Transformation temperatures of the various TiNi-based alloys, determined by DSC as described in paragraph 2.

alloy	composition (at.-%)	As (°C)
TiNi	Ti51.3 Ni48.7	55.61
TiNiZr (I)	Ti49.0 Ni49.5 Zr1.5	41.26
TiNiZr (II)	Ti49.7 Ni49.0 Zr1.27 (*)	40
TiNiFe	Ti50.2 Ni48.2 Fe1.6	-16.85
TiNiZrFe	Ti49.2 Ni47.9 Zr1.56 Fe1.37	65.28

(*) Due to problems with the microprobe the nickel content is measured lower than it should be.

The difference of the measured A_s and the A_s from (10) may be explained from the composition. Since the Zr not entirely displaces Ti in the composition formula, the lowering of the transformation temperatures is in agreement with (11). In (11) it is found that elements X that raise transformation temperatures in TiNi-TiX or TiNi-XNi could lower these temperatures in TiNi-X. Whether Zr lowers or raises the transformation temperatures should be further investigated.

Nevertheless, we melted TiNiZrFe, using the ΔA_s from (10). The result is shown in Table 1. The A_s of the quaternary TiNiZrFe alloy is as it is expected to be by the above hypothesis, i.e. nearly the same as in the binary TiNi alloy. Although these are only preliminary results, we conclude that the reverse transformation is determined by the position of the Fermi level. This also shows that core level states themselves are not important and that the effects of these states on the states near the Fermi level can be canceled. XPS measurements will be done for further investigation of this conclusions.

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