# TRANSFORMATION TEMPERATURES OF NI-TI BASED ALLOYS MEASURED BY RESISTOMETRIC AND THERMO-DILATOMETRIC METHODS

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# TRANSFORMAČNÍ TEPLOTY SLITIN NI-TI MĚŘENÉ METODAMI REZISTOMETRICKOU A TERMODILATOMETRICKOU

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**Abstrakt**

Intermetalická sloučenina obsahující cca 50 at. % Ni a 50 at. % Ti je považována za standardní paměťovou slitinu. Základním předpokladem pro metalurgii těchto materiálů je striktní dodržení chemického složení slitiny, které je hlavní podmínkou pro výrobu slitiny s požadovanými transformačními teplotami. Slitiny na bázi Ni-Ti jsou obvykle taveny při teplotě cca 1500°C. Pro přípravu drátů je nejvhodnější použití technologie rotačního kování v kombinaci s tažením. Slitiny s jevem tvarové paměti mají zpravidla více variant tvarově paměťového chování. Patří mezi ně pseudoelasticita, jednocestný tvarově paměťový jev, vratný tvarově paměťový jev a všestranný tvarově paměťový jev. Transformační metody je možno měřit několika metodami, jako deformačními, DCS, DTA nebo rezistometrickými metodami. Rezistometricá metoda umožňuje jednoduché, přesné a rychlé měření transformačních teplot. V závislosti na složení slitiny, respektive přídavku legujících prvků nebo tepelného či mechanického zpracování, je možno získat různé typy závislostí rezistivity na teplotě. Při dilatometrické metodě jesou základní data generována ve formě křivek závislostí změřeného rozměru na teplotě. Experimentální slitina byla připravena ve vf. indukční vakuové peci, následně tvářena a nakonec podrobena tepelnému zpracováni. Tento příspěvek je zaměřen na měření transformačních teplot Ni-Ti slitin s jevem tvarové paměti rezistometrickou a dilatometrickou metodou a jejich porovnáním.

**Abstract**

Intermetallic compound containing approx. 50 at. % Ni and 50 at. % Ti is considered as standard shape memory alloy. The basic requirement to metallurgy of these advanced materials is strict adherence to chemical composition of the alloy, which is the main condition for obtaining of the alloy with the required transformation temperatures. Ni-Ti based alloys are usually melted at the temperature of approx. 1500 °C. For obtaining of wire it is best to use technology of swagging in combination with subsequent drawing. Alloys with shape memory effect have generally several variants of shape memory behaviour. Generally speaking these are pseudo-elasticity, shape memory phenomenon (irreversible), reversible shape memory phenomenon and all-round shape memory effect. It is possible to measure transformation temperatures by deformation methods, by DSC method (differential scanning calorimetry) or DTA method (differential thermal analysis), by resistometric methods. Resistometric method enables simple, precise and rapid evaluation of transformation temperatures. In dependence on constitution of alloys, or additional alloying or heat treatment or mechanical treatment, it is possible to get different types of dependence of electric resistivity on temperature. The dilatometric method utilises either transformation strains or thermal strains; the basic data generated are in the form of curves of dimension against time and temperature. Experimental alloy was prepared in vacuum induction furnace and then forged and heat treated. This article deals with measurement of transformation temperatures of Ni-Ti shape memory alloys by resistometric and dilatometric method and gives their comparison.

**Keywords:** Ni-Ti alloys, transformation temperature, resistometric method, dilatometric method

## 1. Introduction

Shape memory effects were observed for the first time in the sixties in Ni-Ti based alloys. Since then a considerable attention is paid to these issues. Approximately from the mid-seventies investigation was oriented on explanation of mechanisms of shape reversible deformation in metallic materials [1]. The biggest attention (and this is valid till present times) is focused on systems Cu-Zn-Me and Ni-Ti-Me, where Me represents another alloying component. These alloys are characteristic by their structural arrangement at long distance, thermo-elastic martensite and crystallographically reversible phase transformation [2].

In the system Ni-Ti particular attention is paid namely to intermetallic compound NiTi, which demonstrates shape memory effect. This effect is, however, highly sensitive to stoichiometry of intermetallic phase TiNi, which is connected to specific requirements concerning metallurgy of these intermetallic compounds. There exists strange dependence of transformation sequence on different alloying elements.

## 2. Transformation temperatures measurement

It is necessary to measure transformation temperature of the alloys on the base of Ni-Ti. The knowledge of transformation temperatures is necessary for optimal utilisation of construction parts. At present, there exist many methods for transformation temperature measurement. Some of the most popular are DSC/DTA and restistometric methods. One of the less common is dilatometric method.

## 3. Resistometric method

Resistometric method enables simple, precise and rapid evaluation of transformation temperatures. In dependence on constitution of alloys, or additional alloying or heat treatment or mechanical treatment we get different types of dependence of electric resistivity on temperature. At cooling, when $M_s > T_r$ the martensitic transformation is defined by drop of electric resistivity and the point of change of the line of dependence of electric resistivity on temperature determines the temperature $M_s$. If there occurs transformation to the R–phase, electric resistivity increases due to structural changes and the change determines the temperature of the beginning of formation of R–phase. During the subsequent drop of electric resistivity there occurs transformation to martensite B19‘ by transformations B2→B19‘ and R→B19‘. Width of the area of increase of electric resistivity and modification of the shape of the recorded line is defined by the difference $T_R$ and $M_s$.

During heating there occurs reverse transformation to the phase B2. According to the transformation scheme B19‘→B2 there occurs only change of inclination of the line of electric resistivity dependence. If the reverse transformation occurs in relation with formation of the R-phase B19‘→R→B2, the course of dependence is characterised primarily by increase of resistivity. In case of some ternary alloys, e.g. Ni-Ti-Cu only rhombic martensite is formed (B2→B19). In dependence on degree of alloying (up to 30%) it is possible that only this martensitic transformation takes place. Record of dependence of electric resistivity on temperature shows at such transformation sufficient peak in connection with increase of internal resistivity [3, 4].

## 4. Dilatometric method – measurement of thermal expansion

The dilatometric method utilises either transformation strains or thermal strains; the basic data generated are in the form of curves of dimensions against time and temperature. We obtain two transformation curves (one for heating and one for cooling) as well as resistometric method. Every divergence from linearity signalizes there the transformation.

At high temperatures, the atoms of a crystal oscillate around their equilibrium position. This motion leads to an increase in the interatomic distance as the temperature increases. This phenomenon, called thermal expansion, is closely related to the crystal structure and the cohesive force between atoms. Consequently, the coefficient of thermal expansion (CTE) can vary from one phase to another for the same material [5].

## 5. Experiment

The investigated Ni50.6-Ti49.4 (at. %) alloy was prepared by vacuum induction melting in graphite crucible. Pouring off was realized into graphite mould without preheating. In this way there was obtained a round bar, which was 300 mm high and the diameter was 10 mm. For preparation there was used 4N Nickel (impurities - C 0.01 %, Fe 0.0048 %, Al < 0.0002 %, Ti 0.0056 %, $O_2$ 0.002 %, $N_2$ 0.0002 %), forged 2N8 Ti (impurities - C 0.025%, Fe 0.016 %, Al < 0.002 %, Ni 0.051 % $O_2$ 0.061 %, $N_2$ 0.0002 %).

After metallurgic preparation the alloy was forged by swagging and hot drawing into a wire with diameter between 2.4 – 1.4 mm. Specimens, cut off from the wire, were used for applying different types of heat treatment.

Basic heat treatment was made as solution treating with quenching: 850°C / 30 min / water. This heat treatment was realized in atmosphere of argon with purity 4N6. Next heat treatment step was aging of selected specimens at low pressure (1 – 2 kPa). The specimens were heated between 500 – 900°C with dwell of 0.5-10 h. Selected specimens were subjected to thermal cycling without applied stress in thermal range -15 to 200°C. For measurement of transformation temperatures by both selected methods there were used specimens with length of 60 mm. Table 1 shows description of the samples.

For measurement of transformation characteristics by resistometric method there was used the equipment (Fig. 1), composed of the following components: Power supply 2, power supply Tesla BK 125, rheostat with maximum resistivity 6.4 Ω, personal computer with measuring card Axiom, thermocouple NiCr–NiAl, stand for progressive insertion and withdrawing of samples, heating pocket and cooling chamber. Heating of the sample was realised by resistance wire and cooling down was made in vapours of liquid nitrogen. All the samples were heated up to 150°C and cooled down to -160°C. The measured values were processed with use of computer software and arranged to the final form with use of the program MS Excel.

Table 1 Decription of all the samples.

| | quenching | aging | thermal cycling |
|---|---|---|---|
| 8 | 850°C/0,5 h/water | 500°C/0,5h | - |
| 9 | 850°C/0,5 h/water | 500°C/1h | - |
| 10 | 850°C/0,5 h/water | 500°C/2h | - |
| 11 | 850°C/0,5 h/water | 500°C/3h | - |
| 13 | 850°C/0,5 h/water | 500°C/10h | - |
| 21 | 850°C/0,5 h/water | - | - |
| 25 | 850°C/0,5 h/water | - | 1x (-15 to200°C) |
| 26 | 850°C/0,5 h/water | - | 10x (-15 to200°C) |
| 27 | 850°C/0,5 h/water | - | 100x (-15 to200°C) |

For measurement of transformation characteristics by dilatometric method the equipment shown in Fig. 2 was used. The specimen was put into a stainless steel tube and linked with the detector. Over the specimen there was a piece of copper tube for better transmission of heat during heating. At the bottom of the stainless steel tube a heating wire was mounted. The equipment was stationary as it was very sensitive to vibrations. Cooling of the specimen was realized in vapours of liquid nitrogen. All the samples were heated up to 120°C and then cooled down to -80°C. The measured values were processed with use of computer software and arranged to the final form with use of the program MS Excel.

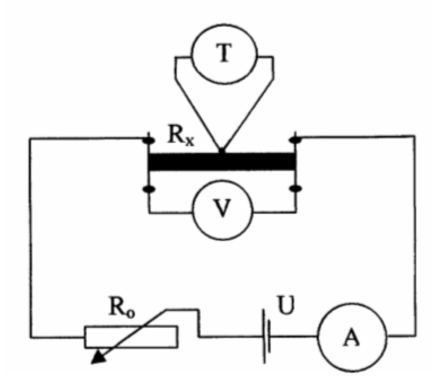


Fig.1 Scheme of the equipment for resistometric measurement.

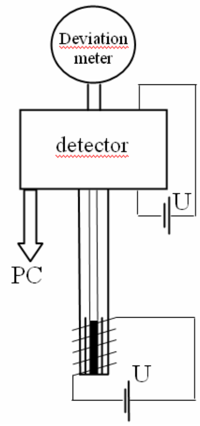


Fig.2 Scheme of the equipment for dilatometric measurement.

## 6. Results and discussion

In the first stage there was investigated effect of ageing at 500°C and various durations on change of transformation behaviour of samples. Fig. 3 shows development of transformation characteristics of the samples 8-13 in dependence on the time of ageing measured with use of resistometric method. It is possible to see on the cooling curve for the sample 8 a small peak, which corresponds to formation of R-phase. Transformation therefore runs in

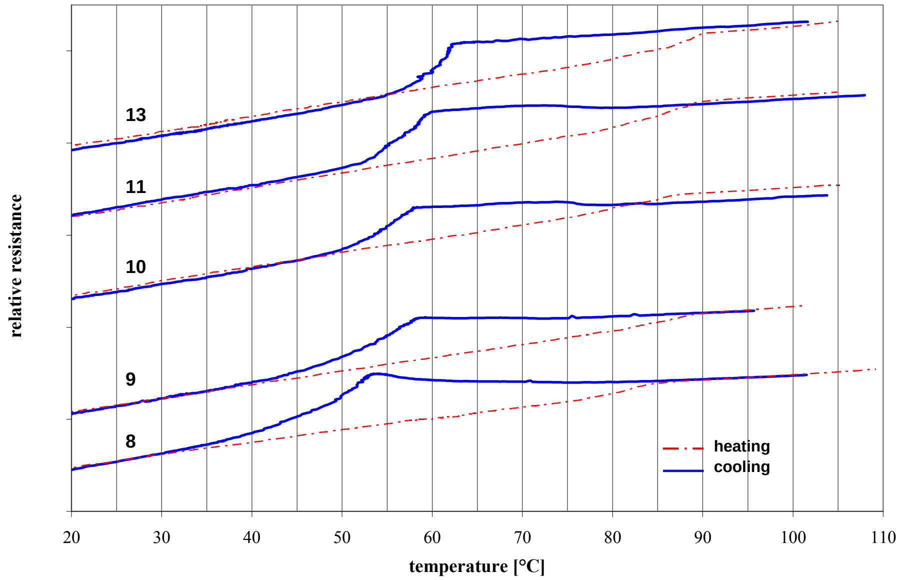


Fig.3 Dependence of relative resistance on temperature for specimens subjected to aging.

accordance with the scheme B2→R→B19′. With increasing time of ageing there occurred suppression of formation of R-phase and transition temperature B2→B19′ increases from $M_s$ = 53°C in the sample D8 to $M_s$ = 62°C in the sample D13. Temperature of the end of this phase transition increases from $M_f$ = 29°C in the sample D8 to $M_f$ = 55°C in the sample D13. Increase of temperature $M_s$ with increasing time of ageing is related to precipitation of the phase $Ti_3Ni_4$ and decline of Ni contents in basic matrix TiNi. During heating of samples there was also monitored development of transformation temperatures. The transformations run here always according to the scheme B19′→B2. The determined transformation temperatures are given in the table 2.

Table 2 Transformation temperatures of samples 8 -13 measured by resistometric method.

| sample | Transformation temperature | | | | |
|---|---|---|---|---|---|
| | $T_R$ | $M_s$ | $M_f$ | $A_s$ | $A_f$ |
| 8 | 58 | 53 | 29 | 75 | 94 |
| 9 | 70 | 58 | 35 | 80 | 88 |
| 10 | 75 | 57 | 46 | 78 | 87 |
| 11 | 75 | 60 | 47 | 80 | 90 |
| 13 | - | 62 | 55 | 86 | 91 |

Effect of thermal cycling without applied stress was also investigated. Fig. 4 shows transformation characteristics of the samples 21-25 measured with use of resistometric method. As it can be seen the treatment described above influenced significantly the transformation characteristics. The sample 21 (which was not cycled) is characterised by graphical dependence relative resistance vs. temperature, when there is no apparent peak characterising presence of the R-phase. In this case it is a single-stage transformation of alloy according to the scheme B2→B19´. Transformation B2→R does not take place in this case. On the cooling curve of the sample D25, which was subjected to one thermal cycle, there is visible a very mild increase of relative resistance at the temperature of approx. 62°C, which is related to the beginning of formation of the R-phase. In the sample D26 or D27 there is already very distinct characteristic peak, corresponding to transformation according to the scheme B2→R→B19´. It can be therefore stated that thermal cycling without applied stress caused changes in character of dependence curves of relative resistance vs. temperature, sand that there occurred also decline of transformation temperatures $M_s$ from $M_s$ = 56°C in the sample 21 to $M_s$ = 38°C in the sample 27. Transformation temperatures of inverse transformation have also a downward trend. There were ascertained the values from $A_s$ = 84°C in the sample 21 to $A_s$ = 58°C in the sample 27. The temperatures of inverse phase transformation declined from $A_f$ = 91°C in the sample 21 to $A_f$= 78°C in the sample 27. In reverse transformation there was not detected transformation of martensite B19´ to austenite B2 via the R-phase. The measured transformation temperatures are given in the table 3.

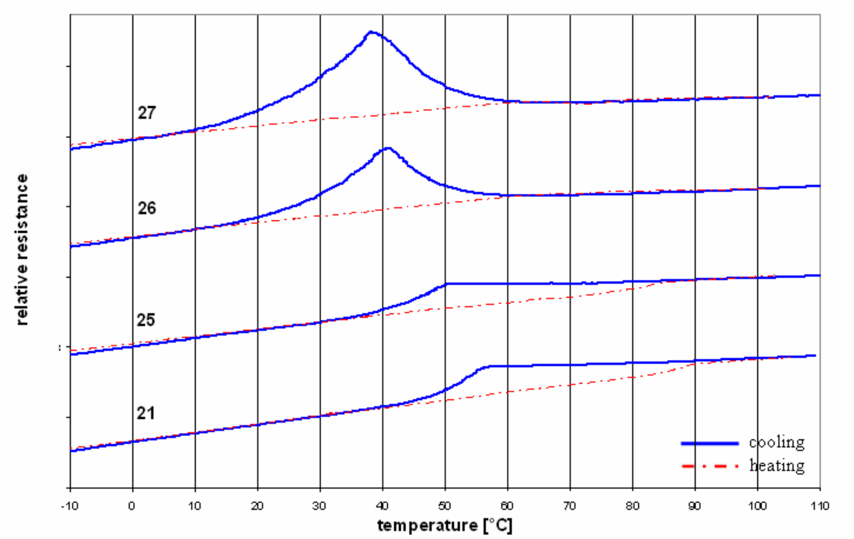


Fig.4 Dependence of relative resistance on temperature for specimens subjected to thermal cycling.

Table 3 Transformation temperatures after thermal cycling without applied stress.

| sample | Transformation temperature | | | | |
|---|---|---|---|---|---|
| | $T_R$ | $M_s$ | $M_f$ | $A_s$ | $A_f$ |
| 21 | - | 56 | 37 | 84 | 91 |
| 25 | 70 | 50 | 32 | 77 | 85 |
| 26 | 60 | 42 | 12 | 62 | 77 |
| 27 | 60 | 38 | 5 | 58 | 78 |

In the next phase there were made measurements of transformation temperatures in selected samples by dilatometric method. Figure 5 shows dependence of expansibility on temperature at linear heating and cooling of the sample 9. It is possible to see on the cooling curve slight undulation around the temperature of 75°C, which can be interpreted as formation of the R-phase (B2→R). This transformation is, however, very quickly suppressed by transformation B2→B19´. Transformation temperature $M_s$ was in this sample determined at 64°C (which is by 6°C more than it was measured by resistometric method). It is possible to observe on the heating curve a deviation from linearity at 78°C, which indicates the beginning of inverse transformation B19´→B2. The determined transformation temperatures confirm the values determined by resistometric method. Transformation temperatures of the sample 9, determined by dilatometric method, are given in the table 4.

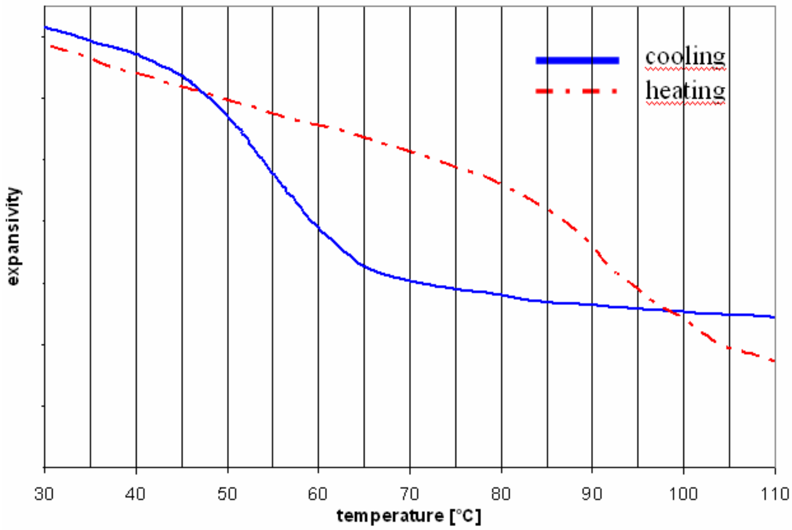


Fig.5 Dilatation curve of the sample 9

Table 4 Tranformation temperatures of the sample 9 (dilatometric method).

| $T_R$ | $M_s$ | $M_f$ | $A_s$ | $A_f$ |
|---|---|---|---|---|
| 75 | 65 | 44 | 78 | 103 |

Figure 6 shows dependence of expansibility on temperature at linear heating and cooling of the sample 25. The cooling curve has in this case different character. It can be seen that the sample undergoes a transformation according the scheme B2→R→B19´. The temperature of formation of R-phase is here 73°C. At the temperature of 68°C the transformation B2→R terminates, and then at the temperature of 53°C martensite B19´ is formed. Heating curve evidences that inverse transformation of martensite B19´to austenite B2 occurs at the temperature 75°C. The determined transformation temperatures confirm the values determined by resistometric method. Transformation temperatures of the sample 25, determined by dilatometric method are given in the table 5.

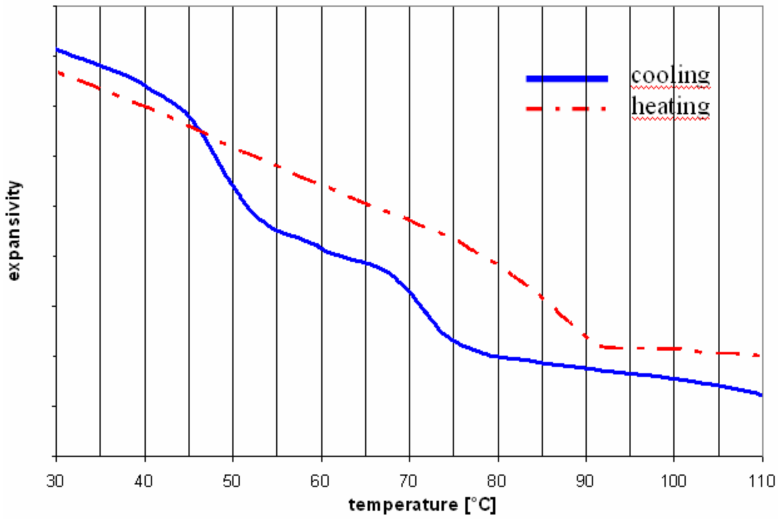


Fig.6 Dilatation curve of the sample 25

Table 5 Tranformation temperatures of the sample 25 (dilatometric method).

| $T_R$ | $M_s$ | $M_f$ | $A_s$ | $A_f$ |
|---|---|---|---|---|
| 73 | 53 | 38 | 75 | 91 |

## 7. Conclusion

Measurement of transformation temperatures of the alloy Ni50.6-Ti49.was realised with use of resistometric and dilatometric methods. It was ascertained that both methods are suitable for this measurement and that they can be added to the currently most frequently used methods DTA and DSC. It is obvious from the enclosed tables that transformation temperatures measured by these methods do mutually correspond. Resistometric method appeared to be less sensitive to capturing of formation of the R-phase at cooling of samples, while dilatometric method captures very distinctly formation of the R-phase.

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