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THERMOKINETIC EMF DURING A REVERSE PHASE TRANSITION IN TITANIUM NICKELIDE AS A WAY OF INFORMATION RECORDING

Abstract. The external factors that influence on the thermokinetic EMF value in the Ti – 50 at.% Ni samples were determined. A method for setting thermokinetic EMF in certain sections of the TiNi wire was developed. The thermokinetic EMF value was measured directly using a digital millivoltmeter MNIPI V7-72. The sections of the Ti – 50 at.% Ni wire samples were subjected to tensile tests on a tensile machine IP 5158-5. On the basis of calorimetric studies, the kinetics of martensitic transformations was investigated. It was found that the direct phase transition affects the thermokinetic EMF value of the Ti – 50 at.% Ni during thermal cycling. Thermal cycling in the temperature range of the complete martensitic transformation causes the thermokinetic EMF value reduction by 0.16 mV by the 15th temperature cycle. The degradation of the thermokinetic EMF value by 0.04 mV took place during thermal cycling in the temperature range of the incomplete martensitic transformation by the 70th thermal cycle. The thermokinetic EMF value was restored to 0.22 mV with increasing temperature to 240 °C, as in the case of annealing at temperatures of 400÷800 °C. The thermokinetic EMF value is associated with a change in physical and mechanical properties of the alloy during thermal cycling. It is characterized by a change in stages of the phase transition and a shift of the characteristic temperatures. On the basis of the obtained experimental data, a method was proposed for a purposeful setting of extended TiNi wire sections with the thermokinetic EMF value from 0 to 0.6 mV, using different methods of influence on its value (thermal cycling, deformation, temperature change in heating zone). The proposed technical solution can be used as a method for information recording.

Keywords: shape memory, titanium nickelide, thermokinetic EMF, martensitic transformation, thermal cycling, deformation, information recording

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ТЕРМОКИНЕТИЧЕСКАЯ ЭДС ПРИ ОБРАТНОМ ФАЗОВОМ ПЕРЕХОДЕ В НИКЕЛИДЕ ТИТАНА КАК СПОСОБ ЗАПИСИ ИНФОРМАЦИИ

Аннотация. Установлены закономерности влияния внешних факторов на термокинетическую ЭДС в образцах Ti – 50 ат.% Ni, а также разработан способ задания термокинетической ЭДС на определенных участках TiNi-проволоки. Термокинетическую ЭДС измеряли прямым способом с помощью цифрового милливольтметра МНИПИ В7-72. Деформирование участков проволочных образцов Ti – 50 ат.% Ni осуществляли на испытательной машине ИП 5158-5. На основании результатов калориметрических исследований исследовали кинетику мартенситных превращений. Установлено, что на величину термокинетической ЭДС Ti – 50 ат.% Ni при термоциклировании влияет степень прямого фазового перехода. Термоциклирование в интервале температур полного мартенситного превращения к 15-му термоциклу стабилизирует значения термокинетической ЭДС на 0,16 мВ. Тогда как термоциклирование в интервале температур неполного мартенситного превращения приводит к вырождению термокинетической ЭДС: к 70-му термоциклу она составляет 0,04 мВ. Увеличение температуры в зоне нагрева до 240 °С позволяет восстановить значение термокинетической ЭДС до 0,22 мВ, как и для случая отжига при температурах 400÷800 °С. Величина термокинетической ЭДС при термоциклировании связана с изменением физико-механических свойств сплава и характеризуется изменением стадийности и смещением характеристических температур фазового перехода. На основе полученных экспериментальных данных предложен способ целенаправленного задания протяженных участков TiNi-проволоки со значением термокинетической ЭДС от 0 до 0,6 мВ, используя различные способы воздействия (термоциклирование, деформирование, изменение температуры в зоне нагрева) на ее величину. Предлагаемое техническое решение может быть использовано в качестве способа записи информации.

Ключевые слова: память формы, никелид титана, термокинетическая ЭДС, мартенситное превращение, термоциклирование, деформирование, запись информации

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Introduction. Titanium nickelide-based (TiNi) alloys are widely used as functional materials and have unique set of properties. The field of their application is extremely wide – from medical implants to intelligent structures of space technology [1]. It was found earlier that the displacement of heating zone in the Ti – 50 at.% Ni wire samples causes the appearance of the thermokinetic EMF in them, which is constant in magnitude and sign. This is due to the occurrence of thermoelastic phase transformations in heating zone and the appearance of a contact potential difference between the sections of the TiNi sample in different phase states. The change in the direction of movement of heating zone induces changes in the polarity of the thermokinetic EMF [2–4]. The thermokinetic EMF value depends on the temperature in heating zone: it arises at the temperature of the beginning of the reverse phase transformation and reaches a maximum at the temperature of the end of the reverse phase transformation. The temperature and duration of heat treatment, thermal cycling, oxide layer, preliminary deformation, loading influence on the functional properties of the TiNi alloy and, therefore, should influence on the thermokinetic EMF value [2–6].

The purpose of this work is to determine methods of influence on the thermokinetic EMF value in the TiNi wire as a possible information recording method.

Equipment and research methods. The studies were carried out on the wire samples made of titanium nickelide of Ti – 50 at.% Ni composition produced by Industrial Center MATEK–SPF (Moscow, Russia) [7] of 40 cm length and 0.6 mm in diameter annealed at 700 °C for 30 min after quenching in air.

The kinetics of martensitic transformations was studied by differential scanning calorimetry (DSC) on a DSC822e METTLER TOLEDO calorimeter (heating and cooling rates of 10 °C/min). The temperatures of the beginning (A_s, M_s) and the end (A_f, M_f) of martensitic transitions were determined from DSC curves by the tangent method according to the ASTM F2004-00 standard (Standard Test Method for Transformation Temperature of Nickel-Titanium Alloys by Thermal Analysis: ASTM F2004-00, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA, 19428). The samples were in the martensitic phase after annealing, the characteristic temperatures of the alloy were M_s = 45 °C, M_f = 33 °C, A_s = 57 °C, A_f = 78 °C. The material undergoes direct transformation B2 $\leftrightarrow$ B19′.

A direct method using a digital millivoltmeter MNIPI V7-72 was applied to measure the thermokinetic EMF value. The tests were carried out on an experimental setup, the design of which allows heating region to be transferred over the sample at a given rate. The contact points of the sample with the measuring copper wires were thermally insulated. The temperature was monitored with a thermal imager with an accuracy of ± 2 °C. The surface of the wire was blackened. The movement rate of heating region was 0.4 cm/s. The maximum temperature of the wire in heating region was higher than the temperature of the end of the reverse phase transition A_f.

Uniaxial tensile testing with a rate of 30 mm/min at 20 °C on an IP 5158-5 testing machine was performed on the sections of the Ti – 50 at.% Ni wire samples, when the material was in martensitic state. The deformation of the samples was accompanied by the reorientation of the martensite plates at stresses of ~ 250 MPa. The yield strength was 500 MPa.

Results and its discussion. It was found that thermal cycling in the temperature range of the complete martensitic 0÷100 °C transformation resulted in a decrease of the thermokinetic EMF value to 0.16 mV for 15 thermal cycles of measurement (Figure 1, red). Thermal cycling in the temperature range of the incomplete martensitic transformation 20÷100 °C during 70 thermal cycles appeared to result in a decrease of the thermokinetic EMF value from 0.22 to 0.04 mV (Figure 1, black). After that, cooling the sample below the temperature of the end of the direct phase transition M_f allows the thermokinetic EMF value to be restored to 0.16 mV in the next 71st thermal cycle, which corresponds to the thermokinetic EMF value in the 15th measurement cycle (Figure 2). Further induction of the thermokinetic EMF of the sample leads to a sharp drop in its value to 0.1 mV during incomplete phase transition. If the sample is cooled again below M_f, the thermokinetic EMF value restores its value to 0.16 mV.

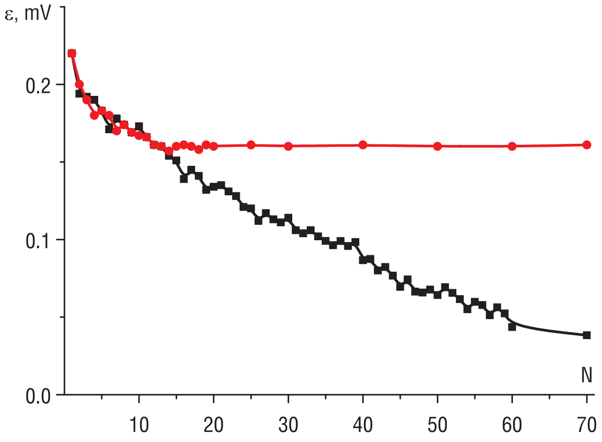

Figure 1. Change in the thermokinetic EMF value during thermal cycling of a Ti – 50 at.% Ni sample in the temperature range of the complete martensitic transformation (red); in the temperature range of the incomplete martensitic transformation (black)

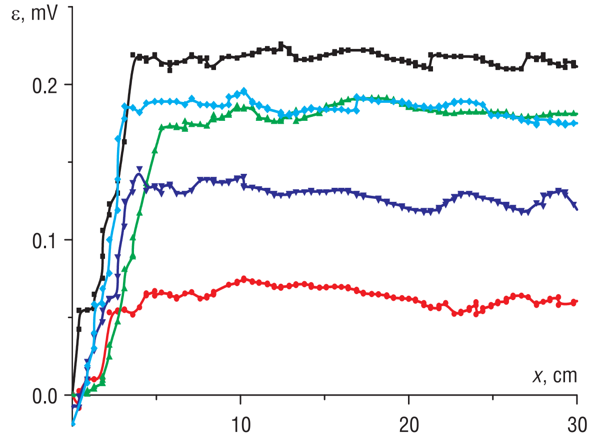

Figure 2. Change in thermokinetic EMF value depending on the location of heating region of the Ti – 50 at.% Ni sample: the 1st cycle (black); the 70th cycle (red); the 71st, the 72nd cycles after cooling the sample to 0 °C (green and blue, respectively); the 73rd cycle after cooling the sample to 0 °C (light blue)

It is known that thermal cycling of a TiNi alloy causes an increase in the density of defects [8, 9] and leads to a decrease in the characteristic temperatures of the phase transition and a change in the stages of transformations. The characteristic temperatures obtained from DSC curves (Figure 3) showed that starting from the 15th thermal cycle in the temperature range of the incomplete martensitic transformation the material does not completely transform into the martensitic state, and the direct transition proceeds with the formation of the intermediate martensitic R-phase.

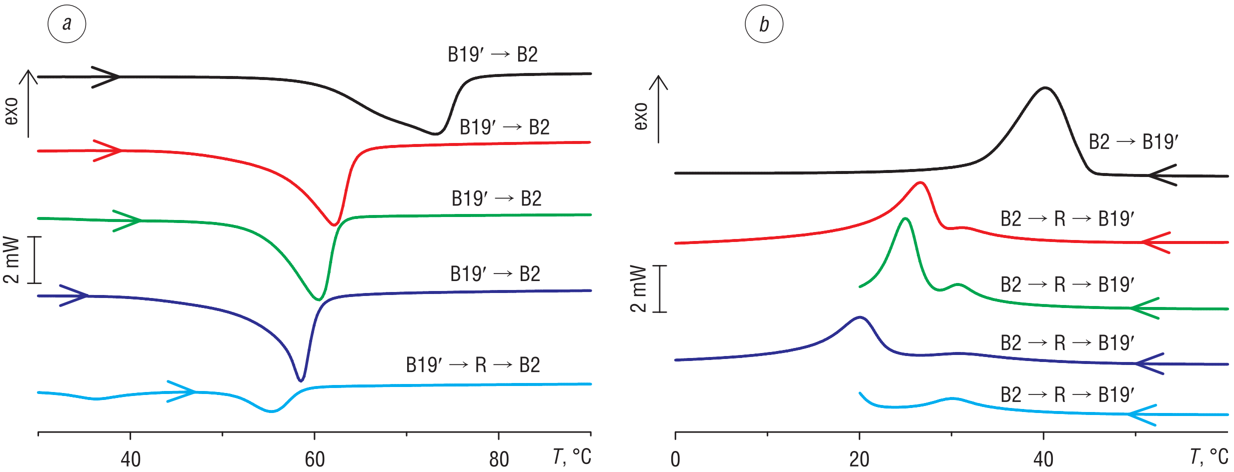

Figure 3. DSC heating (*a*) and cooling curves (*b*) of the Ti – 50 at.% Ni samples after thermal cycling: the 1st cycle (black); the 15th cycle in the temperature range of the complete martensitic transformation (red); the 15th cycle in the temperature range of the incomplete martensitic transformation (green); the 70th cycle in the temperature range of the complete martensitic transformation (blue); the 70th cycle in the temperature range of the incomplete martensitic transformation (light blue)

The kinetics of the reverse phase transformation changes by the 70th thermal cycle. The transition takes place according to the B2 ↔ R ↔ B19′ scheme, i.e. the formation of the intermediate martensitic and austenitic R-phases. Thermal cycling in the temperature range of complete martensitic transformation during 15 thermal cycles also leads to a decrease in the transition temperatures and a change in the stages of transformations. The temperature of the end of the reverse phase transition M_f becomes higher than room temperature, and the transition is realized according to the scheme B2 → R → B19′. However, further thermal cycling during 70 thermal cycles does not significantly affect the kinetics of martensitic transformations.

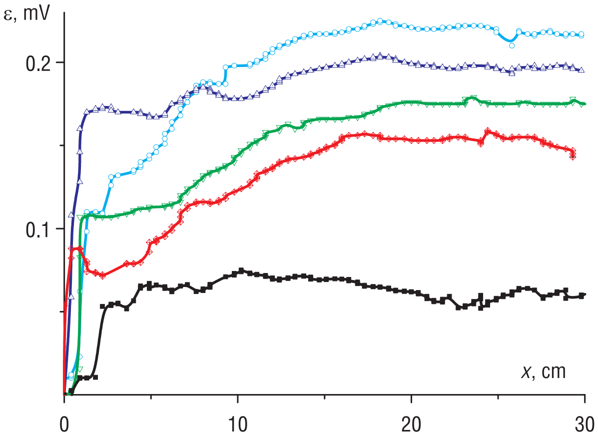

Figure 4. Dependence of the thermokinetic EMF value on the location of heating region of the Ti – 50 at. % Ni sample for the 70th thermal cycle (black) and the 72nd thermal cycle after heating to 160 °C, 180 °C, 220 °C and 240 °C (red, green, blue and light blue, respectively)

In [9, 10], the temperature increase in Ti – 50 at.% Ni is found to influence on the defect structure and the parameters of martensitic transitions. The defect structure should change irreversibly at high temperatures, as is observed in conventional alloys. This should also affect the thermokinetic EMF value. It was found that the thermokinetic EMF value restores to 0.22 mV due to an increase in temperature in the heating region (Figure 4).

The heating temperature was increased to 240 °C in the next 71st thermal cycle after the decrease in the thermokinetic to 0.04 mV during 70 thermal cycles in the temperature range of the incomplete martensitic transformation. Then, the recovery of the value to the initial value of 0.22 mV was observed in the 72nd thermal cycle. The temperature was 160, 180, 220 and 240 °C in the 71st thermal cycle. It was found that the thermokinetic EMF value is restored to 0.14 mV at a temperature of 160 °C, at a temperature of 180 °C – up to 0.18 mV, at a temperature of 220 °C – up to 0.2 mV.

Calorimetric studies of such samples showed that an increase in temperature in heating zone leads to a shift in temperatures and a change in the stage of the phase transition (Figure 5). However, the material does not completely transform into the low-temperature martensitic state at heating temperatures of 160, 180 and 220 °C upon cooling. The reverse transition occurs with the formation of an intermediate R-phase according to the scheme B2 → R → B19′. At a heating temperature of 240 °C, the temperature of the end of the reverse phase transition M_f becomes higher than room temperature. Phase transitions are realized according to the B2 ↔ B19′ scheme, as in the initial sample. This allows the maximum thermokinetic EMF value to be restored.

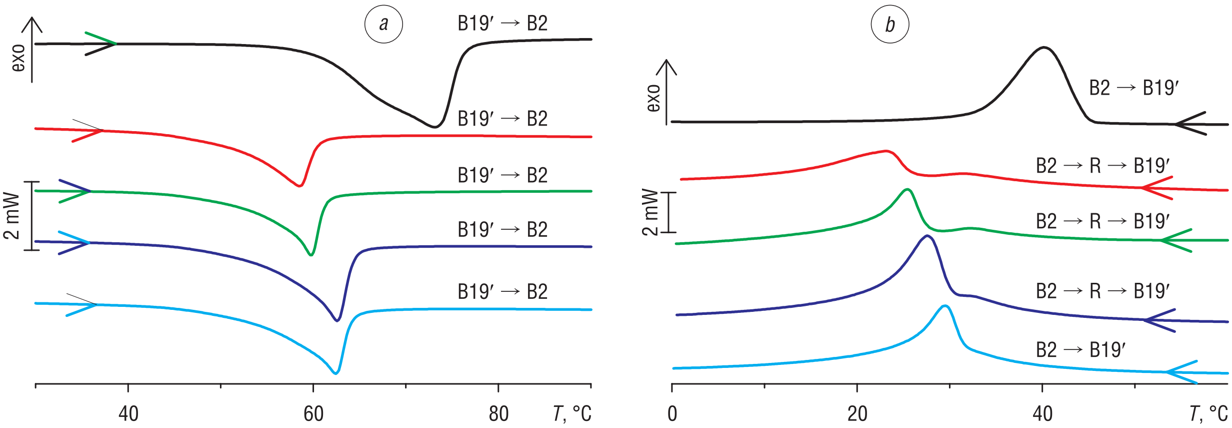

Figure 5. DSC heating (*a*) and cooling curves (*b*) for the initial Ti – 50 at.% Ni sample (black) and after heating to 160 °C, 180 °C, 220 °C and 240 °C (red, green, blue and light blue, respectively)

Using the described methods of influence, it is possible to purposefully change the thermokinetic EMF value in particular sections of the TiNi wire and thus record information on the TiNi wire, for example, using thermal cycling of the sample in the temperature range of the incomplete martensitic transformation or deformation. The length of the information sections corresponds to the size of the affected area.

Figure 6, *b* shows a stepwise change in the thermokinetic EMF value. The samples were processed as follows: the area CD ≈ 4 cm was subjected to heating, then the area BE ≈ 13 cm, and then the area AF ≈ 23 cm (Figure 6, *a*, *c*). Thus, the CD area was thermocycled three times, the BC and DE areas –

twice, and the AB and EF areas – once. The subsequent movement of heating zone along the whole sample causes the induction of thermokinetic EMF of different values (Figure 6, *b*). The method described above shows the possibility of setting the thermokinetic EMF value in the range of 0÷0.22 mV. By the above-described method the setting of the thermokinetic EMF value in the range of 0÷0.22 mV is possible.

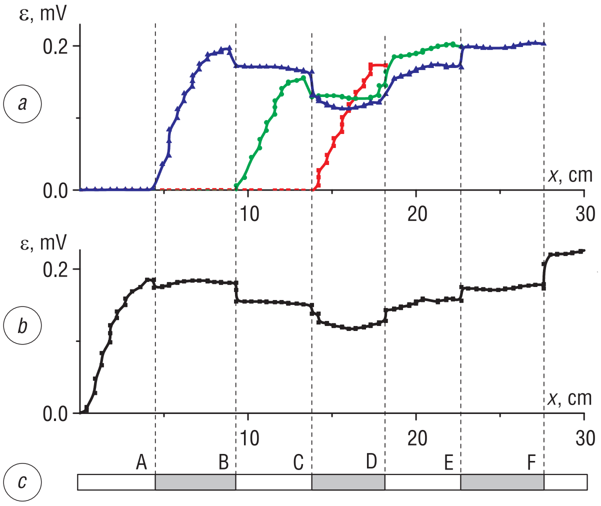

Figure 6. Change in the thermokinetic EMF value depending on the location of heating region of the Ti – 50 at.% Ni sample: *a* – 1–3 heating (red, green and blue, respectively); *b* – the 4th thermal cycle for the whole sample; *c* – the scheme of sample

The areas of the Ti – 50 at.% Ni sample were subjected to deformation up to different values that causes a stepwise change in the thermokinetic EMF value (Figure 7). Previously, the sample areas were alternately deformed by 16, 10, 6, 3, and 1.5 %. After that, heating zone was moved along the sample. It was observed an increase in the thermokinetic EMF value by 0.03÷0.29 mV. The thermokinetic EMF value at each area of deformation is constant and depends on the specified amount of deformation: at 16 % – 0.51 mV, at 10 % – 0.42 mV, at 6 % – 0.37 mV, at 3 % – 0.28 mV and at 1.5 % – 0.26 mV. The thermokinetic EMF value in the deformation zone decreases in the 2nd thermal cycle from 3 to 16 %. The thermokinetic EMF value is 0.09 mV at 16 %, 0.11 mV at 10 %, 0.16 mV at 6 %, 0.21 mV at 3 % and 0.22 mV at 1.5 %.

However, it is possible to obtain a thermokinetic EMF from 0.22 to 0.60 mV in a given area only in the first measurement cycle with this method of influence. In the 2nd thermal cycle, the thermokinetic EMF value will fall and range from 0.10 to 0.22 mV. The restoration of the thermokinetic EMF value to 0.22 mV occurs when the sample is deformed in the elastic region.

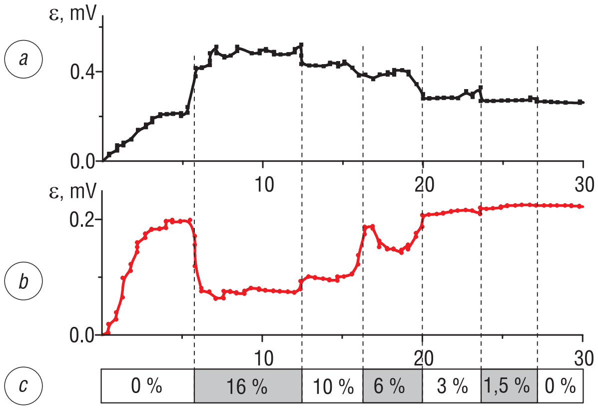

Figure 7. Change in the thermokinetic EMF value depending on the location of heating region of the Ti – 50 at.% Ni sample at different deformation values in heating zone: *a* – the 1st cycle; *b* – the 2nd cycle; *c* – the scheme of sample (the percentage of deformation is indicated at the top)

Thus, it is possible to set sections in the Ti – 50 at.% Ni wire that generate a thermokinetic EMF in the range from 0 to 0.6 mV by combining different methods of influence. Heating the sample above 240 °C allows it to return to its initial state with the maximum generated thermokinetic EMF value of 0.22 mV.

Conclusion. It was established that thermal cycling of the Ti – 50 at.% Ni samples in the temperature range of the complete martensitic transformation leads to stabilization of the thermokinetic EMF value equal to 0.16 mV by the 15th temperature cycle. During thermal cycling in the temperature range of the incomplete martensitic transformation, the thermokinetic EMF value decreases and it is 0.04 mV by the 70th thermal cycle. Heating to a temperature above 240 °C allows the thermokinetic EMF to be restored to 0.22 mV, as in the case of annealing. Thermal cycling in the temperature range of the complete and incomplete phase transformation, the maximum temperature in heating zone change functional properties of titanium nickelide and the thermokinetic EMF value.

A method is proposed for the purposeful setting a thermokinetic EMF value from 0 to 0.6 mV on the TiNi wire areas, using different methods of influence: thermal cycling, deformation, temperature change in heating zone. The thermokinetic EMF value is changed in the range of 0÷0.22 mV during thermal cycling of the wire sections in the range of the incomplete martensitic transformation. The value in the selected area is set by the number of heat changes. The thermokinetic EMF value is changed from 0.22

to 0.60 mV in the 1st thermal cycle for the sample sections deformed at different values. The thermokinetic value decreases and ranges from 0.1 to 0.22 mV in the 2nd thermal cycle. The length of the information sections corresponds to the size of the affected area. The proposed technical solution can be used as a method of recording information on a thermogalvanic carrier (Method for recording analog and digital information onto a thermogalvanic carrier: pat. 2 239 241 C2 Russian Federation, Int. Cl. G 11 B 9/00 / A. M. Gorovoj, M. A. Portnov; date of publication: 10/27/04). The product can be returned in its original condition, i.e. to erase information it is enough to heat the required area of the product above 240 °C.

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