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PHASE TRANSITIONS AND SHAPE MEMORY PROPERTIES OF NICKEL-TITANIUM ALLOYS USED TO MAKE MEDICAL IMPLANTS

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This paper presents the results of phase transitions studies in NiTi shape memory alloys designed for medical applications. The X-ray diffraction technique (XRD), differential scanning calorimetry (DSC), electrical resistivity measurements (ERM) and the shape recovery measurements (SRM) were used for the studies of the reversible martensitic transitions after various thermal treatment. Changes in temperature and time of annealing have influence on a sequence and the characteristic temperatures of transitions as well as on the properties of alloys. The obtained results were applied during processing and thermo-mechanical treatments of these alloys for making the shape memory medical implants which act under the influence of the human body heat. The optimal thermo-mechanical treatment for obtaining the superelastic implants was also selected.

Prepared Nitinol implants prototypes were applied as the shape memory staples for bone joining of mandible fractures and as superelastic springs for skull reshaping during treatments of children with craniostenosis.

Key words: NiTi SMA, phase transitions, medical implants.

The NiTi shape memory alloys offer very attractive properties for medical applications [1]. Binary alloys, containing 49–51 at. % Ni after solution treatment exhibit reversible B2⇔B19' transformations between a high temperature B2 (CsCl) phase (austenite) and a low temperature B19' phase (martensite). Characteristic transformation temperatures during cooling are noted as M_s (Martensite start) and M_f (Martensite finish) and during heating A_s (Austenite start) and A_f (Austenite finish) respectively [2]. Often in those alloys, below the characteristic T_R temperature, the intermediate rhombohedral R-phase occurs [3]. The B2⇒R transition is characterized by a rapid increase in electrical resistance, extra diffraction spots at 1/3 positions of the B2 reciprocal lattice, extra peaks on the DSC curves and splitting in the {110} and {211} X-ray diffraction reflections [4]. One- or two-way shape memory effects are accompanied by reversible thermoelastic transitions and changes of internal stress in the material during cooling and heating. Superelasticity takes place when the change of shape is caused by external stress. The course of transitions, its temperature range, and shape memory properties of these alloys strongly depend on the chemical composition, alloying of other metals and processing conditions [5, 6].

NiTi implants for medical applications must have shape memory or superelastic effects at temperatures below the human body temperature [7, 8].

In this article, the investigations of transformations and shape memory properties of alloys designed for medical implants are presented. The purpose was to select a suitable thermal treatment to obtain implants with a shape recovery temperature below 30°C.

$Ti_{50}Ni_{48,7}Co_{1..3}$ and $Ni_{50,5}Ti_{49,5}$ shape memory alloys have been obtained by vacuum induction melting. After homogenization treatment the ingots were processed to flats and wires by hot and cold rolling as well as drawing. Samples were mechanically cut and polished. Solution treatment at 700°C and ageing in the temperature range 300–600°C and annealing below recrystallization temperatures after cold deformations were used.

The phase transitions were recorded by X-ray Philips diffractometer equipped with a temperature attachment. Diffraction patterns in CuK_{α} radiation were recorded during cooling and heating rates of 1°C/min in the temperature range from +100 to –120°C. DSC curves were recorded by a Perkin-Elmer DSC–7 calorimeter during cooling from ambient temperature to –120°C and reheating to +80°C at the rate of 10°C/min. Changes of electrical resistivity were recorded by a 2-point probe using a Diesselhorst compensator. The shape memory effect of wires was recorded by the ASTM 2082-01 test on the measurement state equipped with a PT–100 temperature indicator and LVDT linear variable differential transformer.

The phase transformation courses recorded by XRD technique after solution treatment are shown in Fig. 1. The reversal phase transitions B2⇔B19’ in NiTi alloy and B2⇔R⇔B19’ sequence in TiNiCo alloy were recorded.

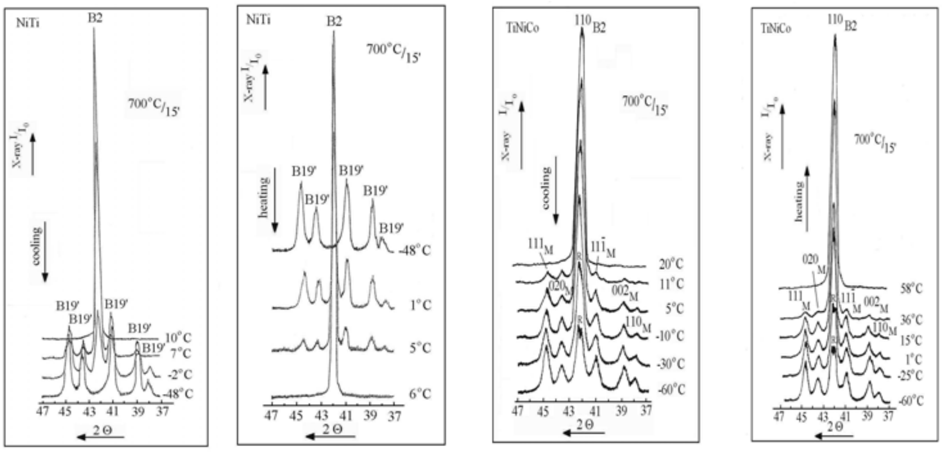

Fig. 1. Transition courses recorded during cooling and heating of $Ni_{50,5}Ti_{49,5}$ and $Ti_{50}Ni_{48,7}Co_{1..3}$ alloys after solution treatment

A very strong peak 110_{B2} of the parent phase on the diffraction patterns of NiTi alloy is visible above 10°C . During cooling the 110_{B2} peak intensity decreases and the diffraction reflections from (110), (002), ($11\bar{1}$), (020) and (111) planes of martensitic phase appear. The intensities of reflections from the martensitic phase increase, whereas the intensity of the 110_{B2} peak decreases together with the decrease in temperature. The very visible reflections of the martensite B19’phase are shown at -48°C. During heating the martensite transforms to parent phase immediately. In TiNiCo alloy during cooling and heating is visible the splitting of 110_{B2} peak which to demonstrates the transitions courses with rhombohedral R-phase contribution.

Reversible phase transitions B2⇔R⇔B19’ in the TiNiCo alloy during cooling and heating after solution treatment and ageing are visible on the DSC curves (fig. 2).

Thermally reversible transformations in these alloys were confirmed by electrical resistance changes versus temperature during the cooling-heating cycles. During cooling the transition of the parent phase B2 to the R-phase occurring below the T_R temperature is characterized by a rapid increase in electrical resistance (fig. 3).

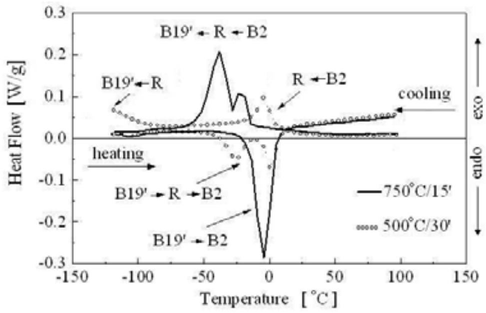

Fig. 2. DSC curves of TiNiCo sample after solution treatment and then ageing at 500°C for 45 minutes

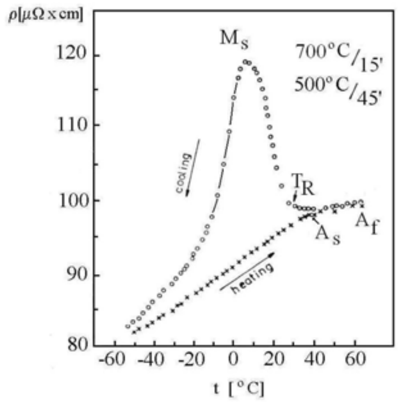

Fig. 3. Electrical resistance as a function of temperature for TiNiCo alloy after quenching and ageing

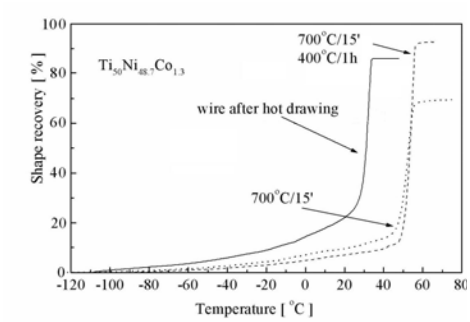

Fig. 4. Shape recovery curves vs temperature after various treatments

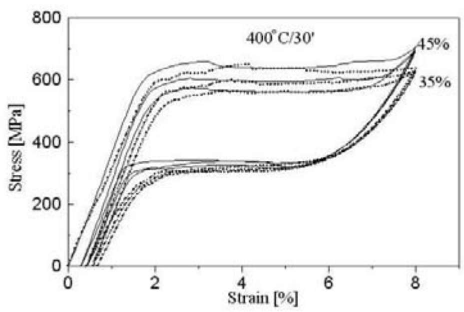

Fig. 5. Superelastic tensile curves of TiNiCo wires after cold drawing and annealing

In fig.4 is seen the increase of shape recovery temperature after quenching and ageing causes by changes of composition and defects structure of wires in comparison with state after hot drawing. The wires with good superelastic loops were selected from wires with 35 and 45% deformation which were annealed at 400°C for 30 minutes (fig. 5). The shape memory staples were made from the wires with shape recovery temperature below 37°C. Two kinds of prototypes implants for clinical treatments were prepared from wires with desired properties. The staples with shape recovery acted by patient's body temperature and superelastic springs to cranial reshaping of children with craniostosis. Figures 6 and 7 show the examples of using the shape memory staples for joining mandible fracture and superelastic springs for cranial correction.

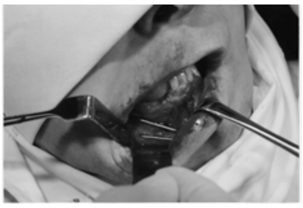

Fig. 6. Example of mandible fracture joining by TiNiCo shape memory staples [7]

Fig. 7. Application of superelastic NiTi ring for craniostosis treatment [8]

The characteristic temperatures of transformations in wires after different working can be easily influenced by the thermomechanical treatments. In the cobalt doping alloys is possible obtainment of good superelastic properties, similar as in Ni-rich alloys, by cold working with large deformation and short time annealing. The implants from obtained wires with desirable properties were successfully applied in craniomaxillofacial surgery.

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ФАЗОВІ ПЕРЕХОДИ ТА ВЛАСТИВОСТІ ФОРМ ПАМ'ЯТІ НІКЕЛЬ-ТИТАНОВИХ ШАРІВ, ЯКІ ВИКОРИСТОВУЮТЬСЯ ДЛЯ ВИГОТОВЛЕННЯ МЕДИЧНИХ ІМПЛАНТАТІВ

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У статті подано результати досліджень фазового складу в NiTi-шарах пам'яті, спроектованих для медичних застосувань. Для дослідження зворотних мартенситних переходів після теплової обробки використано техніку рентгенівської дифракції, диференціальної скандувальної калориметрії, вимірювань електричного опору та вимірювання розпізнавання форми. Зміни температури та часу відпалу впливають на послідовність та характерні температури переходів, а також на властивості сплавів. Одержані результати застосовували під час термомеханічної обробки цих шарів для створення медичних імплантатів форм пам'яті, які реагують на температуру людського тіла. Підібрано оптимальну термомеханічну обробку для одержання суперэластичних імплантатів. Виготовлені прототипи нікелевих імплантатів використані як основні елементи пам'яті з'єднання кісток нижньої щелепи у разі перелому та як суперэластичні пружини для черепа, які дають змогу визначити профіль у разі діагностування дітей з краніостенозом.

Ключові слова: NiTi-форми пам'яті, фазові переходи, медичні імплантати.

ФАЗОВЫЕ ПЕРЕХОДЫ И СВОЙСТВА ФОРМ ПАМЯТИ НИКЕЛЬ-ТИТАНОВЫХ СЛОЕВ, КОТОРЫЕ ИСПОЛЬЗУЮТСЯ ДЛЯ ИЗГОТОВЛЕНИЯ МЕДИЦИНСКИХ ИМПЛАНТАТОВ

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В статье представлены результаты исследований фазового состава в NiTi-слоях памяти, спроектированных для использования в медицине. Для исследования обратных мартенситных переходов после тепловой обработки использована техника рентгеновской дифракции, дифференциальной сканирующей калориметрии, измерений электрического сопротивления и измерения распознавания формы. Изменения температуры и времени отжига влияют на последовательность и характерные температуры переходов, а также на свойства сплавов. Полученные результаты применяли во время термомеханической обработки этих слоев для создания медицинских имплантатов форм памяти, которые реагируют на температуру человеческого тела. Подобрано оптимальную термомеханическую обработку для получения суперэластичных имплантатов. Изготовленные прототипы никелевых имплантатов использованы как основные элементы памяти соединения костей нижней челюсти в случае

перелома и как суперэластичные пружины для черепа, которые дают возможность определить профиль при диагностировании детей с краниостенозом.

Ключевые слова: NiTi-формы памяти, фазовые переходы, медицинские имплантаты.

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