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CHANGES IN SELECTED STRUCTURAL CHARACTERISTICS OF SHAPE MEMORY ALLOYS

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Key words: TiNi and TiNiCu alloys, shape memory, thermal and mechanical loads, annealing, X-ray diffraction measurements, structural characteristics.

Abstract

The first part of this paper presents some experimental results relating to the study of evolution of residual elastic fields in the TiNi alloy subjected to a cyclical reversible martensite transformation (thermal and mechanical loads). Two selected structural parameters were assumed to characterize residual stresses generated in the cycled material. The analysis was conducted in the high-temperature austenitic phase in categories of progressing shape memory degradation.

Taking into account crystalline structure and changes in the phase composition, the TiNiCu amorphous ribbons were examined under various times of heat treatment (annealing). Measurements were performed using mainly X-ray diffraction (XRD) methods. Changes in selected diffraction profiles and mathematical computations provided the basis for determining the structural parameters of TiNi alloys, and changes in the crystalline structure of TiNiCu alloys.

ZMIANY WYBRANYCH CHARAKTERYSTYK STRUKTURALNYCH STOPÓW Z PAMIĘCIĄ KSZTAŁTU

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Słowa kluczowe: stopy TiNi i TiNiCu, pamięć kształtu, obciążanie termomechaniczne, wyżarzanie, pomiary dyfrakcyjne, charakterystyki strukturalne.

Streszczenie

W pierwszej części artykułu przedstawiono wybrane wyniki badań doświadczalnych ewolucji resztkowych pól sprężystych w stopie TiNi na skutek wielokrotnego powtarzania przemiany martenzytycznej (obciążanie termomechaniczne). Dwa wybrane parametry strukturalne przyjęto jako wielkości charakteryzujące naprężenia resztkowe generowane w obciążanym materiale. Analiza była prowadzona w wysokotemperaturowej fazie austenitu w kategoriach postępującej degradacji efektu pamięci kształtu.

Mając na uwadze strukturę krystaliczną oraz zmiany składu fazowego, w stopie TiNiCu przeprowadzono obróbkę cieplną przy różnych czasach jej stosowania. W pomiarach stosowano głównie metody dyfrakcyjne. Na podstawie zmian w wybranych profilach rentgenowskich i korzystając z odpowiedniego aparatu matematycznego prześledzono w badanych materiałach wybrane parametry strukturalne (stopy TiNi) oraz zmiany w strukturze krystalicznej (stopy TiNiCu).

Introduction

Today shape memory materials are often main elements of intelligent structures and mechanisms. This is connected with their unique properties, such as shape memory effect (SME) and pseudoelasticity effect (PE). These materials are used in the case of cyclical changes in motion of elements (e.g. repeated bending). Such elements make use of a one-way shape memory effect (OWSME) and a two-way shape memory effect (TWSME). The practical application of shape memory alloys depends first of all on the stability of their functional properties (e.g. shape memory recovery). According to literature data, a cyclical reversible martensite transformation leads to changes in the functional characteristics of these materials, especially reduced shape memory recovery, or even its complete failure. It follows that the stability of functional properties is one of the most important parameters, deciding about common application of the above materials. This fact and insufficient knowledge about the complex thermal and mechanical relationships may considerably limit the design and development of structures and devices containing shape memory alloys.

ACCORDING to J. HUMBEECK van (1991), there are three major reasons for reduced reliability of shape memory alloys, i.e. damage caused by cracks, changes in physical, mechanical and functional characteristics, and progressing reduction in the shape memory effect caused by stresses, strains and temperature. Many authors claim that residual elastic fields are responsible for the "degradation" behavior of shape memory alloys. Taking this into account, the paper presents some results of experiments concerning changes in selected structural parameters of the TiNi alloy caused by repeated thermal and mechanical loads. Selected structural characteristics, in the form of root-mean-square microstrains $\langle\varepsilon^2\rangle^{1/2}$, and sizes of coherent blocks D, were assumed to characterize residual elastic fields generated in the cycled material. The presence of residual stresses in the TiNi alloy was confirmed applying X-ray diffraction methods. Despite the complex nature of the prob-

lem, the analysis of the above structural parameters may provide new insights into the materials examined in the aspect of changes in their functional properties caused by a repeated shape memory effect.

It is a well-known fact that the shape memory effect can be observed in a variety of materials. In recent years three-component alloys have become more and more popular. An example may be TiNi-Cu alloys, showing more stable functional characteristics, which makes them better suited for practical applications. Due to their good thermal and mechanical properties, TiNi alloys are used mostly in cases of a high number of transformation cycles. On the other hand, these materials are sensitive to thermal fatigue, and additional changes in their properties caused by a cyclical martensite transformation limit their practical application. In order to overcome these problems and improve the fatigue properties of the alloys discussed, they are modified with such elements as Cu or Fe. The introduction of the third element affects the course of a martensite transformation, and causes significant changes in the thermal and mechanical characteristics of these materials.

Compared with two-component alloys (TiNi), three-component ones show much better properties. For instance, replacing nickel with copper allows to reduce the sensitivity of the martensite start temperature to changes in the chemical composition of a given alloy. It also enables to limit pseudoelastic hysteresis and flow stresses in the martensitic state (Nam et al. 1990, Es--Souni et al. 2001, Fu & Du 2003). Moreover, copper makes it possible to avoid the formation of Ti3Ni4 precipitations (Nam et al. 1990). To sum up, the enumerated advantages of TiNiCu alloys make them better suited for technical applications (e.g. sensors, servo-motors).

In the present study three-component alloys (TiNiCu) in the form of thin amorphous films were analyzed in the process of annealing lasting 1.5 and 4 minutes. Changes in their crystalline structure and phase composition were determined using X-ray diffraction methods.

Description of sample and experiments

The shape memory effect was produced in TiNi sample by repeated thermal and mechanical loading. The experimental material was a two-component alloy (TiNi) in the form of 0.5 mm rolled sheet containing 50.6 at % nickel. Before the experiment the alloy was subjected to heat treatment by annealing at a temperature of 500°C for 60 minutes, followed by furnace cooling to ambient temperature. Diffraction measurements performed after this treatment showed that the material contained only the austenitic phase with a low amount of TiNi2 precipitations. Small (100 × 3 × 0.5 mm) samples, cut out of sheet by electric spark machining, were used for thermomechanical load tests and diffraction measurements, using a tube with a cobalt anode.

The characteristic temperatures of transformations were: M_s = 18°C, M_f = 10°C, A_s = 27°C, A_f = 35°C. The specimens were subjected to thermal and mechanical loading 400 times, and strain was executed by bending (Fig. 1). The thermo-mechanical procedure adopted in the study included the following stages:

1. A sample of the TiNi alloy was placed in a holder of a stand for thermo-mechanical load testing (at a temperature above A_f). The sample was subjected to loading and elastic strains were recorded.
2. Then the sample was bent at a 90° angle around a sleeve, with simultaneous cooling with liquid nitrogen vapors. This resulted in the formation of martensite microstructure. After deformation the sample was unloaded, to observe elastic recovery of the martensite.
3. The sample was subjected to resistance heating to a temperature above A_f, and its partial recovery to the original high-temperature shape was observed.
4. The above experimental procedure was repeated cyclically for a given number of thermo-mechanical loads.

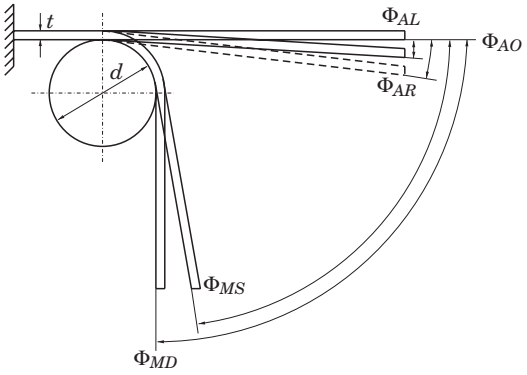

Fig. 1. Schematic illustration of bending examination of SME. The specimen was bent around an ebonite sleeve; Φ_{A0} – arc angle of the specimen in the initial position (austenitic state), Φ_{AL} – arc angle of the specimen in the spring position under load (austenitic state), Φ_{MD} – arc angle of the specimen in the deformed position under load (martensitic state), Φ_{MS} – arc angle of the specimen in the spring-back position without load (martensitic state), Φ_{AR} – residual arc angle of the specimen after 'n' thermal and mechanical cycles (austenitic state)

The strain of external layers of the sample $å$ during bending was determined from the following dependence:

$$\varepsilon = \frac{t}{d} \tag{1}$$

where:

t – sample thickness,

d – diameter of the sleeve used for sample bending.

The diameter of the ebonite sleeve was adjusted to achieve a given degree of strain in the sample. The estimated strain of external layers of the sample was about 6%.

The other material examined was an alloy containing Ti – 50 at %, Ni – 25 at % and Cu – 25 at %. It was used for analyzing crystalline structure and changes in the phase composition caused by annealing heat treatment. The material had the form of amorphous film, 2 × 0.05 mm, produced by melt-spinning preceded by arc remelting of pure titanium, nickel and copper. The crystallization temperature for this material was about 460°C.

In the present experiments the specimen was annealed at a temperature of 500°C for different periods of time (1.5 and 4 minutes). This treatment resulted in obtaining the crystalline state of the material. Annealing was carried out in a resistance furnace, at a temperature range comprising crystallization. Only one sequence of martensite transformation was observed in the material examined, i.e. B2⇒B19. The characteristic temperatures of this alloy were as follows: M_s = 57°C, M_f = 52°C, A_s = 61°C and A_f = 60°C. Microstructure and changes in the phase composition were determined on the basis of diffraction measurements with λ_{CuKa} radiation.

Results and Discussion

Evolution of residual elastic fields resulting from thermal and mechanical loads was examined during 400 cycles divided into separate series, 50 cycles each. Structural parameters, i.e. root-mean-square microstrains $(<\varepsilon^2>)^{1/2}$ and sizes of coherent blocks D, were determined in the austenitic phase, taking diffraction measurements in the most deformed parts of samples, i.e. directly over the sleeve used for bending tests (Fig. 1). Structural characteristics were determined on the basis of broadening of selected diffraction profiles. Changes in diffraction reflections caused by repeated thermo-mechanical loading have been described by Breczko and Kuś (2002). Progressing broadening of diffraction profiles resulting from repeated thermal and mechanical loading was observed. Figure 2 presents changes in the full-width at half maximum intensity peak $(110)_{B2}$,

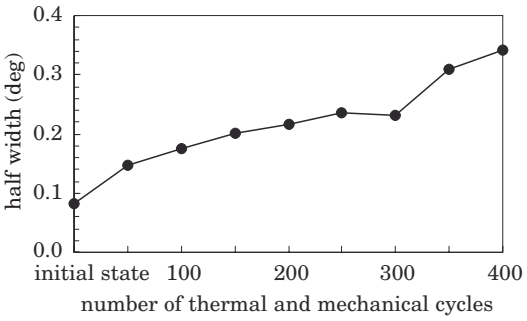

Fig. 2. Changes in the half-value width of the $(110)_{B2}$ peak vs. the number of thermal and mechanical cycles

representing the radiation component $K_{\alpha 1}$, versus the number of thermal and mechanical cycles. The separation into the components $K_{\alpha 1}$ and $K_{\alpha 2}$ was performed with the Pearson function type VII, according to the appropriate algorithm (GUPTA 1998).

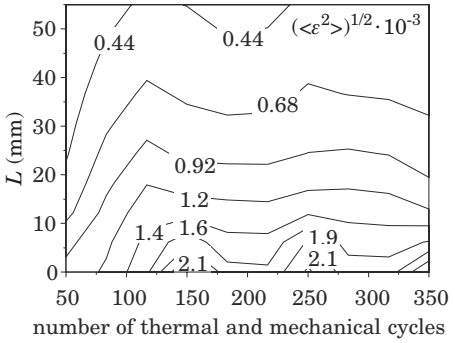

Fig. 3. Changes in the $(<\varepsilon^2>)^{1/2}$ parameter vs. the number of thermal and mechanical cycles; L denotes base length

It is common knowledge that repeated induction of the shape memory effect in consequence of e.g. thermomechanical loads leads to changes in crystalline microstructure, due to the generation of structural defects. This is confirmed by the development of residual elastic fields in the austenitic phase, following repeated martensite transformations. Figures 3 and 4 illustrate evolution of root-mean-square microstrains and sizes of coherent blocks, resulting from repeated thermal and mechanical loading. The Figures show that root-mean-square microstrains increase with a growing number of thermomechanical cycles, reaching the maximum value at 250 cycles (Fig. 3). This parameter stabilized at further loading, but its slight increase was still recorded. As regards the sizes of coherent blocks, an opposite tendency was observed – the value of this parameter was decreasing during the first 250 cycles. The source of these changes may be the crystalline microstructure of the material analyzed, affected by structural defects. It seems that these observations may be important from the perspective of practical applications of shape memory alloys, dependent upon their functional properties, especially the stability of the shape memory effect after many thermal and mechanical cycles.

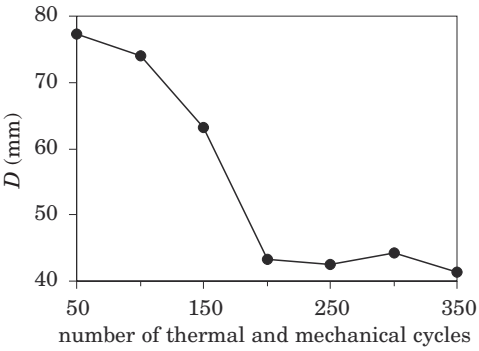

Fig. 4. Changes in the D parameter vs. the number of thermal and mechanical cycles

In the case of the amorphous $Ti_{50}Ni_{25}Cu_{25}$ alloy, changes in the crystalline structure were executed by means of annealing heat treatment at a temperature of 500°C for 1.5 and 4 minutes. Diffraction measurements were performed to observe changes in microstructure and phase composition. XRD patterns of the material examined are given in Figure 5. At the initial stage, at room temperature, only the amorphous phase, in the form of a single broadened diffraction peak, is visible. After annealing at 500°C for 1.5 minutes, the material started to show crystallization, so various phases appeared in the amorphous matrix. This means that the process of

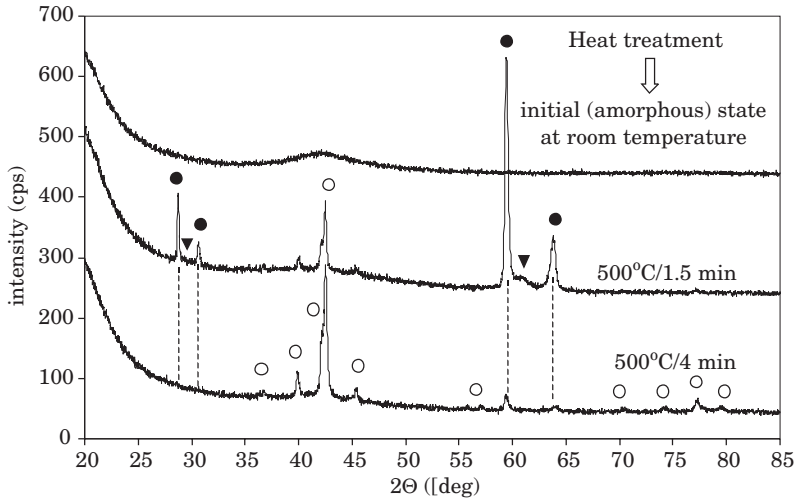

Fig. 5. XRD patterns of the $Ti_{50}Ni_{25}Cu_{25}$ ribbon annealed at 500°C for a different period of time; • – (011), (100), (022), (200) peaks from martensite; – peaks from martensite; t – (100), (200) peaks from the B2 parent phase

crystallization occurred at a temperature close to the temperature of annealing (500°C). The XRD pattern obtained for the sample for which the annealing time was 4 minutes also shows characteristic changes (Fig. 5). The crystalline structure became visible after a longer period of annealing, with martensite as the dominant phase. In Figure 5 the reflections with darkened triangles correspond to the parent austenitic B2 phase with the space group *Pm3m;* the peaks with blank circles represent the martensitic phase with the space group *Pmmb* (SCHRYVERS et al. 2001); the reflections with darkened circles correspond to a strongly preferred orientation of martensite with an orthorhombic unit cell (plane orientations (011) and (100)). The occurrence of such sharp peaks of martensite or residuals of the parent B2 phase could be caused by incomplete martensite transformation. During this transformation, the planes (100) of the parent B2 phase are transformed into the planes (011) and (100) of martensite. No other precipitations of the TiCu and Ti_4Cu_3 phases were recorded.

On the basis of the structural data presented by POTAPOV et al. (2003), an XRD pattern of an orthorhombic unit cell of martensite B19 was also simulated in the study. The parameters of a unit cell of martensitic structure B19 were as follows: a = 2.914 Å, b = 4.284 Å, c = 4.515 Å.

Conclusions

Two shape memory alloys were examined in the study: TiNi and TiNiCu. In the case of the first material, the development of residual elastic fields in consequence of thermo-mechanical load was analyzed, paying

particular attention to the evolution of selected structural parameters. It was assumed that these parameters characterize residual elastic fields in the material subjected to loading. Repeated, cyclical thermal and mechanical loading in categories of shape memory degradation caused a decrease in the sizes of coherent blocks over the first 250 cycles, whereas root-mean-square microstrains increased significantly. During successive cycles, both parameters stabilized. This may indicate changes in microstructure as a result of generation of structural defects, which is confirmed by the development of residual elastic fields within the range of load cycles studied, whose presence was proved by X-ray diffraction. This can disturb the reversible martensite transformation in the aspect of progressing shape memory degradation.

At the second stage of the experiment the amorphous NiTiCu alloy was tested for changes in the crystalline structure caused by annealing heat treatment carried out for different periods of time. Diffraction measurements revealed the effect of annealing on the structure and phase composition of the material. At the initial stage only the amorphous phase, in the form of a single broadened diffraction peak, was visible. After annealing at 500°C for 1.5 minutes, the material started to show crystallization. The crystalline structure became visible after a longer period of annealing (4 minutes), with martensite with the space group *Pmmb* as the dominant phase.

On the basis of the structural data provided by professional literature, an XRD pattern of an orthorhombic unit cell of martensite B19 was also simulated in the study. The results obtained were consistent with experimental data.

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