Journal of Applied Mechanics and Technical Physics, Vol. 39, No. 2, 1998

EFFECT OF DEFORMATION AND EXTERNAL LOAD ON THE CHARACTERISTICS OF MARTENSITE TRANSFORMATIONS AND SHAPE-MEMORY EFFECTS IN ALLOYS BASED ON TITANIUM NICKELIDE

V. É. Gunter, T. Yu. Maletkina, and A. A. Klopotov

UDC 669.295:539.376

The effect of plastic deformation and external load on the characteristics of shape-memory effects is studied for alloys based on titanium nickelide of nearly equiatomic composition. A nonmonotonic dependence of the characteristic temperatures of martensite transformations on the strain degree of deformation is obtained. This phenomenon is explained in relation to the stages of development of plastic deformation. Optimal loading and deformation conditions for obtaining maximum values of reversible deformation are determined.

Alloys based on titanium nickelide, which exhibit the shape-memory effect and other unusual physicomechanical properties, are very sensitive to changes in the external structure of the material. Preliminary thermomechanical treatment allows one to purposely change the parameters of the shape-memory effect and the physicomechanical properties of the alloys. Although this problem has been extensively studied in the literature [1–6], there has been no complex investigation of the effects of external stresses and temperature on alloys based on titanium nickelide and the effect of stresses and deformation on the parameters of the shape-memory effect and the characteristic temperatures of martensite transformations (MT) in these alloys. The present paper is devoted to this problem.

1. Materials and Experimental Procedure. The alloys studied were produced from titanium iodide and NO-graded nickel in an arc-discharge furnace. The alloys had the same compositions as TN-10 and TN-20 alloys [7]. The alloys were shaped into a wire of diameter 1.5 mm by hot extrusion through dies. After chemical treatment by etching, the specimens were held in vacuum (10^{-5} Pa) at 1080 K for 1 h and cooled with the furnace. The temperatures of MT were determined from the variation of the electrical resistance with temperature and x-ray structural analysis data. Curves of electrical resistance were measured by the conventional potentiometric four-point method. X-ray structural studies were performed on a DRON-2 apparatus. The parameters of the shape-memory effect were studied by measuring macrostrain during stretching under load on an "Instron" device in the cycle loading–cooling–heating. Wire specimens of the alloys 60 mm long and 1 mm in diameter were loaded at various temperatures: 77, 223, 323, 373, 423, and 473 K. The external loads corresponded to stresses of 40, 120, and 230 MPa. The influence of prestrain on the shape-memory effect was also studied after rolling of specimens 60 mm long with a square cross section 1 mm^2. The specimens were rolled in one pass at room temperature with an average reduction of 4–6% per pass.

2. Crystal Structure and MT in the Alloys. In the high-temperature region, the alloys are in the one-phase state: the Ti_2Ni phase with the B2 structure. The presence of a minor portion of the Ti_2Ni phase in the form of highly disperse inclusions has little effect on the characteristics of the shape-memory effect. As the temperature decreases from 473 K, TN-20 alloy undergoes the martensite transformation B2 ↔ B19′ which begins at $M_{\text{in}} \approx 300$–$335$ K. Here B2 is a cubic body-centered structure ordered by the CsCl type, and B19′ is a rhombic martensite with an additional slight monoclinic distortion [1]. In the TN-10 alloy, the

---

Russian Medical-Engineering Center, Tomsk 634034. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, Vol. 39, No. 2, pp. 175–181, March–April, 1998. Original article submitted July 9, 1996.

0021-8944/98/3902-0312 $20.00 © 1998 Plenum Publishing Corporation

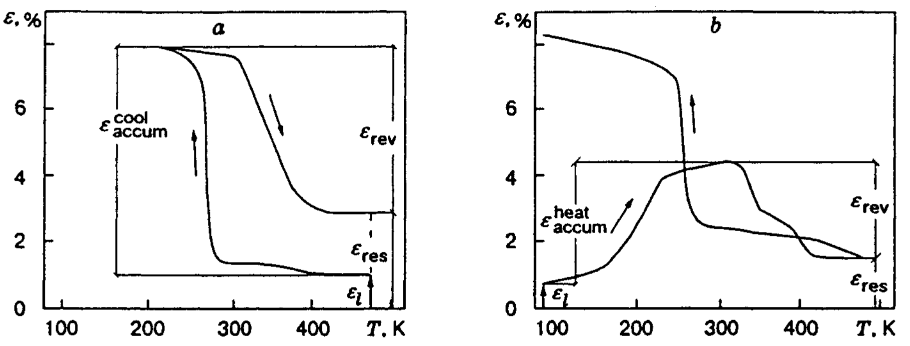

Fig. 1

transformation proceeds in two stages: B2 ↔ R ↔ B19′ (the R phase is rhombohedral). The temperature of the beginning of the phase transformation B2 ↔ R is $T_R \approx 290$ K, and the temperature of the beginning of the martensite transformation R ↔ B19′ is $M_{\mathrm{in}} = 265$ K.

3. Shape-Memory Effect in Nondeformed Specimens. The shape-memory effect is manifested in the curve of strain versus temperature $\varepsilon(T)$ for specimens of TN-10 alloy under constant external loading (Fig. 1a and b, the arrows show the direction of temperature variation). The shape-memory effect in alloys based on titanium nickelide results from the inelasticity in the direct and reverse martensite transformations (B2 ↔ R ↔ B19′) under loading [1, 2].

The main characteristics of the shape-memory effect studied in this paper are shown in Fig. 1a and b, where ε_l is the loading strain, $\varepsilon_{\mathrm{rev}}$ is the reversible strain in heating under load, $\varepsilon_{\mathrm{res}}$ is the residual strain after recovery of shape under heating, $\varepsilon^{\mathrm{cool}}_{\mathrm{accum}}$ is the strain accumulated under cooling, $\varepsilon^{\mathrm{heat}}_{\mathrm{accum}}$ is the strain accumulated during heating of the specimen after loading in the martensite state, and $\varepsilon_{\mathrm{gen}}$ is the general accumulated strain. The parameters are related by $\varepsilon_{\mathrm{gen}} = \varepsilon^{\mathrm{cool}}_{\mathrm{accum}} + \varepsilon_l = \varepsilon_{\mathrm{rev}} + \varepsilon_{\mathrm{res}}$.

4. Effect of External Load on the Shape-Memory Effect. Figure 2a gives the temperature dependence of the stress developed in a constrained specimen of TN-10 alloy in an attempt to recover the initial shape during heating from the low-temperature region after it has been strained by 6% at 77 K (below the temperature range of MT). As shown in [8], the curve obtained coincides with the temperature dependences of the martensite-shear stress and the yield point. The yield point for the alloys with thermoelastic MT is shown by the dashed curve in Fig. 2a; the martensite-shear stress corresponds to the stress level required for the formation and reorientation of martensite crystals [1]. The dashed curve is the actual resistance to plastic shear, determined by extrapolation from high to low temperatures. The minimum region on the curve of $\sigma(\varepsilon)$ corresponds to the beginning of martensite transformation M_{in}, i.e., roughly to the temperature of formation of the martensite phase without loading. The maximum region corresponds to the temperature M_s at which the martensite phase can form under the action of stress.

Figure 2b shows curves of the strain ε_l accumulated at the moment of application of load versus the loading temperature (curves 1–3 correspond to stresses of 40, 120, and 230 MPa). Analysis of the curves in Fig. 2 shows the following regularities. Irrespective of the stress, the highest values of ε_l are observed in the temperature range that corresponds to minimum values of the martensite-shear stress in the two-phase region of the alloy. The strain ε_l in this temperature range is determined by the formation of a single domain of the martensite R phase and transformation and reorientation of crystals of the B19′ phase in accordance with the direction of the applied stress [9]. The slight accumulation of the loading strain ε_l, as shown in Fig. 2, in the austenite and martensite states is due to the high level of internal stresses of the alloys in these states. In the alloys cooled to low temperatures (below M_f), the formation of the martensite has already been completed and the accumulation of strain in loading proceeds as a result of reorientation and retwinning of the martensite. The formation a deformational martensite by loading in a high-temperature state below M_s

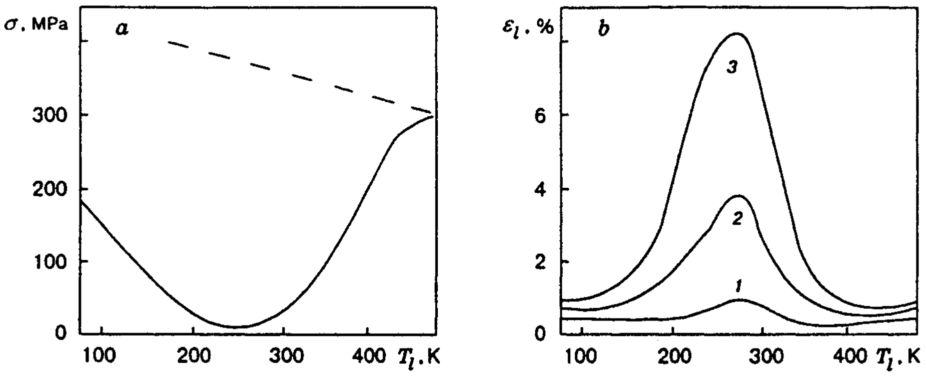

Fig. 2

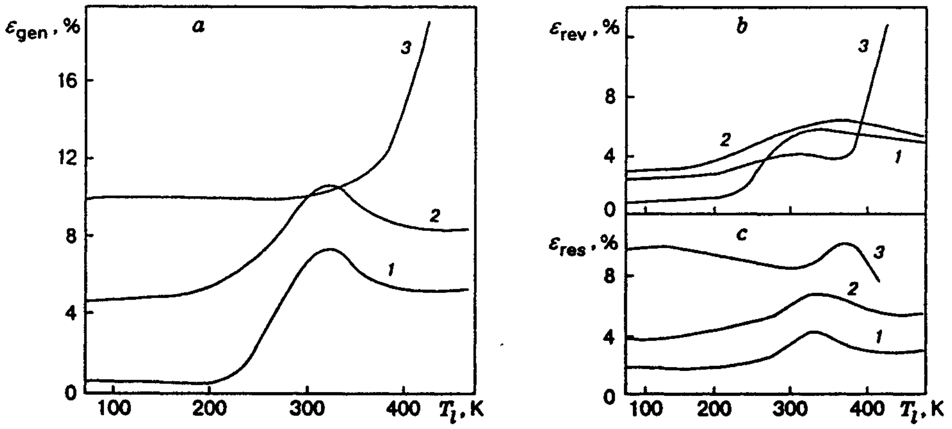

Fig. 3

requires stresses that correspond to the martensite-shear stress. As the temperature increases, the loading strain ε_l grows and the temperature range in which ε_l takes high values is extended. This agrees with the temperature dependences of the martensite-shear stress and the yield point.

Analysis of the curves for TN-10 alloy in Fig. 1 leads to the following dependences of the general strain ε_{gen}, the strain $\varepsilon_{\text{accum}}^{\text{cool}}$ accumulated during cooling in the martensite-temperature region, and the components of the latter on the external load (in Fig. 3, curves 1–3 correspond to stresses of 40, 120, and 230 MPa). As can be seen from Fig. 3a, an increase in load enhances the accumulation of strain. It should be noted that this effect is most pronounced for loading of the alloy in the martensite state. To attain a marked increase in strain accumulation in the austenite state, it is required to apply a more considerable stress than in the martensite state. In addition, at applied stresses of 40 and 120 MPa in the temperature region of pretransition states (~300–400 K), a certain increase in the general strain is observed (Fig. 3a).

Figure 3b shows the reversible strain ε_{rev} with increase in the specimen temperature to 474 K (this phenomenon is called the shape-memory effect [1, 2]) versus the loading temperature T_l. The results obtained suggest that loading of specimens of the alloy in the two-phase and austenite states gives a higher reversible strain compared to loading of the alloy in the martensite state. This conclusion is of great practical importance, because it allows one to predict regions of effective deformation of the alloys.

When a small external load is applied to the alloys (a stress not exceeding 120 MPa), the material shows an improved ability to recover the initial shape with a low level of residual strain [1, 4]. On the other

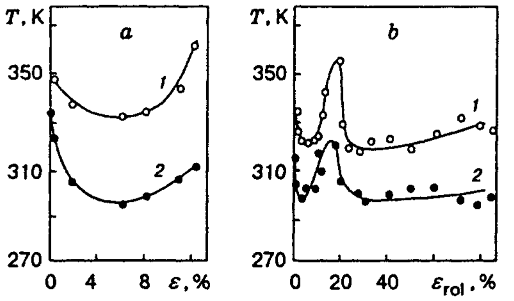

Fig. 4

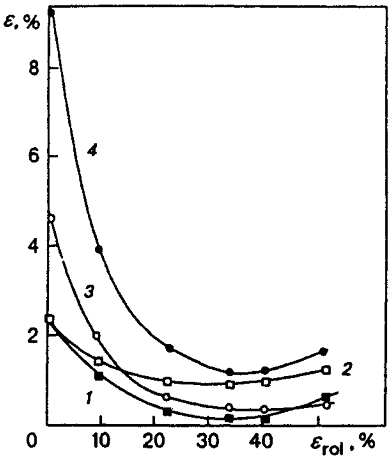

Fig. 5

hand, the reversible strain decreases under heating at load (at a stress of 230 MPa, Fig. 3b). All this suggests that the reversible strain is suppressed as a result of contribution of plastic strain in the temperature region of MT. The sudden increase in the reversible strain when the alloy is loaded in the austenite state and the applied load exceeds the critical value appears to be related to the effective distribution of internal microstrains, which orient martensite crystals with a maximum shift.

Analysis of the results leads to the following regularities: an increase in the level of external stresses extends the temperature region of MT, the hysteresis loop is not closed, and smoothing of the two-phase character of the shape-recovery curve is observed (see Fig. 1). In this case, the residual strain ε_{res} is determined by the relative contribution of the dislocation mechanism to the general strain of the alloy. This contribution is the main cause of dissipation of elastic energy during MT in alloys based on titanium nickelide.

From analysis of the curve of ε_{res} (Fig. 3c) versus T_l the following regularity can be inferred: an increase in load leads to a shift of the maximum of ε_{res} to higher temperatures. In this case, the residual strain is more sensitive to an increase in load in the martensite state (the temperature region 100–250 K) than in the high-temperature state. Heating to high temperatures at small loads (~40 MPa) brings the specimen to the initial state (complete removal of the accumulated strain). At large loads (~230 MPa) there is a considerable residual strain ($\varepsilon_{res} \sim 8\%$), which is due to the irreversible character of redistribution and reorientation of martensite crystals, and accumulation of defects as the temperature changes from 100 to 450 K.

5. Effect of Deformation on the Shape-Memory Effect and Characteristic Temperatures of MT. Figure 4 (curve 1 corresponds to T_R and curve 2 corresponds to M_{in}) gives the results of investigation of the effect of prestrain on the characteristic temperatures of MT in the alloys based on titanium nickelide. It is obvious that for TN-20 alloy subjected to plastic tensile deformation, the dependence of T_R and M_{in} on the strain degree is nonmonotonic (Fig. 4a). The minimum on the curves in Fig. 4a corresponds to a 6% strain. When deformation was performed by rolling of the alloy, the dependences of T_R and M_{in} on the strain degree are also nonmonotonic with a minimum in the region of 3–5% strain (Fig. 4b, ε_{rol} is the rolling strain). According to concepts available in the literature [9], the minimum on the curves of T_R and M_{in} versus the strain degree is due to the occurrence of defects in the alloy under insignificant plastic deformation. The defects prevent motion of the interfaces, thus causing a decrease in the MT temperatures T_R and M_{in}. With a further increase in the plastic-strain degree, the density of defects and elastic fields increases, and, as a result, martensite crystals form at higher temperatures (according to the Clapeyron–Clausius equation [3]). At large strains (more than 20%), the temperature ranges of existence of the low-temperature phases R and B19′ begin to depend in a complex manner on the dislocation substructure of the alloys. Simultaneously, the formation of the dislocation substructure leads to partial suppression of MT. In the TN-10 alloy, MT were not completely suppressed even under very large deformation action (rolling to 80%). This is supported by data obtained in studies of curves of electrical resistance versus temperature in relation to the strain degree.

Analysis of the curves of electrical resistance versus temperature shows that the temperature range of phase transformations in TN-20 alloy increases from ~30 K in the nondeformed material to 100 K in the material deformed to 80% by rolling. In this case, the electrical resistivity increases from 65 ($\varepsilon = 0$) to 125 $\mu\Omega \cdot$ cm ($\varepsilon = 80\%$). This agrees with the numerical results obtained by Akhiezer et al. [10].

Figure 5 shows curves of the general strain and its components versus the degree of rolling strain for TN-20 alloy (curve 1 refers to the residual strain ε_{res}, curve 2 refers to the loading strain ε_l, curve 3 refers to the reversible strain under heating at load ε_{rev}, and curve 4 to the general strain ε_{gen}). Deformation considerably decreases the parameters that characterize the shape-memory effect. The largest decrease in these parameters occurs before ~20% strain. As a rule, defects are accumulated most actively in stages associated with the formation of oriented dislocation substructures before attainment of about 20–30% strain [11, 12]. Upon increase in the dislocation density, the mobility of interfaces decreases and the probability of motion of interfaces from one grain to another also decreases. This affects the completeness of the MT, prevents growth of favorably oriented martensite crystals under applied external loads, and, hence, leads to suppression of the shape-memory effect.

A further increase in strain leads to an insignificant increase in ε_{rev}. Apparently, this phenomenon is associated with transition from the cross-linked dislocation substructure to a cellular dislocation substructure [13, 14]. Since, inside the cells of the dislocation substructure, the scalar density of dislocations decreases (redistribution of dislocations occurs: some of them move to the low-angle boundaries in the dislocation substructure), the probability that martensite crystals form at these local sites increases.

Thus, the shape-memory effect is most pronounced after preloading of the alloys in the austenite state. The largest strain of the material at the moment of loading is observed in the two-phase region, which corresponds to small values of the martensite-shear stress. Minimum residual strain after shape recovery under heating is observed in the case where loading (to 120 MPa) is performed in the two-phase temperature range. The dependence of the characteristic temperatures of MT on the strain is nonmonotonic with a minimum that corresponds to ~3–6% strain.

REFERENCES

1. V. É. Gyunter, V. I. Itin, L. A. Monasevich, et al., *Shape-Memory Effects and Their Applications in Medicine* [in Russian], Nauka, Novosibirsk (1992).
2. V. A. Likhachev, S. A. Kuz'min, and Z. P. Kamentseva, *Shape-Memory Effects* [in Russian], Izd. Leningrad Univ. (1987).
3. S. Rodriguez and L. S. Braun, "Mechanical properties in alloys that exhibit shape-memory effects," in: *Shape-Memory Effect in Alloys* [Russian translation], Metallurgiya, Moscow (1979).
4. Yu. K. Kovneristyi, S. G. Fedotov, L. A. Matlakhova, and S. V. Oleinikova, "Shape-memory effects and shape recovery in TiNi alloy in relation to strain," *Fiz. Met. Metaloved.*, **62**, No. 2, 344–348 (1986).
5. V. B. Fedorov, I. D. Morokhov, I. V. Zolotukhin, and E. G. Galkina, "Effect of severe plastic deformation on the properties of titanium nickelide," *Dokl. Akad. Nauk SSSR*, **277**, No. 5, 1131–1133 (1984).
6. Yu. I. Paskal', V. Ya. Erofeev, L. A. Monasevich, and V. A. Pavskaya, "Martensite deformation of titanium nickelide," *Izv. Vyssh. Uchebn. Zaved., Fiz.*, No. 6, 103–117 (1982).
7. V. É. Gunter, V. V. Kotenko, V. K. Mirgazizov, et al., *Shape-Memory Alloys in Medicine* [in Russian], Izd. Tomsk Univ., Tomsk (1986).
8. V. É. Gunter, T. Yu. Serikova, L. A. Monasevich, and Yu. I. Paskal', USSR Inventor's Certificate No. 1698688, "Method of determining the temperature dependence of the yield point," *Otkr. Izobr.*, No. 46 (1991).

9. V. É. Gunter, "Shape-memory alloys and constructions in medicine," Doct. Dissertation in Tech. Sci., Tomsk (1989).
10. I. A. Akhiezer, L. N. Davydov, and T. P. Chernyaeva, "On polymorphous transformations in highly disperse polycrystalline structures," in: *Questions of Atomic Science and Engineering*, *Physics of Radiation Damage and Radiation Materials Science*, No. 2 (1987), pp. 3-8.
11. V. E. Panin, Yu. V. Grinyaev, V. I. Danilov, et al., *Structural Levels of Plastic Deformation and Damage* [in Russian], Nauka, Novosibirsk (1990).
12. V. A. Pavlov, *Physical Foundations of Plastic Deformation of Metals* [in Russian], Izd. Akad. Nauk SSSR, Moscow (1962), pp. 85–107.
13. A. A. Klopotov, O. B. Perevalova, and N. A. Koneva, *Evolution of the Dislocation Structure, Hardening, and Failure of Alloys* [in Russian], Izd. Tomsk Univ., Tomsk (1992), pp. 84–93.
14. N. A. Koneva and É. V. Kozlov, "Mechanism of substructural hardening," *Izv. Vyssh. Uchebn. Zaved., Fiz.*, No. 3, 56–70 (1991).