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Superelastic Deformation in Polycrystalline Fe-Ni-Co-Ti-Cu Alloys

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This article presents the deformation behavior of aged ferromagnetic alloys of Fe-Ni-Co-Ti-Cu system caused by phase transitions. The basic characteristic temperatures of martensitic transformation (MT) of the alloys were determined from temperature dependences of low-field magnetic susceptibility. The coefficients of thermal expansion of high- and low-temperature phases, as well as values of volume effect were obtained from dilatometric data. Peculiarities of deformation behavior were studied from the analysis of stress-strain curves, registered at uniaxial tension. It was found that investigated alloys have a substantial superelastic deformation and a low value of the temperature hysteresis of MT with the volume effect of 2%, which is typical for thermoelastic alloys of Fe-Ni-Co-Ti-Cu system.

Keywords martensitic transformation, shape memory effect, superelastic deformation

1. Introduction

The discovery of shape memory effect (SME), superelasticity, and magnetic deformation in alloys undergoing reversible martensitic transformation (MT) promoted their wide applications. These effects can be caused by the reversible changes of specimens shape under the action of the temperature, applied stress, and magnetic field. Martensite induced by stress can be formed by different types of loading.

In Fe-Ni alloys, undergoing $\gamma \leftrightarrow \alpha'$ MTs, where γ is the high-temperature phase (austenite) and α' is the low-temperature phase (martensite), the temperature hysteresis $\Delta T \sim 300$-350 K is observed (Ref 1, 2). Such MTs are nonthermoelastic because of significant volume changes $\Delta V_{\gamma-\alpha}$ as a result of the generation during MT of crystal structure defects of dislocation type (Ref 2-4). In aged ferromagnetic Fe-Ni-Co-Ti alloys, precipitation of disperse γ'-phase particles strengthens the high-temperature γ-phase and suppresses plastic flow processes. Moreover, it is known that γ'-phase does not undergo MT; precipitation of γ'-phase modifies the degree of tetragonality of martensite and favors the accumulation of the elastic energy in martensite crystals, and volume changes $\Delta V_{\gamma-\alpha'}$ become $<1\%$ (Ref 1-4). As a result, MT becomes thermoelastic, the temperature hysteresis reduces to 30-50 K, and the SME and superelasticity can be observed (Ref 4).

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Alloying of Fe-Ni with copper (Ref 5) leads to the reduction of austenite elastic moduli value and the increase of the Curie temperature and saturation magnetization. Furthermore, copper doping of ferromagnetic Fe-Ni-Co-Ti alloys allows for reduction of MT thermal hysteresis width to $\Delta T \approx 60$ K, keeping the Curie temperature around 300 °C (Ref 6). Significant amount of cobalt in Fe-Ni-Co-Ti alloys can lead to the increase of the Curie temperature T_c, magnetization, and volume magnetostriction, and enhance of austenite invar anomaly. Fe-Ni-Co-Ti-Cu alloys exhibit effect of superelasticity (Ref 7-10) which occurs as a result of formation of elastic martensite crystals or a reversible motion of interfaces in martensitic state. Theoretical calculations of MT strain under tension-compression predict high values of deformation from 2% to 10% depending on crystallographic orientation and the method of loading (Ref 8). All these factors make Fe-Ni-Co-Ti-Cu alloys promising materials to obtain large reversible deformations in stress fields. Therefore, further investigations of these alloys are required.

The Fe-Ni-Co-Ti-Cu alloys composition, aging time in austenite state, as well as the temperature of deformation T_d affect superelastic properties. Variation of alloys composition by doping, along with thermal treatment, can substantially modify the parameters of materials with SME, dramatically changing their reversibility characteristics. However, the influence of alloys composition and heat treatment on superelastic properties of Fe-Ni-Co-Ti-Cu alloys has not been adequately studied, and the clarification of the mechanisms resulting in the increase of superelastic deformation is of both scientific and practical interest.

Thus, the aim of the present study is to establish general regularities of MTs behavior in ferromagnetic shape memory Fe-Ni-Co-Ti-Cu alloys and the physical factors that influence on the increase of superelastic deformation.

2. Experimental

The polycrystalline alloys with the following composition, 1—Fe-37.0 Co-15.2 Ni-8.0 Ti-6.17 Cu (wt.%), 2—Fe-36.6 Co-15.2 Ni-6.72 Ti-7.62 Cu (wt.%), have been chosen for the investigation.

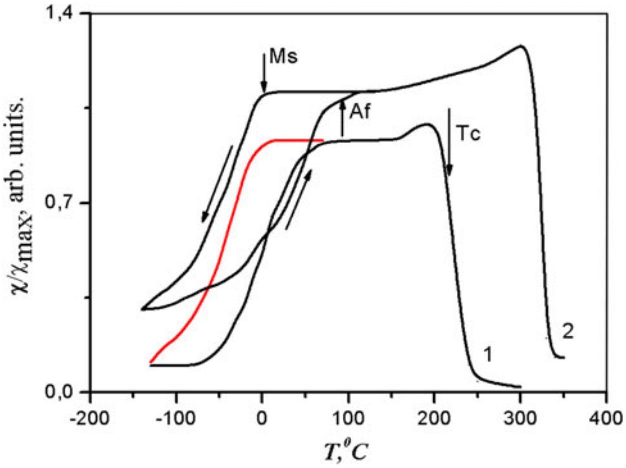

Fig. 1 Temperature dependences of low-field magnetic susceptibility of Fe-Ni-Co-Ti-Cu alloys as a result of quenching and aging: (1) alloy 1 and (2) alloy 2

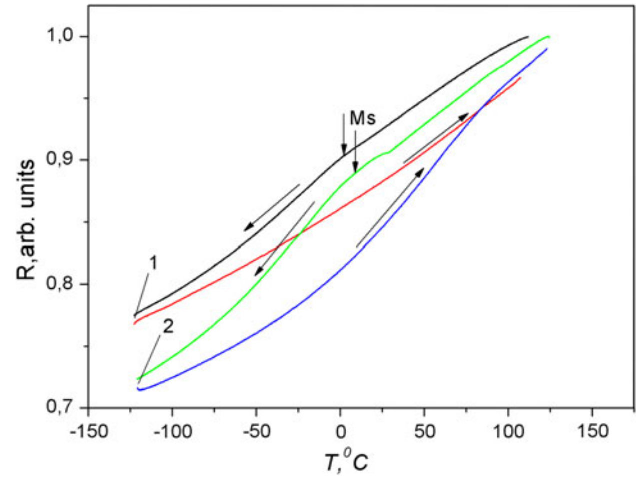

Fig. 2 Temperature dependences of electrical resistance of Fe-Ni-Co-Ti-Cu alloys as a result of quenching and aging: (a) alloy 1, and (b) alloy 2

The alloys were melted in an induction furnace in an argon environment, annealed for homogenizing at 1000 °C for 60 h, and quenched in water from 1150 °C for the formation of tetragonal martensite. The specimens were aged in a vacuum at 500 °C for 3 h.

Characteristic temperatures and hysteresis of MT were determined from the temperature dependences of magnetic susceptibility and electrical resistivity data measured by a four-point method. The value of volume effect of MT and the coefficient of thermal expansion (cte) of the high- and low-temperature phases were determined using dilatometric analysis. Deformation behavior was studied from the stress-strain (σ-ε) dependences measured under the uniaxial tension with the strain rate $\varepsilon/\tau \approx 4 \times 10^{-4}\ s^{-1}$ (τ is the strain time) at room temperature.

3. Results and Discussion

The most sensitive and effective method to determine the characteristic temperatures of MT in ferromagnetic shape memory alloys is the measurement of low-field magnetic susceptibility, as it allows us to determine not only the magnetic transition temperature but also the temperature of the martensitic transition. Figure 1 shows the temperature dependencies of low-field magnetic susceptibility for alloys 1 and 2. A characteristic feature of these alloys is the reversible structural transition in ferromagnetic austenite. The temperature dependence of the magnetic susceptibility of alloy 2 shows that the direct MT starts at M_s = 0 °C, while the temperature of the end of the reversible transformation is A_f = 80 °C (Fig. 1, curve 2).

The curve of electrical resistance (shown in Fig. 2) demonstrates a temperature hysteresis that confirms the first-order phase transition which is typical for shape memory alloys (Ref 4). Atypical behavior of electrical resistance can be explained by a strong contribution of magnetic component to the total resistance, which is described as follows: $\rho = \rho_0 + \rho_p + \rho_m$, where ρ_0 represents impurities and crystal lattice defects dependent resistance (temperature independent), ρ_p stands for resistance associated with scattering of electrons by phonons (temperature dependent), and ρ_m is related to magnetic state resistance (temperature dependent). The temperature dependence of resistivity has an anomalous character $\rho \sim T^n$, like the one observed in invar Fe-Ni alloys at low temperatures (Ref 11). The data on MT parameters in alloys 1 and 2 are summarized in Table 1.

The microstructure of the investigated alloys is typical for iron-nickel alloys. Figure 3 shows the microstructures of aged alloy 1 in single-phase (left) and two-phase regions (right). It should be noted that the martensite in these alloys has a plate-like structure. The average austenite grain size is of about 100 μm.

Relatively narrow hysteresis of MT in the investigated Fe-Ni-Co-Ti-Cu alloys ($\Delta T = 50$ K for alloy 1 and $\Delta T = 80$ K for alloy 2) as compared with binary Fe-Ni alloys is explained by first, thermoelastic nature of this transformation, and second, copper doping, which leads to the reduction of the austenite elastic moduli and, correspondingly, the elastic energy of growing martensite crystals. The elastic energy of martensite crystals' formation during cooling down process according to (Ref 12) is proportional to the width of a thermal hysteresis, which depends on volume fraction and tetragonality degree of precipitated particles, which arise as a result of aging. According to the measurement of low-field magnetic susceptibility (χ), alloys 1 and 2 become ferromagnetic at $T_c \approx 200$ °C and $T_c \approx 300$ °C, respectively.

The study of the variation of specimens linear sizes as a function of aging time during cooling down and heating up cycles was carried out by a dilatometer. The temperature change rate was of about 2 °C/min. According to the $\Delta l/l_o$ curves (Fig. 4), the alloys in quenched state do not undergo transformations. The aging at 500 °C for 3 h significantly changes the elongation character. When the temperature reaches M_s, a sharp increase of specimen sizes takes place because of the transition to martensitic phase, which has a larger volume. The main specimens parameters obtained from dilatometry for the studied alloys are presented in Table 2.

The value of volume effect of MT was calculated from the following relation: $\Delta V/V \approx 3\Delta l/l_o$, and their actual value were 2.34 and 1.89% for alloys 1 and 2, respectively (Fig. 4). In invar alloys, an usual compression caused by temperature decrease is compensated by expansion as a result of the spontaneous volume magnetostriction. As has been noted, the coherent γ′-phase particles

Table 1 Summary of characteristic temperatures and thermal hysteresis of MT, Curie temperature and temperature interval between magnetic and martensitic transition for different ferromagnetic Fe-Ni-Co-Ti-Cu alloys

Alloy, thermal treatment	M_s, °C	M_f, °C	A_s, °C	A_f, °C	$T_c - M_s$	ΔT, °C	T_c, °C
Alloy 1, quenching and aging	−5	−100	−80	45	205	50	200
Alloy 2, quenching and aging	0	−115	−60	80	305	80	305

M_s, M_f, A_s, and A_f are characteristic temperatures of MT; $\Delta T = A_f - M_s$ is the hysteresis of MT, where M_s and M_f are the temperatures of start and end of direct MT, respectively; A_s and A_f are the temperatures of start and end of reverse MT, respectively; T_c is Curie temperature; and $T_c - M_s$ is temperature interval between magnetic and martensitic transition

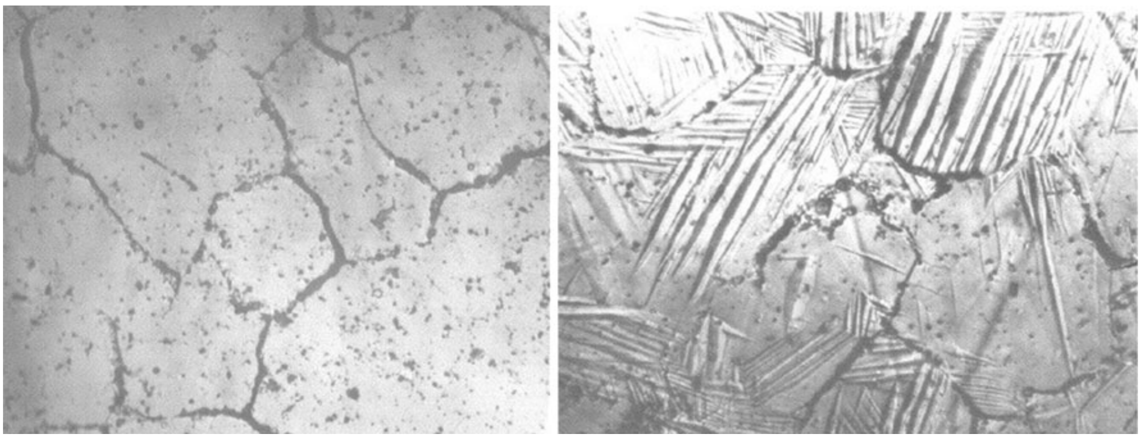

Fig. 3 Microstructures observed in an optical microscope at the room temperature for the alloy 1 after quenching and aging: (left) austenite one phase region; (right) two phase regions (martensite and austenite) after cooling in liquid nitrogen. Magnification is ×250

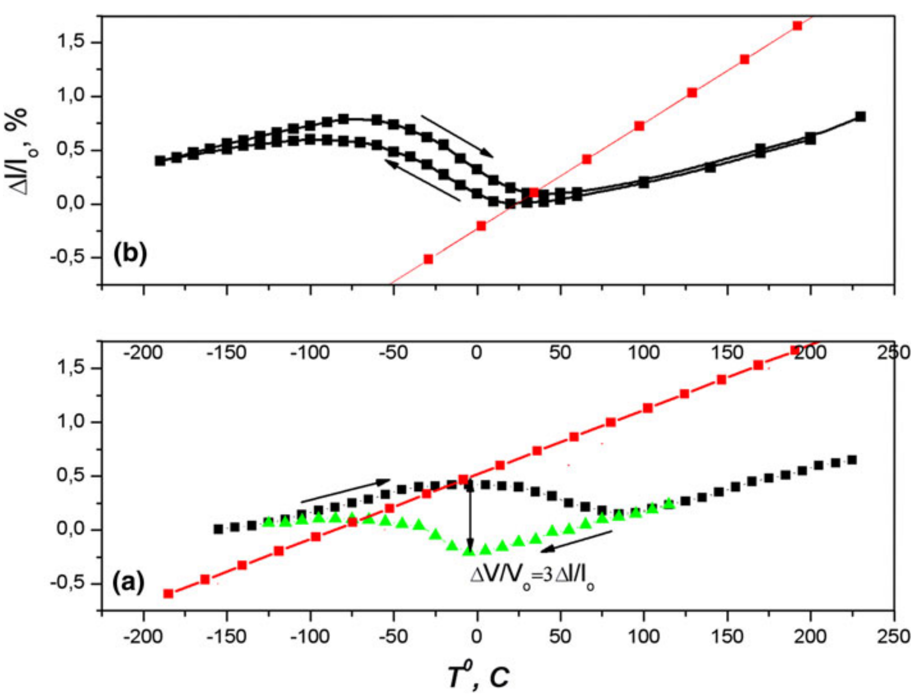

Fig. 4 Dilatograms of Fe-Ni-Co-Ti-Cu alloys under quenching and aging: (a) alloy 1, and (b) alloy 2

precipitate during the aging of the high temperature phase. As a result, the depleted austenite has a composition close to invar (29.85-35.74 at.% Ni). This eventually leads to a decrease of volume effect $\Delta V/V$ during MT due to an increase of $T_c - M_s$ temperature range (Ref 13). Alloy 1, with the smaller temperature hysteresis width, has larger value of $\gamma \leftrightarrow \alpha$ transformation volume effect in comparison to the corresponding effect in alloy 2. An increase of $\Delta V/V$ at MT in alloy 1 is associated with a decrease in the temperature interval between magnetic and martensitic transition $T_c - M_s$ due to an invar anomaly in ferromagnetic austenite (Ref 14).

Table 2 Coefficients of thermal expansion of austenite and martensite and volume effect of MT for different ferromagnetic Fe-Ni-Co-Ti-Cu alloys

Alloy	α_{cte} of austenite after quenching, degree^{-1}	α_{cte} of austenite after aging, degree^{-1}	α_{cte} of martensite, degree^{-1}	$\Delta V/V$, %
Alloy 1	6.5×10^{-5}	4.5×10^{-5}	3.8×10^{-5}	2.34
Alloy 2	7.14×10^{-5}	4.17×10^{-5}	3.4×10^{-5}	1.89

$\alpha_{cte} = 1/l(\partial l/\partial T)_p \approx 1/3V(\partial V/\partial T)_p$ is a coefficient of thermal expansion; $\Delta V/V$ is a volume effect of MT

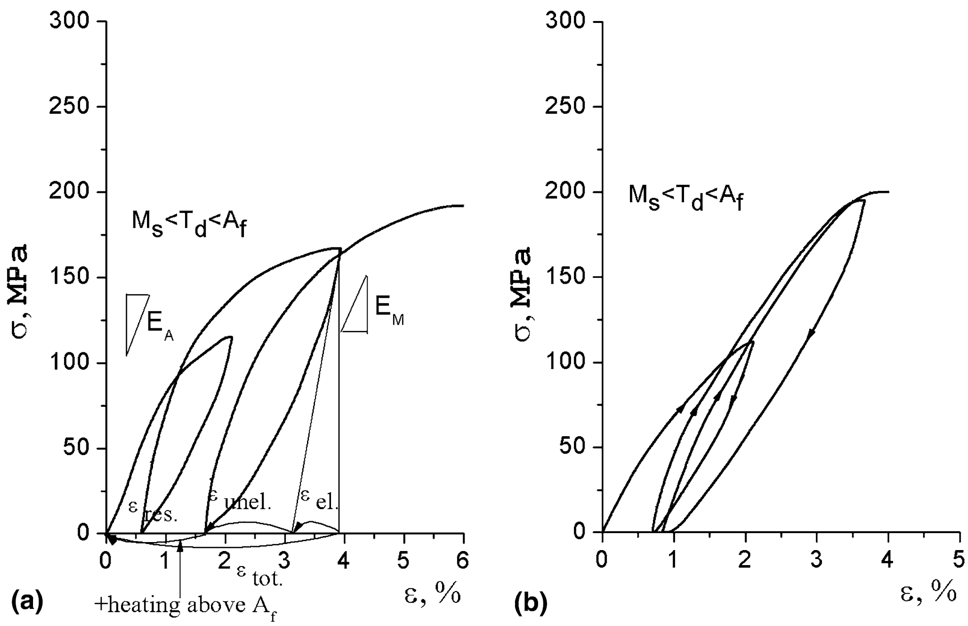

Fig. 5 σ-ε dependences at cyclic loading and unloading of alloy 1 (b) and alloy 2 (a) at the room temperature

The relation between mechanical stress σ and strain ε for both alloys is shown in Fig. 5. At same σ value, which is typical for the definite experiment temperature, the dependence σ(ε) starts deviating from linear. This value corresponds to the formation of martensite crystals under the stress which values are 50 MPa and 85 MPa for alloys 1 and 2, correspondently. The elasticity moduli for both alloys determined from the slope angles of initial sections of loading and unloading curves have values in the range of 70÷75 and 52÷55 MPa for austenite and martensite, respectively. The phenomenon of sample shape recovery after the action of a load in materials where formation of martensite phase accompanied by strong strains appearance is called superelasticity. The superelastic deformation is determined by a sum of components of macroscopic shear of all martensite crystals in the direction of applied load. As the deformation of specimens takes place in the temperature range $M_s < T_d < A_f$ (where T_d is the strain temperature), where without strain, martensite is thermodynamically stable, the load removal just leads to partial recovery of strain. Each subsequent cycle of loading, the stress associated with the formation of martensite increases as a result of mechanical hardening, and the specimen temperature increases as a result of a local heating due to the friction on interfaces ($T_d = 300$ K). With the increasing of the number of loading-unloading cycles, the part of superelastic deformation increases. The total deformation ε_{tot} during the phase transition can be written as follows: $\varepsilon_{tot} = \varepsilon_{el} + \varepsilon_{unel} + \varepsilon_{res}$ (where ε_{el}, ε_{unel}, and ε_{res} are the elastic, inelastic, and residual strains, respectively, are presented in Fig. 5(a) with braces under the corresponding curve). The maximum stresses underwent by specimens before their fracture are approx. 200 MPa in both alloys and the strain in this case is 6% for alloy 1, versus 4% for alloy 2. For polycrystalline alloys of this system, superelastic deformation of about 4.5% can be reached (Ref 15) as a result of multiple cycles of loading-unloading. Heating of deformed specimens above A_f leads to complete recovery of residual strain of the alloys.

4. Conclusion

Aging of ferromagnetic Fe-Ni-Co-Ti-Cu shape memory alloys can affect the course of thermoelastic martensitic $\gamma \leftrightarrow \alpha$ transformation, and significantly change their deformation behavior both under an external tensile stress and temperature variation. The studied alloys with a thermoelastic MT demonstrate a superelastic behavior in two-phase region. Moreover, larger value of superelastic deformation has the alloy with lower value of the temperature hysteresis of MT. This is in correlation with the results of Ref 16. However, at the same time, this alloy has a larger volume changes at MT. The modification of heat-treatment regime allows us to control not only the parameters of thermoelastic MT, but also the value of superelastic deformation in aging shape memory alloys. Deformation behavior of such alloys shows the perspective of their potential application in power executive devices or elastic energy storages.

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