Narrowing of the martensite transformation temperature hysteresis in ferromagnetic Fe–Co–Ni–Ti alloys doped with Cu

V.V.Kokorin, L.E.Kozlova, A.E.Perekos, Yu.S.Levchuk, T.V.Ruzhitskaya**

Institute for Magnetism, National Academy of Sciences of Ukraine, 36-B Vernadsky Ave., 03680 Kyiv, Ukraine

*G.Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine, 36 Vernadsky Ave., 03680 Kyiv, Ukraine

Received October 14, 2007

Using optical metallography and magnetic measurements, the structure and magnetic characteristics of the martensitic transformation have been studied in the Fe–Co–Ni–Ti alloys with copper additive. The copper doping has been found to reduce the temperature hysteresis width of the martensitic transformation down to $\Delta T \approx 60°$, the Curie point being maintained at a level near 300°C. It has been shown that the Fe–Ni–Co–Ti–Cu alloys may be of good prospects as materials where the mechanical characteristics could be controlled by magnetic field influence.

Методами оптической металлографии и магнитных измерений исследованы структурные и магнитные характеристики мартенситного превращения в сплавах системы Fe–Ni–Co–Ti с добавками меди. Установлено, що легирование медью позволяет уменьшить ширину температурного гистерезиса мартенситного превращения до $\Delta T \approx 60°C$, при этом температура Кюри сохраняется на уровне ≈300°C. Показано, что по уровню магнитных характеристик сплавы Fe–Ni–Co–Ti–Cu могут оказаться перспективными для их применения в качестве материалов, в которых реализуется возможность управления механическими свойствами под влиянием магнитного поля.

Ferromagnetic shape memory alloys are a new class of active materials with an ability to be deformed by magnetic field in the martensitic state. A magnetic field induced twinning strain was observed in a Ni–Mn–Ga alloy single crystal [1]. The strains induced by magnetic field have been observed in martensite of Fe-based alloys such as Fe–Pd [2], Fe–Pt [3], Fe–Co–Ni–Ti [4]. The wide practical use of magnetic field induced plastic strains in Ni–Mn–Ga alloys is hampered by several factors, including the fragility of high temperature phase, relatively low saturation magnetization and low Curie temperature. The alloys of Fe–Ni–Co–Ti system exceed Ni–Mn–Ga ones in the above parameters and, in principle, could be considered as an alternative material for the use in actuators.

The complete reversibility and narrow temperature hysteresis in Fe–Ni–Co–Ti alloys is attained due to formation of the structure micro-inhomogeneities at the austenite aging and use of the magnetic ordering effect on the subsequent martensitic transformation [5]. The disperse particles precipitated in austenite maintain the coherency with the martensite crystal lattice, causing its tetragonal distortion, and also increase the elasticity limit, hindering the development of relaxation processes [5]. In order to decrease the temperature hysteresis

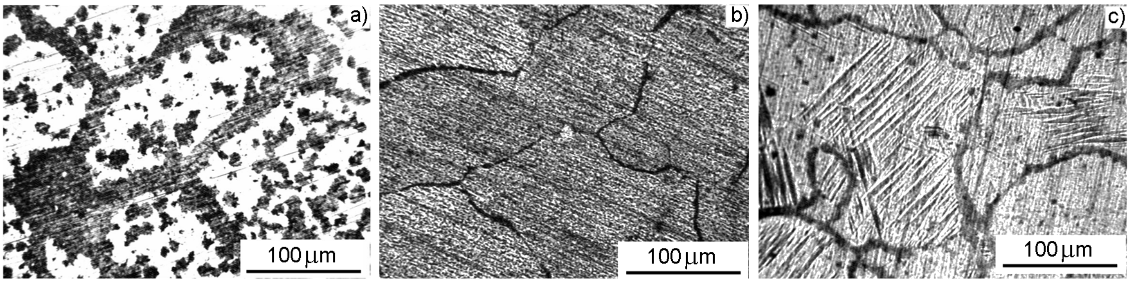

Fig. 1. Microstructure of Fe–Ni–Co–Ti–Cu alloy at room temperature: (a) alloy 1 aged for 6 h at 550°C; (b) alloy 1 aged for 20 h at 500°C; (c) alloy 2 aged for 20 h at 500°C (the sample was cooled in liquid nitrogen and then heated to room temperature).

width of martensitic transformation in Fe–Ni–Co–Ti alloys, it is desirable to lower the shear modulus of austenitic phase, thus providing an elastic energy reduction in the growing martensitic crystals which are coherently connected with an austenitic matrix. The elastic energy decrease, in its turn, gives rise to the hysteresis narrowing [6]. A shear modulus decreasing of Fe–Ni austenite occurs at their doping with copper [7], the Curie temperature and saturation magnetization being increasing in this case, too. Therefore, the purpose of this work is to ascertain how Cu doping influences the characteristics of martensitic transformation in Fe–Ni–Co–Ti ferromagnetic alloys with shape memory. The alloys of similar composition but without Cu were considered before [8], there was fixed a hysteresis $\Delta T \approx 100$ K.

Two alloys were investigated: (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.%). The alloys were melted in an induction furnace under argon atmosphere, annealed at 1000°C for 60 h and then water quenched from 1150°C. The samples were then aged in a vacuum furnace at 600°C, 550°C, and 500°C (1–20 h). The microstructure of the samples after heat treatment was studied by optical microscopy. The martensitic transformation parameters were determined from the low-field magnetic susceptibility temperature dependences ($\chi(T)$ measured in alternating field at amplitude ≤1 Oe and frequency 1 kHz. The dependences $\chi(T)/\chi_{max}$ were plotted, where χ_{max} is the maximum χ value obtained for Fe–Ni–Co–Ti alloys in a specific measurement cycle. The characteristic temperatures, hysteresis and Curie point (T_c) were found as the intersections of corresponding linear parts of $\chi(T)/\chi_{max}$ dependences. The measurements were carried out at an accuracy to 2 K. The magnetization was measured in magnetic fields from 0.25 to 10 kOe by ballistic method at an accuracy to 1 %.

A volume fraction and grain size of γ' phase (Ni_3Ti) have been shown before to rise during the early stages of austenite aging in Fe–Ni–Co–Ti alloys. The γ' phase inclusions inherited in martensite crystals are transformed into shear centers in martensite; as a result, the martensite crystal lattice tetragonality degree (c/a ratio) increases [8]. In the Cu-doped alloys of the Fe–Ni–Co–Ti system, decomposition of the homogeneous solution is observed during austenite aging, too. It is known that formation of solid solution particles based on Cu in the Fe–Ni–Cu alloys influences only insignificantly the martensitic transformation onset temperature and the c/a ratio of martensite lattice [9]. This is explained by low elasticity modulus value of the particles as compared to the matrix.

Aging of Fe–Ni–Co–Ti–Cu alloys above 500°C results in formation of the hardening precipitation colonies near the grain boundaries (Fig. 1a). As the annealing temperature increases from 550 to 650°C, these colonies are observed to grow. The incoherent phase precipitates appear during the cellular decomposition [10], as a result, martensitic transformation is not occurred in the sample areas occupied by the cellular precipitated phase colonies. The aging temperature lowering down to 500°C results in diminishing of the areas occupied by cellular precipitations (Fig. 1b). The cellular precipitation colonies are formed not only near the grain boundaries but also within the grain body, that is a characteristic feature of these alloys.

The temperature dependences of low field magnetic susceptibility for alloys 1 and 2 are shown in Fig. 2. The reversible structural transition is seen to occur in ferromagnetic austenite. In the samples where

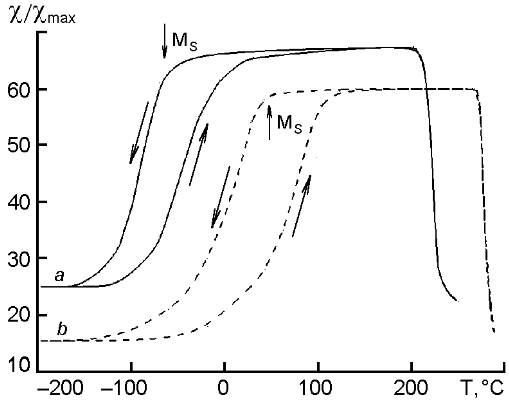

Fig. 2. Temperature dependences of low-field magnetic susceptibility for Fe–Ni–Co–Ti–Cu alloys: (a) alloy 1 (aging at 500°C, 20 h); (b) alloy 2 (500°C, 20 h).

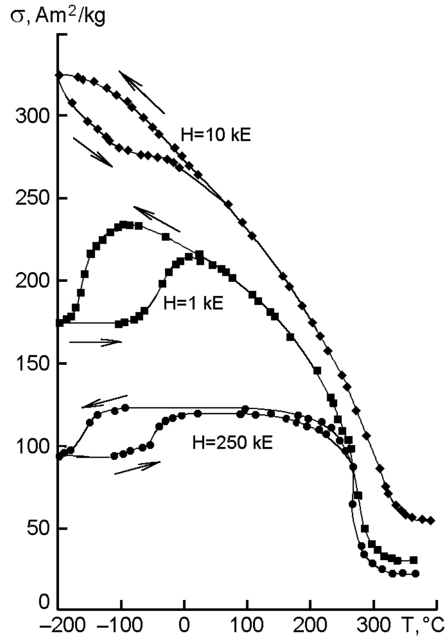

Fig. 3. Temperature dependences of magnetization for alloy 1 at different magnetic field values.

cellular precipitation is present, the fraction of martensitic phase decreases. It is evident that the martensitic transformation takes place only in the areas free from the cellular precipitations.

According to the temperature dependences of susceptibility, for the alloy 2 it was found that $M_s = 40°C$ (M_s is the martensitic transformation onset temperature), $A_f = 104°C$ (A_f is the finish temperature of reverse martensitic transformation) (Fig. 2b). There is a martensitic phase at the room temperature in the sample 2, because A_f exceeds the room temperature. The martensitic transformation parameters in alloys 1 and 2 obtained from the magnetic measurements are listed in Table (M_f is the temperature of martensite transformation finish; A_s, the reverse transformation onset temperature; T_C, Curie temperature, Δ**T**, temperature hysteresis width).

The martensite in these alloys consists of thin plates with plane boundaries (Fig. 1c). It is to note that the relatively narrow hysteresis of martensitic transformation in investigated Fe–Ni–Co–Ti–Cu alloys (ΔT = 55°C for alloy 1 and 65°C for alloy 2) is due to thermoelastic nature of this transformation as well as to Cu doping. As a result, the austenite elasticity modulus decreases and, correspondingly, the elastic energy of martensitic crystals decreases, too. The elastic energy value is proportional to the temperature hysteresis width [6]. According to [8], the tetragonality degree of martensite crystal lattice (c/a) approaches to 1.15 in alloys with narrow hysteresis width. The martensite lattice tetragonal distortion causes an uniaxial magnetic anisotropy in the low-temperature phase of those ferromagnetic shape memory alloys.

The low-field magnetic susceptibility decreases essentially when the martensitic crystals appear (Fig. 2). This may be explained by lower mobility of magnetic domain boundaries in martensite in comparison with an austenite. The domain boundaries contribution is dominant, since χ was measured in low field (≤1 Oe).

The temperature dependences of magnetization measured in the magnetic fields 0.25 to 10 kOe for the samples of the investigated ferromagnetic Fe–Ni–Co–Ti–Cu alloys aged in a vacuum furnace at 500°C for 20 h are shown in Figs. 3 and 4. As follows from

Table.

Alloy No.	Heat treatment: quenching 1150°C; annealing 500°C, 20 h					
	M_s, °C	M_f, °C	A_s, °C	A_f, °C	ΔT, °C	T_c, °C
1	−65	−138	−101	−10	55	208
2	40	−44	32	104	65	274

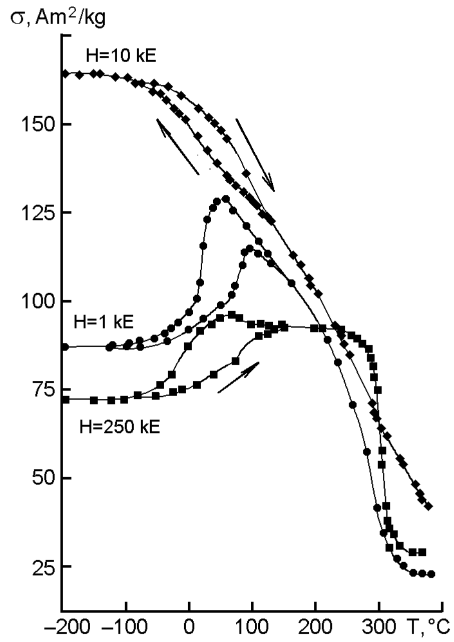

Fig. 4. Magnetization temperature dependences, alloy 2.

the curves $\chi(T)$, the alloys 1 and 2 pass into the ferromagnetic state at the Curie temperatures of $T_c \approx 200°C$ and $T_c \approx 270°C$, respectively. The dependences of Figs. 3, 4 were obtained in the fields, where the magnetization occurs mainly due to rotation of magnetic moments. A characteristic loop and decrease of magnetization at cooling are observed in the temperature range of thermoelastic martensitic transformation.Thus, the magnetocrystalline anisotropy of the martensitic phase exceeds the austenite anisotropy. The martensitic phase magnetization of alloy 1 does not achieve the saturation even in the field $H = 10$ kOe (Fig. 3). Meantime, the consideration of Fig. 4 evidences that the field of 10 kE is sufficient to provide a state close to the saturated magnetization of martensite in the alloy 2, because the σ value corresponding to two-phase state (near $T \approx M_s$) at heating exceeds σ at cooling. This means that martensite has a higher magnetization than an austenite at the same temperature.

Thus, it has been shown that doping of ferromagnetic Fe–Ni–Co–Ti alloys with copper allows to decrease the temperature hysteresis width of martensitic transformation to the value $\Delta T \approx 60°C$ without decreasing Curie temperature from a level of 250–300°C. The temperature dependences of martensitic phase magnetization in alloys 1 and 2 in 10 kOe field are different due to a difference of magnetic anisotropy constant. This seem to be connected with the differences in tetragonality degree of martensite lattice in these alloys. As a whole, it can be concluded that Fe–Ni–Co–Ti–Cu alloys may be of interest as materials of good prospects for studies of the magnetic field induced plastic deformation.

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Звуження температурного гістерезису мартенситного перетворення у феромагнітних сплавах Fe–Co–Ni–Ti, легованих Cu

В.В.Кокорін, Л.Е.Козлова, А.Е.Перекос, Ю.С.Левчук, Т.В.Ружицька

Методами оптичної металографії та магнітних вимірювань досліджено структурні та магнітні характеристики мартенситного перетворення у сплавах системи Fe–Ni–Co–Ti з домішками міді. Встановлено, що легування міддю дозволяє зменшити ширину температурного гістерезису мартенситного перетворення до $\Delta T \approx 60°C$, зберігаючи при цьому температуру Кюрі на рівні $\approx$300°C. Показано, що за рівнем магнітних характеристик сплави Fe–Ni–Co–Ti–Cu можуть бути перспективними для їх використання як матеріалів, в яких реалізується можливість керування механічними властивостями під впливом магнітного поля.