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OBTAINING Fe–Ni–Co–Ti ALLOYS HAVING A THERMOELASTIC MARTENSITE TRANSFORMATION

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Using powder metallurgy methods, we have produced Fe–Ni–Co–Ti alloys that have a thermoelastic martensite transformation, which is the basis of the shape-memory effect manifested by such materials. Since pores are believed to improve the shape memory, specifically the reversible nature of the strain, attention was focused on development of the technology and investigation of the characteristics of porous Fe–Ni–Co–Ti alloys. The problems that arise during sintering of such alloys from sputtered powders are due to the chemical inhomogeneity of the initial structure and of the structure formed when the liquid phase appears. Various forms of activation, such as cyclic sintering and a stepped increase in temperature, were used to prevent the liquid phase from appearing. The properties of Fe–Ni–Co–Ti alloys with a shape memory effect can be improved if the porosity is increased by obtaining larger powder grains with a more complicated shape.

The shape-memory effect in aged alloys of the Fe–Ni–Co–Ti system is due to a thermoelastic martensite transformation [1-4]. Such alloys obtained by conventional methods (casting and subsequent deformation) have substantial shortcomings: a tendency to dendritic liquation with an attendant structural microinhomogeneity, which is very difficult to alleviate by homogenizing annealing. Hence, the stability of other properties and cellular decomposition along grain boundaries during aging, with subsequent brittleness during deformation. In this work we have undertaken to obtain those materials in compact and porous form by means of powder metallurgy. The porous materials are very promising for practical use because of their fairly high reversible strain, which is due to the ability of individual fragments to change shape.

The structure of the indicated alloys was studied with a Neophot-2 optical microscope and a Superprobe-733 scanning microanalyzer. The salient features of the martensite transformation were studied with an induction-sensor dilatometer.

Fe–Ni–Co–Ti alloy powder was obtained by plasma sputtering of cast homogenized forged electrodes. It constituted a mixture of spherical particles 60-250 μm in size, which crystallized in free-fall, and platy particles measuring (10-20) μm × (200-800) μm × (1.2-4) mm, which formed when drops of metal fell onto surface of a water-cooled crystallizer. The specimens were obtained in several ways: extrusion of vacuum-sintered compacts, sintering of powder in a pressing die with an electric current, and vacuum sintering of free-flowing powder.

In the initial stage of the work we extruded compacts (T = 1423 K), previously pressed and vacuum-sintered at 1453 K. In that case the powder was not separated by particle shape or size. For subsequent investigations the powder obtained by sputtering was previously separated: into spherical and platy by flotation and into fractions by screening.

Extrusion produced almost pore-free rods with a layered structure, consisting of former spherical powder particles elongated in the direction of the deformation, with platy particles between them (Fig. 1a, b). After heat treatment the structure was finely divided and had various grains (the grain size is determined by the powder particle size). Powder alloys of the Fe–Ni–Co–Ti system prepared in this way have a martensite transformation of low degree and extended interval (Fig. 2), since it takes place in coarse-grain regions and is suppressed in fine-grain regions. Furthermore, since fine grains promote stabilization of the austenite, the aging time must be much longer for the temperature M_{on} of the onset of the martensite transformation to be close to that of cast alloys.

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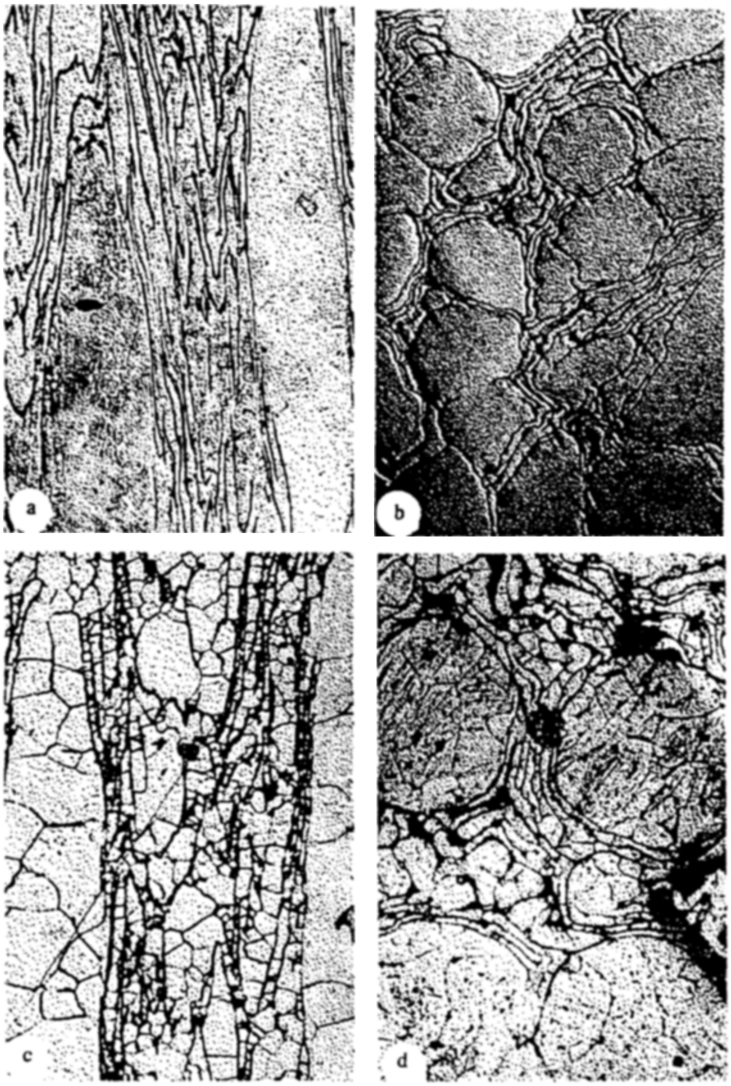

Fig. 1. Structure of extruded Fe–Ni–Co–Ti powder alloys. ×100. After extrusion along (a) and transverse to (b); homogenization at 1223 K for 1 h (c) and 1423 K for 5 h (d) with water quenching and aging.

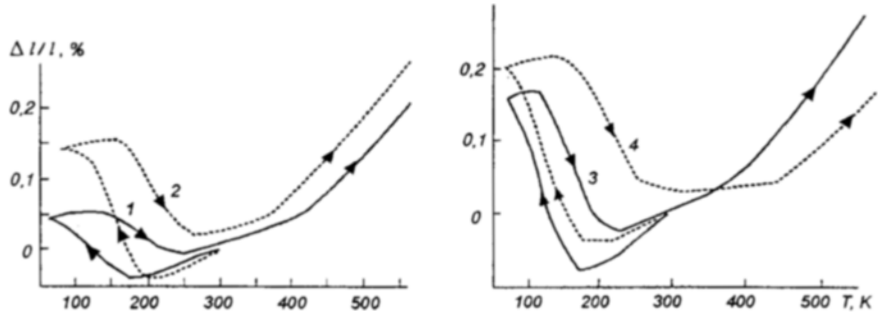

Fig. 2. Dimensional variation of N28K29T6 alloy specimens with cooling and heating after quenching and aging at T = 950 K for 2 h: 1) vacuum sintering, extrusion, and homogenization at 1423 K for 5 h; 2) vacuum sintering at 1523 K for 2 h; 3) cyclic sintering; 4) sintering with a stepped rise in temperature.

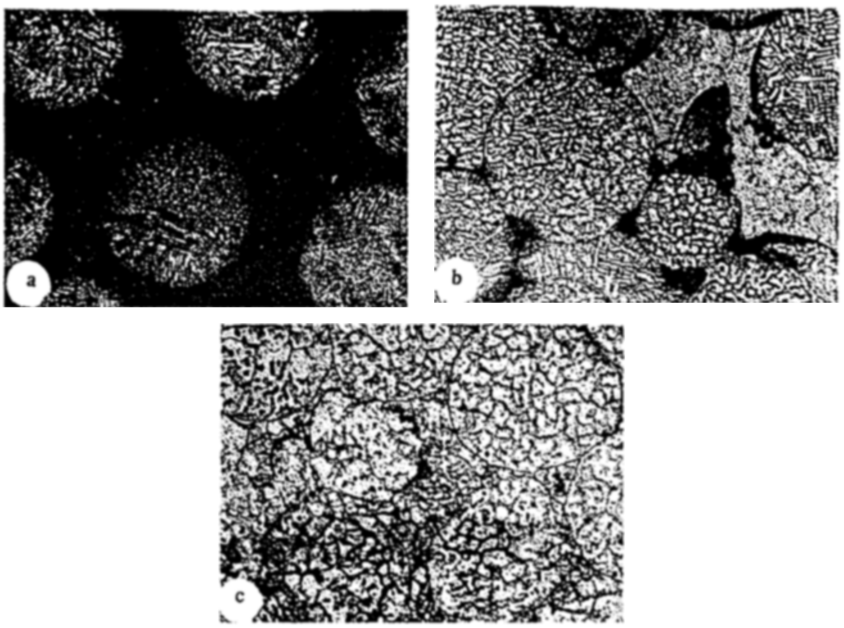

Fig. 3. Structure of Fe–Ni–Co–Ti powder alloys, sintered by an electric current. ×100. a) initial structure (after sputtering); b, c) after sintering at 1173 K for 15 min and at 1223 K for 20 min, respectively.

In the case of sintering with an electric current most spherical particles retain their shape and boundary; they shrink slightly because some particles flow into pores that exist between them (Fig. 3). When sintered at 1173 K for 15 min the material has a low mechanical strength, the powder particles retain a dendritic structure (Fig. 3b) that is close to the initial structure (Fig. 3a). When the temperature is raised and the sintering time is extended the dendrites begin to be "resorbed" (Fig. 3c) and the porosity of the specimen in this case is roughly 28%. Additional homogenization is required for complete elimination of the structural microinhomogeneity.

When free-flowing powder is used it begins to sinter in an evacuated quartz ampule when the temperature 1473 K is reached. The specimens acquire satisfactory strength when sintered at 1523-1573 K for 2 h in the presence of a liquid phase (it arises because of the chemical microinhomogeneity of the dendritic structure of powder particles). Liquid interlayers appear at the junction of powder particles and, here and there, between them when the temperatures at the points of contact are at the indicated values. After cooling those interlayers constitute (Fig. 4b) more etchable spots, inside which are white films of a metastable eutectic formed by titanium nitride and a saturated solid solution of titanium [4]. The appearance of the liquid phase activates the sintering process; the specimens become substantially stronger than those obtained by solid-phase sintering at 1473 K. After the sintering their porosity is about 32% and the boundaries between the separate particles disappear. When the sintering temperature is raised to 1623 K the material is fused completely and crystallizes, forming a coarse dendritic structure. These changes result in large shrinkage, the residual porosity of the material decreases to 7%. According to the results of x-ray spectral microanalysis (Fig. 5), the formation of a new dendritic structure is accompanied by the formation of a strong liquation inhomogeneity. The maximum titanium liquation coefficient, i.e., the ratio of its content in the eutectic interlayer in the interdendrite interval (region 2) to the amount on the dendrite axis in the center of the dendritic cell (region 1), reaches 3.3.

After quenching and aging the liquation inhomogeneity of the structure persists in the form of eutectic interlayers, which grow during decomposition of the solid solution, as well as in the form of high-temperature martensite in nickel- and titanium-depleted regions (Fig. 4c) The volume of metal where a thermoelastic martensite transformation can occur becomes smaller, as is reflected by the smaller dilatometric dimensions of the porous specimen in comparison with the cast homogenized specimen (Fig. 2), even though the grain size of the powder material is comparable with that of the powder particles. (Comparing the degree of change in the dimensions of specimens with different porosities as a result of the martensite transformation, we must also take into account the volume occupied by pores that does not participate in the transformation and reduce the results to zero porosity.) Because of the higher titanium and nickel content here, a longer aging time is also necessary to reach the point M_{on} characteristic of the cast alloy.

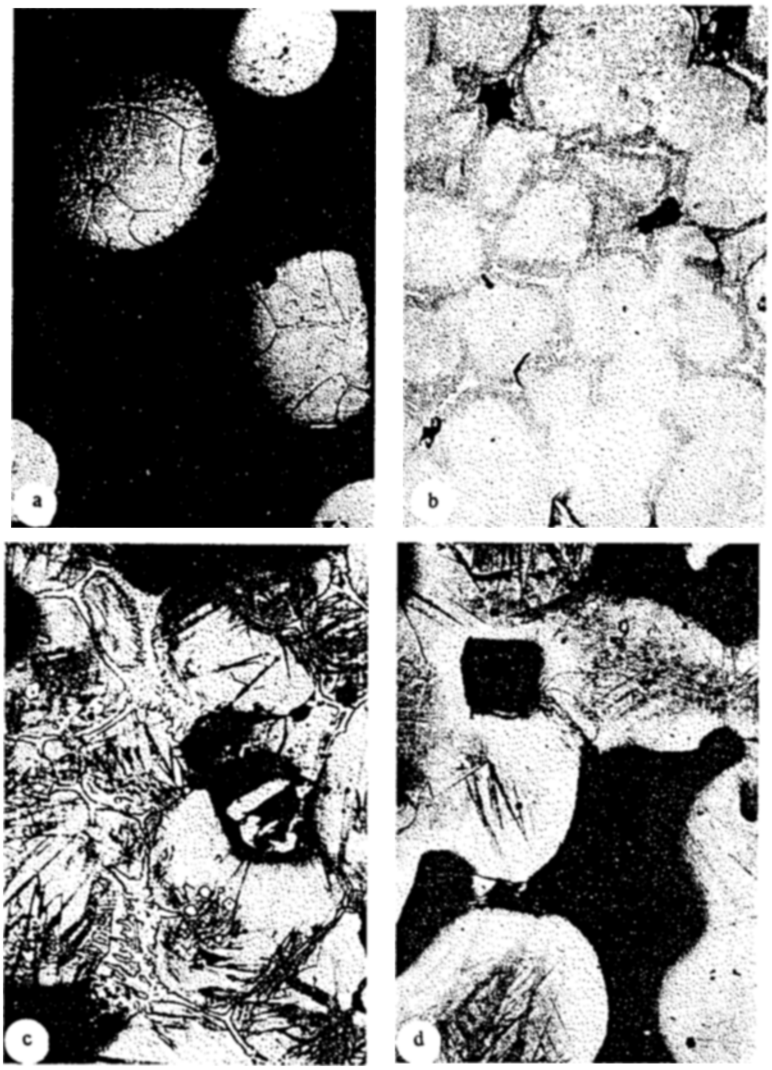

Fig. 4. The structure of porous Fe–Ni–Co–Ti alloys, vacuum-sintered from free-flowing powder. ×100. Sintering at 1223 for 1 h and 1473 K for 2 h (a); 1223 for 1 h and 1523-1573 K for 2 h (b); 1223 K for 1 h and 1523 K for 2 h, water quenching and aging for 950 K for 2 h (c); 1223 K for 1 h and 1523 K for 2 h, homogenization for 1473 K for 5 h, quenching and aging for 950 K for 2 h (d).

After homogenization at 1473 K for 5 h the eutectic interlayers are resorbed but the structure continues to be inhomogeneous, as indicated by the presence of high-temperature nonthermoelastic martensite. (Fig. 4d). Cyclic sintering and sintering followed by a stepped rise in temperature were used to preclude the formation of liquid interlayers and the attendant liquation inhomogeneity.

Cyclic sintering was carried out at 1473 K for 5 min → 1400 K for 1 h → 1500 K for 5 min → 1473 K for 1 h → 1523 K for 5 min → 1500 K for 1 h → 1550 K for 5 min → 1523 K for 2 h; that is, a brief rise in temperature to the appearance of the liquid phase was followed by holding at a lower temperature, for resorption of the newly formed liquation. Since the initial structural inhomogeneity was also smoothed, it was possible to execute the next sintering cycle at a higher temperature. Even though the structure of the material was similar to that obtained by solid-phase sintering (Fig. 6a), specimens prepared from it had good mechanical strength. The martensite transformation in the given case took place with a narrower hysteresis as a consequence of the increased structural homogeneity of the material (Fig. 2, curve 3); the degree of the transformation was higher than under solid-phase sintering, but remained lower than in the cast state because of the small grain size.

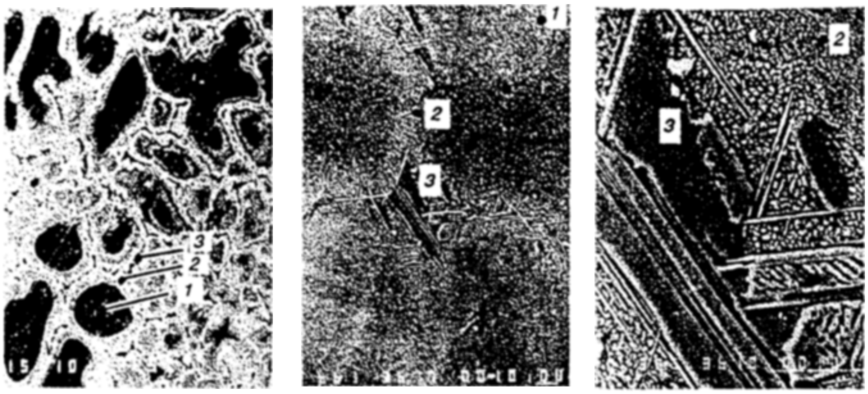

Fig. 5. Structure and distribution of elements in N28K19T6 powder alloy, sintered at T = 1623 K. Composition of the alloy, mas %: 52.86 Fe–25.42 Ni–18.24 Co–3.0 Ti– 0.48 Mo (region 1); 33.60 Fe–37.94 Ni–18.29 Co–9.91 Ti–0.26 Mo (region 2); 20.35 Fe–42.02 Ni–19.14 Co–18.46 Ti–0.03 Mo (region 3).

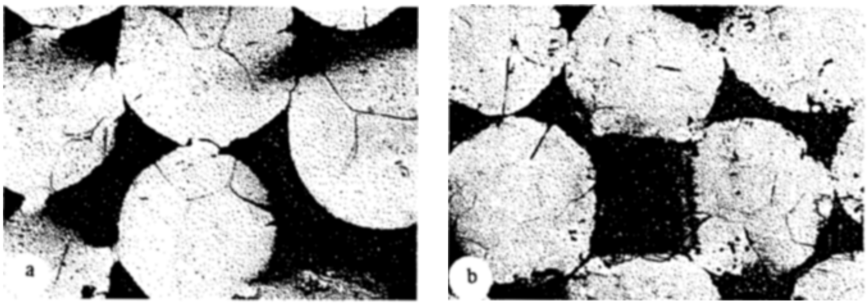

Fig. 6. Structure of Fe–Ni–Co–Ti alloys formed by cyclic sintering (a) and sintering with a stepped rise in temperature (b). ×100.

In sintering with a stepped rise in temperature the lower temperature limit was chosen at the site where the liquid phase was formed (T = 1453 K, t = 1 h). Next the temperature was raised to 1553 K in 20 K steps, with a 1-hour hold at each step. In this case thin liquid-phase interlayers appeared inside power particles, at the junctions of the initial crystallites (grains of the cast state, having an identical orientation of dendrite axes), where the liquation is maximum (Fig. 6b). Evidently, the melting point of those liquates was exceeded and a preliminary hold at a lower temperature for 1 h was insufficient for them to dissolve. Nevertheless, the degree of chemical inhomogeneity in this case is lower than under ordinary solid-phase sintering, since after heat treatment there are no regions of high-temperature martensite. Similar results were obtained by sintering with two-stage preliminary holding at 1223 K for 1 h, 1473 K, and a final hold at 1523 K for 5 h. When alloys of the Fe–Ni–Co–Ti system are sintered with a subsequent stepped rise in temperature the martensite transformation had a wider hysteresis than in the case of cyclic sintering (Fig. 2), but the degree of transformation was fairly high because the initial crystallites did not break up into finer particles. On the basis of the above we can conclude that this sintering method gives good results, but needs further development and an appropriate adjustment of the heat-treatment conditions.

As for specimens made of powder with platy particles, sintered from a free-flowing bulk, when the porosity is very high (of the order of 60-80%) the degree of their transformation is less than 0.15% (because of the smaller grain size for a plate thickness of 10-20 μm). Their reversible strain, however, may be higher than in less porous specimens of powder with spherical particles.

In summary, in the course of developing a technology for obtaining porous Fe–Ni–Co–Ti powder alloys with a thermoelastic martensite transformation we have determined that the porosity and grain size of such materials must be increased if their properties are to be improved. In turn, this can be accomplished by sputtering so as to obtain a powder with particles of maximum size and a more divided shape.

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REFERENCES

1. V. V. Kokorin, The Martensite Transformation in Inhomogeneous Solid Solutions [in Russian], Nauk. Dumka (1987).
2. V. V. Kokorin, Yu. N. Samsonov, V. A. Chernenko, and O. M. Shevchenko, "Superelasticity in Fe–Ni–Co–Ti alloys," Fiz. Met. Metalloved., **67**, No. 5, 1035-1037 (1989).
3. V. V. Kokorin, L. P. Gunko, and O. M. Shevchenko, "Martensite $\gamma \Leftrightarrow \alpha$ transformation in ausaged Fe–Co based alloy," Scr. Met., **28**, No. 1, 35-40 (1993).
4. O. M. Shevchenko and G. V. Gavrilyuk, "Change in the structure of Fe–Ni–Co–Ti alloys during production and heat treatment," in: Electron Microscopy and Strength of Materials [in Russian], Inst. Probl. Materialoved., Akad. Nauk Ukrainy, Kiev (1993), pp. 159-167.