

V.G. Gavriilyuk, V.M. Nadutov, S.P. Oshkaderov, J. Pietikäinen and K. Ullakko, Phase and magnetic transformations in the Fe–Ni–C alloy at low temperatures, *Physics of Metals and Metallography*, Vol. 70, No. 1, pp. 120-125, 1990.

© 1990 MAIK Nauka/Interperiodica

Reprinted with permission.

PHASE AND MAGNETIC TRANSFORMATIONS IN THE Fe–Ni–C ALLOY AT LOW TEMPERATURES*

V. G. GAVRILYUK, V. M. NADUTOV, S. P. OSHKADEROV,
J. PIETIKAINEN and K. ULLAKKO

Institute of Metal Physics, Academy of Sciences, Ukr.S.S.R.
Helsinki Technological University

(Received 28 February 1989, final version 24 August 1989)

The change of the phase composition and magnetic properties of steel Fe–25.3 Ni–0.65 C (wt%) below room temperature is investigated with nuclear gamma resonance, magnetic susceptibility and electrical resistivity methods. Undercooling to liquid helium temperature stabilizes the retained austenite and prevents the isothermal martensitic transformation taking place during subsequent heating. Magnetic ordering is discovered in the retained austenite.

Fe–Ni–C alloys with martensitic point below room temperature are suitable for the investigation of as-quenched and aged martensite (see [1–3] for example). It has been established that in Fe–Ni–C alloys with more than 20% nickel the as-quenched martensite has abnormally high tetragonality, which is reduced during heating to room temperature, but remains above the c/a value of a normal carbon steel.

A feature of the behaviour of the quenched Fe–Ni–C alloy during heating from liquid nitrogen to room temperatures is the isothermal martensitic transformation of part of the retained austenite, which hampers investigation of the fine structure of martensite in as-quenched and aged states.

Fe–Ni alloys with high nickel content are characterized by short-range order [4, 5]. The dissolution of the interstitial impurity assists short-range ordering of solid substitutional solutions [6], and Mössbauer studies of Fe–Ni–C austenite with nickel concentration close to that in invar alloys [7] can be interpreted, according to [6], as evidence of non-uniform short-range ordering, accompanied by decomposition of the solid solution into submicroregions which are nickel-enriched or denuded, leading to an appreciable change of the physical properties [8]. Inhomogeneity of the distribution of nickel and carbon atoms might affect the magnetic and phase transformations during heating of the as-quenched martensite.

Our purpose here was to study changes of the hyperfine structure during heating of the as-quenched Fe–Ni–C alloy in the absence of the isothermal martensitic transformation.

The investigation was done on alloy Fe–25.3 Ni–0.65 C (wt%). Foil 20 μm thick was heated in a silicate slag melt and cooled in water at 20°C, after which it was immersed in liquid nitrogen and then in liquid helium, to obtain martensite. The NGR spectra were taken at 77 and 293

* *Fiz. metal. metalloved.*, No. 7, 128–133, 1990.

K on the NP-255 spectrometer. The γ quanta source was ^{57}Co in chromium. The BESM-6 computer was used to describe the spectra.

The NGR spectra of the investigated alloy (Figs 1, 2) are the superposition of paramagnetic (1) and ferromagnetic (2, 3), with the parameters given in the table. The central line in the spectrum corresponds to iron atoms in retained austenite, sextets 2-3 with hyperfine field 33.5 and 35.5 T belong to iron atoms in the martensitic phase. The quantity of retained austenite was estimated from the relative area of the central spectrum component $S_1/\Sigma S_i$, without allowance for the difference between the Debye-Waller factors of iron atoms in austenite and martensite (see table).

Parameters of NGR spectra, mm/sec.

T_{tr} , K	T_{meas} , K	1			2		3	
		δ_1^*	Γ_1	$S_1/\Sigma S_i$	δ_2^*	H_2 , T	δ_3^*	H_3 , T
4.2	77	0.31	0.71	0.143	0.43	34.0	0.43	36.0
193	77	0.30	0.77	0.141	0.40	33.0	0.42	35.5
293	293	0.21	0.37	0.136	0.30	33.0	0.31	34.5
293	77	0.30	0.76	0.143	0.42	34.0	0.42	36.0
293	293	0.21	0.39	0.139	0.31	33.0	0.30	34.5

* Relative to nitroprusside Na, mm/sec; $\Delta\delta = \pm 0.01$ mm/sec; $\Delta\Gamma = \pm 0.01$ mm/sec; $\Delta H = \pm 0.5$ T; $\Delta S_1/\Sigma S_i = \pm 0.005$.

Irreversible changes are made in the NGR spectrum when the specimen is heated after undercooling in liquid nitrogen (Fig. 1b). The integral intensity of the paramagnetic component diminishes, indicating that an isothermal martensitic transformation has taken place.

For the alloy undercooled in liquid helium, ageing of the martensite at 193 K or room temperature does not cause any change in the spectra taken at the same temperature (Fig. 2a, b, c), which means that the phase composition is unchanged. An appreciable increase in intensity of the central line and reduction in its width to about half was observed after the alloy was heated to room temperature and the spectra taken at that temperature (Fig. 2c). No change was registered, to within the measurement error, in the integral intensity of the central component (see table). The decrease of the isomeric shift δ for the austenitic part of the spectrum (1) and

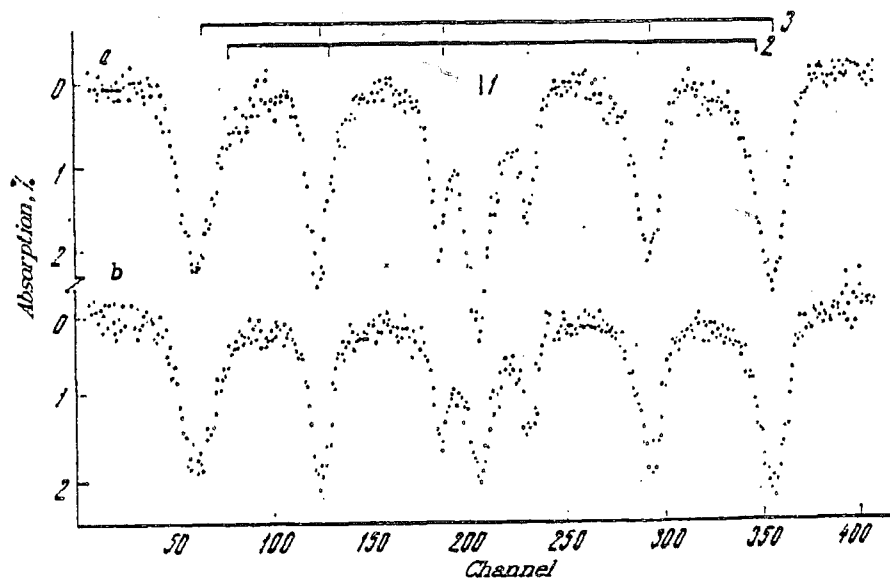


Fig. 1. NGR spectra of alloy Fe-25.3 Ni-0.65 C after heating to 1100°C, cooling to 77 K (a) and subsequent heating to 293 K (b). Photograph taken at 77 K.

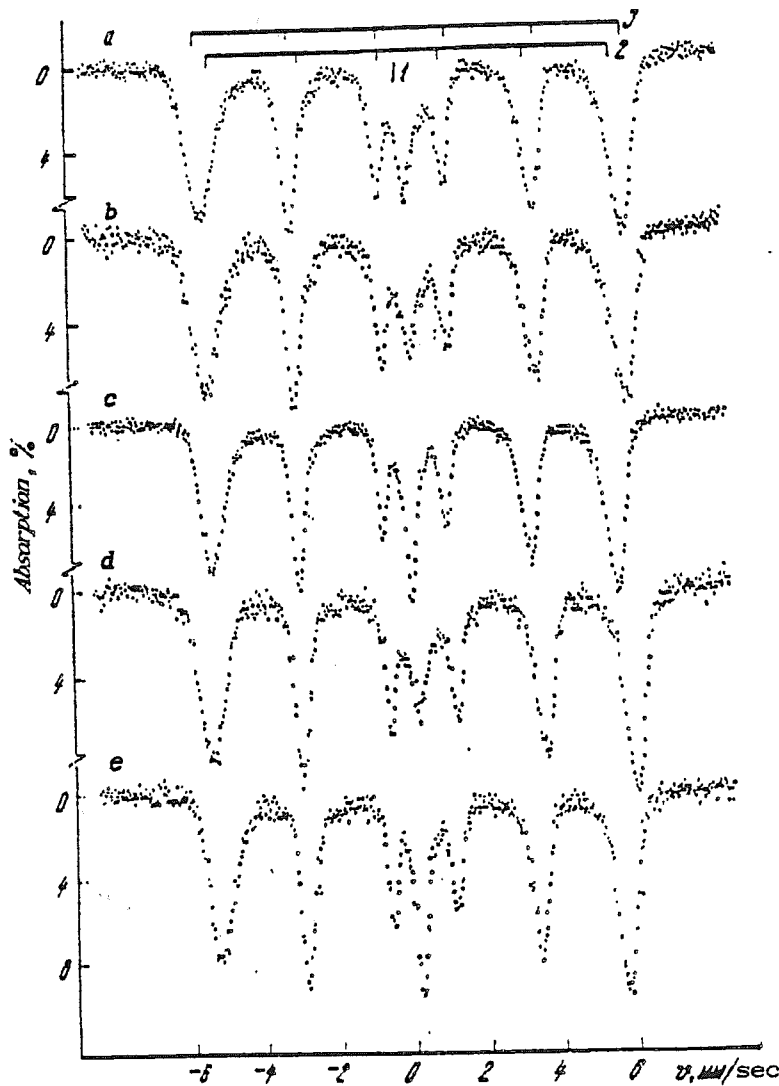


Fig. 2. NGR spectra of Fe-25.3 Ni-0.65 C after heating to 1100°C and cooling to 4.2 K: *a* — taken at 77 K; *b* — heating to 193 K, taken at 77 K; *c* — 293 K, taken at 293 K; *d* — cooling to 77 K, taken at 77 K; *e* — heating to 293 K, taken at 293 K.

martensitic components (2) and (3) (see table) accorded with the expected temperature dependence $\delta(T)$. Subsequent photographs of the NGR spectrum of the alloy at 77 and 293 K showed that the spectral changes of retained austenite were reversible (see Fig. 2*d, e* and table).

Measurements of the magnetic susceptibility of the alloy during cooling to liquid helium temperature (Fig. 3*a*) revealed two effects, the first of which was reversible in the range 200–120 K and did not involve any change of resistivity (Fig. 3*b*). The irreversible change of susceptibility at 120 K corresponded to the effect on the resistivity curve associated with the martensitic transformation. During heating of the as-quenched alloy, a small reversible change of susceptibility was observed (see Fig. 3*a*) and the temperature dependence of resistivity was almost linear (Fig. 3*b*).

DISCUSSION

The fact that the integral intensity of the line of retained austenite in the NGR spectra does not change after ageing of the alloy (see Fig. 2*a, b, d*) and the absence of characteristic changes of a phase transition on the temperature dependence of resistivity during heating in the range

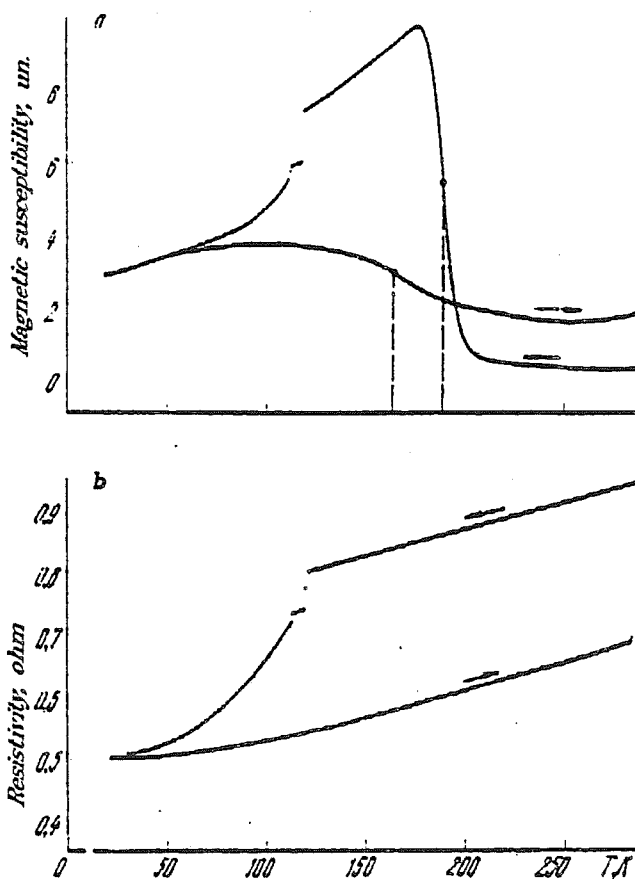


Fig. 3. Change of longitudinal component of susceptibility of alloy Fe-25.3 Ni-0.65 C (a) and resistivity (b) in alloy Fe-25 Ni-0.7 C during cooling to helium temperatures and subsequent heating.

77–293 K (Fig. 3b) show that the retained austenite has stabilized, that is, there is no isothermal martensitic transformation when alloy Fe-Ni-C is cooled to 3.2 K. Current ideas on austenite stabilization are mainly based on the ageing of austenite and martensite [9–11]. Kinsman and Shyne [9] have shown that the kinetic curves of austenite stabilization are similar to the ageing curves, and the temperature range where the stabilization effect was evidenced in [11] corresponded to a model in which carbon diffusion in austenite and martensite results blocks the phase interface of the growing martensite nucleus. Pietikainen [11] has investigated Fe-Ni-C alloys with martensitic point below room temperature, where ageing of the austenite is excluded, and has come to the conclusion that the austenite stabilizes as the result of ageing of the as-quenched martensite, accompanied by an increase in its hardness and, correspondingly, a decrease in the deformability required for relaxation of stresses which arise during the martensitic transformation.

The stabilization of retained austenite caused by cooling of the Fe-Ni-C alloy to 4.2 K cannot be explained on the basis of the existing models, because the austenite and martensite do not age in the range 77–4.2 K. The morphology of the martensite formed during cooling from 77 to 4.2 K appears to be such that the retained austenite is effectively blocked by the rigid martensite framework, preventing any transformation which involves a volume increase.

The absence of an isothermal martensitic transformation owing to undercooling of the Fe-Ni-C alloys in liquid helium helped us to observe another interesting effect — a magnetic transformation of the retained austenite.

Evidence for change of the magnetic state of the retained austenite is given by the reversible change in width and intensity of the central component of the NGR spectrum when the temperature

at which the photograph was taken was changed (see Fig. 2). The susceptibility results also show that the effect is magnetic (see Fig. 3). During cooling of the initial austenite to the temperature of the magnetic transformation, the susceptibility changes nonmonotonically with a maximum (Hopkinson peak), which is typical of ferromagnetic specimens of finite size when the alloy passes through the Curie point. The Curie point of the alloy, found from the second derivative of the susceptibility, was registered at 190 K (see Fig. 3).

The heating curve of the dual-phase alloy after the martensitic transformation, like the cooling curve, is nonmonotonic (see Fig. 3). The fall of susceptibility in the range 100–250 K shows that there is a transition from ferromagnetic to paramagnetic state of one of the phase components. Since the Curie point of martensite is much higher than the temperature range in which the investigation was done, the effect observed during heating of the alloy is due to a magnetic transition in the retained austenite. A large decrease in the fraction of the austenitic phase in the specimen after the martensitic transformation (see table) resulted in a large reduction of the height of the Hopkinson peak.

Since the heating curve coincides with the curves of repeated cooling and subsequent repeated heating of the dual-phase alloy, the observed magnetic transition in the retained austenite is reversible, in agreement with observed reversible changes in the NGR spectrum (see Fig. 2).

It should be noted that the magnetic transition point moved to the left on the temperature scale to 160 K (see Fig. 3). According to the results given in [12, 13] on the influence of pressure [12] and nickel concentration [13] on the Curie point of Fe–Ni alloys with fcc lattice, decrease of the Curie point of retained austenite can be due to two causes: cubic compression of the lattice of the austenite phase or a change of nickel content in the composition of the retained austenite from the original composition. In [14] we have used the neutron diffraction method to show that the martensitic transformation initiates stresses in the austenite, although the unit cell volume of retained austenite does not change, that is, there is no cubic compression effect. The most likely reason for fall of the Curie point is therefore the lower concentration of nickel in the retained austenite than the initial austenite [13]. This result indirectly provides evidence of a nonuniform distribution of nickel in the initial austenite of the alloy, that is, of inhomogeneous short-range ordering, in agreement with the theory developed in [6].

CONCLUSIONS

1. The retained austenite in alloy Fe–25.3 Ni–0.65 C (wt%) stabilizes owing to cooling to liquid helium temperature. The stabilization mechanism cannot be explained on the basis of existing models.

2. The addition of carbon to the Fe–Ni alloy and stabilization of the retained austenite make it possible to observe magnetic ordering of retained austenite with nickel concentration characteristic of paramagnetic austenite.

The authors wish to thank G. A. Takzey and I. I. Sych for helpful advice.

REFERENCES

1. I. M. Georgiyeva and O. P. Maksimova, (On the relation between the kinetics and structure during martensitic transformations), *Fiz. metal. metalloved.*, **32**, 365 (1971).
2. M. Hayakawa, Y. Uemura and M. Oka, Discussion of "atom displacement due to C in Fe–Ni–C martensite", *Met. Trans.*, **12A**, 1545 (1981).
3. K. Ullakko and J. Pietikainen, Effects of tetragonality reduction in Fe–Ni–C martensite, in: *Proc. Int. Conf. Martensitic Transformations, Japan Inst. Metals, Japan Inst. Metals*, 291 (1986).
4. J. Gros and J. Pauleve, Etude par effet Mössbauer de l'ordre dans un alliage Fe–Ni 50–50 irradié par des neutrons ou des électrons, *J. Phys.*, **31**, 459 (1970).

5. S. S. Aliyev, P. L. Gruzin, A. Z. Men'shikov *et al.*, (Low-temperature phase transformations in iron-nickel alloy during electron bombardment), *Metallofizika*, 7, No. 5, 80 (1985).
6. M. A. Krivoglaz and A. A. Smirnov, *Teoriya uporyadochivayushchikhsya splavov (Theory of Ordering Alloys)*, Moscow, FIGML (1985).
7. V. G. Gavriilyuk and V. M. Nadutov, (Influence of carbon on magnetic and atomic ordering in the iron-nickel alloy), *Fiz. metal. metalloved.*, 56, 555 (1983).
8. V. G. Gavriilyuk and V. M. Nadutov, (Influence of carbon on the invar effect in iron-nickel alloys), *Fiz. metal. metalloved.*, 57, 188 (1984).
9. K. R. Kinsman and J. C. Shyne, Thermal stabilization of austenite in iron-nickel alloys, *Acta Met.*, 15, 1527 (1967).
10. M. Ye. Blanter and B. G. Serebrennikova, (On the nature of thermal stabilization of austenite), *MiTOM*, No. 7, 5 (1972).
11. J. Pietikainen, Thermal stabilization of austenite in high nickel-carbon steels, *J. Phys.*, 43, C4, 479 (1982).
12. G. T. Dubovka and Ye. G. Ponyatovskiy, (On the influence of pressure on the magnetic transformation in fcc alloys of the iron-nickel system), *DAN SSSR*, 206, No. 1, 83 (1972).
13. A. Z. Men'shikov and Ye. Ye. Yurchikov, (The Curie temperature of iron-nickel alloys with fcc structure), *Izv. AN SSSR, ser. fiz.*, 36, 1463 (1972).
14. O. Antson, V. G. Gavriilyuk, V. A. Kudryashov *et al.*, (Neutron diffraction study of the martensitic transformation in Fe-Ni-C alloys), Preprint LIYaF AN SSSR No. 1538, Leningrad (1989).