Functional Materials 19, No.3 (2012)

Magnetic and Invar properties of Fe–35 %Ni alloy after grinding of structure by hydroextrusion

V.M.Nadutov, D.L.Vashchuk, Ye.O.Svystunov, V.A.Beloshenko*, V.Z.Spuskanyuk*, A.A.Davidenko*

G.Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine, 36 Vernadskii Acad. Blvd. Vernadskii, 03680 Kyiv, Ukraine
*O.Galkin Institute for Physics and Engineering, National Academy of Sciences of Ukraine, 72 R.Luxemburg Str., 83114 Donetsk, Ukraine

Received March 20, 2012

The impact of deformation of Invar Fe–35 %Ni alloy by hydroextrusion at room temperature on structure and its properties was studied. Grinding of grains, the structure fragmentation on 60 nm blocks and continuous increasing microstresses with growing ε within the strain range of $\varepsilon = 0.45$—3.47 was shown. The multiple extrusion leads to a non-monotonic change of magnetic properties of the alloy (specific magnetization and the Curie temperature) and as a consequence to thermal expansion measured along the direction of the extrusion due to the microstresses growth and their partial relaxation. The hypothesis concerning the microstresses induced change of a balance between ferromagnetic and antiferromagnetic contributions to exchange interspin interaction is supposed.

Исследовано влияние деформации инварного сплава Fe–35 %Ni методом гидроэкструзии при комнатной температуре на структуру и его свойства и показано, что с ростом степени деформации в диапазоне $\varepsilon = 0{,}45$–$3{,}47$ происходит измельчение зерен и фрагментация структуры на блоки размером до 60 нм и непрерывное увеличение уровня микронапряжений. Показано, что, из-за процессов роста микронапряжений и частичной их релаксации многократное экструдирование ведет к немонотонному изменению магнитных свойств сплава (удельной намагниченности и температуры Кюри) и, как следствие, термического расширения, измеренного вдоль направления экструзии. Высказывается гипотеза относительно меняющегося за счет микронапряжений баланса между ферромагнитным и антиферромагнитным вкладами в обменное межспиновое взаимодействие.

1. Introduction

Application of Invar Fe–Ni alloys in constructions operated under conditions of large and continuous cyclic loads is limited due to their relatively low mechanical properties. One of the methods of their increasing is the grinding of grain structure of the alloys under cold plastic deformation. However such a treatment leads to a change of thermal expansion coefficient α (TEC) increasing it in some cases up to the values which correspond to loss of Invar properties although the reason of this effect was not studied at all and the existing data are contradictory and ambiguous [1].

Effect of plastic deformation on thermal expansion of Invar was already described in the first works on the Invar effect [1] and the effect explained by changes of fraction and orientation of Fe–Fe pairs relative to strain direction as most unstable spin systems providing Invar anomaly. As shown in [2] the plastic tensile strain of Fe–35.8–

36.7 %Ni–0.53–0.55 %Cr–0.48–0.49 % Mn alloy with the degree of 5–15 % leads to reduction of TEC within the temperature range 77–293 K that was explained as resulting from destruction of short-range atomic order FeNi or Fe_3Ni.

The reduction of TEC and broadening of the Invar temperature range (to 165°C) of Fe–36 at% Ni alloy deformed by equal-channel angle pressing (ECAP) with the deformation degree of $\varepsilon = 3.5$ was explained by the formation of submicrocrystalline (SMC) structure (100–200 nm) [3]. The authors [4] observed non-monotonic change of α under ECAP with growing ε of Invar Fe–36.1 %Ni–0.02 %C alloy. Taking into account the notions of [5] the reduction of α from $0.4\cdot10^{-6}$ K^{-1} to negative value of $-0.4\cdot10^{-6}$ K^{-1} was explained by destruction of microareas of short-range atomic order by moving dislocations and then its following growth by the structure fragmentation along the deformation accumulation and renewal of submicroareas of short-range atomic order.

Within the existing models, the low thermal expansion of f.c.c.–Fe–Ni alloys within the temperature range below the Curie point is conditioned by competition of two contributions: (i) Gruneisen contribution and (ii) magnetic one characterized by large volume magnetostriction ω_{ms} of the order of 10^{-3} [1]. In this connection the change of magnetic properties of Invar under the different types of plastic deformation leading both to appearance of texture and grains grinding and their fragmentation can give addition information about the nature of Invar anomaly.

In [6] the relationship between decrease of the reduced saturation magnetization σ/σ_0 and the TEC of Invar Fe–36 %Ni alloy was found out after the deformation by torsion under the hydrostatic pressure ($\varepsilon = 7$) that resulted in the structure fragmentation (100–500 nm) with the wide and ragged boundaries of fragments. The growth of α of the deformed alloy and the following its reduction with the elevating temperature to 500°C during the dilatometric measurements is explained by changes of the magnetic characteristics caused by the formation and dissolution of the ordered $FeNi_3$ phase on non-equilibrium 10 nm grain boundaries showing different magnetic properties from those for Fe–Ni basis (T_C = 611°C for $FeNi_3$, T_C = 260°C for large-grain unordered Fe–36 %Ni alloy [6]). However, there are no direct confirmations of the effect of structural elements boundaries in Invar on magnetic characteristics although according to [7] the formed by the deformation non-equilibrium large length-scale boundaries in SMC and nanocrystalline (NC) pure metals Fe and Ni provide changing their magnetic properties and thermal expansion.

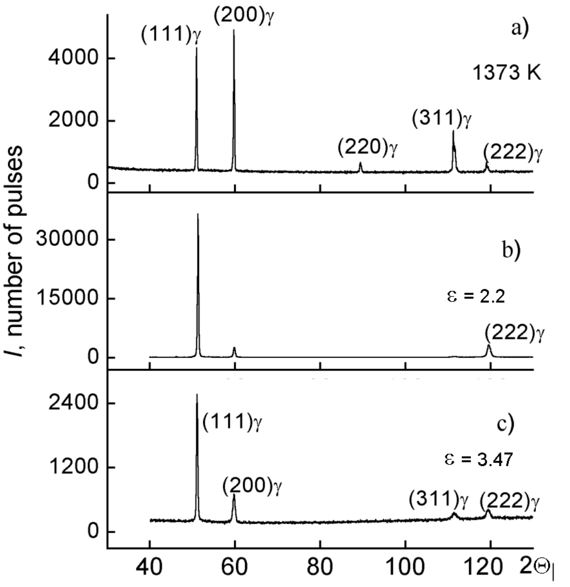

Fig. 1. X-ray diffraction patterns of Fe–35.0 %Ni alloy after homogenization at 1373 K and cooling (a); strains (b) $\varepsilon = 2.2$, (c) $\varepsilon = 3.47$ derived from the sample surface perpendicular to HE direction.

One of the methods of influence on the grain structure is hydroextrusion (HE) which is widely used for hardening and manufacturing of a number of metallic products. There are no any data on the effect of HE on magnetic and Invar properties of Fe–Ni alloys. In this connection the main goal of this study was to reveal changes in magnetic and Invar properties of f.c.c.–Fe–35 %Ni alloy and their dependences on the structure grinding resulted from cold plastic deformation by HE.

2. Objects and methods of study

The standard Invar Fe–35.0 %Ni alloy (containing 0.49 %Mn and Cu, Co, C impurities as well) was studied in this work. Cylindrical samples of 100 mm in length and of 21 and 12.5 mm in diameter were machined from initial work-piece for HE, which was conducted using equipment of O.Galkin Institute for Physics and Engineering of NAS of Ukraine. The samples before HE were annealed at 1373 K during 30 min in slag and subsequently quenched

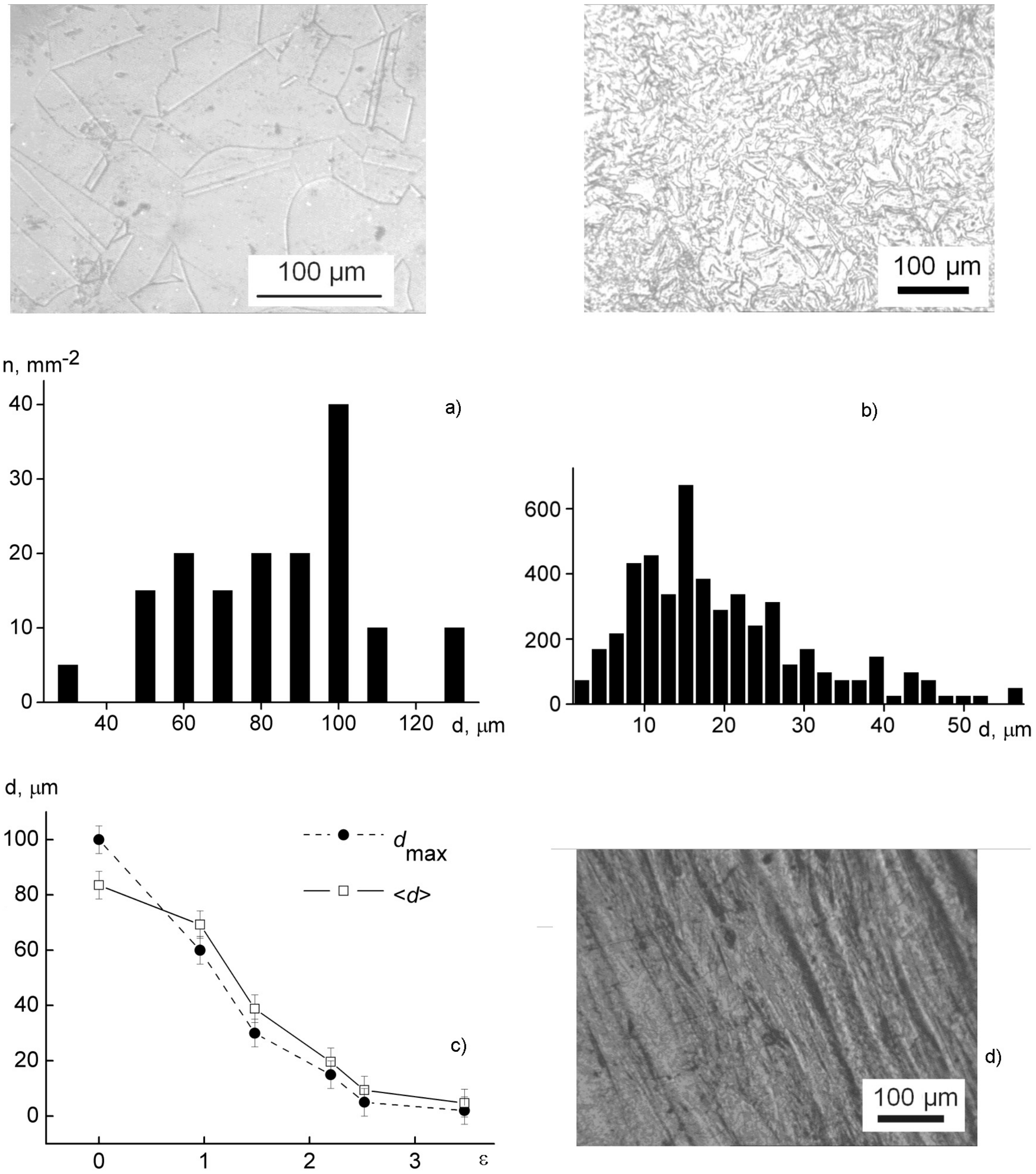

Fig. 2. Microstructure and grain size distribution diagrams of Fe–35.0 %Ni alloy: a) ε = 0 and b) after deformation ε = 2.2; c) average grain size $<d>$ and the most likely their size d_{max} in cross-section of the sample to HE direction vs. strain degree ε of the alloy ($<d> = \sum_i d_i n_i / \sum_i n_i$, where d_i is i-th grain size, n_i is the number of grains of i-th size); d) microstructure derived from a lateral face of the sample with ε = 0.96.

in room temperature water. The work-piece of the alloy was forced away through a die under the liquid pressure of 1.5 GPa and in order to collect deformation this procedure was repeated several times using dies of smaller diameter. Degree of total deformation was calculated using standard relationship $\varepsilon = 2\ln(d_0/d)$, where d_0 and d are diameters of initial and deformed sample after the pass through die. The alloy samples studied were obtained with the degree of total deformation ε = 0.45; 0.85; 0.96; 1.16; 1.48; 2.2; 2.52; 2.9; 3.27; 3.47. The rectangular shaped samples (length of 15 mm and cross section of 2×2 mm and 4.6×4.6) and cylindrical samples (length of

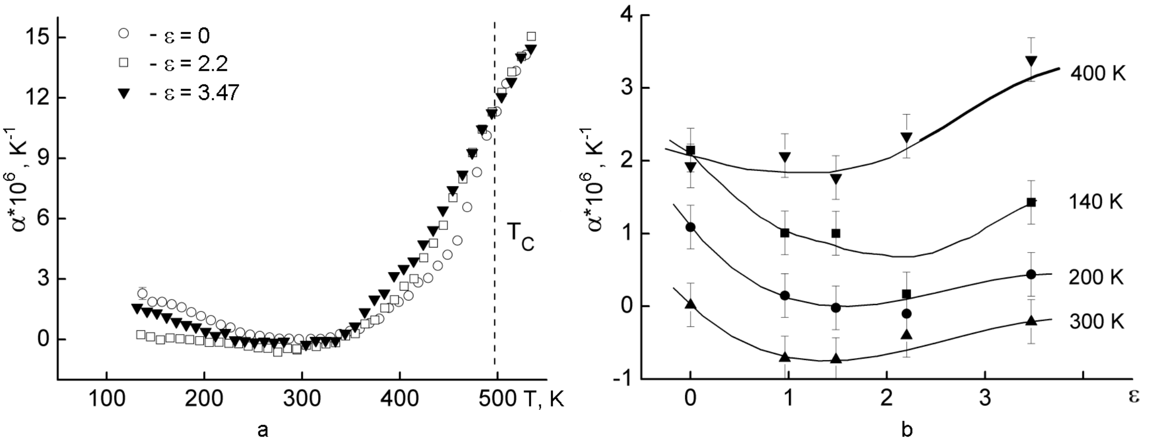

Fig. 3. The value of TEC of Fe–35.0 %Ni alloy vs. temperature (a) and strain ε (b). $\alpha(\varepsilon)$ curves at the corresponding temperatures have drown after smoothing of the experimental curves $\alpha(T)$. T_C is the Curie point, 495 K, of the alloy before deformation.

5 mm and diameters 21–4 mm) were obtained for different measurements.

Structure of the alloy before and after HE was studied by X-ray and metallographic analysis. The X-ray measurements was carried out on diffractometer "DRON-3M" using $\mathrm{Co}_{K\alpha}$ radiation. Microstructural images were obtained by means of "NEOPHOT-21" microscope with zooming of ×100–800. Dilatometric measurements were carried out by means of inductive quartz dilatometer within the 135–530 K temperature range. The initial sample dimension was determined at room temperature with the accuracy of ±0.005 mm and the accuracy of TEC calculation was $\pm 0.3 \cdot 10^{-6}$ K^{-1} including smoothing of experimental curves. Saturation magnetization was measured by ballistic magnetometer in constant magnetic field of 800 $kA \cdot m^{-1}$. The measurements of field dependences were carried out at the temperatures 77 K and 293 K. The Curie point of the alloy was determined by measurement of temperature dependence of magnetic susceptibility within the temperature range of 77–570 K. The magnitude of magnetic field and frequency were 400 $A \cdot m^{-1}$ and 1 kHz correspondingly.

3. Results and discussion

The results of X-ray analysis showed that Fe–35.0 %Ni alloy after homogenization at 1373 K and the following rapid cooling was in austenitic state (Fig. 1a) and the phase composition after HE was not changed within the range of plastic deformation $\varepsilon = 0.45–3.47$ (Fig. 1b,c).

Fig. 2 shows the results of metallographic analysis of the structure in cross-section of the sample perpendicular to HE direction (*a*, *b*) and in longitudinal-section (*d*). Along with ε increasing the gradual refinement of the alloy structure and significant broadening of the grain boundaries is observed. The average grain size in the cross-section to HE direction in the investigated range of values decreases monotonically with increasing strain degree: from 80–100 μm in initial state of the sample to 2–5 μm in the most deformed sample state with $\varepsilon = 3.47$ (Fig. 2c).

Broad and smeared grain boundaries are the result of accumulated stresses under deformation forming their non-equilibrium state. Their relaxation leads to a fragmentation of grains into blocks as evidenced by noticeable inner contrast (Fig. 2b) and subgrain structure revealed by transmission electron microscopy (TEM) [8]. The microstructure of the alloy obtained from lateral face of the sample with $\varepsilon = 0.96$ is shown in Fig. 2d. The grains having an average size of 200–300 μm are elongated along strain direction and indicate an appearance of texture, which is consistent with the distorted ratio of the diffraction line intensities (Fig. 1) and the data of TEM studies [8].

The results of dilatometric studies of the alloy before and after HE showed a change of the behaviour of the TEC temperature dependence: the value of α decreases in the temperature range 140–370 K and it reaches negative value $-0.7 \cdot 10^{-6}$ K at 300 K. The growth of the TEC and $\alpha(T)$ curve shifting to the left on the temperature scale is

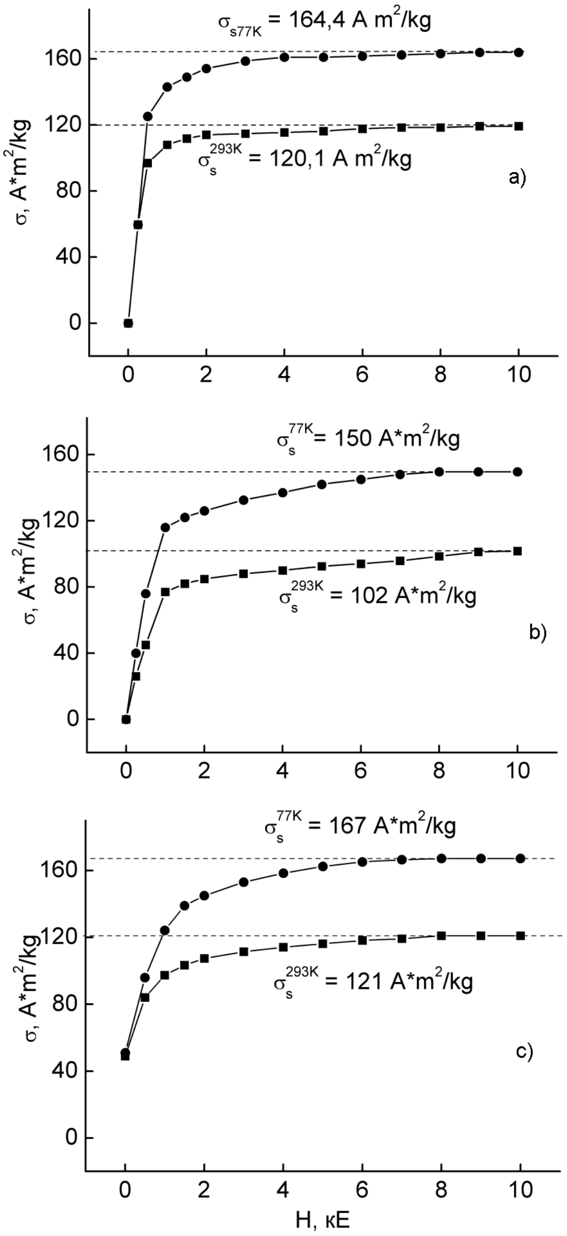

Fig. 4. Field dependences of specific magnetization σ of Fe–35.0 %Ni alloy (at 77 K and 293 K) after homogenization at 1373 K (ε = 0) (a) and plastic deformation by HE: ε = 2.2 (b); ε = 3.27 (c). The dotted lines indicate the magnitude of saturation magnetization σ_s.

observed above 370 K including the vicinity of the Curie temperature (495 K) (Fig. 3a). Minimum on the deformation curve is observed nearby the value ε = 1.48 (Fig. 3b). It exists temperature and only at temperatures above 400 K growth of α observed.

The reduction of TEC for Fe–35 %Ni alloy after HE is consistent with the data of dilatometric studies of Invar alloys after

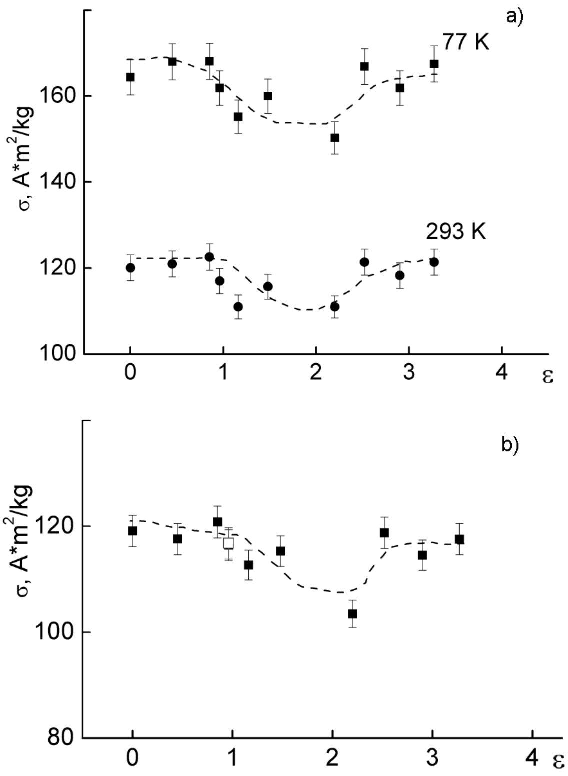

Fig. 5. Dependences of specific saturation magnetization σ_s of Fe–35.0 %Ni alloy on the strain degree ε at 77 K and 293 K obtained: by a) field dependence of σ; b) temperature dependence of σ, extrapolated to 293 K. The error indicated in the graphs is 2.5 %. The dashed curves are shown for ease of visualization. The open dot on curve is related to the alloy after ageing at 800 K.

plastic deformation by different methods at room and below room temperatures [2–6, 9]. For example the non-monotonic variation of the TEC of Fe-36.1 % Ni-0, 2 % C alloy after ECAP was found in [4] as in our case after the HE (Fig. 3) and it was explained as destruction of short-range atomic order by the moving dislocations and then in further refinement of the structure as the formation of dislocation-free fragments and restoration of the ordered state.

The atomic order has not been detected in TEM study of Invar alloy Fe–35 %Ni in [8]. Therefore the explanation of the TEC changing in f.c.c. Fe–Ni Invar alloy after deformation is necessary to search in correlation with the magnetic order vary, which determines the Invar anomaly [1] as a result of distortion of the interatomic distances by strain and as a consequence of the appearance of elastic stresses. The simultaneous change of TEC, saturation magnetization

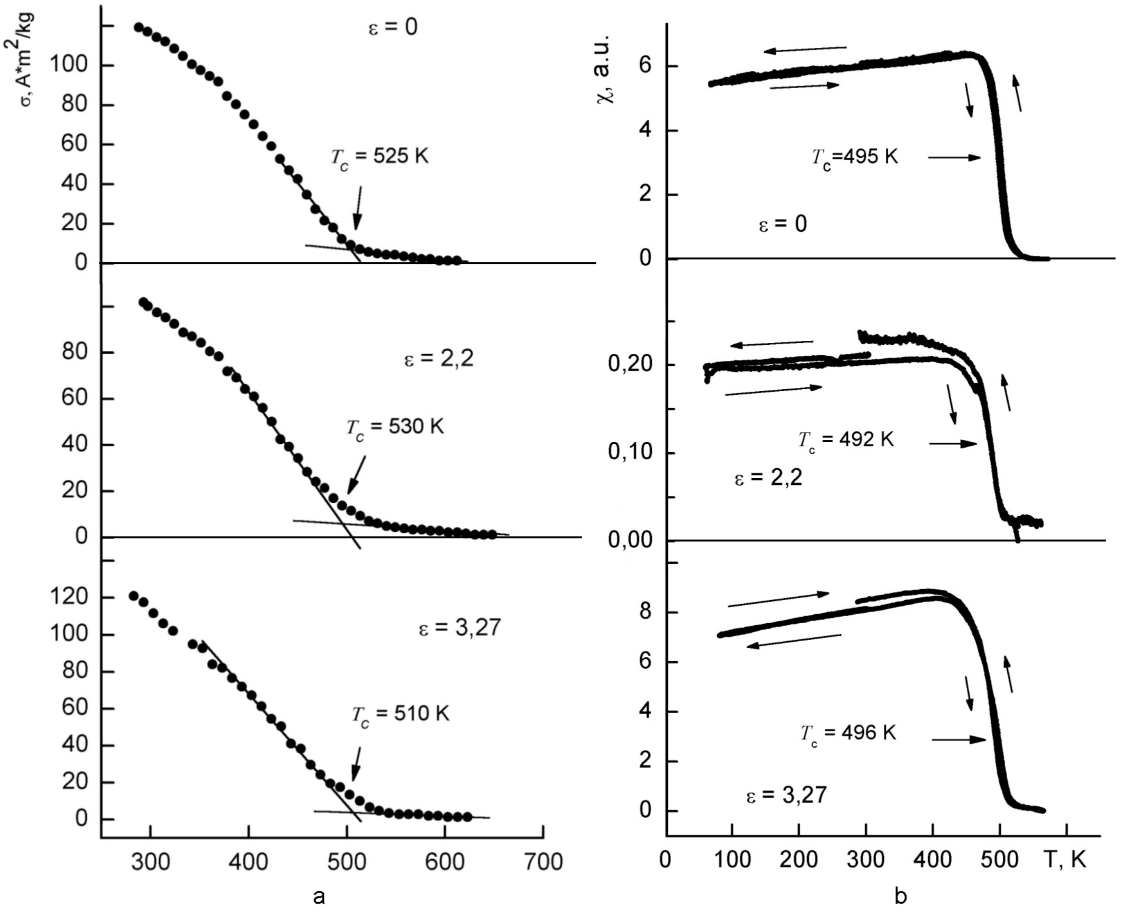

Fig. 6. Dependences of magnetization a) and the real part of magnetic susceptibility b) of Fe–35.0 %Ni alloy on temperature and strain degree ε.

and the Curie temperature of Invar $Fe_{64}Ni_{36}$ alloy was revealed after mechanical alloying as a result of selective increase of Fe–Fe interatomic distances due to the emerging local microstresses [9].

Field, temperature and strain dependences of specific magnetization σ and the Curie point T_C were obtained to reveal the correlation between thermal expansion and magnetic properties of Fe–35 %Ni alloy after HE. Specific saturation magnetization σ_s of the alloy was determined on $\sigma(H)$ and $\sigma(T)$ dependences.

Fig. 4 shows field dependences of the specific magnetization of the alloy Fe–35 %Ni for $\varepsilon = 0$ and after deformation ($\varepsilon = 2.2$ and $\varepsilon = 3.27$) taken at 77 K and 293 K. At low degrees of HE (up to $\varepsilon = 0.96$) the saturation specific magnetization σ_s lies on the same level within the error however magnetization begins a gradual reduction with growing ε reaching the minimum nearby $\varepsilon = 1.16$–2.2 and then its growth to almost initial values (Fig. 5). Similar dependence $\sigma(\varepsilon)$ is observed at 77 K but with the higher values of magnetization.

The obtained data on non-monotonic $\sigma(\varepsilon)$ dependence is only partially consistent to the results shown in [6], in which decrease of the reduced saturation magnetization of Fe–36 % Ni alloy after torsion deformation under hydrostatic pressure was revealed.

The Curie temperature of the alloy before and after HE was determined by means of two independent methods: on temperature dependence of magnetization and magnetic susceptibility of the sample. The examples of the temperature dependences $\sigma(T)$ and $\chi(T)$ for the samples before and after HE are shown in Fig. 6.

The generalized data of the Curie point of Fe–35 %Ni alloy are shown in Fig. 7. A decrease in T_C of the alloy with strain degree increasing for small ε, then a weak rise of the T_C in the range of $\varepsilon = 1.16$–2.2 and its further reduction in the vicinity of $\varepsilon = 3.0$ are observed. At that this tendency is observed for T_C values found out in the measurements of saturation magnetization (Fig. 6a) and magnetic susceptibility (Fig. 6b). The growth of T_C after the strains of $\varepsilon = 1.16-2.2$ qualitatively correlates with the observed changes in the specific magnetization in the same ε range (Fig. 5).

The great attention should be drawn to higher values of temperatures of the magnetic phase transition by approximately of 20–40 K obtained from the magnetization measurements in comparison with the T_C values found on the magnetic susceptibility data. According to [10, 11] this is due to the effect of relatively strong external magnetic field (800 kA/m) at measurements of thermomagnetic curves which greater by several orders of a magnitude of the field strength in the case of magnetic susceptibility measurement (400 A/m).

Taking into account the data on compressibility of the Invar alloy [12], the effect of hydrostatic pressure on the T_C [13] and the crystal lattice expansion with the alloying of fcc–Fe–Ni alloy with carbon [11, 14] as well as high sensitivity of the exchange interspin interaction in the Invar alloys to a distance between neighboring atoms providing according to Weiss model the antiferromagnetic low-spin low-volume or ferromagnetic high-spin high-volume state [15] it should be stated the following. The observed decrease in the Curie temperature at small ε and then the rise of T_C with a simultaneous reduction of the saturation magnetization after deformation $\varepsilon = 1.16-2.2$ (Fig. 5, Fig. 7) are most probably caused not by destruction of the atomic order during deformation or its reduction [4] but by microstresses causing a deviation from the equilibrium interatomic distances and by the processes of their dynamic relaxation as grinding grain structure. As shown in TEM studies of Invar Fe–35 % Ni alloy the plastic deformation by HE leads to the formation of substructures with dimensional parameters in the 50–120 nm range and above it having particularities in fragments disorientation and organization of boundaries between them causing a non-monotonic change of the elastic microstresses level [8].

The analysis results of the degree of structure fragmentation and the level of microstresses in Invar alloys by increasing X-ray diffraction lines broadening with increasing degree of deformation are shown in Fig. 8. The size of coherently scattering domains (CSD) D and the level of microstresses η were determined by approximation of X-ray diffraction line widths (111) (200) (311) and (222) β^1 by using Williamson-Hall method.

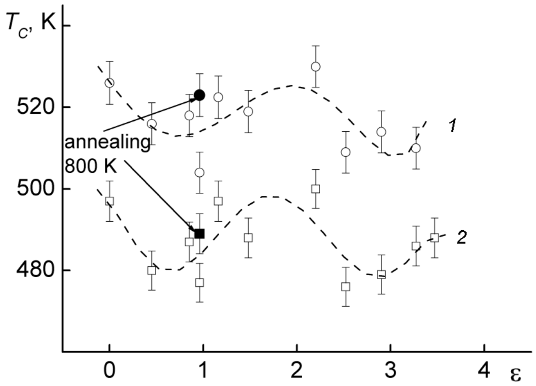

Fig. 7. Dependences of the Curie point of Invar Fe–35.0 % Ni alloy on the degree of deformation, obtained on the thermomagnetic measurements data, σ (*1*) and the measurements of magnetic susceptibility χ (*2*). The error shown on the dependences is 0.5 %. The dashed curves are shown for visualization. The filled dots indicate the values of T_C after ageing of the deformed alloy in vacuum at 800 K.

Along with the CSD size decrease from 110 nm to 60 nm with increase of deformation degree (Fig. 8b) the increase of microstrains occurs with noticeable slowing-down after the $\varepsilon = 1.16-2.2$ (Fig. 8c). The decrease and then weak rise of the crystal lattice parameter of austenite a_γ is observed with increase of straine degree ε (Fig. 8d), which also testifies about monotonically increasing compressive internal microstresses partially relaxing at large ε.

Exclusion of the contribution from boundaries of substructural elements and removal of internal microstresses as the sources of the lattice distortion by ageing at 800 K of the deformed ($\varepsilon = 0.96$) alloy (Fig. 8c) has led to an increase of the Curie temperature (Fig. 7) and the lattice parameter a_γ (Fig. 8d) almost to their initial values, i.e. to properties recovery (filled points in the figures).

Thus the peculiarities of subgrain structure of the alloy and its stressed state after HE, which distort the equilibrium interatomic distances and variate the character of exchange interspin interactions in accordance with Bethe-Slater curve, are the cause of the non-monotonic variation of the magnetic properties and the thermal expansion.

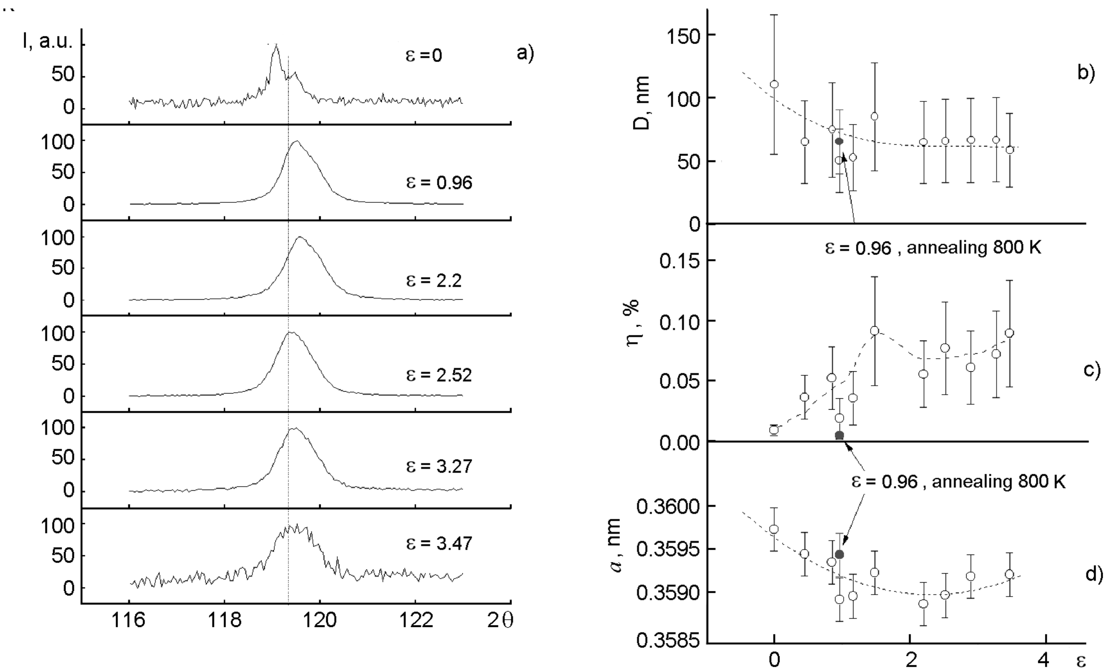

Fig. 8. X-ray diffraction line (222) taken after homogenization of Fe–35.0 %Ni alloy at 1100°C and subsequent HE with the strain degree ε: 0.96; 2.2; 2.52; 3.27; 3.47 (a). Dependence of size of the CSD D (b), level of microstresses η (c) founded by Williamson-Hall method along the line series (111) and (200) (311) (222) and the crystal lattice parameter a_γ (d) on the strain degree. The filled points correspond to the alloy after annealing at 800 K.

4. Conclusions

The non-monotonic change of the Curie point of Invar Fe–35.0 %Ni alloy and its specific saturation magnetization with minimum of σ_s at $\varepsilon = 1.16–2.2$ with the increase of strain degree by hydroextrusion was revealed. Hydroextrusion of the alloy principally does not change its Invar properties measured along direction of strain however it decreases the TEC at $\varepsilon = 1.16–2.2$ within the temperature range 140–370 K and reduces it up to the negative value ($-0.72\cdot10^{-6}$ K) nearby 300 K. Growth of α occurs at 400 K and higher temperatures exhibiting distinctly at the strain degrees $\varepsilon = 2.2–3.47$.

The changes of magnetic properties and as a consequence the TEC of Invar Fe–35.0 %Ni alloy after hydroextrusion are conditioned by the structure fragmentation induced by deformation (with the CSD size that is monotonously changed from 110 nm to 60 nm) and by compressed and then partially relaxed microstresses varying interatomic distances and changing balance between ferromagnetic and antiferromagnetic contributions into exchange interspin interaction.

These studies were conducted within the budget program of G.Kurdyumov Institute for Metal Physics of the NAS of Ukraine at partial financial support of the projects 92/10-H and 92/11-H of purposeful complex program of the fundamental investigations of NAS of Ukraine "Fundamental problems of nanostructural systems, nanomaterials, nanotechnologies". The authors express gratitude to V.P.Zalutsky for X-ray measurements, to T.V.Efimova for magnetic measurements.

References

1. Physics and Applications of Invar Alloys (Honda Memorial Series on Materials Science), Maruzen Company Ltd., Tokyo (1978).
2. V.P.Voroshilov, A.I.Zakharov, V.M.Kalinin et al., *Fiz. Met. i Metalloved*, No.5, 953 (1973).
3. I.Kh.Bitkulov, V.AKazantsev, V.I.Kopylov et al., *Izv. Vuzov. Fiz.*, No.2, 69 (2001).

---

* The half line-width β was obtained by subtraction of instrumental component determined by Rietveld method. The diffraction patterns of lanthanum hexaboride (LaB_6) were measured in order to obtain the resolution function of diffractometer. The diffraction lines were fitted by Lorentzian function. The angular dependence of their half line-width $\beta(2\theta)$ was found, which was approximated by function $\beta(2\theta) = \sqrt{u\,\mathrm{tg}^2\theta + v\,\mathrm{tg}\theta + w}$, where u, v, w are the fitting parameters.

4. V.I.Izotov, V.V.Rusanenko, V.V.Kopylov et al., *Fiz.Met.i Metalloved*, No.3, 123 (1996).
5. V.V.Sagaradze, V.V.Uvarov, E.I.Anufrieva, *Fiz.Met.i Metalloved*, No.6, 156 (1994).
6. R.R.Mulyukov, V.A.Kazantsev, Kh.Ya.Mulyukov et al., *Rev.Adv.Mater Sci.*, No.11, 116 (2006).
7. R.Z.Valiev, I.V.Aleksandrov, Nanostrukturnye Materialy, Poluchennye Intensivnoj Plasticheskoj Deformaciej, Logos, Moscow (2000) [in Russian].
8. V.M.Nadutov, D.L.Vashchuk, P.Yu.Volosevich et al., *Metallofiz.i Nov.Tekh.*, **34**, 395 (2012).
9. P.Gorria, D.Martinez-Blanko, M.J.Perez et al., *Phys.Rev.*, **B 80**, 064421-1 (2009).
10. A.Chernenko, V.V.Kokorin, F.V.Minkov, *Phys.Stat.Sol.*, **134**, 193 (1992).
11. V.M.Nadutov, Ye.A.Svistunov, S.G.Kosintsev et al., *Izv.RAN, Ser.Fiz.*, No.10, 1475 (2005).
12. L.Dobrovinsky, N.Dobrovinskaya, I.Abrikosov et al., *Phys.Rev.Let.*, No.21, 4851 (2001).
13. S.Wei, R.Duraj, R.Zach, M.Matsushita et al., *J.Phys.Condens.Matter*, **14**, 11081 (2002).
14. V.M.Nadutov, Ye.O.Svystunov, S.G.Kosintsev et al., *Hyperfine Inter.*, **168**, 929 (2006).
15. V.L.Moruzzi, P.M.Marcus, J.Kubler, *Phys. Rev.*, **B 39**, 6957 (1989).

Магнітні та інварні властивості сплаву Fe-35%Ni після подрібнення структури методом гідроекструзії

В.М. Надутов, Д.Л. Ващук, Є.О. Свистунов, В.О. Белошенко, В.З. Спусканюк, О.А. Давиденко

Досліджено вплив деформації інварного сплаву Fe–35,0 %Ni методом гідроекструзії при кімнатній температурі на структуру і його властивості і показано, що із зростанням ступеню деформації у діапазоні $\varepsilon = 0{,}45$–$3{,}47$ відбувається подрібнення зерен, фрагментація структури на блоки розміром до 60 нм і безперервне збільшення рівня мікронапружень. Показано, що багаторазове екструдування веде через процеси росту мікронапружень і часткову їх релаксацію до немонотонної зміни магнітних властивостей сплаву (питомої намагніченості і температури Кюрі) і, як наслідок, термічного розширення, виміряного вздовж напрямку екструзії. Висловлюється гіпотеза щодо мінливого за рахунок мікронапружень балансу між феромагнітним і антиферомагнітним вкладами в обмінну міжспінову взаємодію.