DOI 10.1007/s11041-015-9801-x
Metal Science and Heat Treatment, Vol. 56, Nos. 9 – 10, January, 2015 (Russian Original Nos. 9 – 10, September – October, 2014)

UDC 621.762:669.15’26’24’74’786.56

A STUDY OF THE PROCESS OF MECHANICAL ALLOYING OF IRON WITH AUSTENITE-FORMING ELEMENTS

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Translated from *Metallovedenie i Termicheskaya Obrabotka Metallov*, No. 10, pp. 53 – 59, October, 2014.

Results of experimental studies of the effect of treatment time on the processes of phase formation and dissolution of alloying elements during mechanical alloying of iron with austenite-forming elements in a nitrogen-containing atmosphere are presented. The special features of the nanocrystalline structure of a Fe – 18% Cr – 8% Ni – 12% Mn – *x*N powder alloy obtained by mechanical alloying and the effect of the method of compaction on the mechanical properties of articles are determined.

Key words: high-nitrogen austenitic steel, microstructure, phase composition, powder alloys, mechanical alloying.

INTRODUCTION

Solid-phase processes initiated by mechanical action have recently become a subject of intense research. This is connected with the perspectives of such reactions in engineering, especially in the field of creation of new materials that are safer ecologically and more profitable economically than the materials used today [1, 2].

The wide possibilities of mechanochemistry as the chemistry of nonthermal low-temperature reactions are illustrated by the fact that refractory substances and intermetallics, inorganic and organic compounds, molecular complexes, modified polymers, pharmaceuticals, and novel composite materials have been synthesized in a solid phase without dissolution or melting or the reagents. Mechanochemical synthesis is performed at a comparatively low temperature, when the formation of a perfect crystal structure is hard. This paves the way to synthesizing substances and materials in nanocrystalline and amorphous states [1, 2].

A promising class of modern materials are austenitic steels and alloys many of which find application as nonmagnetic, corrosion- and wear-resistant, and cryogenic materials. The main advantages of austenitic steels are their high service characteristics (strength, ductility, corrosion resistance in many operating environments) and adaptability to manufacture. The austenitic steels with nitrogen used as an alloying element present special interest.

Nitrogen-alloy steels possess a high strength combined with ductility and corrosion resistance and a steady austenitic structure in a wide temperature range. The introduction of nitrogen into a steel lowers the need for expensive alloying elements, for example, nickel, manganese or molybdenum. Alloying with nitrogen not only solves the problem of raising the strength and saving the alloying components but also enhances the ecological safety.

Recent methods of production of high-nitrogen steels (melting under elevated nitrogen pressure, plasmochemical saturation of melt, use of nitrides and nitrogen-enriched alloys as the initial substances, etc.) require intricate equipment. In addition, the high temperatures required for melting the steel makes fabrication of coarse-grain materials possessing low mechanical properties virtually inevitable. Since the grains in an austenitic steel cannot be refined by heat treatment, grain refinement requires multiple pressure treatment, which finally prolongs the production cycle and raises the consumption of power and the cost of the material. For this reason, it is expedient to apply the method of mechanical alloying for the production of nitrogen-containing steels.

Powder high-nitrogen austenitic alloys Fe – 18% Cr – 8% Ni – 12% Mn – *x*N with nitrogen content of up to 1 wt.% and a nanocrystalline structure of up to 30 nm have been produced at the laboratory of functional materials of the St. Petersburg Polytechnic University by the method of mechanical alloying of iron in a nitrogen-containing atmosphere [3, 4].

The aim of the present work was to determine the regular features of the action of the treatment time on the processes of phase formation and dissolution of alloying elements dur-

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ing mechanical alloying of iron with austenite-forming elements in a nitrogen-containing atmosphere.

METHODS OF STUDY

To study the effect of the duration of mechanical alloying on dissolution of the alloying elements we performed a series of tests where powders with composition Fe – 18% Cr – 8% Ni – 12% Mn were treated in an atmosphere of nitrogen for 15, 30, 45 and 60 min and for 3.5 h at room temperature. The mechanical alloying was conducted in an energy-intensive vibration mill by the method described in [3, 4]. The changes in the phase composition and in the lattice parameters of the materials obtained by mechanical alloying were determined by x-ray phase analysis using a Bruker D8 Advancer in the characteristic copper radiation ($\lambda = 0.154031$ nm). The parameters of the tube were 30 kV and 30 mA. The phase composition was determined by Mossbauer spectroscopy using a SM4201TERLAB device. The volume distribution of the elements in a powder particle was determined on laps by the method of x-ray microanalysis using a Mira 3 Tescan scanning electron microscope with an Oxford INCA Wave 500 attachment. The fine structure of the powders was studied under a high-resolution JEOL-2100F transmission electron microscope at an accelerating voltage of 200 keV. The powders were rolled in a shell in a DUO 180 laboratory mill. The compact preform for the rolling was obtained in an HP D 25 facility for spark plasma sintering (SPS) produced by FCT Systeme Gmbh. The heat treatment was performed in an OTF-1200X-HP-55 horizontal pusher furnace (MTI Corp.) in an atmosphere of argon or nitrogen. The mechanical tests were performed using Zwick Roelle testing machines.

RESULTS

The study of the effect of the parameters of the process of mechanical alloying on the phase composition of the alloy has shown that the first alloying element to dissolve in the iron lattice is nickel ($a = 0.3524$ nm, $r_a = 124$ pm), then follows chromium ($a = 0.2885$ nm, $r_a = 130$ pm) and then manganese ($a = 0.8890$ nm, $r_a = 135$ pm) (Fig. 1). This succession is a result of the fact that Ni, Cr and Mn form substitutional solid solutions with iron, and the atomic radius of nickel is the closest to that of iron, i.e., 126 pm; the next in this row is chromium and then follows manganese. It has been shown that when the time of the mechanical alloying is increased, the content of not dissolved alloying elements decreases gradually and, simultaneously, the lattice is rearranged from a bcc one to an fcc one. After 30 min of mechanical alloying the content of the γ-phase in the alloy attains about 3 – 5 vol.%. Note that the rearrangement of the crystal lattice occurs without heating, and the formed γ-phase has nanometer sizes. When the time of the mechanical treatment is prolonged still more, the alloying elements dissolve in the iron completely, and the proportion of the γ-phase in the structure increases, while that of the α-iron decreases (Fig. 1*b*).

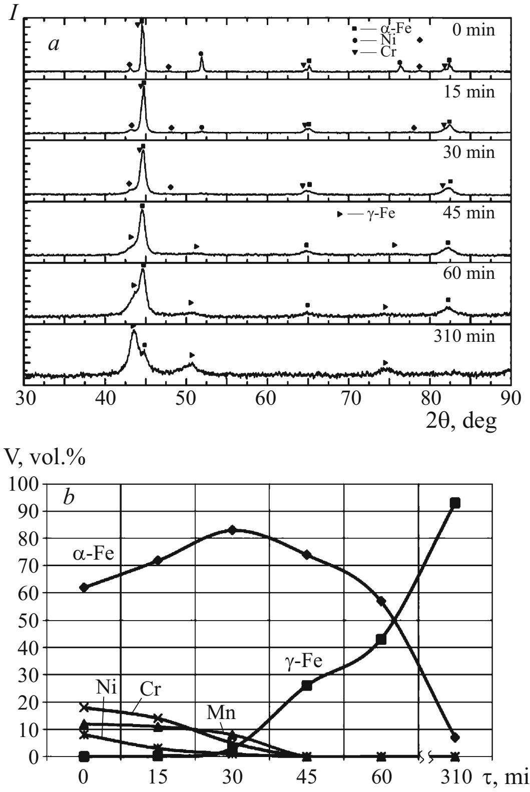


Fig. 1. Diffraction patterns (*a*) and volume content of phases (*b*) in a Fe – 18% Cr – 8% Ni – 12% Mn – *x*N powder as a function of the duration of the process of mechanical alloying.

We used microscopic x-ray spectrum analysis to plot a map of the distribution of the components in the volume of the initial powder (Fig. 2). It can be seen from the data obtained that the initial powder is represented by a mechanical mixture of powders of pure Fe, Cr, Ni, and Mn distributed unevenly over the whole of the volume.

We studied the variation of the structure of the powder mixture during mechanical alloying for 15, 30, 45 and 60 min and during 3.5 h. At the start of the process the intense plastic deformation causes sticking of the powder particles of the initial components, which is then followed by "strain-induced atomic mixing" due to irreversible changes in the shapes and sizes of the powder particles [1, 2]. In short-term mechanical alloying the resulting powders have the form of a "layer-cake." The elements are distributed in a powder particle not uniformly; some zones are enriched with one of the alloying elements and some are depleted of it (Fig. 3). The alloying elements distributed so unevenly in the powder can give quite intense peaks in the diffraction patterns (Fig. 1). The results of a spot chemical analysis (Fig. 3*a*) show that a powder particle contains regions with chemical composition corresponding to the range of existence of the γ-Fe phase in Scheffler's diagram, but the x-ray

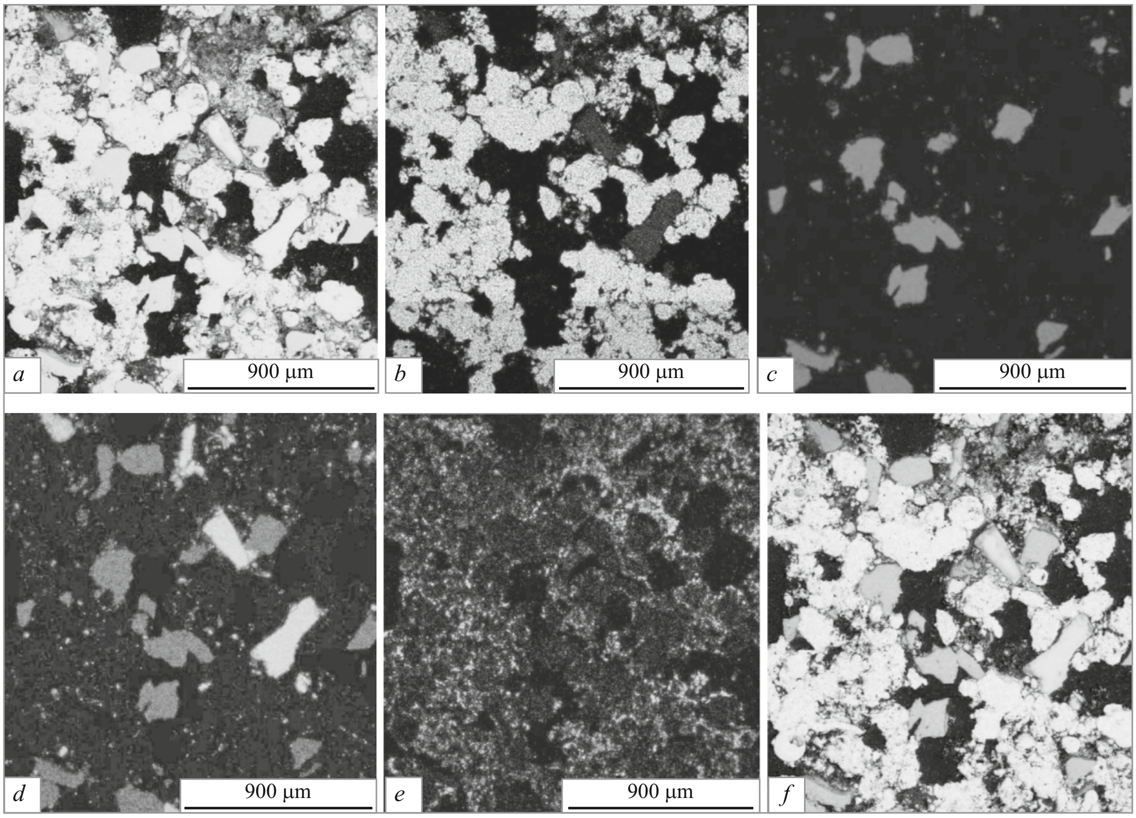
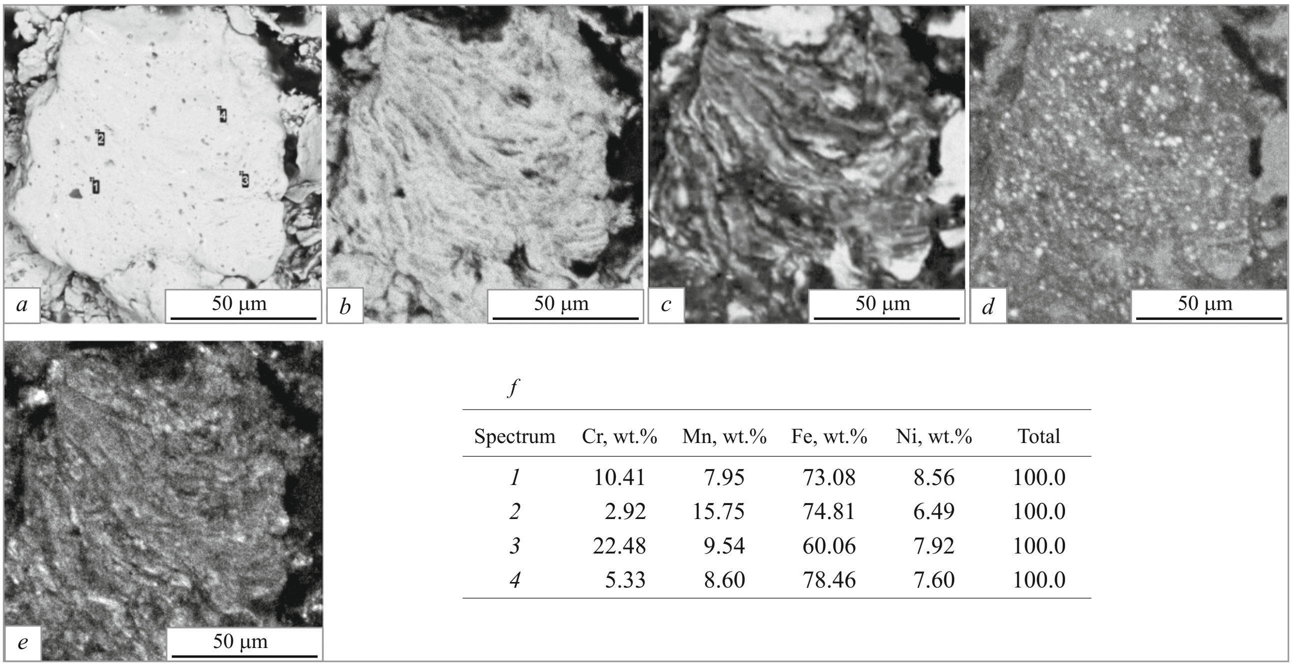


Fig. 2. Distribution of components in the volume of the initial Fe – 18% Cr – 8% Ni – 12% Mn powder: *a*) structure of the region studied; *b*) Fe; *c*) Cr; *d*) Mn; *e*) Ni; *f*) general distribution of the elements.

phase analysis does not detect such regions (Fig. 1). This is a result of the short duration of the mechanical alloying, i.e., the doze of the energy supplied in the short time of the synthesis is insufficient for the elements to form a solid solution



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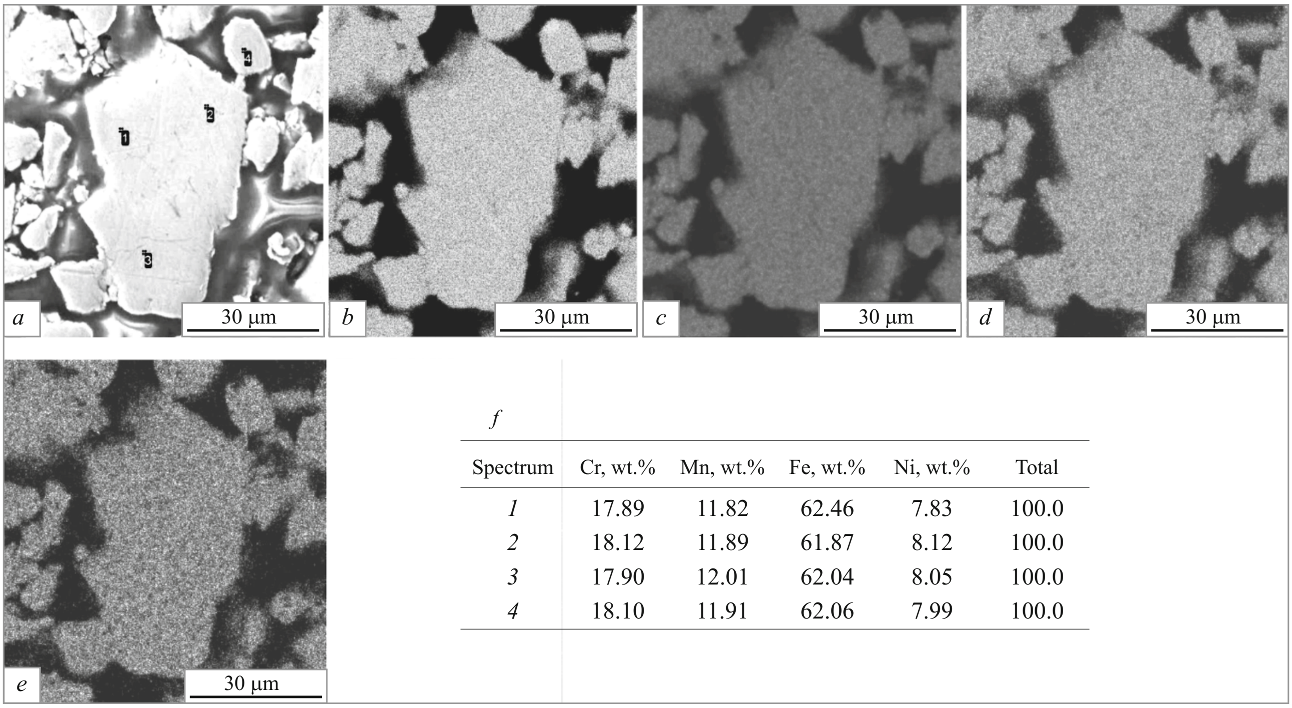
Spectrum	Cr, wt.%	Mn, wt.%	Fe, wt.%	Ni, wt.%	Total
1	10.41	7.95	73.08	8.56	100.0
2	2.92	15.75	74.81	6.49	100.0
3	22.48	9.54	60.06	7.92	100.0
4	5.33	8.60	78.46	7.60	100.0

Fig. 3. Distribution of components in the volume of a particle of Fe – 18% Cr – 8% Ni – 12% Mn powder after mechanochemical synthesis for 15 min: *a*) structure of the region studied; *b*) Fe; *c*) Cr; *d*) Mn; *e*) Ni; *f*) results of spot chemical analysis.



Spectrum	Cr, wt.%	Mn, wt.%	Fe, wt.%	Ni, wt.%	Total
1	17.89	11.82	62.46	7.83	100.0
2	18.12	11.89	61.87	8.12	100.0
3	17.90	12.01	62.04	8.05	100.0
4	18.10	11.91	62.06	7.99	100.0

Fig. 4. Distribution of components in the volume of a particle of Fe – 18% Cr – 8% Ni – 12% Mn powder after mechanochemical synthesis for 3.5 h: *a*) structure of the region studied; *b*) Fe; *c*) Cr; *d*) Mn; *e*) Ni; *f*) results of spot chemical analysis.

and hence for the lattice to transform from a bcc one to an fcc one. When the time of the mechanical alloying is increased, the doze of the supplied energy grows, and this causes gradual leveling of the distribution of the alloying elements over the volume of the matrix of the powder obtained (Fig. 4) and transition from a bcc lattice to an fcc one (Fig. 1). According to the results of the spot chemical analysis after 3.5 h of mechanochemical synthesis the alloying elements are distributed in the volume of the powder uniformly and match the initial chemical composition (Fig. 4*a*).

According to the data of the high-resolution transmission electron microscopy intense plastic deformation of alloys Fe – 18% Cr – 8% Ni – 12% Mn – *x*N yields a homogeneous nanocrystalline structure already at room temperature (Figs. 5 and 6). The sizes of the nanocrystals range within 6 – 20 nm, and the grain boundaries are chiefly not straight. The grain boundaries bear many dislocations; the atomic planes are partially coherent. At the same time, there are many boundaries with poorly defined images, and the diffraction contrast in the grains is inhomogeneous and often varies in a complex manner indicating a high level of internal stresses and elastic distortions of the crystal lattice. Such a complex contrast is present both in the grains containing lattice dislocations and in flawless grains. This means that the sources of the internal stresses are grain boundaries. A detailed study of structural regions at a high magnification resolving individual atoms of the crystal lattice allows us to infer that the grain boundaries are periodic stepped formations. The images of the atomic

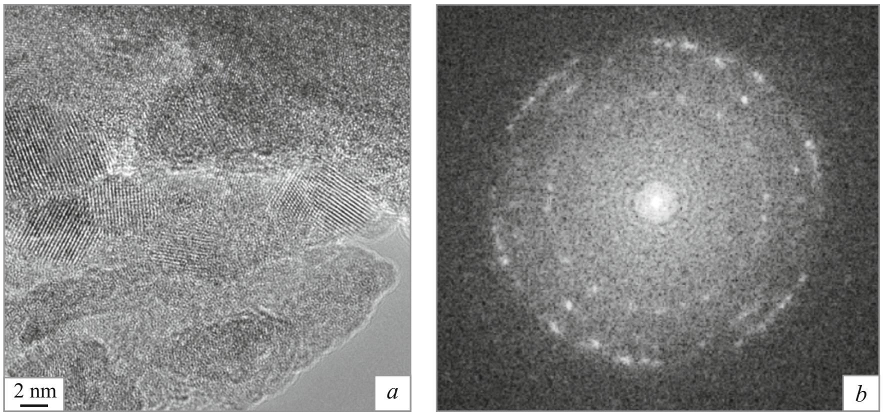


Fig. 5. Nanocrystalline structure (*a*) and electron diffraction pattern (*b*) of high-nitrogen powder alloy Fe – 18% Cr – 8% Ni – 12% Mn – 0.9% N after mechanical alloying for 3.5 h in an ammonia atmosphere.

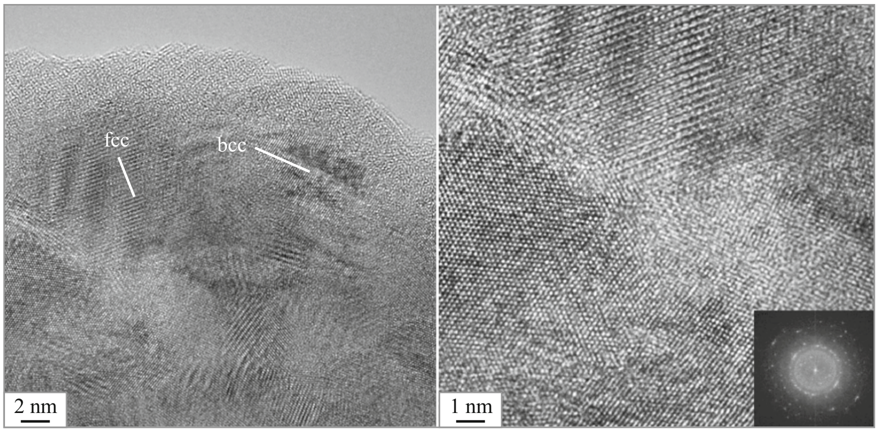


Fig. 6. Nanocrystalline structure and electron diffraction pattern from powder alloy Fe – 18% Cr – 8% Ni – 12% Mn – 0.04% N after mechanical alloying in a nitrogen atmosphere for 3.5 h.

planes near grain boundaries often exhibit substantial distortions or bending of the crystal lattice. Some images of atomic planes break, which indicates the presence of dislocations. The diffraction pattern from regions 0.5 μm in size is represented by numerous reflections arranged on concentric circles (Figs. 5 and 6). This is a sign of the presence of large-angle off-orientations of neighbor grains and of considerable internal stresses in a strongly strained structure. The reflections on the circles are related to the diffraction on the crystal lattice of iron.

The structural features of the grains of nanocrystals studied by high-resolution electron microscopy are quite similar and match the Gleiter model, i.e., the majority of the grain boundaries are large-angle arbitrary ones. This corresponds to the data of the diffraction studies. In addition, the grain boundaries are commonly narrow; their width is 1 – 5 atomic spacings, i.e., is close to the width of grain boundaries in ordinary coarse-grained materials.

We used the methods of spark plasma sintering (SPS) and hot rolling in a shell to obtain compact specimens from powders of a high-nitrogen austenitic alloy. The minimum porosity of the specimens was 0.62 vol.%. Mechanical tests of the compact specimens showed that the maximum strength characteristics were provided by the SPS, rolling with two passes (1100°C, 50% + 900°C, 50%), and austenitizing at 1150°C ($\sigma_r = 1170$ MPa, $\delta \sim 16\%$, see Table 1). The mechanical properties of specimens obtained by the same regime were 1.5 times higher in the case of alloying with 0.9 wt.% nitrogen than in the case of alloying with 0.04 wt.% nitrogen.

DISCUSSION

Several models describing formation of metastable solid solutions and compounds have been suggested to explain the mechanisms of fusion of the substance during mechanical alloying. Works [5] and [6] are examples of investigation of mechanochemical transformations in multicomponent materials. According to the models developed, compounds are formed in such systems in several stages. At first, intense plastic deformation flattens the particles of the initial powders and welds them together forming a composite. In this stage the composite particles have a typical layered structure represented by various combinations of the initial components (Fig. 7). Upon prolongation of mechanical alloying the reaction mixture transforms into a nanosize composite; the formed nanostructure consists of blocks about 10 nm in size. Then the diffusion of the alloying elements from grain boundaries into the bulk of grains yields mixed solid solu-

TABLE 1. Mechanical Properties of the Tested Alloys with Nitrogen

Material	Method of fabrication	N_{ret}, wt.%	$\sigma_{0.2}$, MPa	σ_r, MPa	δ, %	$HV_{0.2}$, kg/mm^2
Alloy Fe – 18% Cr – 8% Ni – 12% Mn – 0.9% N	Rolling at 900°C, 50% (2 passes)	0.78	Rupture behind the mark*			560
	Rolling at 900°C, 50% (2 passes) + 1150°C	0.75	850	970	15	410
	Rolling at 1100°C, 81% + 900°C, 10% + 1150°C	0.74	830	900	16	430
	SPS + rolling at 1100°C, 50% + 900°C, 50% + 1150°C	0.68	1030	1170	16	540
Alloy Fe – 18% Cr – 8% Ni – 12% Mn – 0.04 % N	Rolling at 900°C, 50% (2 passes) + 1150°C	0.03	560	620	15	280
	Rolling at 1100°C, 50% + 900°C, 50% + 1150°C	0.03	570	600	15	270
Steel 08Kh18N10T	Rolling for sheets	–	200	490	40	180

* The rupture occurred in a brittle manner, without formation of a neck or in the grips of the testing machine.

Notes. 1. The specimens of the high-nitrogen austenitic alloy were obtained by rolling in a shell.
2. After the austenitizing at 1150°C the specimens were cooled in air.

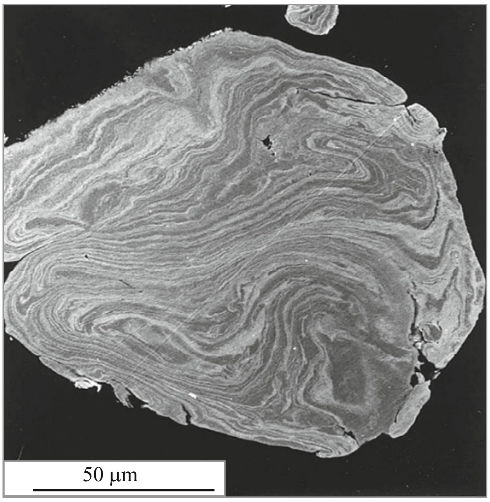


Fig. 7. Layered structure of a particle of a powder of the Ag – Cu system obtained by mechanical alloying [6].

tions. The mixture is homogeneous. The components start to interact, and the products of the synthesis have a chemical composition matching the initial one. Figure 8 presents the evolution of the structure of particles of a Fe – 18% Cr – 8% Ni – 12% Mn powder in the process of mechanical alloying. The powder particles have a layered structure (after 15 min of mechanical alloying the thickness of the layers attains 5 μm; after 30 min it is 100 – 350 nm; after 45 min it is < 100 nm). When the duration of the mechanical alloying is increased, the size of the layers decreases and the structure acquires a nanocrystalline condition, which is confirmed by the results of the x-ray diffraction analysis. Further increase in the time of mechanical alloying causes diffusion of the alloying elements into the iron matrix; the lattice parameter changes due to substitution of the iron atoms in the lattice by atoms of the alloying elements. With allowance for the proportion of the sizes of the components in the Fe – Cr – Ni – Mn system we may assume that the diffusion in mechanical alloying develops in our case primarily over interstices.

The relevant literature suggests different mechanisms of diffusion in mechanical alloying. This is the interstitial diffusion at the moments of pulsed mechanical actions and the diffusion over crystal lattice defects (dislocations, vacancies, grain boundaries etc.). However, there is no direct evidence in favor of this or that diffusion mechanism in mechanical alloying. Direct experiments of many authors have shown that mechanical alloying is a result of a high plastic strain. According to [7], mechanical alloying in a high-power mill is a high-energy pulsed process, where the temperature and the pressure change in a short time interval. At the moment of collision of particles with metallic balls the pressure can reach several thousand atmospheres. Therefore, the pressure appearing in the process should be taken into account when considering the thermodynamics of mechanical alloying.

CONCLUSIONS

We have studied the process of mechanical alloying of iron with austenite-forming elements Cr, Ni and Mn in a nitrogen-containing atmosphere for different periods of time. It has been shown that the first alloying element to dissolve is nickel, then goes chromium, and then manganese. In the initial stage of mechanical alloying each powder particle is a kind of “layer-cake,” i.e., the distribution of the elements in the particle is not uniform. When the time of mechanical alloying is increased, the distribution of the alloying elements over the volume of the powder levels. The powder particles have a layered structure (after 15 min of mechanical alloying the thickness of the layers is 5 μm, after 30 min is attains 100 – 350 nm, and after 45 min it is less than 100 nm). The size of the layers decrease with growth of the time of the process. The nanocrystalline structure of mechanically alloyed powder alloys Fe – 18% Cr – 8% Ni – 12% Mn – xN has special features. It is represented by two structural components, namely, crystalline grains and grain-boundary regions, which agrees with the model of Gleiter. The sizes of the nanocrystals are 6 – 20 nm.

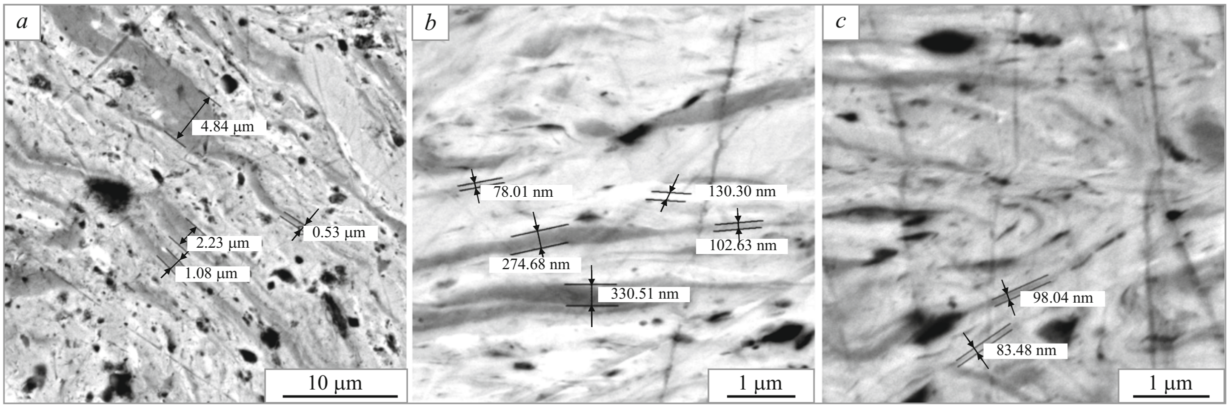


Fig. 8. Evolution of the layered structure of particles of Fe – 18% Cr – 8% Ni – 12% Mn powder during mechanical alloying for 15 min (*a*), 30 min (*b*) and 45 min (*c*).

The work has been performed at the St. Petersburg State Polytechnic University within the subsidy for implementation of complex projects aimed at creation of high-technology productions to fulfill the Ordinance of the Government of the Russian Federation No. 218 of 9.04.2010 "On Measures of State Support of the Development of Cooperation of the Russian Higher Educational Institutions and Organizations Implementing Complex Projects on Creation of High-Technology Productions," by the Ministry of Education of the Russian Federation, Agreement No. 02.G25.31.0094.

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