www.amlett.com, www.vbripress.com/aml, DOI: 10.5185/amlett.2014.6585 Published online by the VBRI press in 2014

Dissolution of alloying elements and phase formation in powder materials Fe-18Cr-8Ni-12Mn-xN during mechanical alloying

Anatoly A. Popovich, Nikolay G. Razumov*

Institute of Metallurgy, Mechanical Engineering and Transport, St. Petersburg State Polytechnical University, Polytehnicheskaya 29, St. Petersburg, 195251, Russia

*Corresponding author. Tel/Fax: +7 (812) 5526623; E-mail: n.razumov@onti.spbstu.ru

Received: 20 June 2014, Revised: 29 July 2014 and Accepted: 03 August 2014

ABSTRACT

In this work, we investigated the effect of the treatment duration on the phase formation and dissolution of alloying elements in the process of mechanical alloying (MA) of iron with austenite forming elements in the nitrogen-containing atmosphere. The influence of MA parameters on the phase composition of the alloy showed the first of the alloying elements dissolved in the lattice of iron are nickel, then chrome and manganese. According to experimental data, the dissolution proceeds through the formation of a layered composite. Also the features of the nanocrystalline structure of powder materials Fe-18Cr-8Ni-12Mn-N, synthesized by mechanical alloying are presented. The nanocrystalline structure of these alloys consists of two structural components: grain-crystallites and grain boundary regions. Such type of structure corresponds to the Gleiter model. Dimensions of nanocrystals are in range from 6 to 20 nm. Copyright © 2014 VBRI press.

Keywords: High-nitrogen austenitic steel; powder alloys; mechanical alloying; nanocrystalline structure.

Popovich Anatoly A. (DSc., Prof.) received doctoral thesis in Powder Metallurgy from Far Eastern State Technical University, Vladivostok, Russia, in 1993. He is serving director of Institute of Metallurgy, Mechanical Engineering and Transport, St. Petersburg State Polytechnical University. The current research interests are powder metallurgy, mechanical alloying, additive technology, materials for lithium-ion battery.

Razumov Nikolay G. is a full time research scholar in laboratory of "Functional materials", St. Petersburg State Polytechnical University. He received Ph.D. in 2014 in Powder Metallurgy. His research interest includes powder metallurgy, mechanical alloying, additive technology, cathode materials for lithium-ion battery.

Introduction

High-nitrogen stainless steels have been extensively investigated lately due to their excellent combination of mechanical properties and corrosion resistance **[1]**. Steel, alloyed with nitrogen, have high strength and ductility, corrosion resistance and stable austenitic structure in a wide range of temperatures.

Today's high-nitrogen steels are commonly produced by high-pressure melting including electroslag remelting processes. Under these conditions, the nitrogen solubility is strongly dependent on the thermodynamic equilibrium achieved between the melt and the nitrogen pressure. From Sievert's law, high-nitrogen contents can only be attained under high-N_2 pressures. However, the need for expensive equipment for high-pressure steel melting is a major constraint **[1]**. Furthermore, because of high temperatures, required to melt the steel, it is absolutely unavoidable to receive coarse materials with poor mechanical properties. The grain size in austenite steels cannot be reduced by heat treatment, which requires multiple pressure processing and eventually leads to the longer process cycle, higher energy consumption and higher material price. In this regard, the powder metallurgy and in particular mechanical alloying method is of considerable interest for nitrogen-containing steels.

Recently, solid-state processes, initiated by mechanical action, have become the subject of the intense research. Apparently, this is due to the prospects of using such reactions in engineering, especially in the field of developing new materials or for improving the properties and performance of existing materials **[2, 3]**.

Mechanical alloying (MA) is a solid-state powder processing technique involving repeated welding, fracturing, and rewelding of powder particles in a high-

energy ball mill **[4]**. MA is carried out at a relatively low temperature, when the formation of a perfect crystal structure is difficult. MA has now been shown to be capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from blended elemental or prealloyed powders. The non-equilibrium phases synthesized include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys **[2, 3, 4]**.

In this method, powder mixtures corresponding to the alloy of interest are mixed and ball milled together under a nitrogen-containing atmosphere. Under these conditions, nitrogen gets absorbed and forms a solid solution with the metallic powder mixture. Enhanced nitrogen solubility can be achieved through these means, concomitant with the development of a nanometric grain structure **[1]**. The "Functional Materials" laboratory, St. Petersburg State Polytechnical University, via MA of iron in the nitrogen-containing atmosphere, obtained the powder of high-nitrogen austenitic alloy Fe-18Cr-8Ni-12Mn-xN with a nitrogen content of 1% (wt) and nanocrystalline structure with a grain size to 30 nm **[5, 6]**.

The present work is focused on establishing regularities between the influence of the treatment time on the phase formation, dissolution of alloying elements in iron during mechanical alloying in the nitrogen-containing atmosphere and investigation features of the nanocrystalline structure obtained alloys.

Experimental

As raw components, we procured powders of iron (99.9 pct), cromium (99.9 pct), nickel (99.9 pct), and manganese (99.9 pct) (Sigma-Aldrich). The nitrogen-containing atmosphere was used gases of high purity nitrogen and ammonia (Linde Gas).

To investigate the influence of the mechanical alloying duration on the dissolution of alloying elements performed a series of experiments in which the powders of Fe-18Cr-8Ni-12Mn were treated in the reactor nitrogen atmosphere for 15, 30, 45, 60 min or 3,5 hrs. Mechanical alloying was carried out in a high-energy ball mill according to the method, described in **[5, 6]**.

Variations in the phase composition and lattice parameters of materials, obtained during MA, were determined using the X-ray diffractometer (XRD, Bruker D8 Advancer) with Cu Kα radiation (λ = 0,154031 nm) at 30 kV and 30mA. The phase composition was studied by the Mossbauer spectroscopy (SM4201TERLAB). The distribution of elements in the volume of the powder particles was determined by the X-ray microanalysis on polished samples by using a scanning electron microscope (Mira 3 Tescan with additive Oxford INCA Wave 500). The fine structure of the powder was studied using the transmission high resolution electron microscope (JEOL-2100F) at an accelerating voltage of 200 keV.

Results and discussion

Investigating the influence of MA parameters on the phase composition of the alloy showed that the first of the alloying elements dissolved in the lattice of iron are nickel (a = 0.3524 nm, r_a = 124 pm), and then chrome (a = 0.2885 nm, r_a = 130 pm) and manganese (a = 0.8890 nm, r_a = 135 nM) (Fig. 1). The reason for this regularity is that the alloying elements Ni, Mn, Cr form a substitution solid solutions with iron, and nickel has the closest to Fe atomic radius - 126 pm. Further in this row have chromium and manganese. It is found that with the increasing time of mechanical alloying the amount of undissolved alloying elements gradually decreases and, at the same time, the process of restructuring the BCC lattice in FCC (**Fig. 1**) begins. After 30 min of MA the contents of γ-phase in the alloy reaches ~3 - 5% (vol.). It is obvious that the rearrangement of the crystal lattice occurs without heating, and the formed γ-phase has a nanometric dimensions. With further increase of the MA duration alloying elements are completely dissolved in the iron and, accordingly, the share of γ-phase in the structure increases, but share of α-iron - decreases.

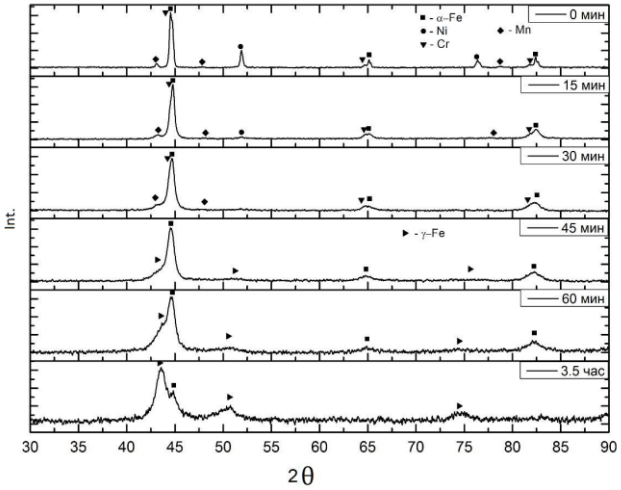


Fig. 1. XRD patterns of the powder Fe-18Cr-8Ni-12Mn-xN at the different mechanical alloying duration.

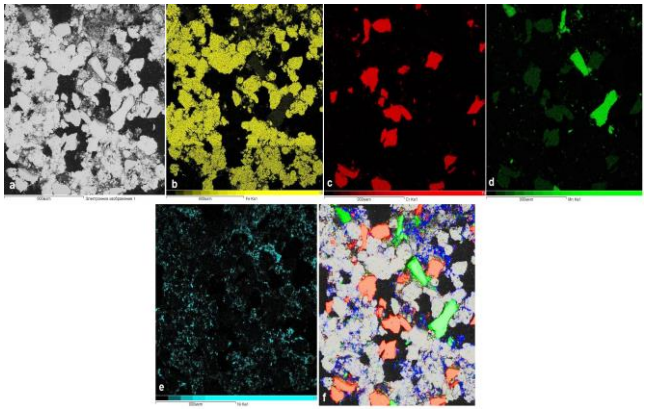
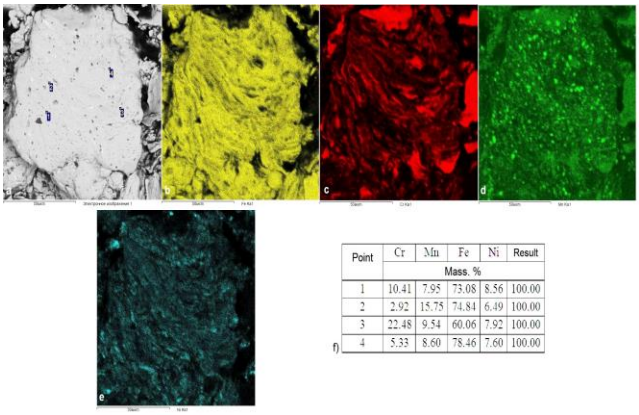


Fig. 2. Distribution of components in the initial powder Fe-18Cr-8Ni-12Mn: a - the structure of the investigated area; b - Fe; c - Cr; d - Mn; e - Ni; f - total distribution of elements.

With the help of the X-ray microanalysis obtained the map of the distribution of components in the volume of the initial powder (**Fig. 2**). From the obtained data it is clear, that the initial powder is a pure mechanical mixture of powders with elements Fe, Cr, Ni, Mn, which are evenly distributed over the entire volume.

We have investigated the change in the structure of the powder mixture during MA for 15, 30, 45, 60 minutes or

3.5 hours. It was found, that at the beginning MA - due to severe plastic deformation - shows the coalescence of the initial component powder particles, and then the process of "deformation atomic mixing ", which is caused by irreversible changes of the shape and size of the powder particles **[1, 2]**. At the short MA duration the obtained powders look like a "layered pancake". It means that the distribution of elements on the powder particles is uneven: there are areas that are rich in one of the alloying elements, and areas with its very low containing (**Fig. 3**). Alloying elements with such an uneven distribution of the powder can give very intense peaks on XRD patterns (**Fig. 1**). The results of the spot chemical analysis (**Fig. 3a**) show that there are areas in the powder particles, where the chemical composition corresponds to the existence of γ-Fe on the Scheffler diagram, but XRD does not reveal it (**Fig. 1**).



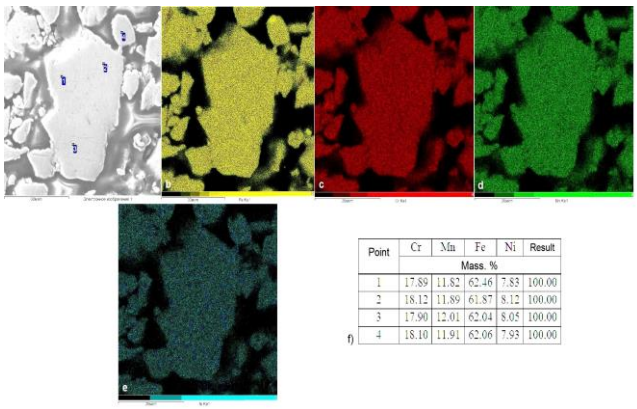
f)

Point	Cr	Mn	Fe	Ni	Result
	Mass. %				
1	10.41	7.95	73.08	8.56	100.00
2	2.92	15.75	74.84	6.49	100.00
3	22.48	9.54	60.06	7.92	100.00
4	5.33	8.60	78.46	7.60	100.00

Fig. 3. Distribution of components in the particles Fe-18Cr-8Ni-12Mn, after 15 minutes MA synthesis: a - the structure of the investigated area; b - Fe; c - Cr; d - Mn; e - Ni; f - spot chemical analysis results.

This is connected with the short duration of the MA process. Due to little synthesis time there are no enough doses of the supplied energy to the elements for solid solution forming, and consequently, there are no shifts in the BCC-FCC lattice. With the increasing MA time, the dose of the supplied energy grows, whereby there is a gradual alignment of the alloying element distribution in the volume of the resulting powder (**Fig. 4**) and BCC transition in the FCC lattice (**Fig. 1**). The results of the spot chemical analysis of powder particles after 3.5 hours of the synthesis show that the alloying elements are uniformly dispersed in the powder and correspond to the chemical composition of the initial powder (**Fig. 4 a**).

Using the high resolution transmission electron microscopy, it was revealed, that the intensive plastic deformation leads to the formation in the Fe-18Cr-8Ni-12Mn-xN alloys the uniform nanocrystalline structure even at an indoor temperature (**Fig. 5** and **Fig. 6**). Nanocrystal sizes are in the range from 6 to 20 nm, and the grain boundaries are not straight. At the grain boundaries there are many dislocations, and atomic planes are partially coherent. However, many boundaries, whose image is badly defined, and the diffraction contrast in the grains is heterogeneous. It is often changed by the complicated method, resulting from high internal stresses and elastic distortion of the crystal lattice. This complex contrast takes place both in the grains, containing lattice dislocations, and in the defect free grains. This demonstrates that the internal stresses result from grain boundaries. The detailed study of structure areas at a higher magnification, when it is possible to resolve individual atoms of the crystal lattice, led to the conclusion, that the grain boundaries are the periodic step formation. The images of the atomic planes near the grain boundaries often present significant bending or distortion of the crystal lattice. Some images of the atomic planes are ragged, indicating dislocations. The diffraction pattern, obtained on the areas with size 0.5 micron, represents a set of reflexes, which are located on concentric circles (**Fig. 5** and **Fig. 6**). This confirms the large-angular disorientation of the neighboring grains in the highly deformed structure and considerable internal stresses. Reflexes on the circles are associated with the diffraction on the iron crystal lattice.



f)

Point	Cr	Mn	Fe	Ni	Result
	Mass. %				
1	17.89	11.82	62.46	7.83	100.00
2	18.12	11.89	61.87	8.12	100.00
3	17.90	12.01	62.04	8.05	100.00
4	18.10	11.91	62.06	7.93	100.00

Fig. 4. Distribution of components in the particles Fe-18Cr-8Ni-12Mn, after MA synthesis for 3,5 hour: a - the structure of the investigated area; b - Fe; c - Cr; d - Mn; e - Ni; f - spot chemical analysis results

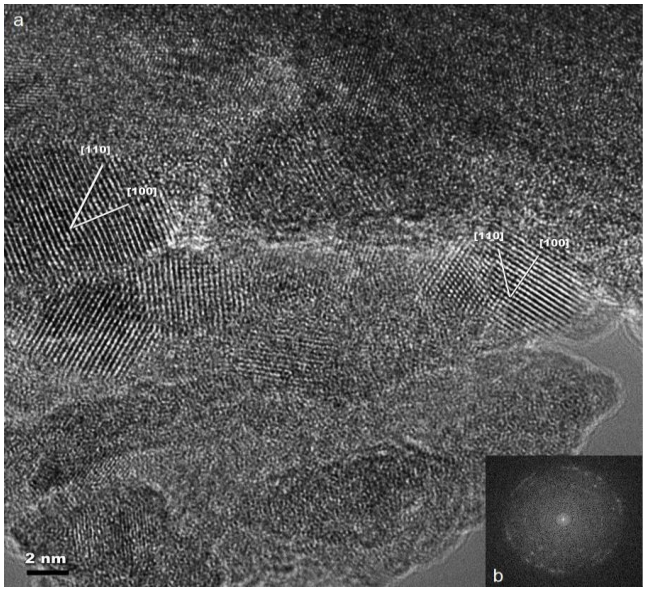


Fig. 5. Nanocrystalline structure of the high nitrogen alloy powder with Fe-18Cr-8Ni-12Mn-0,9N, after MA for 3.5 hours in the atmosphere of ammonia **(a)** and electron diffraction pattern **(b)**.

Structural properties of nanocrystals grains, investigated by the high-resolution electron microscopy, are quite similar and comply with the Gleiter model, where the majority of grain boundaries are large- angular arbitrary boundaries. These data are in line with the diffraction studies. In addition, grain boundaries are usually narrow:

their width is about 1-5 interatomic distances, which is close to the width of the grain boundaries in conventional coarse materials.

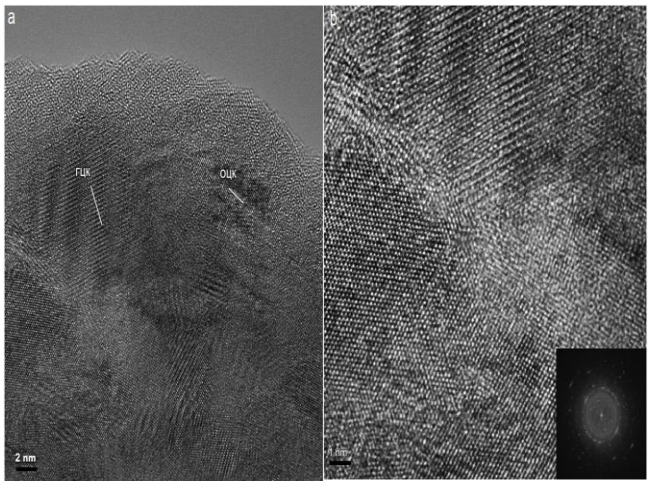


Fig. 6. Nanocrystalline structure and electron diffraction pattern of the powder alloy Fe-18Cr-8Ni-12Mn-0,04N after the MA in the nitrogen atmosphere for 3.5 hours.

In order to explain the alloying mechanisms of materials in the process of MA, proposed a number of models, describing the processes of forming metastable solid solutions and compounds. As examples of studies of MA transformations in multicomponent materials can be taken the work of Suryanarayana C. **[4]** and Elsukov E.P. **[7]**. Under the proposed model, the formation of compounds in these systems occurs in several stages. First, due to the intense plastic deformation the initial powder particles are flattened and welded together to form a composite. The composite particles at this stage have the characteristic of the layered structure, consisting of various combinations of the original components (**Fig. 7**). With the increase of MA processing time, the reaction mixture turns into a nanoscale composite; forms the nanostructure with block size ~10 nm. Then, the diffusion of alloying elements from the border into the grain core causes the formation of mixed solid solutions. The mixture becomes homogeneous. Components begin to interact and form fusion products with a chemical composition corresponding to the initial composition. **Fig. 8** shows the evolution of the particle structure of the Fe - 18 % Cr - 8 % Ni - 12 % Mn powder during MA process. It was established that the powder particles have the lamellar structure (after 15 min of MA layer thickness reaches 5 mkm, after 30 min - 100 - 350 nm, after 45 min - <100 nm). With the increasing MA duration time layers size decreases and the nanocrystalline structure is formed. This is confirmed by XRD analysis. Further increase of the MA duration results into the diffusion of alloying elements in the iron matrix, which leads to a change in the lattice parameter due to the substitution of iron atoms for atoms of the alloying elements.

Currently, the scientific literature discusses different mechanisms of diffusion under MA. These are interstitial diffusion at the moment of pulsed mechanical impacts and diffusion along the crystal lattice defects (dislocations, vacancies, grain boundaries, etc.). However, the direct evidence of the diffusion during MA does not exist. Direct experiments of many authors found that mechanical alloying – is caused by large plastic deformations. The paper **[8]** shows that MA in high-energy mills is a high-energy pulse process, when in a short period of time both temperature and pressure change. At the moment of particle collision with metal balls the pressure can reach several thousand atmospheres. Thus, in reviewing MA thermodynamics, it is necessary to take into account the pressure which arises.

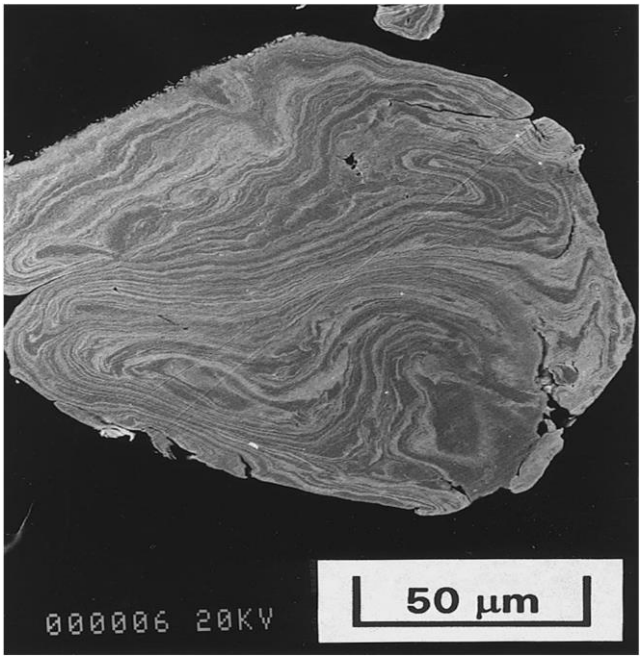


Fig. 7. Layered structure of the powder particles in Ag - Cu system, obtained via MA **[6]**.

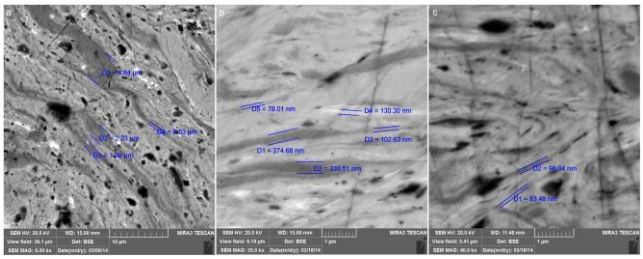


Fig. 8. Evolution of the layered structure of the powder particles Fe-18Cr-8Ni-12Mn during MA with the duration of 15 min **(a)**; 30 min **(b)** and 45 min **(c)**.

Conclusion

Studied MA of iron with austenite forming elements Cr, Ni, Mn in the nitrogenous atmosphere for various periods of time. It was revealed that the first of the alloying elements to dissolve is nickel, then chrome and manganese. At the initial stage of MA each powder particle is like a "layered pancake", and the distribution of elements in the particle volume is uneven. With increasing MA duration, the distribution of alloying elements in the powder volume levels off. It was established, that the powder particles have the lamellar structure (15 min after MA layer thickness reaches 5 µm, after 30 minutes - from 100-350 nm, after 45 min - less than 100 nm). With the increasing MA time, the

size of layers decreases. It revealed the properties of the nanocrystalline structure of MA powder alloys Fe-18Cr-8Ni-12Mn–xN. The nanocrystalline structure of these alloys consists of two structural components: grain-crystallites and grain boundary regions, which corresponds to the Gleiter model. Dimensions of nanocrystals range from 6 to 20 nm. Due with the foregoing will increase the mechanical characteristics of a compact material by 40-60% compared with the conventional method for producing this material.

Acknowledgements
This work has been performed within the framework of scientific research under the project of the state task in the field of scientific activities (contract № 11.2027.2014/K).

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