JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 6 No 3, 03060(5pp) (2014)
ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 6 № 3, 03060(5cc) (2014)

Influence of Magnetic Pulseprocessing on Oxide Materials Physics and Mechanical Properties

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(Received 19 May 2014; revised manuscript received 02 July 2014; published online 15 July 2014)

Internal stresses, specific single-crystal blocks, stoichiometric impurity of oxides composition and other factors lead to low strength properties of ferromagnetic iron oxides. Weakening of such defects and increasing iron oxides microhardness, their fracture and mechanic strength are possible by using magnetic pulse processing. The results of experimental studies of the magnetic pulse field effecting on the iron oxides strength properties are shown. Mössbauer spectroscopy, porosimetry, X-ray structure analysis are used to find the mechanisms of this effect. The strength properties change is the result of set of microscopic and quantum effects superposition. It provides easy defects restructuring of solids: vacancies, dislocations, voids.

Keywords: Magnetic pulse processing, Low-frequency field, Hardening, Defects, Vacancies, Dislocations, Mössbauer spectroscopy, Porosimetry.

PACS number: 62.20. – x

1. INTRODUCTION

The creation and employment of new treatment methods is one of the priorities of modern materials technology. It is often a difficult task to find new invention conceptions and to bring them to their implementation. At the same time, the ways, allowing to obtain structural materials with high performance properties by their electromagnetic pulsed treatment, have already been known. Preliminary results, obtained by the authors of current work, showed that using of weak electric pulsed and magnetic fields was a perspective direction for the development of technologies for performance properties of solids materials and various types of raw materials based on them improvement [1,2]. Using of magnetic pulsed influence for materials hardening undoubtedly predetermines the necessity to find the mechanisms of this hardening. The basis of such mechanisms is changing of the defects concentration and their electric or magnetic state under the influence of electromagnetic fields [3].

It is known that dislocation motion increases under the influence of the magnetic field as spins in the dislocation cores are ordering [4]. However, the problem of the increasing of physical nature macro plasticity of materials in the magnetic field is complicated by indirect measuring the defects motion. Moreover, it is assumed that the mechanism of the fields effect on the defects state, mesostructure of materials and as a result, their strength and ductility properties significantly differ in terms of the nature of solid materials. In particular, the main reason of the field effect on the ductility of crystalline ferromagnetic bodies is changing intensity of the interaction of dislocations with the domain walls. However, the possibility of weak magnetic fields influence on the Coulomb interaction energy of atoms and defects is not considered in this work.

The purpose of this work is realizing the complex research of the nature of magnetic pulsed effects impact on the ferrimagnetic iron oxides microhardness and fracture toughness.

2. THEORETICAL BASIS OF MAGNETIC PULSE TREATMENT

For a long time it was considered [4, 5] that a magnetic field (even the strong one) cannot have a significant impact on the process of oxides crystal lattice reconstruction. However, according to home and foreign authors, if the field impact is carried out on crystals with nonzero magnetic moments of the atoms, situation can change even in the relatively weak magnetic fields. Such fields, changing the particles spin state, can accelerate the lattice reconstruction, can change the defects energy state and, as a consequence, can cause the physico-chemical properties of crystals changing. These ones may lead to ferrimagnetic transition from direct state to the domain structure state after processing in weak low-frequency pulsed magnetic field.

Despite the fact that a large amount of experimental data about the presence of the crystalline materials properties very strong changes in the weak electromagnetic fields has accumulated now, the mechanisms of these changes is remaining poorly understood. It hinders their practical application and conditions of use optimization. This is partly explained by the fact that even traditional methods of materials processing have not received the full explanation in the framework of existing ideas about the strength and plasticity of the solid materials nature. The quantum effects dominate in the mechanisms of magnetic (MF) and electric (EF) fields on crystals influence. The possible mechanisms of these fields action are [6]:

1. The field impact on the point defects state (electrical and magnetic ordering, electron spectrum, aggregation, drift).

2. The impacts on the crystal structure (phonon spectrum, electron spectrum, magnetic and electric ordering, phase transfer).

3. The impacts on dislocations and on the energy of their interaction with the stoppers.

4. The influence on mesostructure (macro effect geometry, porosity, thermal stress, clusters).

The mechanisms of these solid materials parameters

The article was reported at the International Conference «The Advanced Technology, Equipment and Analytical Systems for Materials», Kursk, 13-14 May, 2014 influence differ depending on the solids nature, the self-organization degree, the field strength, etc.

The transformation from metallic to semiconducting state can be under the fields influence in the weakly magnetic materials and because of the new constant-energy surfaces emergence (closed surface turns into open one) and the lattice properties changes. Changes in the strength properties of solid materials under the relatively weak fields influence are in the most cases determined by the type and nature of the point defects interaction with dislocation surfaces (pores) [7, 8].

Such interactions character depends on a lot of factors: possibility of the existence of defect dipole magnetic moment, the elastic anisotropy. As a result, electric or magnetic field can affect the dislocations motion, accelerate the free carriers drift diffusion and electro migration. Then the association of some regions and super saturation other vacancies, the depletion of existed point defects decay aggregates and the formation of new ones may occur [7]. Moreover, the fields can induce metastable states or provide forceful action on items charged nucleus or on the magnetic moment of the dislocation core [8]. However, these factors can not affect the motion of dislocations in weakly magnetic crystals. In such cases, it is necessary to exclude direct physical impact of EF or MF on the dislocation line and to take into consideration the changes in the dislocations structure and condition [9, 10]. Such opportunity has not registered for a long time.

The possibility of the MF effect on the appearance process and the fracture between the dislocation electrons and the stopper should be considered. It is necessary to apply to the energy interaction between dislocations and stoppers change mechanism for these effects explanation.

The reduction of dislocation density in some polycrystalline, the development of ultra fine cell structure and other specific phase transformation have been observed in the grains under the action of MF. The macroscopic defects presence (cracks, pores, external phase inclusions) complicates the transformation of the microstructure processes due to the redistribution and local field enhancement, causing magnetic hydrodynamic instability of the material, the local mechanic stress concentration.

The crystalline iron oxides mechanical properties depend on complex of various factors interaction, which has both direct and indirect effects on the strength characteristics. For instance, the presence of defects and their ordering affect to the strength characteristics in addition extra drag of the dislocations. The defects indirect effect is the nature of the interatomic interactions change. The potential theoretical strength of Fe_3O_4 is $(900\text{-}600)\cdot 10^6$ n/m^2.

It is expected that the low level of iron oxides strength properties is due: the internal mechanical stresses in individual single-crystal blocks, the grain sizes dispersion, nonstoichiometric oxides, and the appearance of Fe^{2+} Jahn-Teller ions.

The parameters, which characterize the brittle materials mechanical properties, are their resistance to cracking, estimated by the load a crack appearance, by the cracks at the prints number and by the microhardness.

Reducing the materials tendency to brittle fracture can be achieved by increasing the mobility of dislocations due to:

1) Facilitating of their detachment from stoppers;

2) Reducing the concentration of these stoppers, as composition homogeneity increases, reducing the concentration of external phases, surfacial and internal porosity;

3) Formation of a coarse-grained structure with low-angle boundaries (in the case of polycrystalline);

4) Reducing the dislocations density and the dislocations ordering.

The most common stoppers for dislocations for polycrystalline samples are dissolved atoms, crystallite boundaries, micro- and nanopores. It depends on the higher solubility of foreign atoms near dislocations than in the undistorted part of the crystal. The atom, which has a large size, is energetically favorable to localize in regions of tension near the dislocation edge; other atoms, witch size is less, are favorable to localize in the compression edge dislocation.

On the other side, the dislocations are the points of vacancies concentration, as the dislocations formation is often due to the precipitation of vacancies. The vacancies are also the main factor for dislocation motions. The dislocations motion hangs on the absorption of the extra half-plane atomic vacancies. As the vacancies deposition nano- and micropores at dislocations can form. As a result of dislocation motion porosity is reduced.

The grain boundaries are similar stoppers as they are sinks for dislocations and they consist of a plurality of dislocations. Therefore, the formation of coarse-grained structure with a grain size of > 6 mm (~ 10 microns) helps to reduce the tendency of the material to brittle fracture.

Some of the factors can be optimized in technological processes: during annealing, quenching, cooling materials. The others can be optimized during the further (non-thermal) processing. For example, a dislocations motion change can be achieved due to dislocations detachment from the retainers (diamagnetic or paramagnetic particles) as a result of the spin-sensitive phenomena; or it can be achieved by creating additional stress in the volume of materials (due to the magneto-electrostriction), as well as by reducing the dislocation density, their ordering and domain walls moving (for ferrimagnetic and ferroelectrics samples). Therefore the inner surface porosity decreases. All these factors contribute to the material fracture toughness. The most probable that such a mechanism is shown in magnetic ordering materials, to which the majority modification of iron oxides relate.

3. EXPERIMENTAL

In the current work the ordering polycrystals and crystals of magnetite (Fe_3O_4) were researched. Magnetite is one of the most important component of the electrical industry and it serves for the preparation of pig iron and steel. The effect of the weak (8-10 kA/m) low-frequency (10-20 Hz) pulsed magnetic fields on the spin state of the iron atoms, the local characteristics of the crystal lattice of the material, as well as their physical and mechanical parameters were investigated. Processing of polycrystalline and crystalline magnetite samples was performed on a device with an automatic control pulse parameters.

During processing, the pulse, their amplitude duration and intervals between pulses were controlled. The Mössbauer spectroscopy investigation of the crystal lattice local characteristics was carried out by spectrometer Ms Em 1104 with automatic processing of Mössbauer spectra. The phase analysis of the samples was carried out by X-ray diffractometer DRON-4M. The determination of specific surface area, total volume, and pore radius distribution by volume performed on the Nova 1200. The microhardness and tendency to brittle fracture performed by standard methods.

4. EXPERIMENTAL RESULTS AND DISCUSSIONS

The Fe_3O_4 strength characteristics, as hardness and cracking load, after treatment in the pulsed magnetic field were increased. So cracks in the initial samples Fe_3O_4 appeared under the load of 30-50 N and the distraction usually took place at the grain boundaries. After treatment Fe_3O_4 cracks appeared under the load of 45-70 N. The microhardness of the sample was increased. Its relative change depended on the number of pulses, and on the initial sample microhardness (Fig. 1).

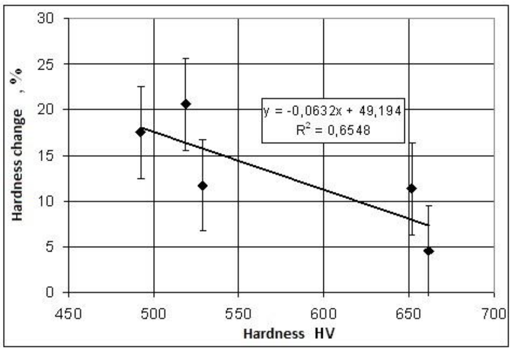


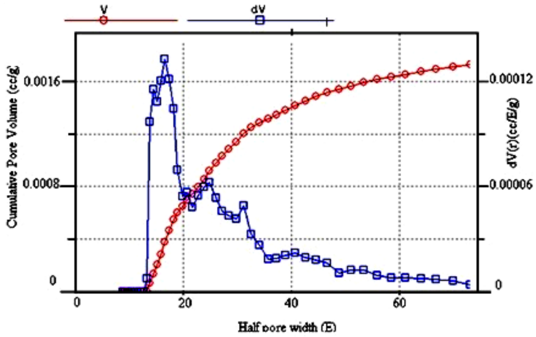
Fig. 1 – Dependence of the Fe_3O_4 samples after magnetic pulse processing relative hardening from the initial samples

This figure shows that the effect depends on the hardness initially Fe_3O_4 increasing. Moreover, such treatment helps to reduce the defects concentration, which is reflected on the change of surface porosity. As an example, Fig. 2 shows the diagram of the pore size distribution for Fe_3O_4.

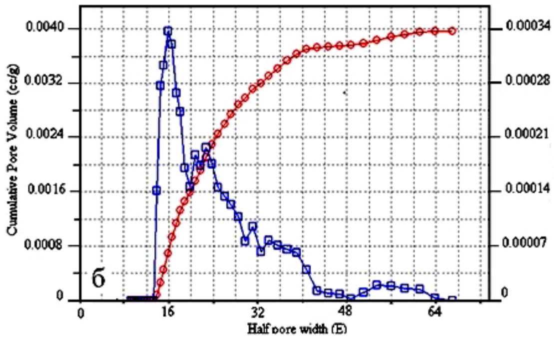
Table 1 – Determination results of the specific surface area and total pore volume of the sample before and after the Fe_3O_4 magnetic pulse treatment

Parameters / Fe_3O_4 sample	pore surface, m^2/g	total pore volume, 10^6 m^3/g
initial state	1,83	0,028
after the magnetic pulse processing	1,61	0,024

Within the Fig. 2 is contained the magnetic pulse processing affects the pore surface, their total amount and size distribution. To explain the observed changes under the influence of magnetic pulse field, it can be used the vacancy- healing defects dislocation mechanism (nano-and micropores). Such a mechanism follows



a



b

Fig. 2 – Pore distribution in the Fe_3O_4 sample:initial (a), after the magnetic pulse processing (b)

from the results of γ- resonance investigations of the crystal structure of the samples. For instance, Fig. 3 shows the Mössbauer spectra of Fe_3O_4, and in Table 2 there are their parameters, which characterize the iron atoms in the structure of magnetite distribution. The table shows that after magnetic pulse treatment the greatest change has been got by the Mössbauer effect probability (from 8 to 10.5 %) Fig. 4, Fig. 5 resonance line has changed of 6-7 %.

The resonance effect ε depends on the isotope content in the sample and Fe_{57} Mössbauer effect probability f, which depends on the mean-square thermal vibrations of atoms $\langle x^2\rangle$, in the direction of γ-radiation or the quantum wavelength of γ-quanta

$$f = \exp\left(-\left\langle x^2\right\rangle / \gamma^2\right), \tag{4.1}$$

where γ is the wave-length of γ-quanta. Then $\langle x^2\rangle$ is less, then more associated atom in the material lattice, and then f and ε is respectively more.

The value f is an integral characteristic of the phonon spectrum. In contrast to macroscopic measurements data, the integral characteristics refer tothe local areas, containing crystal different types of defects, such as vacancies.

After magnetic pulse processing with 30 pulsesvalue of the resonant effect ε increases. Such a variation may be caused by a change of the amplitude atoms fluctuations for two reasons.Firstly, it is change in the force constants for iron atoms, and secondly, it is change in the vibration frequency of the atoms as a result of polymorphic transformations.

In addition the integrated intensity varies relations

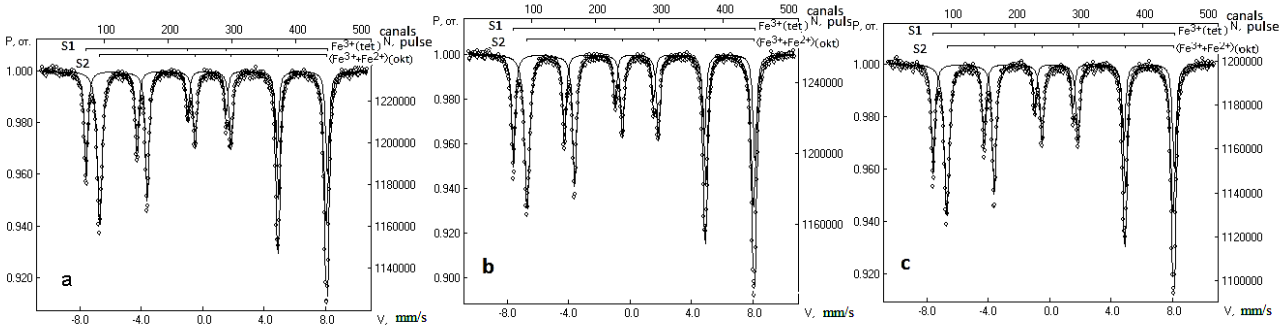


Fig. 3 – Mössbauer spectra of Fe_3O_4 before and after the magnetic pulse processing with the follow magnetic pulses: 0 (the initial state) (a), 10 (b), 50 (c)

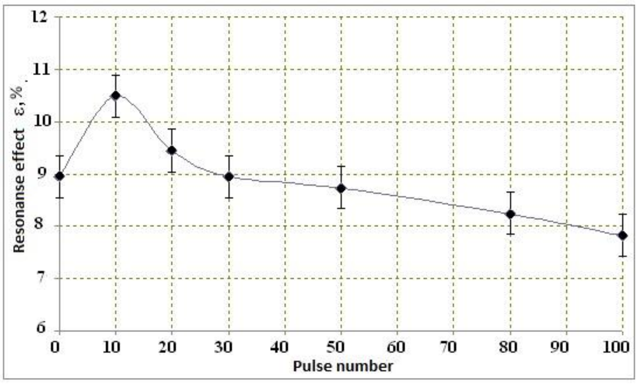


Fig. 4 – Dependence of the Mössbauer resonance effect on the magnetic pulses number

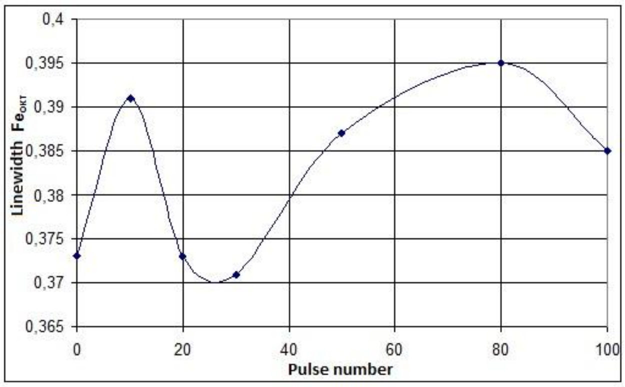


Fig.5. – Dependence of the resonance linewidth *Gokt* on pulse number

Table 2 – Mössbauer parameters of magnetite before and after the magnetic pulse processing

Sample	δ(t)*, mm/s	δ(okt), mm/s	Δ(tet), mm/s	Δ(okt), mm/s	*H*(tet), kOe	*H*(okt), kOe	*S*(tet), %	*S*(okt), %	S_A/S_B	*G*(tet), mm/s	*G*(okt), mm/s	ε, %
Initial	0,268	0,667	-0,008	0,003	489,3	458,9	35,0	65,0	0,539	0,288	0,373	8,94
Pulse	after the magnetic pulse processing											
10	0,264	0,671	-0,008	0,007	489,3	459,4	34,5	65,5	0,529	0,288	0,391	10,4
20	0,270	0,666	-0,003	0,001	489,2	458,6	35,1	64,9	0,540	0,288	0,373	9,44
30	0,267	0,667	-0,003	-0,002	489,1	458,6	34,6	65,4	0,530	0,285	0,371	8,94
50	0,267	0,667	-0,004	0,004	488,8	458,4	34,7	65,3	0,530	0,289	0,387	8,73
80	0,262	0,672	-0,012	0,009	488,3	458,9	34,5	65,5	0,526	0,285	0,395	8,24
100	0,267	0,669	-0,009	0,004	488,8	458,3	35,4	64,6	0,548	0,294	0,385	7,83

* Relatively α-Fe. Mistakes: $\delta = \pm$ 0,001 mm/s; $\Delta = \pm$ 0,002 mm/s; $H = \pm$ 0,1 kOe; G = 0,004 mm/s; $\varepsilon = \pm$ 0,09 %; $S = \pm$ 0,1 %

component of tetra- and octahedral iron ions from 0.52 to 0.55, which is associated with the redistribution of vacancies of iron atoms between octahedral and tetrahedral sites. Such a redistribution of vacancies of iron atoms is accompanied by a change in the width of the resonance absorption line for the octahedral sub lattice (Fig. 5).

The increasing of the resonance line is determined by broadening variations near atomic environment of the resonating nuclei (i.e., the nature of defects), as well as time - limit residence time of the atoms in a localized state (limited type electron transfer $Fe_{2+} \leftrightarrow Fe_{3+}$). The most probable defects in magnetite can be cationic and anionic vacancies. In turn, vacancies are the major factor that provides dislocation motion, as well as the formation of nano- and micropores source, which obstructs the motion of dislocations. This fact is correlated with the Mössbauer research results – Fe_3O_4 (Table 2).

The lack of change in the isomer shift for Fe_3O_4 the observed variation in the areas of components and their relations can be associated with the redistribution of vacancies. This process can be explained as the vacancy-dislocation mechanism of crystal defects healing materials. The magnetic field can stimulate the dislocations motion due to the following processes: separation from stoppers dislocations (defects) and their subsequent displacement- under the influence of internal stress fields increase the dislocation motion domain walls with magnetostrictive stress. All these processes contribute to the reinforcement of materials, a nano - healing and micropores.

5. CONCLUSION

The results show, a magnetic pulse processing result of ferromagnetic materials, their hardness 1.5-1.8 times, crack 1.5-3 times .The reason for magnetic pulse processing hardening of ferromagnetic materials is the impact pulses of magnetic field on the spin system of atoms and defects as a result of which facilitates the process of dislocation and, as a consequence, there is healing pinholes. Use of weak magnetic pulsed fields is a promising direction for the development of technology to improve the performance properties of different materials, from metals to dielectrics.

ACKNOWLEGEMENT

The authors would like to thank Prof. B.A. Staroverov for participating in experimental part of the work and providing the necessary facilities for the preparation of the paper.

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