

Powder Metallurgy Research Trends

Lotte J. Smit
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Editors

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**LOTTE J. SMIT
AND
JULIA H. VAN DIJK
EDITORS**



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POWDER METALLURGY RESEARCH TRENDS

PREFACE

Powder metallurgy is a forming and fabrication technique consisting of three major processing stages. First, the primary material is physically powdered, divided into many small individual particles. Next, the powder is injected into a mold or passed through a die to produce a weakly cohesive structure (via cold welding) very near the dimensions of the object ultimately to be manufactured. Finally, the end part is formed by applying pressure, high temperature, long setting times (during which self-welding occurs), or any combination thereof. In powder metallurgy or ceramics it is possible to fabricate components which otherwise would decompose or disintegrate. All considerations of solid-liquid phase changes can be ignored, so powder processes are more flexible than casting, extrusion, or forging techniques. Controllable characteristics of products prepared using various powder technologies include mechanical, magnetic, and other unconventional properties of such materials as porous solids, aggregates, and intermetallic compounds. This book provides new research on this field from around the globe.

Chapter 1 - The corrosion behavior of finely dispersed powders based on Fe and Fe-Si in 0.85% NaCl solution at 37°C has been studied. The powders were prepared by mechanical milling in organic media and in the presence of graphite. It has been demonstrated that together with the increase of dispersion the corrosion stability of the powders can grow in the process of mechanoactivation. First of all, it can be the case when a surface protective layer is formed when milling occurs in the presence of long-chained surfactants such as oleic acid. If iron is milled in the absence of long-chained surfactants, for example in acetic acid, isopropyl alcohol, and vinyltriethoxysilane, the surface protective characteristics are much worse despite the formation of thick oxide films and doping of the surface layer with silicon. Second, a considerable corrosion stability increase can result from the formation of amorphous phases (Fe-Si-C) in particle bulks in the process of mechanoactivation. At the same time, the increase of the carbide phase content, the encapsulation of the particles in graphite, and the change of grain size (5-100 nm) do not essentially influence the powder corrosion stability.

The second part of the paper is focused on the corrosion-electrochemical behavior of Fe-C powders prepared by dynamic compaction at 500°C, which represented nanocomposites (grain size 40 nm) α -Fe+Fe₃C with the cementite content starting from 9-92 wt.%. It has been stated that the pitting corrosion stability in borate solutions with the admixture of NaCl increases stepwise with the increase of Fe₃C (~50 wt.%) content or with the formation of the ordered net-like cementite structure.

Chapter 2 - Fine and ultrafine powders in the form of metal, ceramic, pharmaceutical, and food ingredients have numerous applications in manufacturing and powder metallurgy, development of sensors, thermal barrier coatings, catalysts, pigments, drugs, and biotechnology, to name a few. There are several methods of powder production, such as wet chemistry, e.g., sol-gel and emulsion, mechanical methods, e.g., ball milling, gas phase methods, e.g., chemical and physical vapor deposition, liquid phase spray methods, e.g., molten metal spray atomization, spray pyrolysis, and spray drying, and liquid/gas phase methods, e.g., flame spray pyrolysis.

Chapter 3 - Factors determining kinetics of physical and chemical conversion, structure of reaction product, and parameters of dynamically loaded reacting powder body surface radiation are investigated by the computer simulation method. The model takes into account structural parameters of the powder material capable of exothermal chemical reactions, an opportunity for phase transfers, formation of a product of chemical reaction, change of an aggregative state of the reacting medium, mechanical activation of the reacting components, the forced filtration of the molten component of a mixture, and change of parameters of a condition on each step of physical and chemical conversions. The algorithm of the numerical solutions of imitating simulation problems of physical and chemical behavior of reactive powder materials has been developed on the basis of the created model, providing the solution of the related problems of a macrokinetics of chemical transformations, mechanical modification of powder materials during dynamic loading, thermal balance and a filtration of a liquid phase. All parameters of the model are repeatedly specified during each step of time. The method for interpretation of experimental results of investigation of physical and chemical processes in the multicomponent reacting systems received by optical pyrometry methods for an estimation of a degree of realization of various stages of physical and chemical conversions, structure modification and other state parameters of reacting powder body, registration of changes of chemical reactions stages, both on the surfaces and in the bulk of the model compact has been developed. The governing factors of researched processes have been investigated during the computer simulation results analysis.

Chapter 4 - Powder metallurgy techniques have been extensively used to fabricate net shape components, and are popular in the current trends in materials processing. Laser Engineered Net Shaping (LENS[®]) is one of the fastest growing laser metal deposition processes, which has combined high power laser deposition and powder metallurgy technologies with advanced methodologies of rapid prototyping, to convert complex virtual objects (CAD solid models) into functional advanced structural components without the need for part-specific tooling. It is an additive versus a subtractive material forming process. With LENS[®] processing, the microstructure can be tailored by controlling both process parameters and composition. In addition to fabricating complex geometries of fully dense metals that require minimal finish machining, the mechanical properties have typically been found to be superior to those of components obtained by conventional processes. In this chapter, recent research and progress associated with the LENS[®] process are reviewed, such as laser materials processing and rapid manufacturing; metal alloys, composites, and cermets development with the LENS[®] process; the effect of process parameters on microstructure, properties, and build of part height; the application of *in-situ* molten pool sensor and Z-height control subsystems; thermal behavior measurement with thermal imaging and thermocouple methods, and numerical simulation; as well as a cost-benefit analysis of the LENS[®] process.

Special emphasis is placed on LENS[®] deposited materials and process control, along with trends and challenges of laser direct fabrication of bulk metallic glasses and nanocrystalline materials, and analysis of residual stress and porosity in deposited materials.

Chapter 5 - In order to further disclose the indirect SLS process, Forming mechanisms and behaviors of selective laser sintering of metal/polymer composite powders within one laser beam point, one laser scanning line and one laser scanning domain are mainly theoretically investigated. Some mathematical and physical models are built to explain these mechanisms and behaviors. It is indicated that all forming behaviors result from the same thermodynamic mechanism which is the decreasment of powders surface energy. The interaction between rigid powders and variable materials decides the energy states during a certain period. Mover, the variation of forming behaviors in laser beam spots, scanning lines and scanning areas are affected by energy distribution of laser beam spot, laser energy accumulation in the prolonged orientation of scanning line and powder material's effective energy density absorbed from laser respectively. The difference between the initial surface energy and final one is the indicate how stable the final mixed material system is. This work enlarges the theory of laser forming during indirect SLS and provides basis for indirect SLS process, which is a good contribution to the development of indirect SLS technology.

Chapter 6 - In order to evaluate distributions of mechanical properties and fracture toughness in ceramic-metal FGMs, mechanical properties and fracture toughness have been investigated on ceramic-metal non-graded composites (non-FGMs) and FGMs. The materials were fabricated by powder metallurgy using partially stabilized zirconia (PSZ) and austenitic stainless steel (SUS 304). Vickers hardness, Young's modulus and bending fracture strength are examined on smooth specimens of non-FGMs. The Vickers hardness continuously decreases with an increase in a volume fraction of SUS 304 metal phase, while the Young's modulus and fracture strength exhibit the low value in the non-FGMs with balanced composition of each phase. This suggests that the interfacial strength between the ceramic and metal phases is very low. The fracture toughness is determined by conventional tests for several non-FGMs with each material composition and by a method utilizing stable crack growth in FGMs. In contrast with the Young's modulus and fracture strength, the fracture toughness increases with an increase in a content of SUS 304 on both FGMs and non-FGMs and it is higher in the FGMs than in the non-FGMs. Under the assumption that the high fracture toughness in FGMs is attributed to the residual compressive stress in the ceramic-rich region created in the fabrication process, the residual stress distribution in the FGMs is estimated from the difference in fracture toughness between the FGMs and non-FGMs.

Chapter 7 - Conventionally, hardness is a primary parameter to determine the wear resistance of high volume ceramic reinforced metal matrix composites. However, this study reports that the friction coefficient and wear characteristics of these metal matrix composites are strongly controlled by their microstructural parameters and are independent of their hardness. Ratio of average grain size to the mean free path of binder phase was found to be a controlling microstructural parameter for wear performance. Metal matrix ceramic reinforced composites with higher ratio of grain size to mean free path of the binder phase can exhibit higher wear resistance and lower friction coefficient.

Chapter 8 - Reactive hot pressing (RHP) is widely recognized as an effective technique to prepare dense metal matrix composites (MMCs) reinforced with in-situ ceramic particulates/whiskers in one processing step. Ultrafine ceramic reinforcements are formed in-

situ by exothermic reactions between elemental and/or compound powders during hot pressing. They are distributed uniformly within the metal matrix of MMCs. Moreover, the reinforcement-matrix interfaces are clean, resulting in a strong interfacial bonding. These enable effective load transfer from the metal matrix to ceramic reinforcements during mechanical loadings. Inherently, the in-situ MMCs exhibit improved mechanical strength, rendering them potential candidate materials for structural engineering applications. In the present review article, recent developments in the structure and mechanical properties of the RHP prepared aluminum, copper and titanium-based composites reinforced with in-situ ceramic particulates/whiskers are addressed and discussed. Particular attention is paid to the beneficial strengthening effects of in-situ TiB_2 particulates or TiB whiskers in the composites.

Chapter 9 - A simple route to produce high strength bulk nanostructured aluminium is presented in this work,. Firstly, a thermally stable nanocomposite Al powder is prepared by attrition milling of elemental Al in the presence of ammonia gas or urea. Both substances are dissociated during milling, enriching the nitrogen and carbon content of aluminium powder.

Then, the milled powder is consolidated to full density by a conventional press-and-sinter powder metallurgy (P/M) technique. Sinterability was improved by using copper powder, as additive, during milling. Shaped specimens possess a stable microstructure, with a grain size of about 150 nm, and their ultimate tensile strength (550MPa) surpass that of most commercial Al alloys, especially at high temperatures.

This new consolidation method may be of interest with a view to manufacturing large batches of small parts, a typical task for the automotive industry.

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Chapter 1

FORMATION OF CORROSION STABILITY OF FE-BASED POWDERED AND COMPACTED MATERIALS

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ABSTRACT

The corrosion behavior of finely dispersed powders based on Fe and Fe-Si in 0.85% NaCl solution at 37°C has been studied. The powders were prepared by mechanical milling in organic media and in the presence of graphite. It has been demonstrated that together with the increase of dispersion the corrosion stability of the powders can grow in the process of mechanoactivation. First of all, it can be the case when a surface protective layer is formed when milling occurs in the presence of long-chained surfactants such as oleic acid. If iron is milled in the absence of long-chained surfactants, for example in acetic acid, isopropyl alcohol, and vinyltriethoxysilane, the surface protective characteristics are much worse despite the formation of thick oxide films and doping of the surface layer with silicon. Second, a considerable corrosion stability increase can result from the formation of amorphous phases (Fe-Si-C) in particle bulks in the process of mechanoactivation. At the same time, the increase of the carbide phase content, the encapsulation of the particles in graphite, and the change of grain size (5-100 nm) do not essentially influence the powder corrosion stability.

The second part of the paper is focused on the corrosion-electrochemical behavior of Fe-C powders prepared by dynamic compaction at 500°C, which represented nanocomposites (grain size 40 nm) α -Fe+Fe₃C with the cementite content starting from 9-92 wt.%. It has been stated that the pitting corrosion stability in borate solutions with the admixture of NaCl increases stepwise with the increase of Fe₃C (~50 wt.%) content or with the formation of the ordered net-like cementite structure.

INTRODUCTION

In recent years, interest in nanocrystalline metal materials has been spurred by the discovery that a decrease in the crystallite size below a certain threshold value can dramatically change the properties of crystallites. Such effects arise when the average grain size does not exceed 100 nm and are most pronounced for sub-10-nm grains. Because of such small sizes, the specific area of the grain boundaries is very high and developed, and hence, nanocrystalline materials significantly differ in their properties from common polycrystals [1].

One of the simplest and most effective ways of producing nanocrystalline materials is mechanoactivation (mechanical milling and fusion) [2, 3]. A variety of processes that occur during its performance result in the production of nanocrystalline composite materials and make it possible to control their structural, phase, morphological, thermal and other properties. The Fe-based powders thus prepared can be applied as magnetic data carriers, magnetic drug carriers, in magnetic liquids, etc.

It is known that ductile metals are milled only in the presence of adsorbents [4-6]. Mechanoactivation in organic media both increases the dispersivity of powders and stabilizes them by forming a protective surface layer that can vary in composition and structure depending on a milling medium and time [7-11]. The powders prepared by mechanoactivation can be used as precursors for producing compacted nanocomposites.

The focus of the present study has been the influence of phase composition and surface layer structure on the corrosion behavior of nanocrystalline Fe and Fe-Si powders formed in the course of milling in organic media. Namely, the influence of the cementite content and its nanocrystalline state on the electrochemical characteristics of α -Fe+Fe₃C composites prepared by compacting powders mechanoactivated in carbon-containing media will be studied.

MATERIALS AND METHODS

The powders were prepared by mechanical milling of carbonyl iron, containing less than 0.03wt.% of carbon, or a Fe-Si alloy (20at.%Si) in a Pulverizette 7 planetary ball mill in the following organic media:

- 1 Fe or Fe-Si in heptane alone and heptane with oleic acid (0.3 wt %). The milling time (t_{mil}) varied from 1 to 99 h;
- 2 Fe in heptane with triethoxy(vinyl)silane (0.3 wt %), $t_{\text{mil}}=1-99$ h;
- 3 Fe in oleic acid and triethoxy(vinyl)silane (10wt.% solutions in heptane, 100%), in acetic acid and isopropyl alcohol (100%), $t_{\text{mil}}=24$ h. An excess of oleic acid taken in concentrations 10% and 100% was removed by a multiple washing of the powders in heptane;
- 4 Fe with graphite in the atomic ratio 85:15 in argon atmosphere; $t_{\text{mil}}=16$ h.

Vessels and balls were made of ShKh15 steel containing C 1% and Cr 1.5% in order to minimize external contamination of the powders during pulverization. Forced air cooling was used to prevent the vessels from being heated above 60°C during milling.

To prepare α -Fe+Fe₃C composites, powders obtained by milling Fe with graphite taken in proportion Fe_{100-x}C_x (x=5, 10, 15, 20, 25 at.%) in Ar medium (t_{mil} = 16 h) as well as by milling Fe in 0.3 weight % vinyltriethoxysilane (t_{mil} = 48 h) were used. The powders were compacted by a magnetoimpulse compacting method [12], which makes it possible to prepare materials whose densities approach theoretical values and which preserve their nanocrystal state due to relatively low heating temperatures (500°C). The compacting was attended with a continuous pump-down using a high-pressure impulse 3 GPa in amplitude and 300 μ s in duration. Before compacting the samples had been subjected to vacuum degassing and held at the temperature of the following compaction (500°C) for an hour. The samples obtained were disks with a diameter of 15 mm and thickness from 2 to 4 mm.

The powders were annealed under argon at 400, 500 and 800°C for an hour. The annealing scheme involved heating to a given temperature at a rate of 60 K/min, holding at this temperature, and cooling at a rate of 100 K/s.

X-ray diffraction analysis was performed on a DRON-3M diffractometer (FeK α radiation). When detecting structural and substructural parameters, the shapes of the K α 1 and K α 2 reflections were approximated by the Voigt function. Carbonyl iron powder annealed at 850°C for 2 h was used as a standard. The mean grain size was determined by harmonic analysis [13].

Mössbauer resonance studies were carried out on a YaGRS-4M spectrometer (constant acceleration mode, ⁵⁷Co in the Cr matrix as a γ -radiation source). The distribution functions P(H) of hyperfine magnetic fields (HFMFs) were determined from the spectra by using the generalized regular algorithm [14].

The analysis of the chemical states of the elements in the surface layers of particles was carried out by X-ray photoelectron spectroscopy (XPS) on an ES-2401 spectrometer with a magnesium anode. The spectrometer chamber was evacuated to a residual pressure of 10⁻⁵ Pa; line positions were measured to within 0.2 eV. The spectrometer was calibrated against the Au4f_{7/2} line (84.0 eV). The bonding energy E_b of the line of C1s electrons in the alkyl group was taken to be 285.0 eV.

IR spectra were recorded on an FSM-1202 FTIR spectrometer (resolution 4 cm⁻¹) in the 1000÷4000 cm⁻¹ range. The spectra of the powders obtained with oleic acid were recorded for the particles forming a sol in heptane. The sol was applied to CaF₂ windows and dried.

The size distributions of the particles were determined on an Analysette 22 laser diffraction microanalyzer. The surface morphology of α -Fe+Fe₃C composites was examined by atomic force microscopy with a P47-SPM-MDT scanning probe microscope.

Electron microscopy studies were performed with a Jeol JEM2000 FXII microscope (accelerating voltage 200 kV) and a JAMP-10S Auger spectrometer.

CORROSION AND ELECTROCHEMICAL TESTS

Just like meaningful real-life corrosion processes, the corrosion of the majority of finely dispersed Fe-based powders runs in neutral media. For example, the powders can be affected by atmospheric corrosion; and in the case of magnetic biomaterials the powders represent water-based pulp with pH close to 7. Therefore, saline (0.85% NaCl at 37°C) was selected as a model medium for corrosion tests.

As opposed to acid media, where direct monitoring of the evolving hydrogen volumes is possible, no straightforward methods of detecting corrosion losses in Fe-based finely dispersed powders exist. Circumstantial methods based on measuring magnetic characteristics are used here to estimate the stability of finely dispersed materials [15, 16].

To determine metal corrosion losses in neutral and alkaline media a weight method has been widely used. After the test all surface and pitting products of metal corrosion must be removed by acid etching in the presence of an inhibitor or by cathode polarization, with weight losses in unoxidized metal being as low as 3-5% of the total corrosion losses. Such an approach was shown inapplicable in the case with finely dispersed iron (300-500 nm) [17], since a few seconds was enough for the powder to dissolve in the etching solutions recommended, even if the inhibitor content was increased an order of magnitude.

A technique for investigating corrosion stability of Fe powders in neutral media was suggested in [17], which was based on determining the difference in the volumes of hydrogen evolved during dissolution of the sample in acid before and after the corrosion test. Hydrogen volumes were equivalent to the content of unoxidized metal in samples, while their difference – to corrosion losses.

In kinetic studies this method requires multiple tests to be taken with different times of samples exposure in corrosion medium. Furthermore, it is invalid for the investigation of the powders with the increased stability to acid etching, for example the ones based on Fe-Si alloys.

The basic reaction during iron corrosion in neutral media is oxygen reduction. This is why we suggest direct monitoring of the content of oxygen absorbed in the course of the powder corrosion. This approach is appropriate for acid-stable powders and does not require multiple tests for corrosion kinetics study. In case a protective layer is present on the powder particle surface, an incubation period is observed during which oxygen absorption speed is relatively small. The destruction of this stabilizing layer results in a more intense oxygen absorption, which is reflected on the absorbed oxygen volume – exposure time curve as a distinct bend. There is a correlation between the incubation period duration and the surface layer protective characteristics.

The speed of the powder corrosion after the protective layer destruction can be determined with a tangent of a tilt angle of straight areas of exposure time - absorbed oxygen volume curves. This technique is however not very exact, since not only metal is oxidized by oxygen, but iron (II) compounds formed during corrosion as well.

Electrochemical investigations of compacted composites $\alpha\text{-Fe}+\text{Fe}_3\text{C}$ were conducted in 1) borate buffer solution 0.3M H_3BO_3 (in the presence of 5M NaOH to reach $\text{pH} = 7.4$) 2) the same borate buffer solution + 0.01 M NaCl. The investigations were performed with a potentiometer IPC-Pro at room temperature in conditions of natural aeration. Chloride-silver and platinum electrodes were taken as reference and auxiliary electrodes, respectively. All the potentials are given with reference to a standard hydrogen electrode, and currents are converted to the visible area of the sample surfaces. Epoxy resin was used to isolate the samples. Distilled water was used to prepare the samples. Before the electrochemical tests the sample surfaces were smoothed out with abrasive paper and polished with Al_2O_3 wetted in distilled water.

Corrosion potential was determined and potentiometric studies were held after the electrode had been held in the solution for no less than 1 h until a steady state was reached. Anodic polarization was conducted starting with corrosion potential with the scan velocity –

0.5 mV/s. Cathodic activation of the samples was conducted at -0.8 V for 10 minutes. Local activation potential was determined at current density of $20 \mu\text{A}/\text{cm}^2$.

RESULT AND DISCUSSION

1. Corrosion of finely dispersed iron-based systems

1.1. Milling in Heptane and Heptane with Addition (0.3wt.%) of Oleic Acid

The micrographs of the powders ($t_{\text{mil}}=24$ h) are shown in figure 1. Upon milling in heptane, particles have a stonelike form, whereas those milled in oleic acid solution represent thin (to $1 \mu\text{m}$) plates. Figure 2 demonstrates the particle size distributions ($t_{\text{mil}}=24$ h). The mean size of the particles prepared in heptane at $t_{\text{mil}}=24$ h is equal to $18 \mu\text{m}$; in oleic acid solution, to $8 \mu\text{m}$; and at $t_{\text{mil}}=99$ h, to 30 and $4 \mu\text{m}$, respectively. Over long-term treatments, the fine milling in heptane reaches its limit and a reverse process (coagulation) becomes prevalent. The use of a surfactant (oleic acid) preventing aggregation allows us to obtain small particles with narrow particle size distribution.

The phase composition of powders prepared by milling in both media over $1\div 47$ h is identical and does not differ from the initial composition: powders contain only one bcc-phase, although the lines in diffractograms are broader (figure 3). On milling over 99 h, peaks corresponding to cementite Fe_3C appear in diffractograms. The grain sizes were calculated by broadening the X-ray lines (figure 4a). After just one hour of milling in heptane, the grain size falls to 11 nm; after milling in oleic acid solution, to 24 nm; i.e., $t_{\text{mil}}=1$ h was enough to obtain $\alpha\text{-Fe}$ in a nanocrystalline state. An increase in treatment time leads to a decrease in the grain size to 4 nm.

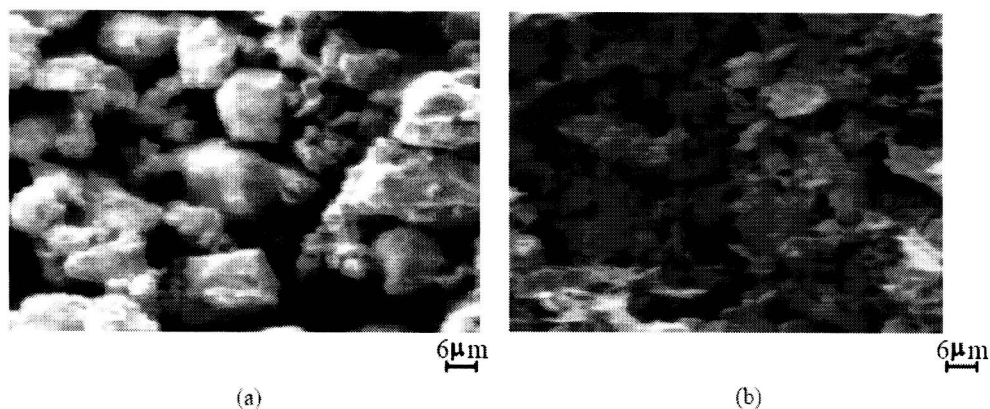


Figure 1. Micrographs of powders after 24 h milling in heptane alone (a) and heptane with oleic acid (b).

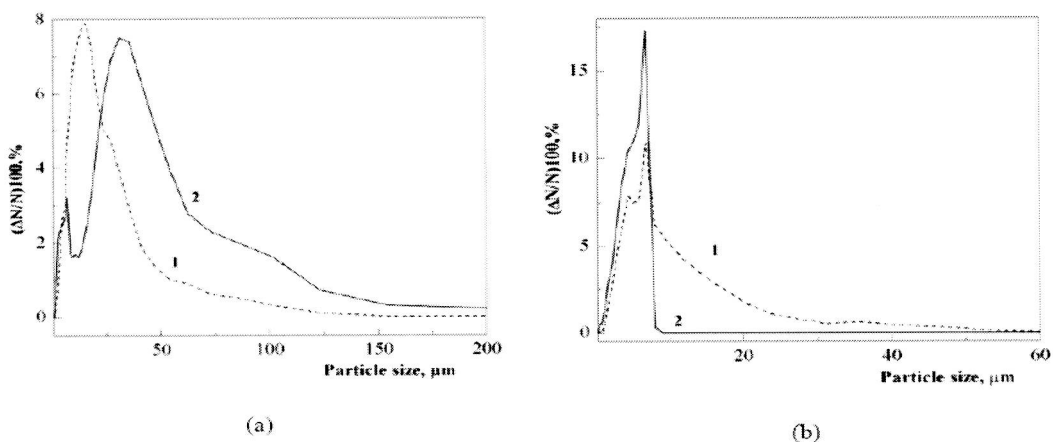


Figure 2. Size distributions of particles prepared by iron milling in heptane alone (a) and heptane with oleic acid (b) for (1) 24 h and (2) 99 h.

No changes (compared with the initial powder) are observed in Mössbauer spectra of the powder after milling over 1 h in heptane (figure 5). A new component with a lower value and wide distribution $P(H)$ of HFMFs appears after milling for 3 h and more (Fig. 5b). Its appearance is clearly seen from the positions of the spectra with respect to the nonresonance level represented by horizontal solid lines (figure 5b). After the thermal treatment of the samples (heating up to 500°C), a second sextet appears in the spectra of the powders milled over 3–47 h; the value of $H=208$ kOe obtained for this sextet agrees well with that for carbide Fe_3C [18, 19]. At $t_{\text{mil}}=99$ h, carbide Fe_3C begins to form directly in the course of milling.

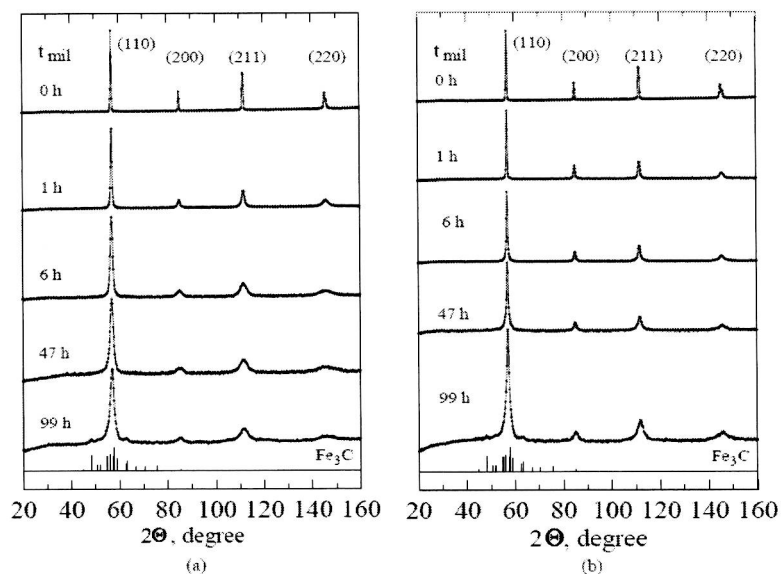


Figure 3. X-ray diffractograms of iron powder milled in heptane alone (a) and heptane with oleic acid (b) over various times. Indices of reflection of the bcc-structures are indicated at the top of the figure, positions of the most intense reflections of Fe_3C are shown at the bottom part of the figure.

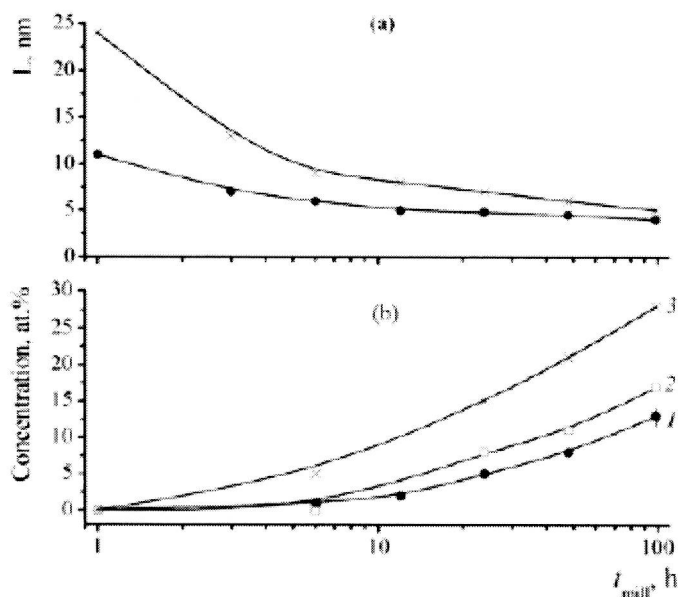


Figure 4. (a) The mean grain size $\langle L \rangle$ and (b) concentration of impurities (1 – carbon, 2 – oxygen, 3 – total concentration of carbon and oxygen) as function of the time of iron milling in heptane alone (solid points) and heptane with oleic acid (crosses, squares).

Mössbauer spectra of the powders prepared in a surfactant solution at $t_{\text{mil}}=1\text{--}24$ h (figure 6) are similar to those described above; however, the formation of Fe_3C begins after just 47 h of milling. After annealing of the powders milled over 12 h and more, sextets appear, for which H_1 and H_2 values are equal to 490 and 460 kOe, respectively, which corresponds to Fe_3O_4 [20].

The amounts of Fe_3C and Fe_3O_4 formed at each milling time were determined from the Mössbauer spectra of the milled and thermally treated powders (500°C). Assuming that, after thermal treatment, all of the carbon is in the Fe_3C phase and all of the oxygen is in the Fe_3O_4 phase, we calculated the dependence of the total content of carbon and oxygen in the particle bulk on the time of milling (figure 4b). The amount of carbon at $t_{\text{mil}}=99$ h reaches 12 at. % in both media, and the amount of oxygen is equal to 17 at.% in oleic acid solution. Carbon and oxygen are the products of the decomposition of heptane and oleic acid during mechanical activation.

The analysis of Mössbauer spectra revealed that the maximum amount of carbon present in the form of a solid solution in iron is as high as 8 at. % (2 wt.%); further saturation with carbon leads to the precipitation of carbide Fe_3C . It follows from all the results obtained that milling of iron in heptane and oleic acid solution results in the diffusion of carbon and oxygen from the particle surface layers along the grain boundaries into the particle bulk with the formation of amorphous-like carbide and oxycarbide phases [21, 22].