Nanostructured Fe-based materials obtained by mechanochemical synthesis in organic liquids

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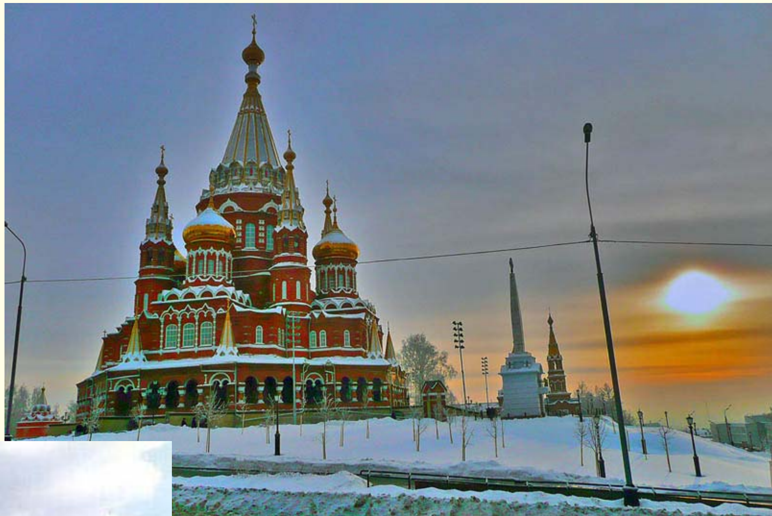
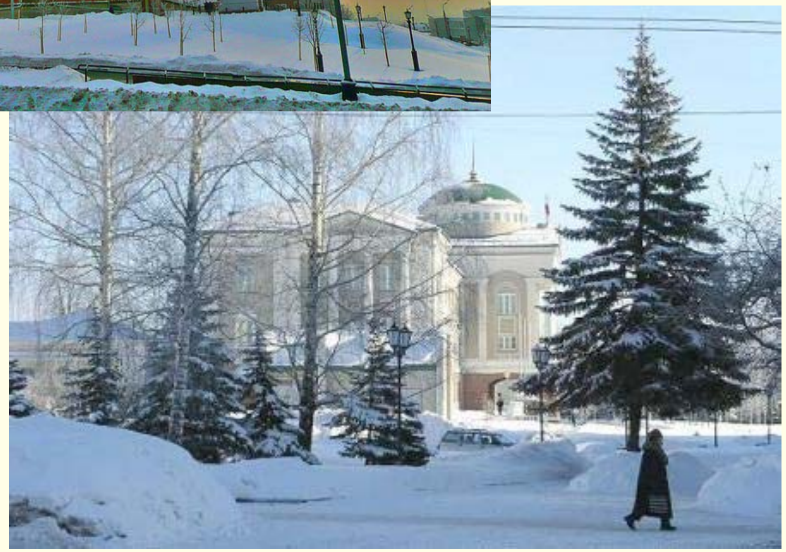




Nanocrystalline materials

New functional materials → High mechanical, anticorrosion, antifriction, thermal stability, magnetic and other properties

Nanocrystalline materials

- Small grain size (~10-100 nm)
- Extended grain boundaries (up to 50% atoms are in the surface state)
- Grains free of structure defects (dislocations, disclinations)

→ New physical properties

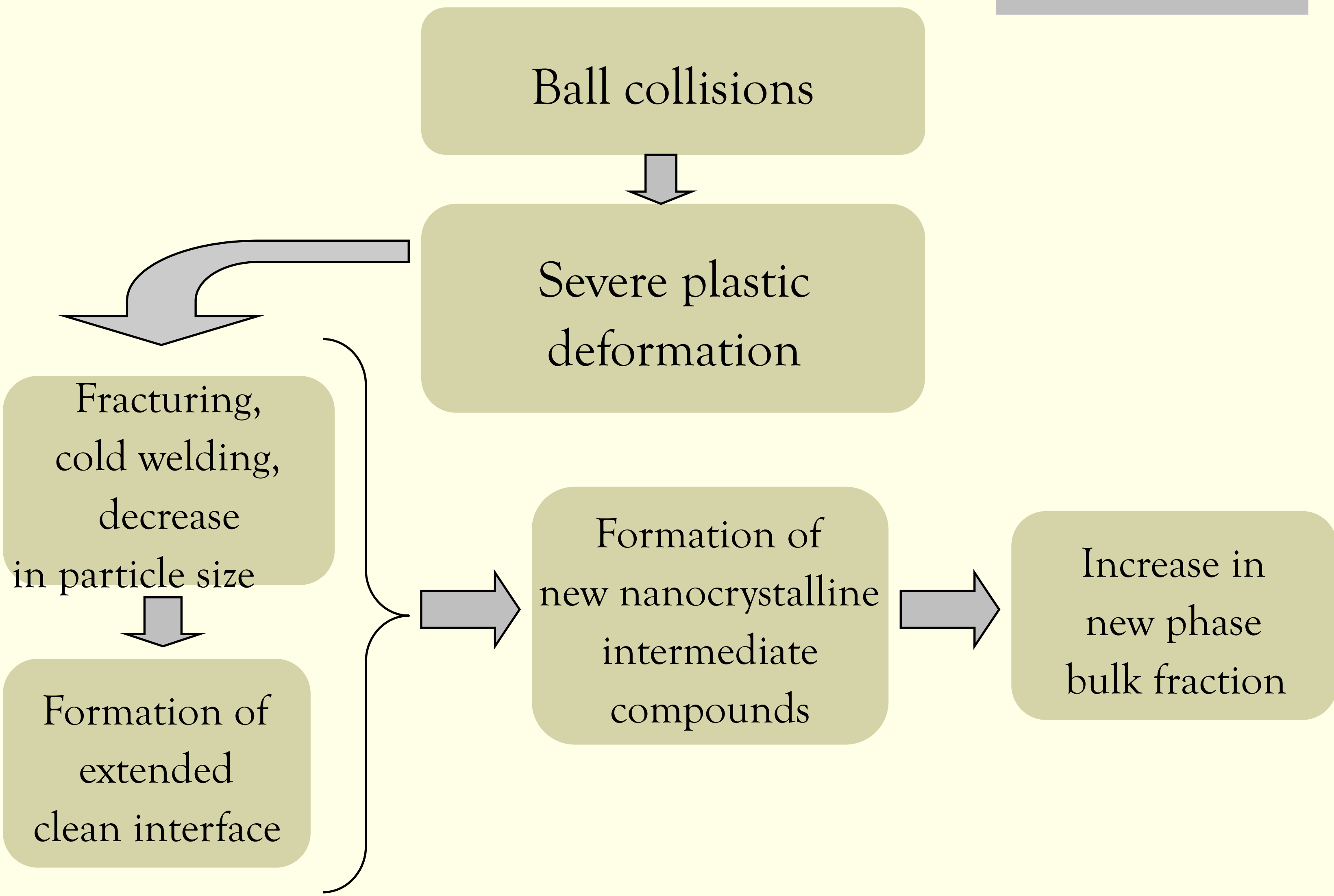
Mechanochemical synthesis:
Its advantages

Mechanoactivation – mechanical milling and alloying – **severe plastic deformation** technique

- Effectiveness
- Simplicity
- Small average **particle** size
- Small average **grain** size

(particle size and grain size: **5-10 nm**)

Mechanochemical synthesis:
What does it mean?

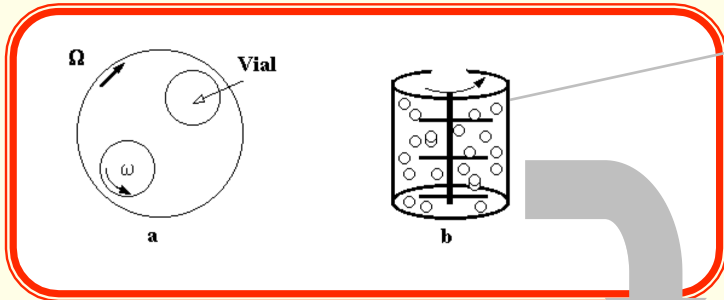


Experimental: Milling Equipment

Mechanical Milling Technique: Equipment

Planetary Ball mill

Fritsch Pulverisette 7



T<80^{o}C

w=25g

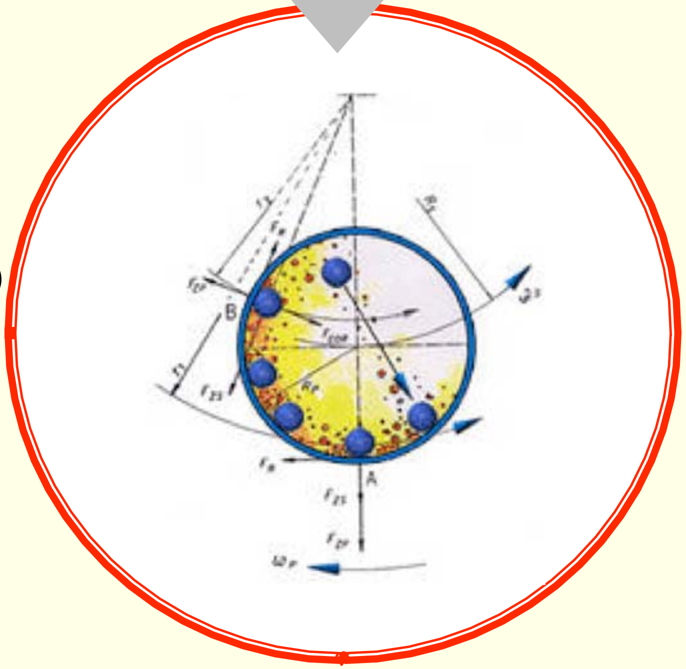
2 vials 45 ml

16 balls (d=12mm)

Hardened steel

(C – 1 wt.%

Cr – 1.5 wt.%)



Experimental: Materials

Powders milled

Fe	$Fe_{80}Si_{20}$ alloy
σ_s = 220 A m^2/kg	σ_s = 150 A m^2/kg
H_c = 8.5 A/cm	H_c = 10 A/cm
T_c = 770 °C	T_c = 592 °C

Fe-based

- Technologically important materials
- Huge basic information accumulated before
- Possibility of using Mössbauer spectroscopy to analyze the local atomic structure

Fe-Si

More disperse and corrosion-resistant powders were supposed to be obtained (compared with Fe) with keeping magnetic characteristics

Fe-Si-C

Technologically important system for iron and steel production

Experimental: Milling conditions

Processes under fine and hyperfine dispersion?

Effect of external environment on the process and energy of destruction?

Milling of metals and alloys in the liquids is used for **rapid reduction of particle size,** obtaining **homogeneous particle size distribution,** changing **structure, phase composition and properties**

Heptane

T_b = 98 °C > temperature of outer vial wall during milling (~ 80 °C)

Surfactant additive

(0.3% solution)

- maximal effect of lowering the mechanical strength
- effective stabilizing layer on the Fe highly-dispersed powder surface

Effects by using surfactant additives:

Plastification,

increase in fragility,

spontaneous self-dispersion

t_{mil} = 1 ÷ 99 hours

Experimental: Milling conditions

- **Milling media**
  - **Organic liquids**
    - **Heptane**
      $CH_3(CH_2)_5CH_3$
    - Heptane + surfactant
      Oleic acid
      ($C_{17}H_{33}$-COOH)
      0.3 % solution
    - Heptane + surfactant
      Viniltrietoksisilan
      (CH_2=$CHSi(OC_2H_5)_3$)
      0.3 % solution
  - **Ar^+**

Experimental: Annealing conditions

- Annealing temperature T_{an} =300, 400, 500, 800 °C
- Atmosphere vacuum (10^{-3} Pa), Ar^{+}
- Annealing regime:

Heating up to T_{an} (60 °C/min) → Soaking at T_{an} for 1 hour → Cooling down to the room temperature (60 °C/min)

Experimental: Measuring techniques

- Structure and phase characterization of the powder bulk:
  - **XRD** (DRON-3M, Cu K_a)
  - **Mössbauer spectroscopy** (NGRS-4M spectrometer)
- Chemical composition and topography of the powder surface:
  - **Laser diffractometry** (Analysette22)
  - **AES**
  - **SEM**

  (AES, SEM: Auger electron microprobe JAMP 10S)
  - **AFM** (Scanning tunneling microscope P4-SPM-MDT)
  - **TEM**
- Magnetic properties
  - **Thermomagnetic behavior**
  - **Coercivity**
  - **Saturation magnetization**

Fe in organic liquids:

The aim of study

◇ Initial stages of synthesis including **formation of the interface** between reagents, **breaking interatomic bonds**, **migration of reagent atoms**, **formation of interstitial compounds**

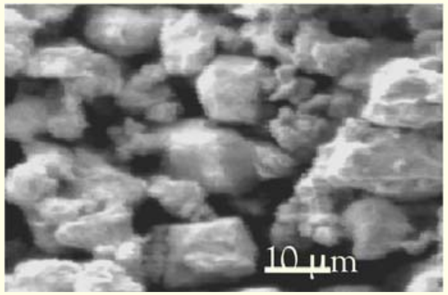
- Processes of formation of:
  - fineness
  - structure and phase composition
  - magnetic properties

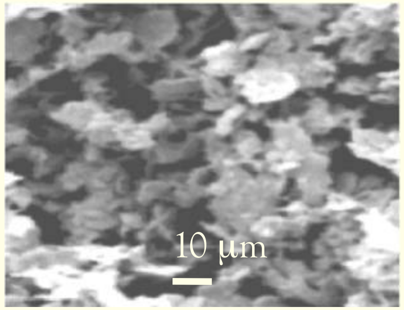
  for the Fe and Fe-Si powders mechanically milled in organics
- The influence of :
  - milling time
  - type of organic liquid
  - surfactant additive

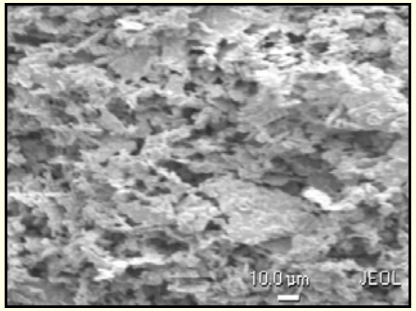
  on the sequence of structure and phase transformations and magnetic properties of the powders

Fe in organic liquids:

Particle shape and size



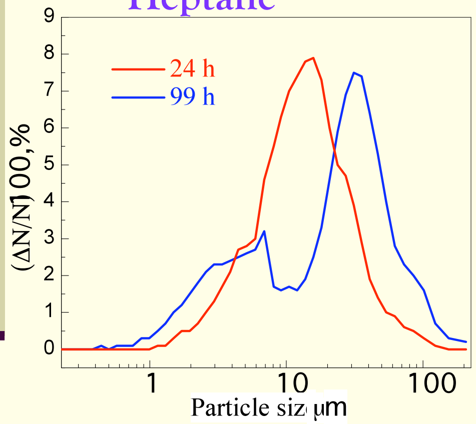


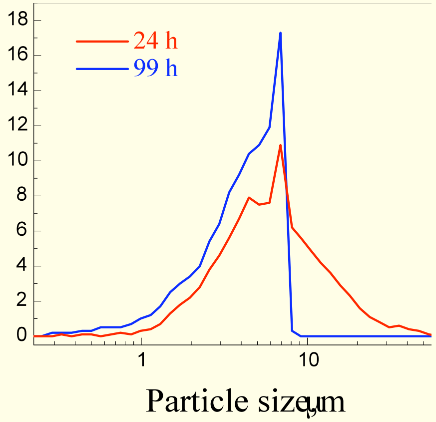


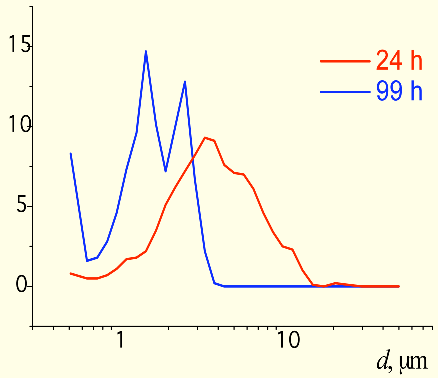
Heptane

0.3% oleic acid in heptane

0.3% VTES in heptane





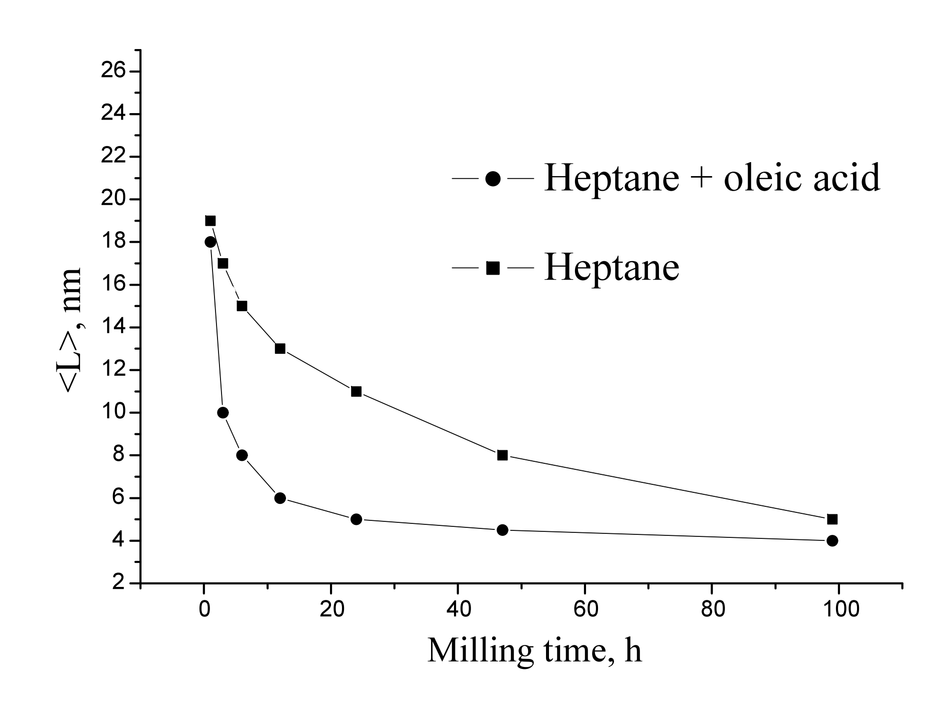


Surfactant presence in milling liquid results in:

- Decrease in the average particle size
- Narrowing of the particle size distribution
- Change in the particle shape

Fe in organic liquids:

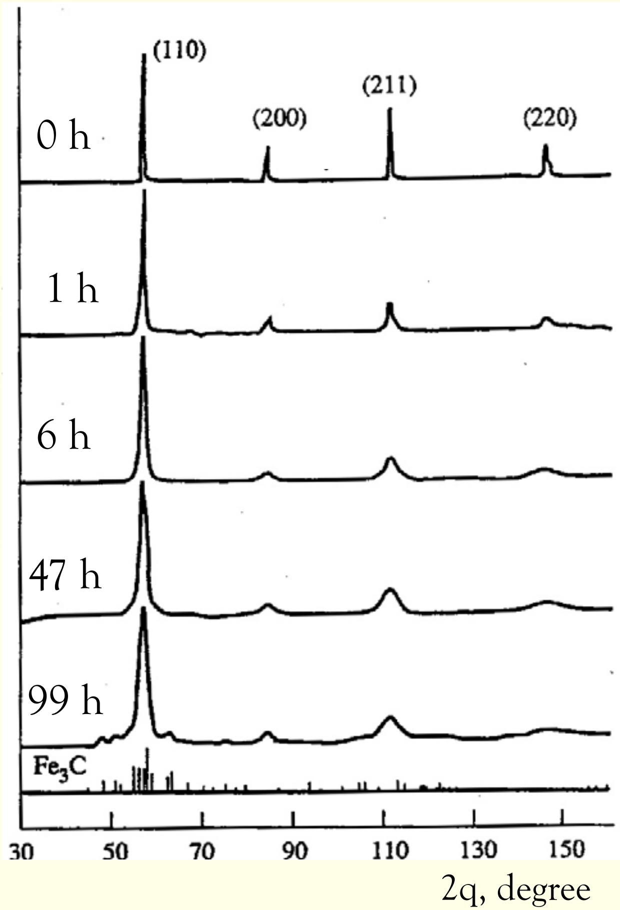
Nanocrystalline structure



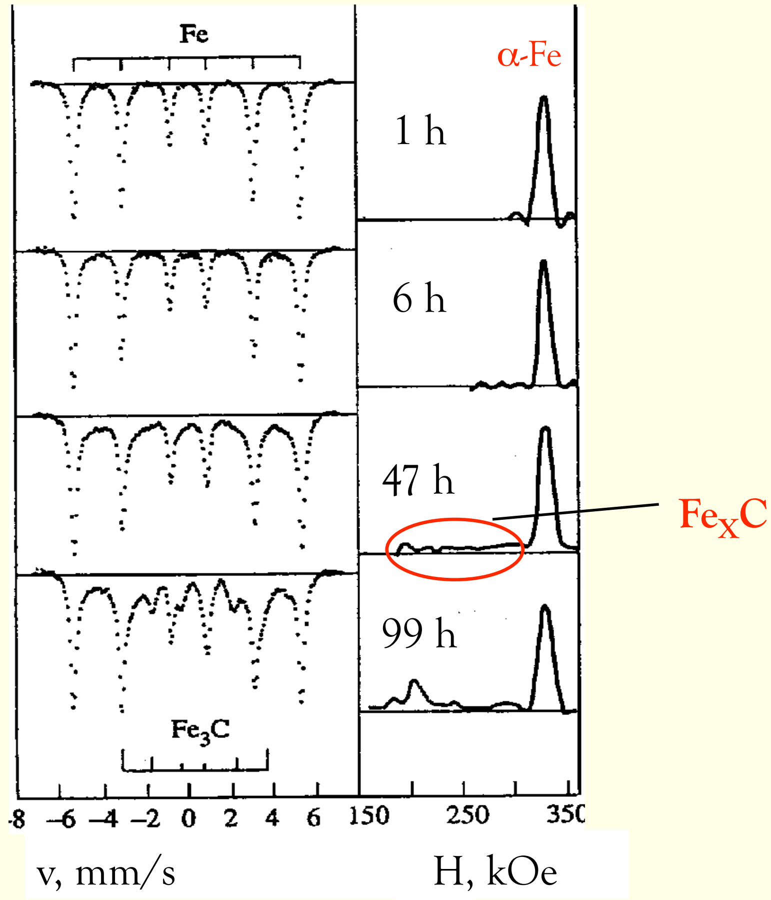
∼ 20 nm after 1h milling

∼ 5 nm by the end of milling

Fe in heptane: Phase transformations

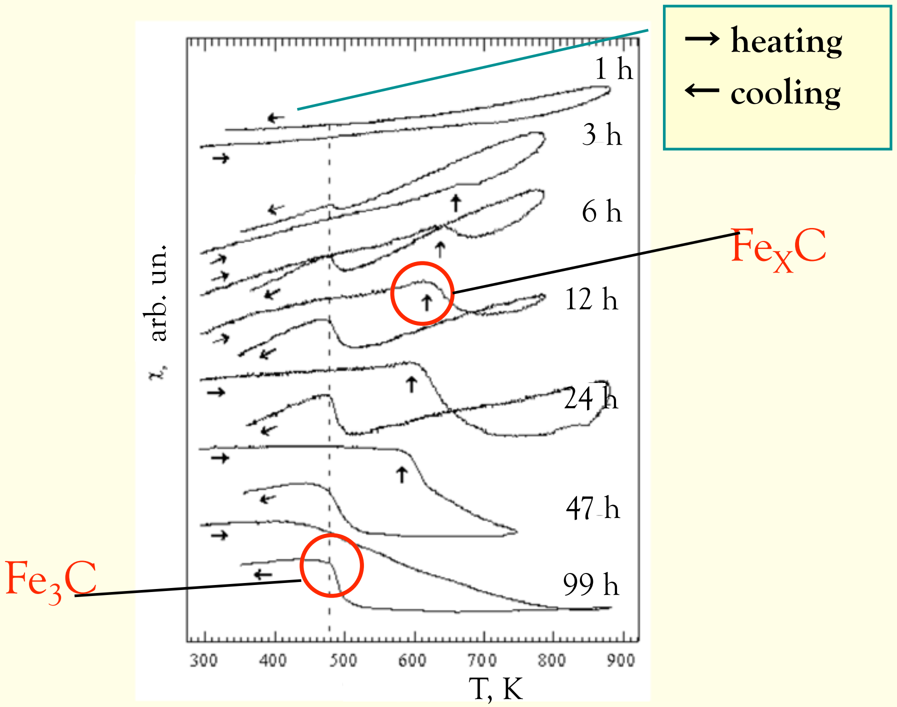


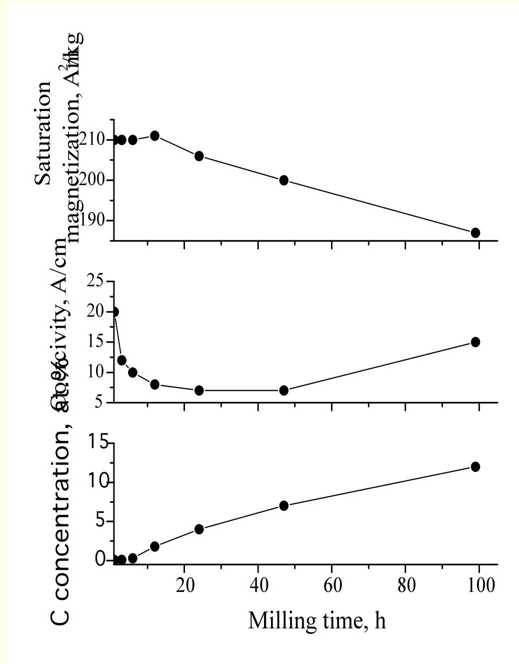
X-ray diffraction



Mössbauer spectroscopy

Fe in heptane: Magnetic characteristics





1) Nanocrystalline structure – after 1 h milling (without changes in structure and properties)
2) Long-time milling → aggregates

$$Fe\ (bulk) + C_7H_{16} \rightarrow \alpha\text{-}Fe + Fe\text{-}C(H) + Fe_3C + C\ (surface\ layers) + H_2$$

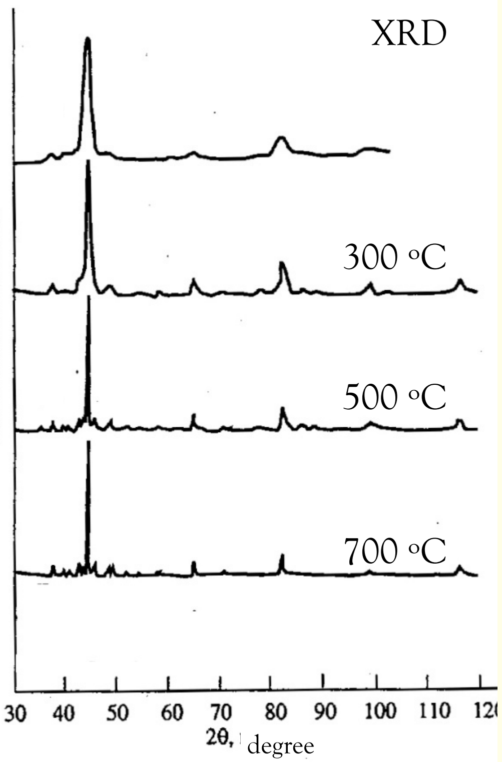
3) Decomposition of heptane (source of C and H) → C, H diffusion → saturation of Fe particles with C, H → Fe-C(H) and cementite Fe_3C phases formation

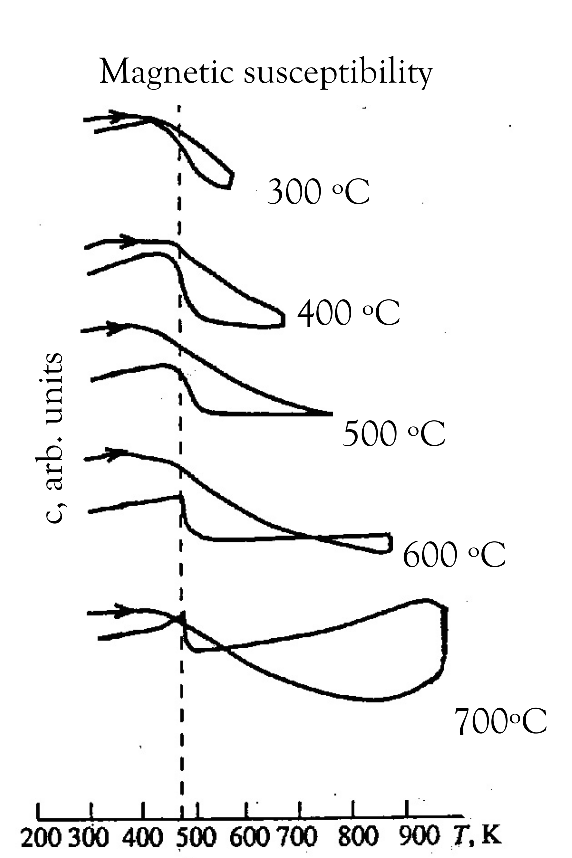
Fe in heptane:

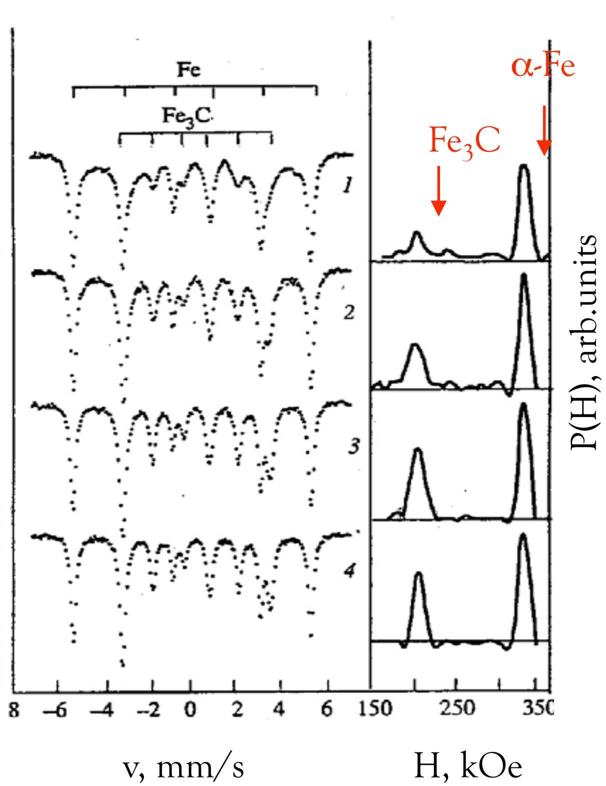
Phase transformations. Effect of annealing

For the powders milled for 99 h

T_{an} = 300÷700 °C, Ar^+





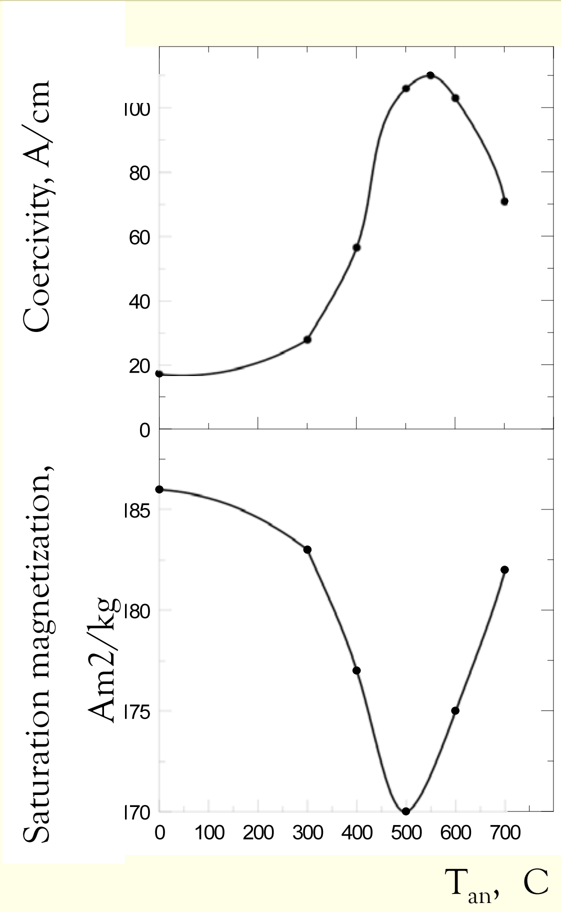


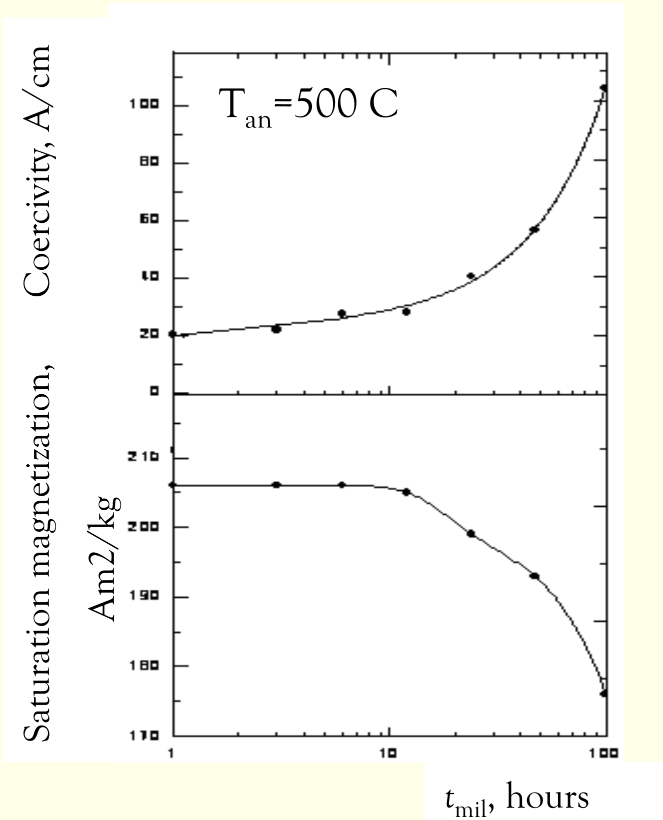
Mössbauer spectra

Fe in heptane:

Magnetic characteristics. Effect of annealing

Structure and phase composition → Magnetic properties





Fe in heptane:

Thermal stability of Fe-Fe_3C nanocomposite

MA of Fe in heptane

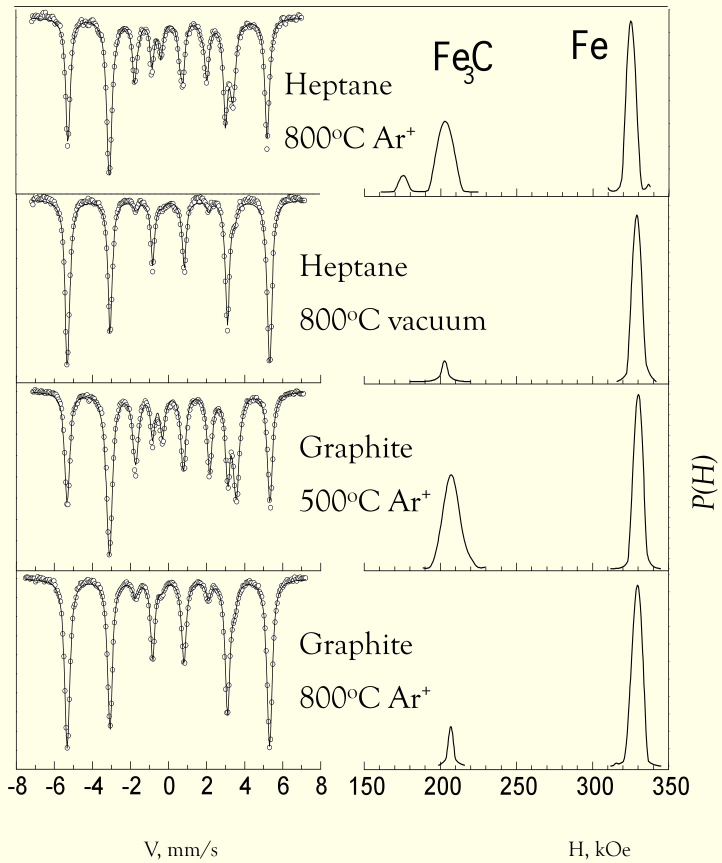
⇩

Annealing, 500°C, 1 h, Ar^+

⇩

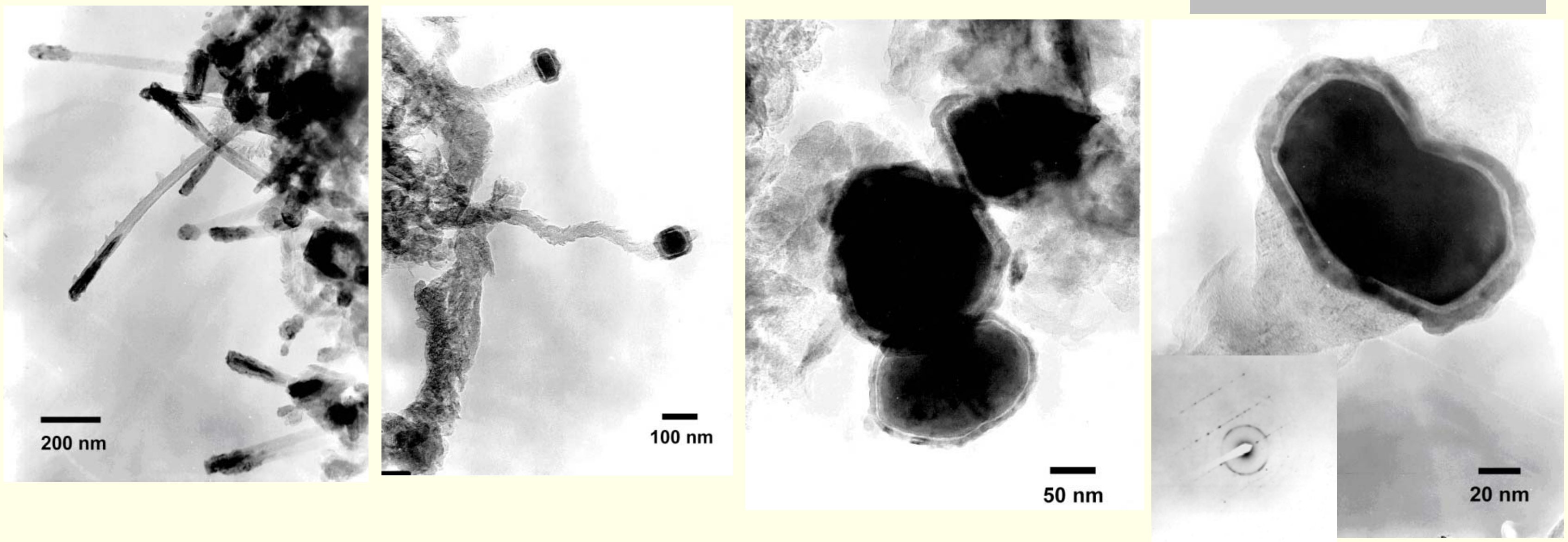
Annealing, 800°C, 1 h

Ar^+ — Vacuum 10^{-4} Torr



Fe in heptane:

Thermal stability of Fe-Fe_3C nanocomposite

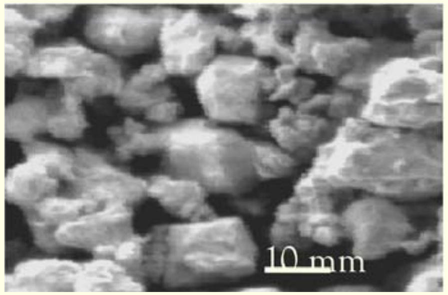


Similar carbon nanofibers and nanotubes are observed under catalytic decomposition of hydrocarbons on fine metal (Fe and its subgroup) and alloys particles (*A.V. Okotrub et al.*)

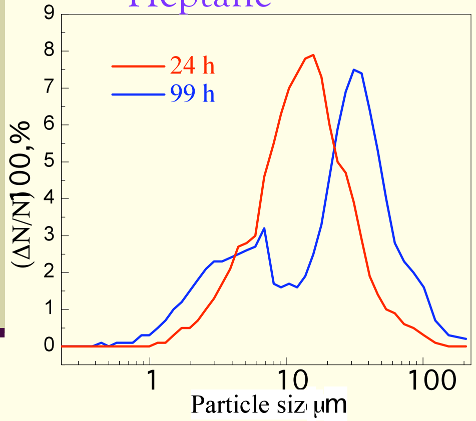
Capsulation of Fe_3C particles in carbon shell → thermal stability under annealing in inert gases up to 800°C (or decomposition in vacuum because of destroying carbon nanotubes)

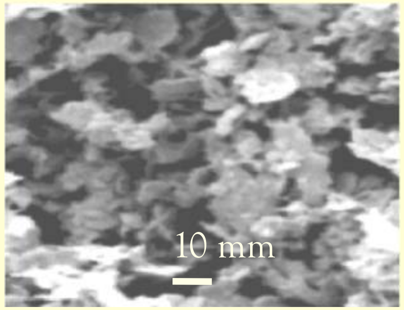
Fe in oxygen-containing liquid:

Particle shape and size

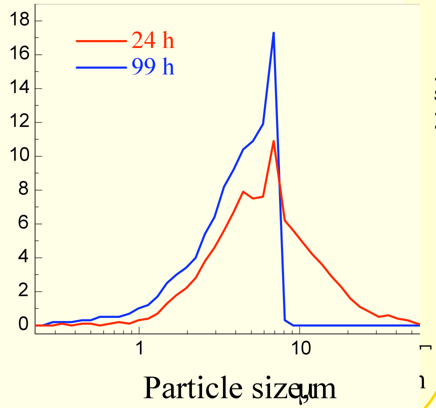


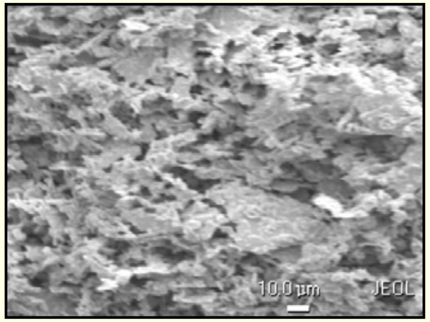
Heptane



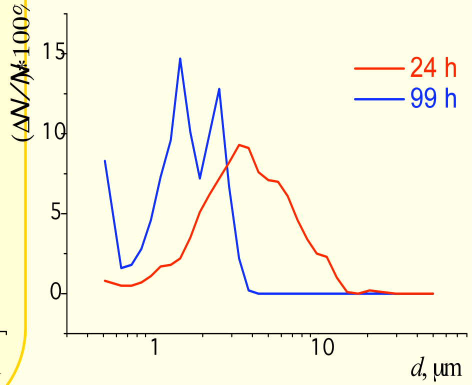


0.3% oleic acid in heptane





0.3% VTES in heptane



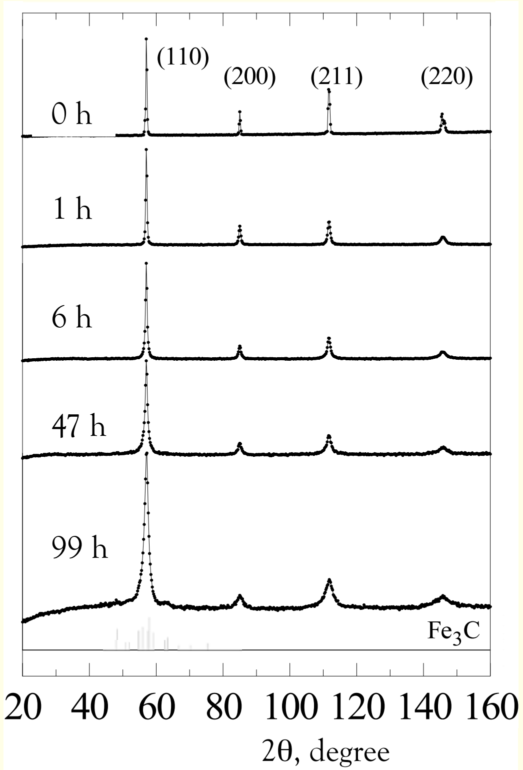
Surfactant presence in milling liquid results in:

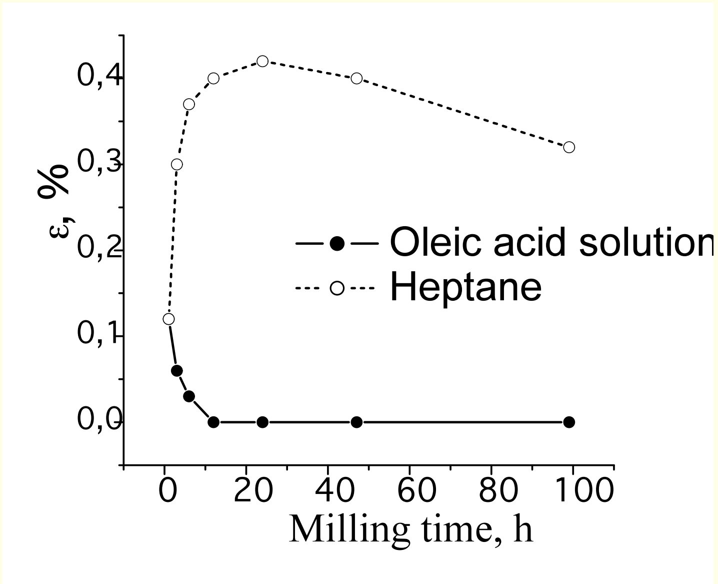
- Decrease in the average particle size
- Narrowing of the particle size distribution
- Change in the particle shape

Fe in oxygen-containing liquid

Phase transformations

Milling liquid – oleic acid solution (0.3 wt.% in heptane)

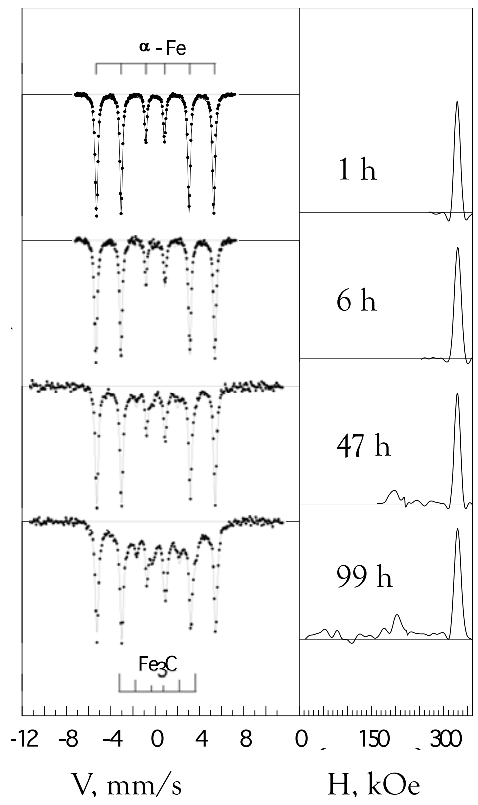




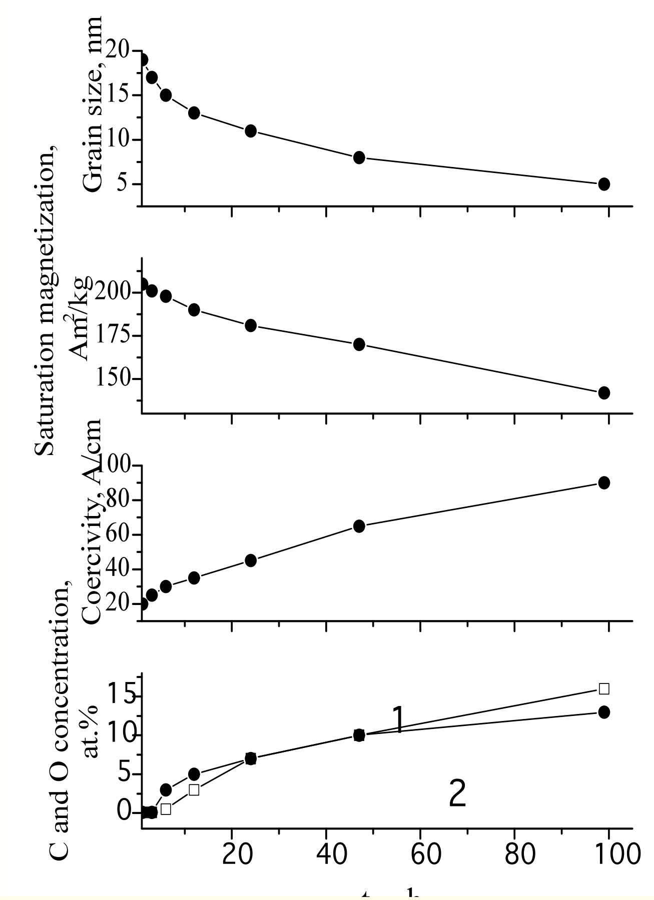
X-ray diffraction

Fe in oxygen-containing liquid

Phase transformations



Mössbauer spectroscopy



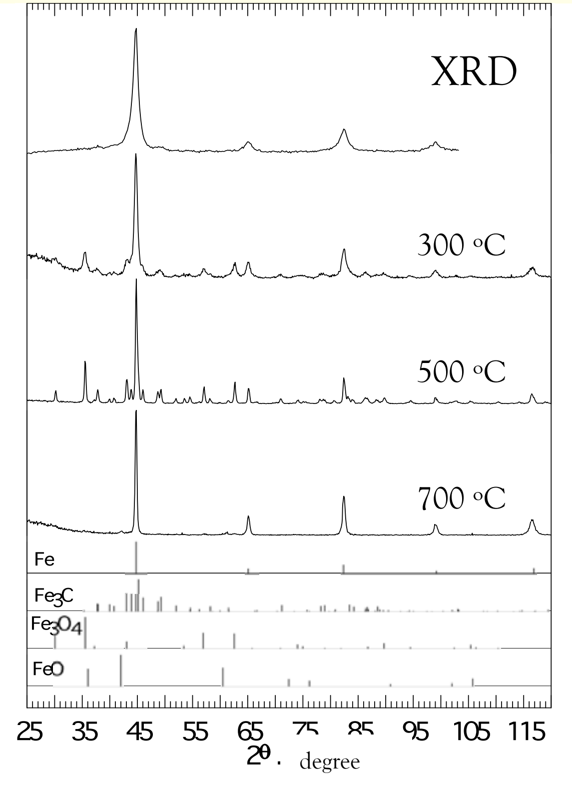
Fe-O-H phases (oxides and hydroxides)

Fe in oxygen-containing liquid

Phase transformations under annealing

For powders milled for 99 h

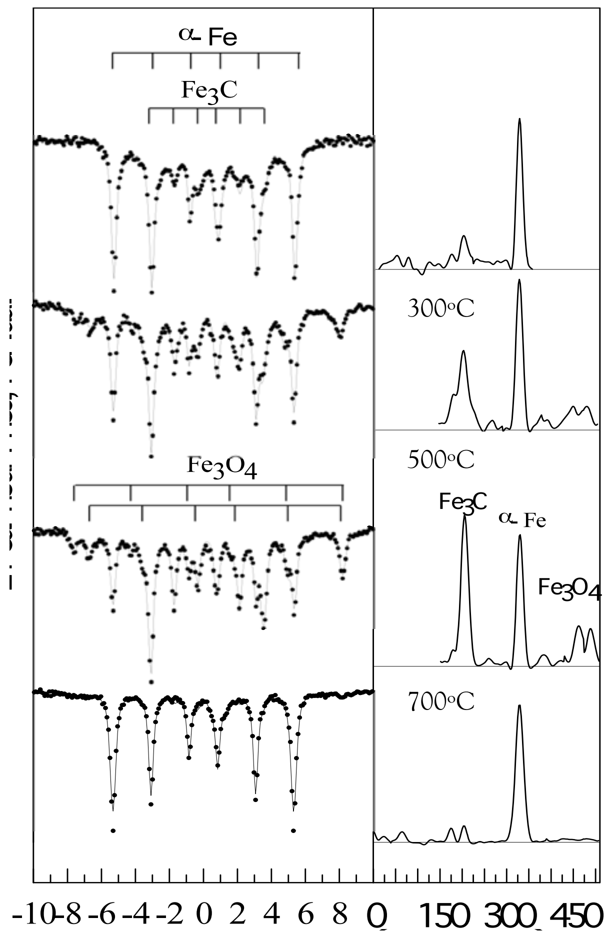
T_{an} = 300÷700 °C, Ar^+



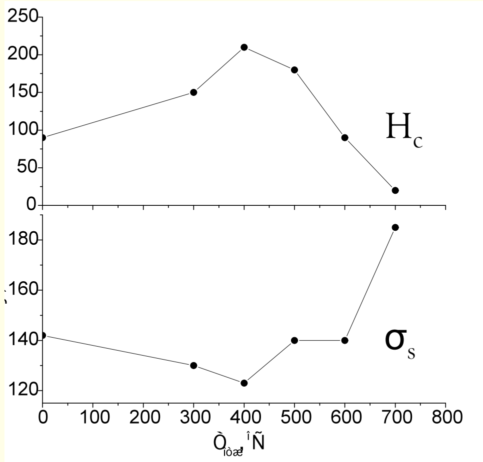
T_{an}, ^{0}C	Fe_3C, wt.%	Fe_3O_4, wt.%	FeO, wt.%	a-Fe, wt.%
300	29	28	_	43
400	44	29	_	27
500	45	28	_	27
600	43	24	6	28
700	_	2	2	96

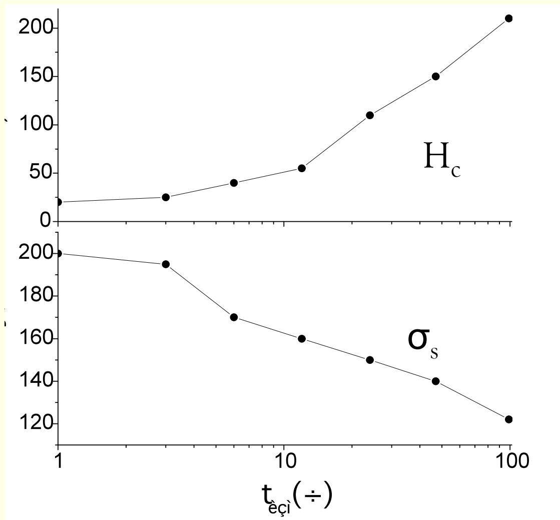
Fe in oxygen-containing liquid

Phase transformations under annealing



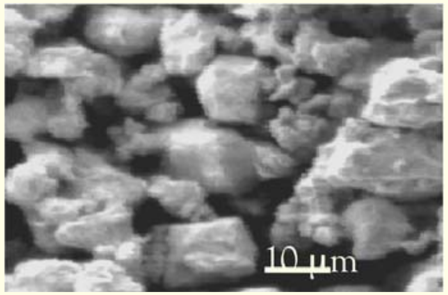
Mössbauer spectroscopy

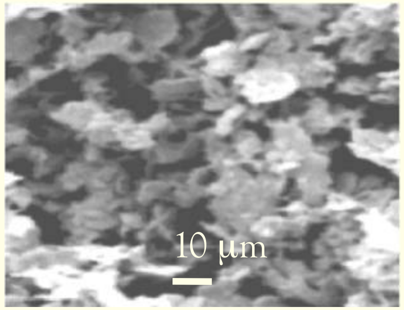


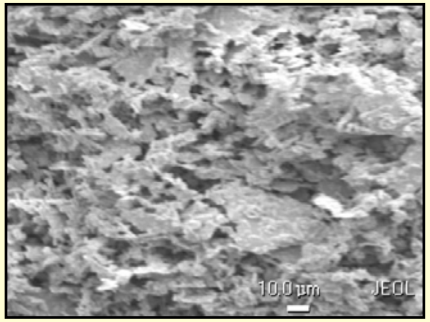


Fe in silicon-containing liquid:

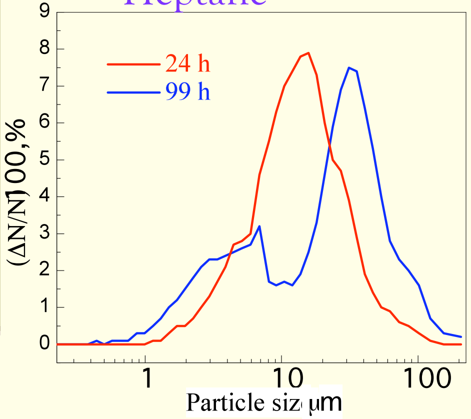
Particle shape and size



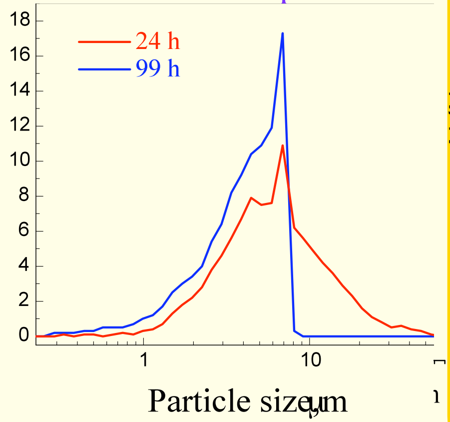




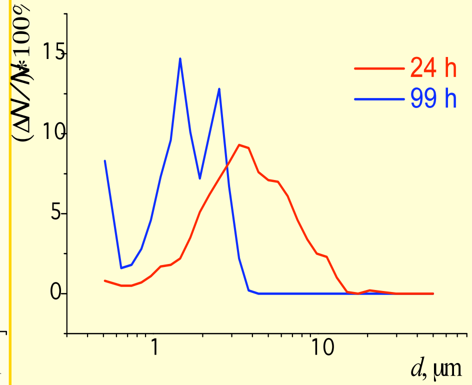
Heptane



0.3% oleic acid in heptane



0.3% VTES in heptane



Average particle size is less than in oleic acid solution

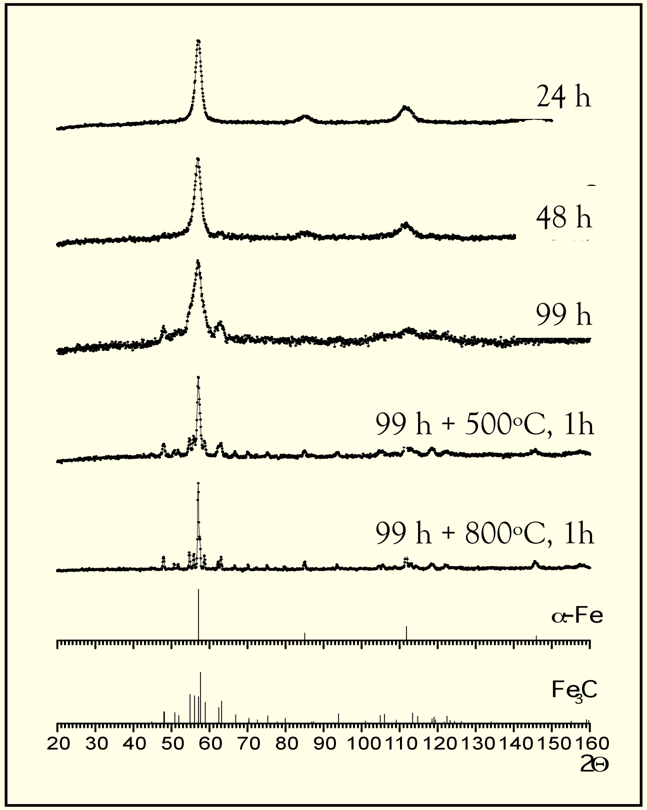
Particle shape – thin crusts due to severe plastic deformation

Melting of particles under electron beam

Fe in silicon-containing liquid

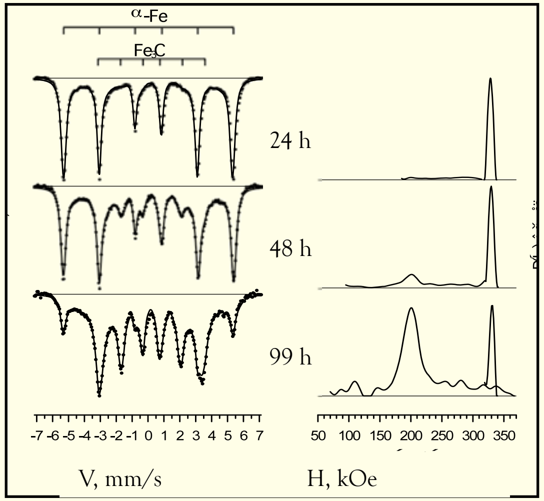
Phase transformations

Milling liquid – vyniltrietoksisilan solution (0.3 wt.% in heptane)



	$t_{mil.}$, h	<L>, nm	*a*, nm	$<\varepsilon^2>^{1/2}$
Fe+ heptane+ VTES	24	2	0.2865	0.3
	48	< 2	0.2863	0.7
	99	*	*	*
Fe+ heptane	24	4	0.2868	0.4
	47	4	0.2866	0.4
	99	3	0.2854	0.3

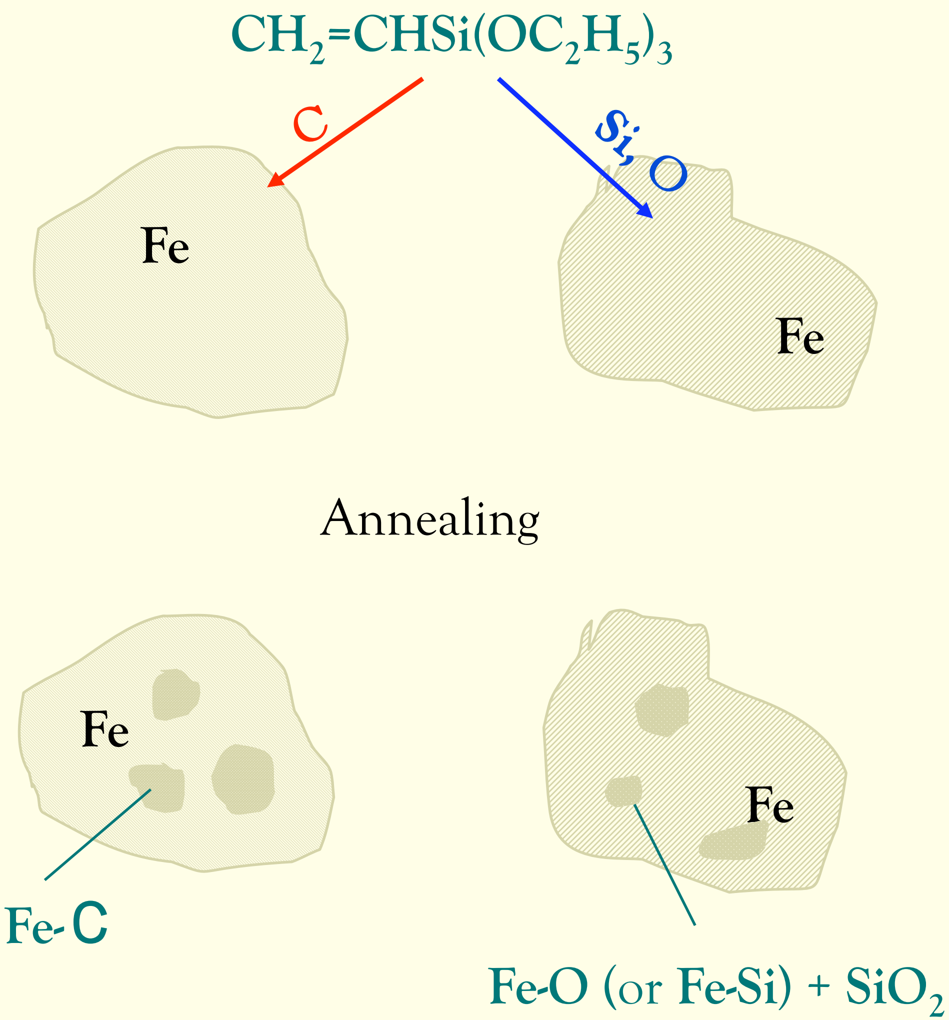
* Were not determined because of strong line broadening

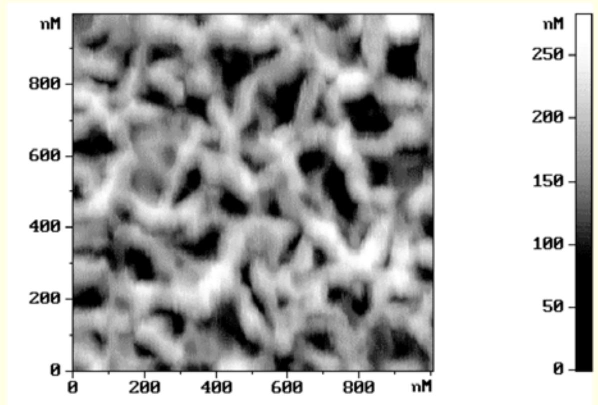


T_{anneal}	Fe_3C, wt.%	
	48 h	99 h
500°C	0.44	0.75
800°C	0.39	0.66

Fe in silicon-containing liquid

Phase transformations





AFM topography

Microhardness ~14 GPa

Fe in organic liquids:
General scheme of phase transformations

1. Severe plastic deformation

2. Developing nanocrystalline structure in Fe powder

3. Thermocatalytical destruction of organic liquid on the as-formed metal surface

4. Adsorption of destruction products and their diffusion out of surface on the grain boundaries

5. Formation of nonperiodic interstitial (amorphous and metastable) phases in the interface

6. After annealing – the formation of new phases in the powder bulk and developing nanocomposite structure

Fe-Si in organic liquids:

Fe-Si-C phases

Manufacturing steels and cast-irons.

Amorphous Fe-Si-C alloys – better mechanical strength, plasticity, corrosion stability and magnetic properties compared to technical cast-iron

Metastable Fe-Si-C phases of different:

Crystal structure (amorphous, bcc, orthorhombic, triclinic, hexagonal and cubic with the structures of α- and β-Mn type;

Chemical composition (Fe_3SiC, Fe_4SiC, $Fe_{10}Si_2C_2$, $Fe_{10}Si_2C_3$, Fe_8Si_2C, Fe_9SiC_2)

Fe-Si in organic liquids

Particle size and shape

$Fe_{80}Si_{20}$

initial

σ_s=150 emu/g

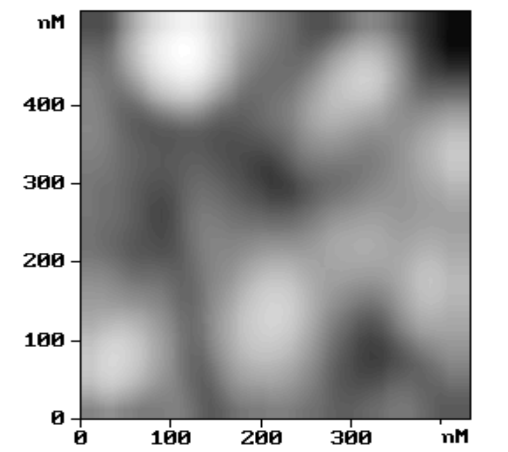
H_c=13 Oe

T_c=592°C

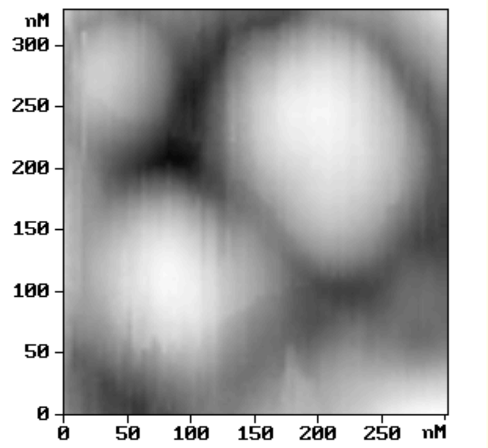
d ≤ 300 μm

<L> = 100 nm

Heptane



Oleic acid solution



Particle size – **0.1-0.2 μm**

(less than for Fe powders)

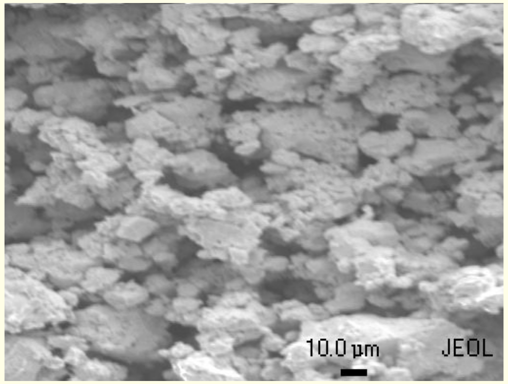
Atomic Force Microscopy

(t_{mil}=99 h)

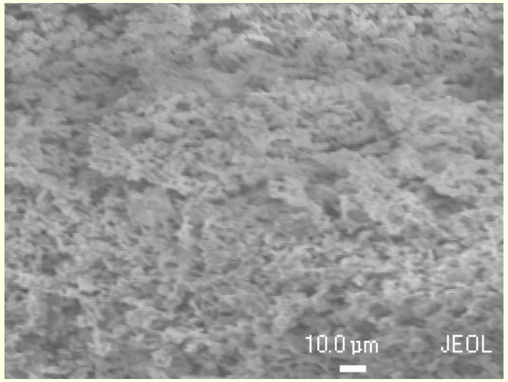
Fe-Si in organic liquids

Particle size and shape

Heptane



Oleic acid solution

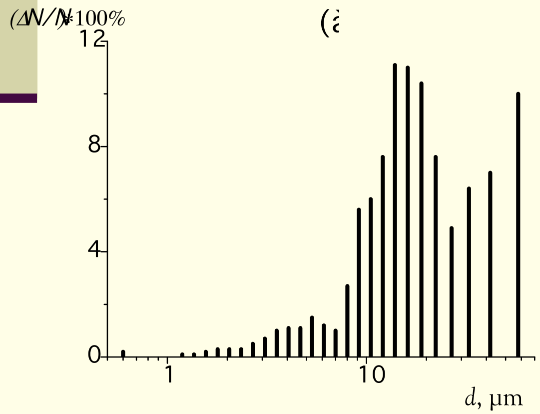


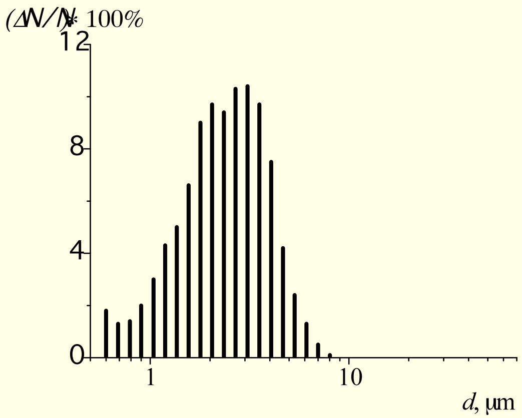
Secondary Electron Microscopy (t_{mil}=99 h)

Agglomerate size

22 µm (heptane)

2 µm (oleic acid)





Unlike Fe powders for Fe-Si powder surfactant additives produce little effect on the particle size but significantly reduces agglomerate size

Fe-Si in organic liquids

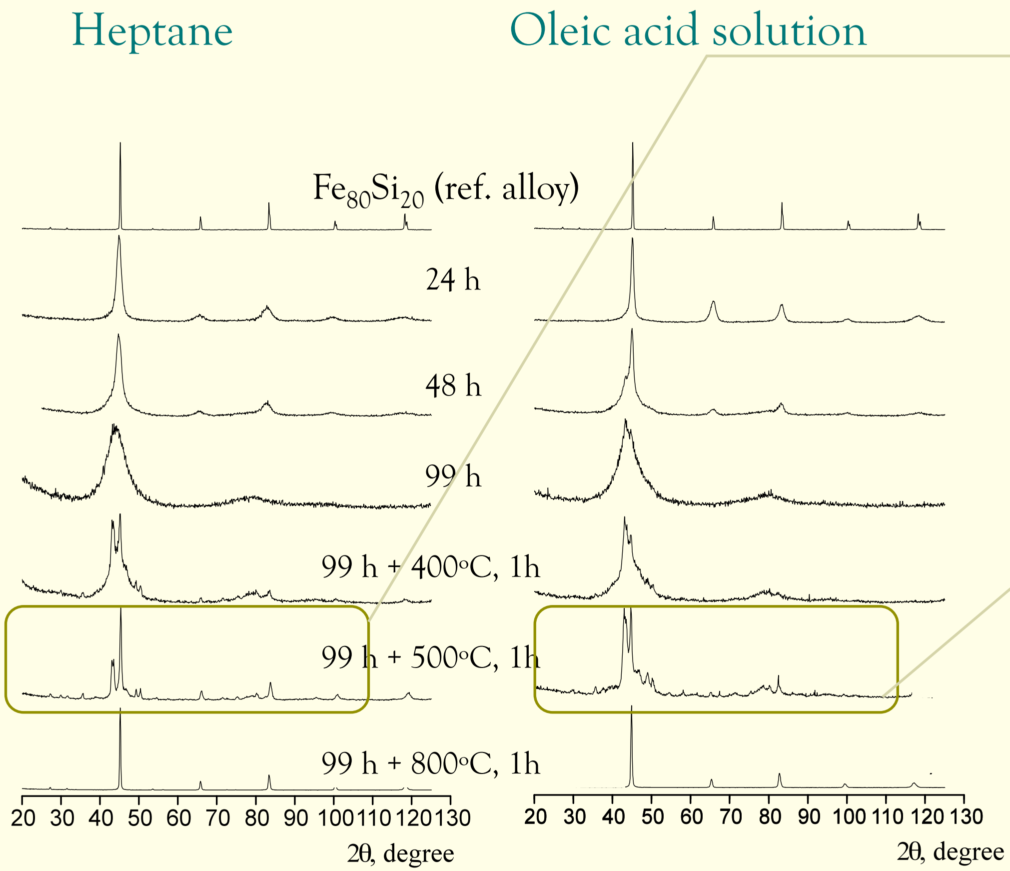
Phase transformations

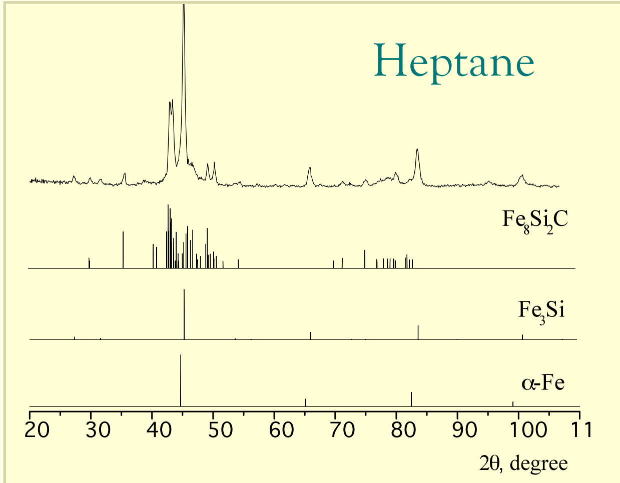
Sequence of structure and phase transformations in Fe-Si under milling in organic liquids

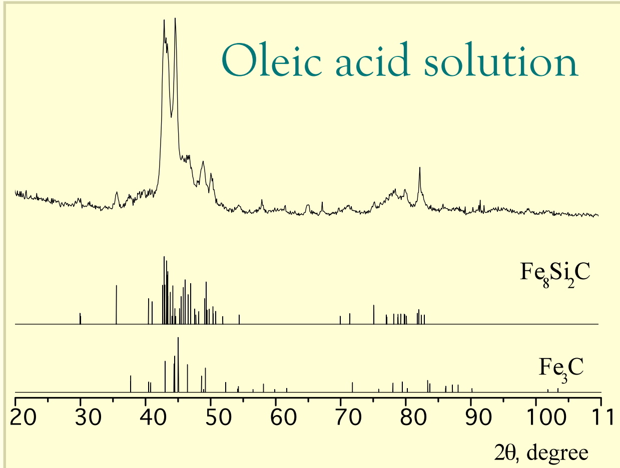
- Formation of nanocrystalline structure;
- Saturation of the particle bulk with the milling environment decomposition products (C, O, H – depending on liquid composition) followed by the formation of solid solutions and amorphous phases;
- After annealing - formation of chemical compounds, for example, iron silicon carbides, iron carbides and so on.

Fe-Si in organic liquids

Phase transformations



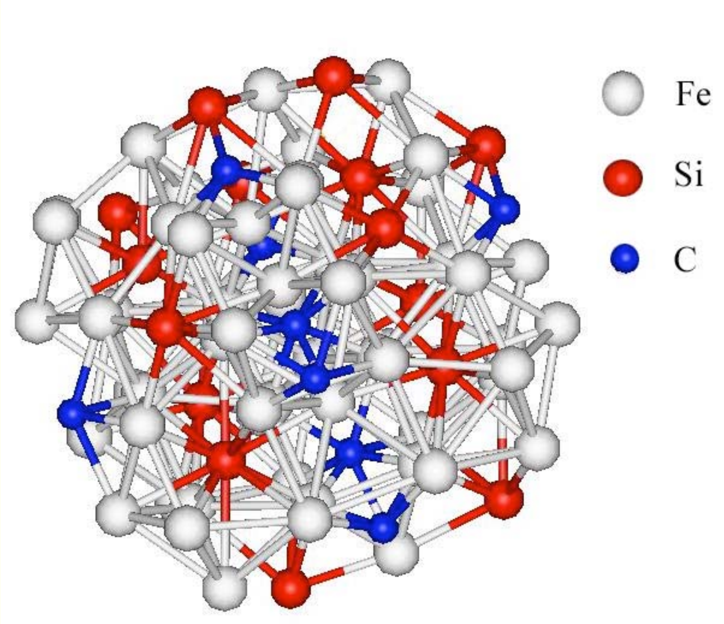




X-ray diffraction

Fe-Si in organic liquids

Phase transformations



Fe_8Si_2C

P1 space group symmetry

Milling liquid	Lattice parameters					
	nm			degree		
	a	*b*	*c*	α	β	γ
Heptane	0.6413	0.6449	0.9724	83.651	99.307	120.423
Surfactant solution	0.6449	0.6469	0.9711	83.550	99.500	120.900

Fe-Si in organic liquids

Phase transformations

Grain size (<*L*>), microdistortions (ε) and lattice parameter (a) for the Fe-Si alloy

Milling liquid	**Heptane**					**Surfactant solution**				
t_{mil} (h)	1	3	6	12	24	1	3	6	12	24
(<*L*>), ±0.5, nm	5.1	4.2	3.5	4.0	3.0	7.7	5.2	5.9	4.2	4.0
(ε), ±0.03%	0.3	0.39	0.42	0.5	0.45	0.31	0.30	0.36	0.28	0.23
a, ±0.0003, nm	0.2841	0.2845	0.2848	0.2848	0.2850	0.2843	0.2844	0.2843	0.2843	0.2843
a^*, ±0.0003, nm	0.2836					0.2855				

Saturation magnetization (σ_s, emu/g)

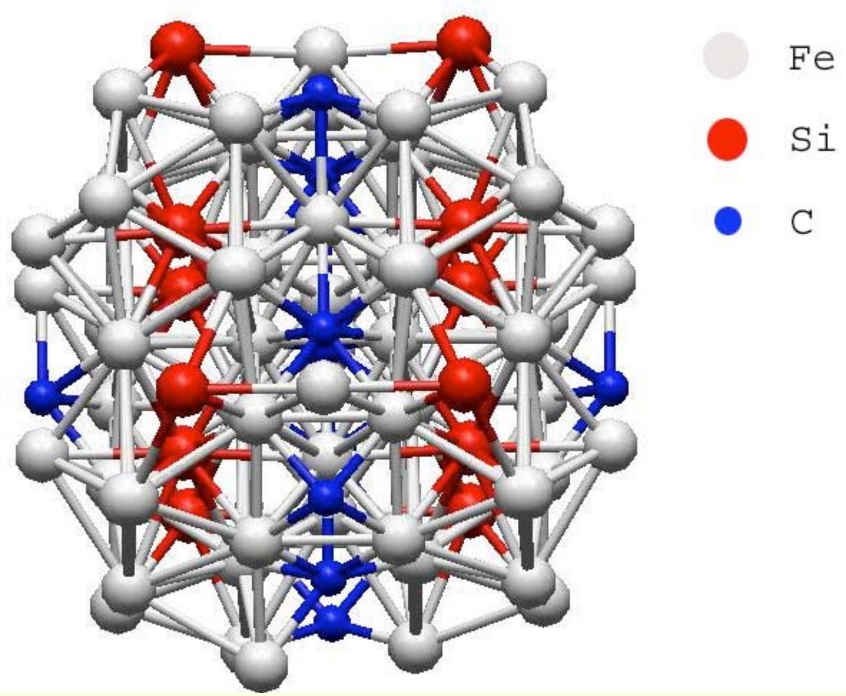
Milling liquid	**Milling time, h**			**Annealing temperature, °C t_{mil} = 99 h**		
	24	48	99	400	500	800
Heptane	150	150	133	139	146	148
Surfactant solution	137	139	121	126	129	157

Coercivity (Hc, Oe)

Milling liquid	**Milling time, h**			**Annealing temperature, ° C t_{mil} = 99 h**		
	24	48	99	400	500	800
Heptane	23	24	26	109	226	13
Surfactant solution	28	39	57	104	194	104

Fe-Si milled in Ar^+

Phase transformations



Dry milling of 70%Fe-13%Si-17%C mixture followed by annealing of the obtained amorphous phase

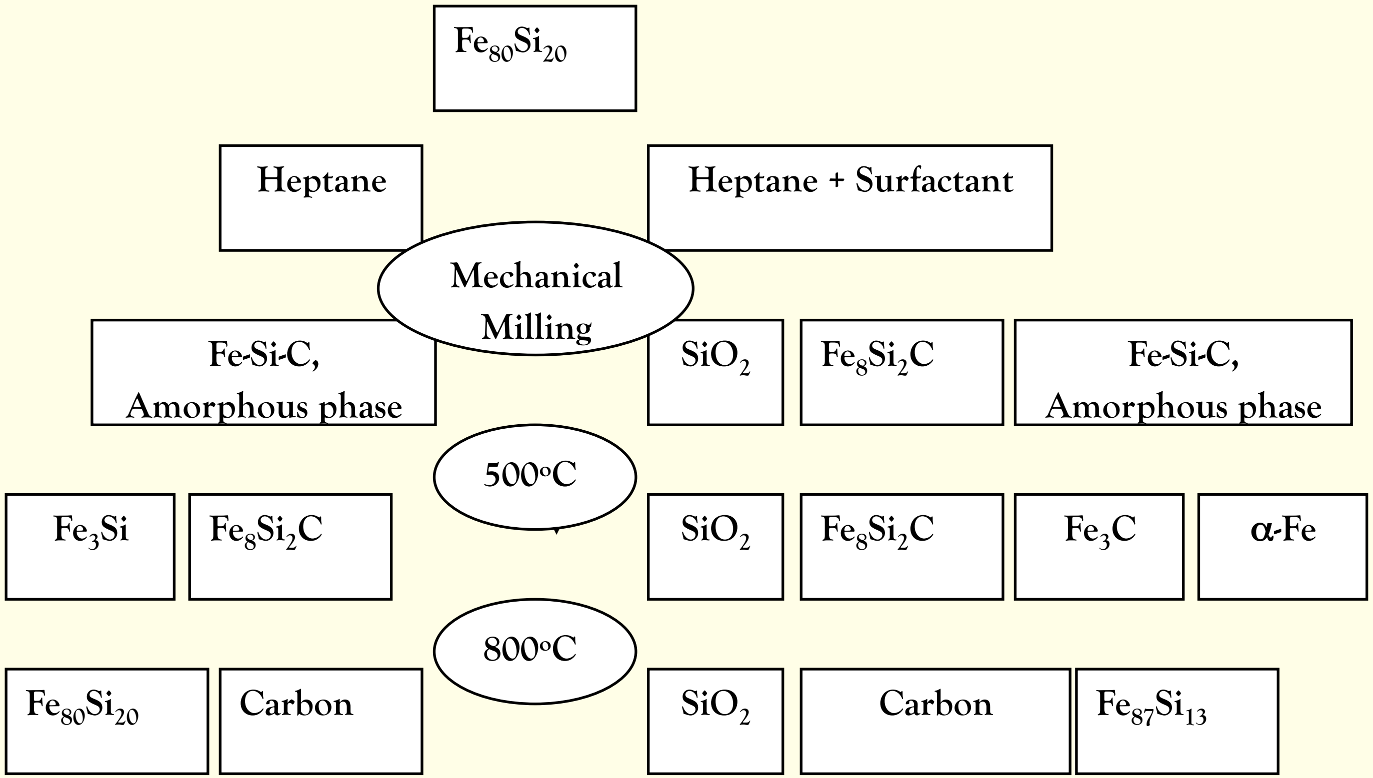
Fe_5SiC

Cmc2.1 space group symmetry (a=1.0422, b=0.7939, c=0.7461 nm)

Ferromagnetic with T_c = 507 °C. Coercivity for the particles of a stone-like shape with an average size of 4 μm was estimated as H_c=470 Oe with the specific saturation magnetization σ_s=150 emu/g.

Fe-Si in organic liquids

Phase transformations



Scheme of the phase transformations occurring under milling the Fe-Si alloy in organic liquids and subsequent thermal treatment

Milling in liquids

Milling of metals and alloys in the presence of liquids (**water, lubricants, protective coatings, etc**.) is connected with the problem of **environment** effect on the **equipment depreciation**

Operation under BOTH **aggressive chemicals** and **mechanical loading** results in STRONGER DESTRUCTION of equipment materials

Mechanical effect leads to changes in structure and chemical composition of **surface layers**

Mechanical milling can be used to simulate the processes of structural and phase transformations under severe plastic deformation of metals in liquid environment

Thank you for your time!

Corrosion properties

- The high specific surface → high chemical activity of powders → resistance to the external environment (especially for Fe-based powders)
- Corrosion behavior in a neutral environment (natural conditions)
- The most common way to stabilize highly-dispersed powders is to develop a protective layer on the surface.
- Difference between materials obtained by mechanoactivation in organic environment from traditional materials is in to high degree of non-equilibrium (highly dispersed, nanocrystalline, with presence of metastable phases).
- Corrosion resistance of Fe-Si alloys in many aggressive environments is due to passive film SiO_2 on the surface – so, they are promising protective coatings and initial material for the synthesis of highly-dispersed powders.
- When milling in the oxygen environment (oleic acid, viniltrietoksisilan) oxide layer formed directly in the milling due to decomposing milling environment . If the liquid does not contain oxygen oxides on the surface are formed after taking powders out on the air after milling with the oxidation of organic component and increasing the oxide layer thickness. For powders doped with Si the surface layer is enriched with Si with the formation of SiO_2.
- **We showed that the protective layer with high anticorrosive properties on Fe and Fe-Si powders forms directly in the milling process in the presence of long-chain surfactant, such as oleic acid. When using silicon-containing environment slight increase in the corrosion resistance takes place due to silicon-organic compounds. Enriching the surface layer with Si and SiO_2 formation does not improve the resistance of the powders.**
- **Corrosive behaviour is determined by phase-structural composition of the particle bulk. The accumulation of amorphous phase (Fe-Si-C, Fe-C) in the milling increases powder corrosion resistance. Reducing the grain size, the formation of carbides and their capsulation into carbon shells do not affect significantly on the corrosive behavior. Formation of oxide phases (FeOOH, Fe_3O_4, SiO_2) in the material bulk degrades corrosion resistance of powders.**
- **Mechanoactivation in the presence of organic surfactant allows one to highly disperse Fe-based powders and simultaneously improve their corrosion resistance.**