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Mössbauer study of Fe powder mechanically alloyed by power ultrasonics

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Outline

- Mechanical alloying
- Ultrasonic method for MA
- Fe-C powder
- Fe-Ni-C
- Conclusion remarks

Mechanical Alloying

- “MA is a technique for processing of powder in a high-energy ball mill. Originally it was developed to produce oxide-dispersion strengthened Ni- and Fe-based superalloys for application in aerospace industry.

- MA has now been shown to be capable of synthesizing a variety of equilibrium and non-equilibrium phases starting from blended elemental or prealloyed powders.

- The non-equilibrium phases include: supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nano structures and amorphous alloys

C. Suryanarayana. Progress in Material Science, 46, 2001, 1-184

Mechanical Alloying

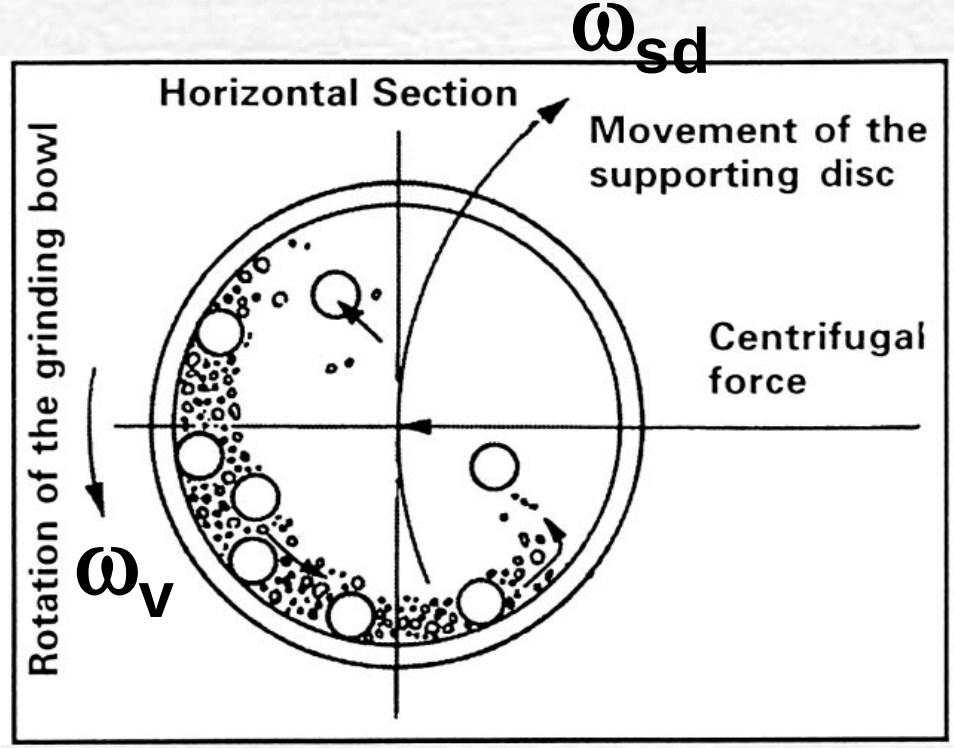
- Different types of high-energy milling equipment are used to produce mechanically alloyed powders.
- They differ in their capacity, efficiency of milling and additional arrangements for cooling, heating, etc.
- A conventional ball mill consists of a rotating drum (horizontal or planet-like movement of its vials) half-filled with small steel balls and powder (few hundred g of the powder can be milled at a time).

C. Suryanarayana. Progress in Material Science, 46, 2001, 1-184

Planetary ball mill (Pulverisette-6)

the vials and the supporting disk rotate in opposite directions
the F_c alternately act in like and opposite directions
This causes
the friction effect
the impact effect

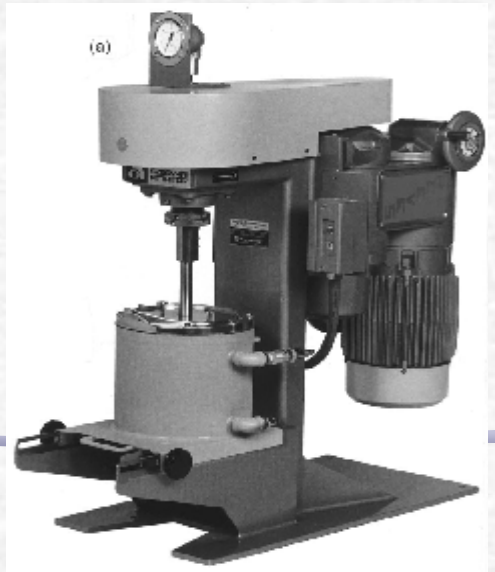
View of ball mill



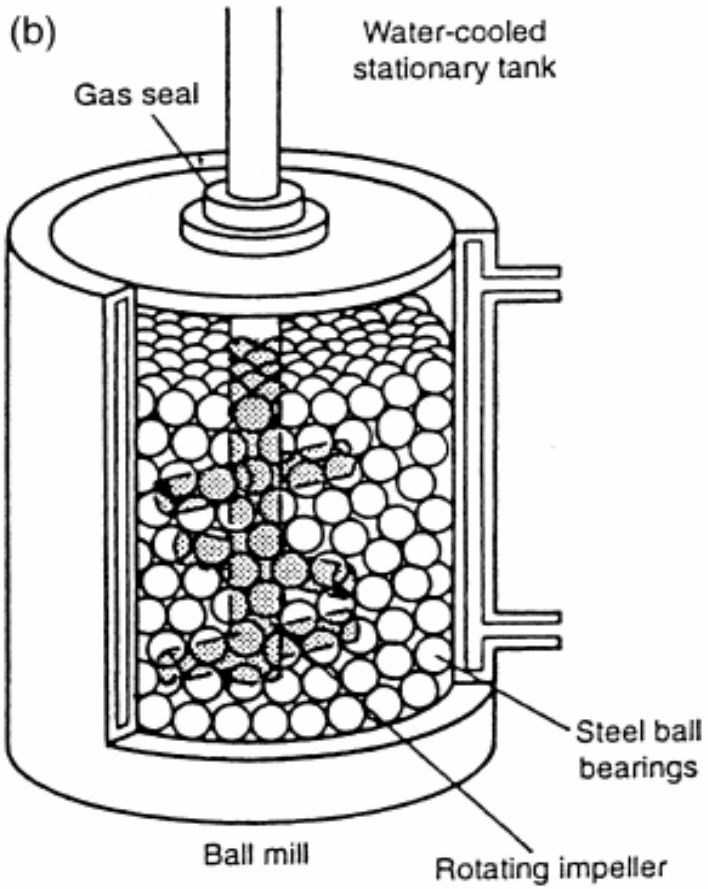
Scheme of grinding

Attritor mills (Model 1-S attrito)

a vertical drum with a series of impellers inside it
this causes shearing and impact forces on the material
ω_v ~ 250 rpm
quantities of powder 0.5 - 40 kg can be milled at a time



View of ball mill

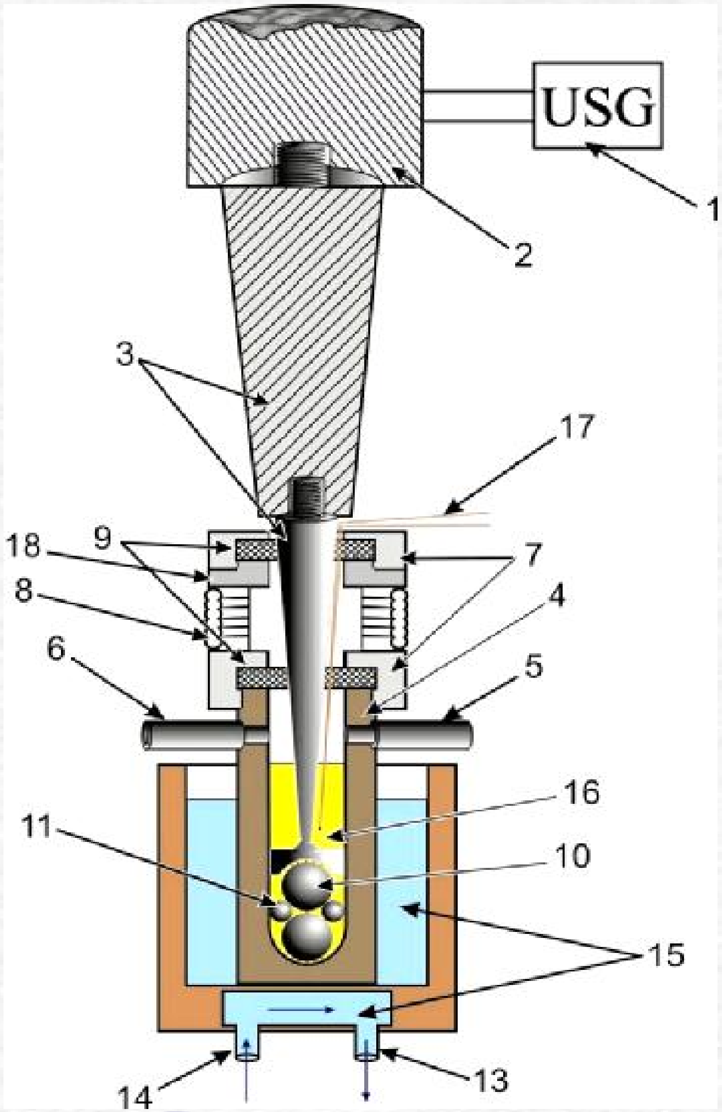


Inside of mill

Ultrasonic Grinding Mill

1 ultrasonic generator
2 ultrasonic vibrator;
3 ultrasonic horn;
15 water-cooled container;
8 – silphon

10, 11 metallic balls;
16 powder;
5, 6 gas inlet and outlet,
4 metal chamber



- **1 kW**
- **F = 20 kHz**
- **A = 10 μm**
- **$\varnothing_{chamber}$ = 14 mm**
- **$\varnothing_{balls}$ = 3 mm, 12 mm**
- **m_{balls}/m_{powder} = 10:1**
- **He environment**
- **t ≤ 60°C**
- **Powder mass ration m_{Fe}/m_C 80:20**

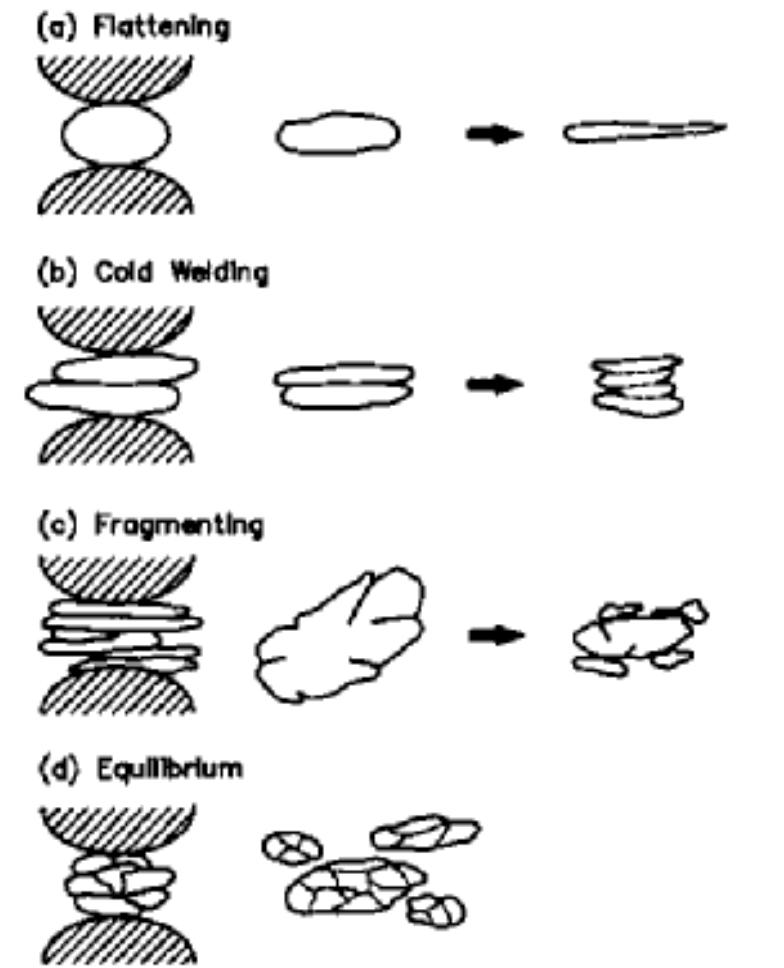
B.M. Mordyuk, G.I. Prokopenko. *Patent of Ukraine, #59770A, Bul.#9*

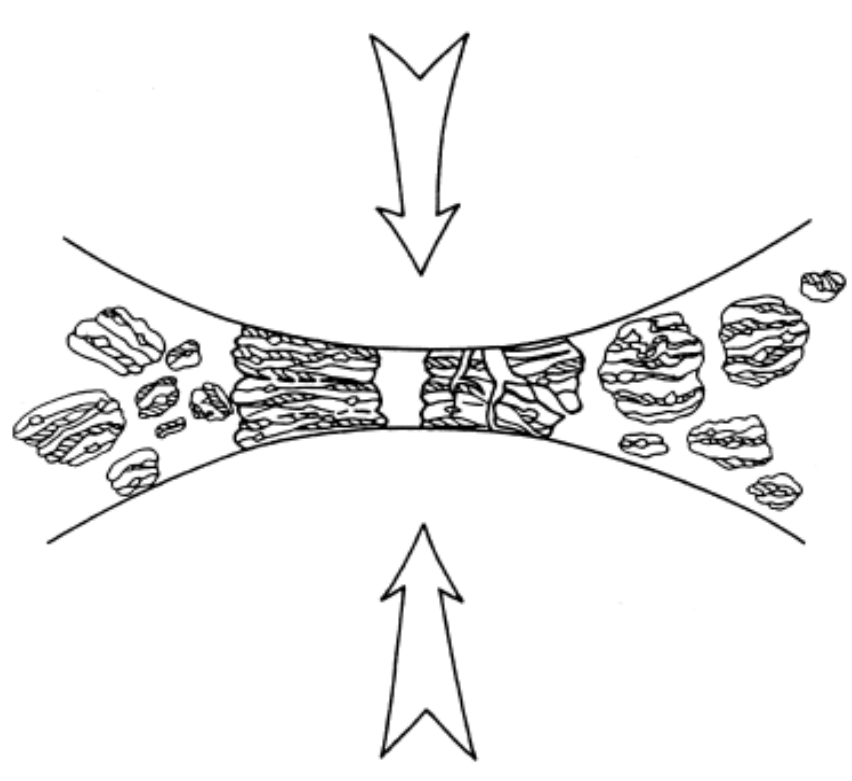
Ultrasonic milling action

One can see how the ultrasonic milling ever can provide a mechanical alloying process.

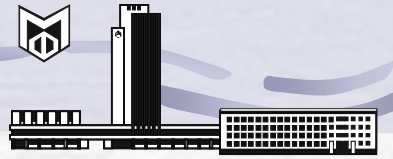
The metallic balls both rotate and collide during treatment. These rotation and impacts lead to grinding, flattening, fraction, fragmenting, cold welding and result in alloying of powders.

During high-energy ball milling the powder particles are repeatedly flattened, cold welded, fractured and rewelded.





Fe-C



- Fe-C system is the basis of a number of steels.

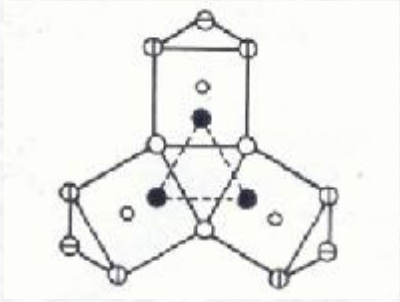
The solubility of C

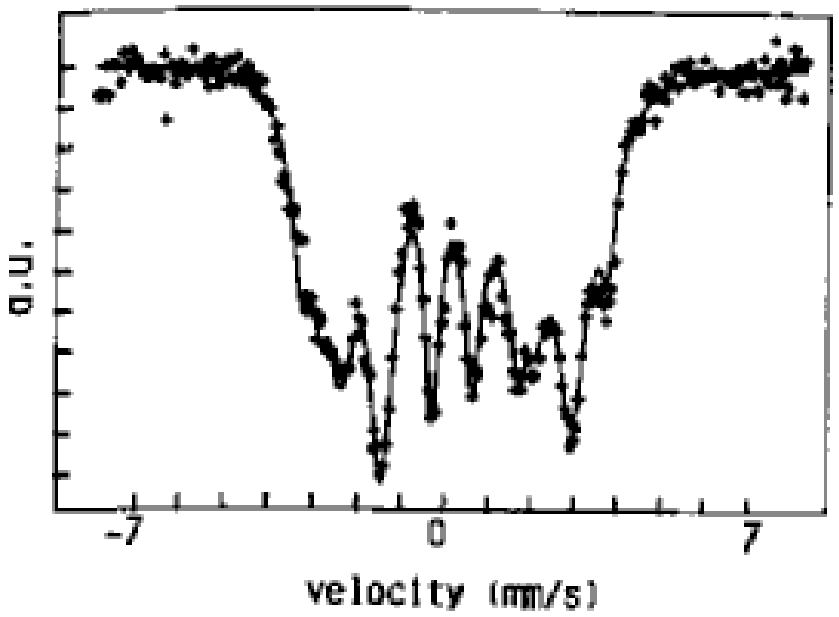
- in α–Fe is approximately 0.02 wt %
- in γ–Fe is 2.1 wt %

High-energy ball milling

Powder atomic ratio at_{Fe}/at_C = 68:32 and at_{Fe}/at_C = 50:50

E.Bauer-Grosse, G. Le Caer → Fe_7C_3
H_1 =23.0 T,
H_2 = 20.5 T,
H_3 =16.5 T



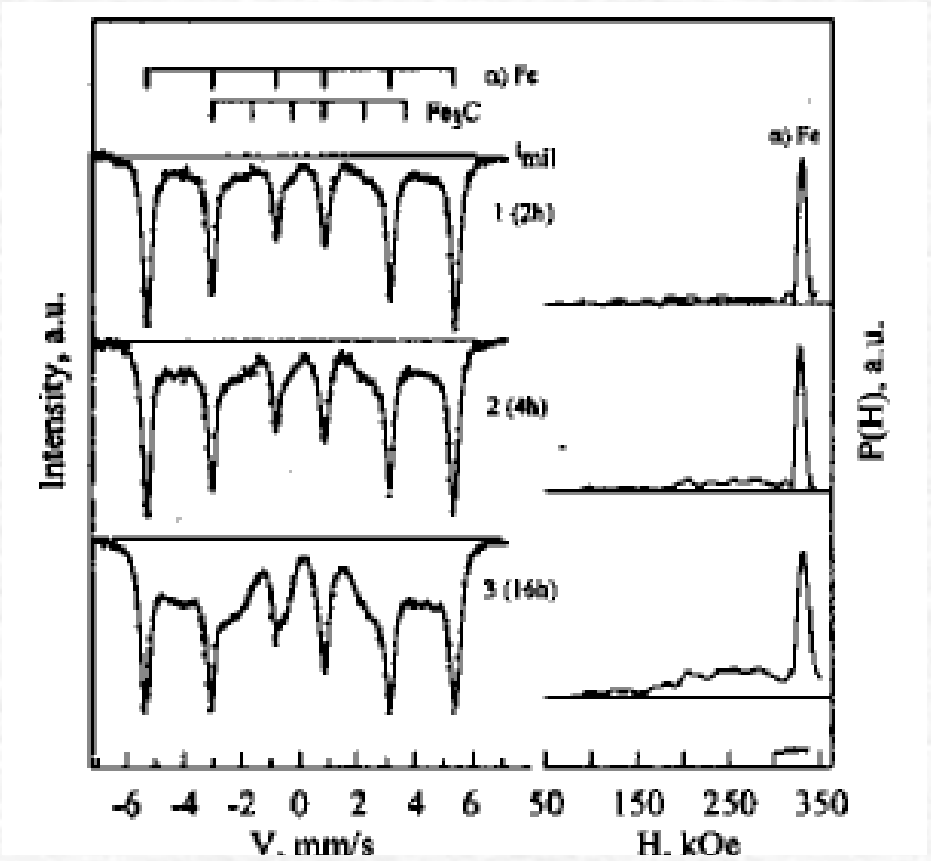


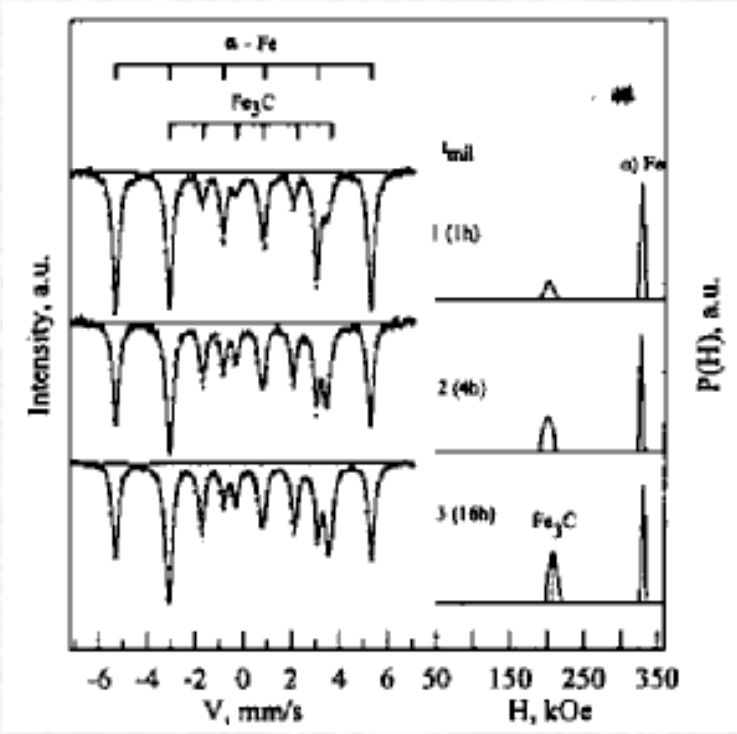
E.Bauer-Grosse, G. Le Caer → Fe_7C_3

- ✓**Stable up to 800 K**
- ✓**Trigonal-prism chains**
- ✓**short-range order typical of ortorombic carbide**
- ✓**Crystalization of amorphous Fe-C alloy,**
- ✓**Synthesized at high temperature (1400C) and pressure (80 kbar)**

High-energy ball milling

Powder atomic ratio at_{Fe}/at_{C} = 85:15 or 75:25



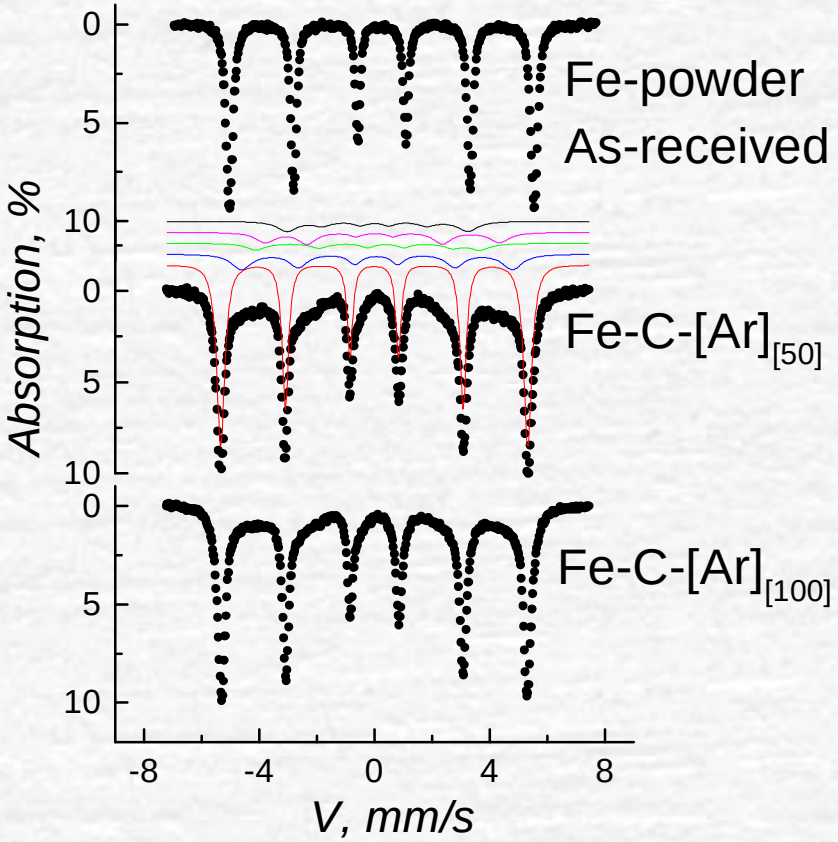


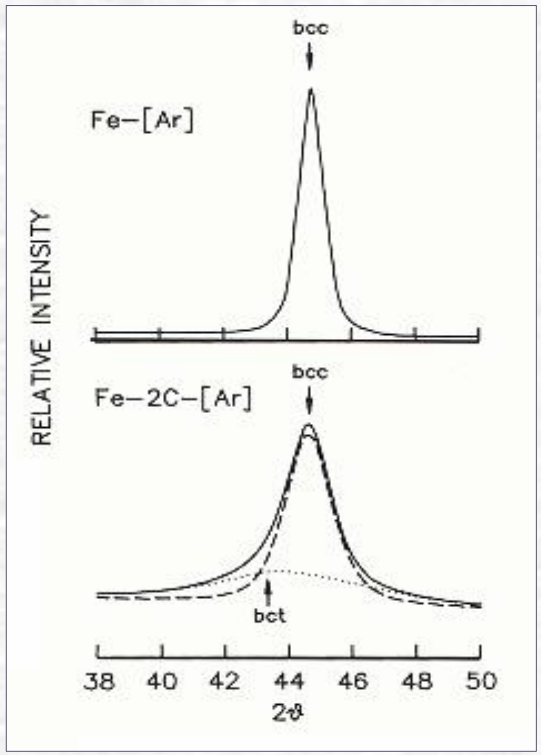
MA Fe+C → AmP Fe-C → Fe_3C

E.P. Yelsukov, G.A. Dorofeev, et al., Mater. Sci. Eng., A 369, 2004, 16-22

High-energy ball milling

Powder mass ratio m_{Fe}/m_C = 80:20





V. M. Nadutov and J. C. Rawers. Mater. Sci. Forum., 278–281, 1998, p.565-70.

J. Rawers, R. Govier, G. Korth. Mat. Sci. Forum, 179-180, 1995, 363-368.

The goal of the work

- to reveal the change in structure and the hyperfine parameters in Fe-particles without alloying and alloyed with C (at_{Fe}/at_{C} = 46:54) by means of power ultrasonics in He environment

Materials

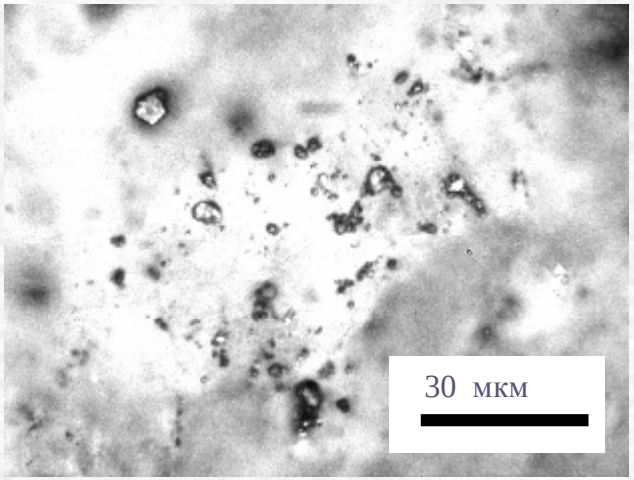
α-Fe-powder

Cr ±0.005	Mn ±0.005	Co	Ni ±0.01	Cu	Ti
0.040	0.09	≤0.016	0.04	<0.01	<0.02

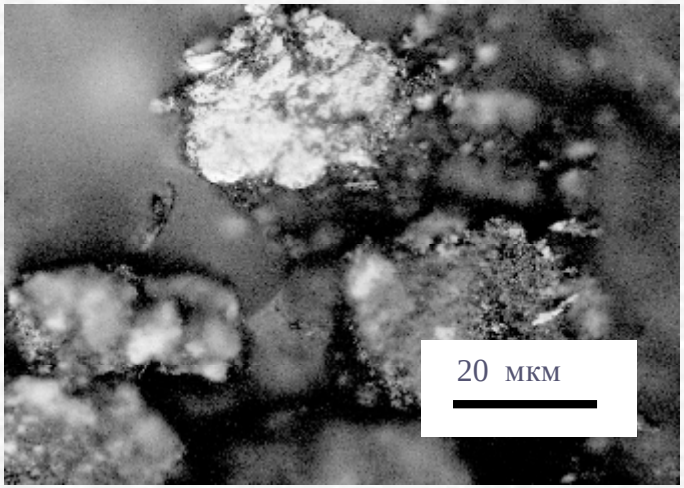
The Fe and C powder atomic ratio m_{Fe}/m_C = 80:20

f.c.c. Fe-30,3%Ni alloy

α-Fe USM in He 50 hrs



General view of part of a sample of processed α-Fe

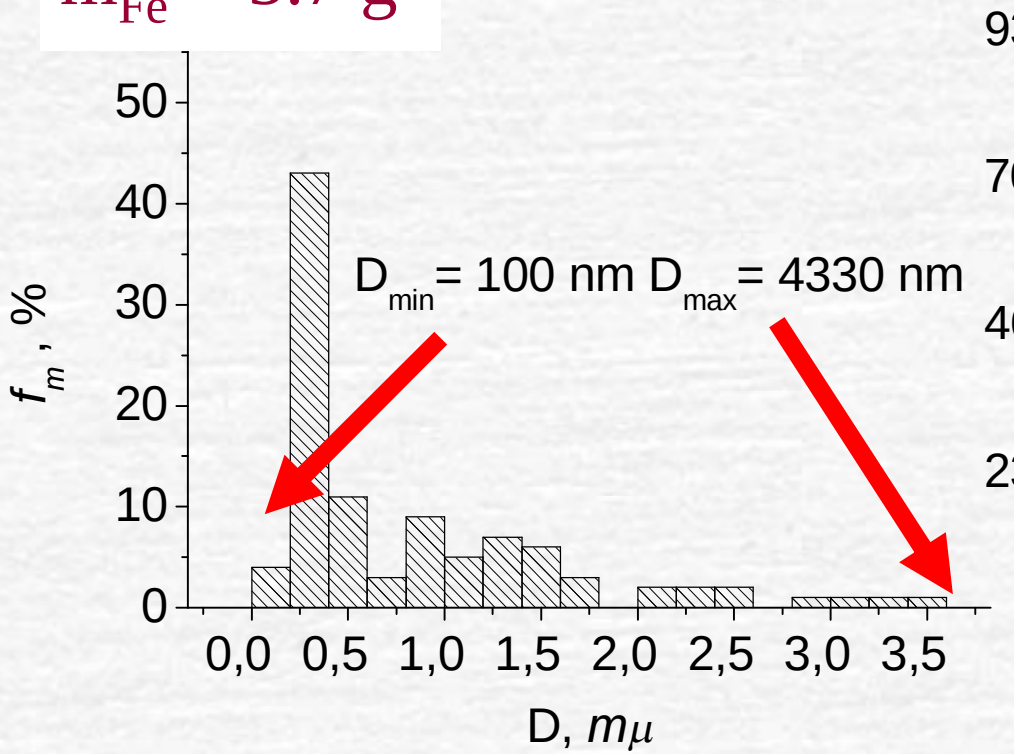


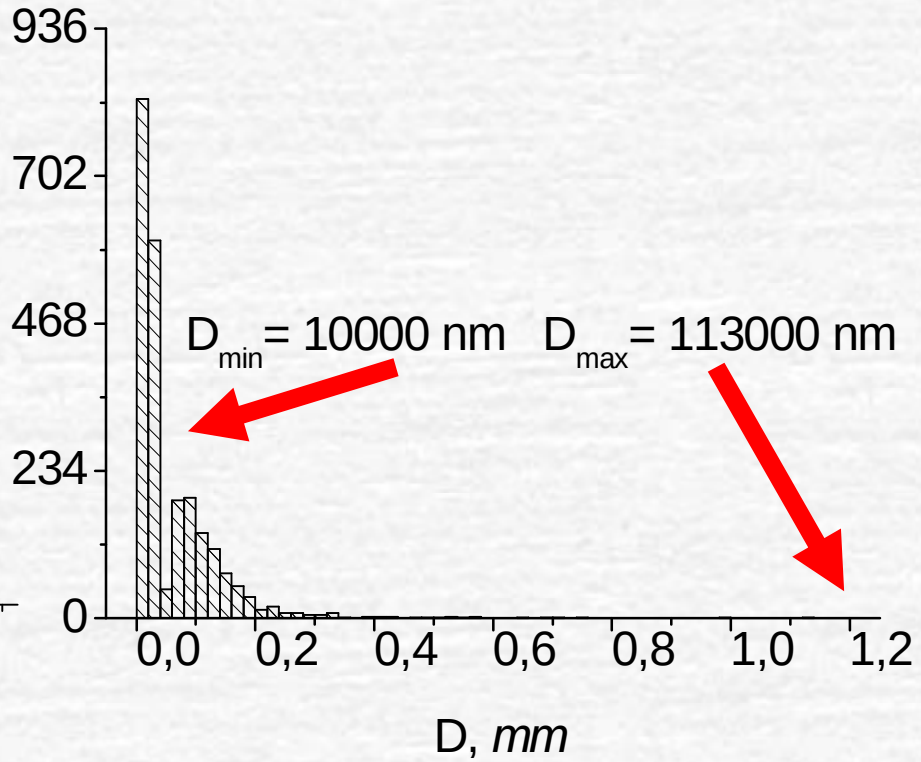
View of separated processed particles of α-Fe

Particles looks like flattened foils (scales)

α-Fe USM in He 50 hrs

m_{Fe} = 5.7 g



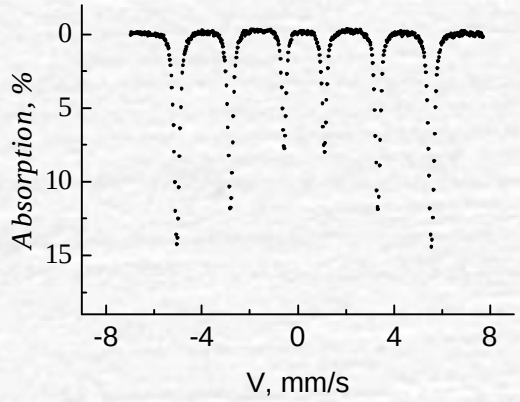


TEM

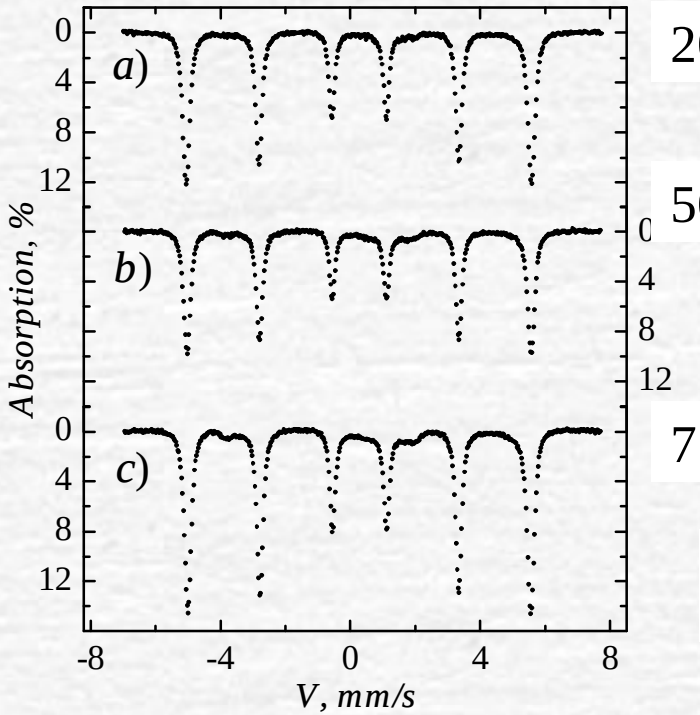
OM

Distribution of sizes of scales is wide, from 100 nm to 1,13 mm

α-Fe-Powder USM in He 50 hrs



1373 K
H = 33 T
G = 0.27 mm/s



20 hrs

50 hrs

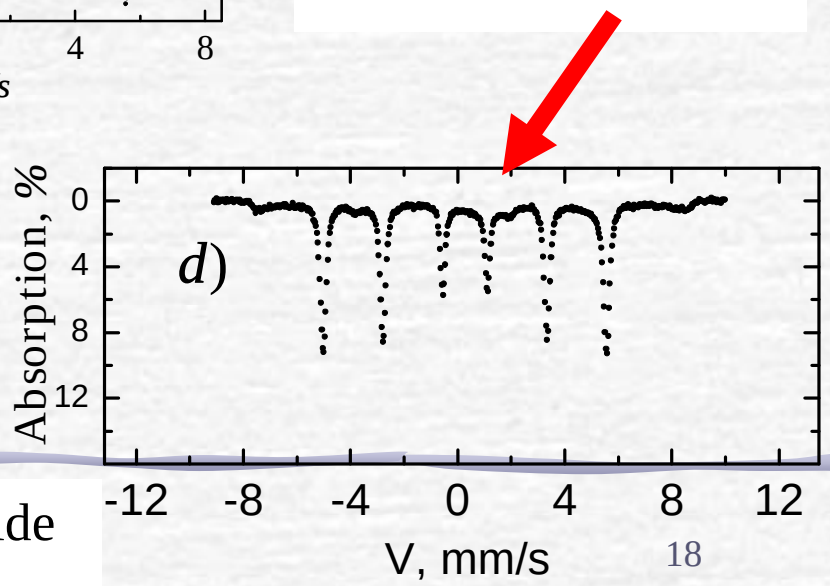
75 hrs

after USM
H = 33 T

USM does not change even G

Fe-O, Fe_2O_3 , Fe_3O_4

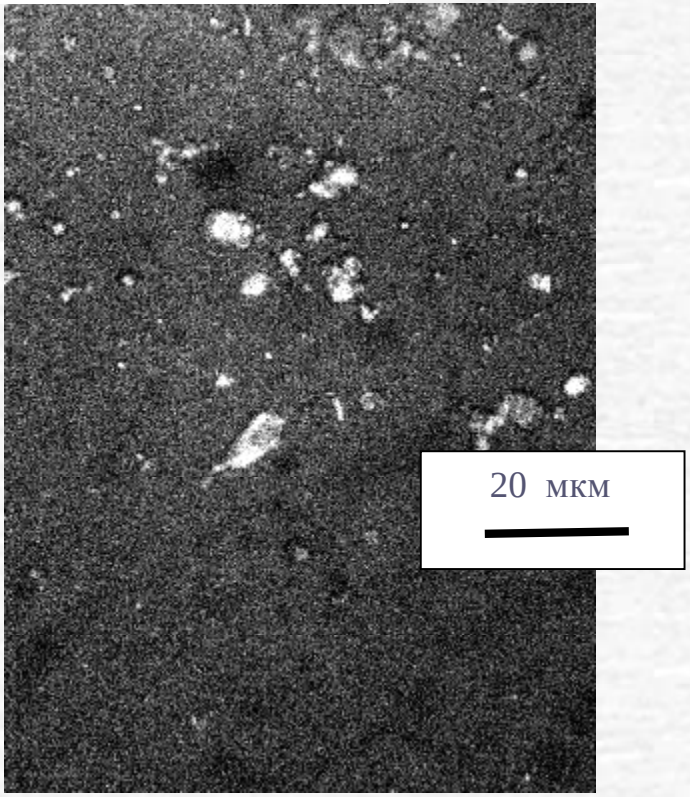
Dislocations were not collected in grains after grinding of particles and they annihilated at their boundaries



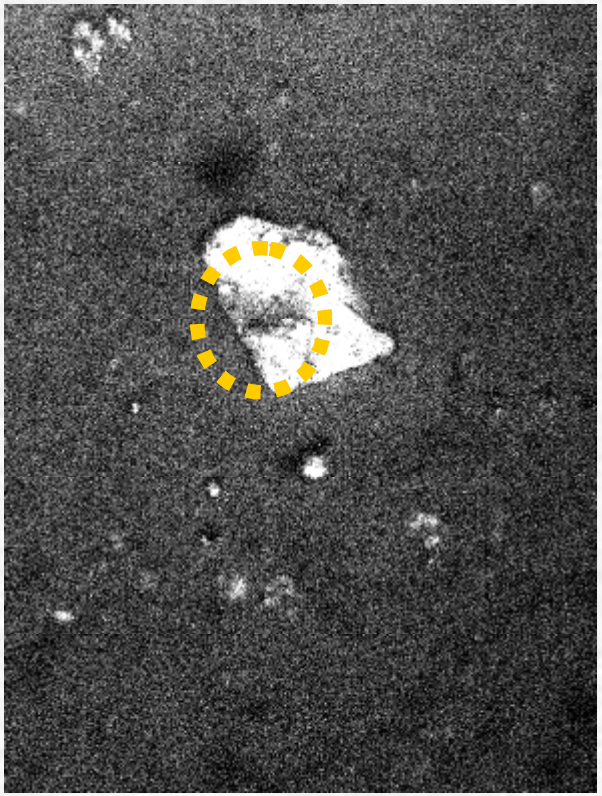
TEM analysis points to Fe-O oxide

$Fe_{46}\ C_{54}$ USM in He 50 hrs

$m_{Fe46\ C54} = 5.7$ g



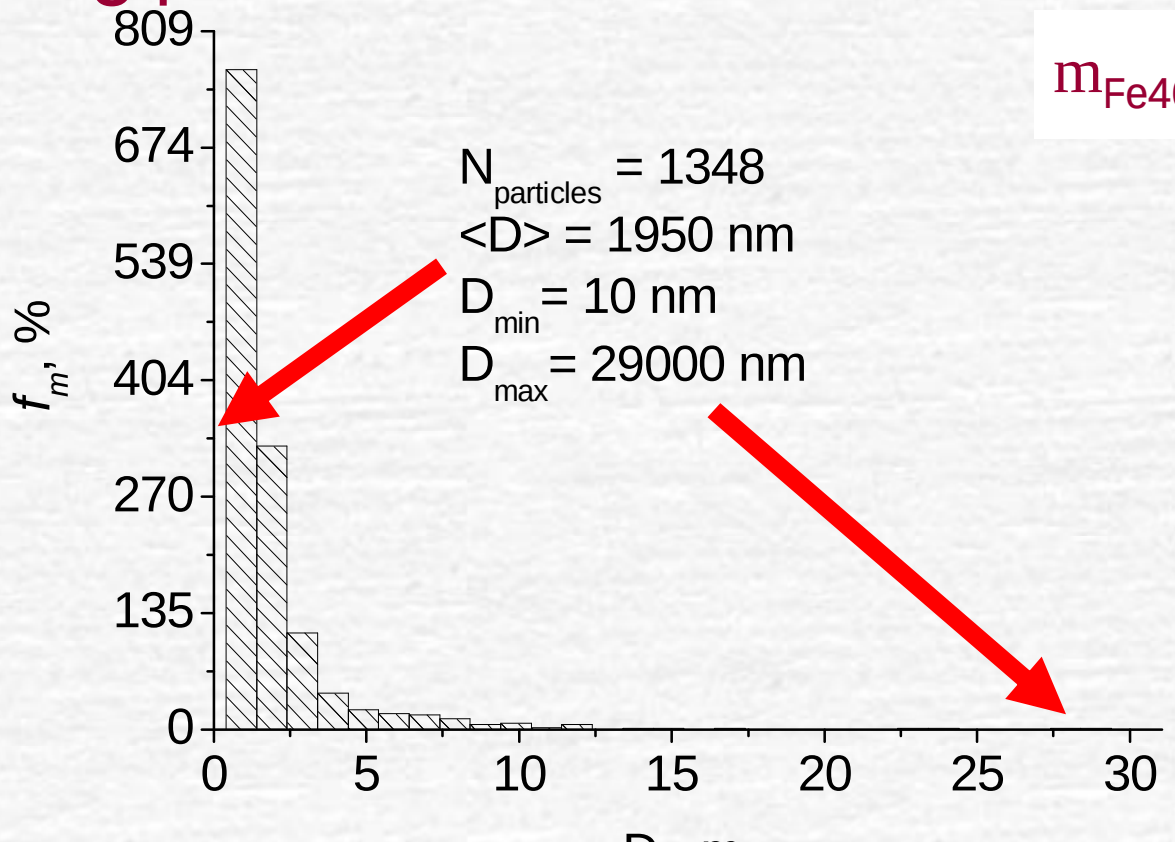
General view of part of a sample of processed $Fe_{46}\ C_{54}$



View of separated particles of $Fe_{46}\ C_{54}$

$Fe_{46}C_{54}$ USM in He 50 hrs

$m_{Fe46\ C54} = 5.7$ g



Distribution of sizes of scales is much narrow, from 10 nm to 29 μm

The process of grinding of Fe powder with C goes more effectively under USM than without C

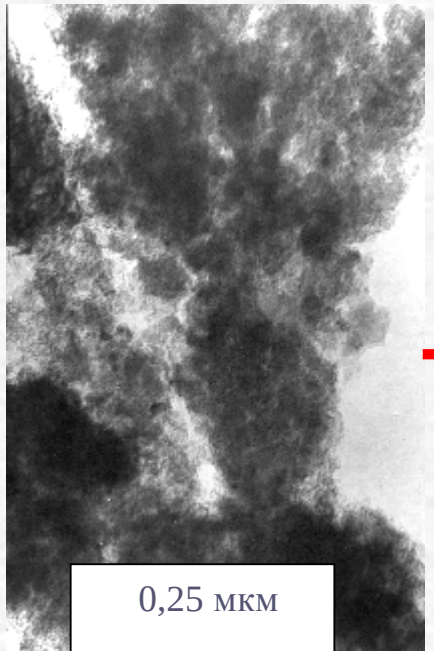
It is consistent to E.P. Yelsukov, G.A. Dorofeev's MA-data ($<L_{fe}>$ = 13 nm, $<L_{Fe-C}>$ = 7 nm)

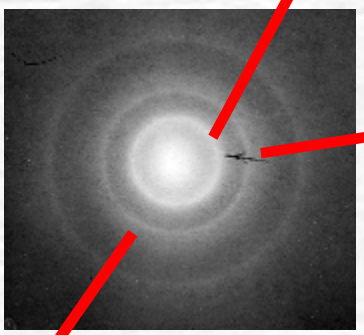
$Fe_{46}C_{54}$ USM in He 50 hrs

I

Distribution of reflections and ring width are close to graphite lattice

$m_{Fe46\ C54} = 5.7$ g





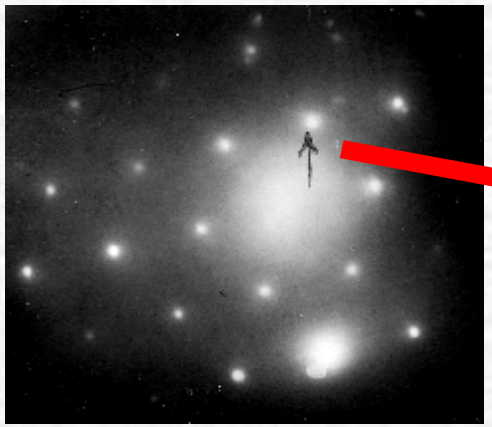
D_{min} = 10-40 nm

dark-field image measured in reflections of graphite

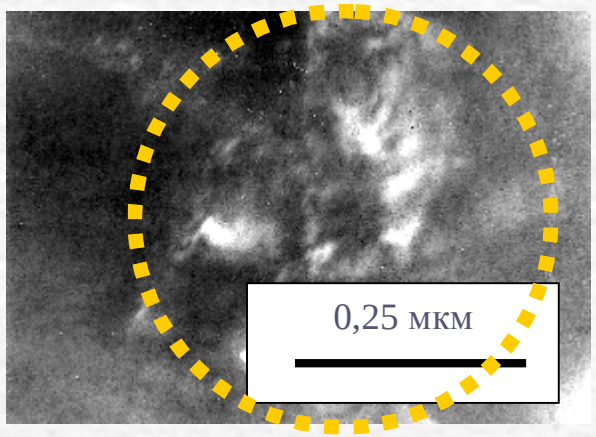
All electron diffraction is formed by complex participation of crystallites of Fe, carbides, oxides. Diffuse character lines is associated with their dispersion.
(no amorphous state)

$Fe_{46}C_{54}$ USM in He 50 hrs

II



b.c.c. Fe
$(111)_\alpha$



dark-field image

- ✓ The elements of ~50 nm are single crystals (without defects)
- ✓ Dislocations and cellular structure in particles of < 50 nm were not revealed

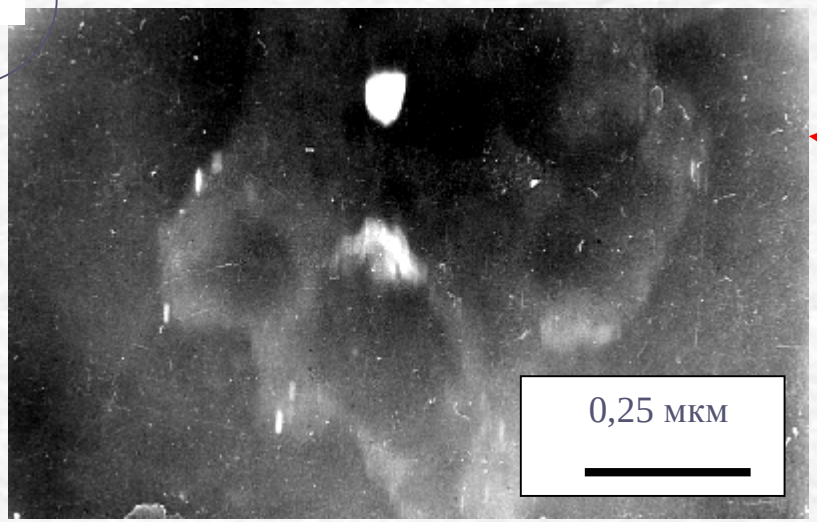
- ✓ Contrast is attributed to high level of strains due to defects of crystal structure in particles larger than 150 nm.

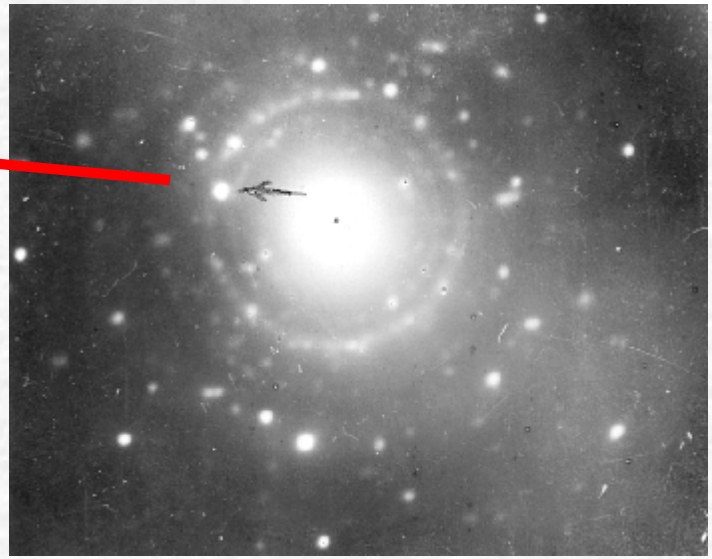
$Fe_{46}C_{54}$ USM in He 50 hrs

III

dark-field image

$m_{Fe46\ C54} = 5.7$ g

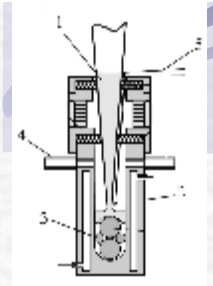




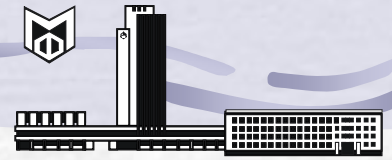
- ✓ In particular the calculation of electron diffractions points to existence of oxides and the the most probable is Fe_3O_4 Diffuse broadening means their dispersion.

- ✓ Some reflections on electron diffractions on their parameters are attributed to Fe_nC_m carbides. However, the data are limited for exact their identification. analysis of dark-field images show the existence of Fe particles and

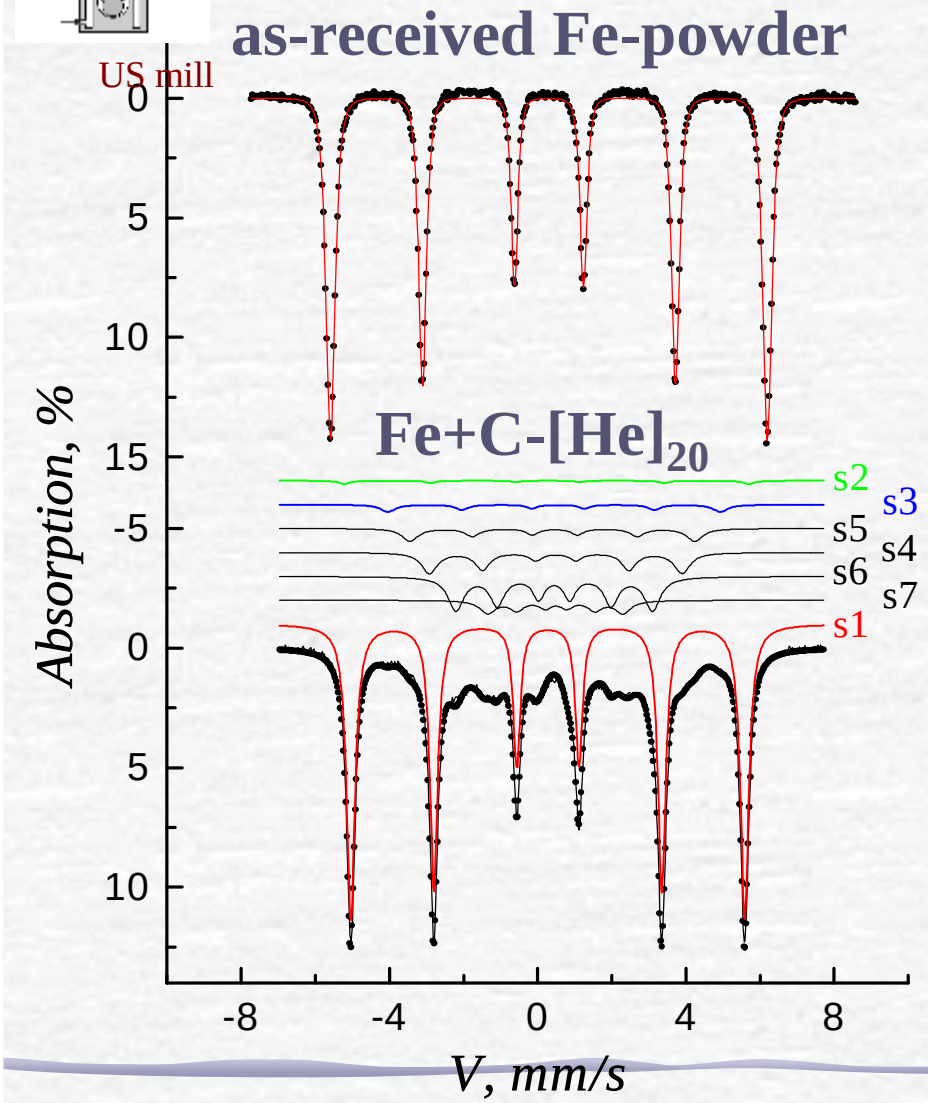
Ultrasonic milling



US mill



High-energy ball milling

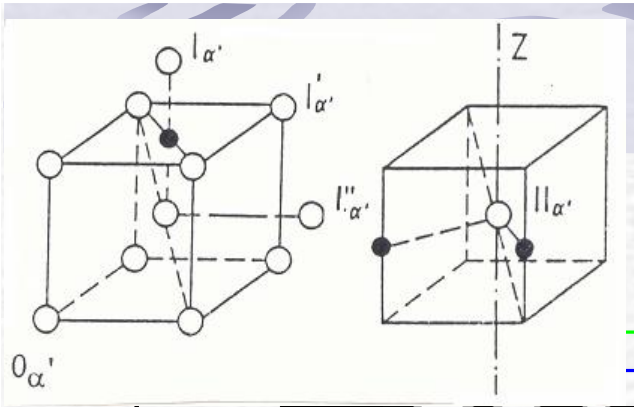


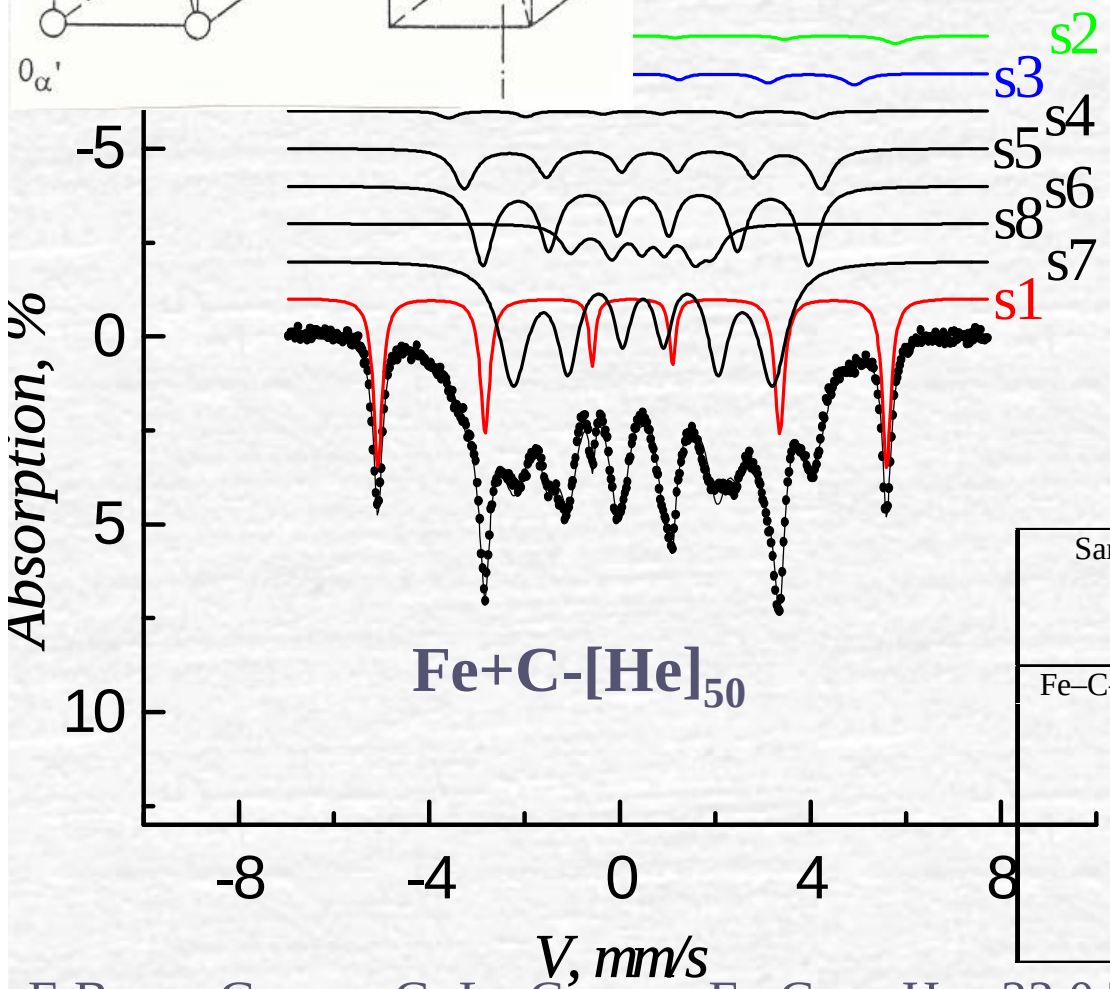
US milling for 20 hrs

Sample	Spectrum component	H_i T ±0.2	δ_i mm/s ±0.008	Δ_1 mm/s ±0.008	$\Gamma^i_{1,6}$ mm/s ±0.008
Fe–C–[He]$_{20}$	s1	33.3	–0.001	–0.006	0.266
	s2	34.2	0.011	–0.054	0.350
	s3	28.1	0.233	–0.378	0.461
	s4	24.0	0.158	–0.157	0.517
	s5	21.3	0.259	–0.021	0.517
	s6	16.6	0.173	–0.002	0.546
	s7	11.5	0.222	–0.134	0.517

E.Bauer-Grosse, G. Le Caer → Fe_7C_3 → H_1 =23.0 T, H_2 = 20.5 T, H_3 =16.5 T

Ultrasonic milling





$Fe_0\,(I'''\alpha')$

$Fe_{1C}\,(I\alpha')$

$Fe_{2C}\,(II''\alpha')$

$Fe_0\,(0\alpha')$

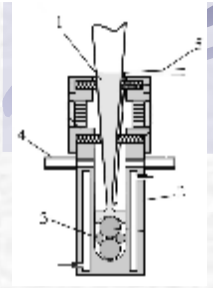
US milling for 50 hrs

Sample	Spectrum component	H_i Тл ±0.2	δ_i mm/s ±0.008	Δ_I mm/s ±0.008	$\Gamma^i_{1,6}$ mm/s ±0.008
Fe–C–[He]$_{50}$	*s*1	33.5	–0.011	–0.005	0.218
	*s*2	34.3	0.034	0.051	0.515
	*s*3	27.7	0.254	–0.078	0.517
	*s*4	24.2	–0.013	–0.001	0.460
	*s*5	23.5	0.280	–0.300	0.517
	*s*6	21.4	0.243	0.113	0.517
	*s*7	17.0	0.213	0.001	0.712
	*s*8	9.4	0.302	–0.482	0.517

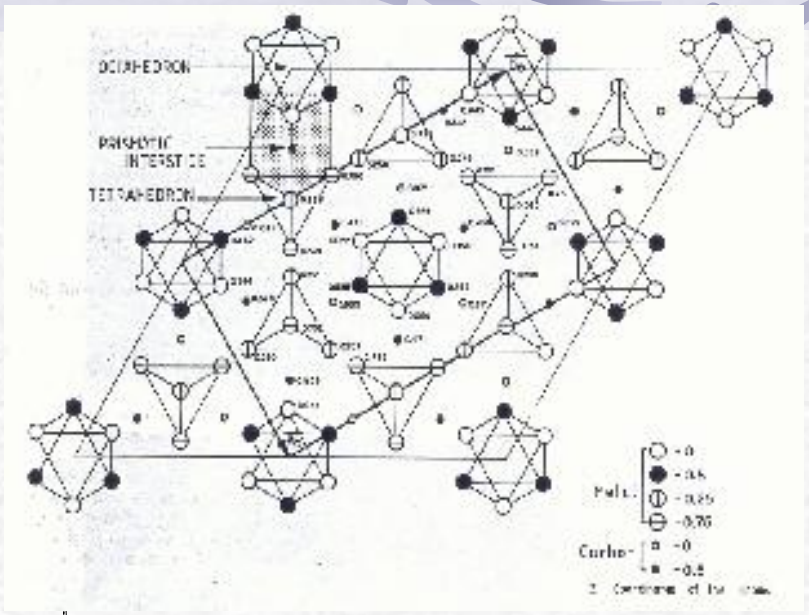
E.Bauer-Grosse, G. Le Caer → Fe_7C_3 → H_1 =23.0 T, H_2 = 20.5 T, H_3 =16.5 T

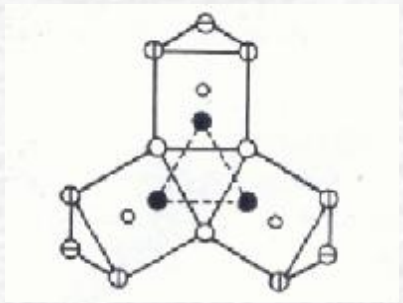
E.P. Yelsukov, G.A. Dorofeev, et al, → AmPase → H =22.0 T - 23.8 T, H =23.5 T - 26.0 T, T_C =550-605 K

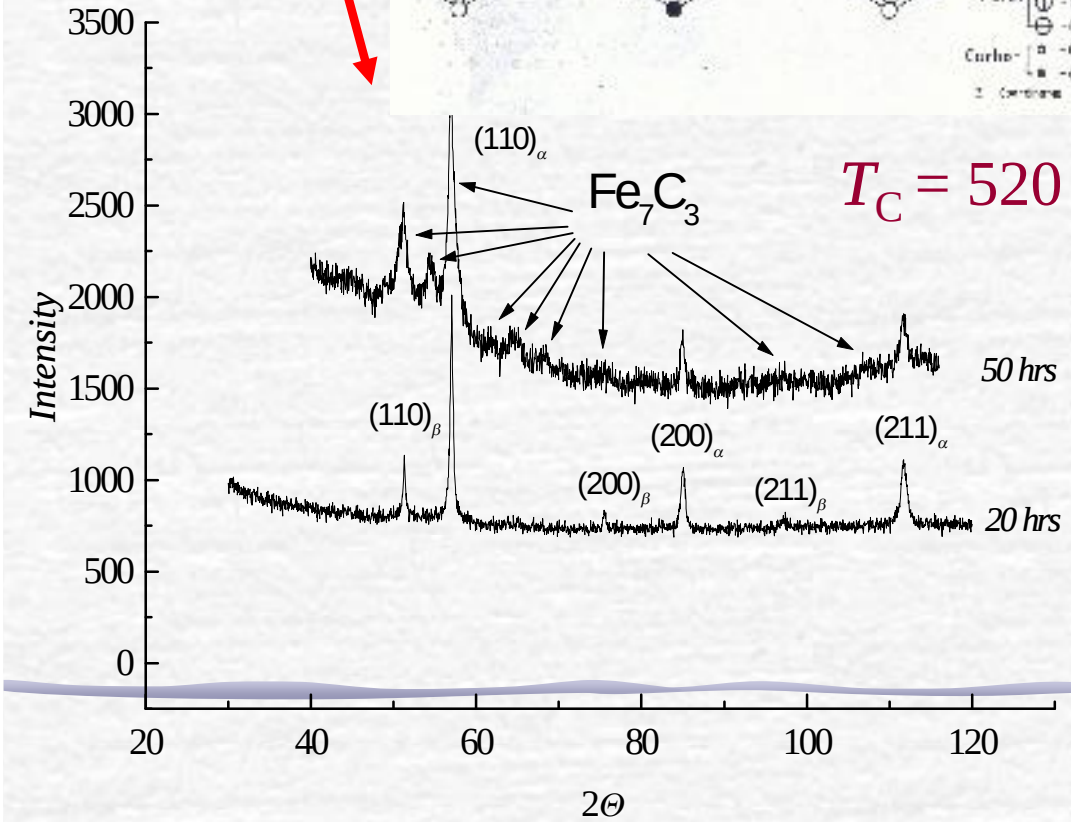
Ultrasonic milling



US mill





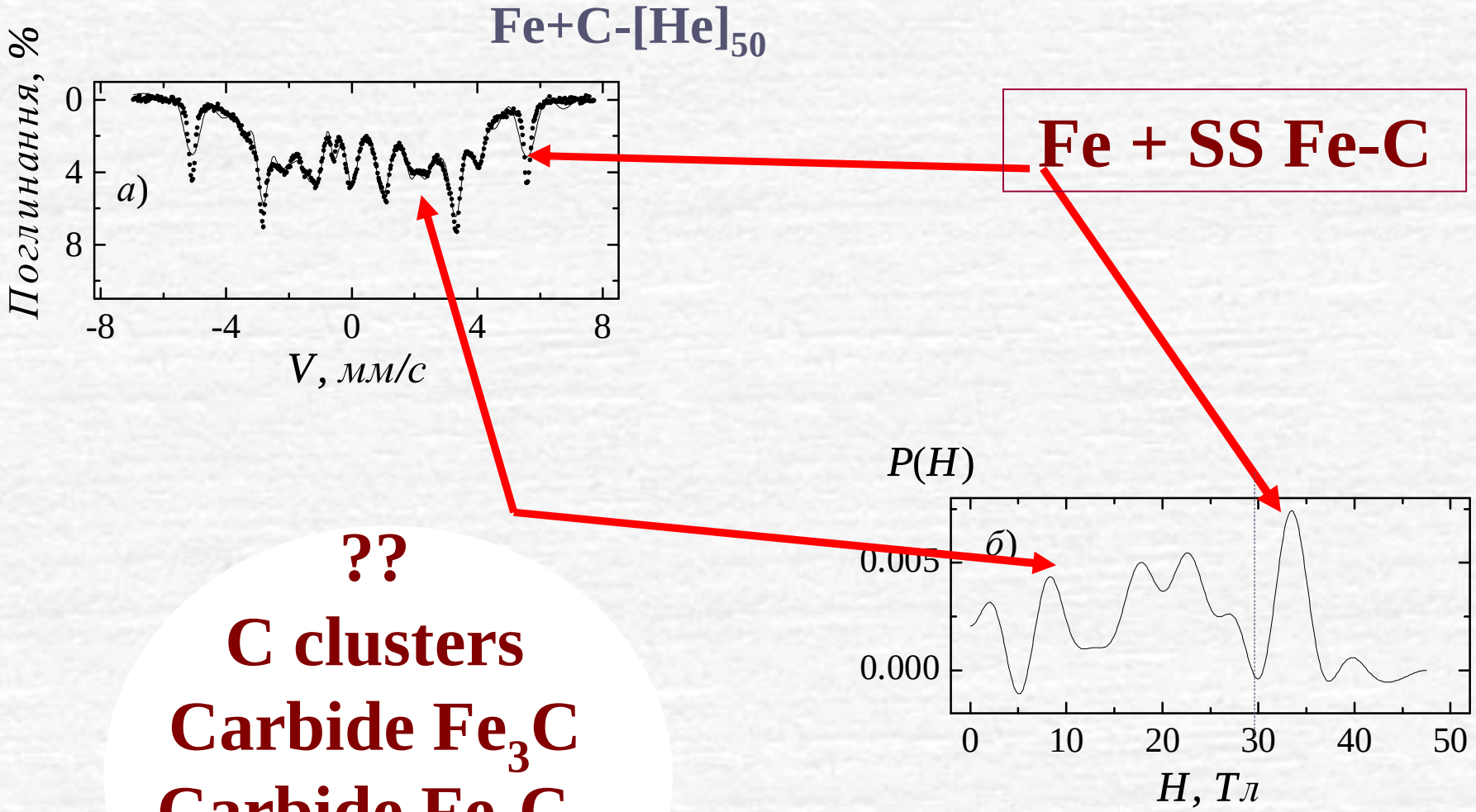


T_C = 520 K

The calculation of diffraction pattern of Fe–powder after ultrasonic milling for 50 hrs.

		α-Fe	Fe_7C_3	
No	d, nm	hkl	d, nm	hkl
1	0,231104	Beta3		
2	0,2243	Beta4	0.2255	210
3	0,212163		0,2122	102
4	0,203164	110		
5	0,202028		0,2019	211
6	0,188757		0,1895	112
7	0,182357		0,182	301
8	0,179615	beta11		
9	0,172352		0,172	220
10	0,163211	?		
11	0,158361	beta 13		
12	0,1435	200		
13	0,141804		0,1417	401
14	0,117067	211		

Ultrasonic milling



??

C clusters

Carbide Fe_3C

Carbide Fe_7C_3

AmPhase Fe-C

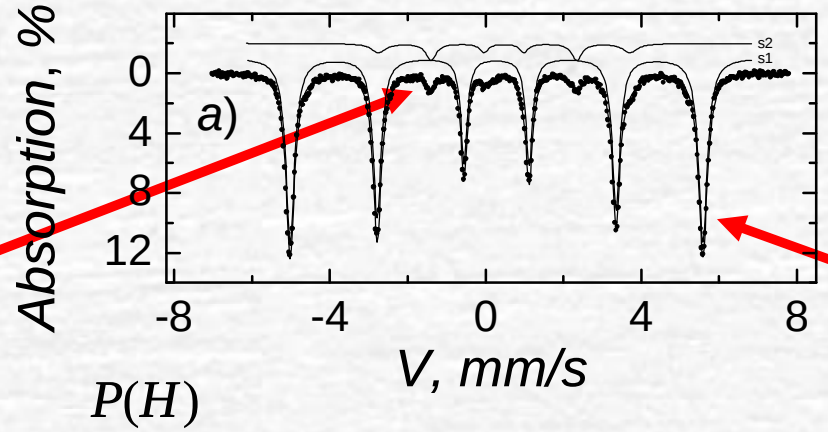
Oxides

81,9%

Ultrasonic milling+ Ageing

Fe+C-$[He]_{50}$ 1273 K

Fe_3C 9,5%



α-Fe

T_C = 480 K
H = 208-210 T

Ultrasonic milling+ Ageing

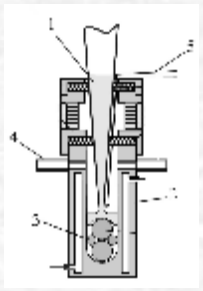
Line No	Experiment *d*, nm	**α-Fe** [1]	Fe_3C [1]
		hkl	*hkl*
1	0.2629539	*β*	
2	0.2550530		020
3	0.2384291		112; 021
4	0.2240548	(110)*β*	
5	0.2107304		121
6	0.2066304		210
7	0.2031318	(110)*α*	
8	0.2014488		022; 103
9	0.1975928		211
10	0.1872829		113
11	0.1856237		122
12	0.1759389		212
13	0.1686038		004; 023
14	0.1583966	(200)*β*	130
15	0.1432947	(200)*α*	
16	0.1289839	(211)*β*	
17	0.1172382	(211)*α*	
18	0.1172327	(211)*α*	

1273 K

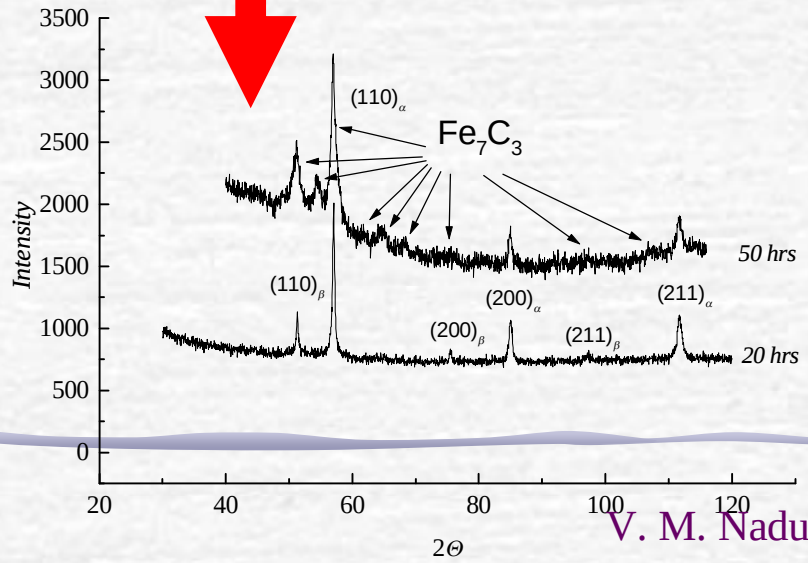
[1] *The International Center for Diffraction Data* (Table 17-0333). .

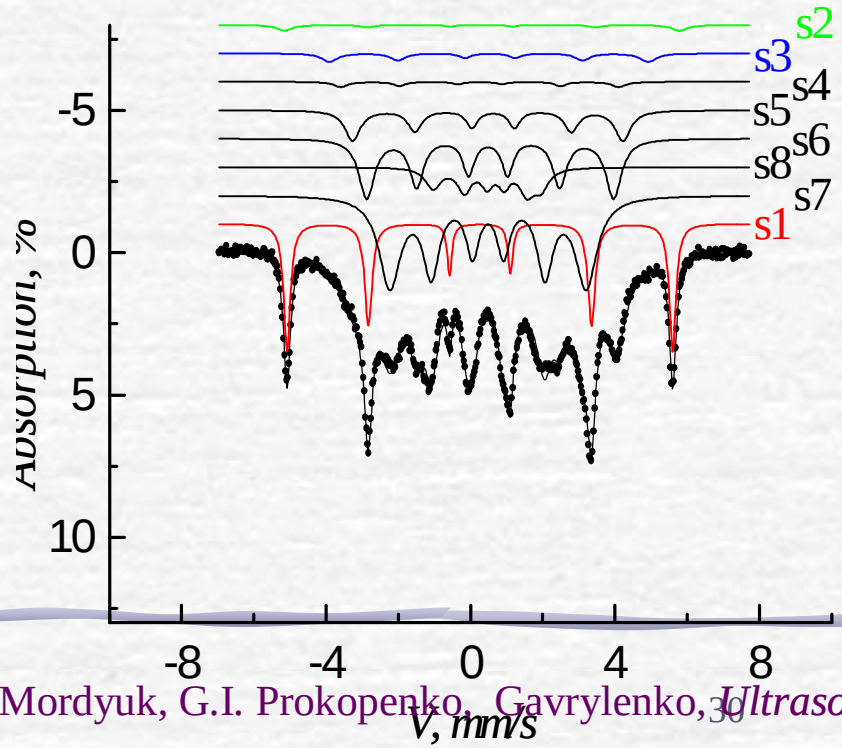
Ultrasonic milling

81,9% (SS Fe-C + Fe_7C_3 + AP Fe-C) → ≠ 9,5% (Fe + Fe_3C)



US mill





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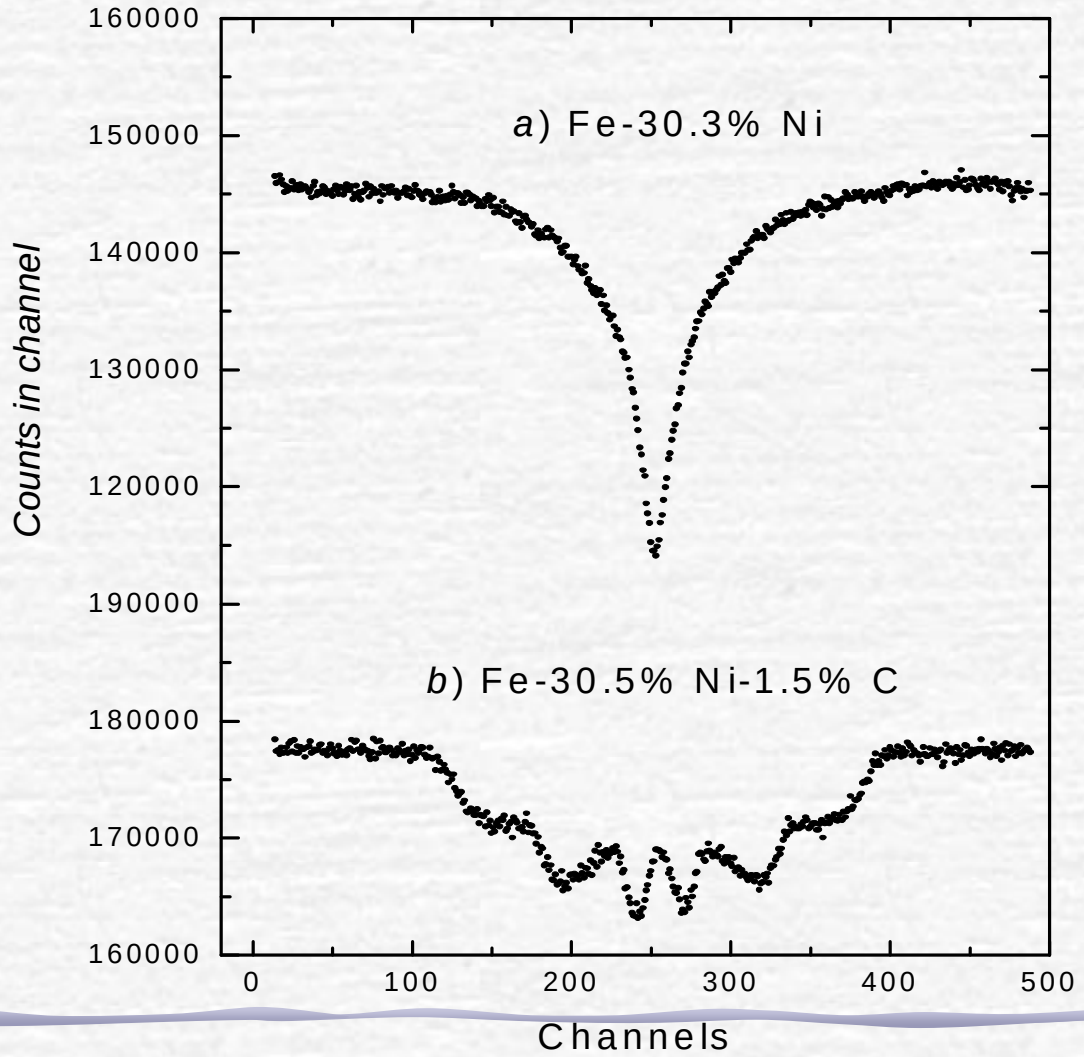
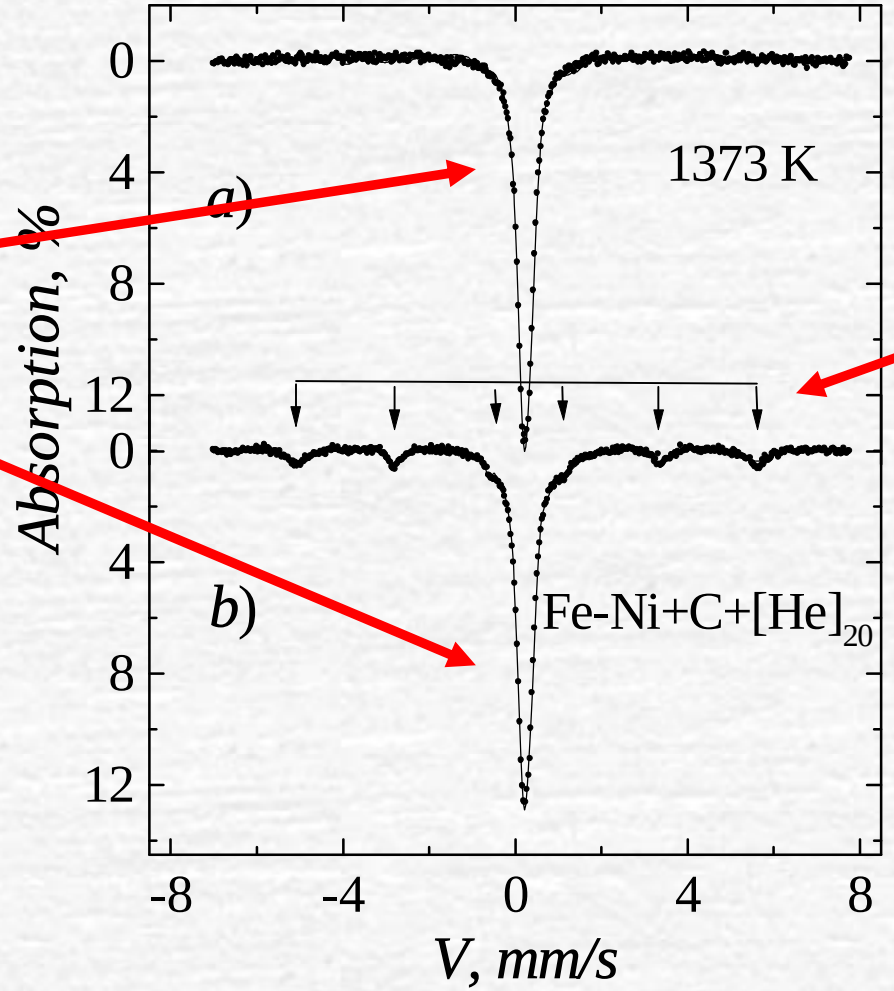
Fe-Ni-C


160000
150000
140000
130000
120000
190000
180000
170000
160000
Counts in channel
a) Fe-30.3% Ni
b) Fe-30.5% Ni-1.5% C
0
100
200
300
400
500
Channels

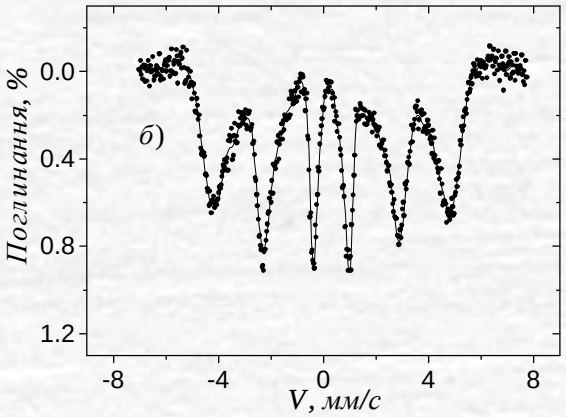
USM FCC $(Fe_{70}Ni_{30})_{46}C_{54}$ He 20 hrs



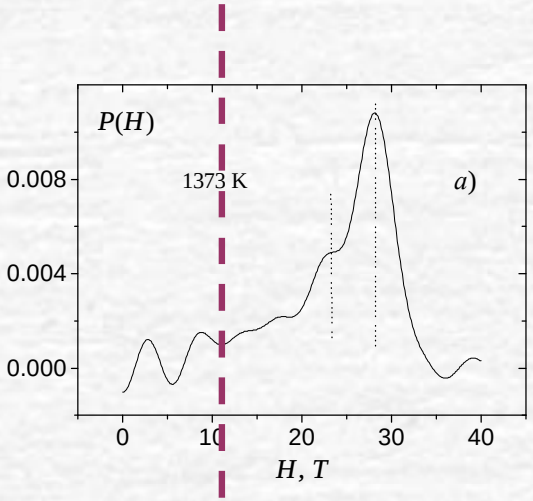
- **Austenite**

- **Martensite**
  d = 0,2029 nm
  $(110)_\alpha$
- **cementit**
  Fe_3C (?)
  crystallites
- **d = 0,168 nm**
- **d = 0,119 nm**

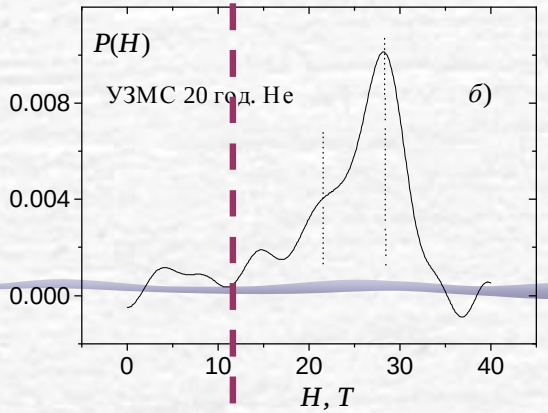
USM $(Fe_{64}Ni_{36})_{46}C_{54}$ He 20 hrs



1373 K

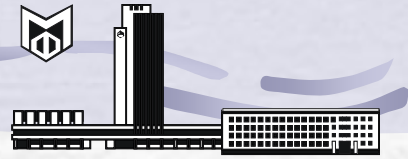


USM



- ✓ No carbides
- ✓ No martensite
- ✓ Solid solution

Conclusions



- The ultrasonic milling in a gaseous He environment results in more effective grinding of Fe particles in blend of Fe-C-powder (at_{Fe}/at_C = 46:54) than without C and dissolution of C in iron particles.

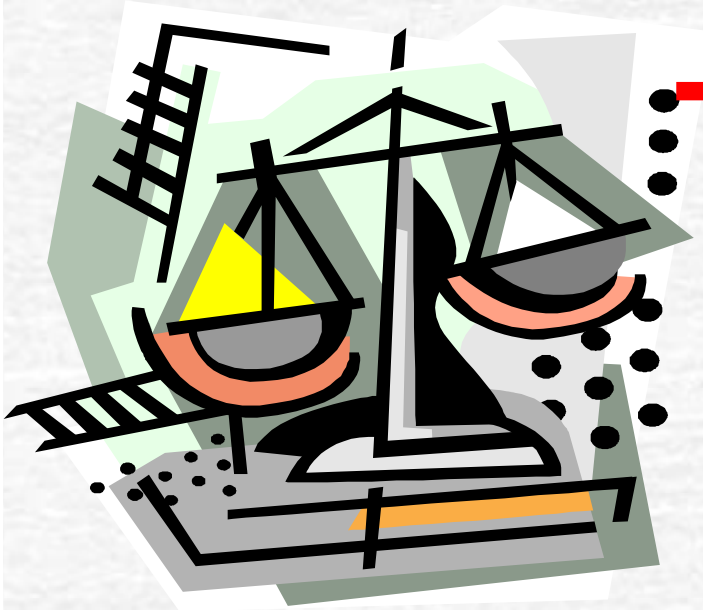
- The distribution of carbon in Fe particles is inhomogeneous and characterised by existing of single C atoms, carbon clusters, iron carbide Fe_7C_3 . The iron oxides are observed and an existence of am.phase is not excluded.

- Ageing of US treated Fe-C powder results in $Fe_7C_3 \rightarrow Fe_3C$ transition.

- The ultrasonic milling is an effective technique for grinding of powders and MA

The #2412 and NN32 STCU projects supported these studies

Дякую за увагу !



Thanks for your attention !