Structure and properties of a chromium-molybdenum steel modified by fullerene and carbon nanotube additions

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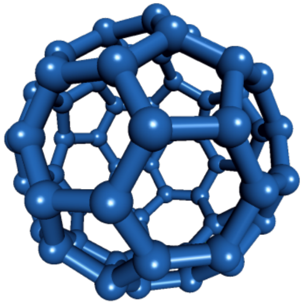
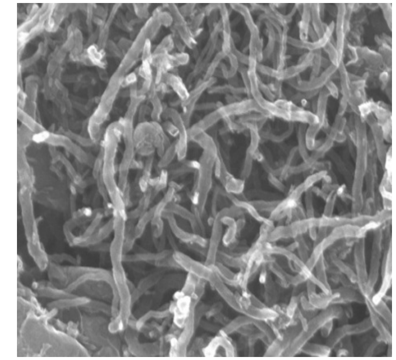
Introduction





In recent years, nanostructured carbon forms, such as fullerenes and carbon nanotubes (MWCNT) become more often used for modifying and preparation of carbon composite materials based on metals, alloys, polymers, and ceramics. Production processes used for these materials exhibit a great variety. More frequently, the modification of materials by nanostructured carbon forms is performed by high-energy milling and hot pressing.

However, no information about studies related to the modifying of high-alloyed steels, in particular, widely used industrial chromium-molybdenum steels, is available in the literature.

Thus, the complex studies of structure and properties formation regularities of the steels, which were prepared by high-energy milling with fullerene and CNT additions and subsequent hot pressing and heat treatment, is the topical both research and practical points of view.

Objectives

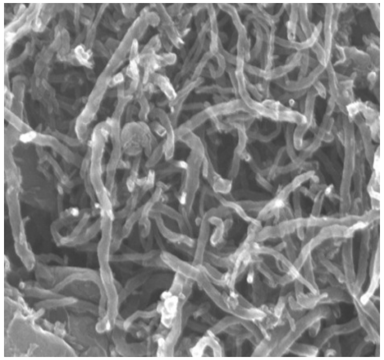
- to investigate features of structure formation of powders produced by high-energy milling process (HEMP) chromium-molybdenum steel with additions of fullerenes and carbon nanotubes;
- to study the structural transformations occurring during hot pressing and rolling of steel samples;
- to investigate the effect of heat treatment on the morphology of the resulting compacts;
- to evaluate the mechanical properties
- to identify the effect of carbon modifiers (fullerenes and nanotubes) on the structure and properties of the materials.

Materials

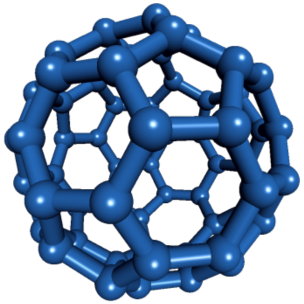
Chromium-molybdenum steel (CM-steel)

Chemical composition, %									
C	Si	S	P	Cr	Ni	Mo	V	Nb	B
0.1-0.15	< 0.5	< 0.15	< 0.025	11.0-13.5	0.05-0.3	1.5-2.0	0.1-0.3	0.15-0.4	< 0.005

Multi-wall Carbon Nanotube (MWCNT)

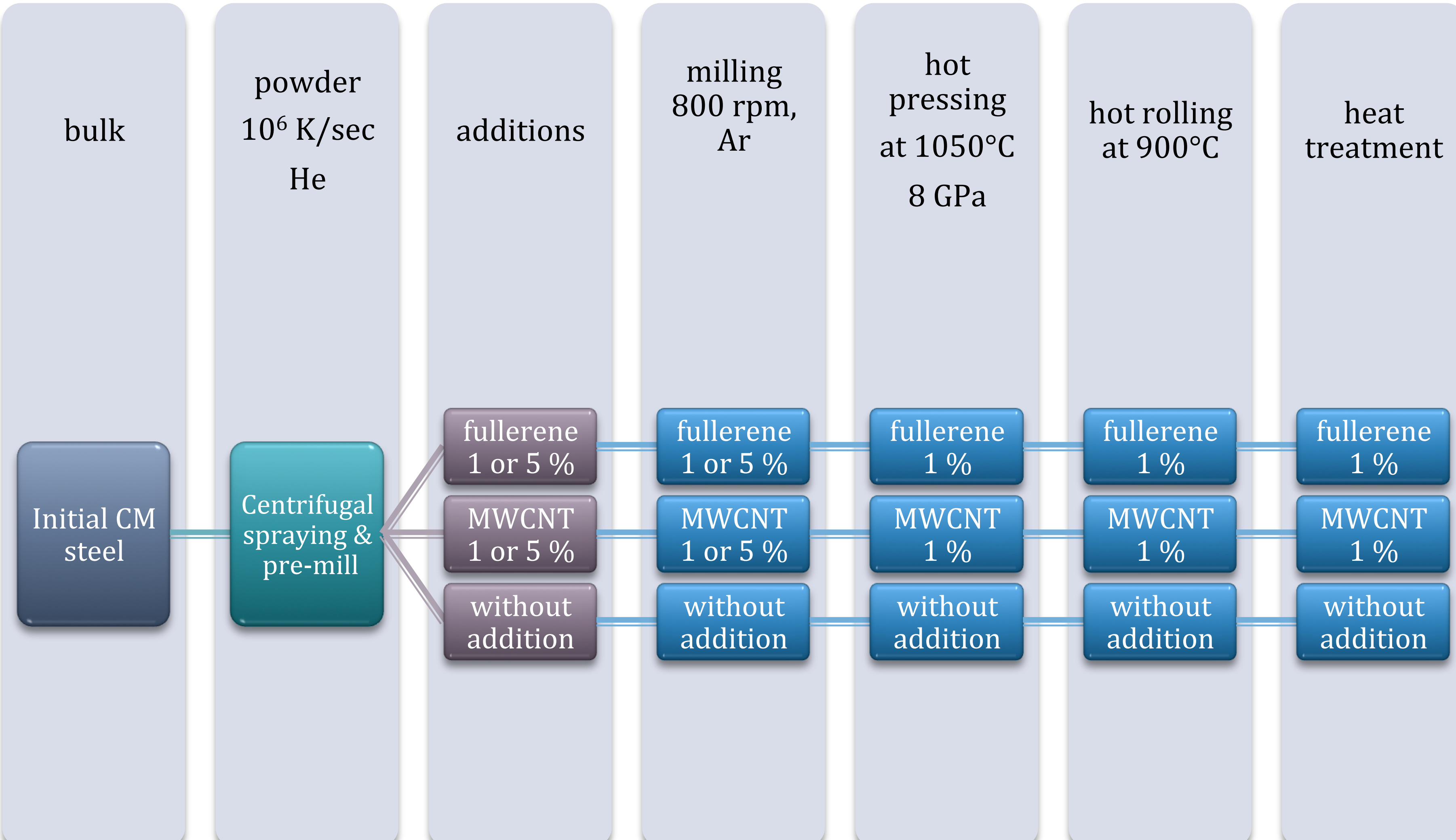


Fullerenes

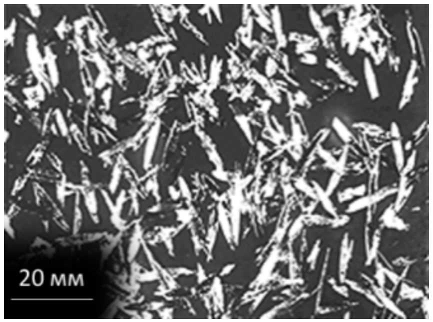


Fullerene concentrate containing
85% C_{60}, 10% C_{70} and 5% of higher fullerenes.

Experimental scheme

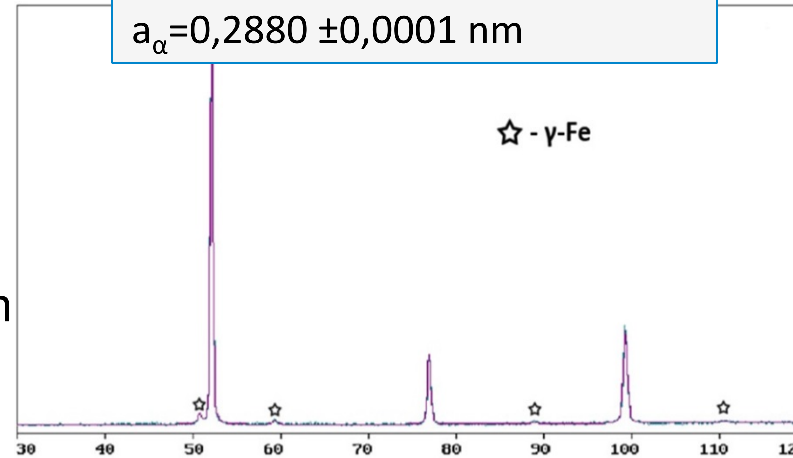


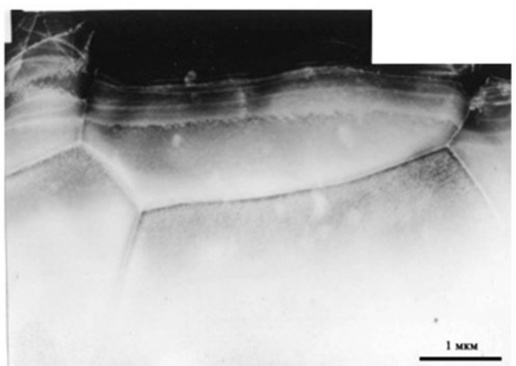
Initial structure of CM-steel

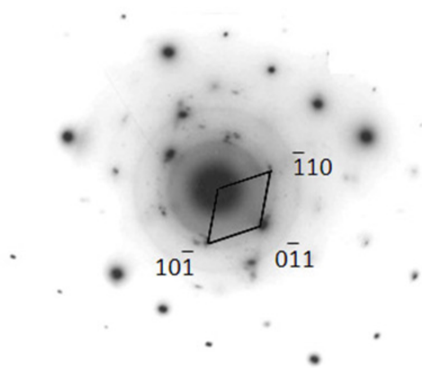


The flakes:
length ≈ 1-3 cm
width ≈ 0,5 cm
thickness of about 10 μm

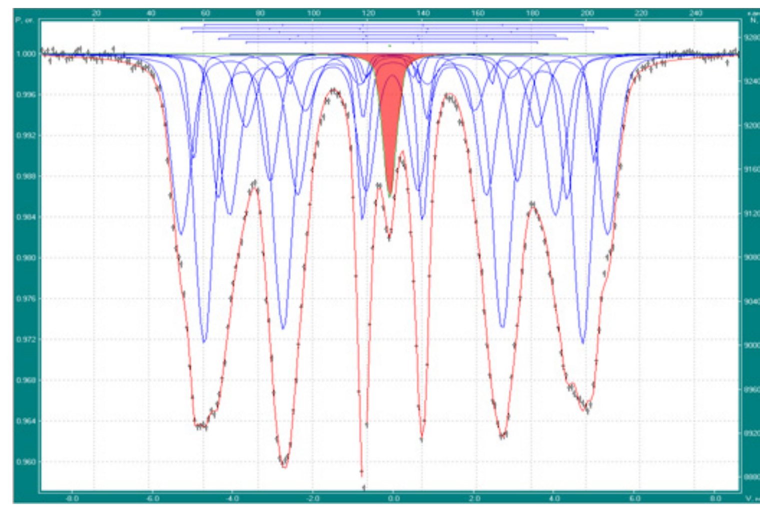
α-Fe + (3-6)% γ-Fe
a_{α}=0,2880 ±0,0001 nm





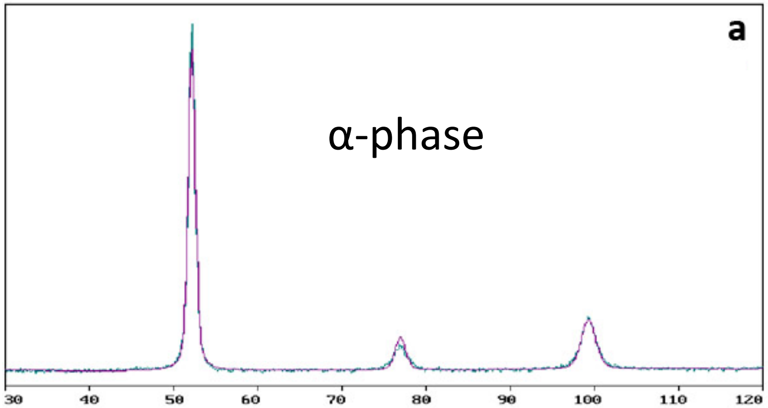


- α-phase
- grain size is 2 - 6 μm

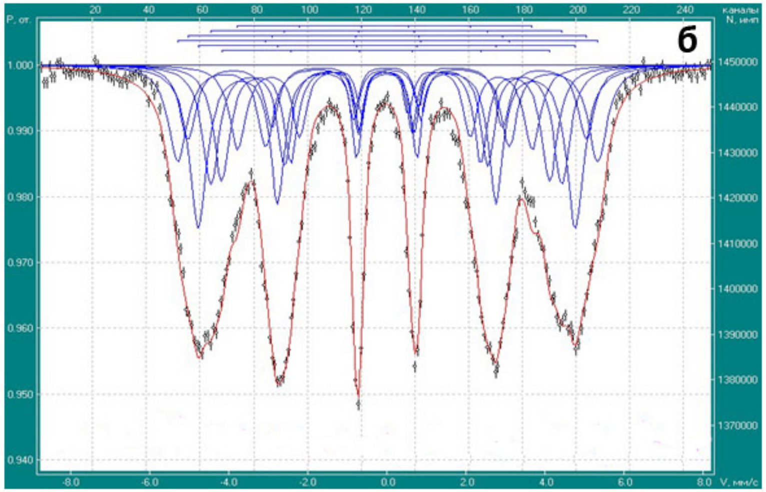


- austenitic singlet
- sextet with distribution of hyperfine field from up to 330-260 kOe (α-solid solution)

CM-steel after pre-milling



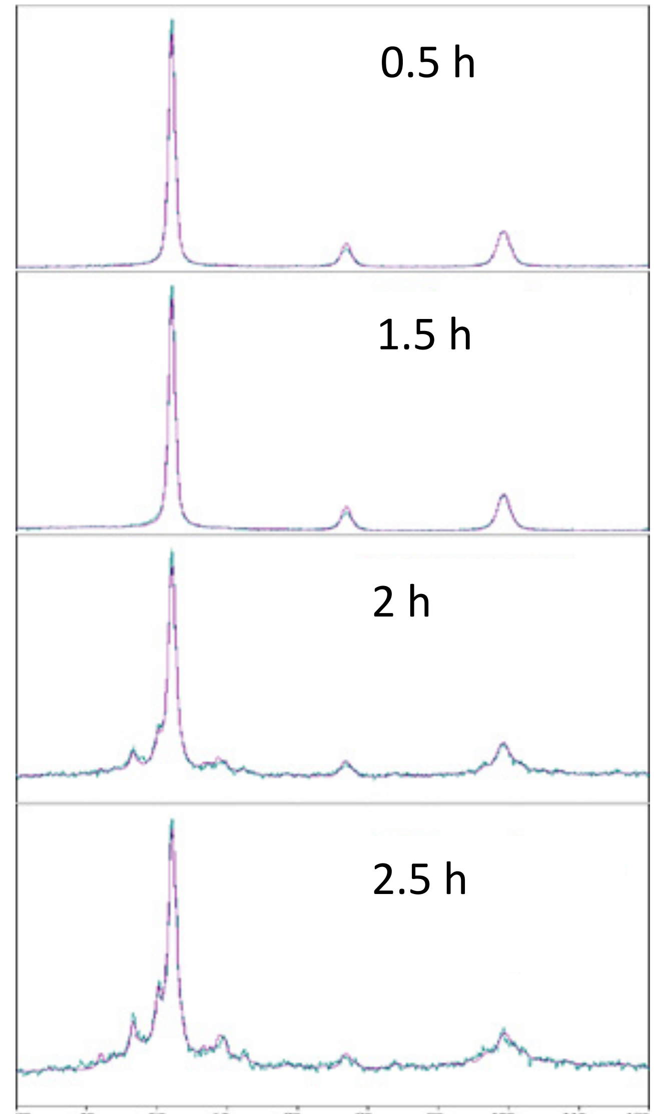
- austenite diffraction peaks is not detected
- α-phase with a_α=0,2880 ±0,0001 nm



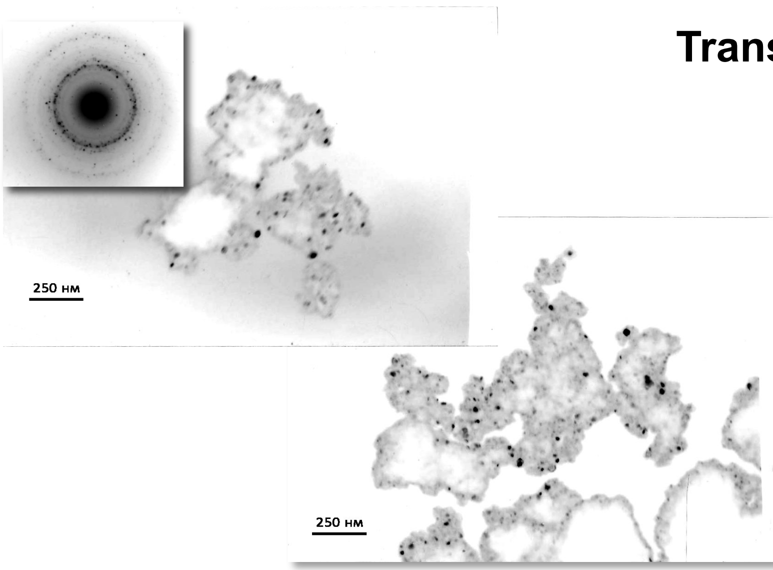
- distribution of the hyperfine magnetic field for sextet is same as in initial state
- austenitic singlet is absent

XRD of CM-steel after milling with 5 % of fullerene & MWCN additions

- halo around the line (110) α-phase (after 2 h in the case of fullerenes additives and after 0.5 hour milling with adding CNTs).
- longer milling resulted in the formation of carbides:
  - (54 ± 5)% Me_7C_3 and (13 ± 1)% Me_3C (in the case of fullerenes additions)
  - (80 ± 3)% Me_3C (in the case of CNT addition)
- the particle size of α-phase and carbides, determined from diffraction line broadening analysis, was about 10 nm.



Structure of CM-steel after milling with 5 % of fullerene addition



Transmission electron microscopy

- powder particles with size of about 1 μm,

- this particles contain mixture of equiaxed particles of α-Fe and carbides with size of 10 - 15 nm

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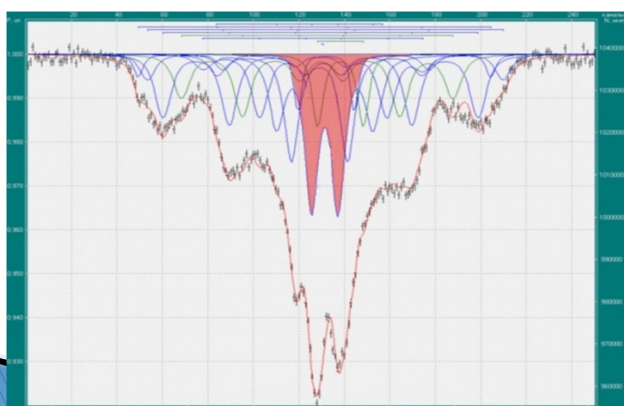


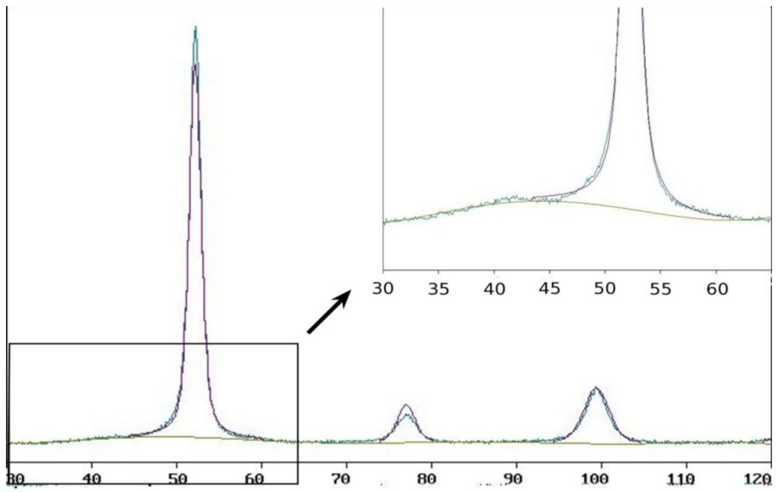
Mossbauer spectroscopy

- there is α-phase with distribution **of** hyperfine magnetic field from 250 up to 330 kOe

- sextets lines with smaller hyperfine magnetic fields (150 - 200 kOe)

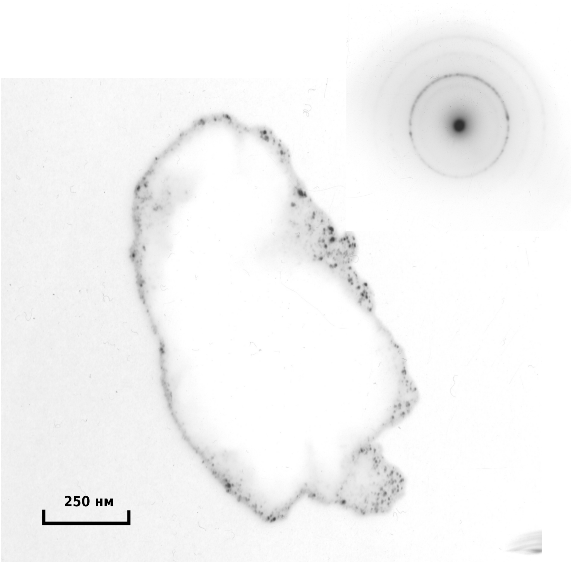
- doublet associated with the presence of the unknown paramagnetic phase.

Structure of CM-steel after milling with 1 % of fullerenes & CNT additions



XRD analysis

- diffraction peaks of α-phase
- halo near the diffraction peak of α-phase (110)
- size nanocrystallites of α-phase is about 10 nm.

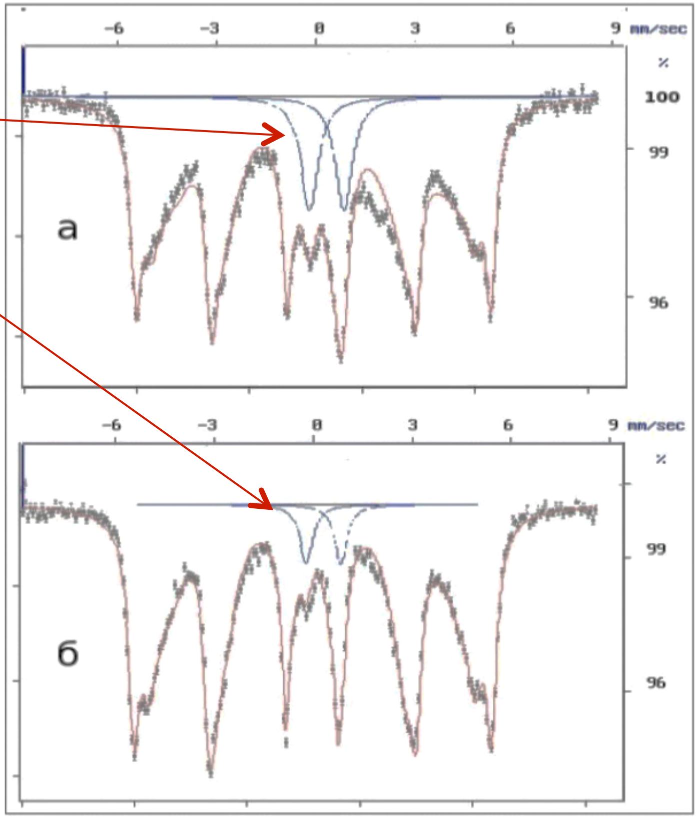


Transmission electron microscopy

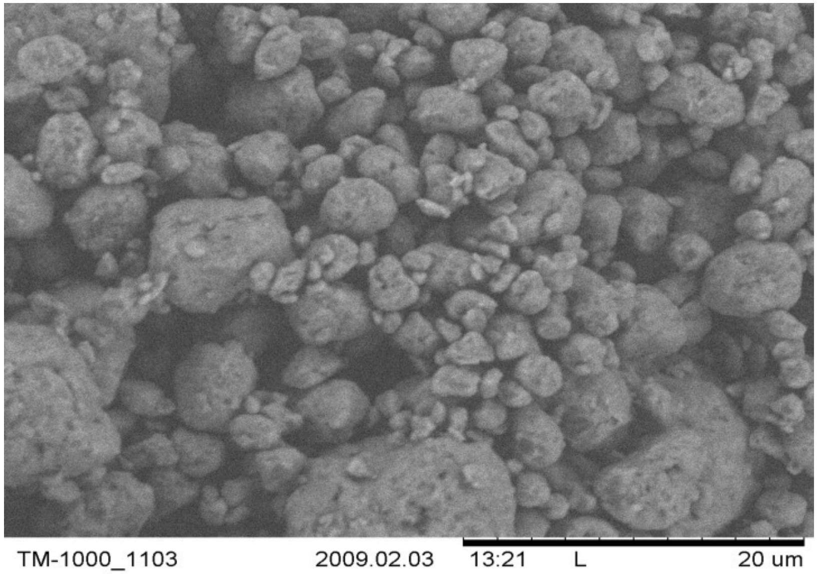
- diffraction reflections of carbides are not detected
- powder particle size is about 1 μm
- powder particles contain small equiaxed crystallites of α-phase with sizes of about 10 - 20 nm

Structure of CM-steel after milling with 1 % of fullerenes & MWCNT additions

Mössbauer spectra

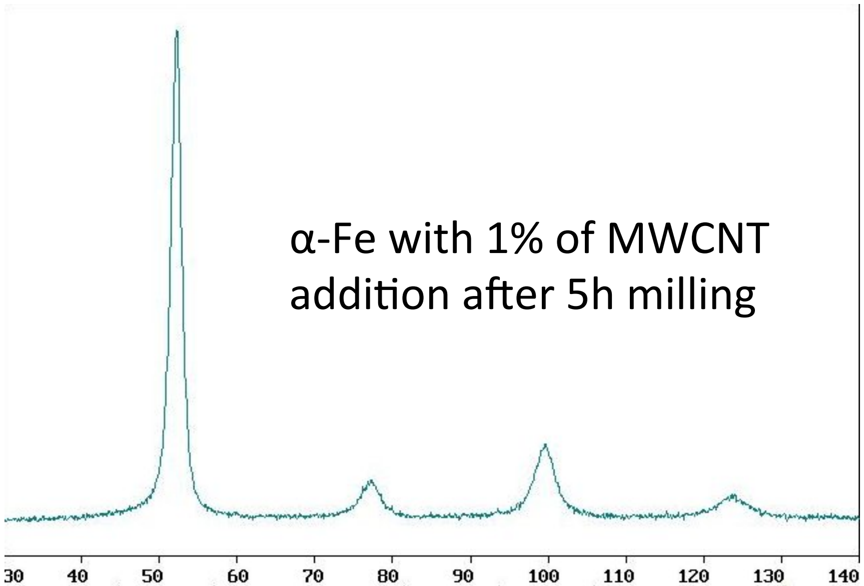


- paramagnetic doublet along with the sextet corresponding to the α phase
- doublet indicates that there is interaction between the components of steel with a carbon additives



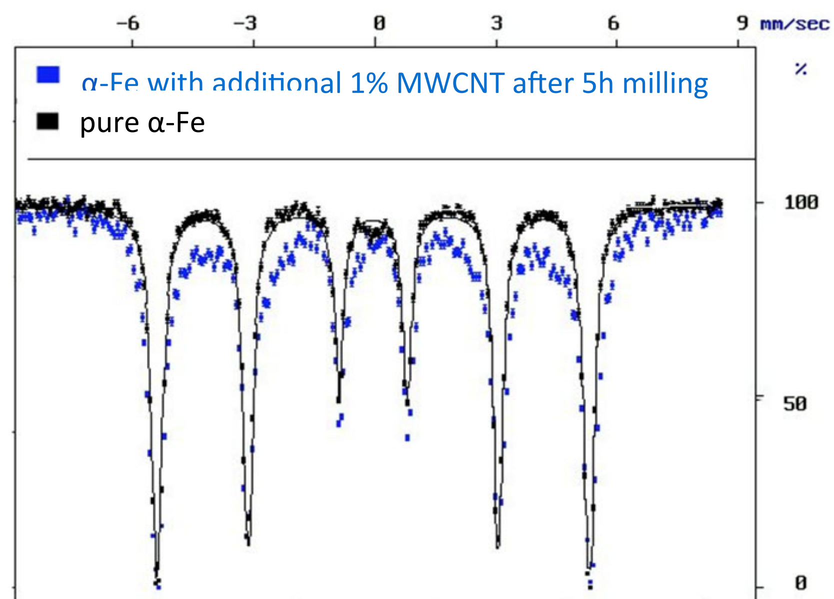
powder particle size is 1-4 μm

Milling of pure iron with 1 % of fullerenes & MWCNT additions

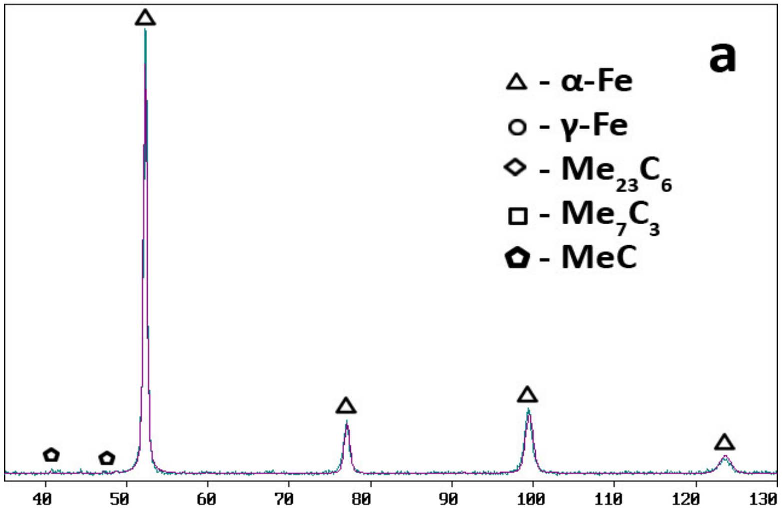


- diffraction peaks of only α-Fe
- other phases are not detected

- there is only one sextet lines
- hyperfine parameters are almost identical to the values characteristic for pure α-Fe



CM-steel after milling & hot pressing

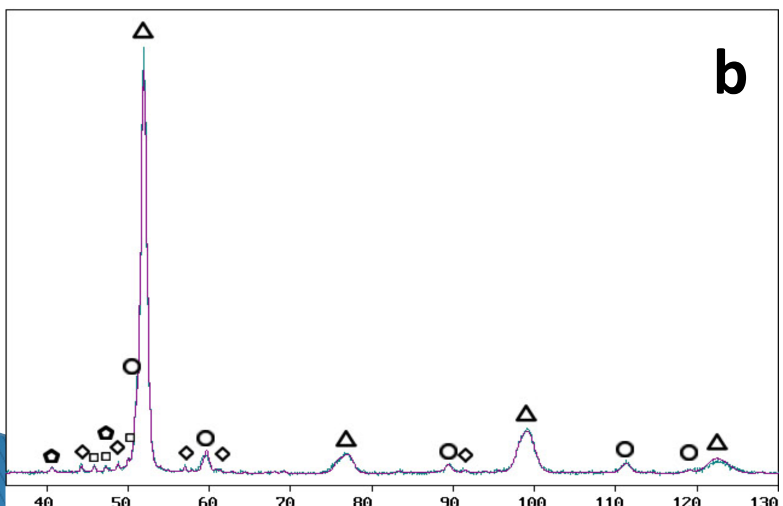


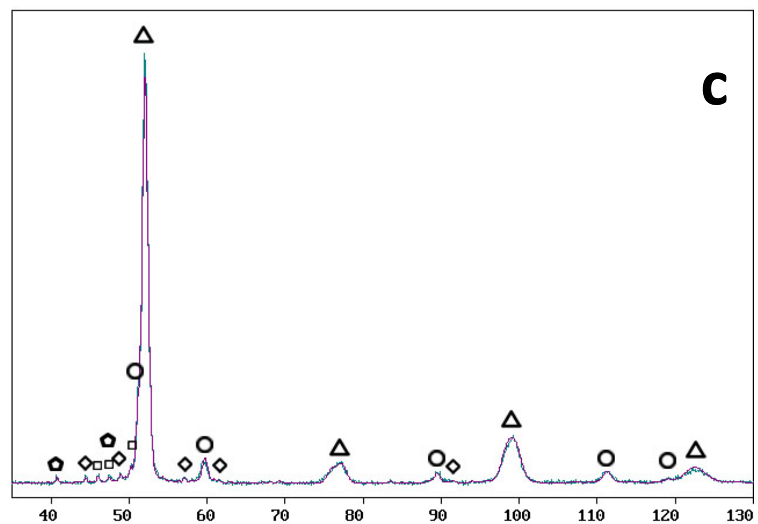
Without additions (a):

- α-phase and traces of carbides

With additions (b, c):

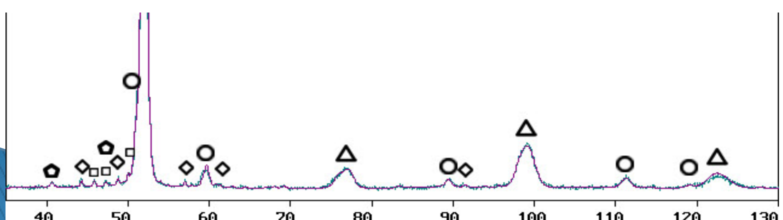
- α-phase +$Me_{23}C_6$ and Me_7C_3 carbides
- γ-phase
- asymmetry of diffraction peak (200) of α-phase that can be explained by the formation of martensite,

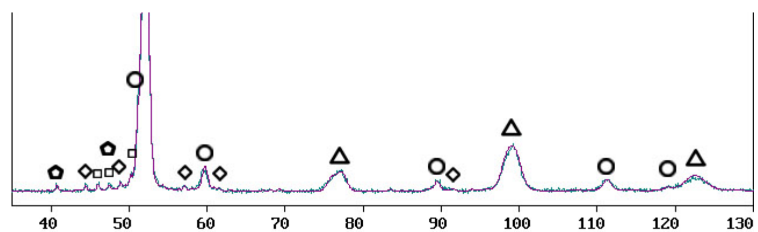




CM-steel after milling & hot pressing

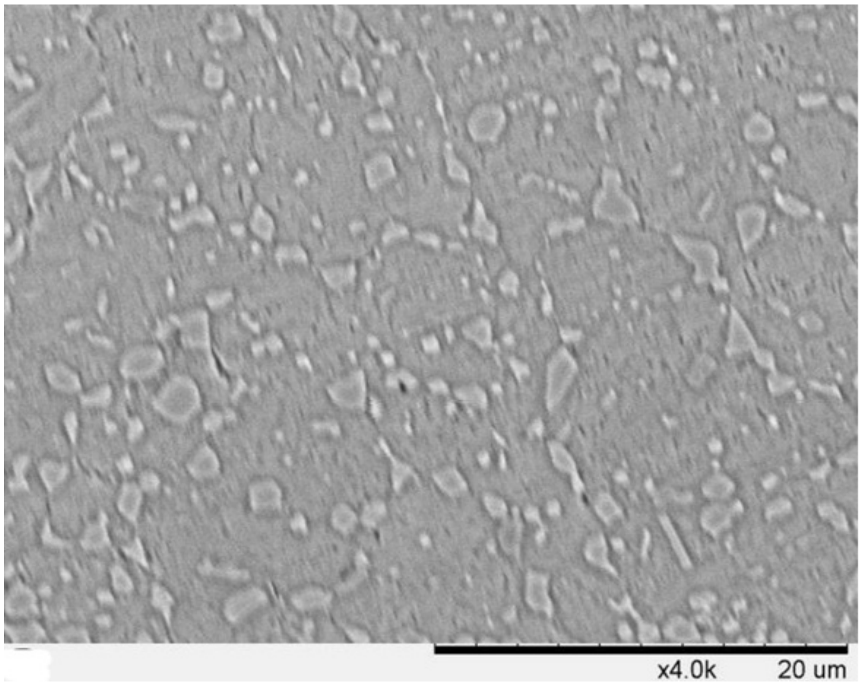
Modificator	Phase	Volume fraction %	Lattice spacing, nm	<D>, нм	<e>, %
fullerenes	α-Fe	77±5	0,2886±0,0002	50±10	0,55±0,10
	γ-Fe	13±3	0,3597±0,0004	19±7	0,16±0,08
	$Me_{23}C_6$	5±2	1,060±0,001	-	-
	Me_7C_3	4±2	-	-	-
	MeC	0,6±0,3	-	-	-
MWCNT	Fe	71±5	0,2882±0,0002	49±10	0,58±0,10
	γ-Fe	19±3	0,3598±0,0003	19±7	0,14±0,08
	$Me_{23}C_6$	5±2	1,060±0,001	-	-
	Me_7C_3	4±2	-	-	-
	MeC	0,5±0,3	-	-	-
-	α-Fe	99,5±0,5	0,2877±0,0002	84±10	0,34±0,1
	MeC	0,5±0,3	-	-	-





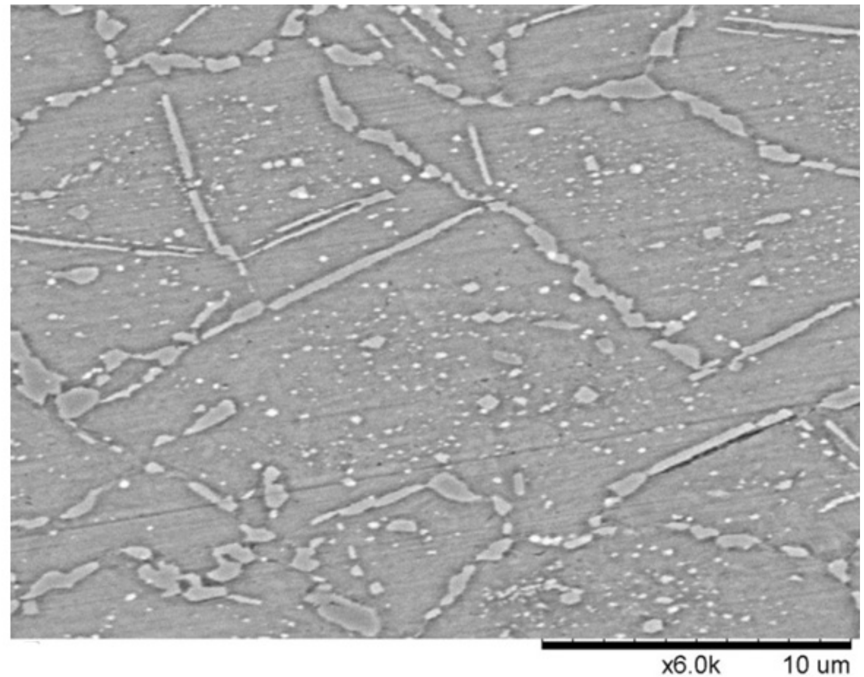
CM-steel after milling & hot pressing

With additions 1 % of fullerenes



- grain size is 10 - 20 μm
- carbides of 1 - 3 μm in size
- carbides have equiaxed shape and are disposed mainly on the grain boundaries.

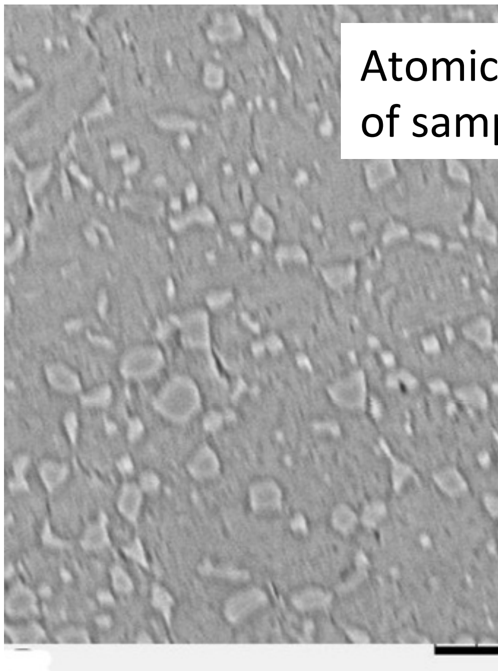
With additions 1 % of MWCNT



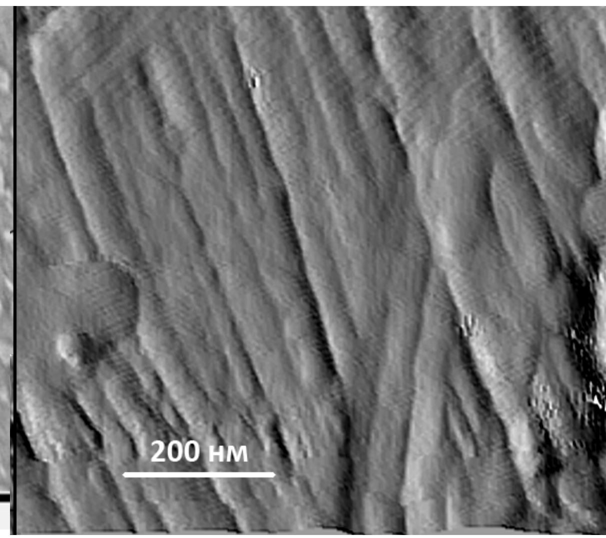
- grain size is 20 - 30 μm
- carbides have elongated shape (1-15 μm long and 1-3 μm wide)
- fine carbides within grains

CM-steel after milling & hot pressing

With additions 1 % of fullerenes

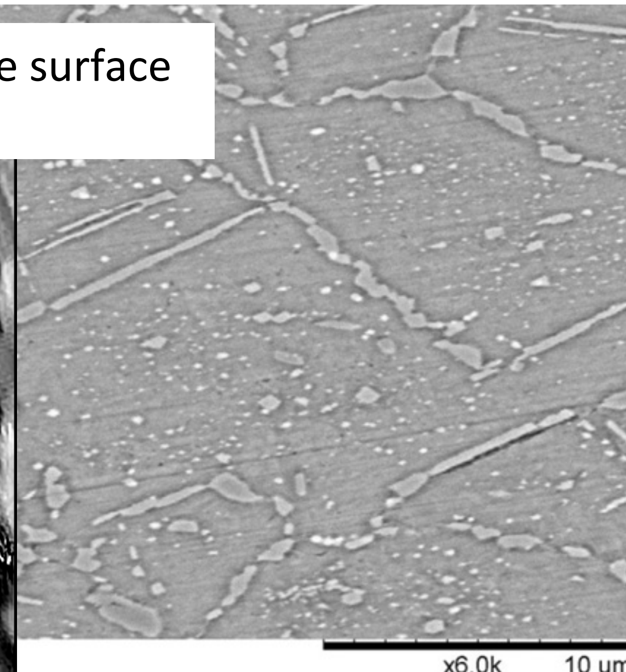


Atomic-force microscopy image of the surface of sample modified by fullerenes



- grain size is 10 - 20 μm
- carbides of 1 - 3 μm in size
- carbides have equiaxed shape and are disposed mainly on the grain boundaries.

With additions 1 % of MWCNT



- grain size is 20 - 30 μm
- carbides have elongated shape (1-15 μm long and 1-3 μm wide)
- fine carbides within grains

Density and microhardness of samples after different treatments

Modifying addition	ρ_{theor}, g/cm^3	Treatment					
		Hot pressing			Hot pressing and hot rolling		
		<ρ>, g/cm^3	η	Microhardness. HV, MPa	<ρ>, g/cm^3	η	Microhardness. HV, MPa
Fullerenes	7,75	7,26±0,07	93,6±0,9%	9310±500	7,53±0,03	97,1±0,5	6860±240
CNTs		7,38±0,05	95,2±0,7%	9020±600	7,62±0,03	98,2±0,5	7370±150
No additions	7,80	7,33±0,05	93,6±0,9%	7400±800	7,55±0,03	96,8±0,4	5090±110

- The microhardness of samples after hot pressing is high and close to that of hardened steel.
- The higher hardness of steel samples modified by carbon-containing additions is likely to be due to the higher carbon content in the martensite and presence of $Me_{23}C_6$ and Me_7C_3 carbides.

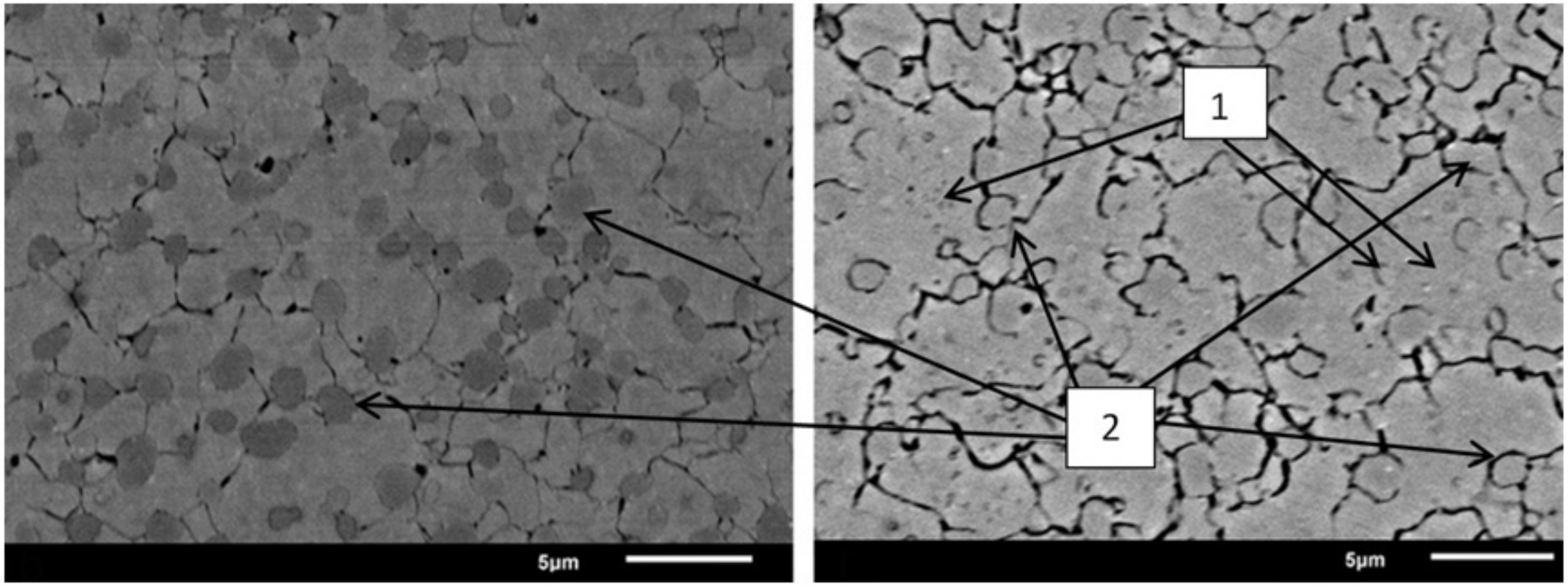
CM-steel after milling, hot pressing & hot rolling

XRD analysis data

Modifiers	Phase	Volume fraction %	Lattice spacing, nm	<D>, нм	<e>, %
fullerenes	α-Fe	79±5	0,2880±0,0002	79±3	0,4±0,1
	γ-Fe	10±2	0,3607±0,0005	21±3	0,12±0,10
	$Me_{23}C_6$	12±2	1,060±0,001	-	-
	MeC	0,6±0,4	-	-	-
MWCNT	α-Fe	79±5	0,2881±0,0002	80±3	0,45±0,1
	γ-Fe	8±2	0,3598±0,0005	23±3	0,15±0,10
	$Me_{23}C_6$	12±2	1,061±0,001	-	-
	MeC	0,5±0,4	-	-	-
Without modifiers	α-Fe	99,5±5	0,2877±0,0002	94±3	0,4±0,1
	MeC	0,5±0,4	-	-	-

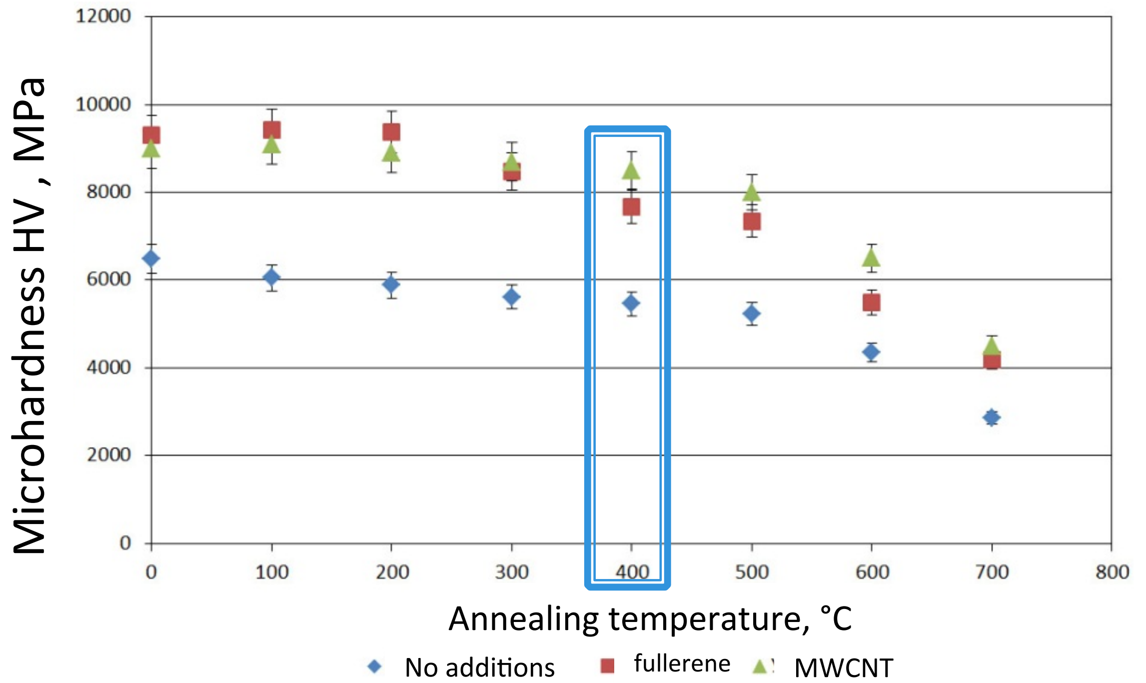
- structural state of the samples without additives has not changed
- the hot-rolled samples modified by fullerenes and CNTs demonstrate the disappearance of Me_7C_3 carbide and formation of the $Me_{23}C_6$ carbide
- reducing the width of α-phase lines as compared to the samples after pressing

CM-steel after milling, hot pressing & hot rolling



- The hot rolling of samples modified by CNTs leads to “refining” plate-like precipitates and formation of more equiaxed carbide inclusions. In this case, relatively large carbide inclusions are present at grain boundaries (2), whereas within grains, disperse particles (1) markedly smaller are found
- In the case of samples modified by fullerene additions, relatively large carbide precipitates ~1 μm in size are mainly located at grain boundaries (2).
- The α-phase grain size for the samples modified by fullerenes and CNTs is 5-10 μm.

CM-steel after milling, hot pressing, hot rolling & heat treatment



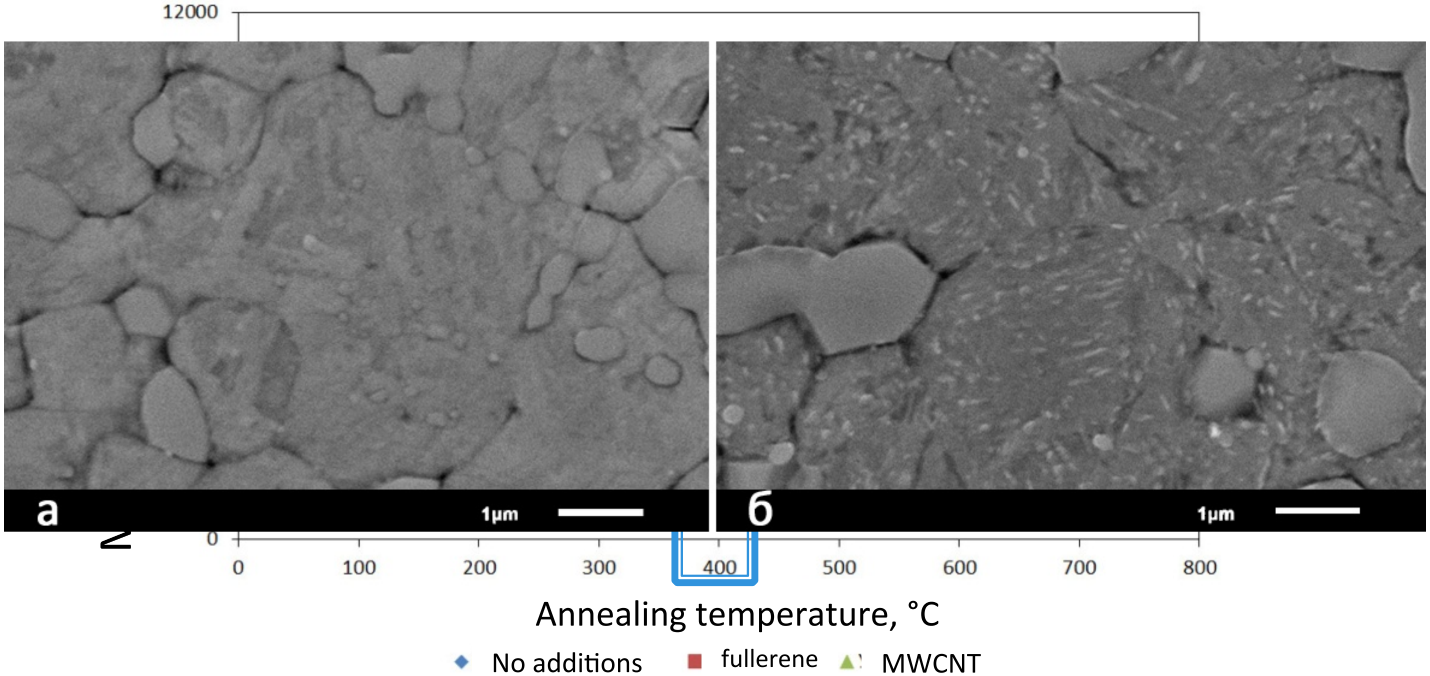
In the case of samples with fullerene addition

- $Me_{23}C_6$ carbide precipitates 0.5-2 μm in size are located at grain boundaries of α-phase;

In the case of samples with MWCNT addition:

- $Me_{23}C_6$ carbide precipitates 1-2 μm in size are located at grain boundaries of α-phase;
- disperse carbide particles 100-300 nm in size are observed within grains.

CM-steel after milling, hot pressing, hot rolling & heat treatment



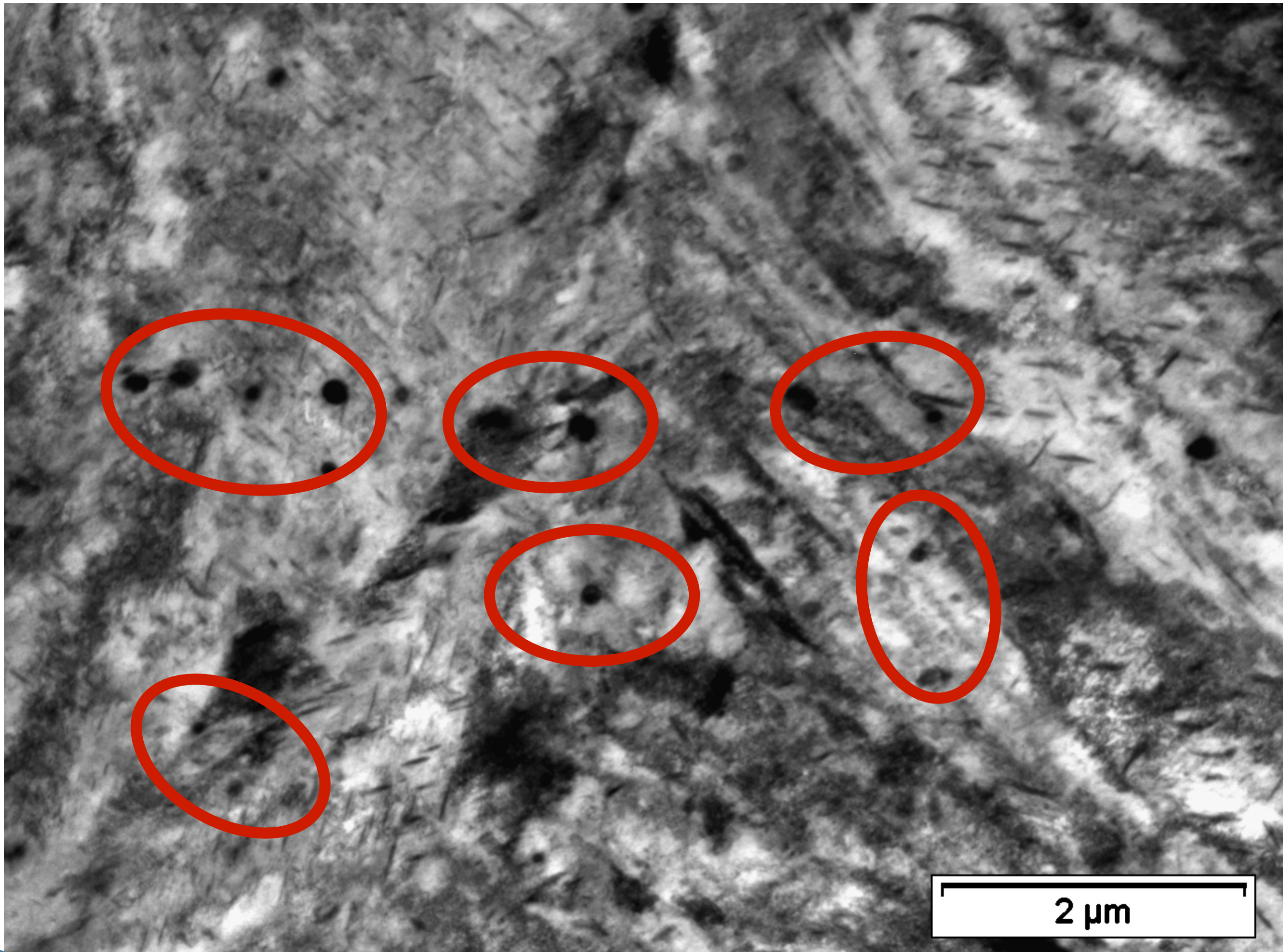
In the case of samples with fullerene addition

- $Me_{23}C_6$ carbide precipitates 0.5-2 μm in size are located at grain boundaries of α-phase;

In the case of samples with MWCNT addition:

- $Me_{23}C_6$ carbide precipitates 1-2 μm in size are located at grain boundaries of α-phase;
- disperse carbide particles 100-300 nm in size are observed within grains.

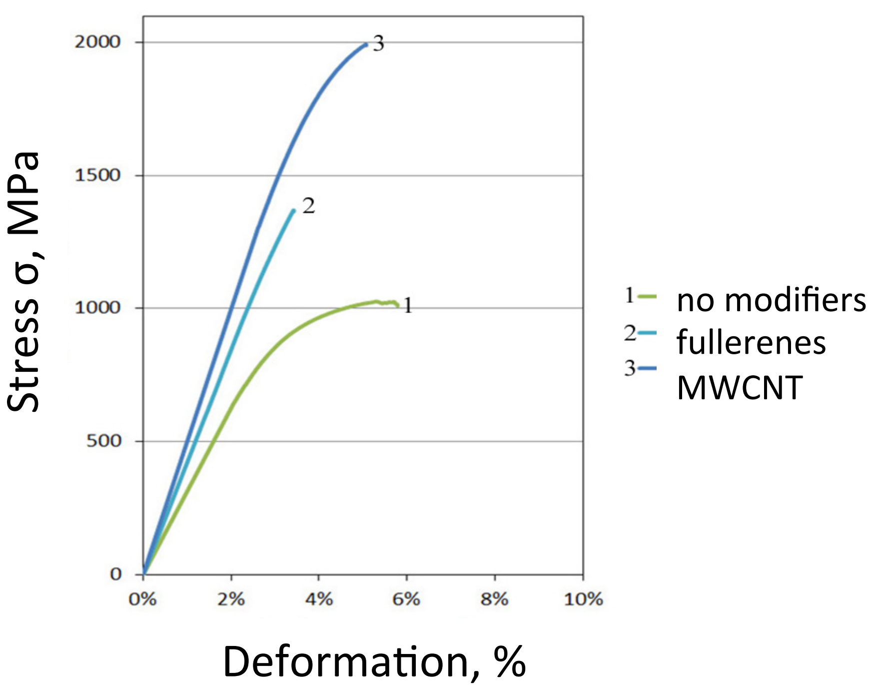
Microstructure of CM-steel with MWCNT after milling, hot pressing, hot rolling & heat treatment

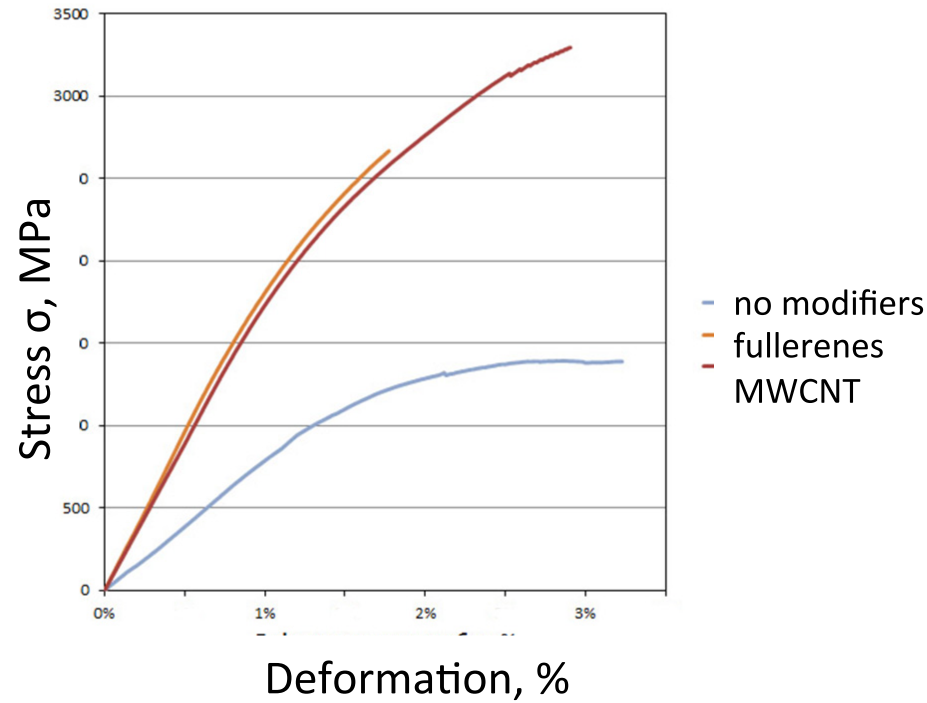


Samples with MWCNT contain:

- bainite
- carbides with size 100-300 nm

Mechanical properties





Results of tension and bending tests

Modifier	Test			
	Tension			Bending
	Yield strength, MPa	Ultimate strength, MPa	Breakdown elongation, %	Maximum bending stress, MPa
Fullerenes	1 080-1 110	1 210-1 370	0,2-0,5	2 420-2 670
CNTs	1 600-1 650	1 910-1 990	0,9-1,1	2 960-3 140
No modifiers	790-850	970-1 030	2,4-2,7	1 390-1 440

Conclusion

(1) During the high-energy milling of the steel powder with fullerene and CNT additions, the reaction between the steel components with the carbon-containing additions takes place.

(2) The fullerene and CNT additions change the character of $\alpha \leftrightarrow \gamma$ transformation during hot pressing. The morphology of carbide particles in the compacts depends on the kind of modifying addition.

(3) The hot rolling allows us to prepare samples with a density of 97-98 % of the theoretical magnitude. The microstructure of the rolled modified sampled depends on the kind of modifying carbon addition.

(4) The heating of hardened samples results in the decomposition of martensite and formation of tempered bainite. The carbide precipitates in the steel modified by fullerenes are about 1 μm in size and located along grain boundaries. In the case of steel modified by CNTs, more disperse carbide particles 100-300 nm in size were found within grains along with more coarse carbide particles located along grain boundaries.

(5) Tension and bending tests showed that the samples modified by fullerenes and CNTs exhibit the higher strength properties but the lower plasticity as compared to those of the samples produced in the absence of modifiers. The strength and plasticity of the samples modified by CNTs are higher substantially than those of samples modified by fullerenes.

Thanks for attention