National Technical University of Ukraine
“Igor Sikorsky Kyiv Polytechnic Institute”

Ye.O.Paton Institute for Materials
Science and Welding
Metals Physics Department

High-Energy Impulse and Vacuum-Plasma Methods for Coatings Production

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OUTLINE

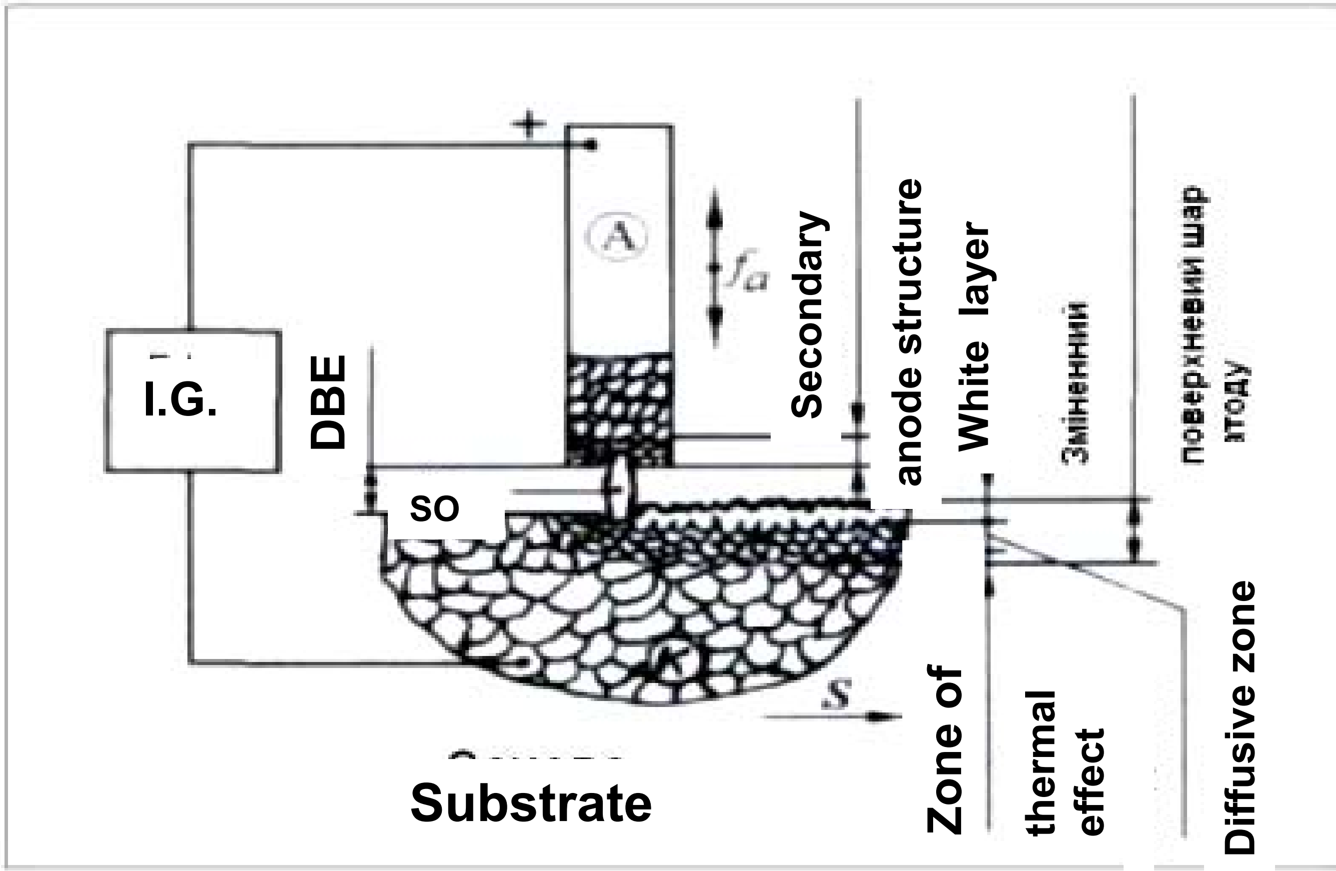
1. **Topics of Investigation**
2. **Electro-Spark Alloying**
3. **Laser Chemical Heat Treatment**
4. **Ion Nitrating**
5. **Biocompatible Coatings**
6. **Magnetron System**
7. **Glass Optical Properties Modification**
8. **Nanocrystalline Magnetically Soft Alloys**
9. **Autoradiographic investigation**

1. TOPICS OF INVESTIGATION

- **VACUUM-PLASMA COATINGS TECHNOLOGY**
  - **Biocompatible protecting coatings on alloys for artificial limbs and medical instrument production**
  - **Coaxial type magnetron spray system for sputtering of magnetic substances and corrosion-resistant, wear-proof, heat-resistant, protective and decorative coatings**
  - **Ion plasma chemical heat-treatment**
  - **Development of carbon nanotubes forming technique by PVD with use magnetron sputtering for obtaining composite nanostructure coatings**
- **HIGH-ENERGY IMPULSE MACHINING AND STRENGTHENED SURFACE PRODUCTION**
  - **Accelerated alloys by chemical heat treatment at pulsing environment pressure variation**
  - **Laser chemical heat treatment**
  - **Combined Electric-spark alloying in the saturate environment**
- **GLASS OPTICAL PROPERTIES MODEFICATION**
  - **Energy saving windows with functional properties of heat protection, reflection, translucent with single-sided review**
  - **Transparent conducting glazing glasses with functional properties of infrared calefactory, guards from an electromagnetic radiation, scan and audition**
- **NANOCRYSTALLINE MAGNETICALLY SOFT IRON ALLOYS**

2. ELECTRO-SPARK ALLOYING

Main scheme of Electro-Spark Alloying (ESA) Processes



I.G. – impulse generator, DBE – distance between electrodes, SO - sparkover, A – anode (contact electrode), К – cathode (sample), f_a – anode vibration frequency, S – strengthened layer growth direction

Three types ESA

Step-by-step
ESA in nitride- and
carbide containing
medium

ESA in liquid
medium with
powder compounds

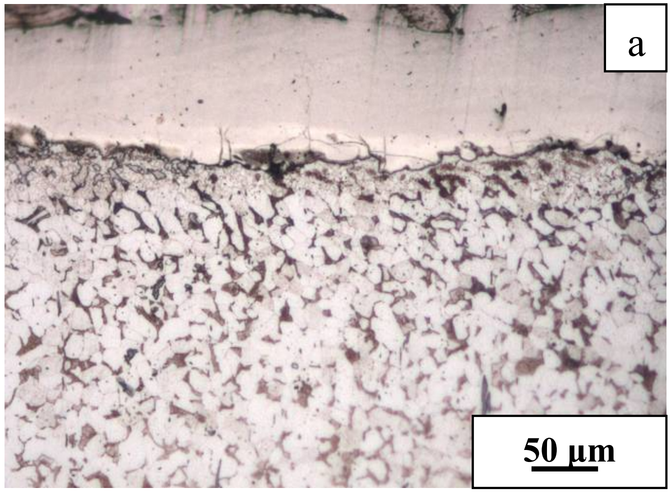
Layer-by-layer ESA
with carbide forming
elements

Combined (ESA + Chemical Thermal Treatment)

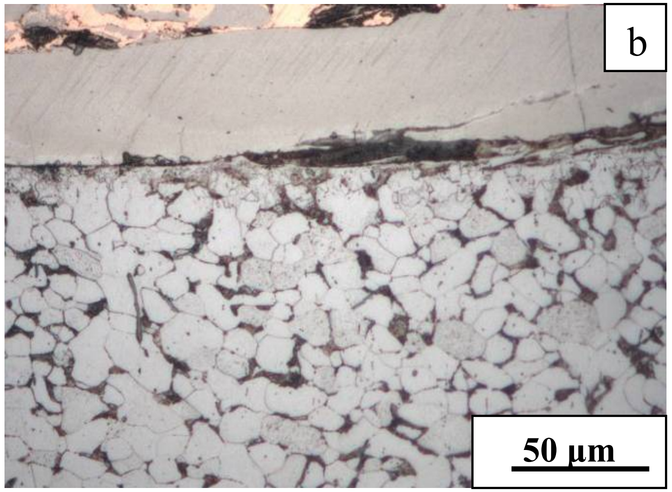
ESA + Nitration

ESA + Carbonitration

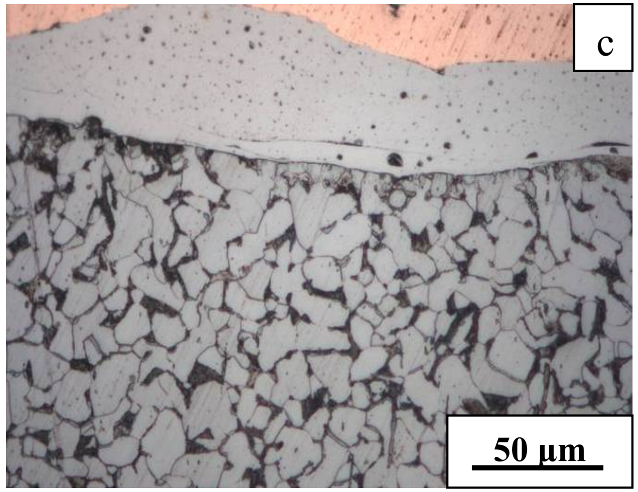
ESA of steel St3 in saturation medium provides strengthened surface in 5 times



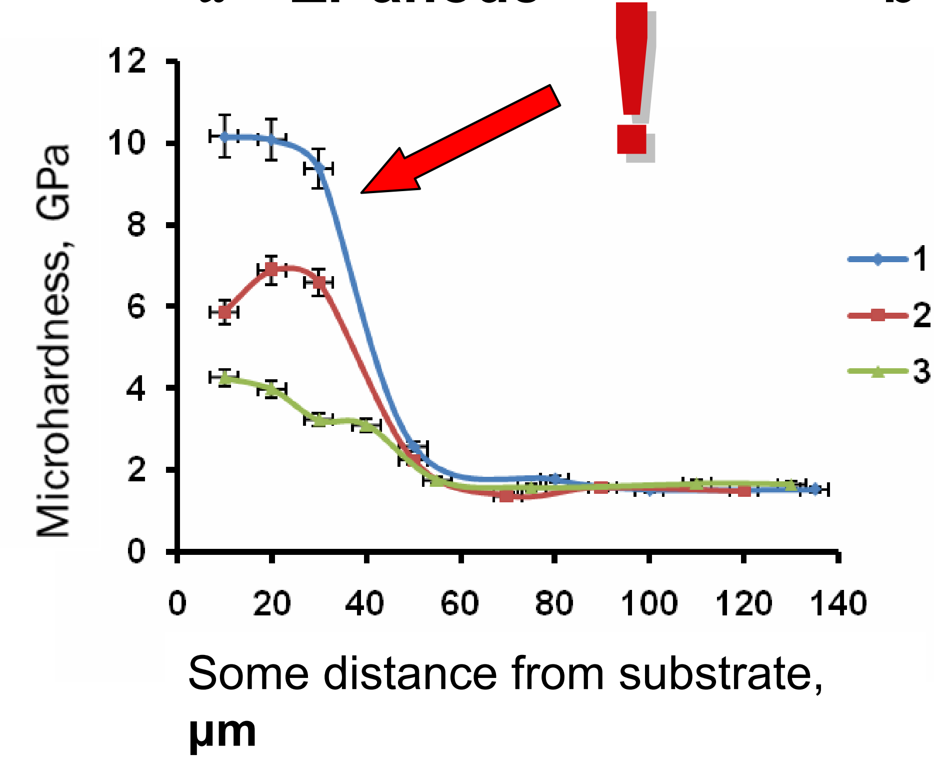
a – Zr-anode

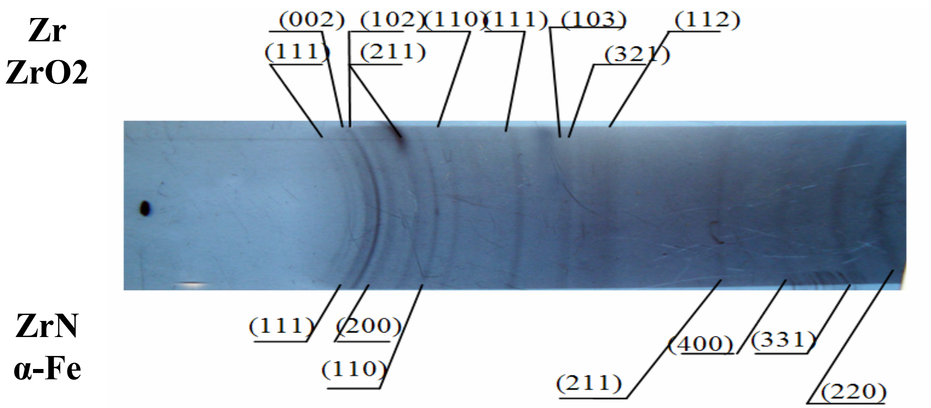


b – Ti-anode

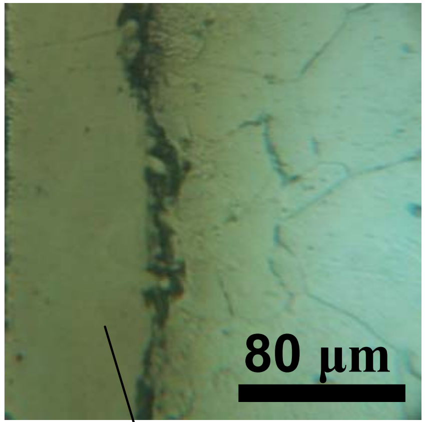


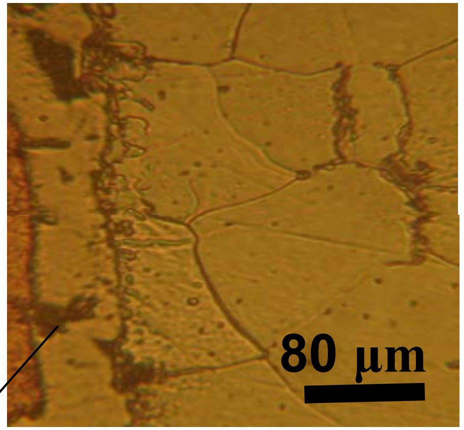
c – Cr-anode



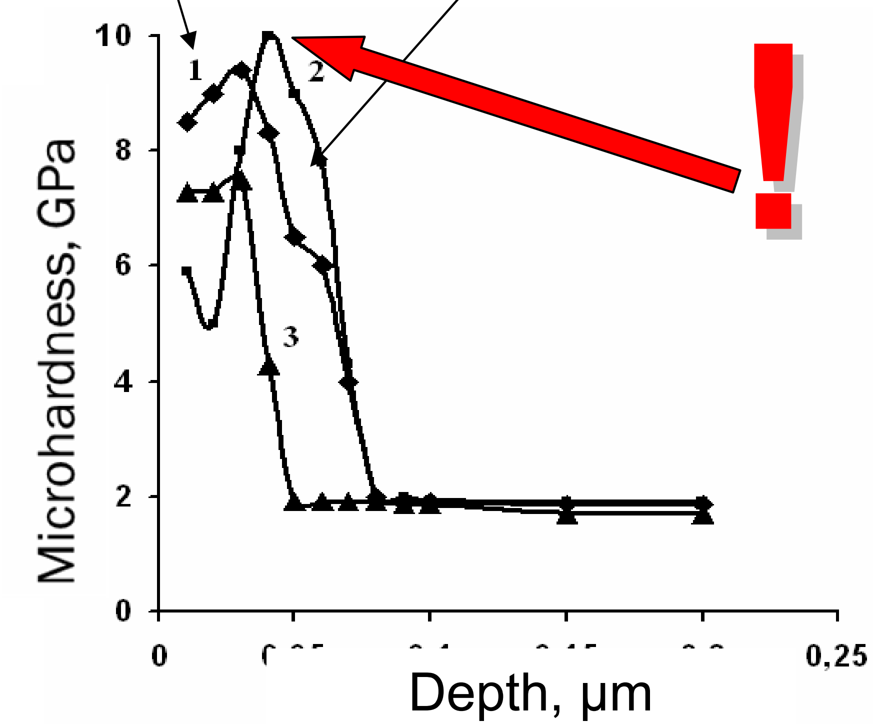


Layer-by-layer ESA carbide forming elements using provide strengthened and wear-resistaned surface

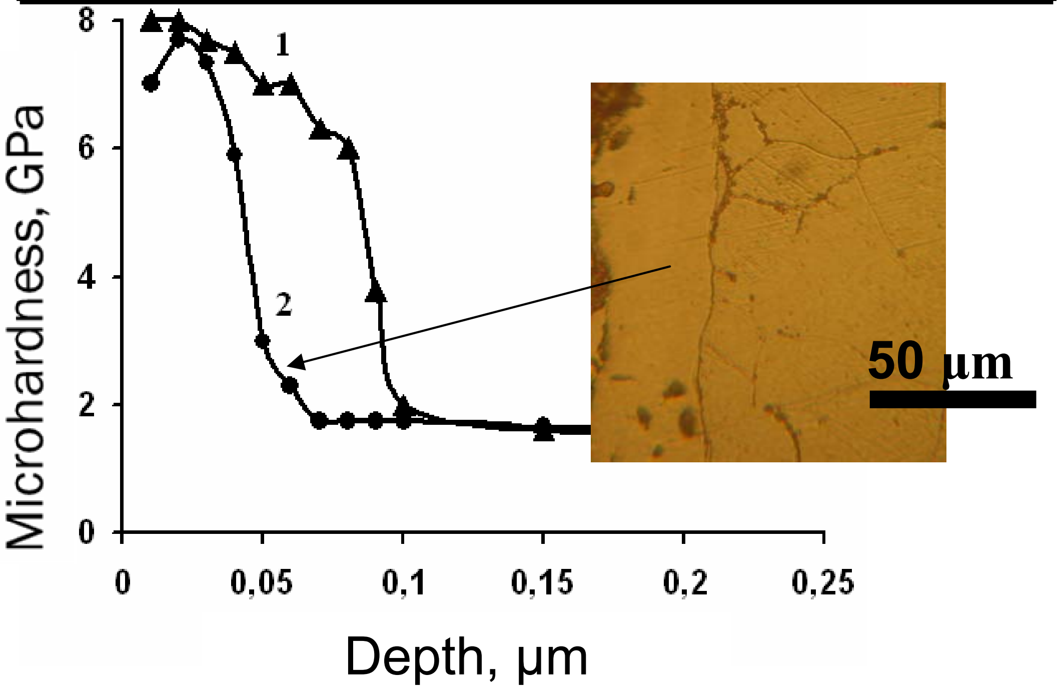




Anode	Phase combination of surface
Zr-C-Zr	Zr, γ-Fe, ZrC
Ti-C-Ti	γ-Fe, Fe_2Ti, TiC.
Zr-Fe-Zr	Zr, Fe, ZrN, ZrO_2, Fe_2O_3
Ti-Fe-Ti	Ti, α-Fe, TiN, TiO_2, Fe_2O_3
Ti-Cr-Ti-Cr	Cr, α-Ti, Cr_2Ti.
Zr-Ti-Zr-Ti	Zr, Ti, Fe, ZrN, TiO_2, Fe_2Ti, FeO

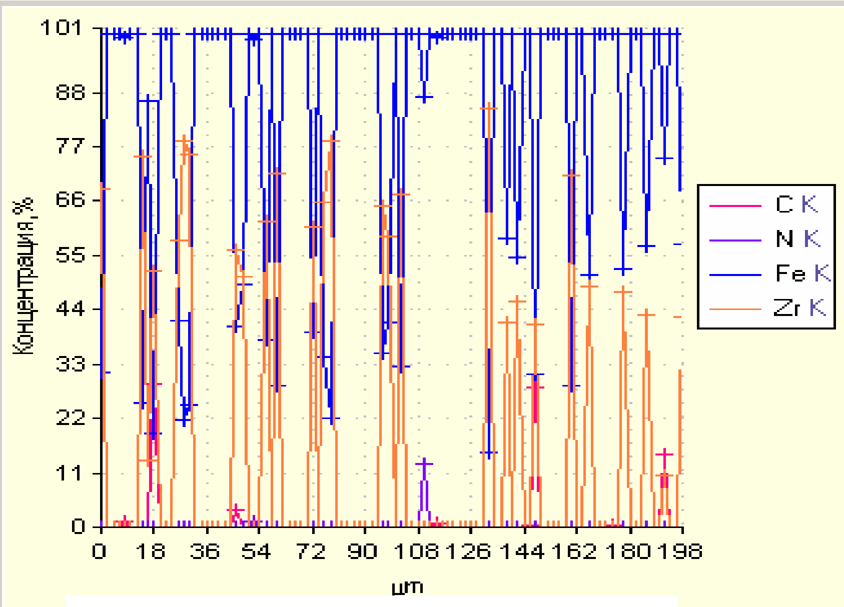


1 – Zr–C–Zr (in LPG);
2 – Ti–C–Ti (in LPG);
3 – Zr–Fe–Zr (on the air)

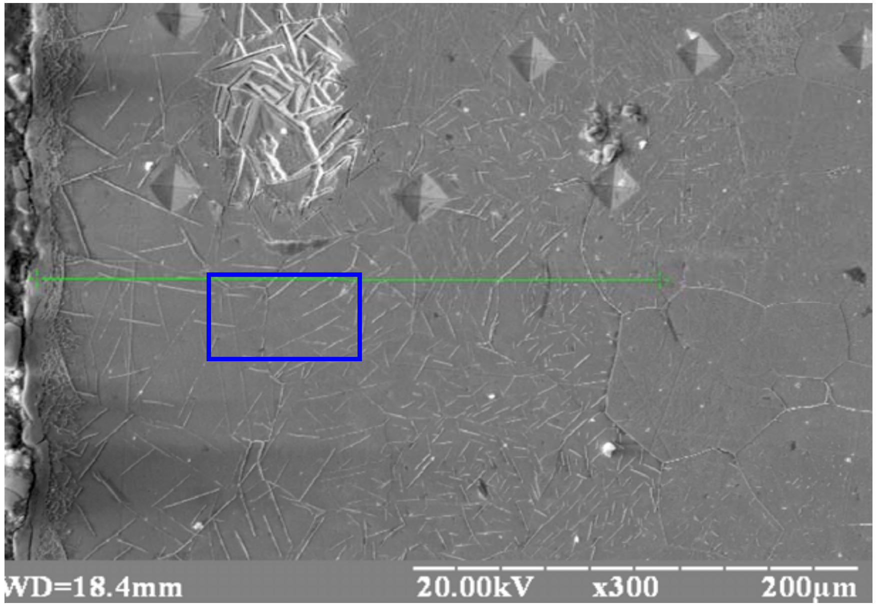


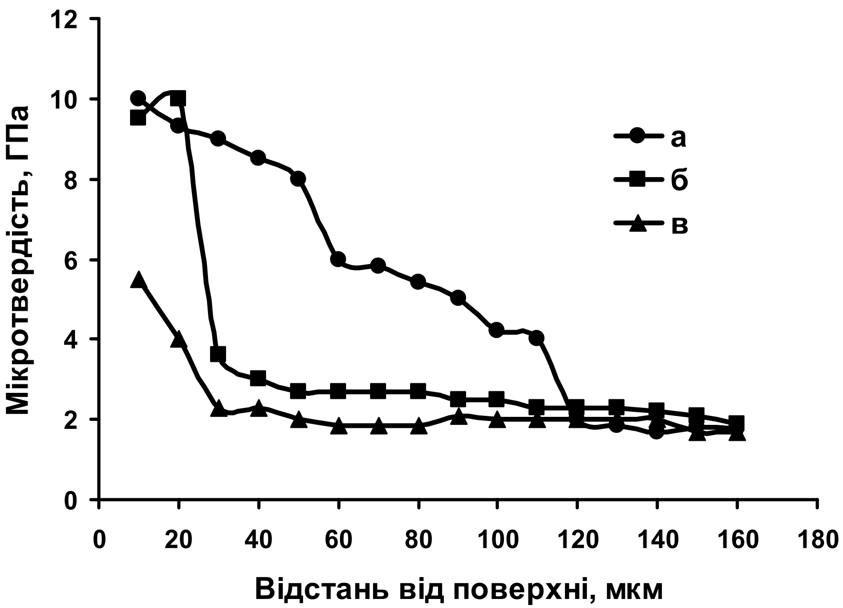
1 – Zr–Ti–Zr–Ti (on the air);
2 – Ti–Cr–Ti–Cr (in LPG)

COMBINED TREATMENT (ESA + NITRATING)

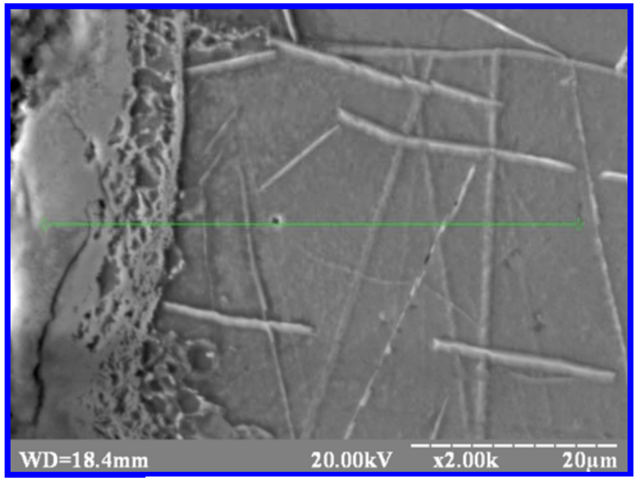


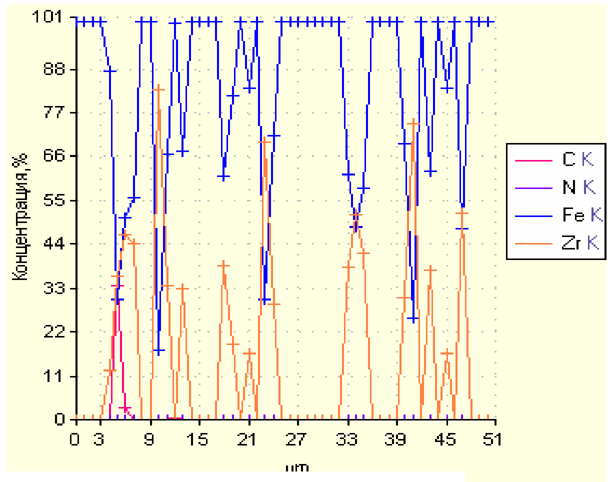
XRD-analysis





а – Zr-anode; б – Ti-anode; в – Cr-anode





Micrographs by SEM obtained in secondary electrons of surface layer

3. LASER CHEMICAL HEAT TREATMENT

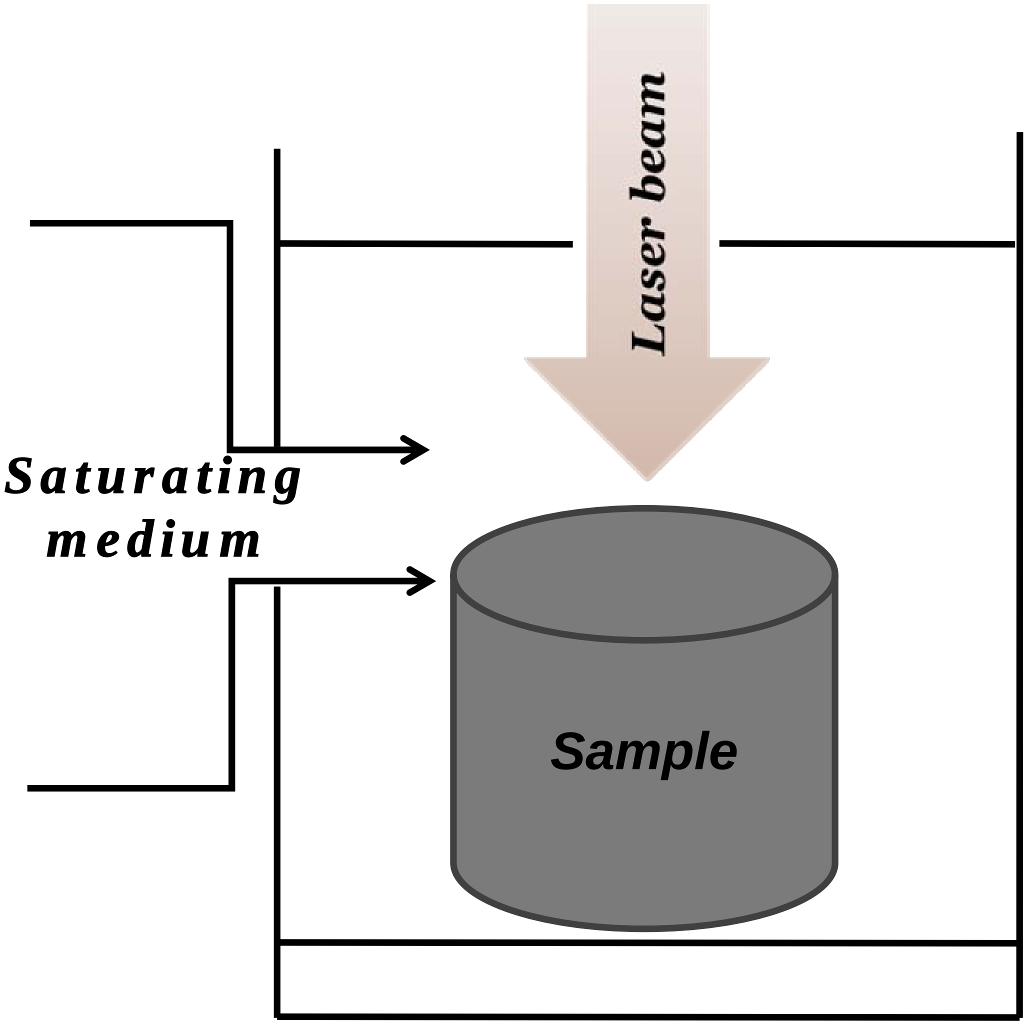
1.Laser treatment in different reactive-active mediums: (nitrogen, LPG and their mix);

2. Laser alloying with solid and like oil paster: (TiC, TiN and diamond paste);

3. Laser chemical-thermal treatment:

- **nitrating + laser treatment**
- **laser treatment + nitrating**

LASER CHEMICAL HEAT TREATMENT



Scheme
of laser chemical-thermal treatment
in reactive-active different types medium

Pulsed laser facility
“КВАНТ-16”

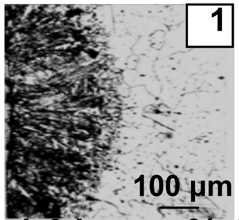
Parameters of treatment	
Energy	E=20÷30 J
Power Density	W_p=5÷8,1 GW/m^2
Duration of impulse	τ=4÷8 ms
Diameter of focus spot	$d_п$≈1÷3 mm

Laser treatment in different reactive-active medium using provide strengthened surface

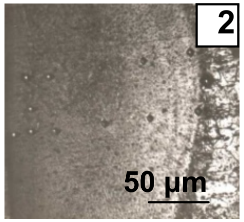
1-100 % N_2; **2**–50%N_2+50%$C_3H_8C_4H_{10}$; **3**–20% N_2+80%$C_3H_8C_4H_{10}$; **4**–100% $C_3H_8C_4H_{10}$

W_p=6,5 GW/m^2

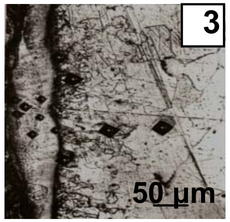
Microstructure of surface layer



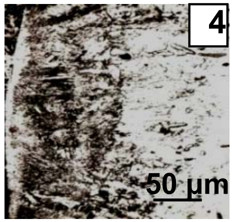
Fe+1,91 mas.% Cr



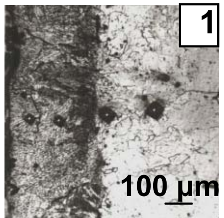
Fe+1,02 мас.% Ti



Fe+1,02 мас.% Ti

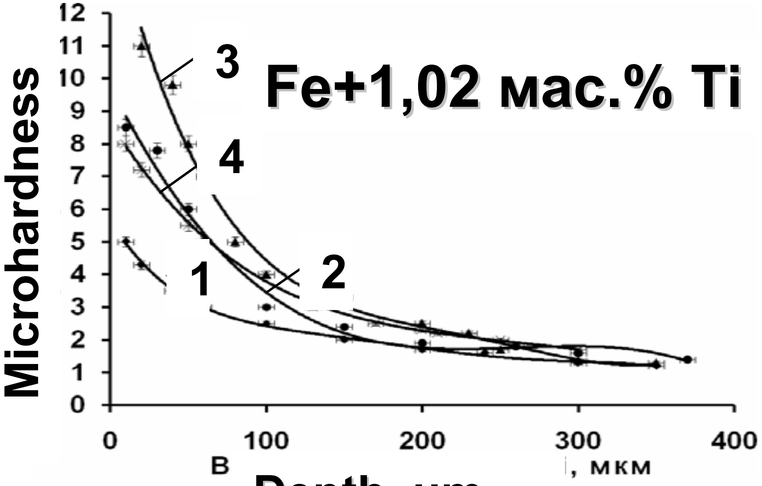


Fe+1,91 мас.% Cr

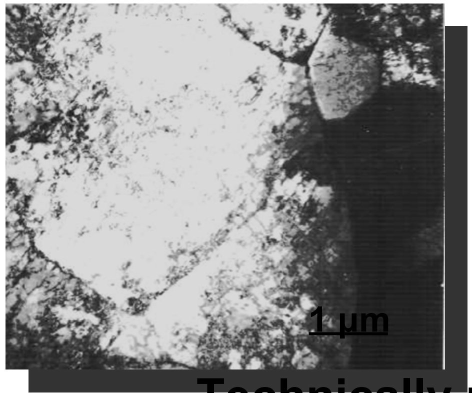


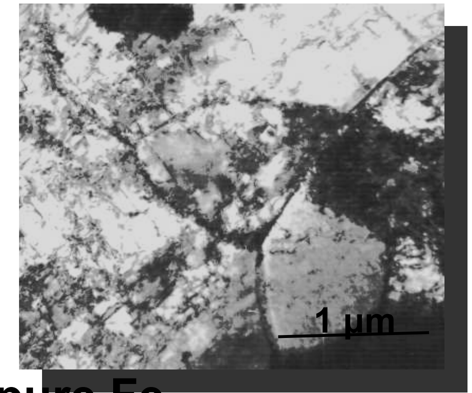
Technically pure Fe

Microhardness of surface layer

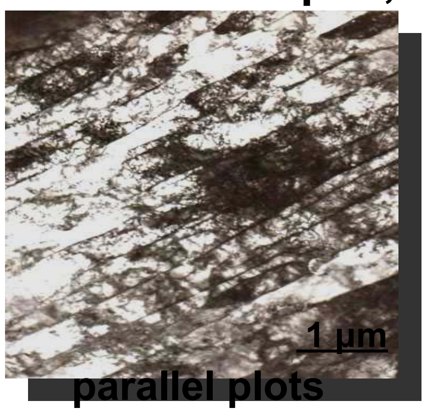


Alloy Fe+ 1,91 mas.% Cr; saturation medium – 50 % N_2+ 50 % $C_3H_8C_4H_{10}$ Power Density - Wp=6,5 GW/m^2

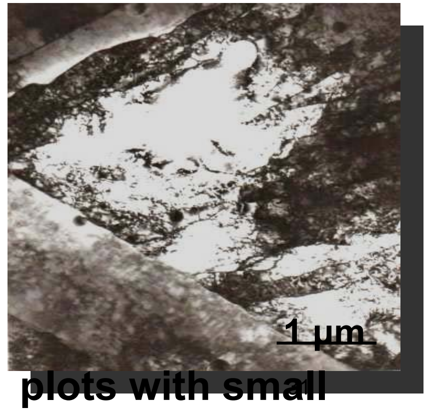




Technically pure Fe, saturation medium - 100 % N_2 Wp=6,5 GW/m^2



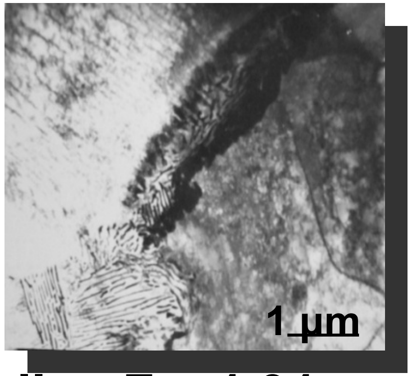
parallel plots of stripped structure

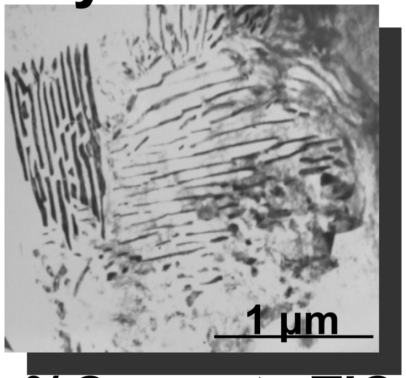


plots with small misorientation

Laser treatment with paste using provide strengthened and wear-resistant surface

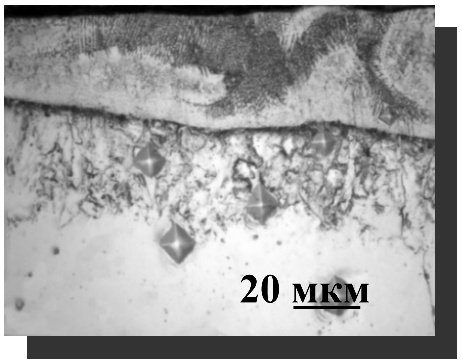
Electron microscope analyze of surface layer

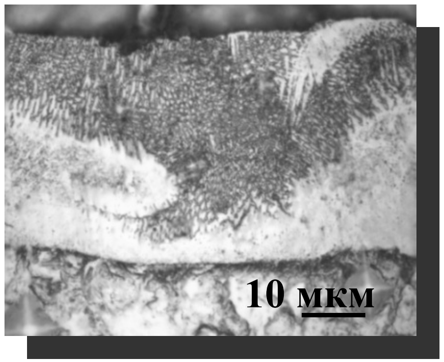




alloy Fe+1,91 mas.%Cr, paste TiC, Wp=6,5 GW/m²

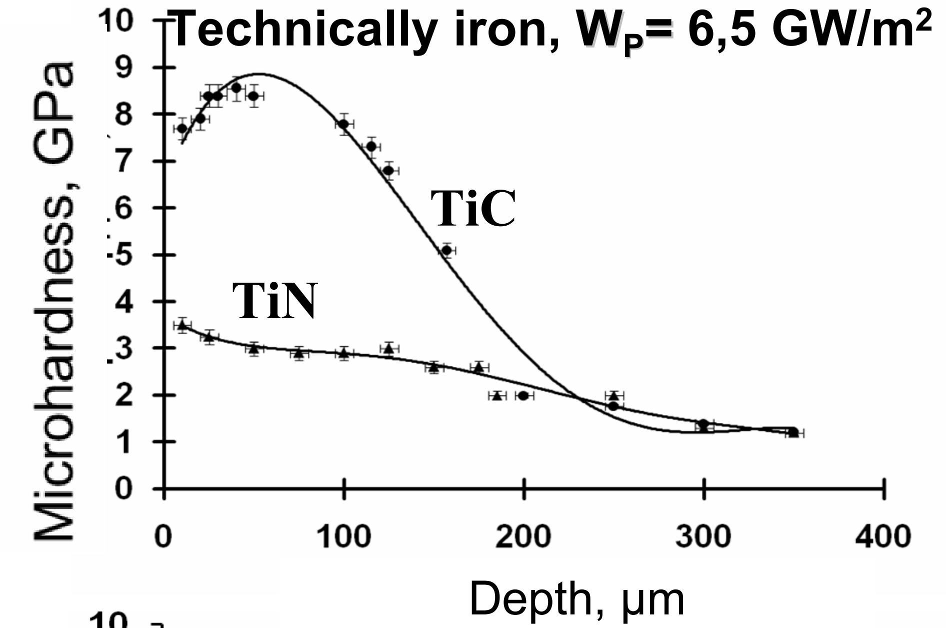
Microstrucure of surface layer

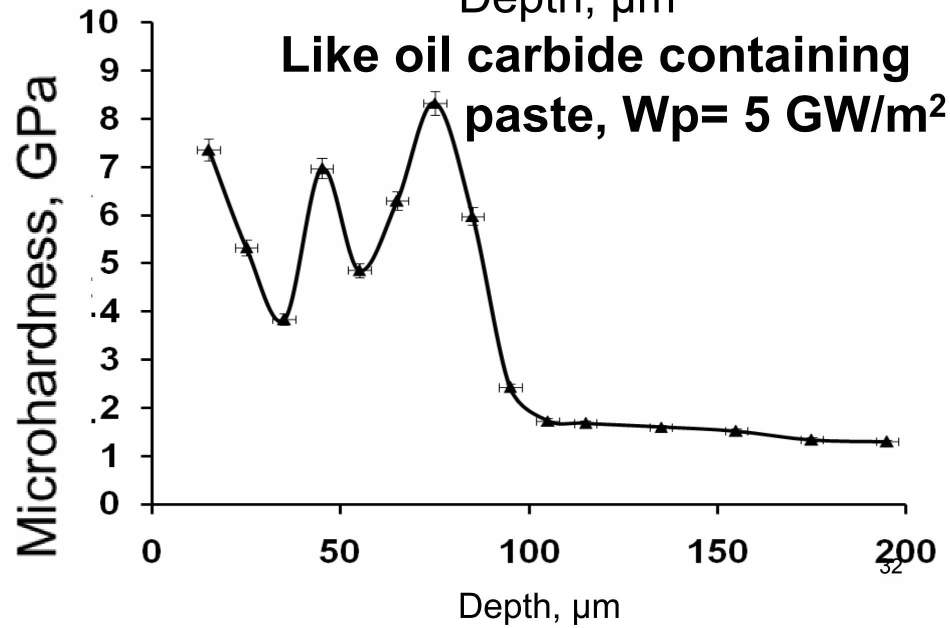




Alloy Fe+1,11 мас.%Cr,
like oil carbide containing paste

Microhardness of surface layer





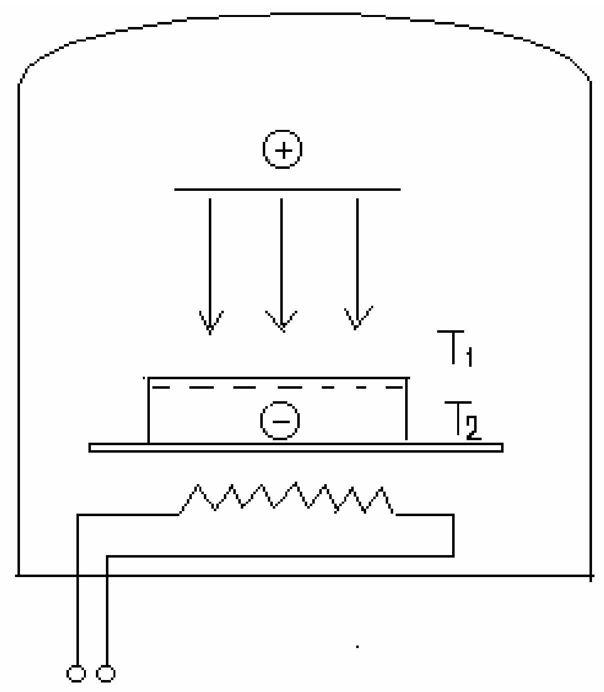
Sphere of laser chemical heat treatment application

- engineering;
- aircraft industry;
- shipbuilding;
- fuel and energy complex;
- medicine.

4. Ion nitrating. Technology of ion nitrating of steels and alloys

Complex technology of ion nitrating of steels and alloys, and the creation of installations for its implementation

Scheme of ion-plasma nitrating

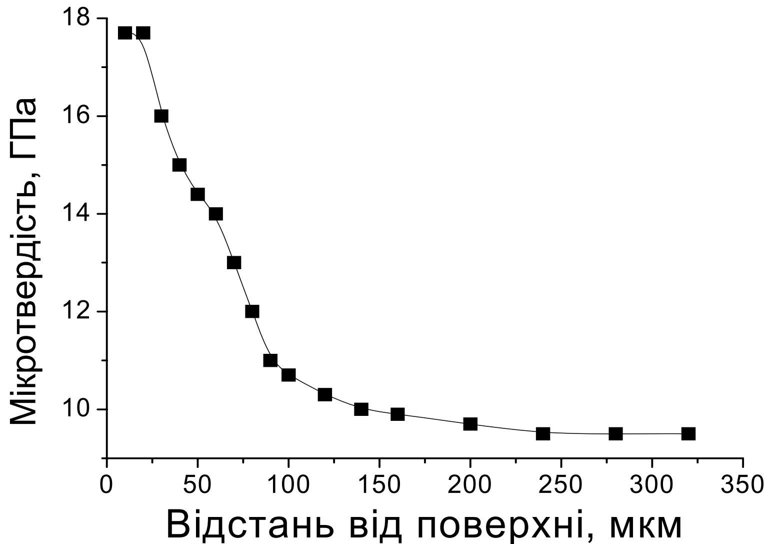


- Speeding up the process of diffusion saturation and increase the microhardness by creating a temperature gradient

$T_1 - T_2 = \Delta T$ for creation internal stress

Technology of ion nitrating of steels and alloys

ION NITRIDING OF STEEL DRILL Р6М5 (ЭИ 298) (ГОСТ-19265-73)



Microhardness distribution over the depth

Chemical composition:
C - 0,82-0,90 мас.%;
Cr - 3,80-4,40 мас.%;
W - 5,50-6,50 мас.%;
Mo - 5,00-5,50 мас.%;
V - 1,70-2,10 мас.%

Parameter of treatment:
U = 950-1000 W; P = 850 Pa;
T = 793 K;
duration of treatment $7{,}2 \cdot 10^3$ sec (2 hours)

At the Metal Physics Department were designed and manufactured equipment for the strengthening of the matrix hot-pressed aluminum, which is used in mass production at enterprises of St. Petersburg and Brovary factory aluminum construction

Technology of ion nitrating of steels and alloys

Advantages:

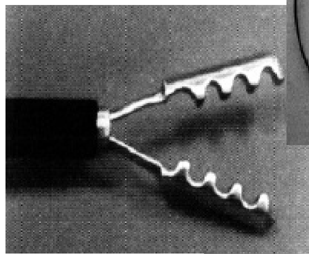
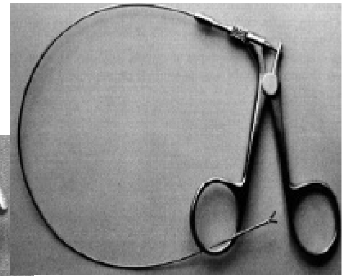
- decrease duration of treatment in 2-3 times;
- increase of microhardness in 2 times;
- for nitride matrix increased speed compression 6 times;
- improving the quality of the surface of aluminum after compression

5. Biocompatible protecting coatings (general)

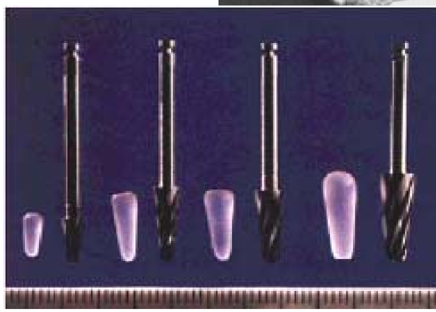
- ❑Formation vacuum-plasma coatings on surgical and orthopedic instruments
- ❑Modification biocompatible coatings by electro-spark alloying and laser treatment

Biomaterials and coatings must have next set of properties:

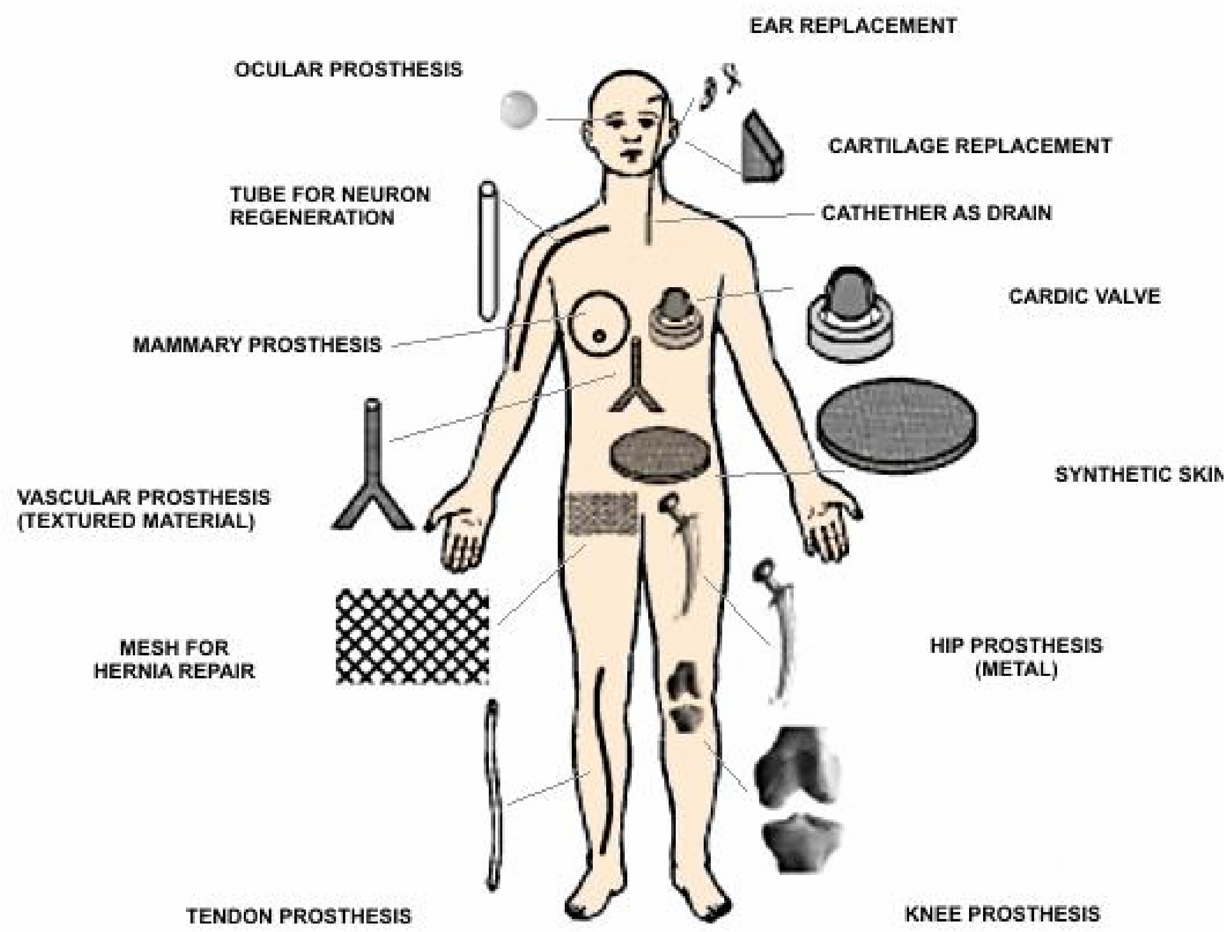
- •Chemical (rustproof finish, without undesirable reactions wit tissues);
- •Mechanical (durability, wear-resistance,
fracture strength);
- •Biological (bony union, stimulation osteosynthesis).






Biocompatible protecting coatings (general)



During last 30 years, about 40 types of different materials (ceramics, metals, polymers) was used for replaced different parts of human body.
Market capacity of biomaterials is about 2,5 billion dollar's

Apparatus for PVD of biocompatible coatings

Co-chamber stuff of apparatus for Ion-Plasma Treatment

Co-chamber stuff of apparatus for High-Vacuum Plasma Treatment

Designing and creation:

1. Special Co-chamber Stuff;
2. Reaction Gas Feeding System;
3. Power Supply System;
4. Monitoring System.

Main idea: formation biocompatible coatings by electro-arc and magnetron sputtering methods with increased adhesion in consideration of use of ascending diffusion effect during ion-plasma treatment

Biocompatible composite coatings formation

Main idea is obtain biocompatible composite coatings by high-energy methods, like electro-spark alloying and laser treatment. Such coatings could be more strengthened and wear-resistant

Alloying surface of titanium by aluminium and zirconium

- Laser melting of surface for increase homogeneity of chemical composition, decrease internal stress and roughness of surface
- Ion-plasma nitration for obtaining AlN layer on surface

Parameters of ESA treatment:

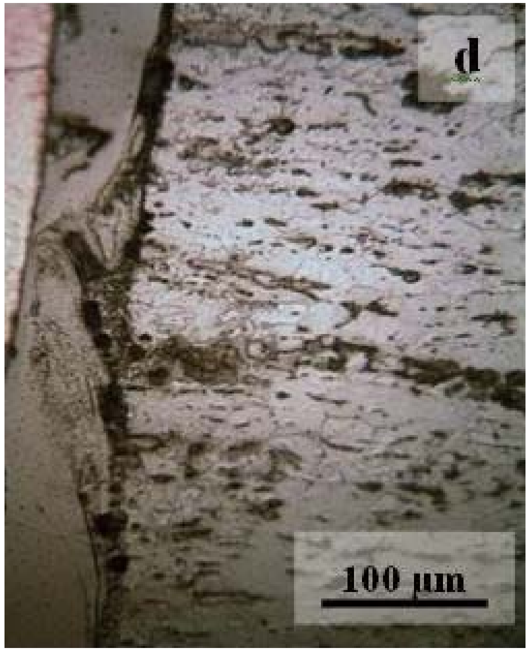
Cathode	Anode	Current I, A	Voltage U, V	Duration τ, sec	Saturation medium
•Steel Ct 3 •Titanium alloy BT1-0	Al	1.8..2	60..80	180..360	Air

Parameters of sequent laser treatment:

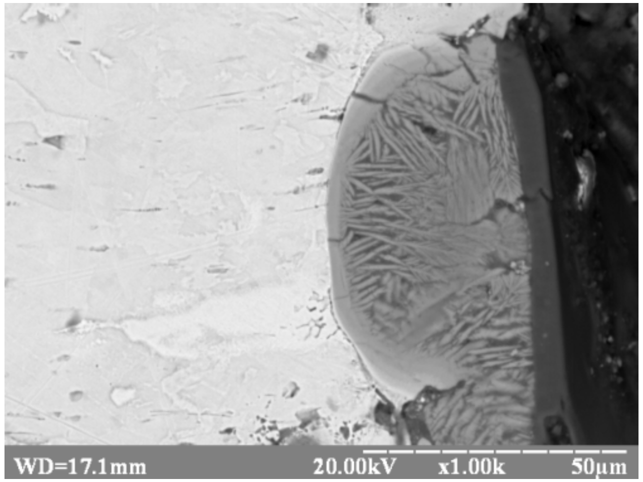
- Power density of laser irradiation Wp = 2,6 GW/m^2
- Saturation medium - air

Biocompatible composite coatings formation

Microstructure of surface layer of specimen steel after ESA by Al

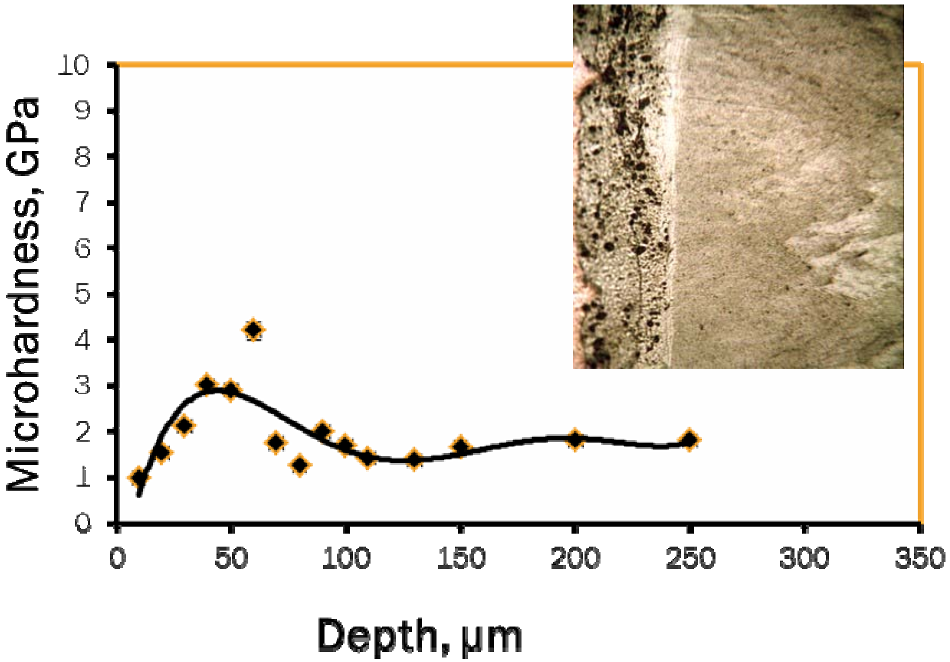


Microstructure of surface layer of specimen steel after ESA by Al with sequent LT

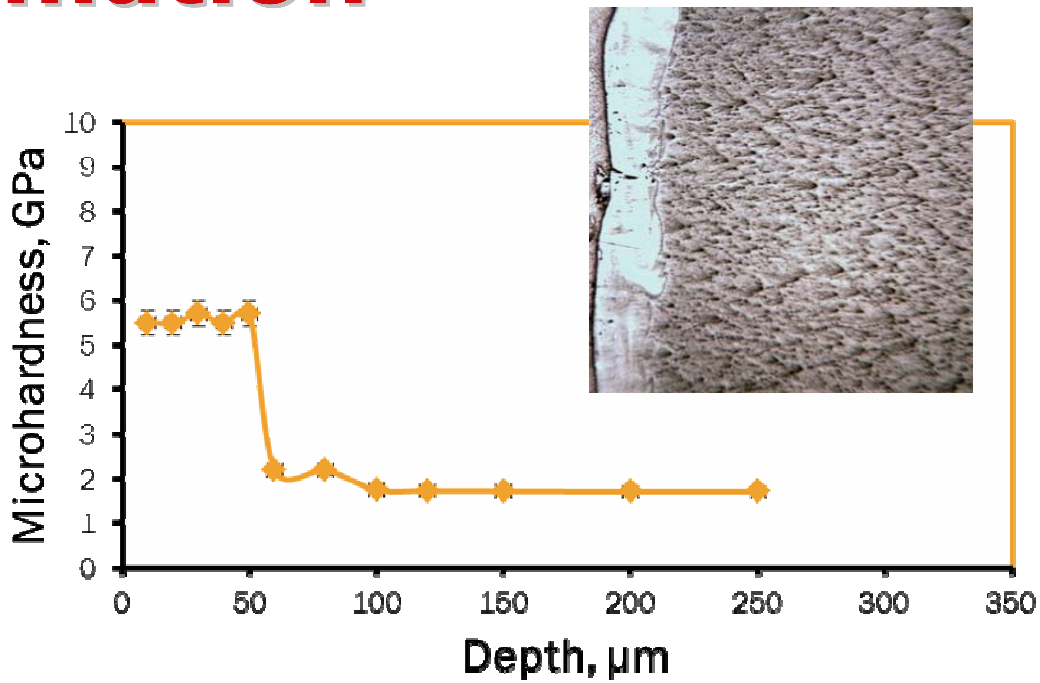


Micrographs by SEM obtained in secondary electrons of surface layer after combined treatment ESA+LT

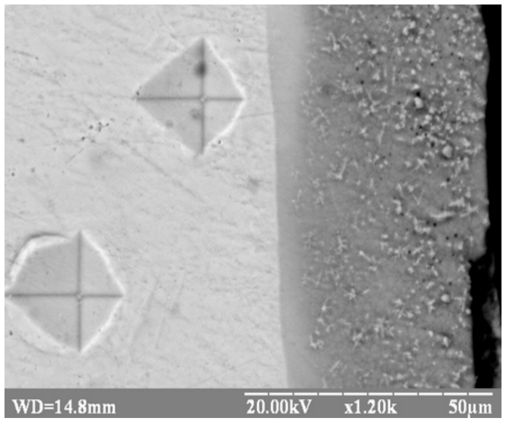
Biocompatible composite coatings formation



Microhardness and microstructure of surface layer of Ti-alloy BT1-0 after ESA-treatment



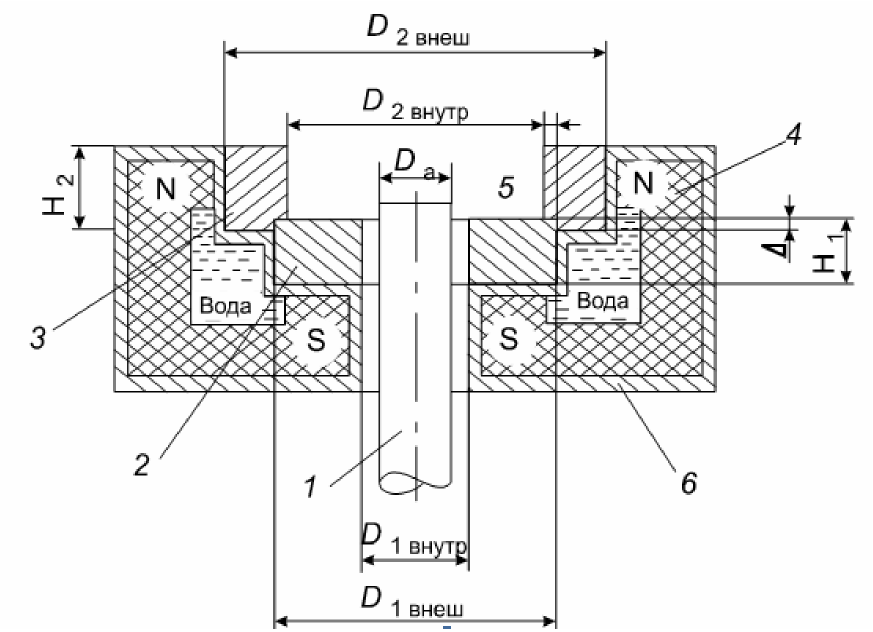
Microhardness and microstructure of surface layer of Ti-alloy BT1-0 after combined treatment ESA+LT



Micrographs by SEM obtained in secondary electrons of surface layer after combined treatment ESA+LT

6. Magnetron System for obtain wear-resistant and strengthened coatings

COAXIAL TYPE MAGNETRON SPRAY SYSTEM FOR SPUTTERING OF MAGNETIC SUBSTANCES AND CORROSION-RESISTANT, WEAR-PROOF, HEAT-RESISTANT, PROTECTIVE AND DECORATIVE COATINGS



- **Products with titanium nitride coating were obtain be electro-arc sputtering of titanium cathode (PVD) with nitride gas-reagent in vacuum chamber**
- **Coaxial type apparatus for magnetron-sputtering system was investigate**
- **Certificate of recognition is get**

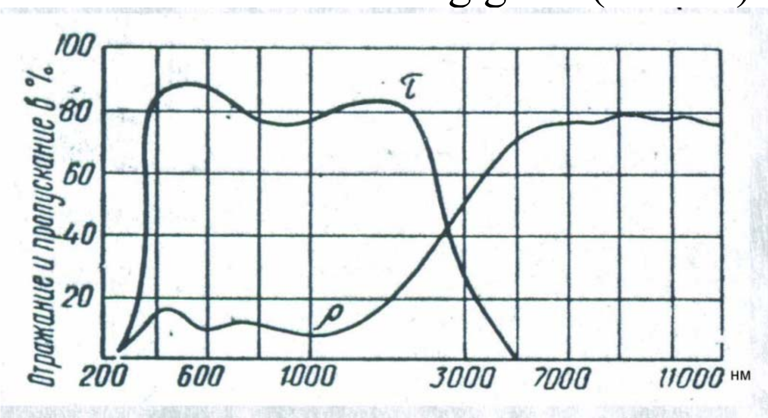
7. Glass optical properties modification for energy saving and dust protection

- **Technological processes of vacuum-plasma coatings, which provide the best effect antiglitter with clarity (glass for automotive rear-view mirrors) was developed.**
- **The way to protect the mirrors in one vacuum cycle of metal-dielectric coating was developed.**

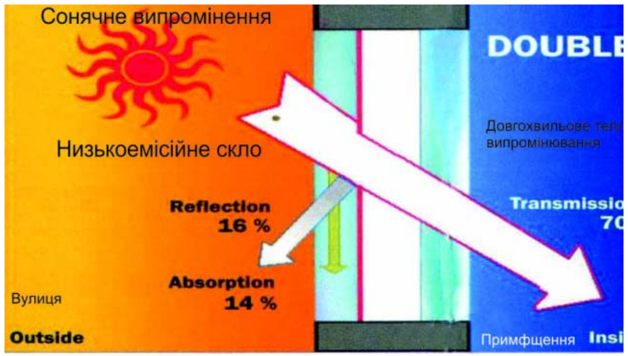
Glass optical properties modification for energy saving and dust protection

Ion-plasma technology for modifying the properties of the construction of energy efficiency of glass with functional purpose of resource conservation: the optical, conductive

Heat reflecting glass (Low-E)

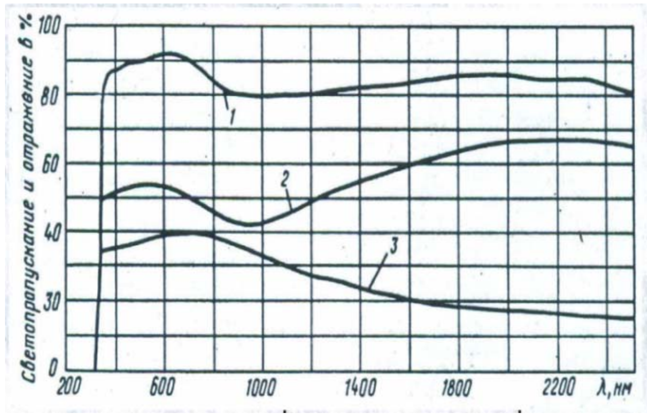


The emission wavelength of the solar spectrum:
T - transmission coefficient,
p - the reflection coefficient



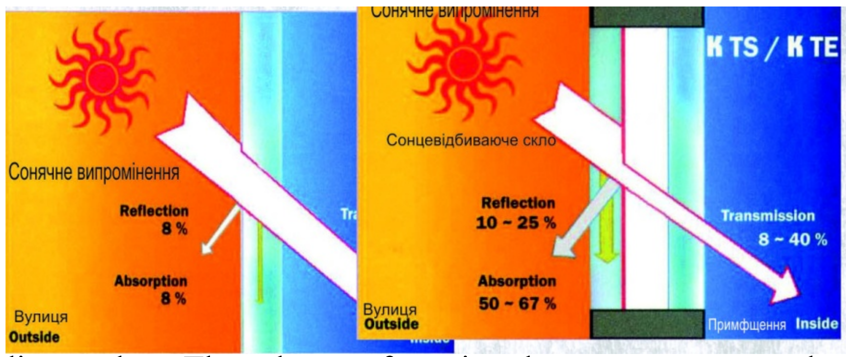
The scheme of passing a sunbeam through the glass

Tinted glass (reflects sunlight)



The wavelength of solar radiation
Optical characteristics of heatproof glass:

1 - transmission of ordinary glass;
2 - transmission glass coated with TiO_2, 3 - a reflection of the glass coated with TiO_2

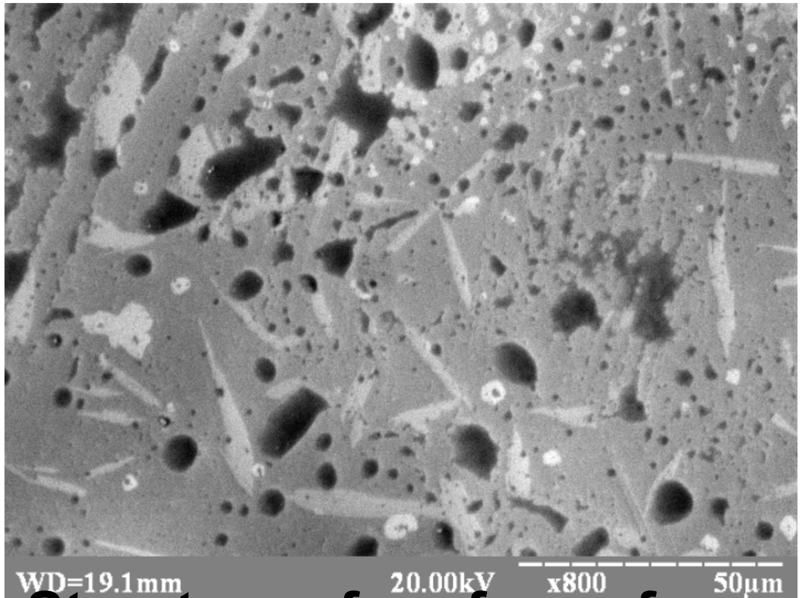


Ordinary glass The scheme of passing the beam through the glass

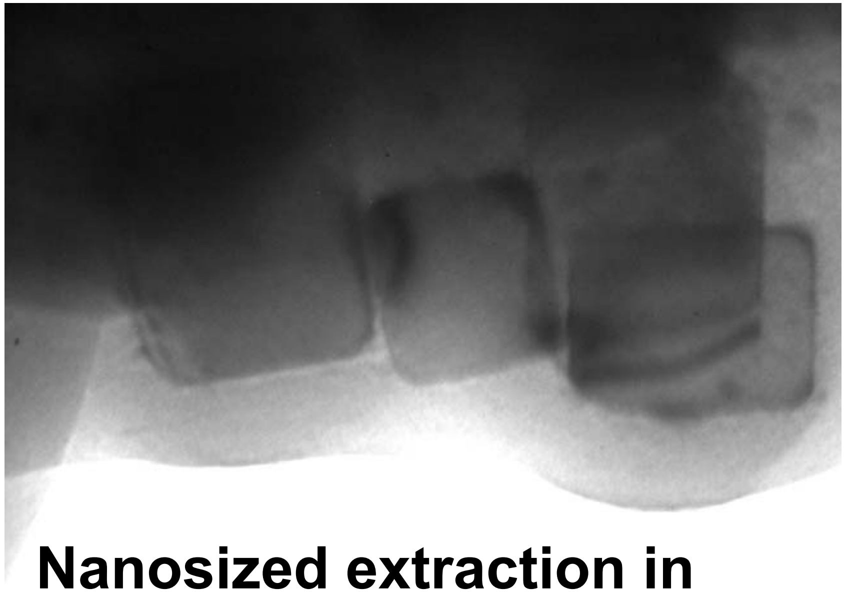
8. Nanocrystalline Magnetically Soft Alloys

Main idea is establish the optimal parameters of nanocrystalline soft magnetic iron alloys heat treatment and to achieve high magnetic properties through analysis of structural and phase state using high-temperature X-ray.

Influence of thermal treatment parameters on structure and properties of nanocrystalline magnetically soft alloys of system Fe-Co-Zr-Nb-Cu-B.

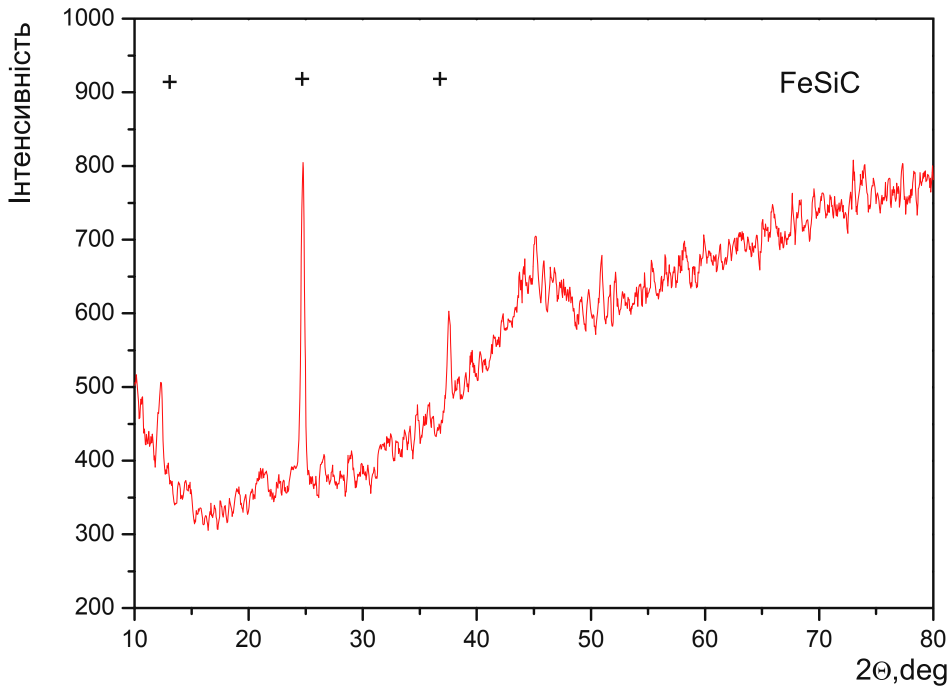


Structure of surface of sample $Fe_{73,5}Cu_1B_9\ Nb_3Si_{13,5}$ (Finemet)

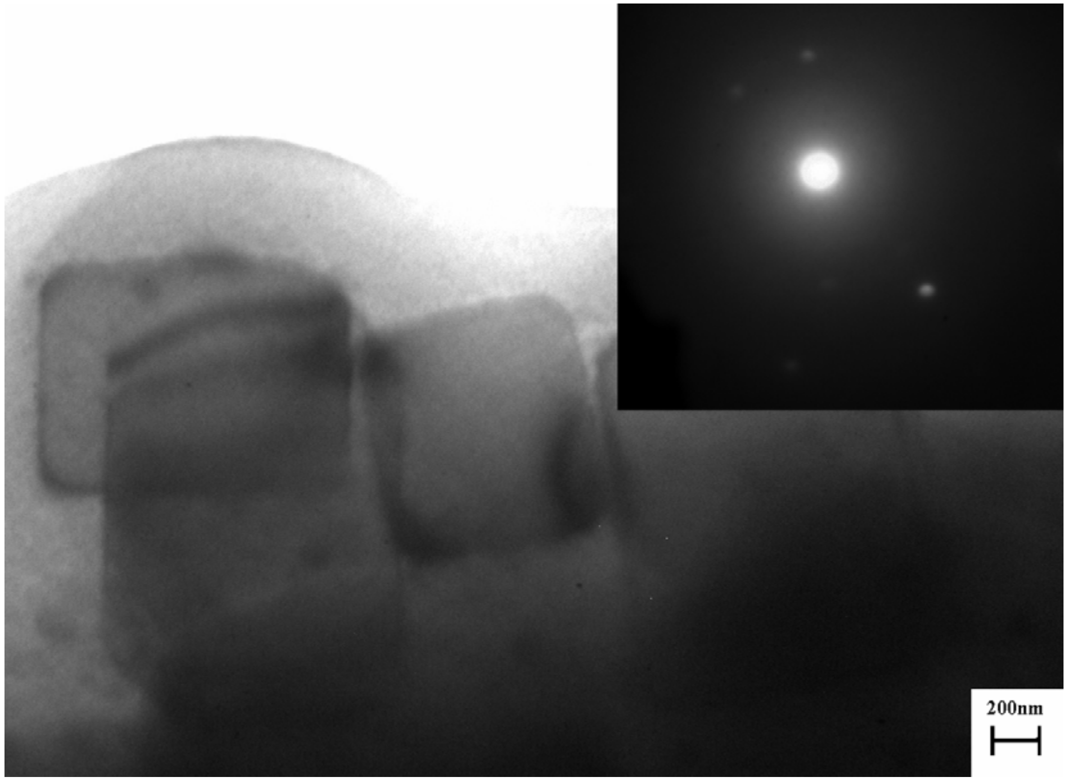


Nanosized extraction in structure of sample $Fe_{73,5}Cu_1B_9\ Nb_3Si_{13,5}$ (Finemet) *340000 Укр2

NANOCRYSTALLINE MAGNETICALLY SOFT ALLOYS

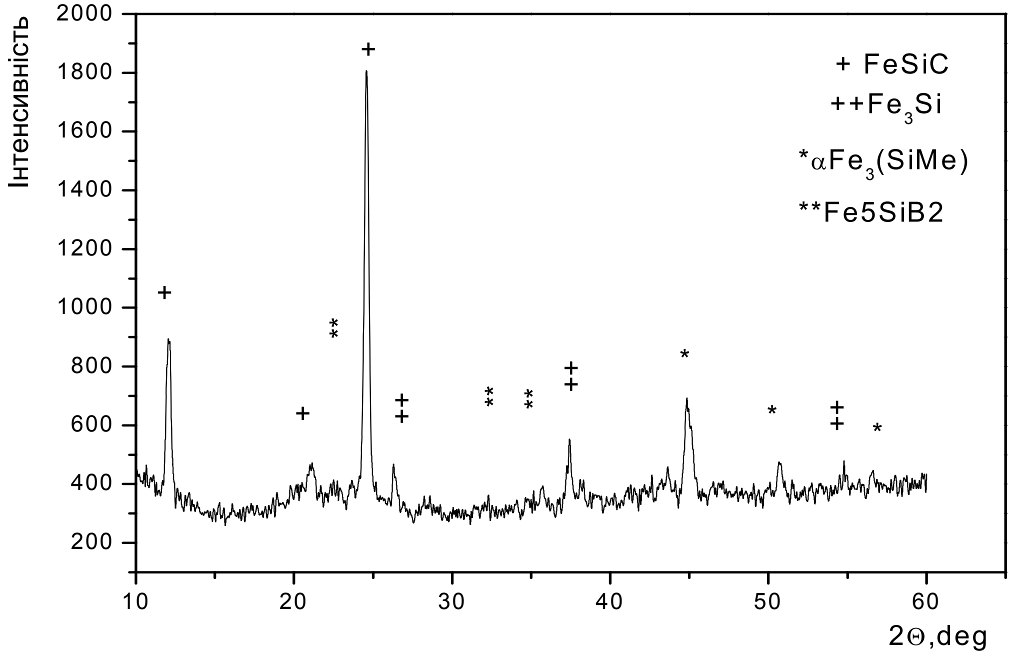


Diffraction pattern of AMS system Fe73,5Cu1B9Nb3Si13,5 initial state, emission of Cu-anode, selective filter



Structure of fragment of AMS $Fe_{73,5}Cu_1B_9$ $Nb_3Si_{13,5}$ with extraction of nanosized phase Fe_3Si Fm3m

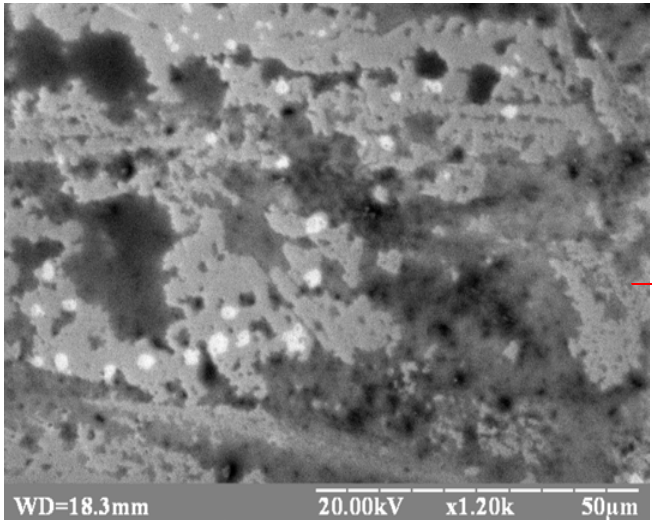
NANOCRYSTALLINE MAGNETICALLY SOFT ALLOYS

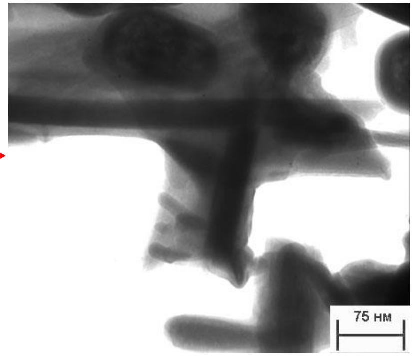


Fragment of structure of AMS $Fe_{73,5}Cu_1B_9Nb_3Si_{13,5}$ with extraction of nanosized phase Fe_3Si $Fm3m$, annealing in vacuum $5*10^{-6}$ Pa during 10 sec at temperature 673K

Diffraction pattern of AMS system $Fe_{73,5}Cu_1B_9Nb_3Si_{13,5}$, annealing in vacuum $5*10^{-6}$ Pa during 10 sec at temperature 773K, Cu-anode emission, selective filter

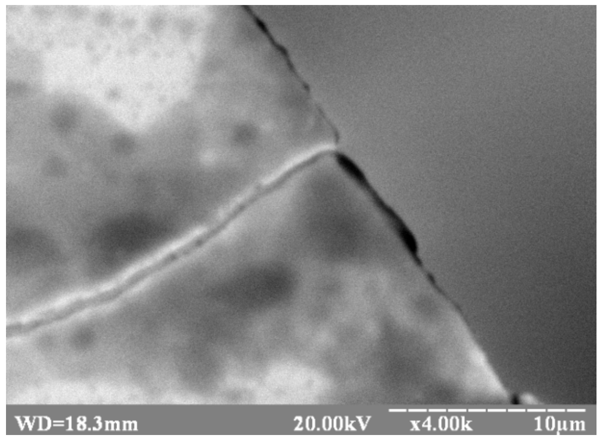
NANOCRYSTALLINE MAGNETICALLY SOFT ALLOYS





Fragment structure of AMS $Fe_{73,5}Cu_1B_9Nb_3Si_{13,5}$ after annealing at temperature 563К

Microstructure of sample surface of fast-hardened ribbon from alloy of system $Fe_{73,5}Cu_1B_9Nb_3Si_{13,5}$ after annealing at temperature 533 К



Structure of sample surface of fast-hardened ribbon from system $Fe_{73,5}Cu_1B_9Nb_3Si_{13,5}$ (Finemet) after annealing at temperature 673К

9. AUTORADIOGRAPHIC INVESTIGATION

Autoradiographic investigation of iron alloys with titanium diffused zone after saturation by carbon and nitrogen

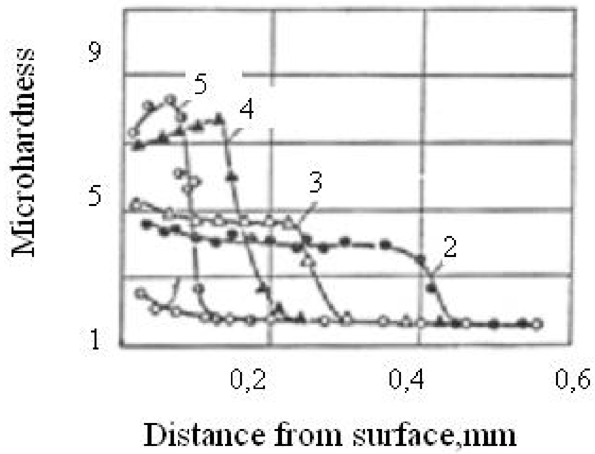


Fig. 1. A microhardness of iron titanium alloys, saturation by carbon at 973 K during 3,6· 10^3 seconds.
1- iron, 2- Fe+ 0,4% Ti, 3-Fe+ 1,04% Ti, 4- Fe +1,43% Ti, 5 – Fe + 1,73% Ti.

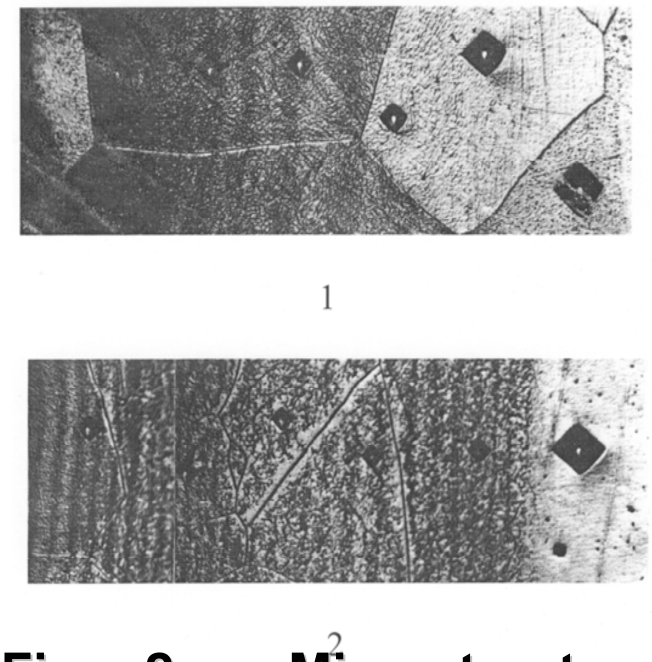


Fig. 2. Microstructure of iron titanium
alloys, saturation by carbon at 973 K during 3,6· 10^3 seconds.
1- Fe+ 1,04% Ti,
2- Fe +1,43% Ti. X 300.