Kuban State Technological University- KSTU
Laboratory dynamics and machine strength

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Structure and properties of coatings made of high-entropy alloy with martensitic transformations obtained by HVOF method in a protective atmosphere

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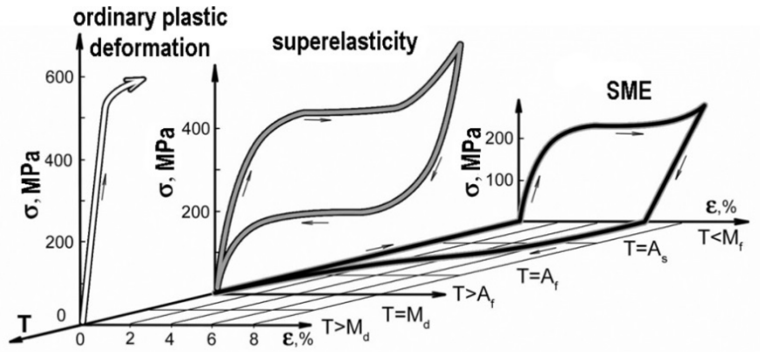
1. Introduction

High-entropy materials with martensitic transformations have improved functional and mechanical properties:

- cyclic durability;
- wear resistance;
- corrosion resistance;
- effects of one and multiple reversible thermomechanical memory;
- high level of reactive stresses, recovery and damping.

3D diagram of the basic thermomechanical properties of SME alloys



However, despite all the advantages, the high cost of the alloy limits their use in industry. Under these conditions, the direction associated with methods of surface modification of steels by high-entropy alloys with SME becomes relevant.

The aim of the work is to study the structure and properties of the highly entropic CoCuTiZrHf coating with martensitic transformations with the development of optimal technological parameters for producing a HEA with the assessment of the specified structural, mechanical properties, which ensure the manifestation of phase transformation.

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Research Objectives:

- we have to study the laws of the mechanical activation effect of highly entropic material powder on the structural phase state and quality of the coating obtained by HVOF in a protective atmosphere;
- this ensures the functional and operational properties of the products;
- we have to develop the optimal technological parameters of HVOF in the protective atmosphere to form a highly entropic CoCuTiZrHf coating that provides reliable adhesion;
- on the basis of complex metallophysical studies it is also necessary to establish the patterns of structure formation in highly entropic coatings after HVOF in a protective atmosphere and subsequent heat treatment;
- we have to develop statistical models of the technological process with optimization of parameters and to reveal the effect of phase transformation during calorimetric tests of the alloy coating;
- we finally have to perform testing of steel samples with coatings from HEAs on "friction-wear" with justification of the coating material influence on improving the mechanical properties of products.

Technologies for the production of composite high-entropy coatings with martensitic transformations

- diffusion metallization;
- ion-plasma, magnetron sputtering;
- plasma spraying in a protective environment (argon);
- argon-arc surfacing;
- laser surfacing;
- self-propagating high-temperature synthesis;
- coating by explosion;
- HVOF in a protective environment (argon).

The optimal technology for the formation of highly entropic coatings with martensitic transformations is HVOF, because it is a high-performance process that allows the formation of bulk composite coatings in a short period of time with low energy consumption.

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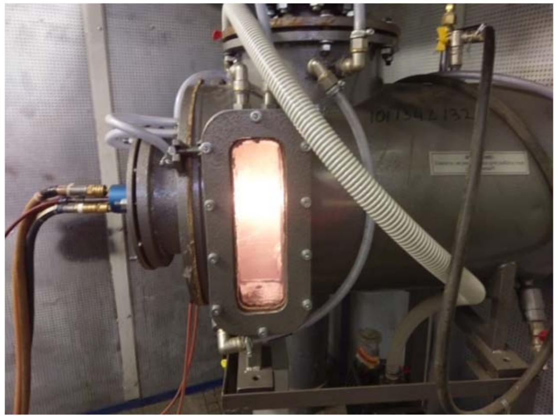
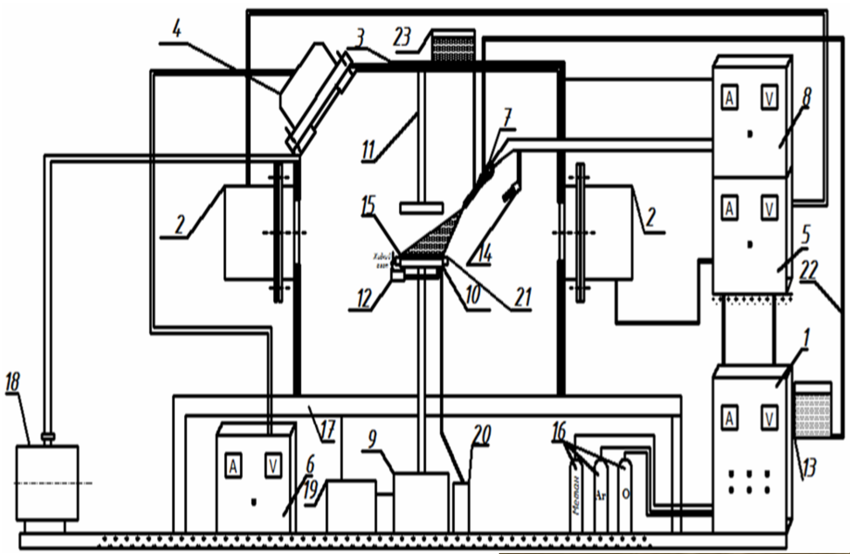
2.Vacuum mounting for producing coatings from highly entropic materials with martensitic transformations by the method of HVOF in a protective environment



Vacuum mounting diagram



Control unit 1, magnetrons 2 for magnetron sputtering of metals located on the vacuum chamber 3, source 4 for ion implantation of metals located on the vacuum chamber 3, power supply 5 for magnetrons 2, power supply 6 for ion implantation source, gas-flame burner 7 for HVOF installed at an angle of 45 ° to the surface of the part, fixed in the housing of the vacuum chamber, a power source 8 for HVOF, a press 9 with a lower 10 on which the workpiece is fixed and the upper 11 traverse for surface plastic deformation of the obtained coating, a device 12 for cooling a part made in the form of two containers filled with liquid nitrogen, a powder dispenser 13 for feeding powder into a subsonic region of the nozzle, a powder dispenser 23 for feeding powder into a supersonic region of the nozzle, a pyrometer 14 for measuring the temperature of the workpiece 15, working gas cylinders 16, frame 17, vacuum pump 18, process module 19 for ionic cleaning of the surfaces of the workpiece 15, step-down transformer 20 connected to the clamp the device 21 of the workpiece 15, the line 22 for transporting powder from the powder dispenser 13

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3. The technological process of coating formation includes the following steps:

-preparation and cleaning of the surface of the steel base;

-mechanical activation of metal powders;

-consistent HVOF coatings in a single production cycle;

-subsequent thermal and thermomechanical treatment;

-optimization of process parameters;

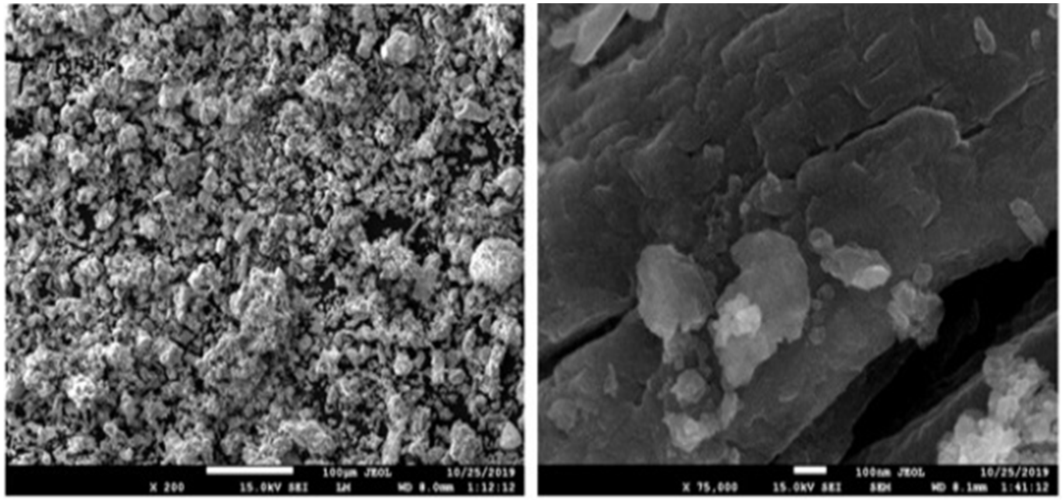
- analysis and experimental verification of the results with an assessment of the functional reliability of the composition.

The mechanical activation of the powder helps to improve the quality of the coating and increase the strength properties while there is a decrease in porosity and an increase in the adhesion of the coating to the base

4.Mechanical activation of powders

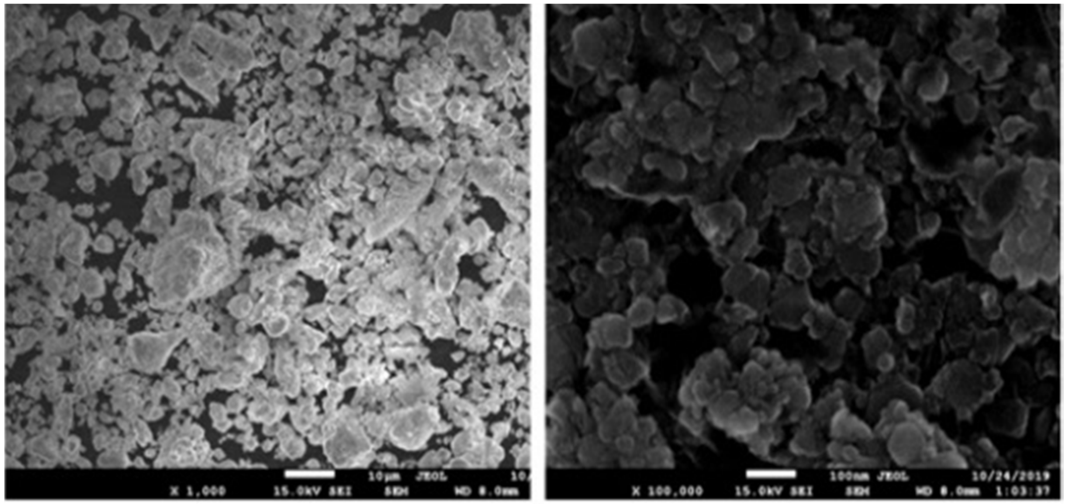
Morphology of Co17.6Cu18.8Ti9.6Zr18.3Hf35.7 powder particles:

before mechanical activation



The particle size of the powder before mechanical activation is 25–50 μm

after mechanical activation



After mechanical activation it is 1–20 μm

5. The effect of temperature in the zone of contact of powder particles with the substrate during high-speed impact on the microstructure and properties of surface layers

Empirical equations of temperature (Tp) and velocity (Vp) of mechanically activated powder particles versus spraying distance

$$T_p = A - B \cdot L - C \cdot L^2,$$
$$V_p = A_1 + B_1 \cdot L - C_1 \cdot L^2,$$

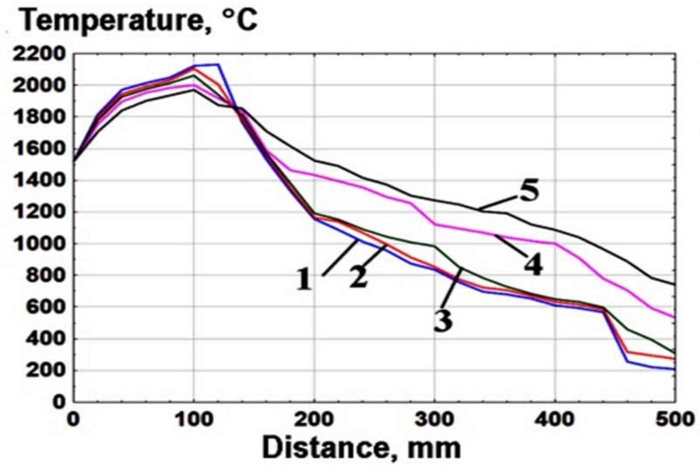
where L - the spraying distance;

A, B, C, A_1, B_1, C_1 - coefficients obtained as a result of statistical processing of experimental data.

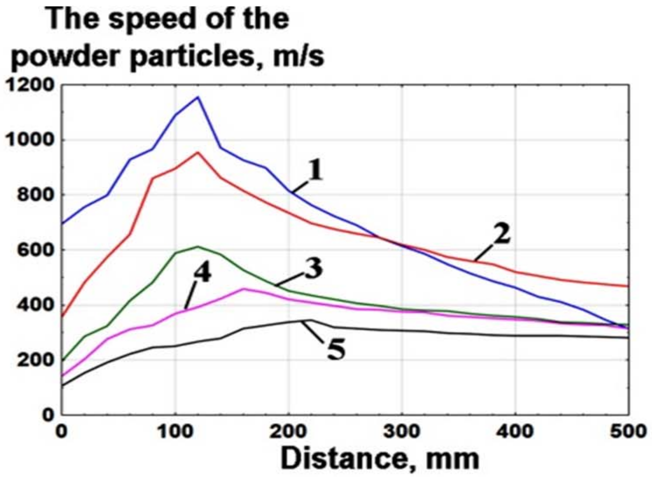
The values of the coefficients

Particle size, microns	A	B	C	A_1	B_1	C_1
3	2074,9	3,6	0,0005	879,3	0,41	0,0034
10	2047,75	3,42	0,0005	580,76	1,64	0,0042
20	2012,29	3	0,0009	346,3	1,12	0,0026
30	1895,6	1,23	0,0031	218,5	1,46	0,0027
40	1836,7	0,54	0,0035	146,77	1,2	0,002

The dependence of temperature particles of mechanically activated powder on the spraying distance

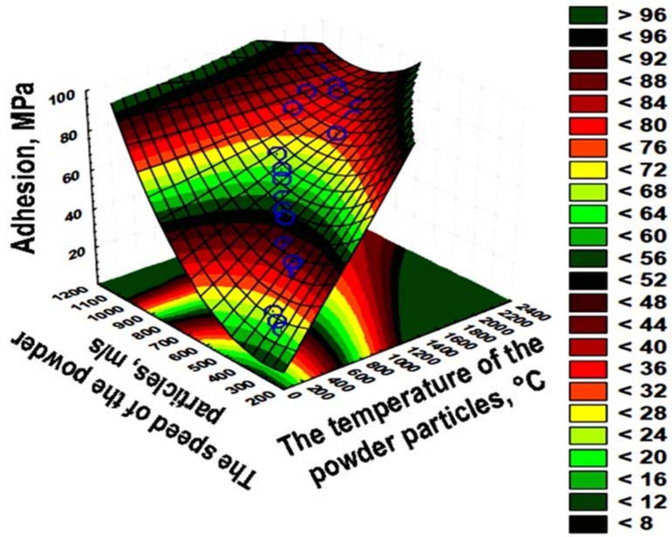


Dependence of the particle velocity of mechanically activated powder on the spraying distance

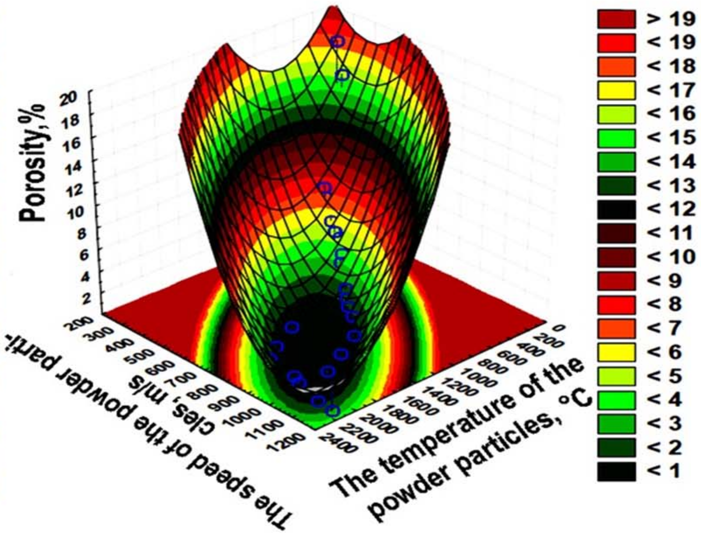


Particle size 3 μm - 1; 10 μm - 2; 20 μm - 3; 30 μm - 4; 40 μm - 5

The dependence of temperature on the velocity of the particles of the powder during HVOF and the adhesion strength of the coating to the base



Dependence of temperature on the velocity of the particles of powder during HVOF and porosity of the coating



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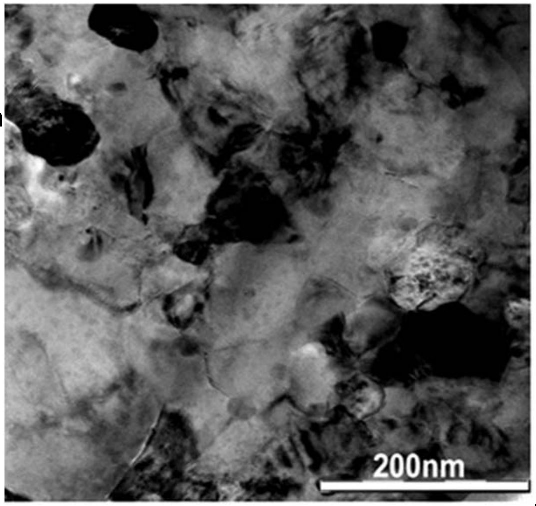
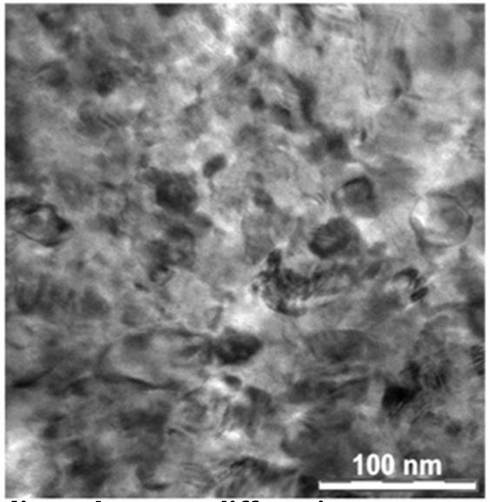
6.The structure and properties of steel 1045 coated with HVOF in a protective atmosphere

Microstructures of CoCuTiZrHf coatings : austenitic structure

grain size of 25-125 nm



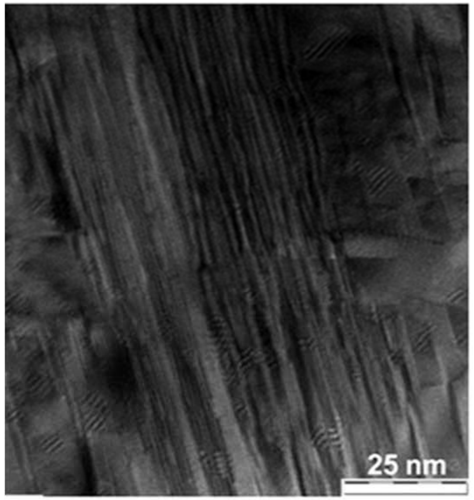


Pore content in the coating is less than 1%

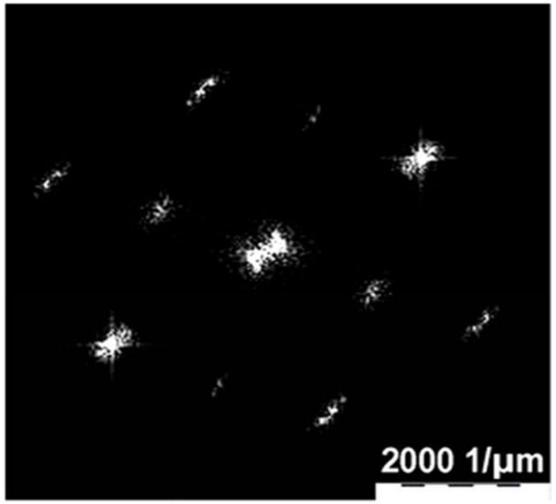
The adhesion of the coating was 78 MPa

Coating thickness 1mm

Martensitic structure

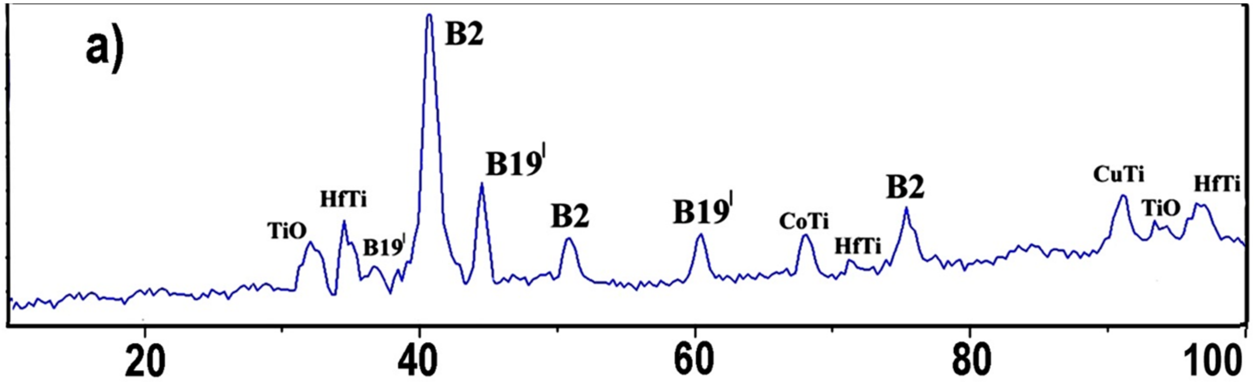


Microelectron diffraction pattern corresponding to the martensitic phase



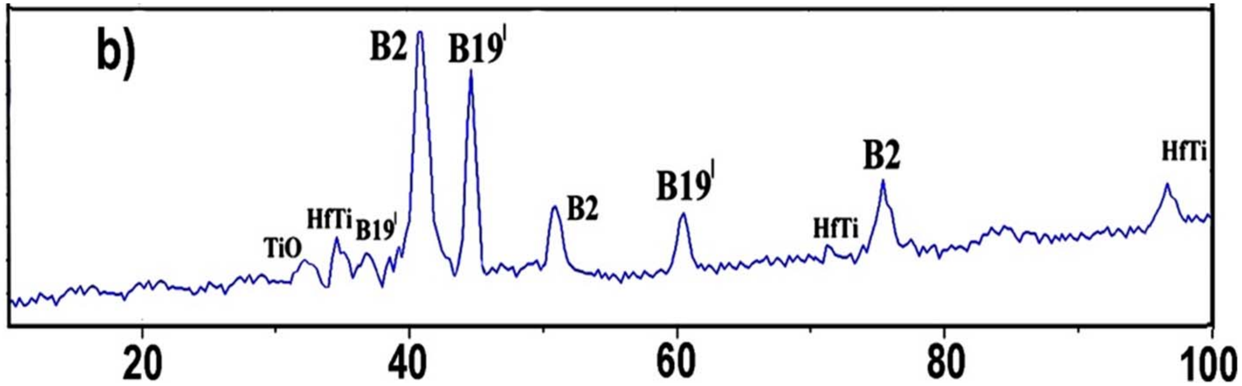
Coating diffractogram CoCuTiZrHf

Obtained by HVOF in a protective atmosphere (argon medium)



At room temperature, the main structural components of the CoCuTiZrHf coating obtained by HVOF in a protective atmosphere are as follows: the austenitic B2 phase with a cubic lattice, the martensitic B19′ phases with a monoclinic lattice, the HfTi phase with a hexagonal lattice, a small CoTi phase, CuTi with a tetragonal lattice, as well as titanium oxide (TiO) of less than 2%

After heat treatment (annealing at a temperature of 1123K)



After heat treatment (annealing at a temperature of 1123 K) we observed: an austenitic B2 phase with a cubic lattice, martensitic B19' phases with a monoclinic lattice, an HfTi phase with a hexagonal lattice, and a small amount of titanium oxide (TiO) of less than 1%

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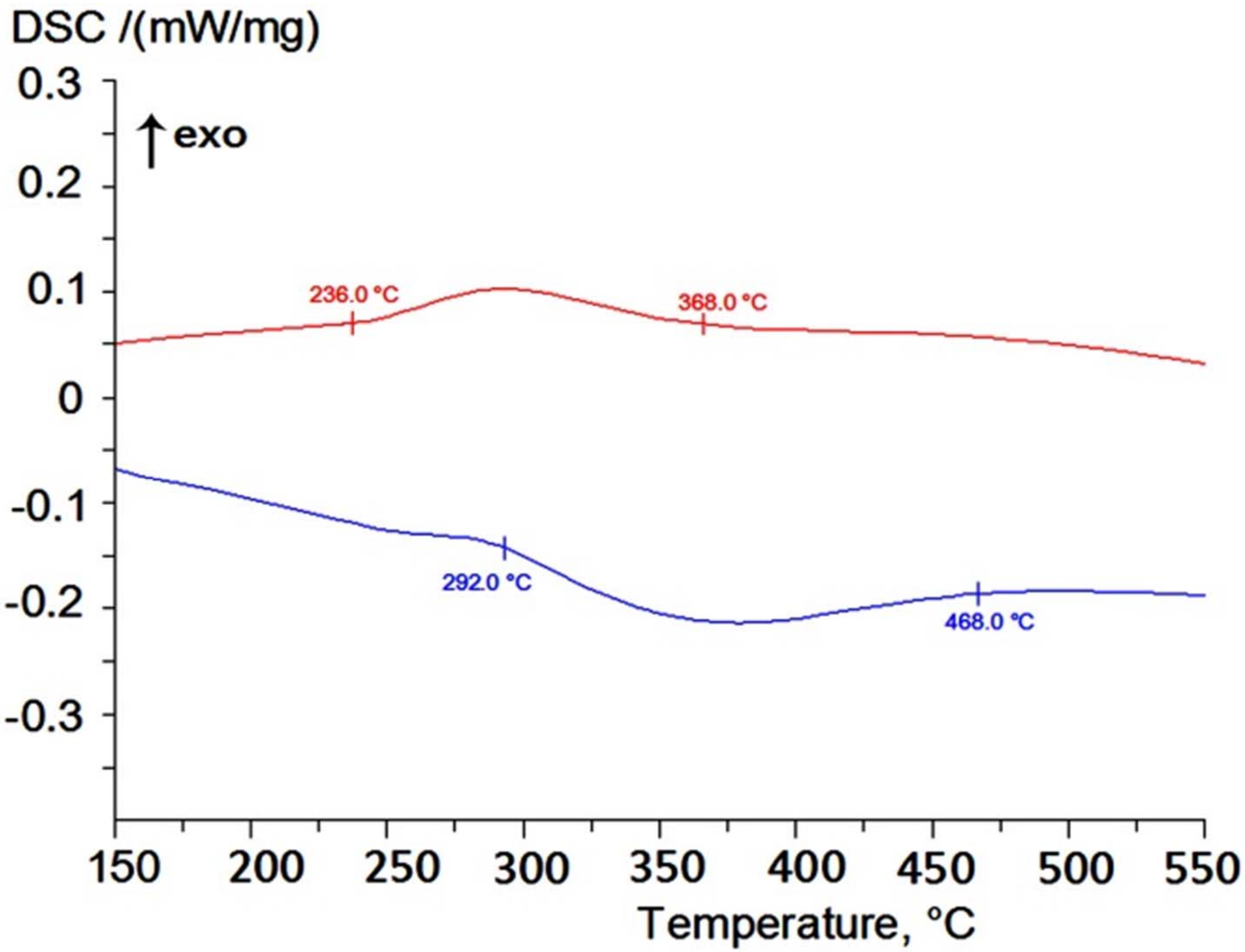
Parameters of the crystal lattices of the phases making up the Co-Cu-Ti-Zr-Hf coating

Phase	a, nm	$V_{at} \cdot 10^3$	b, nm	c, nm	β, degrees
B2 (cubic)	0,3021	27,57	-	-	90,00
B19' (monoclinic)	0,4651	55,56	0,4112	0,2905	98,00
CuTi (tetragonal)	0,316	26,86	0,316	0,269	90,00
CoTi (tetragonal)	0,3971	59,8	0,3971	0,3792	90,00
HfTi (hexagonal)	0,305	45,21	0,305	0,486	90,00
TiO (monoclinic)	0,587	229,11	0,936	0,417	108,12

7. Calorimetric heating-cooling curves of the CoCuTiZrHf alloy

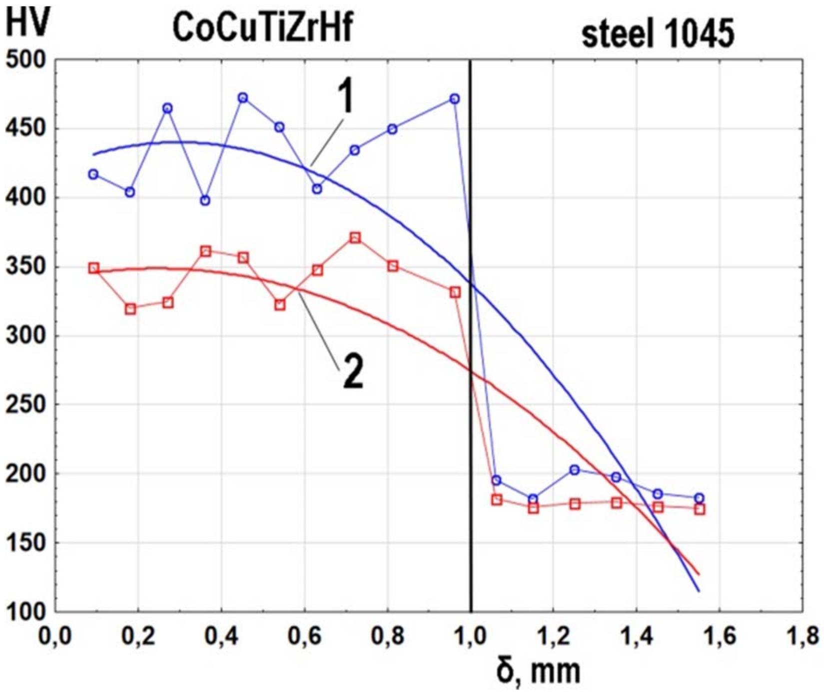


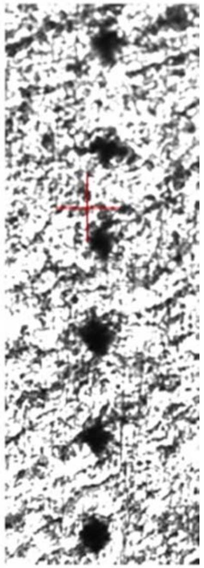
As can be seen from the results of calorimetric studies, the phase transformation in the CoCuTiZrHf alloy is reversible (M↔A), B19'↔B2.

8. Mechanical properties of high entropy coated steel

Hardness of coatings CoCuTiZrHf

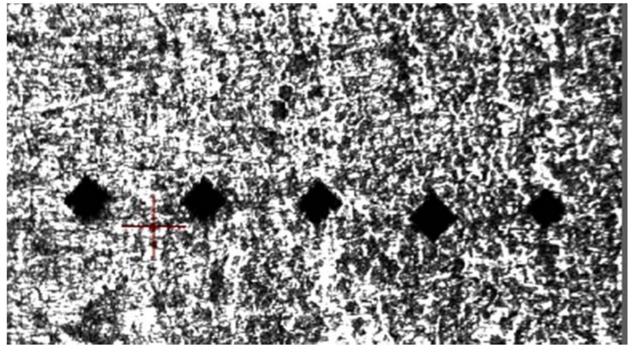
The distribution of microhardness "Co-Cu-Ti-Zr-Hf - steel 1045" by thickness





The distribution of microhardness over the thickness of the CoCuTiZrHf coating is uneven, in the range of 398-472 kg/mm^2 (after HVOF in a protective atmosphere) (curve 1); 320-372 kg/mm^2 (after HVOF in a protective atmosphere followed by heat treatment) (curve 2).

The microhardness of the steel base is in the range 175-203 kg/mm^2



The dependence of the microhardness HV0.1 of the coating on the thickness (δ) is described by equations (3) and (4). Equation (1) corresponds to curve 1, and equation (2) of curve 2.

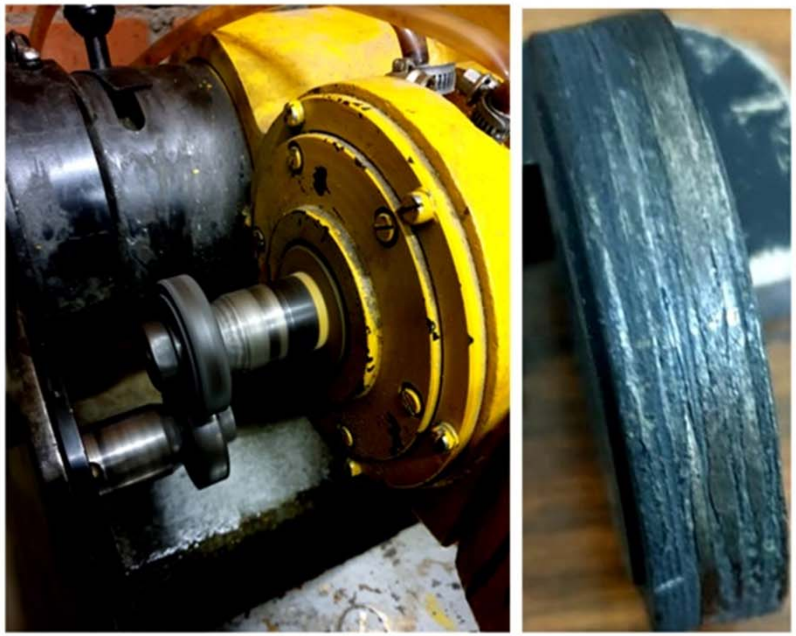
$$HV\ 0.1 = 421{,}79 + 123{,}21 \cdot \delta - 206{,}97 \cdot \delta^2,\ (kg/mm^2) \quad (1)$$

$$HV\ 0.1 = 340{,}86 + 64{,}06 \cdot \delta - 130{,}18 \cdot \delta^2,\ (kg/mm^2) \quad (2)$$

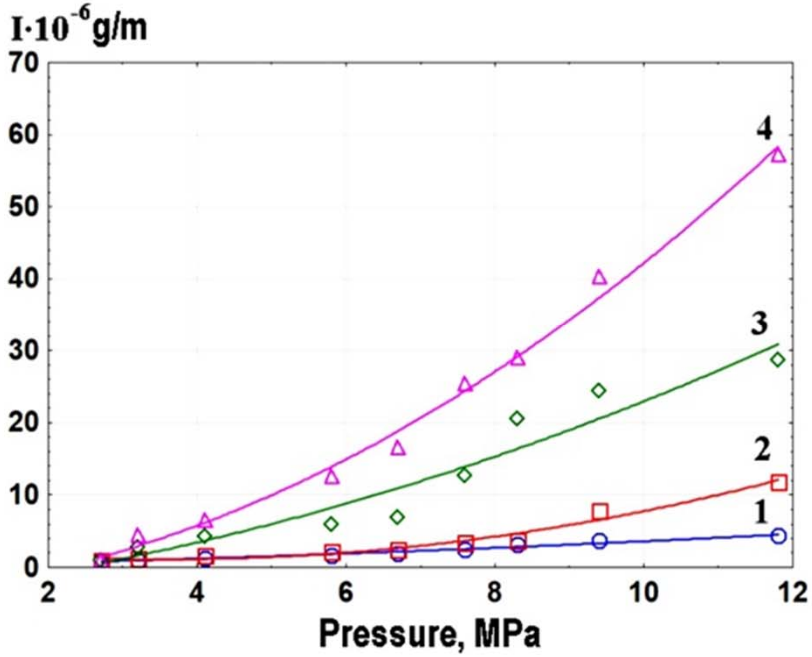
where δ - coating thickness, mm.

Friction-Wear Coated Steel Samples

The process of testing the friction-wear of samples with coatings from HEAs on a testing machine 2070 SMT-1



The dependence of the wear rate I on the disk pressure P with CoCuTiZrHf coating, the sliding speed of the disk



0.5 m / s -1; 1 m / s -2; 1.5 m / s -3; 2 m / s -4

The empirical dependences of the wear rate (I) on the disk pressure (P) for the CoCuTiZrHf alloy are described by equations:

$I = 0{,}1364 + 0{,}2224 \cdot P + 0{,}0127 \cdot P^2$ (disk slip speed 0.5 m/s),
$I = 3{,}264 - 1{,}1816 \cdot P + 0{,}1634 \cdot P^2$ (disk slip speed 1 m/s),
$I = -3{,}8309 + 1{,}2502 \cdot P + 0{,}143 \cdot P^2$ (disk slip speed 1,5 m/s),
$I = -3{,}596 + 0{,}8539 \cdot P + 0{,}3724 \cdot P^2$ (disk slip speed 2 m/s).

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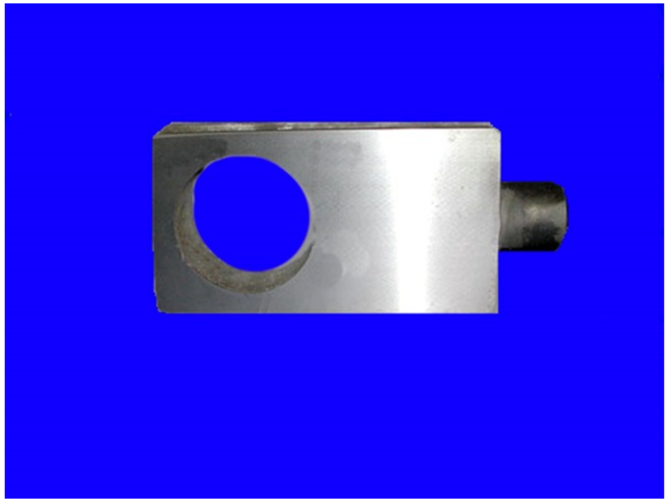
9.Examples of successful applications

Hardened gate valve



Pump impeller hardening

Hardening compressor rotors

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10. Conclusions

- it was shown that the use of mechanical activation reduces the porosity of the coating (the pores are less than 1%), increases the adhesion of the coating up to 78 MPa;

- the optimal technological parameters are determined, which provide the greatest adhesion and low porosity;

- we have developed statistical models of technological process with optimization of parameters such as spraying distance, speed and temperature of powder particles;

- based on complex metallophysical studies we have researched the structure formation in highly entropic coatings after HVOF in a protective atmosphere and subsequent heat treatment. Since the grain size in the coating was 25-125 nm, the structure is mainly austenite-martensite;

- during calorimetric tests of the CoCuTiZrHf alloy, we observed a significant exo-effect corresponding to the manifestation of the B19 '↔ B2 phase transformation;

- we have established experimentally that after HVOF in a protective atmosphere of a mechanically activated SME powder based on CoCuTiZrHf, the wear resistance of the coating increases by 2.32 times compared to that of steel 1045.

Patents

As part of the development of a technology for spraying high-entropy powder materials, a "Installation for producing nanostructured composite multifunctional coatings from a material with a shape memory effect on the part surface" was developed (a positive decision was received on the grant of a patent for the invention No. 2019137463 of 02/14/2020).

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Thank you for your attention!

Questions?
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