Refractory phases synthesis at the surface microalloying using a wide aperture electron beam

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Abstract. The experimental results prove the ability to realize technology of chemical heat treatment of some materials by surface microalloying using a wide-aperture low-energy high-current electron beam. Such layers were produced due to initiating exothermic chemical self-propagating high-temperature reactions in the thermal explosion mode between the base and the thin film covered on the base. New phase compounds in reaction products were found.

1. Introduction

Today there are many methods of surface modification of a wide range of materials with surface allying. The most popular are the methods including chemical and thermal processing (CTP). They include technologies connected to diffuse layer saturation. Usually such processes are carried out as a final operation in technological procedure of instrument production, except for the cases when the surface strengthened with CTP is covered with abrasion resistant coatings [1].

Creation of an alloyed surface layer with increased wear-resistance using self-propagating high-temperature synthesis (SHS), based on the use of internal energy of the source reagents, may be an alternative to the traditional methods of chemical and thermal processing. As a rule, reagents in SHS processes are used in the form of fine-grained powders, liquids and gases. Such processes are known in systems with powder and liquid, gas suspension and multilayered films. In this article we describe the peculiarities of producing microalloying subsurface layers in the systems consisting of a massive object with a thin film cover.

The basis of the process is the synthesis of stable compounds in the surface layer of the product by initiating chemical reaction between metals of IV–V groups with non-metals of the 2nd period. At that, the product should contain such non-metals in its structure or to be saturated by them by producing solid solution or some instable compounds. Metal in the form of the layer is applied on the product surface, for instance, with the use of magnetron sputtering. Then the reaction of self-propagating high-temperature synthesis is initiated in the mode of thermal explosion by impulse heating of the product surface. In some cases, interconnection between metal coatings and substrate produces intermetallic phases.

During creating SHS system it is possible to use rather wide spectrum of the reagents which are chemically active at high temperature [2]. Simultaneously other substances can be used as fillers or dilatants including those, which take part in synthesis process as by-products of the reaction. In this
case not only chemical nature of the reagents is important but also the thermal effect of the reaction, heat flow conditions and kinetics of phase and structural transformations.

2. Microalloying of the surface samples
The main method of SHS reaction initiating is approaching heat impulse with combustion wave along interphase boundary [3]. The process is more effective in case of heating all surface of the object in the mode of thermal explosion. Evaluation of diffusion coefficient in such reactions is up to $10^{10}$ times more that it is usually in solid phase. In case of high thermal losses caused by intensive heat removal of the substrate the process can become less stable. However, with increasing temperature of the surface the speed of SHS front will be increasing exponentially.

In our case material examples were subjected to impulses series of a wide aperture low energy high current electron beam (LEHCEB), to initiate exothermic chemical reactions both in liquid and in solid phases, between metal film and nitrogen, carbon or aluminum which are present in the content of base in the free form or in the content of compounds.

The processing was carried out in RITM-SP unit which is a combination of the LEHCEB RITM, and two magnetron sputtering systems were placed in a single vacuum chamber. The unit allows carrying out sputtering of films made of various materials onto the surface of the product and further liquid phase mixing of film materials and the substrate with intensive electron beam impulse [4], which is called microalloying. LEHCEB generation includes electron emission, creating of beam in a plasma diode and its transportation in plasma channel. Use of such generation scheme allows getting a beam with about 5 microsecond length and with current density up to $10^5$ A/cm$^2$ at accelerating voltage from 15 to 30 kW. The area of processing is about 50 cm$^2$.

During impulse electron processing surface layer covered with an alloying layer is subject to cyclical heating. During quick heating with electron beam with $10^6$ K/s speed and its further quick cooling ($10^4...10^5$ K/s) its external layers cool quicker than the middle that is why there appear tension stresses [5]. The source of excitation of stress waves can be thermo elasticity, caused by the sudden expansion of thin surface layer heated to high temperatures, as well as recoil impulse caused by material vaporizing in the exposure zone and further recession of vapors. The temperature in the subsurface layer reaches the levels which exceeds melting of system compounds. Evaluation of the the impulse surface heating at discharge energy density about 4.5 J/cm$^2$ results in the value approaching 4000 °C. Heat emission caused by exothermal chemical reaction between a thin film and surface layer allows to produce up to 0.5 J/cm$^2$ additionally but with certain time delay. After passing of the elastic wave at the moment of relaxation of elastic tensions a burst-like creation of structural defects occurs there, which enhances the process of substance transfer referred to as remote action effect.

3. Microalloying of solid alloy samples with Nb$_{70}$Hf$_{22}$Ti$_8$ composition
In this section we describe microalloying processes of the materials surface using the reaction of niobium-hafnium carbide creation in the complex carbide on the surface of carbide phase of hard alloy acting as a donor of carbon atoms, including free atoms.

For experiments H13A inserts, produced by Sandvik Coromant, were used as base material. Thin film (thickness 150 – 250 nm) was applied to the samples by means of magnetron sputtering. The content of the film is NbHfTi alloy. The experiment was carried out to obtain a layer from wear resistant nonstoichiometric carbides with face centered cubic lattice at the next processing stage [6].

A high speed melting and solidification process allows creating unusual structures in hard alloy. And, although according to modern concepts the greatest influence on the strength of a hard alloy having the status of the binder, structure changes of which often can lead to softening, also the changing structure of carbide phases exerts influence here.

Here we are dealing with deformation hardening caused by the elastic wave. However, due to short duration of the process (~ $10^{-5}$s) and thermal inertia, heating caused by compression and viscous friction, most likely, is not a physical factor defining substance performance at such conditions. The
main part in this case should play mechanic activating of high rate physical and chemical processes within the substance which are present both in liquid or in solid phases.

Covering of the instrument surface by carbide forming elements as – Nb, Hf and Ti before processing with an electron beam allows to produce multiphase carbide structure due to microalloying during SHS. The external layer is saturated with hard-melting carbide phases of MC type, which keep a small form and are homogeneously distributed due to extremely high speed of cooling. Moreover, chemical potential of the system changes. The appearance in the melt in the neighborhood with more refractory melting particles leads to the sharp increase in the interphase surface and carbide formation reaction. Due to additional energy release during SHS, there is enough time to produce explosion chemical reactions. Moreover, such compounds as γ-WC, TiC, NbC and HfC have an opportunity to create non stoichiometry structures, with a range of stoichiometry varying from 0.5 to 0.97 which means that effects, connected to surface decarburization, can be eluded.

Here we should notice the role of hafnium carbide, having one of most high formation heat (252 kJ/mol). Impact by the electron beam on an alloy film where hafnium is absent, does not result in the formation of homogenous structure without micro fractures. Internal thermal energy of chemical interaction of source reagents is not enough.

X-ray analysis of crystal structure proves phase content changes, and on the surface of the samples characteristic structure appears, which proves successful SHS in each case (figure. 1b). Powerful thermal impact of LEHTEB on the surface of H13A hard alloy insert covered with film made of NbHfTi alloy about 200 nm thick results in creation of face-centered cubic arrangement of carbide phase, identified as (Nb, Hf, Ti) Cx. γ-WC phase reflection with lattice constant of 0.424 nm are appears. We should also consider one-type FCC structure of niobium-hafnium carbide and of high temperature tungsten carbide. The result of the X-ray analysis depicting the above mentioned specifics features is presented at figure 1b. X-ray diffraction analysis was performed with an X-ray diffraction meter PAN analytical Empyrean Series 2 (CoKα).

![Figure 1](image)

**Figure 1.** a) Structure of solid alloy surface after microalloying with LEHTEB by Nb70Hf22Ti8 alloy. b) X-ray diffraction analysis from H13A sheet surface after microalloying with Nb70Hf22Ti8 alloy.

The specific feature of sub-surface area is formation of crystallographic texture caused by heat transfer during cooling. Comparison of spectrums received during symmetrical and asymmetrical analysis showed the change in intensity of reflection of two main phases of face centered cubic lattice connected to crystalloid texture {100} which is parallel to the object surface.

Influence of geometrical factor should be noticed as well. During the use of impulse electron beams energy losses for backscattering depend on atomic size of the target, energy and incidence angle of electron beams and reach the level up 8 to 50 %. In case if angle of the incidence of an electron beam is about 30°, maximal value of temperature distribution will be transferred to the surface, and in case of further angle decreasing the temperature gradient in subsurface layer increases [7]. This means that homogeneity of heating of subsurface area would be influenced by surface roughness of the irradiated
object, especially in case if its value comparable or more than penetration distance of the electrons to the object.

It was noticed that on polished samples of hard alloy when roughness of the surface is 4-5 times less than penetration distance if the electrons the reaction does not flow right which has negative influence on the properties of a forming material. At that, change of angle of incidence of the electron beam to the surface up to 30° can initiate the reaction. The process flows most effectively at roughness of unprocessed surface varying from 0.5–1.5 µm Rₐ.

The concentration of Nb, Hf and W in interlayer proves mixing of solid alloy with alloying cover as a result of high temperature synthesis reaction. Maximal thickness which allows to produce modified SHS structure is 3-4 µm. Multiple initiating of the process practically does not change initial microstructure but it can have negative impact on the substrate due to thermal cycling. To make the modification to the fullest extent, as a rule, it is enough to perform a series of five or six pulses.

At the bottom the layer is created due to the contact melting of tungsten carbide grains. The thickness of contact melting zone increases when it is closer to the surface, but the size of initial carbide grains decreases.

On the other hand, the structure of the modified layer transfers to the structure of source solid alloy. In this area we can observe zone liquation of cobalt. The cobalt content in the transfer zone equals 2-3 µm, which is four times more than its content in the source alloy. The occurrence of such liquation can be described by the fact that cobalt phase acting as crystallizing phase transfers with liquid phase to the boundary of thermal influence area. The displacement process is also influenced by the significant difference in the specific density of carbides and liquid cobalt. Existence of such liquation can lead to cracking of the object surface and the most probable risk is maximal cobalt content in subsurface layer.

4. Microalloying of preliminary nitrified rapid cutting steel

We should analyze the process of zirconium nitride formation where instalable ferric nitrides of preliminary nitrified rapid cutting steel acted as a nitrogen atom donor.

To carry out the experiments preliminary nitrified high speed steel (HSS) S6-5-2 sheets at the depths of 50 µm with two stage vacuum arcing type discharge [8] as a base material were used.

In figure 2 the influence of LEHTEB impulses series with energy density 4.5 J/cm² and about 5 µs lengths to the surface of nitrified steel sample is shown. The heating effect of the electron beam sufficiently below an upper layer of metal not only melted, but also began to evaporate, exposing the carbide component. Irradiation by LEHTEB causes dissociation of ferric nitrides, especially ε-phase; great amount of residual austenite is created on the surface (figure 2b).

After covering the samples by magnetron thin Zr film 150 – 250 nm thick, and further irradiation with an electron beam we have managed to initiate SHS reaction of ZrN formation.

Due to the formation of hard melting nitride film metal vaporizing significantly decreases and the structure becomes finely dispersed. The formation of the nitride phase is proved by the results of X-ray structural analysis (figure 2c). Moreover, we should note that in the latter case the content of residual austenite in subsurface layer significantly decreases.

It can be noted that Zr is discovered in subsurface layer about 2 µm thick.

5. Microalloying of aluminum alloy with titanium and zirconium

Formation of intermetallic phases can be analyzed at the example of aluminum interaction with titan coatings. For electron beam microalloying alloy AlCu4Mg1 was chosen. On flat samples made of these alloy Ti covering were placed in order to get the layer saturated with intermetallic phases of Al-Ti systems after electron beam processing during SHS.

In figure 3 we can see the result of the impact made by an electron beam with the energy density of 4.0 J/cm² on Al alloy of the surface covered with titanium film about 0.2 µm thick. Optical microscopy shows formation of dendrite type crystals of intermetallic phase which is proven by X-ray structural analysis. It confirms the intermetallic phase formation Al₃Ti (structural types tI8, α=0.348
nm, c=0.858 nm and tI32/30, a=0.3875 nm, c=3.384 nm, the melting point of 1390 °C). The energy density increased by 4.5 J cm\(^{-2}\) causes the vaporizing of the covered film along with the aluminum surface layer. The intermetallic phase content decreases drastically in this case.

The “polishing” effect is vividly shown on aluminium alloys. The alloy processing, namely the intense melting with the partial vaporizing of the surface layer, causes its refining, its structure crushed to sub-micron crystals and smoothing the micro relief. The initial roughness equal to 2.5 µm has reduced to 0.8 µm.

The essential practical features that the observed effects possess are their stability and reproducibility.

6. Conclusion
The obtained experimental results confirm a possibility for the formation layers modified by microalloying on the surfaces of the wide variety of materials. The problem is the increasing the thermal stability of non equilibrium structural and phase states that ensure to achieve unique physical and strength properties. These layers were prepared due to chemical reactions initiation conducted between the alloy and its thin film coated on its surface. The formation of new phase components was detected in the reaction products in this case.

The structure formation in the sub-surface material layer arises in our case from the impulse nature of the conducted processing in the microsecond range. The key factors influenced the microalloying are electron beam energy, which is determined by accelerating voltage, and film thickness. The interdependence that occurs between the modified layer and accelerating voltage has an extremal nature. The electron beam irradiation with the lack of energy is unable to initiate the SHS, but its abundance leads to the extreme film vaporizing.

The processing is to be conducted providing the coating thickness equal to half-value penetration distance into the substrate material. It goes up to about 200 nm in our case. At that, it is preferable to have more or less uniform heating of the sub-surface layer by electrons that the geometrical factor enables. The initial roughness correlates with the electron penetration distance into the substrate.

The microalloying finds its application. In particular, the aforesaid processing recommended before conducting the coating enables to make influence on cutting tool depletion ensuring the fact that its resource will be increased [9].

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