FEATURES OF SURFACE MODIFICATION OF COPPER-BASED ALLOYS UNDER POWERFUL PLASMA EXPOSURES

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Paper presents features of plasma alloying of Cu-based materials with Ti-Cr, Ti-Cr-Ti-Nb, Ti-Cr-Ti-Zr, Ti-Cr-Ti-ZrO coatings in different regimes of the QSPA Kh-50. Targets were made from copper samples covered of multilayer PVD coatings have been deposited within a Bulat-type facility. Prepared targets were irradiated with powerful plasma streams with energy loads achieved 0.6 MJ/m^2 and the pulse duration of 0.25 ms. Influence of plasma impacts on modification different copper alloys has been analyzed. Mechanisms of modification of thin multilayered coatings mixed with Cu substrate in a liquid phase under the plasma processing are evaluated.

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INTRODUCTION

Copper-based alloys are widely used in heat transfer elements for electronics, nuclear fusion technology and many other areas due to their excellent thermal conductivity, strength and fatigue resistance. Such alloys, e.g. Cu-Cr-Ti-Zr, could be used as basis to construct heat sinks for first wall and divertor components of ITER. The main benefit of using Cu-base alloy as a heat sink material for high heat flux applications lies in the fact that it offers unique combination of desired properties, namely, excellent thermal conductivity, strength at operation temperature, ductility, toughness, water-tightness, and only moderate activation. However, various changes of mechanical properties could be driven in copper alloys under the plasma exposures with extreme energy and particle loads [1].

In spite of the extraordinary virtues the very harsh conditions environment expected for the fusion reactors (e.g. DEMO) will be highly challenging for Cu-base alloy as heat sink material. For instance, the surface of divertor of a DEMO reactor will be exposed to high heat loads up to 20 MW/m^2 [2]. Given that the heat sink of a divertor has to withstand both cyclic heat loads and neutron irradiation, maintaining a heat conductivity and sufficient mechanical stability is the paramount requirement for heat sink material. In this context, there is a concern whether a Cu-Cr-Ti-Zr alloy heat sink can fulfill the structural design criteria formulated for DEMO divertor targets. This question is primarily related to the mechanical performance of Cu-Cr-Ti-Zr alloy under irradiation.

However, the production of elements of the cooling system of divertor from Cu-base alloy is rather expensive. A thin layer on the surface of the heat sink compound is more cost effective. This problem can be solved with appropriate coatings. Although the coat application method the most common method today, it can suffers problems with insufficient adhesion of coating. One of the prospective ways towards an improvement of the material properties is the alloying during the pulsed plasma processing (the mixing of previously deposited thin ($h_{coat} < h_{melt}$) coatings of a different pre-determined composition with the chosen substrate in the course of its melting driven by powerful plasma impacts).

The alloying of a surface layer in result of the coating (Cr, Ti, Zr, Nb) and substrate (Cu) mixing allows achieve a desirable chemical composition of the processed surface layers [3-7]. Nevertheless, the modification processes in plasma facing materials, which can be induced by repetitive plasma impacts and synergetic effects (caused by different factors) are still not understood.

This paper presents experimental studies of the alloying and modification of the pure copper with Ti-Cr, Ti-Cr-Ti-Nb, Ti-Cr-Ti-Zr, Ti-Cr-Ti-ZrO coatings admixture introduced by the plasma-induced mixing. Accumulation and comparison data for different materials types (coatings, alloys and etc.) might be a basis for choosing the heat sink system material relevant to ITER and DEMO.

1. EXPERIMENTAL DEVICE AND DIAGNOSTICS

Surface modification by powerful pulsed plasma streams were carried out within a quasi-stationary plasma accelerator QSPA Kh-50 [8, 9]. The main parameters of the QSPA hydrogen plasma streams were as follows: ion impact energy was about 0.4…0.6 keV, the maximum plasma pressure reached up to 0.32 MPa, and the plasma stream diameter was about 18 cm. The surface energy loads, as measured with a calorimeter, amounted to 0.6 MJ/m^2. The load pulse shape was approximately triangular, and the pulse duration was 0.25 ms. The target surface before each plasma pulse was maintained at the room temperature in reported experiments.

Samples (10x10 mm and 3 mm in height) were made from copper covered of multilayer coatings of about thickness 3…4 μm (each layer – 1 μm). High quality Ti-Cr, Ti-Cr-Ti-Nb, Ti-Cr-Ti-Zr, Ti-Cr-Ti-ZrO thin multilayer coatings were created using PVD technique [10] in a Bulat type facility. Parameters of arc discharge are as follows: current of arc I_{arc} = 230 A and biasing voltage of U_{bias} = 140 V. Before deposition of coatings, ionic cleaning of the surface (etching duration 2 min, U_{bias} = 1.5 kV and I_{arc} = 100 A) was applied. Ti was used as a binder between the substrate and layers of Cr/Zr/Nb.

Spectroscopy, piezodetectors, electric and magnetic probes, and other diagnostics were applied for measurements of plasma streams parameters. The energy density in free plasma and the surface heat loads were measured by means of the local calorimeters. Observations of plasma interactions with the exposed surfaces were performed with a high-speed 10-bit CMOS pco.1200 s digital camera of the PCO AG type (in the spectral range from 290 to 1100 nm, with an exposure time ranging from 1 μs to 1 s). The surface analysis of the exposed samples was carried out with a MMR-4 optical microscope, equipped with a CCD camera. There were also performed measurements of weight losses, as well as precise measurements of the surface roughness with a Hommeltester T500.

X-ray diffraction (XRD) has been used to study structure, sub- structure and stress state of targets. ϑ-2ϑ scans were performed using a monochromatic Cu-K_α radiation [11-13]. Computer processing of the experimental diffraction patterns was performed using the new profile 3.5 software package [12]. Comprehensive analysis of diffraction peaks intensity, profiles, width (B), angular positions was applied to evaluate texture, coherent scattering region size [12]. Changes of phase state on the surface were evaluated from XRD spectrum analysis.

2. EXPERIMENTAL RESULTS

The cycle of copper alloying consisted of two stages. During first stage the thin multilayer coatings was deposited on the surface by PVD method. The surface roughness is slightly increased after deposition of coatings (R_a < 0.2 μm, R_{max} ≈ 1.2 μm). At the second stage the coated samples were processed with hydrogen plasma streams in QSPA Kh-50 device.

Microscopy observations show that the morphology of the thin multilayer coatings imitates the initial relief of the substrate, and that the surface roughness almost does not change (Fig. 1).

As a result of plasma irradiation modified surface layer with essentially changed structure has been formed in all types of coatings. Origination of a melt layer does not accompanied by surface cracking. Formation of melted and further re-solidified layer cause observed changes of surface roughness after plasma exposure (Fig. 2). The weight loss measurements demonstrate negligible mass decrease under plasma exposures (decreases less than 100 μg). These mass losses are not caused by evaporation and may be the result of selective sputtering during the mixing of the coating with the bulk material. The roughness of exposed surfaces increased up to R_a ≈ 0.3 μm, R_{max} ≈ 2.1 μm (Fig. 3). The delamination of coatings was not observed.

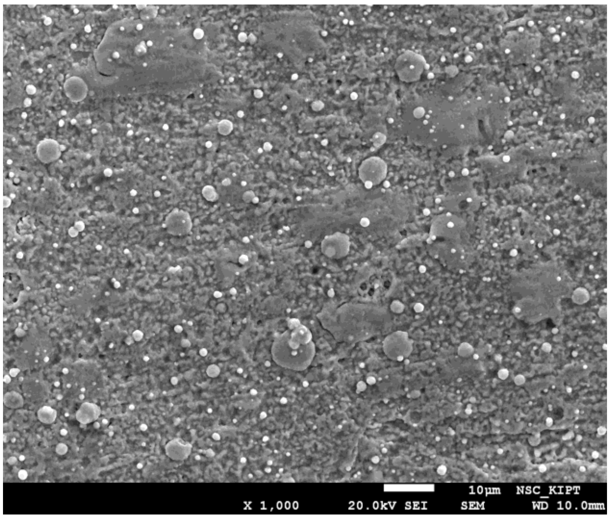

Fig. 1. SEM images of Ti-Cr-Ti-Zr coatings (without plasma exposure)

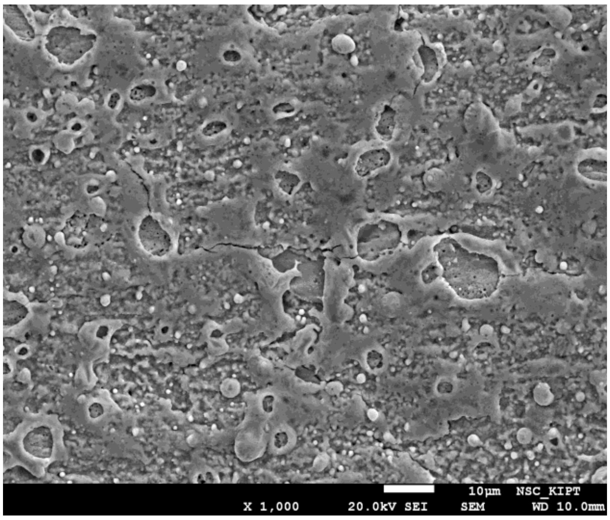

Fig. 2. SEM images of Ti-Cr-Ti-Zr coatings (irradiation with heat load of 0.6 MJ/m^2)

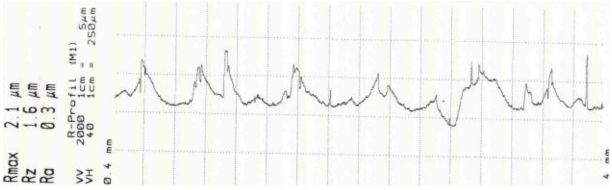

Fig. 3. Surface profile of Cu covered by Ti-Cr-Ti-Zr after QSPA plasma exposed (heat load of 0.6 MJ/m^2)

The typical XRD patterns of the different coatings are presented in Figs. 4, 5. Characteristic reflection peaks of materials of alloying additives and copper are easily identified.

The copper lattice parameter was 0.36152 nm before and after plasma irradiation (which is close reference value). This indicates that alloying elements are not present in the lattice in the form of a solid-solution. However, phases $CuCrO_4$, $CuZrO_4$ are observed on the XRD pattern. On diffraction pattern such phases were not observed before to plasma irradiation. Therefore, mixing of the coating materials with the copper substrate occurred with plasma exposure. Since the penetration depth of X-rays may exceed the modified layer thickness and diffraction peaks intensity in the studied range is almost extreme, the halo is not clearly identified in X-ray spectra.

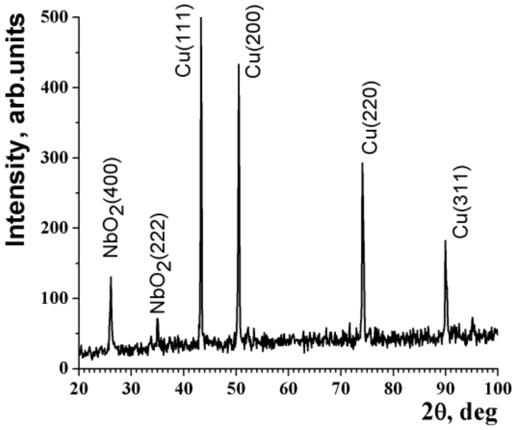

Fig. 4. Diffraction pattern of surface coated by Ti-Cr-NbO and exposed to after 5 QSPA plasma pulses of 0.6 MJ/m^2

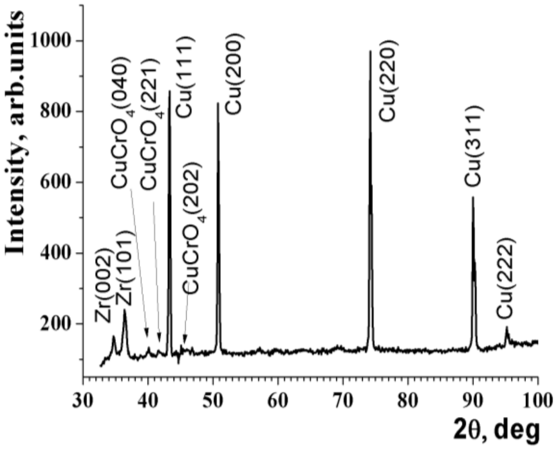

Fig. 5. Diffraction pattern of surface coated by Ti-Cr-Zr and exposed to after 5 QSPA plasma pulses of 0.6 MJ/m^2

The concentrations of material of coatings have been achieved several units wt% in surface layer up to 6 μm (Tables 1 and 2). At the same time, significant changes element content (wt %) are not observed before and after the plasma loads.

The possible way to improve coatings mixing is application of several cycles of plasma treatment. One cycle consist of two stages: 1 – deposition of thinner multilayer coating; 2 – the coated samples should be processed with pulsed plasma.

Table 1

Element content (wt %) of Cu-Ti-Cr-Zr

	Ti	**Cr**	**Zr**	**Cu**
Initial	2.925	2.006	7.058	88.011
Exposed	8.546	2.1	7.032	82.321

Table 2

Element content (wt %) of Cu-Ti-Cr-NbO

	Ti	**Cr**	**Nb**	**Cu**
Initial	7.9	2.575	7.39	82.135
Exposed	8.497	2.784	7.468	81.252

CONCLUSIONS

Experimental studies of surface modification of copper samples covered by different multilayer coatings (Ti-Cr, Ti-Cr-Ti-Nb, Ti-Cr-Ti-Zr, Ti-Cr-Ti-ZrO) have been performed with a quasi-stationary plasma accelerator QSPA Kh-50. Plasma heat load on the surface was about 0.6 MJ/m^2.

Surface modification and copper alloying due to the mixing of thin multilayer coatings with sample substrate under powerful plasma exposures is investigated. The surface morphology is developed mostly by melting and re-solidification processes in the course of plasma treatment. Delamination of coatings was not observed. As a result of plasma irradiation modified surface layer with essentially changed structure has been formed in all types of coatings.

The weight loss measurements demonstrate negligible mass decrease under plasma exposures (less than 100 μg). The concentrations of material of coatings have been achieved several percent by weight in surface layer up to 6 μm.

Obtained results showed the favorable influence of alloying additions (Cr-Zr, Cr-Nb) on behavior of Cu-based materials under the high heat loads.

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ОСОБЕННОСТИ МОДИФИКАЦИИ ПОВЕРХНОСТИ СПЛАВОВ НА ОСНОВЕ МЕДИ ПОД ВОЗДЕЙСТВИЕМ МОЩНОГО ПЛАЗМЕННОГО ОБЛУЧЕНИЯ

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Описаны особенности плазменного легирования материалов на медной основе с покрытиями Ti-Cr, Ti-Cr-Ti-Nb, Ti-Cr-Ti-Zr, Ti-Cr-Ti-ZrO в разных режимах КСПУ Х-50. Проанализировано влияние плазменных нагрузок на модификацию разных медных сплавов. Образцы были изготовлены из меди и многослойных покрытий, осажденных PVD-методом в установке булатного типа. Подготовленные мишени облучались мощными плазменными потоками с энергетическими нагрузками, достигавшими 0,6 МДж/м^2 , с длительностью импульса ~ 0,25 мс. Обсуждаются механизмы модификации тонких многослойных покрытий, смешанных с медной подложкой в жидкой фазе при плазменном облучении.

ОСОБЛИВОСТІ МОДИФІКАЦІЇ ПОВЕРХНІ СПЛАВІВ НА ОСНОВІ МІДІ ПІД ДІЄЮ ПОТУЖНОГО ПЛАЗМОВОГО ОПРОМІНЕННЯ

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Описано особливості плазмового легування матеріалів на основі міді з покриттями Ti-Cr, Ti-Cr-Ti-Nb, Ti-Cr-Ti-Zr, Ti-Cr-Ti-ZrO в різних режимах КСПП Х-50. Проаналізовано вплив плазмових навантажень на модифікацію різних мідних сплавів. Зразки було виготовлено з міді та багатошарових покриттів, які утворювались PVD-методом в установці булатного типу. Підготовлені мішені опромінювалися потужними плазмовими потоками з енергетичними навантаженнями, що досягали 0,6 МДж/м^2, з тривалістю імпульсу ~ 0,25 мс. Обговорюються механізми модифікації тонких багатошарових покриттів, змішаних з мідною підкладкою в рідкій фазі при плазмовому опроміненні.