Pulsed Electron-Beam Melting of Cu-Steel 316 System: Evolution of Chemical Composition and Properties[1]

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Abstract – The surface morphology, chemical composition, nanohardness, and tribological properties of a film (Cu)/substrate (stainless steel 316) system subjected to pulsed melting with a low-energy (20–30 keV) high-current electron beam (2–3 μs, 2–10 J/cm^2) have been investigated. The film was deposited by sputtering a Cu target in the Ag plasma of a microwave discharge. To prevent the local delamination of the film due to cratering, the substrates were repeatedly pre-irradiated with 8–10 J/cm^2. Single pulsed melting of this system results in the formation of a diffusion layer of thickness 120–170 nm near the interface, irrespective of the energy density. In contrast, an increase in number of pulses increases the thickness of this layer. For single irradiation, the nanohardness and the average wear rate of the surface layer of thickness 0.5–1 μm, including the molten film and the diffusion layer, non-monotonically vary with energy density, reaching, respectively, a maximum and a minimum in the range of 4.3–6.3 J/cm^2.

1. Introduction

Pulsed liquid-phase mixing of film/substrate systems with intense pulsed (10^{-8}–10^{-6} s) electron beams is an efficient method of surface modification of materials. In experiments on binary systems with components of various solubility it has been established that this method makes it possible to form, due to fast quenching from melt, metastable supersaturated solid solutions and amorphous and nanocrystalline structures, and to synthesize metal silicides and silicon carbide [1–5]. The attention was mainly given to the investigation of the structure and phase formation for binary systems, while the variation of the properties of the surface layers of structural alloys by their alloying from previously deposited coating was in fact with the development of sources of microsecond low-energy (20–30 keV) high-current electron beams (LEHCEB's) [4], prospects for successful use of the given method for modification of surface-sensitive properties of metallic materials have arisen. This paper describes the evolution of the surface morphology, chemical composition, nanohardness, and tribological properties of a Cu/stainless steel 316 system (Cu/SS316) subjected to pulsed electron-beam melting. This system is of interest because thin-layer copper coatings are used for wear protection of steels. Besides, alloying (to 3–5% Cu) of austenitic SS enhances their corrosion resistance in hydrochloric and sulfuric acids at high temperatures and resistance to the hydrogen action at high pressures and also improves the stability of austenite under intense deformations [6].

2. Experimental

Copper films have been deposited on substrates of 3 mm thickness made of austenitic SS 316 (Fe – 16.25 Cr – 10.15 Ni – 2.17 Mo– 1.63 Mn– 0.36 Cu – 0.69 Si – 0.045 C – 0.025 P – 0.013 S; wt.%). Film deposition was carried out using plasma reactor based on multipolar magnetic confinement, named as distributed electron cyclotron resonance plasma reactor [7]. The thickness of films was measured by optical interferometer and was equal to 512 ± 30 nm.

Pulsed electron melting of the Cu/SS316 system was carried out using an LEHCEB source described elsewhere [4]. The pulse duration was 2–3 μs; the energy density was varied in the range E_s = = 2–10 J/cm^2, allowing gradual transition from the initial melting mode of the Cu film to its appreciable mixing with the substrate. The number of pulses was N = 1–5. To prevent the surface cratering of samples to be treated, the substrates were irradiated, prior to film deposition.

[1] The work was supported by NATO (CLG) through Scientific Affairs Division and by CRDF Program BRHE (Project No. 016–02).

The surface morphology was examined using an AHIOVERT optical microscope and a Philips-SEM 515 EDAX scanning electron microscope (SEM). The surface roughness was measured using a Micromeasure 3D Station Profilometer (STIL, France). The chemical composition of the surface layer was determined by Auger electron spectroscopy (AES) and from EDS spectra recorded in the SEM. The thickness of the layer analyzed by EDS is 0.8 μm at accelerating voltage of 20 kV, and mapping area is 10×10 μm^2.

The mechanical properties were studied by nanoindentation using a Nano Indenter II (MTS Systems, USA) with diamond Berkovich indenter at peak load of 50 mN. Hardness was calculated according to [8, 9]. The pin-on-surface wear tests were carried out using a TAY-1M Tribometer with indenter made of WC-8 Co hard alloy (HRC 87.5) at following conditions: radius of indenter 2 mm, load 1 N, sliding speed 4 mm/s, sliding time 30 min.

3. Results and Discussion

3.1. Characteristics of melting and resolidification

According to calculations performed by the method described in Ref. [10], for bulk Cu and SS316 targets, the surface melting thresholds are attained at 5–5.5 and 2–2.5 J/cm^2, respectively, which is in a good agreement with experiment results. For a Cu (512 nm)/SS 316 system, the threshold of melting of the Cu film is attained at 2–2.5 J/cm^2, which also agrees with experiment. Figure 1 shows the depth dependence of the maximum temperature achieved at E_s = 2.8–8.4 J/cm^2. The time dependence of the position of the melt–solid interface for the same values of E_s is shown in Fig. 2. It can be seen that with increasing E_s the total thickness of the molten layer increases in range of 0.8–5 μm, and the lifetime of the molten substrate increases in range of 0.5–4 μs. As a result, the velocity of the resolidification front decreases from 8 to 4 m/s and the rate of cooling of the substrate in the solid phase decreases from $6.4 \cdot 10^8$ to $2 \cdot 10^8$ K/s.

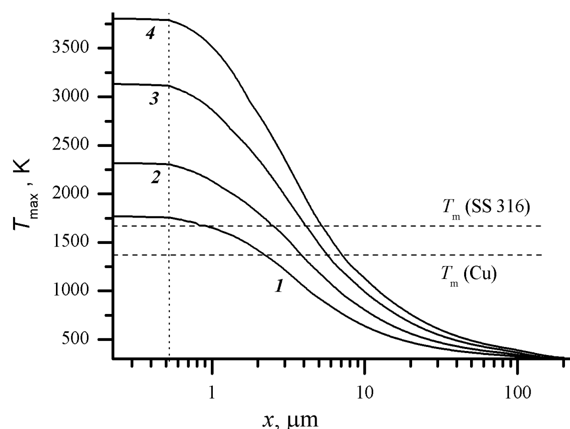

Fig. 1. Maximum temperature of irradiated Cu/SS 316 system vs depth: 2.8 (*1*), 4.3 (*2*), 6.3 (*3*) and 8.4 J/cm^2 (*4*). Vertical dotted line corresponds to thickness of Cu film

After resolidification of the substrate, the Cu film remains in the liquid state for 0.4–4.4 μs, depending on E_s (horizontal lines in Fig. 2), and then it solidifies as well. The comparatively long lifetime of Cu in the liquid state is due to the low thermal conductivity of SS 316. It should be noted that, according to calculations, notwithstanding the substantial overheating (see Fig. 1), the evaporation of Cu is negligible throughout the E_s range.

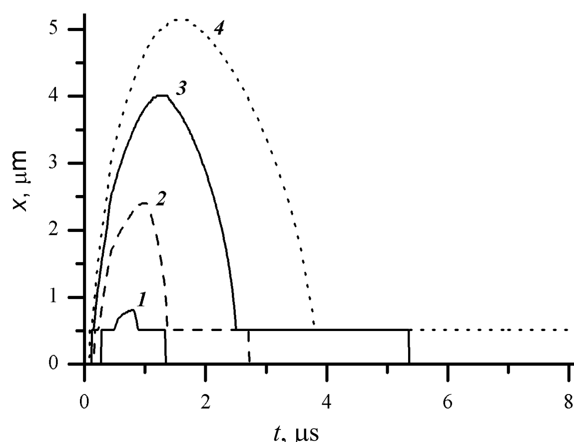

Fig. 2. Kinetics of displacement of melting front in Cu /SS316 system: 2.8 (*1*), 4.3 (*2*), 6.3 (*3*) and 8.4 J/cm^2 (*4*)

3.2. Surface morphology

Experiments have shown that when a Cu film was deposited on a previously polished substrate, the film was observed to exfoliate in separate sections during subsequent pulsed heating even at E_s lower than its threshold value for melting of the film (Fig. 3, *a*). An increase in E_s results in substantial smearing of these sections and in their merging to form extended regions of increased roughness. The local delamination of the film and its non-uniform mixing with the substrate upon irradiation is associated with the formation of microcraters on the film-substrate interface. It has been shown [11] that multiple pulsed melting of type SS 316 substantially reduces the probability of cratering due to the removal of impurities from the surface. In this connection, in all subsequent experiments the substrates were preliminary (before the deposition of a Cu film) irradiated with E_s = 8–10 J/cm^2 and N = 30. After this treatment, delamination of the film was practically not observed in range of E_s = 2.8–8.4 J/cm^2 (Fig. 3, *b*), testifying to a considerably enhanced adherence of the film.

The surface of an unirradiated Cu film has roughness R_a = 0.25–0.35 μm, which corresponds to the surface roughness of the substrate preliminary repeatedly irradiated with LEHCEB [11]. After single-pulse irradiation with E_s = 2.8–8.4 J/cm^2, the value of R_a remains practically unchanged, and this testifies to the dominant role of the surface morphology of the substrate before deposition of the coating.

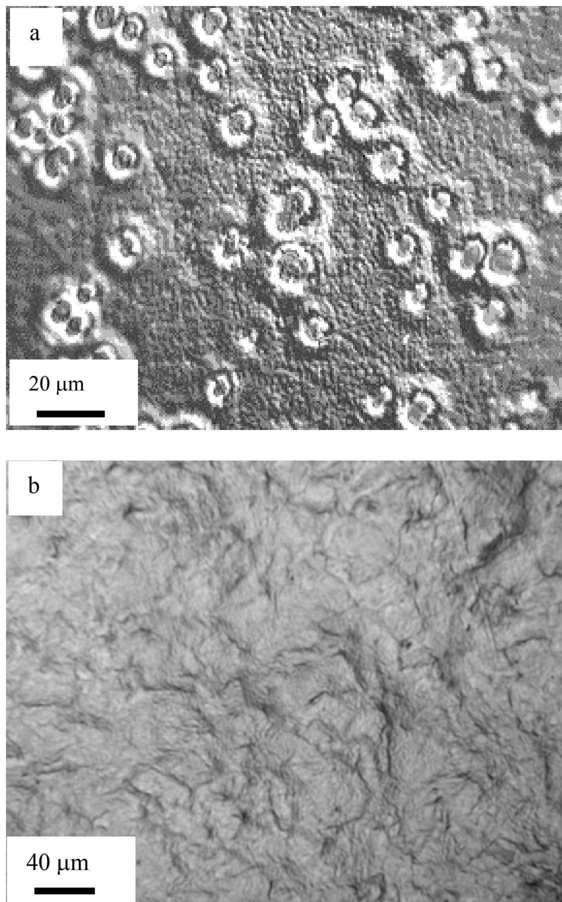

Fig. 3. Optical micrographs of the surface of irradited Cu/SS316 system: (*a*) 1.9 J/cm^2, $N = 1$; (*b*) 4.6 J/cm^2, $N = 2$. In case of (*b*) SS substrate was preirradiated at 8 ± 2 J/cm^2, $N = 30$

3.3. Chemical composition

According to AES data, the original Cu film contains impurities of C and O concentrated, mainly, in the near-surface (~ 250 nm) layer. Figure 4 presents typical concentration profiles for Cu/SS316 samples after single-pulse irradiation. It can be seen that the C and O impurities are removed and a diffusion transition layer is formed on the film–substrate interface. The depth of this layer is 120–170 nm and it weakly depends on the beam energy density. The given layer was formed as a result of liquid-phase mixing of the film and substrate components. Actually, assuming, in accordance with calculations (Fig. 2), that the characteristic time during which the film and the substrate exist simultaneously in the liquid state, $t_m \sim 10^{-6}$ s, and putting the liquid–phase diffusivity $D = 5 \cdot 10^{-5}$ cm^2/s, we obtain the thickness of the diffusion layer $d \sim (2Dt_m)^{1/2} \sim 100$ nm, which is in rather good agreement with experiment.

Since increasing E_s increases the thickness and lifetime of the molten substrate, the thickness of the diffusion layer should also increase. However, according to AES data, this is actually not the case. This can be related to the fact that an increase in thickness and lifetime of the molten substrate is accompanied by a slowdown of the process of its resolidification and by a decrease of the quenching rate from the liquid state. In this connection, it is highly probable that the Cu atoms dissolved in the liquid substrate will be pushed out from the growing crystal into the near-surface layers, restricting the concentration of Cu in the solid solution and, hence, the thickness of the mixed layer.

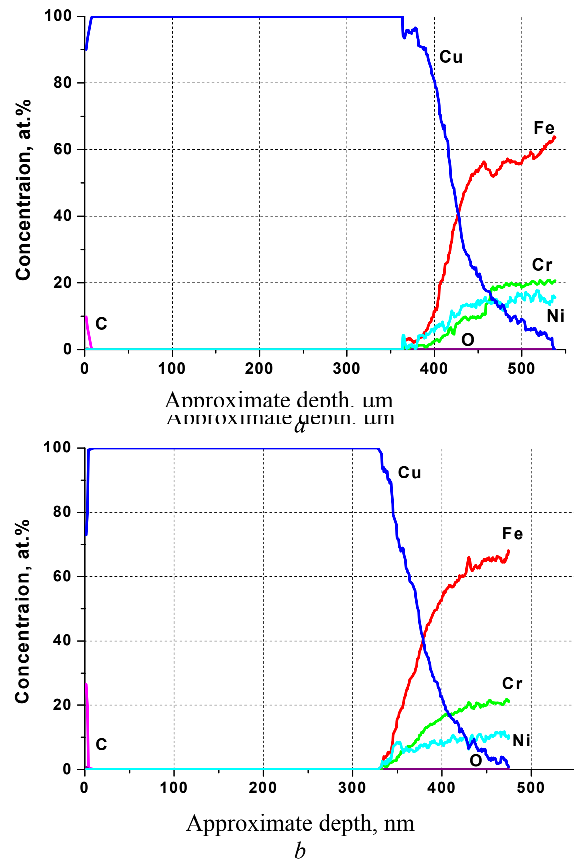

Fig. 4. AES profiles of elements of Cu/SS316 irradiated at 2.8 (*a*) and 6.3 J/cm^2 (*b*). $N = 1$

Multiple ($N = 5$) pulsed melting of the given system with $E_s = 5 \pm 1$ J/cm^2 results in increase the thickness of the diffusion layer and partial evaporation Cu-film. This is judged by the steel tincture appearing on the surface and is confirmed by EDS data (Table 1).

Table 1. Results of EDS examination of Cu/SS316 system

E_s, J/cm^2	N	Cu, at.%	Fe, at. %	Cr, at. %	Ni, at.%
–	–	74.03	18.21	5.03	2.73
6.3	1	73.52	18.48	5.26	2.74
4.6 ± 0.1	2	73.28	18.71	5.25	2.76
5 ± 1	5	37.31	45	11.52	6.17

3.4. Nanoindentation

Preliminary multiple pulsed melting of the substrate with the purpose of improving the adherence of a Cu film results in a loss of hardness of the near-surface layer of thickness more than 1 µm. It is related to the

buildup of residual tensile stresses in the heat-affected zone after irradiation [3]. Figure 5 shows the results of nanoindentation for a Cu/SS316 system as-deposited and after single-pulse irradiation with different E_s. It can be seen that the surface layers of thickness up to 400–600 nm, consisting preferentially of Cu, have a reduced hardness compared to the substrate. The rather small difference in hardness of the film and substrate demonstrated by these curves is due to the fact that the penetration depth of indenter is comparable to the thickness of the film.

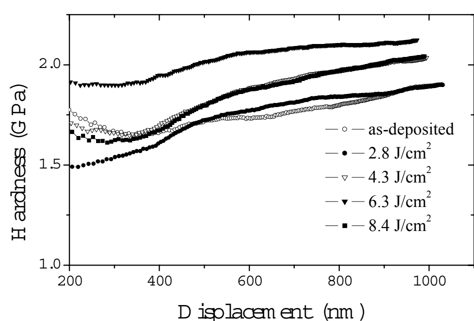

Fig. 5. Nanohardness profiles of Cu/SS316 system as-deposited and after pulsed melting ($N = 1$)

As also follows from Fig. 5, the dependence of the nanohardness of both the Cu film and the diffusion layer on E_s has a maximum at 6.3 J/cm^2. The maximum can be explained as follows. Increasing E_s increases the lifetime of the film in liquid state and decreases the rate of its quenching from melt. This results in an increase in grain size in the film and, hence, in a decrease of the contribution of grain size hardening. On the other hand, increasing E_s decreases the temperature gradients in the film at the stage of cooling. It promotes the lowering of the level of residual tensile stresses in the film and, hence, the decrease of the extent of its loss of strength. Thus, there exists a certain optimum value of E_s at which the hardness of the surface layer is a maximum.

3.4. Wear resistance

The substrate subjected to preliminary multiple irradiation is characterized by a high coefficient of friction ($\mu \sim 0.5$) and its large oscillations (Fig. 6, *a*). The maximum depth of the track of wear, determined by its width, was $h = 4.56$ μm at the end of testing (30 min). From calculations (Fig. 1, *b*) it follows that wear occurred in the layer quenched from melt.

After deposition of the Cu film, the coefficient of friction decreases more than twice, and its spread appreciably decreases (Fig. 6, *b*). This decrease in μ is accompanied by the decrease in h to 1.83 μm and, hence, the severalfold decrease in average rate of volumetric wear in comparison with SS 316. In this case, the track depth is a factor of ~ 3.5 greater than the thickness of as-deposited Cu film. Notwithstanding this, no signs of wear of the substrate (SS316) were detected on the surface of the track. It confirms the dominant role of the Cu film in the improvement of the wear behavior of the friction pair.

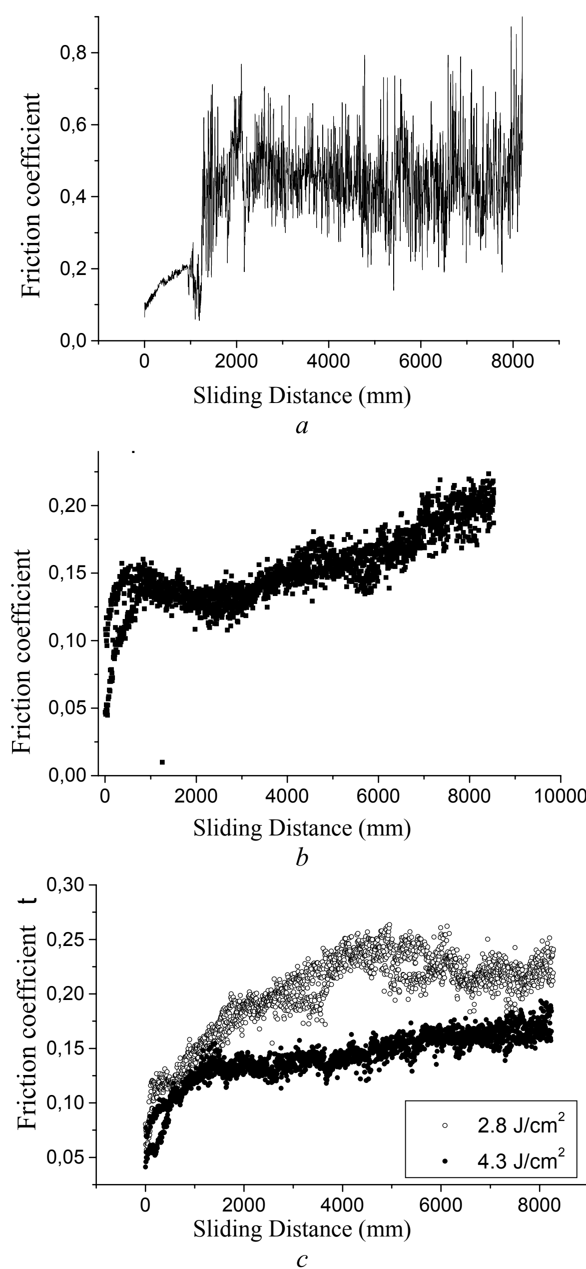

Fig. 6. Friction coefficient vs sliding distance: (*a*) SS316 substrate irradiated at 8 ± 2 J/cm^2, $N = 30$; (*b*) Cu/SS316 as-deposited; (*c*) Cu/SS316 after pulsed melting at 2.8 and 4.3 J/cm^2 ($N = 1$)

Typical dependences of the coefficient of friction on the sliding distance for a Cu/SS316 system subjected to single pulsed melting for two E_s values are shown in Fig. 6, *c*. Analysis of similar data has shown that the minimum average value of the coefficient of friction corresponds to 4.3 J/cm^2, and this is demonstrated in part by Fig. 6, *c*.

Figure 7 shows how the depth of the track of wear corresponding to the end of testing varies with E_s. It

can be seen that this plot has a minimum at 4.3 J/cm^2 at which the track depth is about half that in the as-deposited state. This plot characterizes the dependence of the average wear rate of the surface layer of thickness up to ~2 μm on the pulsed heating mode. It qualitatively agrees, first, with the behavior of the average coefficient of friction depending on E_s and, second, with the results of nanoindentation (Fig. 5).

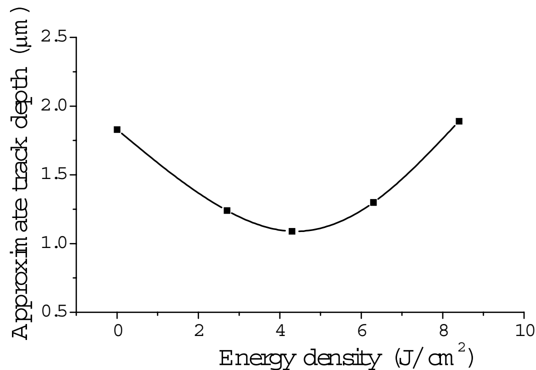

Fig. 7. Wear track depth of Cu/SS316 system vs energy density

The latter allows the conclusion that the improvement in wear behavior is associated, mainly, with the hardening of the surface layer of thickness 0.5–1 μm that is achieved under certain optimum conditions of quenching from the liquid state.

4. Conclusion

1. With a Cu/SS316 system used as an example, it has been shown that pretreatment of the substrate with LEHCEB prevents its local delamination on pulsed melting and, hence, improves the adherence of the film.

2. Single pulsed melting of this system results in the formation of a diffusion layer of thickness 120–170 nm near the interface, irrespective of the energy density in range of 2.8–8.4 J/cm^2. An increase in number of pulses results in increase in thickness of the diffusion layer.

3. For single pulsed melting in the surface layer of thickness 0.5–1 μm, including the Cu film and the diffusion layer, the nanohardness and the average wear rate non-monotonically vary with energy density, reaching, respectively, a maximum and a minimum in the range 4.3–6.3 J/cm^2. The improvement of the properties can be related to the hardening of this layer due to its fast quenching from the liquid state.

Acknowledgements

The authors thank D.I. Proskurovsky and S.F. Gnyusov for fruitful discussions.

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