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Effect of laser irradiation on structure and properties of composite coatings

It is shown that the laser radiation is much «mixes» coating Cr–Mn–Si–Cu–Fe–Al with the near-surface layers of the basics, like changing the structure of the coating and its elemental composition at different points of the sample. From the XPS analysis that the content of coating element deviates from the average content of the coating prior to laser irradiation, but they occur at specific points in the coagulation of the sample. Occurrence coagulates can be associated with diffusion processes coating transfer elements (diffusion rate is usually small in this case), and hydrodynamic processes under the influence of laser shock waves in the liquid phase of the coating. To coating the Cr–Mn–Si–Cu–Fe–Al+Ti in an argon environment friction coefficient decreases after laser processing, and micro-hardness increases. The first effect is associated with a decrease in roughness of the coating when the laser beam reflow. The second effect is due to the formation of the dislocation structure of the coating with a sharp heating-cooling. When coating Cr–Mn–Si–Cu–Fe–Al+Ti in a nitrogen environment are formed in the last field containing chromium and titanium nitrides, and XPS data on the contents of the two components is approximately the same.

Key words: laser radiation, the coating composition, the X-ray elemental analysis, the structure, microhardness, friction surface layer.

Introduction

In recent years, increased interest of researchers to synthesize multi-element vacuum coating methods [1–10]. This is due to the fact that such compositions virtually impossible to obtain by conventional metallurgy techniques.

Modifying the properties of materials by laser radiation on the physical essence boils down to the local thermal effect. Therefore, it is determined by thermal parameters of the material, the power density and the time of radiation exposure are generally specific amount of energy absorbed by the material and the rate of its dissipation.

This paper presents the experimental results of laser irradiation on the properties of composite coatings.

Experimental technique

In this paper we used the cathodes Cr-Mn-Si-Cu-Fe-Al, obtained by the method of induction melting, and titanium cathodes brand BT-1-00 GOST 1908. The coatings were applied to a steel substrate by ion-plasma method to install HHB-6.6I1 while sputtering cathodes mentioned above. A quantitative analysis of the elemental composition of composite cathodes and coating was carried out on JEOL JSM-5910 electron microscope. A study of microhardness of composite coatings was carried out on the Hardness HVS-1000A. The microstructure of the coatings was determined by metallographic microscope Epikvant. Coatings were deposited in argon and nitrogen. As the laser radiation source used in the YAG doped with neodymium λ = 1064 nm. The duration of the flash of the laser pump lamps operating in free-running mode, was 2 10^{-3} s. The energy of the laser pulse was 1 J and before the experiment was measured using IMO-2N, the laser pulse repetition rate was adjusted from 0.1 to 35 Hz.

Experiment results

Figure 1 shows the microstructure of the coating Cr-Mn-Si-Cu-Fe-Al, and Figure 2 — XPS before laser irradiation (tables 1, 2).

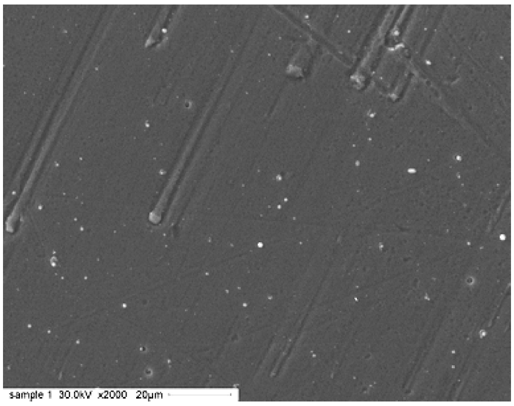

Figure 1. Electron microscope image of a coating
Cr-Mn-Si-Cu-Fe-Al before irradiation

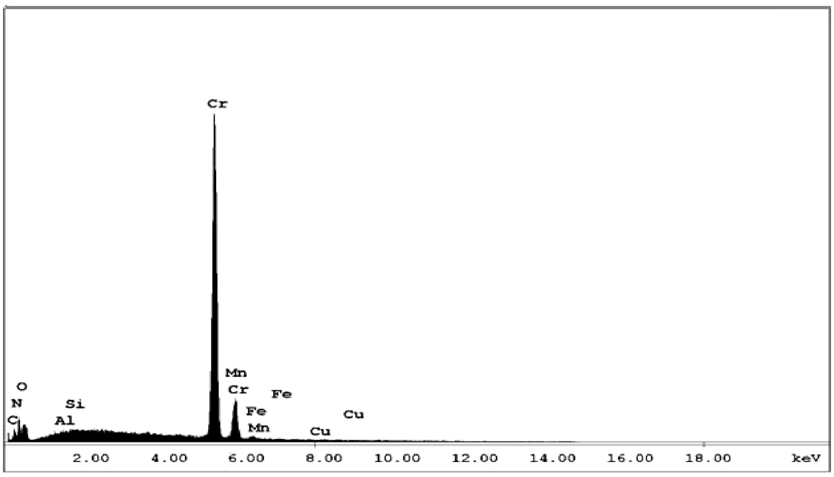

Figure 2. XPS coating Cr-Mn-Si-Cu-Fe-Al

Table 1

Elemental coating composition Cr-Mn-Si-Cu-Fe-Al

Element	Wt %	At %	K- Ratio	Z	A	F
N	2.89	8.88	0.0151	1.1767	0.4433	1.0024
O	5.72	15.38	0.0387	1.1656	0.5765	1.0057
Al	0.17	0.27	0.0010	1.0846	0.5532	1.0010
Si	0.29	0.45	0.0022	1.1226	0.6748	1.0020
Cr	89.08	73.67	0.8754	0.9802	1.0010	1.0015
Mn	0.00	0.00	0.0000	0.9619	1.0029	1.0004
Fe	1.26	0.97	0.0115	0.9794	0.9295	1.0003
Cu	0.58	0.39	0.0053	0.9445	0.9680	1.000
Total	100.00	100.00				

Table 2

Phase composition of the coating Cr-Mn-Si-Cu-Fe-Al in nitrogen atmosphere

Sample	Phase detection	Phase Content, %	The lattice parameters, Å	The size of the AKR, nm	$\Delta d/d*10^{-3}$
Cr-Mn-Si-Cu-Fe-Al in nitrogen atmosphere	$FeN_{0.0324}$	60,6	a = 3,598	103,37	3,460
	$TiN_{0.31}O_{0.31}$	39,4	a = 4,211	25,600	5,143

Figure 3 shows the microstructure of the coating Cr-Mn-Si-Cu-Fe-Al after laser irradiation, Figure 4 — its mapping, and Figure 5 — XPS.

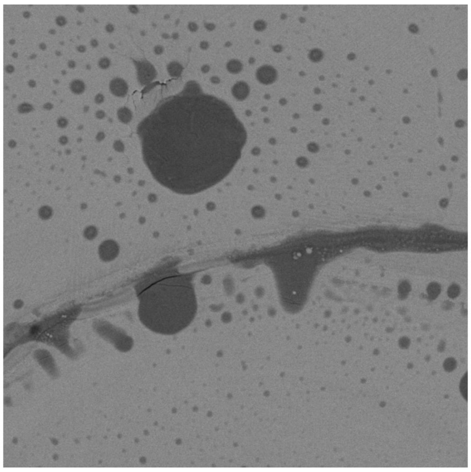

Figure 3. Electron microscope image of a coating Cr-Mn-Si-Cu-Fe-Al after laser irradiation

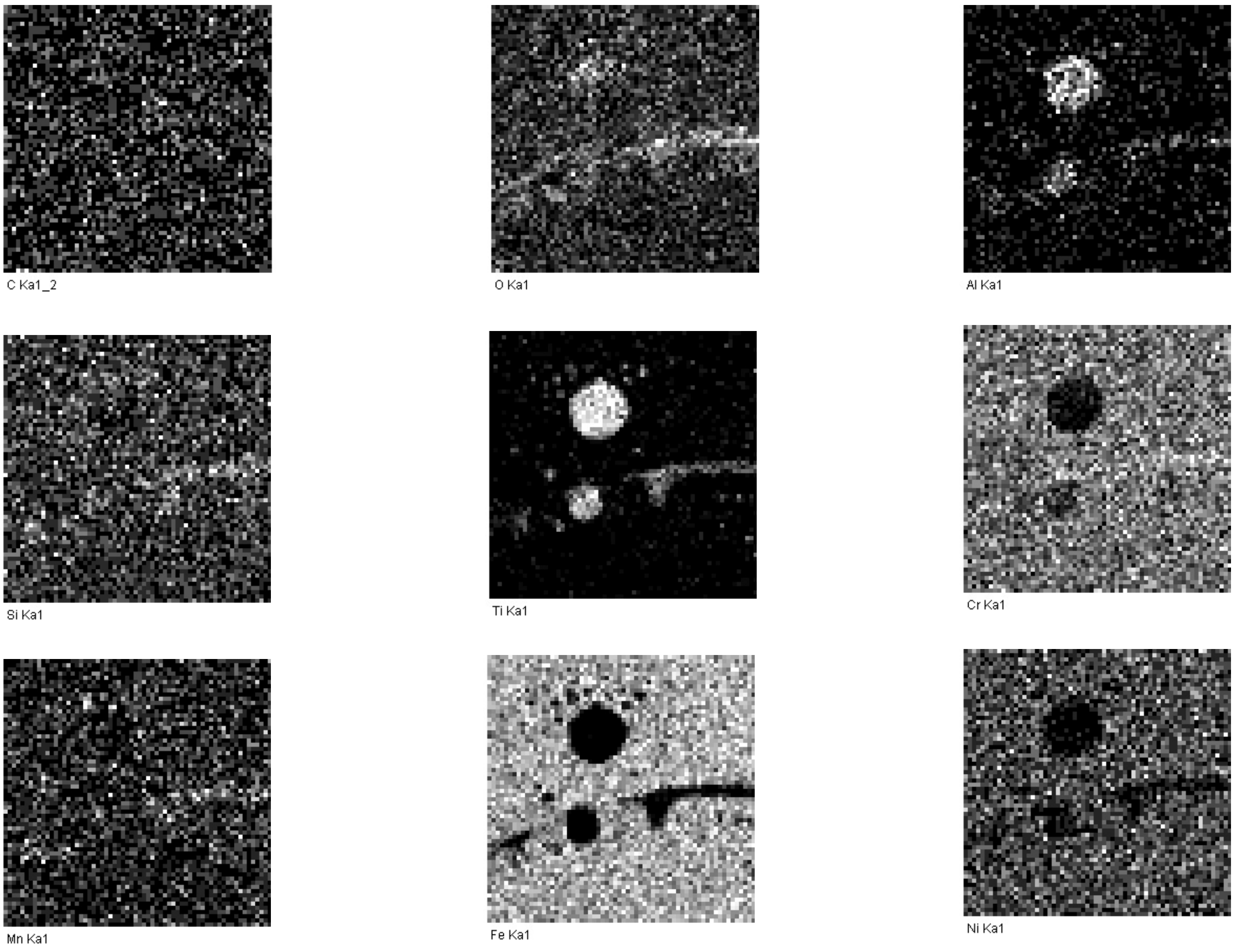

Figure 4. Mapping of electron-microscopic images coating Cr-Mn-Si-Cu-Fe-Al after laser irradiation

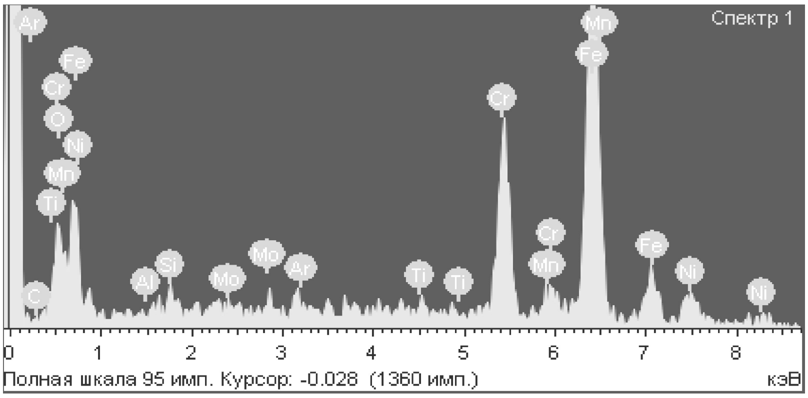

Figure 5. XPS coating Cr-Mn-Si-Cu-Fe-Al after laser irradiation

Tables 3 -5 coating elemental composition represented Cr-Mn-Si-Cu-Fe-Al after laser irradiation at different points in the specimen.

Table 3

Elemental composition of the coating Cr-Mn-Si-Cu-Fe-Al after laser irradiation

Element	Wt, %	At, %
C K	16.41	47.52
O K	0.00	0.00
Al K	0.00	0.00
Si K	0.00	0.00
Ar K	0.00	0.00
Ti K	0.00	0.00
Cr K	16.09	10.76
Mn K	0.00	0.00
Fe K	57.21	35.62
Ni K	10.29	6.10
Zn K	0.00	0.00
Mo L	0.00	0.00
Итоги	100.00	

Table 4

Elemental composition of the coating Cr-Mn-Si-Cu-Fe-Al after laser irradiation

Element	Wt, %	At, %
C K	9.96	19.39
O K	35.92	52.51
Al K	5.51	77
Si K	0.00	0.00
Ar K	0.00	0.00
Ti K	39.62	19.35
Cr K	5.78	2.60
Mn K	3.22	1.37
Fe K	0.00	0.00
Ni K	0.00	0.00
Zn K	0.00	0.00
Mo L	0.00	0.00
Итоги	100.00	

Table 5

Elemental composition of the coating Cr-Mn-Si-Cu-Fe-Al after laser irradiation

Element	Wt, %	At, %
C K	197	27.95
O K	32.99	46.25
Al K	44	3.69
Si K	1.81	1.44
Ar K	0.00	0.00
Ti K	28.68	13.43
Cr K	10.15	38
Mn K	6.97	2.84
Fe K	0.00	0.00
Ni K	0.00	0.00
Zn K	0.00	0.00
Mo L	0.00	0.00
Итоги	100.00	

Discussion of the experimental results

From the experimental data that the laser radiation is much «mixes» with near-surface layers of coating bases, changing as the structure of the coating and its elemental composition at different points of the sample.

From the data it follows that the content of elements in the coating is different from the average content of the coating prior to laser irradiation, but they occur at specific points in the coagulation of the sample. This is clearly seen from Figures 1, 3 and 4.

If one is visible in Figure phase finely dispersed nitrides of titanium and iron, the Figure 3 shows the appearance of coagulates. The latter can be associated with diffusion processes coating transfer elements (diffusion rate is usually small in this case), and hydrodynamic processes under the influence of laser shock waves in the liquid phase of the coating.

The physics of the processes involving laser shock waves quite worked out, although there are some difficulties in the interpretation of the whole variety of phenomena arising in this case.

The action of the laser radiation with an intensity below the threshold of molten splash, then melted or heated sample flow layer different structural and phase transformations. Under the influence of a single laser pulse duration τ warms the layer thickness of the order $\tau\chi^{1/2}$, where χ — thermal diffusivity.

If the thickness of the sample is much larger than the thickness of this layer is due to the thermal conductivity of a rapid cooling and cooling rate characteristic for structural steels reaches values of the order of $10^3/\tau$ K/ s. This means that when using lasers with pulse duration of 10^{-6}–10^{-8} s. Cooling rates are 10^9-10^{11} K/s. At these speeds, you may experience the metastable phases, ultrafine crystalline. This is clearly evident from the Figures 6 and 7.

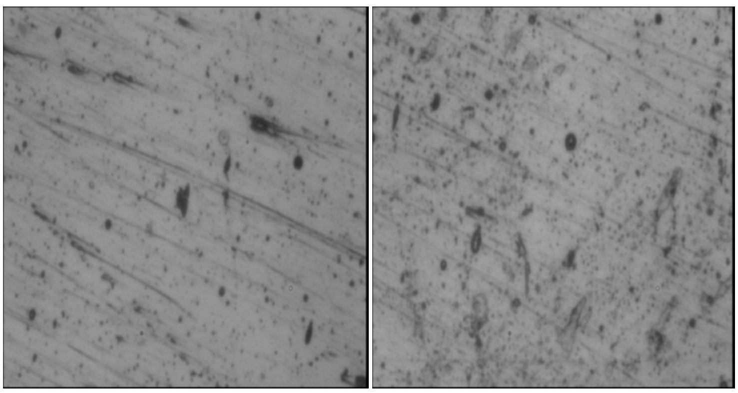

Figure 6. Optical coating microstructure
Cr-Mn-Si-Cu-Fe-Al prior to laser irradiation

The essence of laser hardening iron-carbon steels, as well as conventional hardening methods is diffusionless transformation during rapid cooling of face-centered cubic austenite lattice in a distorted bodycentered lattice of martensite. A characteristic feature is its high martensite hardness on the one hand, and low plasticity and brittleness, on the other hand. In this case, as can be seen from the XPS data, the studied coating contain carbon, despite the high content of iron.

Tempering of non-ferrous metals are not associated with phase transitions in the bulk material, due to the «correct» distortions metal structures encountered during their solidification. Therefore, in this case, the effect of laser radiation on the properties of composite coatings, which are based on aluminum, is not as trivial as it may seem at first glance. To this we must add the nanostructured state investigated coatings, thermal properties that are significantly different from the bulk properties of the substance.

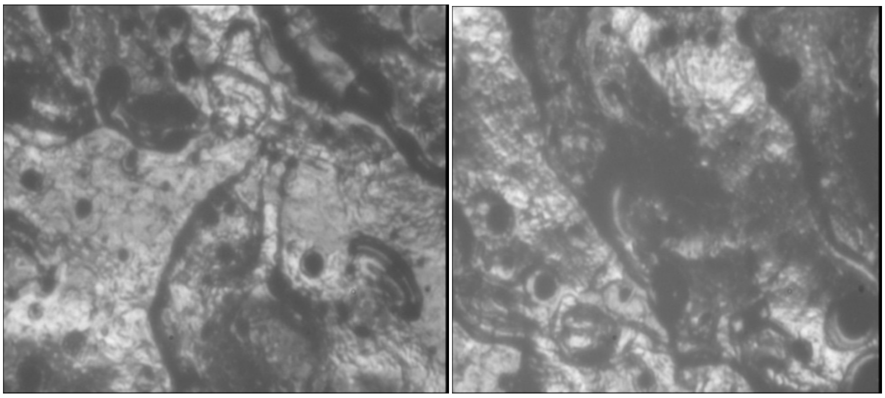

Figure 7. Optical coating microstructure Cr-Mn-Si-Cu-Fe-Al
after laser irradiation

After the laser treatment the coating Cr-Mn-Si-Cu-Fe-Al + Ti, prepared in a nitrogen atmosphere, the friction coefficient varies slightly, and decreases the microhardness of more than 2 times.

When coating Cr-Mn-Si-Cu-Fe-Al + Ti in a nitrogen environment are formed in the last field containing chromium and titanium nitrides, and XPS data on the contents of the two components is approximately the same. The particle size of titanium nitride and chromium by electron microscopy is (100–150) nm. Microcrystallites titanium nitride and chromium are preferred orientation (presumably in the direction (200)), which is different from a spherical symmetry microcrystallites pure titanium. These, along with cellular coverage structure, it leads to a high microhardness.

After the laser treatment the coating Cr-Mn-Si-Cu-Fe-Al + Ti, resulting in reduced nitrogen microhardness of more than 2 times. This means that in this case we are not dealing with a hardening coating and its release as it is observed in hardened steels at high temperatures.

However, the mechanism of softening in this case differs from the release mechanism of steel, where the last phase transition is caused by martensite → austenite. One of the probable reasons for softening coating Cr-Mn-Si-Cu-Fe-Al + Ti, resulting in a nitrogen atmosphere, a coagulation of micro-crystallites of titanium and chromium, can be clearly seen in Figure 7, and occurring when the melt cools after laser irradiation. A similar effect was observed by doping titanium with oxygen-free metal smelting. At the same time the inclusion of titanium nitrides significantly degrade the casting properties. Another reason for the weakening could be the fact that at high temperature, which is achieved by laser irradiation, titanium nitride and chromium «corroded» iron oxides. iron oxide formation can occur either due to its significant content of the coating, and due to the fact that laser irradiation was performed in air.

Conclusion

Coatings formed Cr-Mn-Si-Cu-Fe-Al, to form an infinite substrate and solid solutions are characterized by high porosity and poor denseness. Transition layer formed of these metals and the substrate, after laser exposure, remains virtually unchanged.

Preliminary tests have shown promising industrial use coating formed Cr-Mn-Si-Cu-Fe-Al + Ti in a nitrogen ion plasma technique with subsequent laser processing.

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Құрылым мен композициялық жабындылардың қасиеттеріне лазерлік сәулелендірудің әсері

Мақалада лазерлік сәуле үлгідегі түрлі нүктелерінде жабыны құрылымын және оның элементтік құрамын өзгерту сияқты негіздері жуық беткі қабатымен қаптамасында Cr–Mn–Si–Cu–Fe–Al «қоспаларының» көп екені көрсетілген. РФЭС талдауынан жабынды элементтерінің мазмұны жалпы лазерлік сәулеленуге дейінгі жабынды мазмұнынан өзгешелігі жоқ, бірақ олардың ұюы нақты нүктелер үлгілерінде орындалады. Диффузиялық жабындысы сұйық фазада лазерлік соққы толқындар әсерінен жабындыны аудару элементтерінен (диффузия жылдамдығы бұл жағдайда, әдетте, аз), және гидродинамикалық процестердің қоюлануының туындауына байланысты болуы мүмкін. Cr–Mn–Si–Cu–Fe–Al+Ti жабындысы үшін аргон қоршаған ортасында үйкеліс коэффициенті лазерлік өңдеуден кейін азаяды, және микроқаттылығы артады. Алғашқы әсері оның лазер сәулесімен балқыту кезіндегі жабынды бұдырының азаюымен байланысты. Екінші әсері күрт қыздыру-салқындату кезіндегі жабынды дислокациялық құрылымының қалыптасуына байланысты. Cr–Mn–Si–Cu–Fe–Al+Ti жабынды жағу кезінде азот ортасында хром және титан нитридтерін қамтитын соңғы саласында қалыптасады, және РФЭС екі компонент мазмұнында шамамен бірдей.

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Влияние лазерного облучения на структуру и свойства композиционных покрытий

Лазерное излучение значительно «перемешивает» покрытие Cr–Mn–Si–Cu–Fe–Al с приповерхностными слоями основы, изменяя как структуру покрытия, так и его элементный состав в различных точках образца. Из РФЭС-анализа следует, что содержание элементов покрытия в среднем не отличается от содержания их в покрытии до лазерного облучения, но происходит их коагуляция в определенных точках образца. Возникновение коагулятов можно связать не с диффузионными процессами переноса элементов покрытия (скорости диффузии обычно в этом случае малы), а с гидродинамическими процессами под воздействием лазерных ударных волн в жидкой фазе покрытия. Для покрытия Cr–Mn–Si–Cu–Fe–Al+Ti в среде аргона коэффициент трения после лазерной обработки уменьшается, а микротвердость возрастает. Первый эффект связывается с уменьшением шероховатости покрытия при его оплавлении лазерным лучом. Второй эффект обусловлен формированием дислокационной структуры покрытия при резком нагреве–охлаждении. При нанесении покрытий Cr–Mn–Si–Cu–Fe–Al+Ti в среде азота в последнем формируются области, содержащие нитриды титана и хрома, причем по данным РФЭС содержание обеих компонент примерно одинаково.