Functional Materials 12, No.1 (2005)

Structure formation and wear resistance of TiN–Ni ESA coatings after solar irradiation treatment

A.V.Paustovsky, G.A.Frolov, I.I.Timofeyeva, V.I.Novikova, V.S.Tsyganenko, N.M.Mordovets, A.D.Kostenko, L.P.Isayeva

I.Frantsevich Institute for Problems of Material Science,
National Academy of Sciences of Ukraine,
3 Krzizhanovsky St., 03680 Kyiv, Ukraine

Received December 10, 2004

It has been shown that the emitting ability of TiN electric spark coatings increases in 1.5 time after treatment by concentrated solar irradiation. This is effective for the use in friction pairs of mechanisms in outer space. The concentrated solar energy treatment of TiN–Ni spark coatings increases in 2–3 times the wear resistance due to oxide phase formation in the alloyed layer. The structure of steel 45 changes in the area of concentrated solar radiation action from the ferrite-pearlite to troostite with grain refining and hardness increase. The spark coating of 60 %TiN + 40 %Ni has been found to have optimum frictional and physical-mechanical properties.

Показано, что в электроискровых покрытиях из TiN при добавлении Ni после обработки концентрированным солнечным излучением излучательная способность увеличивается в 1,5 раза, что эффективно при использовании в узлах трения механизмов в космическом пространстве. Применение концентрированной солнечной энергии для обработки ЭИЛ-покрытий из TiN–Ni повышает износостойкость покрытий в 2–3 раза вследствие образования оксидной фазы в легированном слое. В стали 45 в зоне воздействия концентрированной солнечной энергии происходят структурные изменения от феррито-перлита до троостита с измельчением зерна и повышением твердости. Установлено, что оптимальными триботехническими и физико-механическими свойствами и излучательной способностью обладает электроискровое покрытие из материала 60 %TiN + 40 %Ni.

The use and saving of new energy sources becomes more vital every year. Electric spark alloying (ESA) and surface treatment by concentrated solar irradiation (CSI) belong to the new energy-saving methods of hardening technologies. During ESA, a discrete discharge pulse provides formation of a protective layer with changed structure of different thickness, continuousness and roughness on the workpiece surface [1]. To improve the surface quality, additional treatment of ESA coatings with concentrated solar radiation is advisable. This allows to decrease the porosity, cure the microcracks and improve the adhesion. The advantages of CSI method consist in non-contact heating in any medium, in vacuum, pollution-free heating and the possibility to regulate widely the input energy [2, 3].

Titanium nitride is a promising material for wear-resistant coatings [4]. To reduce the fragility and increase the transport factor, ductile nickel should be introduced in the production course of titaniumium nitride electrodes. The structure and hardness of the surface layer after ESA with TiN–Ni system materials is studied in [5], where the following characteristics of ESA process are considered: cathode mass overweight, anode erosion, transport factor. The aim of

this work is to study the concentrated solar radiation influence on some physical-mechanical properties of electric spark coatings of TiN–Ni materials: hardness, thickness, wear resistance.

Steels of 45 and U8 grades were coated by electric-spark alloying using electrodes made of TiN + (1–100) % Ni. The admixture to the titanium nitride was chosen with regard to the fact that nickel forms a continuous series of solid solutions with iron (the main element of the substrate material) and promotes good adhesion of coating material to steel. The ESA was carried out in an EFI-46A unit at I = 1.5 A, C = 300 μF. The CSI treatment of the surface was made in SGU-2 unit being a mirror solar energy concentrator provided with a sun tracking system. The radiant heat flux was regulated by shutters and was in the range of 3000 to 4000 kW/m^2.

The friction tests were carried out in a MT-65) unit at the slip velocity of V = 10 m/s and load P = 5 kg/m^2 in the "bush-in-shaft" scheme in the open air, according to the procedure described in [5]. In the course of experiment, the friction force was registered wherefrom the friction of the movable joint (f) and the linear wear of the friction pair were calculated. The linear wear allows to evaluate the wear intensity of the sample (I), μm/km. The X-ray phase analysis of CSI-treated samples was carried out using a DRON-3M unit in Cu–K_α radiation. The metallographic analysis of electric-spark coatings and steel was carried out by means of optical microscope MIM-9. During the experiment in SGU-2, the temperature was controlled with chromel-alumel thermocouples fixed on the backsides of the samples; it did not exceed 400°C. As the coated samples were made of the same material and all had the same size of 10×10 mm^2, it was possible to evaluate the surface radiant emittance basing on the sample temperature increase intensity at the same density of input heat flux.

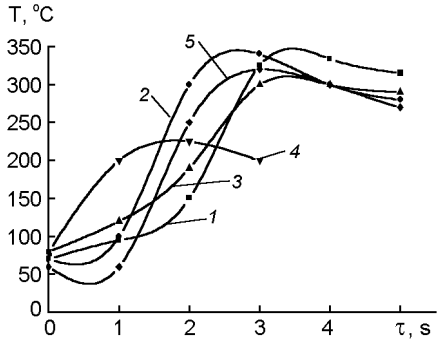

Fig. 1. The heating temperature T,°C, as a function of the treatment time τ, s, for spark coatings of TiN–Cr system:

80 %TiN + 20 %Ni (*1*); 60 %TiN + 40 %Ni (*2*); 90 %TiN + 10 % Ni (*3*); TiN (*4*); Ni (*5*).

It is known that the radiant emittance coefficient (or emissivity) of a surface may change essentially in accordance with the composition and physical nature of the coating material [7]. The higher the emissivity is, the higher is the temperature of the heated surface and the higher the temperature increase intensity on the sample backside. In this work, the dependences of the sample heating temperature T (°C) on the CSI treatment duration (τ, s) have been obtained. The heating curves of the composites under consideration show that even

Table 1. The results of steel and coatings phase analysis after ESA and ESA+CSI

Electrode material composition, %	X-ray phase analysis of the surfaces	
	ESA	ESA + CSI
TiN	TiN, Fe, Fe_2Ti, TiO_2	TiN, Fe, Fe_2O_3, Fe_2Ti^*, TiO_2
90TiN + 10Ni	TiN, TiO_2^*, α–Fe, FeTi, $FeNi^*$, $TiNi^*$, Ni(Fe)	TiN, TiO_2, α-Fe, $Fe_2Ti_3O_9$, Ni(Fe), Ti–Ni–O*
80TiN + 20Ni	TiN, FeTi, Ni^*, Fe^*, $TiNi^*$	TiN, TiO_2, Ni^*, Fe, $NiTiO_3^{**}$, $Fe_{0.43}Ni_{0.53}O_4$, Ti_4Fe_3O
60TiN + 40Ni	TiN, $FeNi^{**}$, TiO_2, Ni^*, Fe, $TiNi_3^*$, $NiTiO_3$	TiN, Ni^*, Fe^*, TiO_2, $FeNi^*$, $Fe_{2.43}Ni_{0.53}O_4$, $NiTiO_3^{**}$, NiO, $FeTiO_3^*$, Fe_2O_3
Ni	Ni(Fe), Ni, Fe^*, FeNi, Fe_2O_3, $Fe_{2.43}Ni_{0.53}O_4$	Ni(Fe), Ni, α-Fe, NiO, α-Fe_2O_3; $Fe_{2.43}Ni_{0.53}O_4$

Note: * traces, ** a large amount.

small quantities of Ni (~10 %) addition increase appreciably the emissivity of the surface compared to the pure titanium nitride coatings (Fig. 1, curves 1–5). The results shown in Fig. 1 let us conclude that TiN coatings with 10 to 40 % Ni were treated at nearly similar heating temperatures of the studied surfaces. The emissivity coefficient values of the coating surface increase due to the introduction of nickel into titanium nitride. The emissivity for TiN–(20–40) % Ni coatings increased by a factor of 1.5 as compared to TiN coating.

The results of the X-ray phase analysis (XPA) of ESA coatings and CSI-treated ESA coatings are shown in Table 1. The studied coatings are polyphase systems formed due to interaction between the elements of steel substintensity material and those of electrode materials and oxygen: solid solutions, intermetallides, and oxides. It is seen from Table 1 that in all compositions of TiN–Ni system coatings, there are the following phases: TiN (the major phase), intermetallides $TiNi_3$, Fe_2Ti, FeNi, simple and complex oxides — Fe_2O_3, Ti_4Fe_3O, $Fe_{2.43}Ni_{0.53}O_4$; solid solution Ni(Fe) (Table 1). Solid solution Ni(Fe) is rvealed in the diffraction patterns of TiN + (10–20 %)Ni ESA coatings and the same coatings treated by CSI. It is noted that after the sun treatment of the studied surfaces, the amount of the dissolved metal (iron) in the solid solution of nickel increases; this means that the diffusion process is more intense. It is found that when CSI is applied to the ESA coatings under consideration, the amounts of solid solution and intermetallide phases reduce while that of the oxide phase increases.

The metallographic examination of the coatings obtained after ESA and CSI showed that the alloyed layer thickness at low content of (10–40) % Ni binder remained almost unchanged (Table 2, Fig. 2, 3). However, for ESA coatings of 20 % TiN + 80 % Ni material and pure nickel, the hardened layer thickness increases by 5 times as compared to TiN coatings (Fig. 1). The alloyed layer microhardness for TiN coating with (1–10) % Ni decreases sligutly after CSI treatment (by a factor of about 1.1) (Table 2). As the nickel content in the coating increases from 20 % to 40 %, the layer microhardness increases 1.2 time after CSI treating (Table 2). When nickel content in the material composition of electrode mate-

Table 2. Physico-mechanical and durometric properties of steel and coatings

Electrode material composition, %	The alloyed layer thickness after ESA, μm	The alloyed layer thickness after ESA+CSI, μm	The alloyed layer continuousness	The microhardness of the alloyed layers and the steel, H_μ, GPa			Steel structure
				ESA	ESA+CSI	The thermal zone of the steel after ESA+CSI	
TiN	10	10	35	1.7	1.5	0.4–0.6 0.18	Troostite Pearlite
90TiN + 10Ni	15	15	50	1.4	1.5	0.7–0.4 0.3–0.2	Troostite Ferrite + pearlite
80TiN+20Ni	40	40	50	0.8	1.0	0.8–0.4 0.23	Troostite with martensite areas Ferrite + pearlite
60TiN + 40Ni	50	50	80	1.1	1.2	0.65 0.23	Troostite Ferrite + pearlite
Ni	50	50	100	0.25	0.7	0.7 0.25	Troostite Ferrite + pearlite

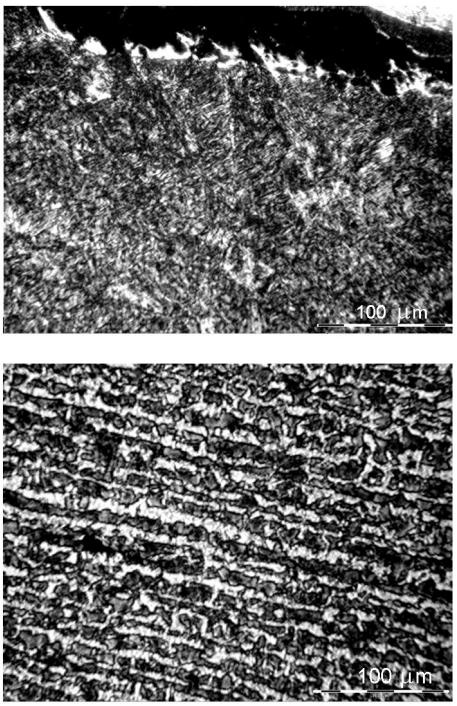

Fig. 2. The structure of TiN and 45 steel spark coating after concentintensityd solar irradiation (CSI): coating + troostite (a); ferrite + pearlite ; basic structure of steel (b). ×240.

rial increases, the continuousness increases 5 times compared to TiN coatings. The alloyed layer consists of "white" unetchable layer from 10 to 100 μm in thick (depending on the metal binder content) and dark layer with thickness of 15 μm and 0.55 GPa microhardness, covering the "white" layer (Fig. 4a). The dark layer seems to consist of complex iron oxides with the elements of electrode material ($Fe_{2.43}Ni_{0.53}O_4$ and others) (Table 1) and forms a dense film on the sample surface. This film cures cracks and rough places and can act as a lubrication during wear and friction tests. There are a lot of taupe-green inclusions, apparently, iron and nickel oxides. In some cases, for instance, in coatings of 60 % TiN + 40 % Ni, grey phase zones of 2.4 GPa microhardness are observed, that probably consist of complex oxides $Ti_4Fe_2O_4$ and $Fe_{4.3}Ni_{0.53}O_4$ (Fig. 4a).

After CSI treating, the structure of steel 45 changes. For example, in the samples with TiN and 80 % TiN + 20 % Ni ESA coatings, the initial structure of steel 45 (ferrite and pearlite streak like) transforms into fine-dispersed troostite one with martensite areas, which results in the 4 times (0.9 GPa) increase of hardness compared to the untreated steel (Fig. 2a; 3a–

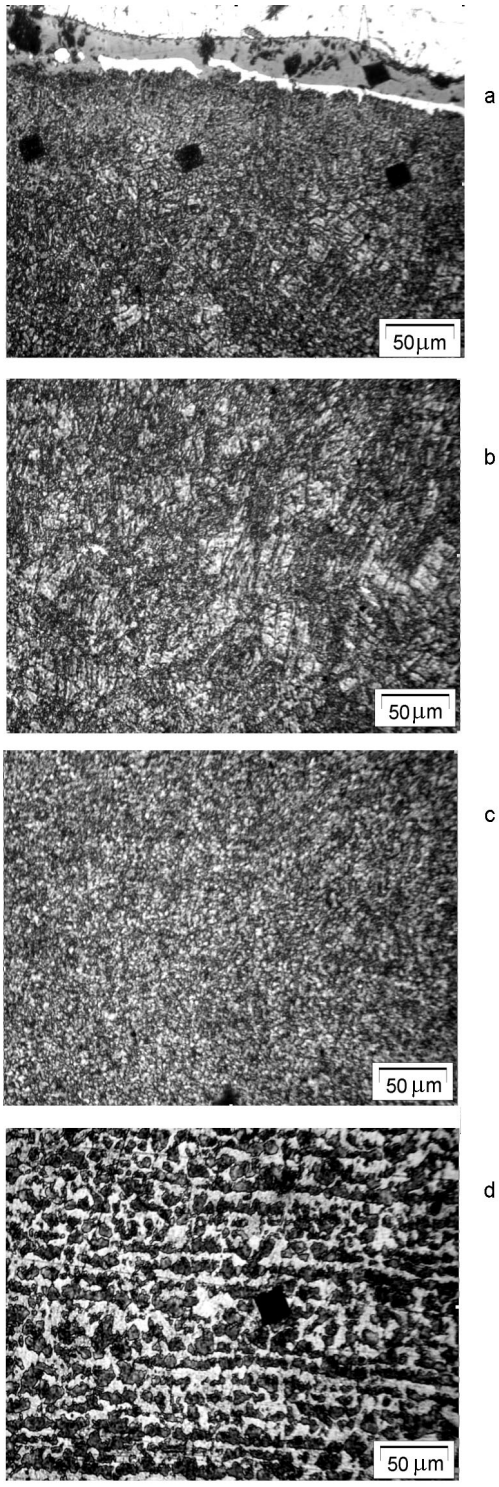

Fig. 3. The microstructure of 80 % TiN + 20 % Ni and 45 steel spark coating after concentintensityd solar irradiation in the sample depth: coating + troostite with martensite areas (a); troostite (b); sorbite (c); ferrite + pearlite (d). ×240.

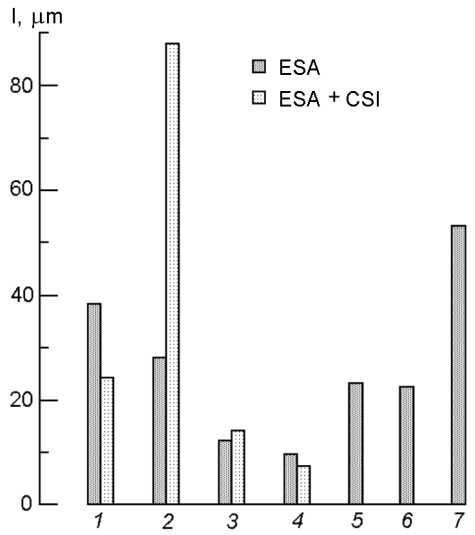

Fig. 4. The wear intensity (I) of coatings: TiN (*1*); 90 %TiN + 10 %Ni (*2*); 80 %TiN + 20 %Ni (3); 60 %TiN + 40 %Ni (*4*); 20 %TiN + 80 %Ni (*5*); Ni (*6*); steel U8, CSI untreated (*7*).

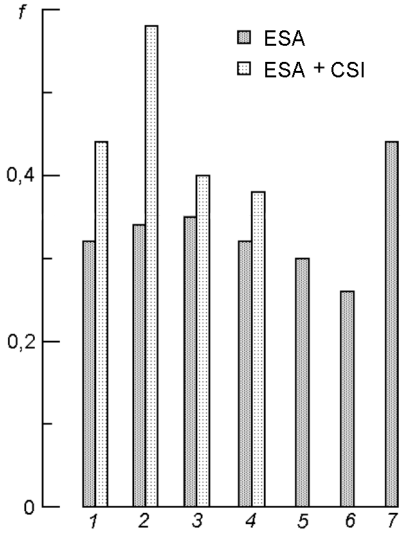

Fig. 5. Friction factor (*f*) for coatings: TiN (*1*); 90 %TiN + 10 %Ni (*2*); 80 %TiN + 20 %Ni (*3*); 60 %TiN + 40 %Ni (*4*); 20 %TiN + 80 %Ni (*5*); Ni (*6*); steel U8, CSI untreated (*7*).

3d). After only electric-spark alloying, the steel structure remained unchanged and consisted of two phases (ferrite and pearlite) with 0.18 GPa microhardness. As to samples with pure TiN ESA coatings, the no martensite areas were observed at metallographic examination of the CSI treated steel.

In friction tests, Ni content increasing to 40 % reduces the wear intensity (I) of the TiN ESA coating from 4 to 1.2 times (Fig. 2). Further increase of Ni > 40 % in TiN ESA coatings causes the double increase of wear intensity, and in comparison with non-hardened steel, even a 5-fold increase. CSI treatment of the ESA coatings under consideration results in a 1,2- to 3-fold decrease of wear intensity as compared to non-irradiated coatings. The exception was 90 %TiN + 10 %Ni ESA coating where the wear intensity increased twice as compared to TiN ESA coating, apparently due to the formation of iron solid solution in nickel Ni(Fe). Thus, the composition 60 %TiN + 40 %Ni shows the minimum wear intensity (I = 9.7 μm/km). The use of CSI reduces 1.2 time the wear intensity of this coating as compared to the untreated one. The wear resistance of 60 % TiN + 40 %Ni ESA coating increases 5 times as compared to the TiN one and 7 times as compared to the CSI untreated steel (Fig. 4). The average friction factor for TiN–Ni ESA coatings is 0.32–0.30 (Fig. 5). As the Ni content in the coating increases to exceed 40 %, the friction factor reduces from 0.30 to 0.26, obviously due to the appearance of free nickel, according to XPA data (Table 1). The friction factor for unhardened steel is 1.3 time higher as compared to TiN ESA coating and 1.8 time higher as compared to Ni ESA coating (Fig. 5). The CSI treatment of TiN–Ni ESA coating causes the increase of friction factor by a factor of about 1.2 time.

To conclude, it has been established that the emissivity of TiN–Ni coating materials increases 1.5 time as compared to the pure TiN coating, which is effective for the use in friction pairs of mechanisms in the outer space. In the zone disposed to concentintensityd solar energy, steel 45 is subjected to structure changes from ferrite-pearlite to troostite with grain size diminution and increase of hardness. The concentintensityd solar radiation treatment at the same temperatures of ESA-surfaces of TiN–Ni increases the wear resistance 2–3 times due to formation of oxides in the alloyed layer, according to XPA data. It has been established that the electric spark coating of 60 %TiN + 40 %Ni material has the optimum friction and physical-mechanical properties. The wear resistance of ESA-coatings made of 60 %TiN + 40 %Ni has increased 1.2 times as compared to the same coatings not treated with CSI.

References

1. V.S.Kovalenko, A.D.Verkhoturov, L.F.Golovko, I.A.Podchernyayeva, Laser and Electro-

erosion Hardening of Materials, Nauka, Moscow (1986) [in Russian].
2. I.A.Podchernyayeva, V.A.Lavrenko, G.A.Frolov et al., *Poroshkovaya Metallurgia*, **39** (1994).
3. T.A.Lyudvinskaya, I.A.Podchernyayeva, A.D.Panasyuk et al., in: Proc. of VIII Intern. Conf. on Hydrogen Material Science and Carbon Nanomaterials Chemistry, Crimea, Sudak, 14–20 September 2003, p.363 [in Russian].
4. G.V.Samsonov, Nitrides, Naukova Dumka, Kyiv (1968) [in Russian].
5. A.V.Paustovsky, V.I.Novikova, N.P.Korzhova, *Poroshkovaya Metallurgia*, No.1/2, 26 (2002).
6. L.F.Kolesnichenko, V.V.Polotay, V.V.Zabolotny et al., *Poroshkovaya Metallurgia*, No.3, 61 (1970).
7. P.P.Latyshev, V.A.Petrov, V.Ya.Chekhovsky et al., Emitting Properties of Solids, Energiya, Moscow (1974) [in Russian].

Структуроутворення та зносостійкість ЕІЛ покриттів з TiN–Ni після обробки концентрованим сонячним випромінюванням

О.В.Паустовський, Г.О.Фролов, І.І.Тімофєєва, В.І.Новікова, В.С.Циганенко, Н.М.Мордовець, О.Д.Костенко, Л.П.Ісаєва

Показано, що у електроіскрових покриттях з TiN при додаванні Ni після обробки концентрованим сонячним випромінюванням випромінювальна здатність збільшується у 1,5 раза, що є ефективним при використанні у вузлах тертя у космічному просторі. Застосування концентрованої сонячної енергії для обробки ЕІЛ-покриттів з TiN–Ni підвищує зносостійкість покриттів у 2–3 рази, внаслідок утворення оксидної фази у легованому шарі. У сталі 45 у зоні дії концентрованої сонячної енергії відбуваються структурні зміни від ферито-перліту до трооститу із подрібненням зерна та підвищенням твердості. Встановлено, що оптимальні триботехнічні і фізико-механічні властивості має електроіскрове покриття з матеріалу 60 % TiN + 40 % Ni.