Functional Materials 10, No.4 (2003)

Phase formation and formation kinetics of Ni–Cr–Al–Y electric-spark coating on steel 45

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Received October 10, 2003

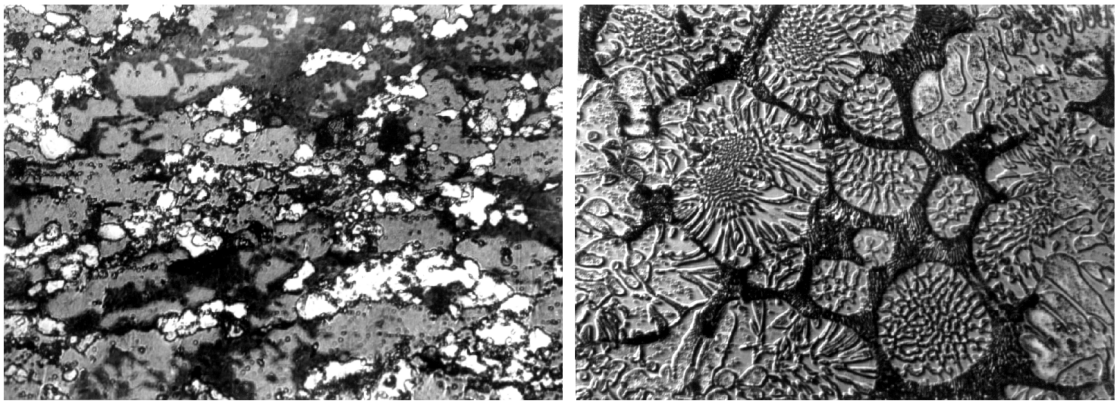
The main parameters of the cast and hot-milled steel 45 electric-spark alloying with eutectic Ni–Cr–Al–Y alloy have been studied, including the anode total erosion, the cathode mass gain and the material transfer mean coefficient. The phase composition and structure state of initial electrode materials and electric-sparked coatings made thereof. The electrode material structure character has been shown to define the kinetic parameters of surface layer growth. The wear resistance of the layers obtained is defined also by the initial structure of electrodes.

Исследованы основные параметры кинетики электроискрового легирования стали 45 сплавом Ni–Cr–Al–Y эвтектического состава в литом и горячепрессованном состоянии: суммарная эрозия анода, привес катода и средний коэффициент переноса материала. Изучены фазовый состав и структурное состояние исходных материалов электрода и электроискровых покрытий из них. Показано, что характер структуры материалов электродов в исходном состоянии определяет параметры кинетики наращивания поверхностного слоя. Износостойкость полученных слоев также определяется характером структуры электродов в исходном состоянии.

The electric spark alloying (ESA) method is one of effective techniques for surface recovery and hardening. It consists in a predominating erosive destruction of anode material and transfer of the erosion products onto the cathode surface with formation of a layer having modified structure and composition. The electric-spark coating ("white layer") structure formation under local action of high pressures ($2\cdot10^6$ to $7\cdot10^6$ MPa), temperatures (5000 to 6000°C) and cooling rates (10^5 to 10^6 deg/s) defines their high physical and mechanical properties. The selection of electrode material is associated in first turn with the considerations of phase formation within the alloyed layer and thus defines its further functional application.

Ni–Cr–Al alloys alloyed with yttrium and refractory metals are used widely in electron-beam, plasma, and detonation-made coatings [1–3].

The common casting technology provides for limitation of chromium (max. 10 to 12 % by mass), aluminum (max. 2 to 2.5 %) and rare-earth metals (max. 0.1 to 0.2 %) content in those alloys. However, the novel technology of high-energy hot powder pressing (in what follows, HP) elaborated at I.Frantsevich Institute for Materials Science Problems, National Academy of Sciences of Ukraine [4] provides essentially pore-free materials where Ni, Cr, and Al can be combined within wide concentration ranges. This makes it possible to use these alloys as electrodes for electric-spark alloying to obtain coatings with pre-specified physical and mechanical properties, first of all, with high heat resistance and wear resistance.



a b

Fig. 1. Microstructure of Ni–Cr–Al–Y alloy (×500): cast (a) and hot-pressed (b).

In this work, studied are kinetic characteristics of Ni–Cr–Al–Y electric-spark coating formation, its phase composition and structure state.

It is known [5] that a four-phase eutectic transformation $L \leftrightarrow \alpha + \gamma + \beta$ occurs in a section of Ni–Cr–NiAl ternary diagram. However, the available data on the eutectics chemical composition [6, 7] are contradictory. Basing on investigations done by the authors, the alloy composition nearest to the eutectic has been found. This alloy containing 2 % (mass) of yttrium (Ni, 50.7; Cr, 38.3; Al, 9.0; Y, 2.0) was obtained using melting and HP.

The melting was carried out in an arc furnace with permanent tungsten electrode under a protecting atmosphere. Electrolytic nickel (N–0), refined chrome (ERCh-0, 99.9 % purity), high-purity aluminum 9-995, and melted yttrium metal (IPM-1) were used as initial materials. The same contents of components were used as powders to prepare the alloy using HP (The grain size values of the powders in μm are indicated in brackets). The powders of electrolytic nickel, GOST 97-22-74 (<40 *m*m), chrome PCh1M, TU 14-1-1470-75 (<40 μm), and aluminum, PAR-91 (<10 μm) were used. Yttrium was introduced as hydride YH_2 (2 to 5 μm). The phase composition and structure of the alloys in the initial state and as electric-spark coatings were studied using optical microscopy, differential thermal analysis (DTA), as well as X-ray and micro-X-ray spectral analysis.

The 45 steel was subjected to electric-spark alloying using cast and hot-pressed electrodes made of the alloy mentioned above. To that end, an EFI-46A unit was used in the following mode: the vibrator frequency 100 Hz, the short-circuit current 1.5 A, the treatment duration for 1 cm^2 area 10 min. To obtain the coatings intended for wear resistance test, an Elitron-52 was used at 100 V and pulse energy 7.5 J.

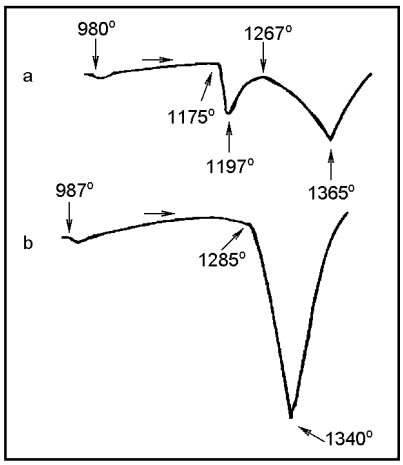


Fig. 2. DTA patterns of cast (a) and hot-pressed (b) Ni–Cr–Al–Y alloy under heating.

The main parameters of electric-spark alloying process were determined from the time dependences of the anode erosion and the cathode mass gain. Those include: the specific anode erosion, Δa, and the specific cathode mass gain, Δk, measured at each minute of the 1 cm^2 area treatment; the total anode erosion and the total cathode mass gain measured over 10 min of the 1 cm^2 area treatment; and the mean material transfer coefficient, $k' = \sum \Delta k / \sum \Delta a$.

In the cast alloy, the ternary eutectic structure is observed consisting of γ (Ni-based solid

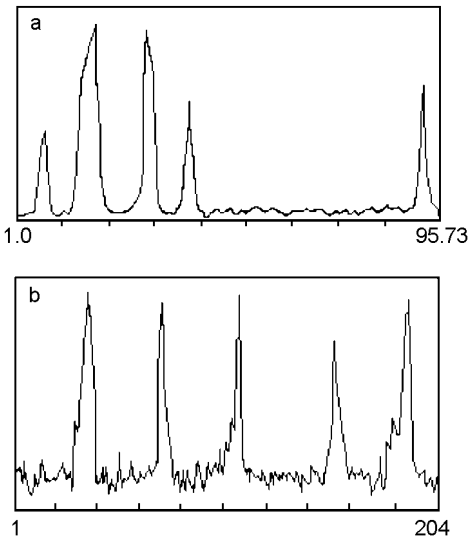


Fig. 3. Yttrium distribution in cast (a) and hot-pressed (b) Ni–Cr–Al–Y alloy.

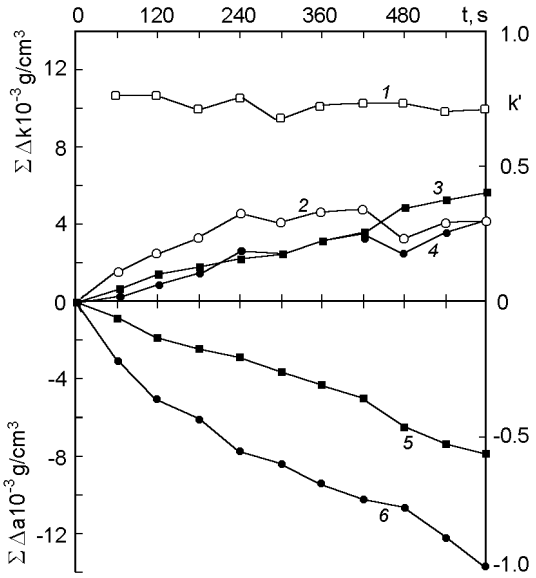


Fig. 4. Kinetic curves of the total cathode mass gain $\sum\Delta k$ (*3*, *4*), total anode erosion $\sum\Delta a$ (5, 6) and mean mass transfer k' at electric-spark alloying of 1 cm^2 of steel 45 with Ni–Cr–Al–Y alloy at the specific alloying duration $t = 600$ s/cm^2 (*1*, *2*). *1*, *3*, *5* for hot-pressed alloy; *2*, *4*, *6* for cast one.

solution with f.c.c. lattice), α (Cr-based solid solution with b.c.c. lattice), and β (NiAl intermetal based solid solution with b.c.c. lattice). Along the boundaries of the ternary eutectic (α + γ + β) colonies, the binary eutectic is arranged consisting of the γ Ni-based solid solution and the Y_2Ni_{17} intermetal phase (see Fig. 1a). As determined by DTA, the melting point of the binary eutectic is 1175°C, that of the ternary one, 1267°C (Fig. 2a).

In contrast to the cast alloy, the hot-pressed one shows a single thermal effect at 1285°C (Fig. 2b). The phase composition of the HP alloy was formed in the course of sintering of the mixture including nickel, chrome, aluminum, and lithium hydride powders. Under heating and exposure for 40 min at 1150°C, α, γ, and β solid solutions were formed having grain structure (Fig. 1b). Yttrium hydride dissociated under heat forming atomic yttrium. The yttrium, when interacting with inclusion impurities adsorbed at the powder particles forms complex oxides and oxynitrides. The micro-X-ray analysis has shown that in the cast alloy, yttrium is distributed non-homogeneously as large conglomerates forming the eutectic (Fig. 3a). In the HP alloy, the oxides oxynitrides, and intermetallic phases containing yttrium are distribute homogeneously over the whole sample volume and form a dispersion-hardened structure (Fig. 3b).

Kinetic curves of the anode erosion, the cathode mass gain, as well as values of the mean material transfer coefficient for cast and hot-pressed electrodes are shown in Fig. 4. The cast anode erosion attains a maximum value of $13.6 \cdot 10^{-3}$ g/cm^3. It is lower for the HP anode.

The material amount thrown out of the anode is determined [8] as $\gamma = kEft$, where γ is the thrown material mass, g; E, the single pulse energy, J; f, the pulse repetition frequency, Hz; k, a proportionality factor depending on the electrode material physical constants, the medium composition, and the pulse duration; t, the treatment duration, seconds.

It the case under consideration, both cast and hot-pressed anodes have the same elemental composition and are subjected to electric sparking in the same conditions, but are different in the phase composition defined by the manufacturing technology. It is just the distinctions in the anode structures that define obviously the erosion difference.

The presence of ternary and binary eutectics containing intermetal phases as large colonies (conglomerates) favors the brittle destruction of the anode by the spark pulse. As a consequence, the erosion products contain the solid phase along with liquid and

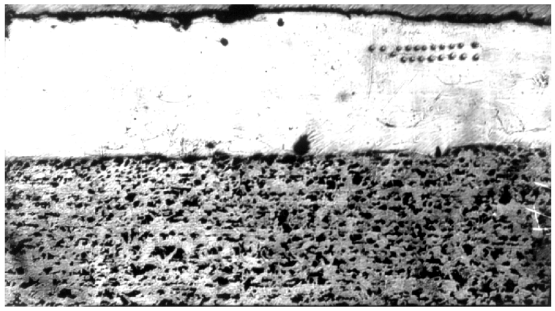


Fig. 5. Microstructure of Ni–Cr–Al–Y electric-spark coating on steel 45 (×50) (alloying using an Elitron-22 unit).

vapor ones. The solid phase has no time enough to melt within the short pulse action period. The solid destruction products are no fixed on the cathode, thus causing the material loss [9].

At the same time, the cathode mass gain is almost the same for alloying with cast and HP anodes. The monotonous cathode mass increase with the alloying duration evidences that the brittle destruction threshold of the surface layer was not attained in 10 min alloying. The obtained layer thickness attains 700 to 800 μm, thus, this alloy seems to be suitable in repairing worn articles. The mean material transfer coefficient for the alloying with HP electrodes exceeds that for the cast electrodes (k' is 0.7 to 0.8 and 0.3 to 0.5, respectively).

The electric-spark coating microstructure (Fig. 5) is the high-density "white layer" that is not etchable. The micro-hardness of electric-spark coatings obtained with both cast and HP anodes is 10.3 to 11.2 GPa, thus, it exceeds that characteristic for individual components of the eutectic (3.5 to 8.3 GPa).

The X-ray phase analysis reveals the nickel and chrome based solid solutions as well as NiAl β-phase in the coatings. Besides, intermetal phases Al_3Y, AlNiY, and oxide Y_2O_3 are found. The X-ray spectral microanalysis has confirmed the X-ray phase data. Nickel, chrome, and aluminum have been found to be distributed homogeneously in the electric-spark coatings (Fig. 6), thus evidencing the thin conglomerate structure of the ternary eutectic phase. In coatings made of both cast and HP alloy, yttrium is distributed in a discrete manner similar to that in the initial HP alloy. This may be due to yttrium-containing oxides or oxynitrides.

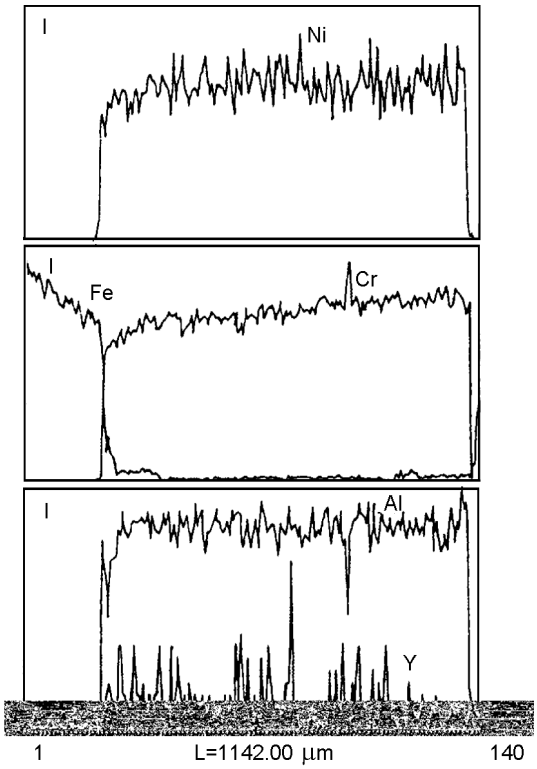


Fig. 6. Ni, Cr, Al, and Y distribution in Ni–Cr–Al–Y electric-spark coating on steel 45.

The formation of mixtures of solid solutions in electric-spark coatings made of eutectic alloys is confirmed by [10] where it has been indicated that when the anode material contains elements (Cr, Ni) limitless soluble in the substrate (Fe), a coating is formed consisting of solid solutions based on those elements. Such layers are characterized by a high solidity and good adhesion to the substrate.

The wear resistance of electric-spark coatings was tested on a MT-68 unit using steel 45 samples (5×5×15 mm^3) provided with electric-spark coatings made of the cast and hot-pressed alloy. The test conditions were as follows: lubricant-free friction in air at room temperature, the 65G steel being used as the second pair member; slipping speed $V = 10$ m/s, loading 2 MPa. The friction coefficient f and the wear intensity in μm/km were monitored during the test. As a wear resistance reference, a steel 45 sample with electric-spark coating made of sintered chromium-doped VK-3U hard alloy (WC, Co, Cr).

The friction coefficient for cast alloy coatings is 0.29, for those of HP one, 0.27. The wear of cast alloy coatings attained 18 to 20 μm/km, while for those of HP one, 10

to 12 μm/km, thus being commensurable with that of VK-3U alloy coatings. The wear resistance of the initial cast alloy is 30 to 35 μm/km, that of the HP one, 14 to 18 μm/km. The friction coefficient is 0.41 and 0.38, respectively.

Thus, the studies carried out have shown that the electric-spark alloying of steel 45 with Ni–Cr–Al–Y eutectic alloy results in formation of surface layer having a structure different from that of the initial alloy. The main distinction consists in a high dispersity of phase components and their homogeneous distribution. This provides an improved wear resistance of the coatings as compared to the initial cast and hot-pressed alloys.

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Фазоутворення та кінетика формування електроіскрового покриття із сплаву Ni–Cr–Al–Y на сталі 45

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Досліджені основні параметри кінетики електроіскрового легування сталі 45 сплавом Ni–Cr–Al–Y евтектичного складу у литому та гарячепресованому стані: сумарна ерозія аноду, привіс катоду та середній коефіцієнт переносу матеріалу. Вивчено фазовий склад та структурний стан вихідних матеріалів електродів та електроіскрових покриттів із них. Показано, що характер структури матеріалів електродів у вихідному стані обумовлює параметри кінетики нарощування поверхневого шару. Зносостійкість одержаних шарів також визначається характером структури електродів у вихідному стані.