High-Nitrogenous Coatings with Ferrovanadium Additives Deposited by Electron Beam Surfacing

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Abstract – Coatings deposited by multipass electron beam surfacing of powders that contain nitrogen in equilibrium concentration and nitrogen-containing ferrovanadium additive was investigated. Abrasive wear resistance of the produced coatings exceeds wear resistance of high-chromium white cast iron by 10 and hardened steel 65G by 50%.

1. Introduction

In Russia and abroad methods for deposition of coatings based on nitrogen solid solutions are intensively developed [1–6]. Nitrogen content in the coatings depends on their functions and deposition technology, and varies in a wide range of 0.2–1.0 mass %. It has become possible to form composite coatings with high-strength matrix on the basis of nitrogen solid solutions, which is reinforced by refractory solid particles. This enlarges the application area of nitrogen materials. Today, there is no accepted concept concerning the optimal phase composition of high wear-resistant nitrogen coatings and their deposition methods.

2. Experiments

Steel powder 60Cr24NMn16 is taken as the base of a deposition material. It is prepared by mechanical milling of steel chips preaged at 700 °C during 3 h. The obtained powder is sieved to separate the fraction for deposition with good flowability, namely, with the particle size 50–400 μm. Then, the nitrogen powder is divided into five parts to obtain deposition mixtures with different content of powdered nitrated ferrovanadium having composition 40% V, 9% N, 3% C, the rest Fe. The content of nitrated ferrovanadium varies in the prepared deposition powders and comprises 5, 10, 20, 25, and 30 mass %.

We have analyzed the literature data on the interaction of vanadium carbonitride particles with a liquid alloy melt [7, 8]. This allows predicting the coating formation by mechanisms of dispersion solidification and hardening if the deposition powder is added with nitrated ferrovanadium.

Electron beam surfacing described in [9] is performed using an ELU-5 installation equipped with a powder feeder. An electron beam is split into two. One beam forms a molten pool on the substrate surface moving with the velocity 3 mm/s, into which the deposition powder is fed through the feeder with the rate 7–10 g/min. The second beam remelts the pool and captures the substrate. A coating 2.5–3 mm thick is obtained after several passages, each of which forms a layer ~0.5 mm thick. We use, as the substrate, 65Mn steel plates measured $20 \times 100 \times 10$ mm, which are heat-treated by induction hardening to provide the hardness 56 HRC.

The coating structure is studied by an Axiovert metallurgical microscope. The X-ray structural analysis is performed using a DRON-4M diffractometer with CoK_α-radiation. Comparison tests for wear resistance of a non-rigid abrasive are conducted by a laboratory installation according to GOST 23.208-79. Quartz sand with the grain size 400–900 μm is taken as abrasive. Abrasive wear-resistance is defined as a ratio between the mass loss of the induction hardened steel 65Mn with the hardness 56 HRC ΔMe (etalon) and the mass loss of the studied material ΔMm: $\varepsilon = \Delta Me / \Delta Mm$. A relative abrasive wear-resistance of coated specimens is found from the results of 10 parallel tests. Coating microhardness is measured by a PMT-3M device under load 100 g.

3. Results and discussion

According to metallographic and X-ray structural investigations, the deposited coating structure with composition 60Cr24NMn16 represents a nitrogen austenitic matrix containing chromium carbide inclusions Cr_7C_3, $(Fe, Cr)_3C_7$ along grain boundaries (Fig. 1, *a*).

The coating has a homogenous phase composition throughout its thickness. Note that coating surface layers are characterized by a more disperse structure as compared to middle layers and those adjacent to the substrate. The average size of austenitic grains comprises 30 μm in surface layers, 40 μm in middle layers, and 100 μm in the vicinity of the fusion zone. Nitrated ferrovanadium added to the initial deposition powder allows reducing the structure so that the average size of austenitic grains is 15 μm in surface layers, 30 μm in middle layers, and 70 μm in the vicinity of the fusion zone. Different grain size is related to thermal cycling governed by multipass electron beam surfacing [6].

Microstructures of coatings based on deposition mixtures with nitrated ferrovanadium additives are almost identical and differ only in volume fraction of particles V (C, N) (Figs. 1, *b* and *c*).
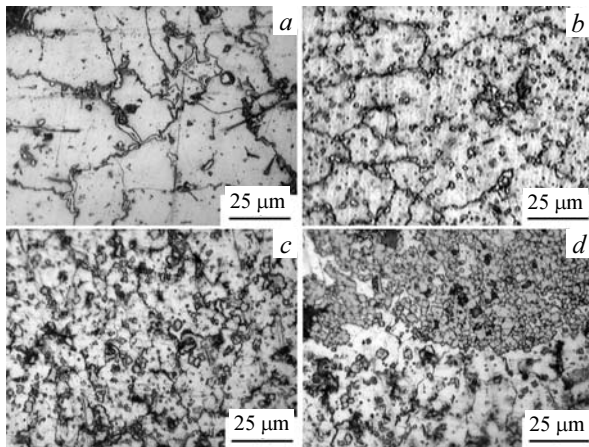
Fig. 1. Coating structure based on steel powder 60Cr24NMn16: without a nitrated ferrovanadium additive (*a*); with a ferrovanadium content of 10 (*b*) and 25% (*c*, *d*) in the deposition powder

After arriving at a molten pool and being remolten by an electron beam the vast majority of initial nitrated ferrovanadium particles "is scattered". The formed structure has a rather homogeneous phase composition with small inclusions of V (C, N) 1–5 μm in size both along boundaries and within austenitic grains. However, initial coarse particles of size from 30 to 200 μm are also found in the structure of dispersion-hardened coatings (Fig. 1, *d*). Iron entering into the composition of nitrated ferrovanadium dissolves in the austenite and changes its chemical composition. This is manifested in a lattice parameter decrease of the nitrogen austenite (Fig. 2, *a*).
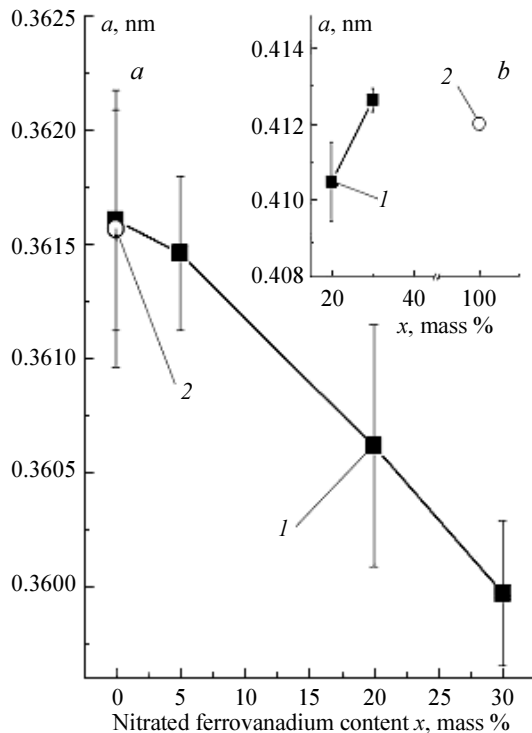

Fig. 2. Lattice parameters of Fe$_\gamma$ (*a*) and V (C, N) (*b*) in electron beam coatings (*1*) and deposition powders (*2*) versus mass fraction of nitrated ferrovanadium added to the deposition powder 60Cr24NMn16

An increase in mass fraction of nitrated ferrovanadium added to the nitrogen steel powder to reinforce the matrix and improve wear-resistance requires an increase in the electron beam power density at surfacing. This leads to a temperature growth in a zone of electron beam action. As a results, some particles V (C, N) in coatings with a nitrated ferrovanadium content of 20, 25, and 30% start to dissolve and form molecular nitrogen. No pores are observed in the nitrogen matrix. All of them are concentrated in initial particles of nitrated ferrovanadium containing 9%t of nitrogen. In some case under residual stresses pores induce crack formation. The lattice parameter of vanadium carbonitride is studied in the initial state (before surfacing) and in coatings with a nitrated ferrovanadium content of 20 and 30% in the deposition powder (Fig. 2, *b*). In coatings without nitrated ferrovanadium and in those deposited using 5 and 10% of the nitrated ferrovanadium powder no gas chambers are observed.

The phase composition of the coating matrix changes from austenitic to austenitic-martensitic (Fig. 3).
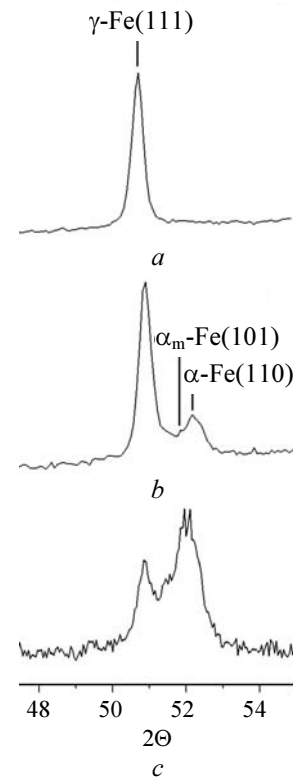

Fig. 3. X-ray patterns of the electron-beam coating deposited using powder 60Cr24NMn16 (*a*) and powder containing 80% of 60Cr24NMn16 and 20% of nitrated ferrovanadium before (*b*) and after the wear test (*c*)

An increase in the dispersed phase fraction and related change in the phase composition of the composite coating has a beneficial effect on hardness and abrasive wear resistance of coatings of the considered composition (Fig. 4). Wear resistance increases most rapidly with 10% of nitrated ferrovanadium. Further an increment in the relative wear resistance coefficient decreases.

ing matrix with the austenitic-martensitic structure is almost unchangeable.

Table 1. Microhardness HV and relative wear resistance coefficient ε of electron-beam coatings

Coating composition	Microhardness H_V, kg/mm^2		ε
	before wearing	after wearing	
60Cr24NMn16	530	630	0.696
75% 60Cr24NMn16 and 25% nitrated ferrovanadium	670	700	1.528

Friction tracks in the studied coatings are also different in structure. Interaction of the abrasive with the 60Cr24NMn16 steel coating results in clearly seen traces of matrix deformation by the same wear mechanism, i.e., scratching.

In the second case, such interaction is prevented by dispersed phase particles that equally to the matrix improve the abrasive wear resistance of the material.

4. Conclusions

1. Electron beam surfacing is used to form a coating with the structure of the metastable nitrogen austenite. Its high wear resistance is governed, firstly, by martensitic transformation $\gamma \rightarrow \alpha$ and formation of nano-sized martensite crystals in the friction surface and, secondly, by dispersion and age hardening of multi-sized particles V (C, N).

2. Electron-beam nitrogen-containing coatings dispersion-hardened by nitrated ferrovanadium have high abrasive wear resistance that is 30–50% higher than that of steel 65Mn with hardness 56HRC.

3. An optimal content of nitrated ferrovanadium in the deposition powder is 10 mass %. Its increase complicates a production technology of electron-beam coatings and degrades their quality.
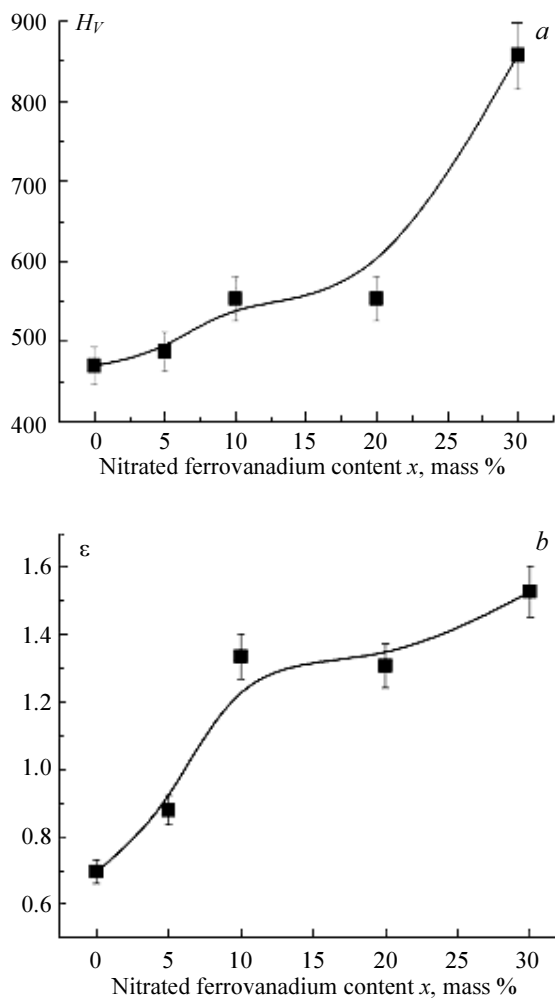
Fig. 4. Microhardness (*a*) and relative wear resistance coefficient (*b*) of electron beam coatings containing different mass fraction of nitrated ferrovanadium introduced into deposition powder 60Cr24NMn16

The abrasive wear resistance tests reveal structural instability of the nitrogen austenite and its capability to martensitic transformation. The comparative analysis of the X-ray patterns in Figs. 2, *b* and *c* shows a change in the relation between intensities of X-ray maxima and main matrix phases, namely, austenite and martensite.

Before the wear test austenite prevails in the structure while after the test martensite becomes predominant. Coherent-scattering regions of martensite crystals are no more than 90 nm in size and it is the structure reduction that governs broadening of X-ray maxima of Fe$_\alpha$. No austenite reduction is found in our studies while a value of microdistortions of the fcc lattice is an order higher than that of the nanostructured martensite. This value comprises 0.0003%, which is governed by its highly defect structure. Friction hardening of the structure in abrasive wear allows increasing microhardness measured in friction tracks in the coating deposited using powder 60Cr24NMn16. According to Table 1, the microhardness increase comprises ≈18% while the microhardness in the coat-

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