Formation of the CoCrCuFeNi high entropy cladding layer by non-vacuum electron beam treatment

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Abstract. Non-vacuum electron beam cladding was applied to obtain CoCrCuFeNi cladding layers with thicknesses of 0.89 and 1.24 mm on a surface of mild steel. The cladding layers possessed the dendritic structure. Interdendritic space was filled with a Cu-rich phase. It was found by X-ray diffraction analysis that FCC solid solution phases were formed during crystallization. The lattice parameter of the dendritic phase was \(a=3.59\) Å, while that of the interdendritic phase was equal to \(a=3.60\) Å. The average microhardness values of the cladding layers were lower compared to the base material and equaled 156HV and 190HV.

1. Introduction

Recently, the multicomponent alloys with equiatomic and near equiatomic compositions, namely high entropy alloys, have attracted the attention of many research groups [1]. These alloys are a breakthrough in physical metallurgy since traditional alloys are usually based on one main component (steel, aluminum alloys, etc.).

Investigations of the high-entropy alloys have shown that this class of materials can have a unique combination of properties and find their application in industries that require high strength, hardness, wear resistance, or heat resistance. Due to these characteristics, high-entropy alloys can be considered as promising materials for protective functional coatings. A large number of studies are being carried out in this area, but most of them are aimed at studying thin films obtained by such technology as magnetron sputtering. However, it is more reasonable from the technological point of view to apply coatings of a large thickness (more than 0.5 mm). Various types of thermal spraying, laser cladding, arc cladding, and electron-beam cladding can be referred to as the methods of forming such thick coatings. Another currently important and actively developing technology is considered to be additive manufacturing with the use of the electron beam as an energy source [2]. Thus, the purpose of this study was to investigate regularities of the formation of materials with protective layers of the composition corresponding to high entropy alloys by the method of non-vacuum electron-beam processing. CoCrCuFeNi layers were applied to the surface of steel 20 workpieces. According to the literature data [3, 4], an alloy of such composition has an FCC structure and can be used at elevated temperatures, or as a corrosion resistant material.
2. Materials and methods

2.1. Preparation of the coatings
Formation of the surface layers was carried out at Budker Institute of Nuclear Physics using an ELV-6 electron accelerator modified to allow the electron beam to be injected into the atmosphere. The energy of electrons in the beam is 1.4 MeV. The advantages of this technology include the fact that energy is released in the subsurface layer. This makes it possible to efficiently melt a powder layer of considerable thickness applied to the surface.

To produce layers, a powder mixture consisting of commercially pure Co, Cr, Cu, Ni powders was used. The metal powders were mixed with a flux (CaF$_2$) powder in a ratio of 70:30 by weight (CoCrCuNi:CaF$_2$) and applied to the surfaces of steel 20 workpieces. Next, the powder-coated workpiece was moved forward under a scanning electron beam. Iron necessary for the formation of the cladding layer of the required elemental composition was received from the melt pool resulted from the melting of the base material. During the experiments, the amount of powder applied to the workpiece, the current of the electron beam, and the moving velocity of the workpiece under the beam were varied. Changing the modes allowed regulating the composition of the cladding layer and finally obtaining the equiatomic surface alloy. Table 1 shows the cladding regimes.

| Regime No | Metal powders | Flux         | Surface density, g/cm$^2$ | Beam current, mA | Moving velocity, cm/s | Energy density J/cm$^2$ |
|-----------|---------------|--------------|---------------------------|-----------------|----------------------|--------------------------|
| 1         | CoCrCuNi 70%  | CaF$_2$ 30%  | 0.45                      | 25              | 15                   | 4.67                     |
| 2         | CoCrCuNi 70%  | CaF$_2$ 30%  | 0.45                      | 22              | 15                   | 4.11                     |
| 3         | CoCrCuNi 70%  | CaF$_2$ 30%  | 0.45                      | 20              | 15                   | 3.73                     |
| 4         | CoCrCuNi 70%  | CaF$_2$ 30%  | 0.6                       | 25              | 15                   | 4.67                     |
| 5         | CoCrCuNi 70%  | CaF$_2$ 30%  | 0.8                       | 25              | 15                   | 4.67                     |
| 6         | CoCrCuNi 70%  | CaF$_2$ 30%  | 0.6                       | 22              | 15                   | 4.11                     |
| 7         | CoCrCuNi 70%  | CaF$_2$ 30%  | 0.8                       | 22              | 15                   | 4.11                     |
| 8         | CoCrCuNi 70%  | CaF$_2$ 30%  | 0.45                      | 25              | 20                   | 3.50                     |

2.2. Characterization of the coatings
Cross-sections of the samples obtained were used for the microstructural investigations. Specimens were grinded and polished according to a standard method and etched with aqua regia (1HNO$_3$;3HCl). Microstructure was studied using a Carl Zeiss Axio Observer Z1m optical microscope (OM), and a Carl Zeiss EVO50 scanning electron microscope (SEM). Elemental compositions were measured by energy-dispersive X-ray spectroscopy using an Oxford Instruments X-Act spectrometer coupled with SEM. Phase compositions and lattice parameters were estimated using a Arl X'tra X-ray diffractometer. X-ray diffraction (XRD) patterns were obtained in Cu Kα1+2 irradiation. 2θ ranged between 30 and 155 °, and a step size was equal to 0.03 °. Samples for the XRD analysis were prepared by grinding and polishing the top surface of cladding layers to the depth ~0.3 mm. Profile analysis was implemented using WinXRD software. Peak profiles were described by Pearson VII function in consideration of Cu Kα2 irradiation. Lattice parameters were calculated using the Nelson-Riley function [5].

The Vickers microhardness was measured on the polished cross-sectional specimens in the direction from the top of the cladding layer down to the substrate by a Wolpert Group 402MVD hardness tester using a 100 g load on a diamond indenter.

3. Results and discussion
Energy dispersive analysis of the cladding layers revealed that modes 3 and 5 provided the composition closest to the required equiatomic one. 1st, 2nd, 4th, and 6th regimes caused excessive
melting of the base material, which led to the formation of layers with an iron content of 30 - 75 at. %. Contrary, regimes 7 and 8 did not provide the required depth of melting of the base material. The elemental composition and the thickness of the cladding layers obtained according to the 3rd and 5th regimes are listed in Table 2. The copper concentration was lower than expected, which can be explained by insufficient protection of the molten bath from air oxygen and more intense oxidation of copper compared to other elements.

Table 2. Average elemental compositions of the cladding layers.

| №  | Co, at. % | Cr, at. % | Cu, at. % | Fe, at. % | Ni, at. % | Thickness, mm |
|----|-----------|-----------|-----------|-----------|-----------|---------------|
| 3  | 20        | 21        | 18        | 21        | 20        | 0.89          |
| 5  | 21        | 22        | 17        | 20        | 20        | 1.24          |

Figure 1 shows a typical microstructure of the materials’ cross-sections. Three main regions can be distinguished in the structure: a cladding layer, a heat-affected zone, and a base material.
The cladding layer had a dendritic structure varying in depth. The lower part of the layer corresponded to the cellular growth of crystallites (Figure 1 d,e). Due to intensive heat removal into the base material, a large number of crystallization nuclei was formed at the border with the unalloyed metal. At some distance from this boundary, the structure was typical dendritic (Figure 1b and 1c): the dendrites in the central part were elongated in the vertical direction, which also can be explained by more intense heat removal towards the base material. It should be noted that a thin interlayer with a thickness of ~10 µm was formed between the cladding layer and a heat-affected zone. In this area, a gradual decrease in the concentration of alloying elements and an increase in iron concentration was observed (Figure 1f). Another peculiarity of the structure of the interface consisted in the formation of local areas where «leakage» of a Cu-enriched phase in the heat-affected zone was observed (Figure 1 d, e). In such areas, the crystallite boundaries extending from the cladding layer to the heat-affected zone can be clearly distinguished.

A similar crystallization character was observed in [6]. In addition, in the cladding layers obtained in our study, as well as in the aforementioned work, the vertical cracks extending along the dendrite boundaries were formed. The formation of these cracks can be associated with the relaxation of stresses arising in the base material during heating in a process of the electron beam cladding.

Energy dispersive analysis revealed that dendrites formed in the cladding layer were depleted in copper compared to the average composition, while the Cu-rich phase crystallized in the interdendritic space (Table 3). The copper concentration reached 65 – 75 at. % in the interdendritic space.

| Sample | Region   | Co, at. % | Cr, at. % | Cu, at. % | Fe, at. % | Ni, at. % | a, Å  |
|--------|----------|-----------|-----------|-----------|-----------|-----------|-------|
| 3      | Dendrite | 23.0      | 22.4      | 10.4      | 24.2      | 19.9      | 3.59  |
|        | Interdendrite | 5.5  | 6.4       | 71.1      | 6.4       | 10.9      | 3.60  |
| 5      | Dendrite | 24.7      | 24.7      | 12.4      | 15.9      | 22.2      | 3.59  |
|        | Interdendrite | 7.2  | 7.9       | 65.4      | 5.4       | 14.0      | 3.60  |

Figure 2 shows XRD patterns obtained from the cladding layers. It was found that the materials had an FCC structure.

![XRD patterns](image)

**Figure 2.** XRD patterns obtained from: 1 - coating No 3, 2 - coating No 5. a - 2θ = 30 – 100 degrees, b - 2θ = 70 – 155 degrees measured for lattice constant calculations.

Detailed analysis revealed a slight asymmetry of the peaks clearly visible at the reflections corresponding to the families of planes (400) and (420) (Figure 2b). It was assumed that the intense peaks corresponded to the dendritic phase (FCC-1), while the asymmetry is due to the presence of an
interdendritic Cu-rich solid solution (FCC-2). Based on these assumptions, a profile analysis was carried out and the lattice parameters of the dendritic and interdendritic phases were calculated (Table 3).

Microhardness of the cladding layers obtained by regimes 3 and 5 was 156±3 HV and 190±3 HV respectively. These values were lower than that of the base material (220±4 HV). The absence of an increase in hardness according to the solid solution hardening model can be explained by the close values of the atomic radii of the elements used for alloying.

Conclusions
Non-vacuum electron beam cladding allows obtaining the CoCrCuFeNi high-entropy surface layers at carbon steel workpieces. The thickness of layers obtained in one pass can reach 1.24 mm.

The cladding layer has a dendritic structure. The interdendritic space consisted of a copper-based phase with the concentration of other elements at a level of 5-10 % at.

Dendrites and the interdendritic space were represented by FCC solid solutions with similar lattice parameters.

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