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Microhardness Gradients and Structural Phase States of the Coating Contact Zone (HEA CoCrFeNiAl) with Substrate (Alloy 5083)

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ФИЗИКА

Научная статья

Градиенты микротвердости и структурно-фазовые состояния зоны контакта покрытия (ВЭС CoCrFeNiAl) с подложкой (сплав 5083)

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Abstract. A non-equiatomic high-entropy alloy (HEA) CoCrFeNiAl coating on the 5083 alloy substrate is produced by wire-arc additive manufacturing (WAAM). It is revealed that microhardness changes significantly at the contact zone of the "coating — substrate" system.

Аннотация. На подложке из сплава 5083 сформировано покрытие из высокоэнтропийного сплава (ВЭС) CoCrFeNiAl неэквиатомного состава методом проволочно-дугового аддитивного производства (WAAM). Установлено существенное изменение

The changes range from 7.6 GPa at the coating boundary and the contact zone up to 1.6 GPa at the substrate boundary and the contact zone. The coating and substrate have the microhardness values of 6.3 GPa and 1.1 GPa, respectively. The structural phase state, defective structure, and elemental composition of the "coating — substrate" system are analyzed using methods of modern physical material science. It is shown that they depend on the distance from the contact zone between the coating and substrate. Also, it is found out that application of the high-entropy coating on the 5083 alloy surface is accompanied by mutual alloying of the coating and substrate. Creation of two types of submicro- and nanosized particles is revealed in the study. Nanosize particles of Al2O3 and MgAlO oxides, Al and HEA subgrains form the first structure. The second structure consists of nanosized HEA subgrains, Al13Fe4 and (NiCo)3Al4 nanoparticles located along the grain boundaries.

Keywords: contact zone, high-entropy alloy CoCrFeNiAl, substrate, alloy 5083, structure, phase composition, elemental composition

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микротвердости в зоне контакта системы «покрытие — подложка». Она изменяется от 7,6 ГПа на границе покрытия с зоной контакта до 1,6 Гпа на границе подложки с зоной контакта. Покрытие имеет микротвердость 6,3 Гпа, подложка 1,1 ГПа. Методами современного физического материаловедения проанализированы структурно-фазовое состояние, дефектная структура и элементный состав системы «покрытие — подложка». Показано, что они зависят от расстояния от зоны контакта покрытия и подложки, а также, что нанесение высокоэнтропийного покрытия на поверхность сплава 5083 сопровождается взаимным легированием покрытия и подложки. Выявлено формирование двух типов субмикро- и наноразмерных частиц. Первая структура образована наноразмерными частицами оксидов Al2O3 и MgAlO, субзернами Al и ВЭС. Вторая структура состоит из наноразмерных субзерен ВЭС и наночастиц (NiCo)3Al4 и Al13Fe4, расположенных по границам субзерен.

Ключевые слова: зона контакта, высокоэнтропийный сплав CoCrFeNiAl, подложка, сплав 5083, структура, фазовый состав, элементный состав

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Introduction

Attention of researchers in the field of physical material science has recently been focused on creation and application of so-called high-entropy alloys (HEA) [1–5]. It follows even from the name itself that the HEA alloys have abnormally high values of the entropy of mixing that exceed considerably the values for complex alloys. A concept of the HEA realization, based on achievement of the maximum entropy of mixing from five and more elements in different atomic relations, specifies a formation of single-phase structures with a severe lattice distortion and a difficulty of diffusion that, in its turn, ensures a growth of strength properties and their stability in a wide temperature range [6–10]. The HEAs, that had already been created, are the perspective materials for application in electronics, nuclear power-engineering, transport machine-building, rocket-spacecraft and other branches of industry [11–15]. An application of HEAs is not limited to the above-mentioned fields, but it will extend as a development of new compositions, and examination of their properties is continued. Nowadays, the extensive information on the methods of HEA production, examination of their structural-phase states, defective substructure, properties [16-17], is being accumulated and interpreted.

A variation in microhardness and structural-phase state in a contact zone of the coating (HEA CoCrFeNiAl) — substrate (5083 alloy) system has been analyzed in the present research.

Material and methods

In the samples of the 'coating-substrate' system, a coating is the CoCrFeNiAl HEA of a non-equiatomic composition formed on the 5083 alloy substrate by wire-arc additive manufacturing [7]. The material hardness was determined by the Vickers scheme on a microhardness tester PMT-3 at a load of 5 N. The studies of structural-phase states, defective sub-structure, elemental composition were carried out by the methods of scanning (instrument SEM 515 Philips with micro-X-ray spectrum analyzer EDAX ECON IV) and transmission electron diffraction microscopy on instrument JEM 2100 [18–20].

Results and Discussion

A determined increase in microhardness in the layer adjacent to the coating (Table) is due to its lamellar structure which is indicative of a reciprocal alloying. A micro-X-ray spectrum analysis of the layer adjacent to the contract zone boundary from a coating side revealed particles of second phase located in the HEA grain wall and enriched in the Cr and Fe atoms. This indicates a layering of the HEA solid solution. By means of TEM analysis of such portions of a foil using dark-field images and technique of indexing the microelectron diffraction patterns it is found that a composition of a second phase is the Al_8Cr_9.

Variation in microhardness of the 'coating (the CoCrFeNiAl HEA)-substrate (the 5083 alloy)' system

Site of measurement	Value HV, GPa
Volume of coating	6.3
Boundary of coating and contact zone	7.6
Midpoint of contact zone	4.0
Boundary of substrate and contact zone	1.6
Volume of substrate	1.1

In the contact zone itself the two types of structure are observed: these have a monocrystalline (10–20 nm) — (1st-type structure) and a subgrain (140–170 nm) — (2nd-type structure) constitution. The 2nd-type structure is more homogeneous in elemental composition whereas in the 1st-type structure a distribution of chemical elements is non-homogeneous. Both regions of a lamellar shape enriched in the Cr atoms and regions of a spherical shape enriched in the Ni, Fe and Co atoms are discovered. By means of the micro-X-ray spectrum analysis the elemental composition of the 1st-type structure (at.%) is found: 10.2Mg-64.7Al-5.2Cr-0.9Mn-9.4Fe-2.3Co-7.3Ni and of the 2nd-type structure (at%): 61.1Al-7.0Cr10.6Fe3.8Co-17.5Ni. Our attention has been engaged in substantially higher concentration of the Ni atoms in the 2nd-type structure and an absence of the Mg and Mn atoms.

The analysis of phase composition of the 1st-type structure of the contact zone of the coating and the substrate, performed by indexing of microelectron diffraction patterns and by using dark-field images, enabled one to find reflections of aluminum oxides of the Al_2O_3 and MgAlO composition and reflections belonging to the HEA coating. TEM images in Figure 1 demonstrate a presence of the MgAlO (Figure 1, c) and Al (Figure 1, d) phases.

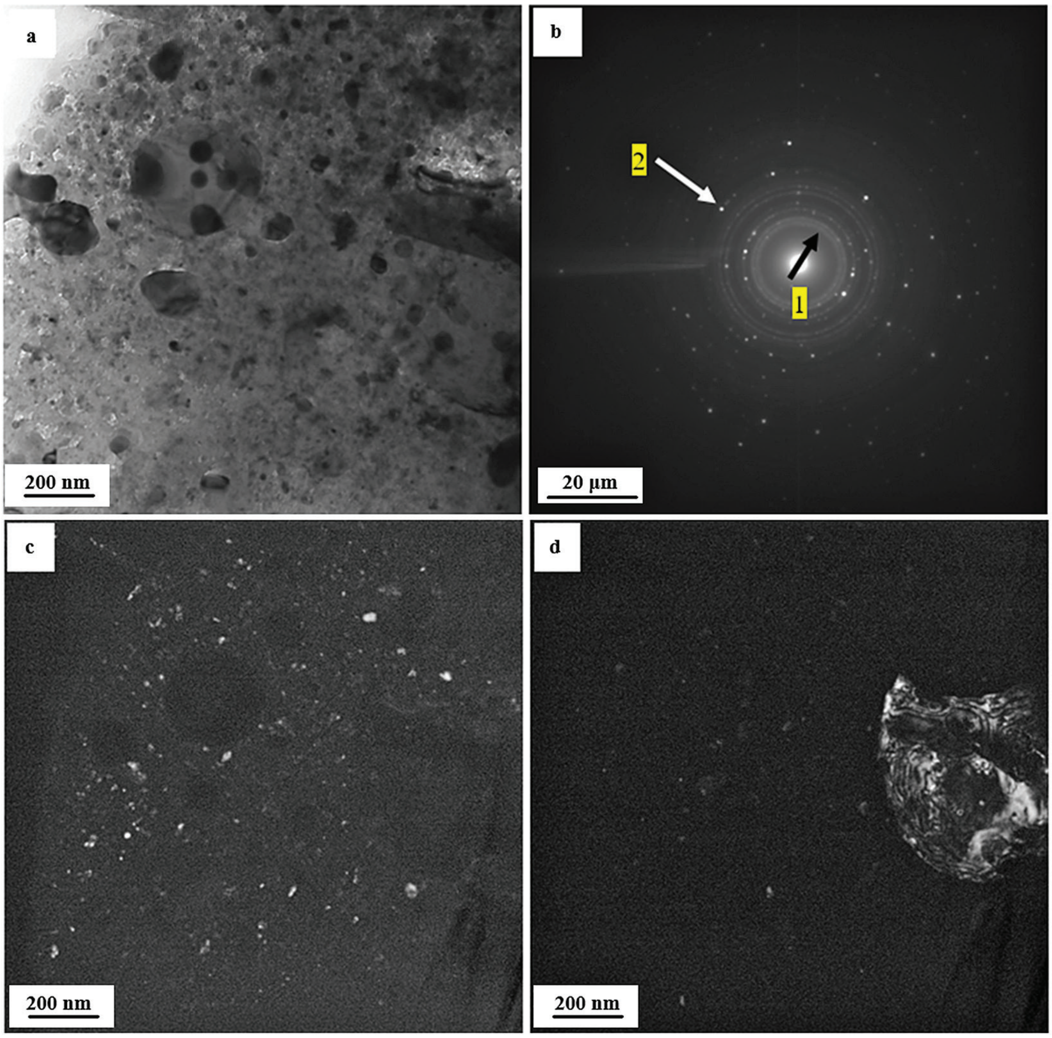

Figure 1. The type 1 structure of the contact zone of the coating and substrate; (a) — a bright field; b-a microelectron diffraction pattern; (c, d) — dark fields obtained in reflections [0-20]. MgAlO (c) and [222] Al; the arrows on (b) indicate, reflections in which dark-field are obtained: 1 — for (c), 2 — for (d)

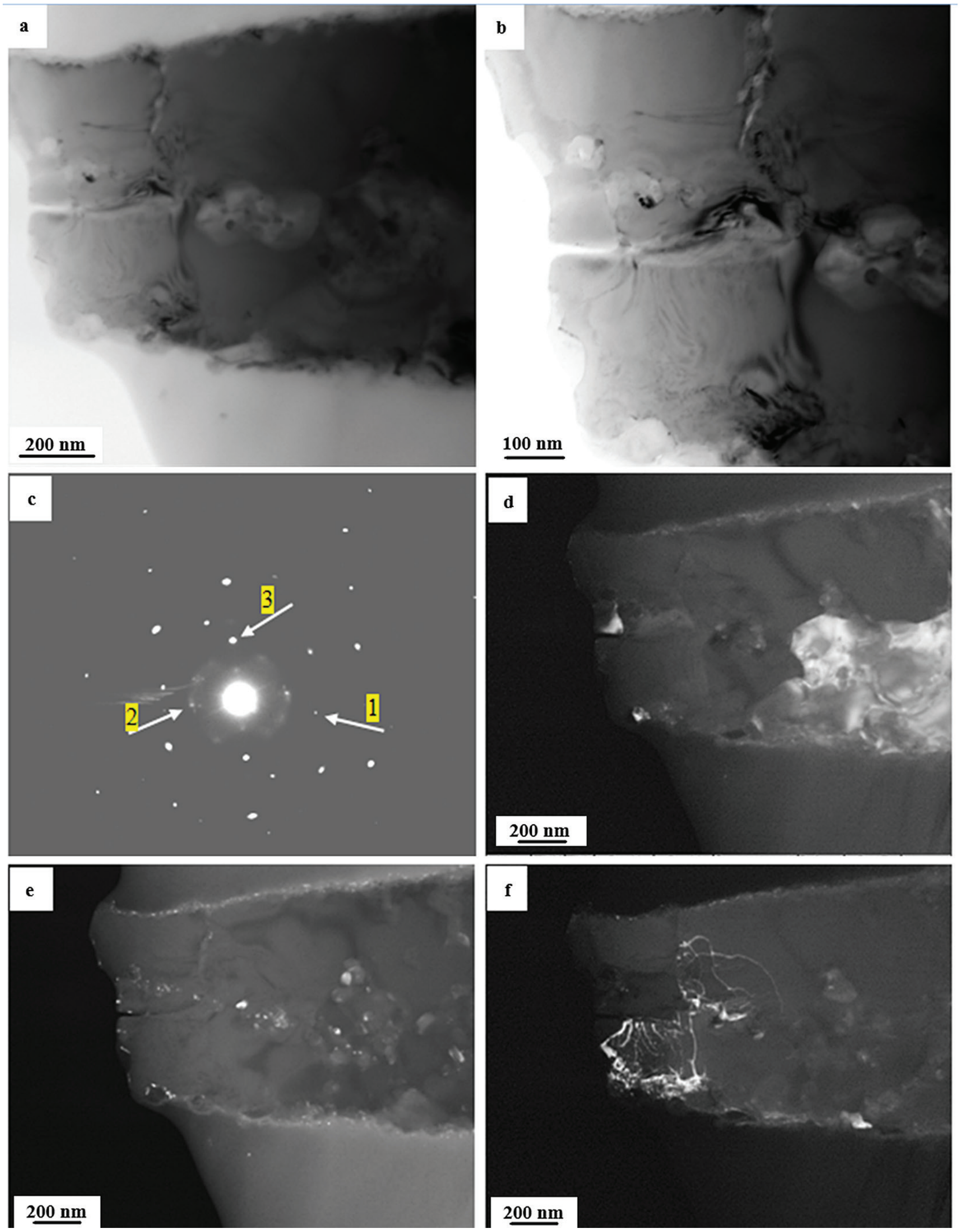

Figure 2. The 2 type structures of the contact zone of the coating and the substrate;(a, b) — bright fields; c–a microelectron diffraction pattern; (d–f) — dark fields obtained in reflections [210] HEA+[840] $(NiCo)_3Al_4$ (d), [620] $Al_{13}Fe_4$ (e), [111] HEA (f); the arrows on (b) indicate reflections in which dark fields are obtained: 1 — for (d), 2 — for (e), 3 — for (f)

Figure 2 presents the TEM images of the 2 type structure of the contact zone and the substrate. The analysis of the microelectron diffraction pattern depicted in Figure 2, c showed that the foil portion is formed by the HEA with a subgrain structure (Figure 2, d, f). The nanodimensional particles $(NiCo)_3Al_4$ (Figure 2, d) and $Al_{13}Fe_4$ (Figure 2, e) are revealed along subgrain boundaries.

Conclusion

By the method of wire-arc additive manufacturing the coating (the CoCrFeNiAl HEA) — substrate (the 5083 alloy) system has been produced. A gradient character of changes in microhardness in the contact zone has been shown. The elemental and phase composition, defective substructure of the HEA CoCrFeNiAl coating depend on a distance to the contact zone of the coating and the substrate. In the contact zone [zone of mixing (alloying) of the coating and the substrate] two types of structure have been detected. First that of the structure formed by nanodimensional (10–20 nm) particles of an oxide phase (the Al_2O_3 and the MgAlO), Al subgrains and the HEA. Second, structure formed by the HEA subgrains (140–170 nm), and nanodimensional particles the $(NiCo)_3Al_4$ and the $Al_{13}Fe_4$ located at subgrain boundaries.

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