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MANUFACTURING LIGHTWEIGHT HONEYCOMB PANELS ON THE BASE OF HIGH-ENTROPY $CoCrFeNiSi_{0.2}$ ALLOY FOIL PRODUCED BY EB-PVD METHOD

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ABSTRACT

The possibility of manufacturing thin foils of high-entropy alloys (HEA) of Co–Cr–Fe–Ni–Si system by the method of high-speed (up to 10 μm/min) electron beam physical-vapour deposition (EB-PVD) is shown in the work. It was established that silicon content in the alloy composition of approximately 5 wt.% improves the values of high-temperature resistance of basic CoCrFeNi HEA. It is shown that at soaking in air for 28 h at the temperature of 1000 °C the specific change in the weight of $CoCrFeNiSi_{0.2}$ sample is not more than 0.9 mg/cm^2. A technological scheme was proposed of manufacturing by welding three-layer thermal protection honeycomb panels with a low specific weight based on thin foils of high-entropy $CoCrFeNiSi_{0.2}$ alloy. It was found that the produced by the proposed scheme three-layer thermal protection panels can stand multiple thermal cycling from 25 to 1000 °C in air without the structure failure. The derived results can be the base for development of the technology of manufacturing lightweight honeycomb structures, capable of ensuring thermal protection of aerospace equipment elements at their interaction with the atmosphere.

KEYWORDS: high-temperature resistance; high-entropy alloys; thin foils; electron beam deposition; three-layer honeycomb panels; thermal protection

INTRODUCTION

Successful operation of modern flying vehicles, moving in the atmosphere at supersonic speeds and designed for multiple takeoff and landing cycles, necessitates reliable thermal protection of their skin from overheating and damage as a result of interaction with the atmosphere [1]. Experience of service of thermal protection structures based on ceramic materials, which were applied in Buran and Space Shuttle flying vehicles, showed their insufficient reliability and difficulty in maintenance. Technical problems of operation of such structures and their low cost-effectiveness make it necessary to carry on investigations aimed at creation of new systems, both in terms of development of the design of thermal protection panels, and high-temperature materials for their fabrication. Lightweight thermal protection honeycomb panels (LTPHP) are considered as one of the most promising and effective methods of solving the problem of protection of structural elements of aerospace equipment from heating at interaction with the atmosphere. Special attention is paid to three-layer honeycomb structures of thermal protection panels based on metal systems. Three-layer panel is a structure, consisting of two thin cover sheets with the core placed between them. The cover sheets take the in-plane longitudinal loads (stretching, compression and shear). The core takes the transverse forces in the bend of three-layer structure and ensures the redistribution of forces between the cover sheets. Such a design of thermal protection panels can provide a combination of high strength and rigidity with the low specific weight, due to application of sheet metal materials [2, 3]. The sheet materials for LTPHP manufacturing should have a set of such properties as high-temperature resistance, strength and low specific weight. Alloys based on Ni–Cr, Ti–Al, Ti–Nb–Al systems and some other widely known high-temperature alloys are the most often used as materials for LTPHP cover sheets. Thin foils are usually produced by rolling bulk billets, which are formed from the melt or by powder metallurgy methods. Such an approach, however, significantly complicates the process of producing sheet materials. Moreover, thermodeformational treatment of the billets is accompanied by formation of a resistant oxide film on the foil surface, which greatly complicates producing permanent joints. In this connection, producing thin foil with the required set of properties and its joining methods remain relevant up to now.

On the other hand, we showed that thin foils based on high-temperature alloys can be produced directly during condensation of the vapour phase in vacuum at evaporation of an alloy of the specified chemical composition [4]. Such an approach allows producing sheet metal materials with a controlled structure and thickness, avoiding the limitations, which are inherent to the traditional metallurgical and thermomechanical treatment methods. It greatly enhances the possibilities of using a wide class of high-temperature alloys, and allows prevention of dense oxide film formation on the foil surface which hinder application of welding in fabrication of structures from such materials.

At the same time, development of new alloys with the required set of properties is also important, when creating the technology of fabrication of thermal protection panels. From this viewpoint, so-called HEA attract considerable attention [5]. It is noted that these alloys are characterized by stability in a broad temperature range, and have relatively high values of strength and high-temperature resistance.

In the previous works, the authors [6–8] showed that the method of high-speed electron beam deposition allows producing thin foils from CoCrFeNiCu HEA with a rather wide range of micromechanical characteristics, high damping properties and weldability. It was also shown that at high-temperature resistance testing at the temperature of 900 °C in atmospheric air, foils from CoCrFeNi alloy demonstrate rather high values of high-temperature resistance due to formation of low-defect continuous scale based on Cr_2O_3 oxide on the surface [9].

In view of that the objective of this work was development of scientific fundamentals of the technology of manufacturing lightweight thermal-protection honeycomb panels, using thin foils of high-entropy alloy based on Co–Cr–Fe–Ni system, produced by the method of vacuum electron beam deposition.

EXPERIMENTAL

Foils of Co–Cr–Fe–Ni–Si system alloy were produced by the method of high-speed electron beam evaporation of the respective target-ingot with subsequent deposition of the vapour phase on a substrate from stainless steel (AISI 302), heated to the specified temperature. Foils of 80–100 μm thickness were deposited at the rate of approximately 8–10 μm/min at substrate temperature of 550–600 °C. To ensure foil separation from the substrate, a thin layer of CaF_2 salt was first deposited on it. Initial target ingots of 50 mm diameter were produced in an induction furnace.

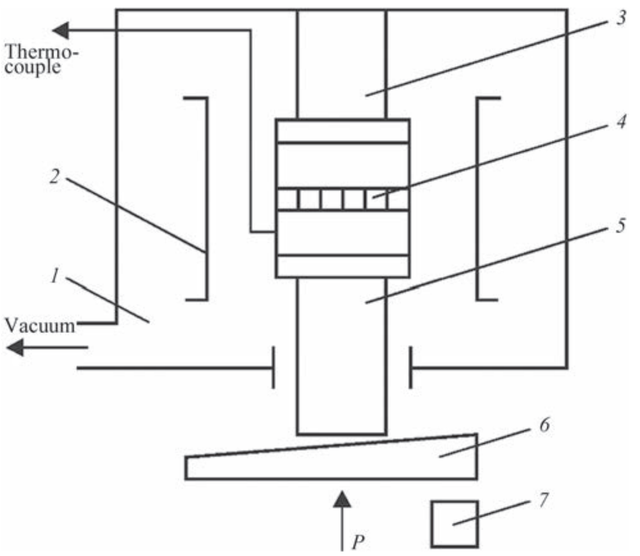

Figure 1. Scheme of the work chamber of diffusion welding unit; *1* — work chamber; *2* — molybdenum heater; *3* — upper rod; *4* — three-layer panel placed into a limiting sleeve; *5* — lower rod; *6* — wedge; *7* — press

Microstructural studies and local chemical analysis were conducted on transverse sections of the produced foils using scanning electron microscope (SEM) CamScan4, fitted with ENERGY 200 microanalyzer. Total thickness of the foil was assessed by electron microscopy images of the transverse section. X-ray diffractometer DRON-4M (Cu-K_α-radiation) was used to conduct phase analysis.

Evaluation of heat resistance of the produced foils was conducted by the change of the sample specific weight during long-term annealing at temperatures of 900 and 1000 °C in shaft-type electric furnace of SShOL-2.4/12.5 type in atmospheric air.

Foil of AISI 304 stainless steel 100 μm thick was used to produce the honeycomb core. Foil cutting up was conducted under the conditions of ensuring the required accuracy by sample length and prevention of appearance of tears or burrs. The profiled strip — honeycomb core was formed using the method of rolling in profiling rollers, which allows manufacturing corrugated strips with a high productivity [10].

The honeycomb core was manufactured by spot welding of the produced profiled strips, according to the scheme described in work [10]. The profiled strip surfaces were degreased with alcohol before their assembly into blocks. The strips were placed on a graphite electrode, which was manufactured, proceeding from overall dimensions of the honeycombs. The optimal process parameters for this foil thickness are current I = 300 mA, voltage U = 5 V at 2 mm diameter of copper electrode.

Joints of the honeycomb core with the cover sheets were produced by vacuum diffusion welding. Welding was performed using a specially designed fixture, which consists of the lower and upper flanges and limiting sleeve. The flanges provide pressing down to the honeycomb core over the entire cover sheet area during welding, and the limiting sleeve allows equalizing the temperature field in the product being welded. Figure 1 shows the schematic of the working chamber of the diffusion welding unit with the fixture installed in it. Welding temperature was monitored by the readings of chromel-alumel thermocouple mounted in the fixture. Pressure was applied to the parts being welded from the press through wedge *6* and lower rod *5*. Pressure value was monitored by a dynamometer. Heating of the fixture with the honey-

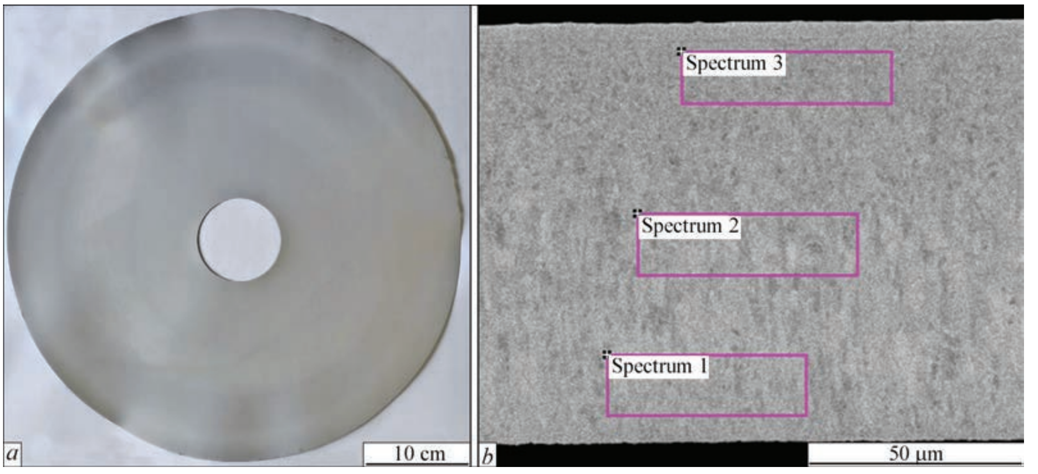

Figure 2. Appearance (*a*) and SEM image of the characteristic microstructure of the transverse section of deposited $CoCrFeNiSi_{0.2}$ HEA foils

comb panel mounted in it was conducted with the rate of 25–30 °C/min; pressure was applied after welding temperature has been reached (800 °C). The time of soaking at the welding temperature was 15 min, and after that the pressure level was lowered to zero and cooling to room temperature was conducted under vacuum.

RESULTS AND DISCUSSION

Earlier research established that copper content has an essential influence on the values of heat resistance of Co–Cr–Fe–Ni–Cu system alloys: with lowering of copper content in the alloy composition its heat resistance increases [9]. Also in works [11, 12] it was shown that alloying of CoCrFeNi base alloy by a small quantity of silicon may lead to a considerable increase of its heat resistance, as a result of formation of combined scale based on Cr_2O_3 and SiO_2 on the alloy surface. It was assumed that silicon content in the quantity of 5 wt.% will not influence the HEA structure, but will promote an increase in heat resistance at higher temperatures, due to formation of protective layers based on silicon oxides or chromium silicides on the foil surface. In view of that, the method of electron beam vacuum deposition was used to produce a series of foils of $CoCrFeNiSi_{0.2}$ alloy 80 to 100μm thick. Figure 2 shows the appearance and characteristic cross-sectional microstructure of the produced foils. Microstructural analysis showed that the optimized modes ensure formation of a homogeneous foil structure without macrodefects (cracks, pores, delaminations, etc.) with a uniform distribution of the components over the thickness (Table 1). The average concentration of elements in the foils corresponds to their concentration in the initial target-ingot. Foil specific weight is $8.1 \cdot 10^3$ kg/m^3.

Table 1. Chemical composition (wt.%) of $CoCrFeNiSi_{0.2}$ sections (Figure 2, *b*)

Section number	Cr	Fe	Co	Ni	Si
Spectrum 1	22.8	22.6	23.7	25.0	5.9
Spectrum 2	24.1	22.3	23.2	24.4	6.1
Spectrum 3	24.3	22.6	23.6	23.9	5.6

Assessment of heat resistance of the produced foils showed that soaking at the temperature of 900 °C for 28 h is accompanied by only a slight increase of sample weight: less than 0.2 mg/cm^2 (Figure 3, curve *2*). At the temperature of 1000 °C the oxidation kinetics of foil of $CoCrFeNiSi_{0.2}$ alloy obeys the parabolic law, which may be indicative of formation of a continuous protective oxide film on the surface. Here, the intensity of increase of the specific weight of $CoCrFeNiSi_{0.2}$ foil samples at the temperature of 1000 °C is lower, even compared to foils of HEA without silicon at the temperature of 900 °C [9]. That is addition of silicon in the quantity of about 5 wt.% promoted an increase of heat resistance, and also allowed raising the potential service temperature of the material application up to 1000 °C (Figure 3, curve *1*).

Analysis of the microstructure and chemical composition of $CorCrFeNiSi_{0.2}$ foils showed (Figure 4, *a*, *b*) that after annealing in air at the temperature of 1000 °C scale layers of up to 10 μm thickness form on the foil surface, foil bulk structure remains poreless,

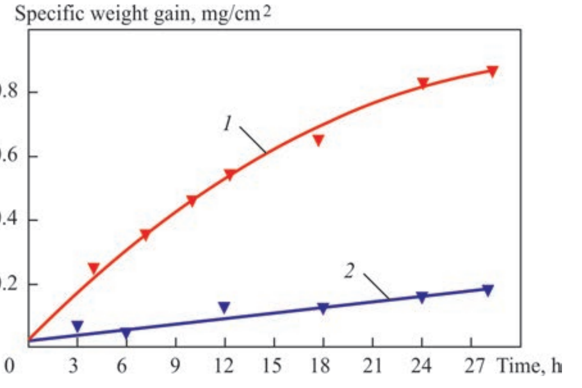

Figure 3. Oxidation kinetics of $CoCrFeNiSi_{0.2}$ alloy foil at the temperature of 1000 °C (curve *1*) and 900 °C (curve *2*)

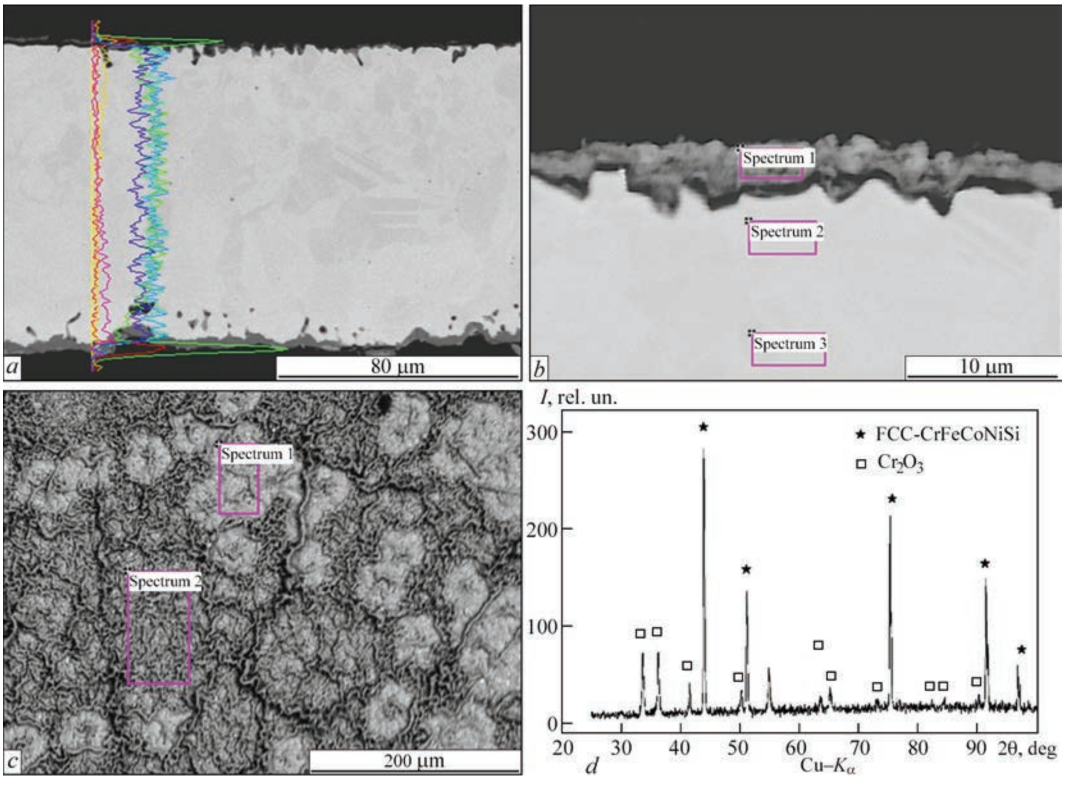

Figure 4. SEM images of cross-sectional microstructure (*a*, *b*) and surface (*c*) and diffraction pattern (*d*) of $CoCrFeNiSi_{0.2}$ HEA foils after heat-resistance testing at the temperature of 1000 °C

and formation of a small quantity of closed micropores located along the grain boundaries, is observed in the subsurface regions. At the same time, no oxygen was found in the subsurface regions of the foil. The scale surface is characterized by a sufficiently high level of continuity and low defect rate (Figure 4, *c*). Chemical analysis shows that scale consists predominantly of chromium, silicon and oxygen with a small content of the rest of the components (Table 2).

X-ray diffraction analysis revealed that the scale structure forms on the base of chromium oxide Cr_2O_3 (Figure 4, *d*). In view of the fact that no diffraction signs of formation of silicides or other silicon compounds were observed, and by the data of energy-dispersive microanalysis the scale and foil surface layer contain silicon, it is assumed that silicon can promote inhibition of oxygen diffusion along the grain boundaries, thus preventing formation of unstable iron oxides and, consequently, rapid "burning out" of the foil material. At the same time, greater chromium affinity for oxygen in such a case promotes formation of a protective layer based on chromium oxide on the foil surface.

In keeping with published data, three-layer panels with hexagonal core, in which the cell walls are normal to the main layers (cover sheets), became the most widely applied. Wide application of such honeycomb cores is associated with their ability to ensure high specific strength and adaptability to manufacture [13].

Moreover, considering that the size of the thermal protection honeycomb panel is usually much smaller than that of the surface, which is to be "protected", the shape of the three-layer panel proper has an important role. It is known that an area can be filled without gaps using three regular polygons: triangle, square and hexagon. A hexagonal panel has a number of advantages over a square or triangular one. First of all, a hexagonal panel can more effectively distribute the loads (for instance, at repeated entering of the dense layers of the atmosphere), as it has more neighbours, leading to a more uniform distribution of the load and smaller extreme values on any specific panel. Stresses are known to concentrate in acute angles, so that regular hexagons with angles of 120° have an obvious advantage over square panels with angles of 90° and

Table 2. Chemical composition (wt.%) of $CoCrFeNiSi_{0.2}$ sections (Figure 4)

Figure	Section number	Cr	Fe	Co	Ni	Si	O
Figure 4, *b*	Spectrum 1	39.3	8.5	6.8	4.7	8.4	32.3
	Spectrum 2	16.4	25.2	27.8	28.3	2.3	0
	Spectrum 3	14.2	25.1	28.9	29.6	2.2	0
Figure 4, *c*	Spectrum 1	44.9	6.3	7.0	6.7	7.4	27.7
	Spectrum 2	54.8	3.5	4.1	3.9	6.5	27.2

triangular panels with angles of 60°. Moreover, in the case of application of square panels straight regions of parallel welds can form along the rows, in which the heated gas flows will be accelerated, causing erosion wear of the panel materials, while application of a hexagonal panel will ensure distribution of the gas flows, as in this case extended continuous welds, parallel to the gas flow, will be absent. Another advantage of a hexagonal panel over a triangular or square one is a more uniform heating and cooling. Usually considerable overheating in the corners is noted in square and triangular parts, compared to the central areas of the parts.

In view of that, it was exactly the hexagonal shape of the thermal protection honeycomb panel, which was selected for making model samples. A sketch of a model sample of the three-layer honeycomb panel is given in Figure 5. Such a shape of the panel can ensure a more rational and effective covering of curvilinear surfaces or surfaces of the bodies of revolution, compared to panels of a square or rectangular shape.

The technological process of manufacturing a mockup of thermal protection honeycomb panel includes the following operations [14]: making skins (cover sheets); making blanks for honeycomb core; formation of profiled strips from the blanks; welding of the honeycomb core; manufacturing the honeycomb panels.

The procedure described above was used to manufacture honeycomb core elements of the required size and to join them to each other by spot welding. The appearance of the produced honeycomb core pack is shown in Figure 6. The outer frame is made from $CoCrFeNiSi_{0.2}$ HEA foil strip, which was joined to the honeycomb core by spot welding. Frame welding mode was the same as in welding the honeycomb core.

To ensure uniform height for all the honeycomb core elements and eliminate the residual cutting, as-

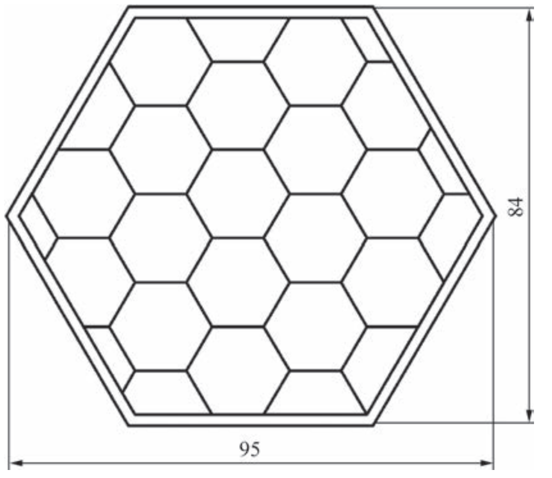

Figure 5. Sketch of the mockup of a three-layer thermal protection honeycomb panel

sembly and welding defects, the manufactured honeycomb cores were ground on a surface grinding machine from both sides. After grinding the honeycomb core height was 10 mm in all the cases.

The cover sheets in the form of a regular hexagon with side length of 48.5 mm were mechanically cut from the produced $CoCrFeNiSi_{0.2}$ HEA foils according to pattern. In such a case the area of the cover sheet working surface is about 60 cm^2.

The manufactured elements of the three-layer panel (lower cover sheet, honeycomb core and upper cover sheet) were placed into the fixture, installed in the working chamber of the diffusion welding unit, and their joining was performed.

In such a way, a series of samples of three-layer honeycomb panels of a hexagonal shape were made (Figure 7) with dimensions according to the drawing given in Figure 5. The structure specific weight was 3.3 kg/m^2.

The made mockups of three-layer honeycomb panels were tested for structure resistance to cyclic thermal loads. Testing was conducted using electric

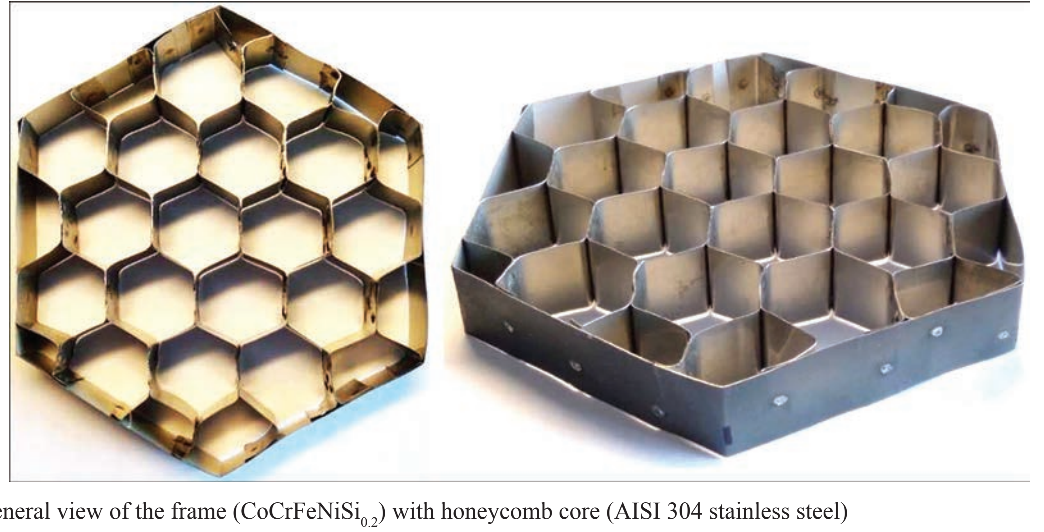

Figure 6. General view of the frame ($CoCrFeNiSi_{0.2}$) with honeycomb core (AISI 304 stainless steel)

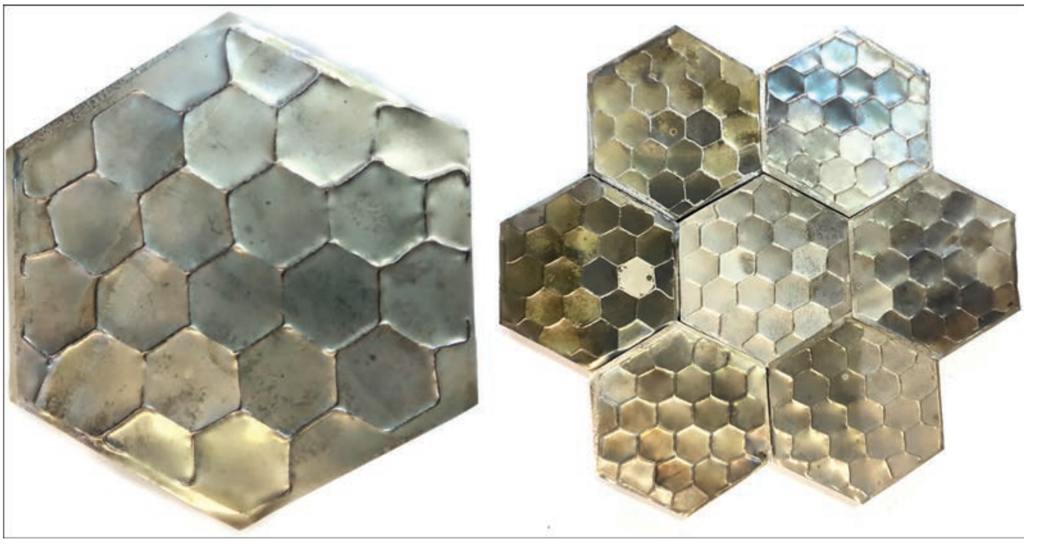

Figure 7. General view of the manufactured three-layer honeycomb panels

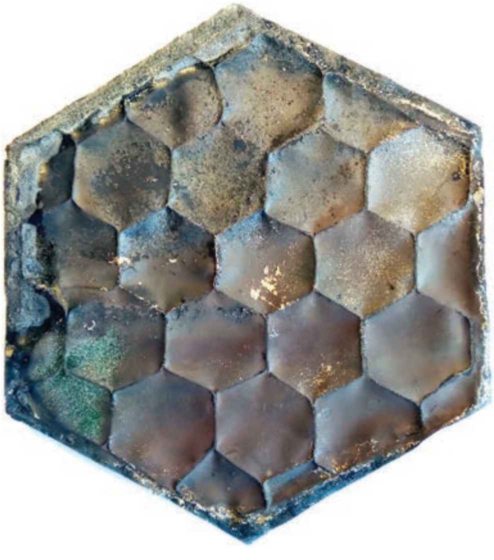

Figure 8. General view of the made mockup of the three-layer panel after 10 heat treatment cycles

furnace SShOL-2.4/12.5 of shaft type by a scheme, in which one cycle consisted of placing the panel into a furnace heated up to the temperature of 1000 °C, soaking for 30 min, removing from the furnace, and cooling to room temperature. Figure 8 shows the appearance of a mockup of a three-layer honeycomb panel after 10 heat treatment cycles. The integrity of the panel skin (cover sheets) and frame (honeycomb core) after thermal cycling should be noted.

Electron microscopy investigations revealed that the developed diffusion welding modes ensure formation of a sound joint of the honeycomb core and the cover sheets: one can see formation of the diffusion zone of up to 20 μm length with a smooth redistribution of elements between the material of the core and the cover sheets (Figure 9). Presence of a linear porosity of predominantly submicron size in the zone of the stainless steel and HEA joint is indicative of intensive

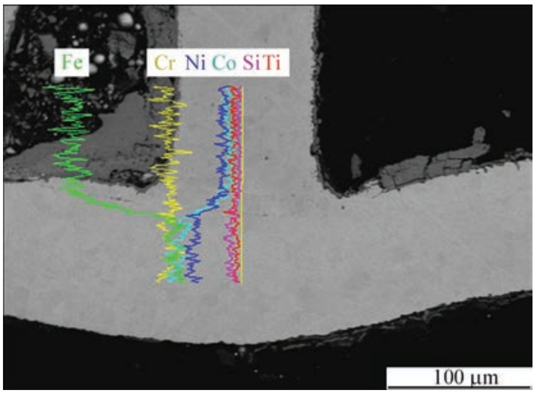

Figure 9. Electron image of the cross-sectional microstructure of the zone of core and cover sheet joint in the three-layer panel after testing at the temperature of 1000 °C

diffusion interaction between them with unbalanced flows of atoms, which causes the Kirkendall effect.

CONCLUSION

1. Modes of high-speed EB-PVD process were optimized, which ensure producing thin foil of high-entropy alloy of Co–Cr–Fe–Ni–Si system with uniform structure across the thickness.

2. It was found that the proposed $CoCrFeNiSi_{0.2}$ alloy ensures a combination of the required level of heat resistance with weldability in the solid phase.

3. Shown is the possibility of manufacturing by solid-phase welding of three-layer honeycomb panels based on thin $CoCrFeNiSi_{0.2}$HEA foils produced by the method of electron beam deposition, which can stand multiple thermal cycling from 25 up to 1000 °C in air without structure failure.

REFERENCES

1. Takayuki, K., Hideyuki, T., Syunsuke, I. et. al. (2011) Conceptual study on heat resistant and cooling system of hypersonic airplanes. In: *Proc. of 17th AIAA Inter. Space Planes and Hypersonic Systems and Technologies Conf. (San Fran-*

cisco, CA, USA, April 11–14, 2011), 1–12. DOI: https:// doi. org/10.2514/6.2011-2378
2. Rakesh, K.K., Hazem, E.S., Summit, V. et al. (2008) Static Analysis of Sandwich Panels with Square Honeycomb Core. *AIAA J.*, **46**, 627–634. DOI: https://doi.org/10.2514/1.28121
3. Boudjemai, A., Amri, R., Mankour, A. et. al. (2012) Modal analysis and testing of hexagonal honeycomb plates used for satellite structural design. *Materials and Design*, **35**, 266–275. DOI: https://doi.org/10.1016/j.matdes.2011.09.012
4. Semiatin, S.L., Gross, M.E., Matson, D.W. et. al. (2012) Microstructure evolution and composition control during the processing of thin-gage metallic foil. *Metallurg. and Mater. Transact. A*, **43**, 4819–4834. DOI: https://doi. org/10.1007/ s11661-012-1255-9
5. Murty, B.S., Yeh, J.W., Ranganathan, S. (2014) *Chapt. 2 — High-entropy alloys: Basic concepts*. Eds by B.S. Murty, J.W., Yeh, S., Ranganathan. In: High entropy alloys. Butterworth-Heinemann, Oxford, UK, 13–35, DOI: https:// doi. org/10.1016/B978-0-12-800251-3.00002-X
6. Ustinov, A.I., Polishchuk. S.S., Demchenkov, S.A. et. al. (2020) Formation of thin foils of high-entropy CrFeCoNiCu alloys by EB-PVD process. *Surf. and Coat. Technol.*, **403**, 126440. DOI: https://doi.org/10.1016/j.surfcoat.2020.126440
7. Ustinov, A.I., Skorodzievskii, V.S., Demchenkov, S.O. et al. (2020) Effect of the structure of vacuum condensates of high entropy alloys of Cr–Fe–Co–Ni–Cu system on their mechanical properties. *Suchasna Elektrometal*., **4**, 16– 22. DOI: https://doi.org/10.37434/sem2020.04.03
8. Ustinov, A.I., Demchenkov, S.A., Melnychenko, T.V. et. al. (2021) Effect of structure of high entropy CrFeCoNiCu alloys produced by EB PVD on their strength and dissipative properties. *J. of Alloys and Compounds*, **887**, 161408. DOI: https:// doi.org/10.1016/j.jallcom.2021.161408
9. Ustinov, A.I., Demchenkov. S.O., Melnichenko, T.V. et. al. (2022) The influence of copper on the heat resistance of thin foils of high-entropy alloys of the Cr–Fe–Co–Ni–Cu system obtained by the electron beam deposition method. *The Paton Welding J*., **11**, 39–44. DOI: https://doi.org/10.37434/ tpwj2022.11.07
10. Gusarova, I.A., Parko, M., Potapov, A.M. et al. (2016) Evaluation of high-temperature resistance of three-layer honeycomb panel produced from YuIPM-1200 alloy by vacuum diffusion welding. *The Paton Welding J.,* **12**, 29–33.
11. Kai, W., Cheng. F.P., Liao, C.Y. et. al. (2018) The oxidation behavior of the quinary FeCoNiCrSix high-entropy alloys. *Materials Chemistry and Physics*, **210**, 362–369. DOI: https:// doi.org/10.1016/j.matchemphys.2017.06.017
12. Li, Y., Zhang, P., Zhang, J. et. al. (2021) Oxidation behavior of AlCoCrFeNiSix high-entropy alloys at 1100 °C. *Corrosion Sci.*, **190**, 109633. DOI: https://doi.org/10.1016/j. corsci.2021.109633
13. Kobelev, V.N., Kovarsky, L.M., Timofeev, S.I. (1984) *Calculation of three-layer structures*. Moscow, Mashinostroenie [in Russian].
14. Bitzer, T.N. (1997) *Honeycomb technology. Materials, design, manufacturing, applications and testing*. New York, Chapman & Hall.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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