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MnFeCoNiCu HIGH-ENTROPY ALLOYS FORMED BY DETONATION SPRAYING OF A POWDER BLEND FOLLOWED BY LASER TREATMENT

MnFeCoNiCu LEGURE VISOKE ENTROPIJE FORMIRANE EKSPLOZIVNIM NANOŠENJEM SMEŠE PRAŠKA I NAKNADNOM LASERSKOM OBRADOM

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Keywords
- high-entropy alloy
- powder
- detonation spraying
- laser treatment

Abstract

Formation of a MnFeCoNiCu high-entropy alloy by detonation spraying of a powder blend followed by laser treatment is reported for the first time. As the blend components differ by the deposition efficiencies, the composition of the deposited material may differ from the composition of the feedstock powder. In the coating formed from an equimolar mixture, the concentrations of iron and nickel are significantly higher than in the feedstock mixture. The composition of the feedstock powder is adjusted via decreasing the concentrations of nickel and iron to render the composition of the deposited layer close to the desired composition. A mixture containing 26Mn+11Fe+22Co+13Ni+28Cu (at.%) forms a $Mn_{20}Fe_{18}Co_{22}Ni_{18}Cu_{22}$ *coating. The laser treatment of the deposited layer allows for producing solid solutions of face-centred cubic structure. In the resolidified material, the interdendritic space is enriched by copper.*

Ključne reči
- legure visoke entropije
- prašak
- eksplozivno nanošenje
- laserska obrada

Izvod

Formiranje MnFeCoNiCu legure visoke entropije eksplozivnim nanošenjem smeše praška sa naknadnom laserskom obradom se ovde iznosi prvi put. S obzirom da se komponente smeše razlikuju u efikasnosti nanošenja, sastav nanesenog materijala može se razlikovati u odnosu na sirovinski sastav praška. U prevlaci sačinjenoj od ekvimolarne mešavine, koncentracije železa i nikla su znatno veće u odnosu na sirovinski sastav. Sastav sirovinskog praška se reguliše smanjenjem koncentracija nikla i železa kako bi se postigao sastav nanetog sloja u bliskim granicama zahtevanog sastava. Mešavinom 26Mn+11Fe+22Co+13Ni+28Cu (at.%) se formira prevlaka $Mn_{20}Fe_{18}Co_{22}Ni_{18}Cu_{22}$. *Laserska obrada nanetog sloja omogućava stvaranje čvrstih rastvora strukture tipa kubne površinski centrirane rešetke. U prekristalisanom materijalu, međudendritski prostor je obogaćen bakrom.*

INTRODUCTION

MnFeCoNiCu high-entropy alloys (HEAs) have been the subject of recent studies owing to their interesting properties /1-3/. In the production of cermets, MnFeCoNiCu HEAs can be used as binders /1/. Nanoparticles of MnFeCoNiCu are found to show a photocatalytic behaviour and are suggested for use in water treatment systems /2/. The alloys have been obtained by electrodeposition /3/, solution combustion synthesis /4/ or induction melting, followed by annealing and ball milling /2/. The phase composition of MnFeCoNiCu HEAs depends on the atomic concentrations of the elements. In the electrodeposited MnFeCoNiCu HEAs, the body-centred cubic (bcc) and face-centred cubic (fcc) phases are found /3/. The crystalline structure of the alloy determines its corrosion resistance. Thermodynamic calculations show that, in the equimolar MnFeCoNiCu HEA, a secondary Cu-rich fcc phase precipitates below 1000 °C /1/. It should be noted that the microstructure of a HEA alloy formed via liquid phase-assisted processing depends on the grain boundary wetting phenomenon /5/. As the melt solidifies, the crystals and liquid coexist for a certain period of time. The remaining liquid can wet the grain boundaries of the solid material to a different extent (complete or incomplete wetting).

For broader applications of MnFeCoNiCu HEAs, the possibilities of forming MnFeCoNiCu coatings with a controlled composition should be sought. In this work, the formation of a MnFeCoNiCu HEA by detonation spraying of a powder blend followed by laser treatment is reported for the first time. To compensate the losses of certain components, the composition of the feedstock powder is adjusted to produce a layer with a composition close to the target composition $Mn_{20}Fe_{20}Co_{20}Ni_{20}Cu_{20}$. The laser treatment is used to homogenise the alloy coating to produce a solid solution structure via melting and solidification processes.

MATERIALS AND METHODS

The initial feedstock powder blends had a composition of 20Mn-20Fe-20Co-20Ni-20Cu (at.%). The mixture is prepared from manganese (95 %), atomised iron (99.8 %), electrolytic cobalt (99.5 %), carbonyl nickel (99.9 %), and electrolytic copper (99.7 %) powders. The composite layers are formed by detonation spraying on a computer-controlled detonation spraying facility (CCDS2000, Novosibirsk, Russia) /6/. The O_2/C_2H_2 molar ratio was 1.0. Composite layers are deposited on steel substrates. As the feedstock of the selected composition could not produce a layer of the same composition, compositional adjustments are made (Table 1).

Table 1. Powder blends and deposited layers (non-adjusted and adjusted compositions). Coating composition is determined by EDS (average values and standard deviations are given).

Blend component	Mn	Fe	Co	Ni	Cu
Non-adjusted					
Conc. in the feedstock, at.%	20	20	20	20	20
Conc. in the coating, at.%	14.5±1.0	31.6±3.5	15.9±1.2	26.6±1.7	12.4±1.1
Adjusted					
Conc. in the feedstock, at.%	26	11	22	13	28
Conc. in the coating, at.%	20.4±1.8	17.1±3.7	22.3±0.8	18.0±1.6	22.1±1.4

For homogenising the deposited layers and producing a HEA, laser treatment in an argon atmosphere is applied. A FL-Clad-R-4 (IPG IRE-Polus, IPG Photonics Corporation, Russia) unit equipped with an ytterbium fibre-optics laser (wavelength 1065-1075 nm, power 4 kW) is used. The laser speed is 25 $mm \cdot s^{-1}$. The laser power is 900 W. This treatment mode allows forming of a HEA structure within a layer 200-250 μm thick.

X-ray diffraction (XRD) patterns of the as-sprayed and laser-treated samples are recorded using a D8 ADVANCE diffractometer (Bruker AXS, Germany) with Cu Ka radiation.

For the compositional adjustment, the analysis of the deposited layers using an EVO MA15 (Zeiss, Germany) microscope equipped with an energy-dispersive spectroscopy (EDS) unit (Oxford Instruments X-Max 80 mm^2, UK) is applied. The spectra are collected from the polished surface of the coatings, 10 rectangular areas 250×300 μm^2 in size are analysed and the average values of concentrations are reported.

The microstructure of the alloys is studied on the polished cross-sections by scanning electron microscopy (SEM) using an S-3400 N microscope (Hitachi, Japan). The back-scattered electron (BSE) imaging mode is used. Analysis of samples by elemental mapping is conducted on an EDS unit (NORAN Spectral System 7, Thermo Fisher Scientific Inc., USA) attached to the S-3400 N microscope.

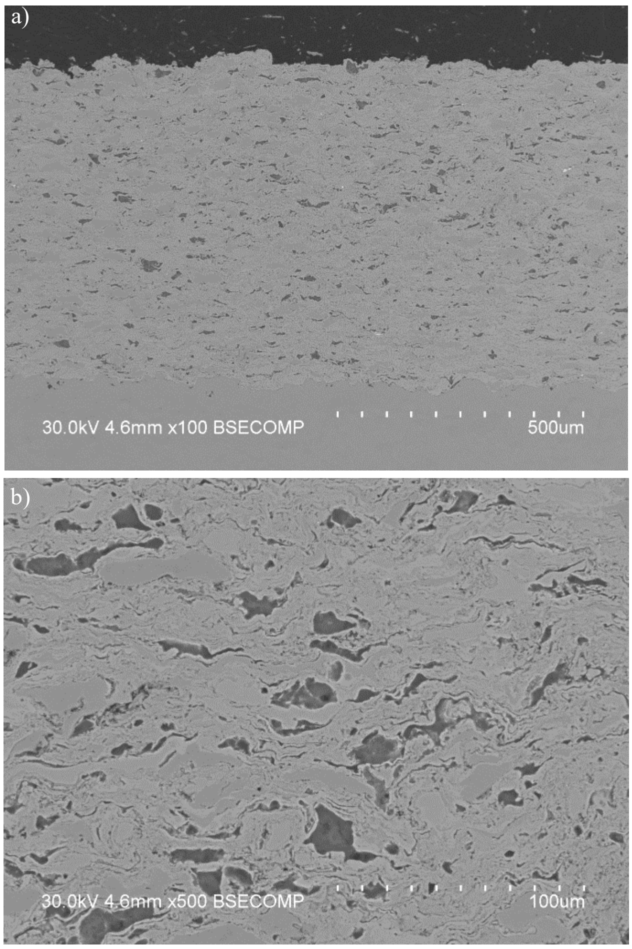
The porosity of the alloys is determined from the optical images of sample cross-sections using OLYMPUS Stream Image Analysis software, 'Stream Essentials 1.9.1' (Japan). The optical images are recorded on an OLYMPUS GX-51 metallographic microscope (Japan).

Vickers hardness of the alloys is measured using a Dura-Scan 50 hardness tester (EMCO-TEST, Austria) at a load of 0.3 kg on the polished cross-sections.

RESULTS AND DISCUSSION

Table 1 shows the composition of the feedstock powder blend corresponding to the target composition of the alloy. The changes in the composition of the coatings relative to the feedstock powder have been previously observed in our studies /7/. In the present work, the concentrations of the elements in the deposited layer sprayed using an equimolar blend are not fully preserved. In order to achieve the desired composition, certain adjustments are made. Based on the results obtained with the 20Mn+20Fe+20Co+20Ni+20Cu mixture, the concentrations of iron and nickel are reduced in the feedstock blend. The adjusted composition of the blend and the composition of the layer formed by spraying of this blend are given in Table 1.

Figure 1(a, b) shows the general view and microstructure of the $Mn_{20}Fe_{18}Co_{22}Ni_{18}Cu_{22}$ coating, which consists of lamellae of different compositions. The XRD patterns of the as-deposited and laser-treated coatings are shown in Fig. 2. The coating formation is accompanied by partial alloying between the metals (early stage of the alloy formation). The porosity of the as-sprayed composite coating was below 2 %. Upon laser treatment, the detonation sprayed layer of composite nature transformed into a HEA consisting of two fcc phases.



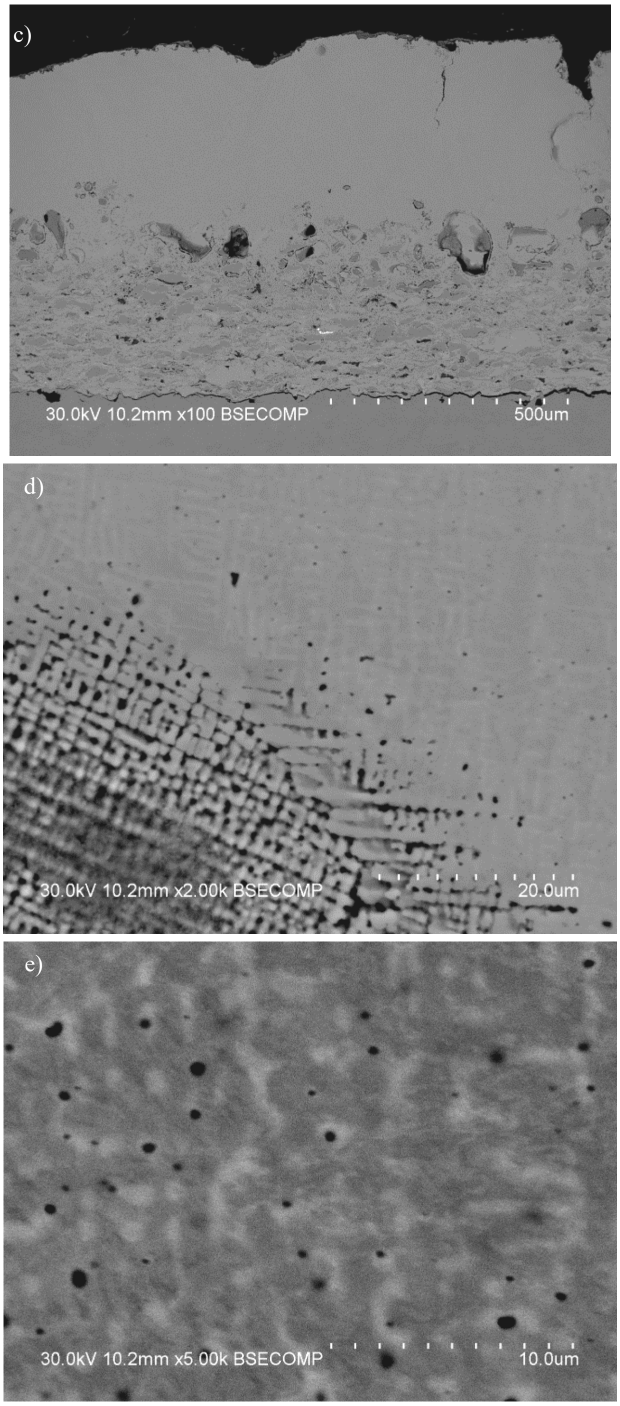


Figure 1. a) General view, and b) microstructure of the composite coating layer of adjusted composition ($Mn_{20}Fe_{18}Co_{22}Ni_{18}Cu_{22}$); c) general view, and d), e) microstructure of laser-treated layer; d) a dendritic non-polished region of the remelted alloy; e) polished area of cross-section at higher magnification.

The mapping results of the as-sprayed coating indicate its composite structure (Fig. 3a). The general view and microstructure of the remelted layer are shown in Fig. 1(c-e). The laser treatment results in partial melting of the deposited layer and its composition is homogenised through approximately half of its thickness. In the structure of the remelted layer, dendritic structures are found (Fig. 1d). In terms of composition, the remelted layer is rather uniform, as can be inferred from results of the EDS mapping (Fig. 3b). However, in a BSE image of the remelted zone (Fig. 1e), the evidence of compositional non-uniformities is present at the scale of the grain size (1 μm). Between dendritic grains, a Cu-rich phase is formed, as confirmed by the point EDS. The segregation effect in MnFeCoNiCu alloys is previously investigated in /8/. In that work, it is shown that non-equilibrium solidification of a $Mn_{35}Fe_{5}Co_{20}Ni_{20}Cu_{20}$ melt leads to the formation of dendrites, while a Cu- and Mn-rich liquid remains. This causes the formation of a grain boundary phase differing in the composition from the grains in the fully solidified material. The presence of XRD peaks from both phases is observed in /8/, which agrees with our results. The Cu-rich phase (solid solution 2, Fig. 2) demonstrates reflections at lower 2θ angles due to its larger lattice parameter compared with that of the phase of the dendrites (solid solution 1).

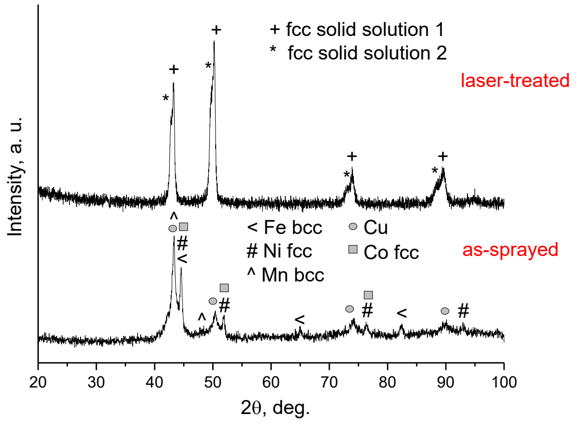


Figure 2. XRD patterns of as-deposited and laser-treated $Mn_{20}Fe_{18}Co_{22}Ni_{18}Cu_{22}$ layer (solid solutions: 1-dendrites, 2-interdendritic phase).

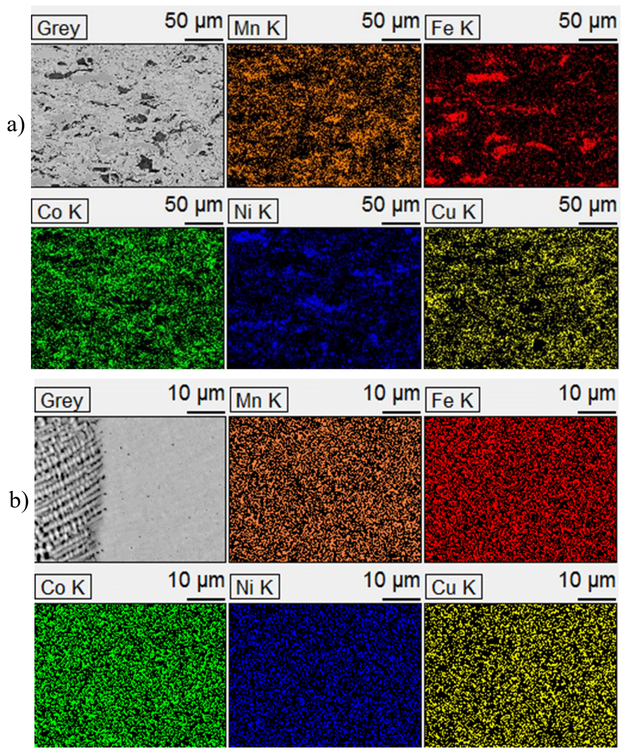


Figure 3. Elemental maps of MnFeCoNiCu layer deposited by detonation spraying (a), and the remelted part of the layer after laser treatment (b).

The hardness of the composite coating obtained in this work is measured to be 350 ± 10 $HV_{0.3}$. This value is close to the hardness of the as-sprayed and spark plasma sintering-treated coatings reported in /9/. The layer remelted by laser treatment shows a diminished hardness of 226 ± 10 $HV_{0.3}$, which is explained by laser treatment-induced grain growth. The porosity of the laser-treated layer is not determined as melting resulted in the formation of macrodefects. Future work should focus on optimising the laser treatment conditions to eliminate the macrodefects in the structure of laser-treated layers.

CONCLUSIONS

A MnFeCoNiCu HEA is obtained by detonation spraying of a powder blend followed by laser treatment for the first time. In order to make up for the losses of the blend components during spraying, the composition of the feedstock powder blend is adjusted to form a composite layer with a composition close to the target composition. A mixture containing 26Mn+11Fe+22Co+13Ni+28Cu (at.%) forms a coating $Mn_{20}Fe_{18}Co_{22}Ni_{18}Cu_{22}$ (at.%). This novel approach has been proven successful and is promising for multi-component coatings of other compositions. The fact that the composite precursor coating can be formed from a powder blend with an adjusted composition eliminates the necessity of the production of pre-alloyed powders with fixed compositions. The laser treatment of the deposited layer allows for producing solid solutions of fcc structure.

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REFERENCES

1. Pötschke, J., von Spalden, M., Vornberger, A. (2023), *TiCN cermets with MnFeCoNiCu high entropy alloy binder*, Metals 13(7): 1259. doi: 10.3390/met13071259
2. Das, S., Sanjay, M, Kumar, S., et al. (2023), *Magnetically separable MnFeCoNiCu-based high entropy alloy nanoparticles for photocatalytic oxidation of antibiotic cocktails in different aqueous matrices*, Chem. Eng. J, 476: 146719. doi: 10.1016/j.cej.2023.146719
3. Aliyu, A., Srivastava, C. (2022), *Phase constitution, surface chemistry and corrosion behavior of electrodeposited MnFeCoNiCu high entropy alloy-graphene oxide composite coatings*, Surf. Coat. Technol. 429: 127943. doi: 10.1016/j.surfcoat.2021.127943
4. Aydinyan, S., Kirakosyan, H., Sargsyan, A., et al. (2022), *Solution combustion synthesis of MnFeCoNiCu and $(MnFeCoNiCu)_3O_4$ high entropy materials and sintering thereof*, Ceram. Int. 48 (14): 20294-20305. doi: 10.1016/j.ceramint.2022.03.310
5. Straumal, B.. Korneva, A., Kuzmin A., et al. (2022), *High entropy alloys for energy conversion and storage: A review of grain boundary wetting phenomena*, Energies, 15(19): 7130. doi: 10.3390/en15197130
6. Ulianitsky, V.Y., Dudina, D.V., Shtertser, A.A. Smurov, I. (2019), *Computer-controlled detonation spraying: Flexible control of the coating chemistry and microstructure*, Metals, 9(12): 1244. doi: 10.3390/met13091519
7. Ulianitsky, V.Yu., Rybin, D.K., Ukhina, A.V., et al. (2021), *Structure and composition of Fe-Co-Ni and Fe-Co-Ni-Cu coatings obtained by detonation spraying of powder mixtures*, Mater. Lett. 290: 129498. doi: 10.1016/j.matlet.2021.129498
8. Schneiderman, B., Chuang, A.C., Kenesei, P., Yu, Z. (2021), *In situ synchrotron diffraction and modeling of non-equilibrium solidification of a MnFeCoNiCu alloy*, Sci. Rep. 11: 5921. doi: 10.1038/s41598-021-85430-z
9. Batraev, I.S., Ulianitsky, V.Y., Shtertser, A.A., et al. (2023), *Fabrication of high-entropy alloys using a combination of detonation spraying and spark plasma sintering: A case study using the Al-Fe-Co-Ni-Cu system*, Metals, 13(9): 1519. doi: 10.3390/met13091519