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Cast Protective Coatings of Nano-Structured Polymetallic HEAs by Means of Centrifugal SHS Process

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Abstract

In this work, we for the first time attempted to fabricate cast HEAs containing $NiCrCoFeMnAl_x$ and $CrCoFeAlCu_x$ *etc.* by SHS-metallurgy. The investigated HEAs were prepared by combined centrifugal casting– metallothermic SHS. Combustion was performed at centrifugal accelerations a = 10–400 g.. Our SEM and XRD data suggest that thus synthesized cast HAEs represent a solid solution based on Fe and Ni containing uniformly distributed elements into volume of ingots. Increasing of Al (and Cu) content into HEAs was found to markedly change the microstructure and phase composition of HEAs. On the second stage we carried out a search for the reactive systems and process parameters that would be favorable for deposition of protective coatings of HEAs directly onto commercially available Ti and Fe alloys. The cast protective coatings are formed due to strongly heat exchange between high temperature alloys and substrate (based on Ti and Fe alloys). The phase composition and microstructure of protective coatings was investigated.

Keywords: Cast protective coatings, centrifugal SHS Process, HEA, polymetallic alloys.

Introduction

In recent years, a new alloy design concept that breaks the traditional principles of alloy design has been studied. High entropy alloys (HEAs) have attracted considerable attention around the World. Usually, alloy systems have been based mainly on one principal element as a matrix, such as iron, copper, aluminium, magnesium, titanium, etc. Many researchers have explored a wide range of bulk amorphous alloys where the concept of multicomponents is taken to drop the melting temperature and to increase the difficulty of crystallization [1-4]. However, one essential component of the alloys is usually more than 50%. It is known that when solubility is high, the solid solution based on one principal element can increase the strength of the solution due to the solution hardening. As the amount of alloying element increases, intermetallic compounds are typically formed in the alloy due to limited solid solubility, and this leads to increased strength, but at the expense of accompanying embrittlement. If the formation of intermetallic compounds were avoided where the alloy has a single crystal lattice, the alloy would have a better combination of strength and plastics. Based on the thermodynamic principle, a new alloy design concept, 'multiprinciple element alloy', was explored by Yeh et al. [5-7], which was named as high entropy alloys (HEAs) and consists of simple fcc or bcc solid solution phases. High entropy alloys as multi component alloys are composed of n major alloy elements with $n \geq 5$ in equimolar or near equimolar ratios. This leads to an increase in stability of the solution due to the maximizing the mixing entropy. Following Boltzmann's hypothesis on the relationship between entropy complexity the configurational entropy change per mole ΔS_{conf}, during the formation of a solid solution from *n* elements with equimolar fractions, may be calculated from $\Delta S_{conf} = R \ln (n)$ equation, where R is the gas constant. When n=5, $\Delta S_{conf} = 1.61\ R$, which comparable with the melting entropy of most intermetallic compounds (about R–2R). As results, intermetallic compounds are absent (or present in minor part) and a single solid solution is built with structures of a single fcc, a single bcc or fcc+bcc. Owing to the above structural and compositional characteristics it has been reported that HEAs possess many attractive properties, such as high hardness [8], outstanding wear resistance [9], good fatigue resistance characteristics [10], excellent high-temperature strength [11], good thermal stability [12] and, in general, good oxidation [9] and corrosion resistance [13]. These properties suggest great potential in a wide variety of applications. Most studies on HEAs are focused on the relationships between phase, microstructure, and mechanical properties. Although less attention was paid to the preparation mode. Nevertheless preparation of the multicomponent materials is not easy science and technological task. The high homogeneity (fine distribution of all elements into volume of alloy) should be provided.

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Currently, the main methods for the obtaining HEAs are classical vacuum furnace and/or powder metallurgy technologies. The common disadvantages of the both methods are high-energy consumptions, multistage (5-7 remelting), quantity/quality of suitable gas or vacuum needed along with the operation time. Besides the alloy consist of high chemical active component (Ti, Al, Zr, Hf *etc.*) requires expensive mold materials.
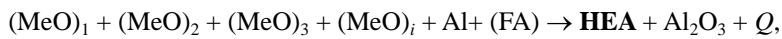
One of energy and cost saving processing method for the synthesis of a wide variety of materials, including cast alloys is Self- Propagating High Temperature Synthesis (SHS) frequently named as Combustion Synthesis. In the SHS process, after initiation, highly exothermic reaction becomes selfsustaining. The chemical conversion takes place in a combustion wave which moves over mixtures producing the desired product. Initial mixtures of metals and nonmetals (C, Si, B etc.) are used for SHS. To obtain cast materials in the combustion mode high exothermic initial mixtures of metal oxides, metal reducer and non-metals are used. The approach combines two material production methods, namely an aluminothermic process and SHS and is called as thermite-type SHS reactions or SHS-metallurgy [14]. Since the adiabatic combustion temperatures (T_{ad}) of the SHS reactions obtained by the high energetic precursor mixtures change between 2500 and 3500 K, the combustion products (alloy and oxide) are in liquid-phase state.

This study aimed at developing a new cost-effective process for fabricating cast $NiCrCoFeMnAl_X$, NiCrCoFeAlCu high-entropy alloys and deposition of such coatings through thermite-type SHS reactions in centrifugal machines.

1. Experimental procedure

1.2. Synthesis technique and processing conditions.

The SHS reaction yielding cast polymetallic HEAs can be represented in the form:

$$(MeO)_1 + (MeO)_2 + (MeO)_3 + (MeO)_i + Al + (FA) \rightarrow \textbf{HEA} + Al_2O_3 + Q,$$

where (MeO) = NiO, Cr_2O_3, Fe_2O_3, Co_3O_4, etc.; FA is an additive facilitating phase segregation, and Q the reaction heat. The flowsheet of the process is given in Fig. 1. Combustion was performed under centrifugal accelerations $a = 10$–$400\ g$.
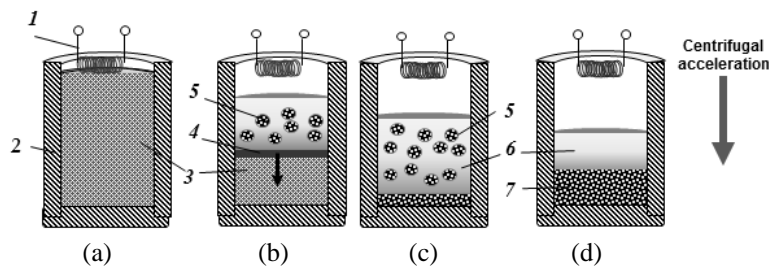

Fig. 1. Schematic of the process for fabrication of cast HEAs: (a) charge preparation, (b) combustion, (c) phase separation, (d) pattern formation: *1*, igniting coil; *2*, refractory mold; *3*, green composition; *4*, combustion front; 5, HAE globules in the melt; 6, oxide melt (Al_2O_3); and *7*, cast HEA.

Stoichiometric amount of aluminum, needed to reduce all the oxides, was added to the charges. Intermixing was performed in planetary mixer for 20 min. The blends were then placed in cylindrical graphite containers (inner diameter 40 mm) lined up with an alumina coating to minimize interaction with carbon. Then the crucible was fixed on rotor of SHS centrifuge machine [14]. After steadied rotation of the rotor the charge was ignited. Because the attained temperatures (up to 3000°C) are well above the m.p. of reaction products, the melt represents a mixture of mutually insoluble metallic (MMC) and oxide (Al_2O_3) phases. Due to strongly different specific weights, these phases undergo gravity-assisted phase segregation and subsequent interaction between high temperature alloys and substrate. As a result, a cast protective coating is formed. Combustion was performed at centrifugal acceleration $a = 10$–$200g$. In this way we expected to (a) improve the yield of target product, (b) remove gaseous byproducts, (c) diminish the grain size in the product, and (d) make product composition more uniform. Combustion products were characterized by SEM/EDS (Zeiss Ultra Plus microscope) and XRD (DRON-3 apparatus, Cu-K_a radiation, $2\theta = 10$–$80°$). Vickers hardness (H_V) was measured using an HVS-50 testing machine.

2. Results and discussion.

2.1. Chemical composition and microstructure of synthesized HEAs.

Table 1 shows the calculated composition of the alloys used in experiments. The comparison of calculated and nominal chemical composition reviled some differences. The amounts of Ni, Co, Cu and Fe were close to nominal values. The Cr and Mn content is slightly lower by 1.2–1.4 and 1.6–2.1 % , respectively. It can be explained by incomplete reduction of chromium and manganese oxides. As a result, excessive Al (by 0.6–0.8 %) is formed. The problem of deviation of nominal/calculated alloy composition was solved by addition some excessive amounts of Cr and Mn oxides into initial mixture as well searching optimal cavity conditions for synthesis. It is revealed that for all systems under study overload effect (centrifugal forces) assist more complete chemical conversion and as the result increase the yield of target products (capacity).

Table 1 Composition of alloys used in experiment.

Alloy	Atomic ratio	Element composition, weight %.						
		Ni	Cr	Co	Fe	Mn	Al	Cu
HEA-I	NiCrCoFeAlCu	18,5	16,8	18,6	17,6		8,5	20,0
HEA-II-0,6	NiCrCoFeMnAl$_{0.6}$	19,9	17,6	19,9	18,9	18,6	5,1	-
HEA-II-1,2	NiCrCoFeMnAl$_{1.2}$	18,7	16,5	18,8	17,8	17,5	10,7	-
HEA-II-1,6	NiCrCoFeMnAl$_{1.6}$	17,8	15,8	18,0	16,9	16,7	14,8	-
HEA-II-2,0	NiCrCoFeMnAl$_{2.0}$	16,9	14,9	17,0	16,1	15,8	19,3	-

In the future, all alloy composition obtained with above mentioned amendments had no deviations from the estimated more than 0.2 %. The obtained alloys with optimized composition were subjected cutting, polishing and subsequent microstructure analysis.

As follows from the SEM micrograph analysis of the obtained cast HEAs exhibits a clearly pronounced nanostructure. By the example of HEA-II-0,6; HEA-II-1,6 and HEA-II-2,0 the SEM micrographs are presented on Fig.2

(a) (b) (c)
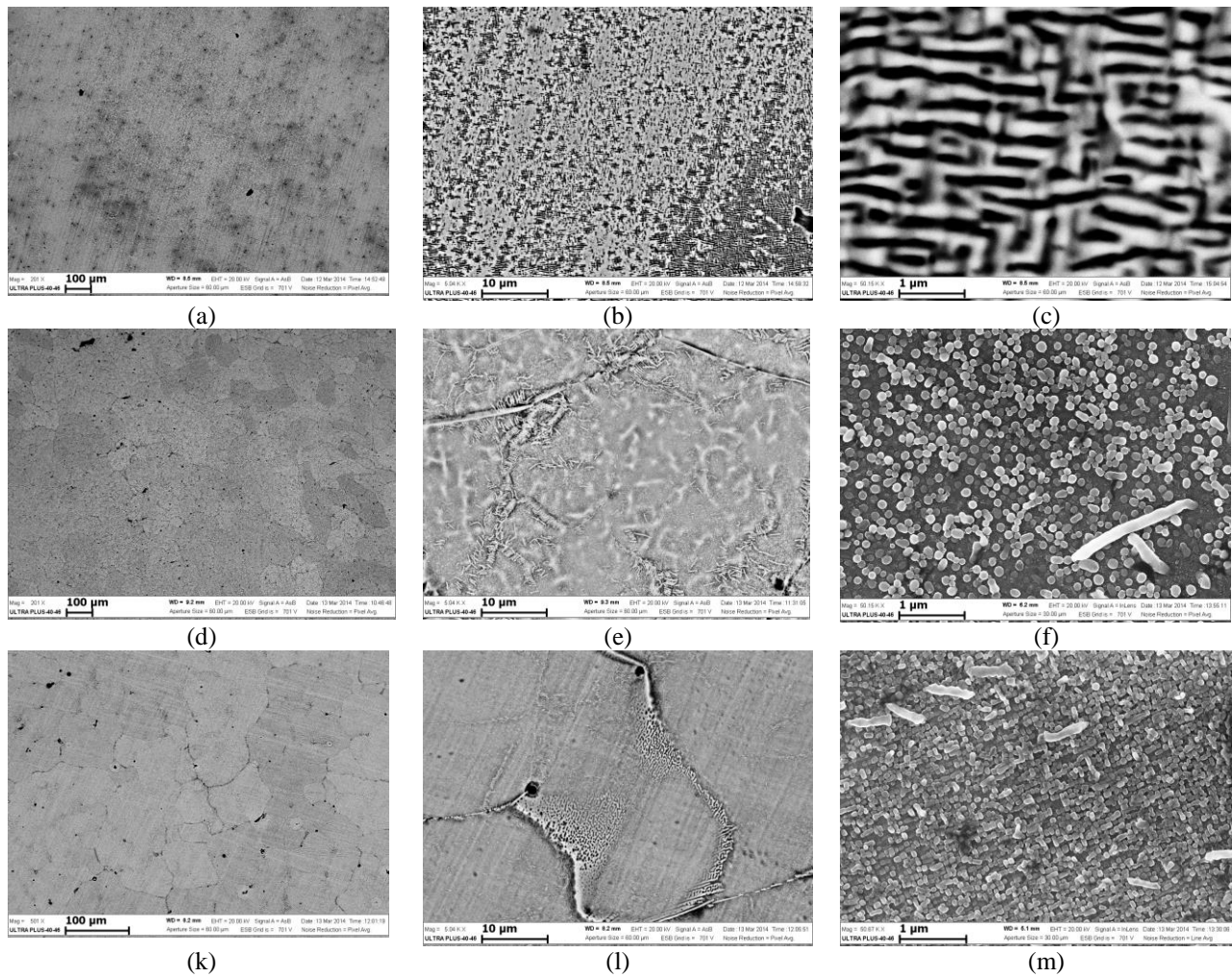
(d) (e) (f)

(k) (l) (m)

Fig. 2. SEM images of micrograph analysis of the obtained cast HEAs (after light etching).
(a-c)-HEA-II-0,6;   (d-f)-HEA-II-1,6;   (k-m)-HEA-II-2,0.

According XRD date cast HAE-I are formed by solid solution with Im3m structure (a=2,874 Å) and Cu reach solid solution with Fm3m structure (a=3,525 Å). Synthesized HEAs-II type alloys NiCrCoFeMnAlx with high Al (up to 19 wt. %) had unique nano-sized composite structure (Fig.2) which consist of NiAl as body phase and nano-sized (rounded shape) precipitates formed of polymetallic solid solution (FCC/BCC).

The Vickers hardness of the synthesized HEA-I was found to vary between 230 and 350 Hv., and HEAs-II type was found to vary between 400 and 800 Hv.

2.32. *SHS surfacing.*

On the second stage we carried out a search for the reactive systems and process parameters that would be favorable for deposition of protective coatings of HEAs directly onto commercially available Fe and Ti alloys. It was released by putting

the Ti (Fe) substrates into bottom of mould. The cast protective coatings are formed due to strongly heat exchange between high temperature alloys and substrate (Fig.3). The optimal experimental parameters for production of the cast protective coating were verified experimentally. The phase composition and microstructure of protective coatings was investigated. The gradient concentration of components over height of coatings was revealed (Fig.4). The Vickers hardness of SHS coatings of the cast HEA-I was found to vary between 240 and 450 Hv (Fig.5). This makes such coatings promising candidates for use in marine and aerospace propulsion engineering, power engineering, gas/oil transportation, structural engineering materials etc. This work can be regarded as the first positive experience of SHS surfacing by HAE.
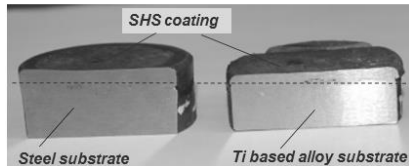

Fig. 3. Exterior view of samples after SHS surfacing *(cut-to-cross)*
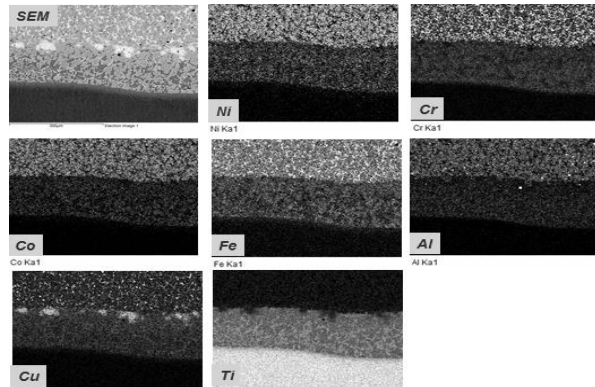

Fig. 4. X-ray element maps of SHS coating (HEA (I) / Ti alloy substrate
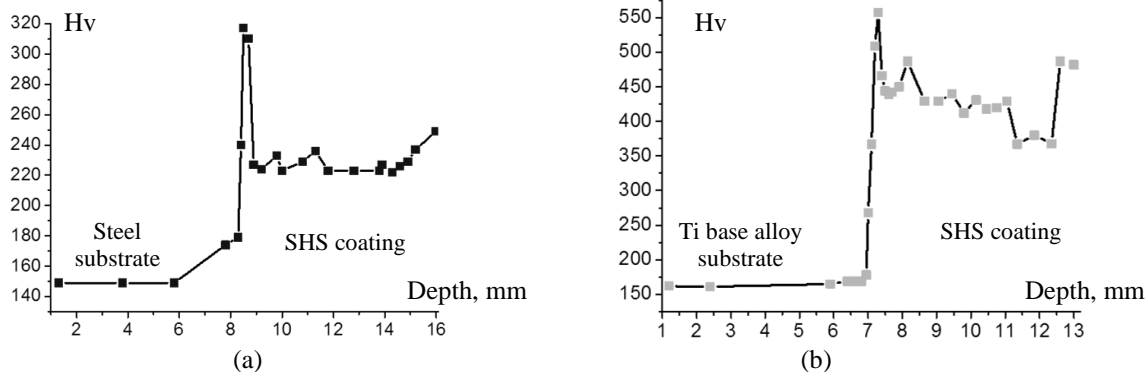

(a)

(b)

Fig. 5. Coating hardness vs. height of surfacing layer. (a)- HEA-I/steel substrate, (b)- HEA-I/Ti based alloy substrate,

Conclusion

For the first time, the equal atomic cast NiCrCoFeAl and NiCrCoFeAlCu high-entropy alloys (HEAs) were prepared by metallothermic SHS, as one of most cost-effective process. This work can be regarded as the first positive experience of SHS surfacing by cast HEAs on Fe/Ti alloy substrates. The present results can be expected to make engineering background for industrial-scale manufacturing of new cost-effective process for fabricating HEAs with valued properties and protective coatings based on them.

Acknowledgements

Reference
1. Takeuchi and A. Inoue: *Mater. Trans. JIM,* (2000) 41, 1372–1378.
2. A. Inoue, T. Zhang and T. Masumoto: *Mater. Trans. JIM,* (1990) 31, 177–183.
3. R. Akatsuka, T. Zhang, M. Koshiba and A. Inoue: *Mater. Trans. JIM* (1999) 40, 58–261.
4. T. Zhang and A. Inoue: *Mater. Trans. JIM* (1998) 39, 857–862.
5. J. W. Yeh, S. K. Chen, S. J. Lin, J. Y. Gan, T. S. Chin, T. T. Shun, C. H. Tsau and S. Y. Chang: *Adv. Eng. Mater.,* 2004, 6, 299–303.
6. J. W. Yeh, S. K. Chen, J. Y. Gan, S. J. Lin, T. S. Chin, T. T. Shun, C. H. Tsau and S. Y. Chang: *Metall. Mater. Trans. A,* 2004, 35A, 2533–2536.
7. Ilouio kmm L . K. Huang, J. W. Yeh, T. T. Shun, S. K. Chen: *Adv. Eng. Mater.,* 2004, 6, 74–78.
8. Tong, C.J.; Chen, M.R.; Chen, S.K.; Yeh, J.W.; Shun, T.T.; Lin, S.J.; Chang, S.Y. *Metall. Mater. Trans. A* (2005) *36*, 1263–1271.
9. Chuang, M.H.; Tsai, M.H.; Tsai, C.W.; Yang, N.H.; Chang, S.Y.; Yeh, J.W.; Chen, S.K.; Lin, S.J. *J. Alloys Compd. (*2013) 551, 12–18.
10. Hemphill, M.A.; Yuan, T.; Wang, G.Y.; Yeh, J.W.; Tsai, C.W.; Chuang, A.; Liaw, P.K. *Acta Mater. (*2012) *60*, 5723–5734.
11. Senkov, O.N.; Wilks, G.B.; Scott, J.M.; Miracle, D.B. *Intermetallics (*2011) *19*, 698–706.
12. Tsai, M.H.; Wang, C.W.; Tsai, C.W.; Shen, W.J.; Yeh, J.W.; Gan, J.Y.; Wu, W.W. *J. Electrochem. Soc. (*2011) *158*, 1161–1165.
13. Kao, Y.F.; Lee, T.D.; Chen, S.K.; Chang, Y.S. *Corros. Sci.* (2010), 52, 1026–1034.
14. V.I. Yukhvid, V.N. Sanin, and A.G. Merzhanov. Processing by Centrifugation. Edited by L.L. Regel and W.R. Wilcox. Kluwer Academic, 2001, ISBN 0-306-46654-6, p.185 -200.