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Secondary hardening in laser rapidly solidified $Fe_{68}(MoWCrVCoNiAlCu)_{32}$ medium-entropy high-speed steel coatings

Hui Zhang [a,b,*], Bang Dou [a], Hao Tang [a], Yizhu He [a], Sheng Guo [c]

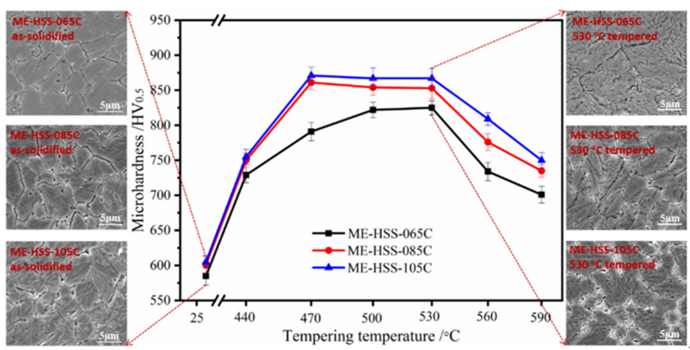
[a] School of Materials Science and Engineering, Anhui University of Technology, Ma'anshan, 243002, Anhui, PR China
[b] State Key Laboratory of Solid Lubricating, Lanzhou Institute of Chemical Physics, Chinese Academic of Science, Lanzhou 730000, Gansu, PR China
[c] Department of Industrial and Materials Science, Chalmers University of Technology, SE-41296 Gothenburg, Sweden

HIGHLIGHTS

- New medium-entropy high speed steel coatings exhibit excellent hot wear resistance
- Secondary hardening due to coherent nano-sized M_2C contributes to the high hardness
- The secondary hardening is enhanced with the increasing C content
- The C content needs to be optimized for high hardness and good hot wear resistance

GRAPHICAL ABSTRACT

Microstructure and hardness variation of novel $Fe_{68}(MoWCrVCoNiAlCu)_{32}$ medium-entropy high-speed steel (ME-HSS) coatings with different C content: 0.65 wt%C (ME-HSS-065C), 0.85 wt%C(ME-HSS-085C) and 1.05 wt%C(ME-HSS-105C).



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ABSTRACT

Novel $Fe_{68}(MoWCrVCoNiAlCu)_{32}$ (at.%) medium-entropy high-speed steel (ME-HSS) coatings, containing various carbon contents from 0.65 to 1.05 wt%, are prepared by laser rapid solidification. The newly prepared ME-HSS coatings are characterized by a hard martensitic matrix enhanced by secondary hardening, and specifically by coherent nano-sized M_2C. The secondary hardening effect is enhanced with the increasing carbon content. The high amount of alloying elements in ME-HSS coatings results in excellent oxidative wear resistance, without leading to serious compositional segregation and coarsening of carbides.

1. Introduction

High-entropy alloys (HEAs), which contain a high amount of alloying elements and tend to stabilize solid solutions due to the contribution from high configuration entropy, can exhibit strong solid solution strengthening, nano-precipitation hardening, excellent corrosion and oxidation resistance, and good thermal stability [1–5]. However, one challenge to HEAs for industrial applications is their high material cost, since most reported HEAs contain a high content of expensive elements like Co and Ni. Recently, the current authors revealed that the concept of Fe-rich medium-entropy alloy (MEAs), which

* Corresponding author.
E-mail address: huizhang@ahut.edu.cn (H. Zhang).

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contains above 50 at.% of iron, can be quite effective to reduce the cost of HEAs, while still maintaining the entropic contribution to stabilize solid solutions over intermetallic compounds. Based on that, they designed the so-called medium-entropy stainless steels (MESS), which are comprised of simple bcc or fcc solid solution phases, and contain 50–65 at.% of Fe, above 13 at.% of Cr, and other 5 to 7 elements with similar atomic percentage [6]. MESS serve as a good example to showcase that the compositional space for the alloy design in traditional high alloy steels can be broadened, potentially with tailored phases, microstructure and properties.

In this work, a series of medium-entropy high-speed steels (ME-HSS) coatings containing various carbon contents are designed. The selection of alloying elements is based on the established knowledge for traditional HSS, which belong to complex Fe-C-X high alloy steels (X = Mo, W, Cr, V) containing a high carbon content, with the microstructure featuring a large volume of hard carbides, formed from eutectic reactions or secondary precipitation, distributing in a martensitic matrix [7,8]. It is already known that the selection and content of strong carbide-forming elements, like Cr, W, Mo and V, are critical in the carbide precipitation and hardness improvement of the HSS [9,10]. However, the traditional alloy design in HSS generally regards that a high amount of alloying elements would result in serious compositional segregation and fast growth of carbides, hence a low toughness of the steels.

Therefore, it is the purpose of this work to use the concept of MEAs to design new HSS with a high amount of alloying elements. There are three considerations that are taken into account when designing the alloy compositions and ways to prepare alloys. Firstly, the laser rapid solidification technique, which is one of the main non-equilibrium processing methods and can enhance solute trapping and relieve compositional segregation, is chosen to prepare ME-HSS. Previous studies have confirmed that laser cladded HSS coatings exhibit ultrafine microstructures, limited amount of precipitates and insignificant coarsening of carbides [11–13]. Secondly, apart from the carbide forming elements W, Mo, V and Cr, non-carbide forming elements Co, Al, Ni and Cu with the same content of 4at.% are also added to increase the number of alloying elements and hence the configuration entropy. Consequently, the calculated configuration entropy in the current HSS coating is about 1.29*R* (assuming in fully random solid solution states, and the carbon content is not counted. R is the gas constant). The current HSS can then be classified as MEAs, based on a widely accepted definition that defines MEAs as alloys having a configuration entropy between *R* and 1.5*R* [14]. Furthermore, it should be noted that the addition of non-carbide forming elements like Al and Co has been proved to benefit the improvement of thermal stability and oxidation resistance in traditional HSS [15,16]. Thirdly, the effect of various carbon contents, is studied in this work, aiming to obtain high hardening with carbide precipitation.

2. Experimental procedure

A series of $Fe_{68}(MoWCrVCoNiAlCu)_{32}$ (at.%) ME-HSS coatings containing various carbon contents, specifically 0.65 wt%, 0.85 wt% and 1.05 wt%, were prepared in this work. The three coatings with increasing carbon content are subsequently referred to as ME-HSS-065C, ME-HSS-085C and ME-HSS-105C, respectively. Powders used for ME-HSS coatings were mechanically mixed starting from pure metal powders. C was added into the mixed ME-HSS powders in the form of the ferrocarbide alloy (C: 4 wt%). The compositions of the ME-HSS alloys in weight percentage are as follows: 11.94 wt% W, 6.23 wt% Mo, 3.38 wt % Cr: 3.31 wt% V, 3.83 wt% Co, 3.81 wt% Ni, 4.13 wt% Cu, 1.75 wt% Al, 61.64 wt% Fe, with additional 0.65 wt%, 0.85 wt% and 1.05 wt% of C. All used powders were in the size range of 50–120 μm. For laser cladding, a 5 kW continuous-wave CO_2-laser system with directly focused laser beam was used. The mechanically mixed powders were preplaced onto the surface of a low carbon steel substrate to form a powder bed with a thickness of 1.0–1.5 mm. By the relative movement between the laser beam and the substrate, the preplaced powder was melted and a rapidly solidified single-track coating strongly bonded with the substrate was produced. The multi-tracks with a 30% overlap of each track were achieved by moving the laser beam back and forth. High-purity argon gas was used as the shielding gas through the coaxial nozzle to prevent oxidation. The laser power, beam diameter and scanning speed used here were 2.0 kW, 4.5 mm and 400 mm min^{-1}. After laser scanning, about 0.8 mm thick coatings together with a thin layer of melted substrate were obtained. Then the laser cladded coatings were tempered three times (triple-tempering) in the temperature range between 440 °C and 590 °C. Each tempering time was 60 min. The triple-tempering process is directly transferred from the routine heat treatment procedure for conventional HSS, and the purpose is to eliminate the influence from the possible existence of retained austenite [7,8].

The phase constitution and microstructure were characterized using a Rigaku X-ray diffractometer (XRD) with the Cu-Kα radiation, transmission electron microscopy (TEM) (Tecnai G2, 200 kV), and a Quanta 450 field emission gun scanning electron microscope (FEG-SEM) equipped with the energy dispersive spectrometer (EDS). SEM specimen was cut from the cross-section of the coatings, and the surface was etched using aqua regia before observation. TEM specimen was cut parallel to the substrate. The microhardness was measured at around the middle of the cross-section of the coatings, by a Vickers hardness tester with a load of 4.9 N and loading time of 30 s. Each alloy was tested for multiple points and the average hardness was calculated. Hot wear resistance was tested on a HT tribometer (MMU-100) with a pin-on-disc wear test device at 500 °C in ambient air. The diameter of contact surface of cylindrical pins was 4.0 mm. All samples were tested under a load of 50 N and a sliding velocity of 100 r/min for 115 min. After the hot wear test, the worn surface from both the coating, and the counterface made of the AISI M2 HSS, were observed by SEM. M2 is the "standard" and the most widely industry-used HSS with the composition W6Mo5Cr4V2 (in weight percentage) and a carbon content of 0.85 wt%.

3. Results

3.1. Hardness

Fig. 1 shows that the hardness variation in ME-HSS coatings after triple-tempering at different temperatures. All ME-HSS coatings show obvious secondary hardening, with the hardness increasing from about 585 HV, 601 HV and 615 HV, to the maximum value of 825 HV, 861 HV and 871 HV in the ME-HSS-065C, ME-HSS-085C and ME-HSS-105C coating, respectively. Apparently, a higher carbon content leads to a higher hardness and lower peak temperature for secondary hardening; secondary hardening peaks appear at 530 °C for ME-HSS-065C and at 470 °C for ME-HESS-085C and ME-HSS-105C. This observation indicates that the secondary hardening effect is enhanced with the increasing carbon content. When the triple-tempering temperature is above 530 °C, the hardness in all three ME-HSS coatings gradually decreases. The hardness variation seen in the ME-HSS coatings here is quite similar to that in the traditional Fe-C-X HSS [7,16,17]. Therefore, by analogy it can be inferred that secondary hardening in ME-HSS coatings should be caused by secondary carbide precipitation, while the decreased hardness after tempering at above 530 °C is due to carbide coarsening and tempering induced softening in the martensitic matrix, which will be proved by microstructural observations later. Darmawan et al. previously studied the laser cladded M2 coating, and they found that the maximum hardness in it is about 840 HV, after triple-tempering at 560 °C [13]. The maximum hardness after tempering in the current ME-HSS coatings is quite comparable with results obtained by Darmawan et al. in the M2 coating, indicating a high amount of alloying