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Paper Title: Atomic-scale investigation of the synergistic impact of Mo and Nb addition on enhancing the performance of laser cladding FeCoCrNi-based high entropy alloy coatings

Content :

1. Introduction

Low-carbon steel is extensively employed in the fabrication of mechanical parts, attributed to its admirable plasticity and welding capabilities. However, its inherent low strength, hardness, and susceptibility to wear often result in premature failures in environments with high temperatures, heavy loads, and corrosive media. To address these limitations, one of the most efficacious strategies involves utilizing high-performance coatings for surface strengthening. High entropy alloys (HEAs) [[1], [2], [3], [4], [5], [6]], alloys composed of five or more primary metals in equal or nearly equal molar ratios, possess exceptional properties such as high strength, ductility, toughness, wear resistance, and corrosion resistance [7,8]. These exceptional characteristics stem from their various strengthening properties, including solid solution strengthening, precipitation strengthening, fine-grained strengthening, dislocation strengthening, phase transformation strengthening, and interface strengthening. And the synergistic effects of the high entropy effect, slow diffusion effect, severe lattice distortion effect, and cocktail effect [[9], [10], [11], [12], [13], [14]]. By fusing a HEA coating onto the surface of the low-carbon steel substrate, it can be effectively shielded from abrasive environments, thereby overcoming the mechanical deficiencies of the base material.

FeCoCrNi-based high entropy alloys have garnered significant attention in research due to their unique properties. It has unique properties such as high strength and hardness, good plasticity and toughness, excellent corrosion resistance, and adjustable phase structure, demonstrating broad application prospects in aerospace, nuclear energy, chemical and other fields. Studies reveal that the closely matched electronegativity of Fe, Co, Cr, and Ni elements facilitates the formation of simple solid solutions [15]. These alloys exhibit both high entropy and lattice distortion effects, resulting in a single-phase face-centered cubic (FCC) solid solution that possesses remarkable thermal stability, fracture toughness, and ductility across a wide range of temperatures, from room to low levels. Nevertheless, the ductility inherent in the FCC structure has detrimental effects on the strength, hardness, and tribological properties of FeCoCrNi MEAs, thereby restricting their industrial applications. Consequently, numerous scholars have utilized FeCoCrNi MEAs as a fundamental composition to explore a broad spectrum of HEAs derived from 3D transition metals, aiming to enhance the applicability of FeCoCrNi-based HEAs [16]. Yang et al. [17] were successful in fabricating FeCoCrNiMoW thermal sprayed coatings with a deposition diffusion layer structure on an iron substrate, utilizing plasma surface alloying technology (PSAT). The coating forms a deposition layer of 6 μm and a diffusion layer of 3 μm, and its wear resistance and high-temperature oxidation resistance are 3.66 and 5.5 times higher than those of the Fe substrate, respectively. He et al. [18], on the other hand, employed a welding ultrasonic impact composite Tungsten Inert Gas Welding (TIG) process to prepare FeCrNiCoMnSi0.1 coatings. The ultrasonic flow's stirring effect further refined the grain structure, enhancing both the mechanical properties and corrosion resistance. Peng et al. [19] utilized the vacuum arc melting method to synthesize AlCoCrFeNiNbx alloys and further surface-modified them through laser remelting technology. The inclusion of Nb enhanced the alloy's hardness and wear resistance. Specifically, NbC particles effectively inhibit HEAs grain growth due to their strong pinning effect, which not only augments strength and hardness but also impacts tribological behavior at both room and high temperatures [[20], [21], [22], [23], [24], [25]]. Post-laser remelting treatment significantly improved the alloy's hardness and wear resistance, with the fine grain strengthening effect being particularly evident. Given their high melting points and large atomic radii, Nb and Mo readily dissolve in elements such as Fe, Co, Ni, and Cr, making them prime candidates for HEAs design. However, there is a scarcity of research investigating the synergistic effect mechanism of Mo and Nb on FeCoCrNi-based high entropy alloys.

Therefore, focusing on the FeCoCrNi-base high entropy alloys, this study incorporated the large atomic radius elements Mo and Nb, utilizing laser cladding technology to fabricate two high entropy alloy coatings, FeCoCrNiMo and FeCoCrNiMoNb, on the surface of low-carbon steel. This innovative attempt aims to explore the synergistic enhancement mechanism of Nb and Mo on the microstructure evolution and mechanical properties of FeCoCrNi-based HEAs. By precisely regulating the composition and structure of the alloys, this study seeks to reveal the inherent laws governing element interactions and their impact on alloy performance optimization. Furthermore, it aims to provide theoretical support and experimental evidence for the development of high entropy alloy coatings in the fields of wear resistance and high-hardness applications.

Surface hardness

The Vickers hardness measurements depicted in Fig. 5 demonstrate a significant enhancement in the hardness of the coated specimens. Specifically, the average surface hardness of the FeCoCrNiMo and FeCoCrNiMoNb coatings was recorded as 365.44 HV and 537.87 HV, respectively, representing a remarkable increase of 253.6 % and 373.2 % compared to the substrate's hardness of 144.12 HV. Evidently, the application of laser cladding to deposit FeCoCrNiMo and FeCoCrNiMoNb coatings profoundly elevates the surface hardness of the substrate. This hardening effect can be attributed to the unique microstructure of these coatings, wherein the transformation of Mo-containing metal compounds into hardened NbC and (Mo, Nb) C particles plays a crucial role. Notably, NbC, a hard ceramic particle, contributes significantly to the enhancement of the hardness of the high entropy alloy coatings.

Mechanical property

Utilizing the phase models depicted in Fig. 9(b), (c), and (d), the elastic constants of the four distinct phases-NbC, (Mo, Nb) C, Mo_3Co_3C, and Ni_3Mo_3C were accurately determined via the VASP simulation. All these phases exhibit a cubic crystal system, characterized by three independent single-crystal elastic constants: C_{11}, C_{12}, and C_{44}. According to the criteria for dynamic (mechanical) stability in cubic structures [43], the satisfaction of $C_{44} > 0$, $C' = (C_{11}-C_{12})/2 > 0$, and $B > 0$ is essential. Here, B represents the bulk modulus.

The hard elastic ratio, defined as the quotient of hardness (H) and elastic modulus (E), has been widely recognized as a pivotal parameter influencing wear resistance. Specifically, a higher H/E ratio, also known as the hard elastic ratio, corresponds to superior wear resistance [45]. Analyzing the data presented in Table 6, it becomes evident that the incorporation of Mo into the NbC lattice elevates the H/E value of the resulting (Mo, Nb)C composite compared to pure NbC. This observation suggests that the synergistic interplay between Mo and Nb in enhancing wear resistance is more potent than that of Nb alone. Consequently, the ranking of wear resistance among four high entropy alloy coatings is: (Mo, Nb)C exhibiting the highest wear resistance, followed by NbC, Mo_3Co_3C, and Ni_3Mo_3C in descending order.

In summary, the synergistic interaction between Nb and Mo leads to the formation of (Mo, Nb)C, a phase exhibiting exceptional wear resistance. Notably, the hardness of (Mo, Nb)C surpasses that of Mo_3Co_3C and Ni_3Mo_3C, marking it as a superbly durable material. Furthermore, the combined strengthening effect of (Mo, Nb)C and NbC contributes significantly to the enhancement of both hardness and wear resistance in FeCoCrNiMoNb high entropy alloy coatings, resulting in their significant improvement.

Mechanical anisotropy plays a pivotal role in material applications, as it profoundly affects the durability and reliability of components. The formation of microcracks in materials, which can significantly degrade their performance, is often linked to anisotropy [46]. Specifically, the direction of high modulus aligns with the direction of high fracture energy, while the converse holds true for low modulus and fracture energy. Wang et al. [47] discovered that the corrosion resistance of materials is intricately tied to the anisotropy of their microstructure. Meanwhile, the anisotropy of materials significantly affects their hardness and wear resistance. Because of the varying internal crystal structure, grain morphology, and orientation in different directions, the mechanical response of materials varies under external loads or during wear, leading to higher hardness and wear resistance in certain orientations. If the anisotropy of the material is excessive, it may result in drastically different properties in different directions, potentially compromising the overall performance of the material. For instance, in components subjected to complex loads, excessive material anisotropy can give rise to stress concentration and premature failure in specific directions.

Fig. 9 depicts the three-dimensional anisotropy diagrams of four phases: Mo_3Co_3C, Ni_3Mo_3C, NbC, and (Mo, Nb)C. The first row portrays the bulk modulus (B), the second row illustrates the elastic modulus (E), and the third row shows the shear modulus (G). The deviation between the three-dimensional surface structure and a sphere quantifies the extent of elastic anisotropy. When the 3D diagram resembles a sphere, the material exhibits isotropic elasticity; otherwise, it is anisotropic. A greater deviation indicates a higher degree of elastic anisotropy [48]. Observing the bulk modulus diagrams, Mo_3Co_3C, Ni_3Mo_3C, and NbC exhibit a uniform color and perfect spherical shape, indicating isotropic behavior. Conversely, (Mo, Nb)C displays a color ellipsoidal shape, signifying anisotropy. Among these phases, Mo_3Co_3C and Ni_3Mo_3C exhibit the lowest anisotropy, while NbC and (Mo, Nb)C possess slight anisotropy. Despite their small differences, these four high entropy alloy phases exhibit good anisotropy characteristics, contributing to their exceptional material properties.