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An analysis of formation mechanism and nano-scale hardness of the laser-induced coating on Ni–17Mo–7Cr based superalloy

Yanming He [a], Jianguo Yang [a, b, *], Wei Fu [c], Limei Wang [a], Zengliang Gao [a]

[a] Institute of Process Equipment and Control Engineering, Zhejiang University of Technology, Hangzhou, 310014, PR China
[b] State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin, 150001, PR China
[c] Shanghai Baosteel Industry Technological Service Co., Ltd., Shanghai, 201900, PR China

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ABSTRACT

The Ni–17Mo–7Cr based superalloy was laser surface treated in argon atmosphere to enhance its tribological property. The formation mechanism of the coating was revealed and its mechanical properties were characterized. The microstructure and phase identification in the coating were investigated by scanning electron microscope, transmission electron microscope and X-ray diffraction techniques. The mechanical properties of the coating, i.e. elastic modulus and hardness, were measured by nanoindentation tests. The SiC particles were used as the coating materials. During the laser treatment, the SiC will first decompose and the decomposition products Si will trigger the formation of MoC carbides in the coating. After complete solidification, the coating consists of the MoC equiaxed dendrites, interdendritic Ni matrix and graphite. Lot of tiny MoC and chromium carbides can also occur in the interdendritic matrix. The elastic modulus and hardness of MoC are characterized to be 394.0 GPa and 22.3 GPa, which are far higher than that of the matrix ($E = 246.8$ GPa, $H = 5.3$ GPa). In addition, the volume fraction of hard MoC can reach about 45.3% in the coating. The method reported in this work will provide us a new approach to fabricate the wear-resisting coating.

1. Introduction

Ni-based superalloys are widely used in several industrial sectors, for instance petrochemical industries and power plants, due to their superior performances in aggressive environments [1]. The Ni–Mo–Cr based Hastelloy alloys exhibit a strong resistance to a wide variety of chemical environments, including strong oxidizers, formic and sulfuric acids, hot contaminated media, chlorine, sea water and brine solutions [2]. The Ni–17Mo–7Cr based superalloy studied in this work was initially designed for use in nuclear industries [3]. Currently, the Ni–Mo–Cr based alloys series constitute an important class of superalloys, attracting interests not only from nuclear industries, but also aerospace, chemical processing, as well as oil and gas industries, owing to their excellent performances at elevated temperatures and corrosion resistance [4,5]. In order to prolong the service life, sometimes it is quite necessary to improve the tribological property of alloys. Introducing a wear-resisting coating on the substrates by laser treatment is extremely common and shows superiorities in many aspects, such as low substrate dilution, minimal distortion and strong metallurgical bonding at the interface [6].

There are two ways to create the coating on substrates by laser treatment. The first is direct laser surface melting (LSM), which will obtain the refined microstructure on the surface due to a high cooling rate of nearly 10^7 °C/s during the process [2]. Incorporating hard particles, such as the SiC [7], WC [8,9], Al_2O_3 [10] and Cr_3C_2 [11], into the coating to form a metal matrix composite is another significant manner to enhance the tribological property. These hard particles can be incorporated directly [7–11] or in-situ precipitated from the melt pool [12,13]. Controlling particles dissolution and excessive reaction between the particles and matrix are very important since they will introduce some undesirable reaction phases in the coating [7,14]. These excessive brittle reaction phases can decrease hardness of the coating, and hence depress its wear resistance. By optimizing laser processing parameters, the degree of particles dissolution may be reduced to some extent. But it is impossible to absolutely eliminate the particles dissolution and excessive reaction since the particles are heated under direct

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[*] Corresponding author. Institute of Process Equipment and Control Engineering, Zhejiang University of Technology, Hangzhou, 310014, PR China.
E-mail address: yangjianguo@hit.edu.cn (J. Yang).

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irradiation of a laser beam. The residual stress built up in the coating during cooling of the melt pool is another significant problem, which is worthy to be seriously considered [15]. The thermal stresses can be developed as a result of differences in mechanical and thermal properties of the different phases (matrix and reinforcement) or layers of materials (coating and substrate). The large stresses will bring the cracks in the coating. They can be decreased via preheating the substrates and optimizing the laser processing technology, but likewise can't be eliminated completely.

As far as the Ni–17Mo–7Cr alloy studied in this work, this kind of alloy consists of the Ni matrix and embedded MoC particles. We found that Si is an important element to promote the formation of MoC in the alloy [16]. Based on this fact, we plan to introduce SiC particles as the coating materials. The basic idea is to make the SiC particles decompose during the laser-particles interaction. After that the decomposition products Si and C atoms will enter the melt pool. During the cooling process, the Si will trigger formation of hard MoC in the coating, which efficiently improves its tribological property. In addition, the graphite can also be precipitated from the supersaturated matrix, providing a necessary lubricating action during the wear process. The aim of this work is, thus, to reveal formation mechanism of the coating during laser surface melting. In addition, an accurate and reliable input of the mechanical property data for the phases in the coating is urgently required to model coating behavior. Nanoindentation technique has the ability to precisely measure the modulus and hardness of subjects with a small volume [17]. We thus employ the nanoindentation to measure the modulus and hardness of related phases in the Ni–17Mo–7Cr alloy before and after the LSM treatment. The solid evidence will be provided to elucidate the wear-resisting mechanism of coating.

2. Materials and methods

The substrates used in this work were Ni–17Mo–7Cr based superalloy with the following composition: Ni-17.29Mo-6.96Cr-3.96Fe-0.627Mn-0.466Si-0.0488C (wt.%), which is similar to that of Hastelloy N. The casting alloys were first prepared by vacuum induction melting, followed by vacuum arc melting. The obtained ingots were hot rolled into sheets and then the sheets were solutionized at 1177 °C for 0.5 h, followed by water quenched. The SiC particles with an average diameter of 10 μm were used. Before LSM treatment, a layer of SiC particles with a thickness of 1 mm was preset on the substrates. A 3 kW transverse-flow CO_2 laser system (Leo HJ-3000) coupled with a four-axis numerical control working table were used to perform the LSM treatment with following processing parameters: laser power 2 kW, scanning speed 150 mm/min, overlap ratio 50%. Argon was used as the shielding gas to protect the melt pool from oxidation. Laser beam was perpendicular to the surface of substrates.

After the laser treatment, the cross-sections of the processed layer were cut and prepared by a standard polishing procedure. Microstructural characterization and composition analysis were performed by scanning electron microscopy (SEM, FEI Quanta 200F) coupled with an energy dispersive spectrometer (EDS, Bruker Nano XFlash Detector 5010). The samples for transmission electron microscope (TEM) analysis were prepared for the coating and observed using a FEI Tecnai G2 F30 operating at 300 kV. The phases in the alloy before and after the LSM treatment were also identified by X-ray diffraction technique (XRD, Bruker D8 Advance). The triboindenter system (Hysitron Inc., USA) in conjunction with a Berkovich tip was introduced to measure the nano-scale elastic modulus (E) and hardness (H) of relevant phases in the coating. A maximum penetration depth was set to 2000 nm during the measurements. The mechanical properties of the material, i.e. elastic modulus and hardness, were determined from the load-displacement curve based on the Oliver and Pharr's method [18].

3. Results

Fig. 1(a) shows the microstructure of the Ni–17Mo–7Cr based superalloy. As can be seen from the figure, the alloy is basically composed of the matrix and embedded blocky precipitates. The matrix, mainly consisting of Ni 67 at.%, C 12 at.%, Mo 8 at.%, Cr 7 at.%, Fe 5 at.% and Si 1 at.%, should be the Ni-based solid solution. The scattered precipitates are made up of Ni 30 at.%, C 28 at.%, Mo 28 at.%, Si 7 at.%, Cr 6 at.% and Fe 1 at.%. Associated with our preceding research [16], they are actually the MoC carbides. In addition, some annealing twins can also be inspected. After the LSM treatment, the microstructure obtained is exhibited in Fig. 1 (b). As shown in the figure, a metallurgical bonding, which is absent of pores and cracks, is formed at the coating/substrates interface. The heat-affected zone (HAZ) with a width of 0.3 mm occurs in the substrates close to the bonding interface. The microstructure in the coating mostly consists of the columnar dendrites, equiaxed dendrites and interdendritic matrix, with the columnar dendrites perpendicular to the bonding interface. It is well-known that the ratio of G/R is a controlling factor to determine the solidified microstructure, where G is the temperature gradient and R is the solidification rate. The temperature gradient G during laser processing can be estimated as follows [19]:

$$G = 2K(T - T_0)^2 \Big/ \eta P \tag{1}$$

where T is the liquid temperature of alloy, T_0 is the initial temperature of substrate, η is the laser absorption coefficient, P is the laser power and K is the thermal conductivity of substrate. In the melt pool, the solidification rate R at the front of isothermal line can be expressed as: $R = V_S \cos\theta$, where V_s is the scanning speed and θ is the angle between the R and V_s. At the coating/substrates interface, the ratio of G/R was very large, and there was hardly any ingredient supercooling. In addition, the temperature gradient G and heat flux density perpendicular to the interface was largest, since the substrates acted as a heat sink and the heat of coating layer chiefly dissipated through the substrates in initial cooling. This would lead to directional growth of grains counter to the heat flux direction and formation of columnar dendrites. As shown in Fig. 1(b), the columnar dendrites grew perpendicular to the substrates, which were also reported in Refs. [20] and [21]. With the cooling proceeding, the ratio of G/R decreased and ingredient supercooling increased. The heat flow via the substrates was no longer predominant, and in such a case it mainly dissipated through the atmosphere. The high supercooling degree would promote the primary dendrites to nucleate. But they had less time to grow, leading to the formation of massive equiaxed dendrites at the upper part of coating.

Fig. 2(a) and (b) display the microstructure of the columnar dendrites at the coating/substrates interface. It can be seen from the figure that the columnar dendrites grow from the substrates. In the HAZ, the original MoC particles disappear and some new microstructures are formed at the grain boundaries and in the grain interiors (Fig. 2(c)). At high magnification, Fig. 2(d) indicates that massive tiny particles are embedded in the new structures. These tiny particles, consisting of C 45 at.%, Ni 26 at.%, Mo 18 at.%, Si 5 at.%, Cr 5 at.% and Fe 1 at.%, have the nearly same constitution with that of original MoC. It can therefore deduce that they are also the MoC. These structures should be produced through local melting during the laser treatment. We mentioned before that the initial liquid occurs in the Ni–17Mo–7Cr alloy when the temperature reaches