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Microstructure and phase transformations in laser clad Cr_xS_y/Ni coating on H13 steel

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ABSTRACT

Laser cladding was carried out onto H13 steel with preplaced NiCrBSi+Ni/MoS_2 powders using CO_2 laser under the optimized experimental parameters of laser power 2 kW, scanning velocity 6 mm/s and laser beam diameter 3 mm. An X-ray diffractometer and scanning electron microscope with energy dispersive spectroscopy were applied to analyze the microstructure and phase compositions of the coating. Thermodynamic calculation was performed with Thermo-Calc software on the basis of a commercially available Ni-based Alloys' database. The experimental results show that MoS_2 decomposed and S reacted with Cr to form nonstoichiometric Cr_xS_y during the laser cladding process. The coating consists of spherical Cr_xS_y particles, primary γ-Ni dendrite, interdendritic eutectic (γ-Ni+NiMo) and precipitated NiMo. The precipitated NiMo was fine and uniformly distributed in primary γ-Ni dendrite. The calculated results and experimental data indicate that the solidification process in the coating during laser cladding process was liquid→liquid+Cr_xS_y→ liquid+Cr_xS_y+γ-Ni→liquid+Cr_xS_y+γ-Ni+ eutectic (γ-Ni+NiMo). A solid state phase transformation (fine and uniformly distributed NiMo precipitated from γ-Ni) occurred after the solidification process. The calculations agree well with the experimental data and it is helpful to understand the phase transformation and microstructure evolution in the coating.

1. Introduction

Due to the extraordinary hot strength and remarkable toughness, H13 steel is used for making hot-forging dies, casting dies, and extruding tools [1]. These tools are subjected to continuous mechanical and thermal loadings and it easily leads to a heavy damage of the tool surface. Thus hot working tools have to be replaced after a certain time of use, which leads to considerable costs associated with machining of tools [2]. To improve the mechanical and tribological properties and lengthen the service life of the tools, surface engineering techniques were always used on these hot working tools [3]. Among the surface engineering techniques, laser cladding shows extraordinarily distinct advantages such as low dilution, minimal distortion of substrate, narrow heat affected zone, metallurgical bond between the coating and substrate and fine microstructure.

There are mainly two laser cladding methods: powder injection and preplaced powder on the substrate. Although powder injection is a commonly used powder deposition method in industry applications, laser cladding with preplaced powder is the simplest method in depositing clad powder. In preplaced powder method, the powder is blended with a binder to form a slurry and then pasted to the substrate surface. It does not require sophisticated powder feeding systems. Minimal dilution rates were observed for a wide range of process parameters due to the thermal barrier effect of the preplaced layer on the substrate. In addition, the preplaced powder method is advantageous for cladding of workpiece with complicated geometry, such as worm gear and bolt screw [4]. Therefore, the preplaced powder method which remains a popular and effective means was adapted in the present study.

Self-lubricating metal matrix coatings combine the superior strength and wear resistance of the metal with the antifriction property. So laser clad self lubricating metal matrix coatings are always fabricated on H13 steel to improve its surface properties. As reported in the literatures, a wide range of self-lubricating coatings were investigated. Yang et al. [5] fabricated high temperature self-lubricating and wear resistant Ni–Cr/Cr_3C_2–30%WS_2 coating on 0Cr18Ni9 austenitic stainless steel by laser cladding. Results indicated that most of the WS_2 phase decomposed during the laser cladding process and the coating was mainly composed of Cr_7C_3 and (Cr, W)C carbides, with minor quantity of lubricating WS_2 and CrS sulfides. Wang et al. [6] synthesized a Ni-based alloy matrix submicron WS_2 self-lubricating coating by Nd:YAG laser cladding. The results show that high energy ball milling of nano-Ni onto submicron WS_2 can significantly prevent the oxidization, reaction

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and vaporization of WS_2 and improve the interfacial compatibility between WS_2 and Ni matrix. Liu et al. [7] clad Ni/Cr/C/CaF_2 mixed powders on γ-TiAl substrate. Buoyancy, decomposition and vaporization of CaF_2 occurred because of its lower melting point, lower density and bad interfacial compatibility with the metal matrix. As a further step in obtaining high performance self-lubricating coating on TiAl alloy, Liu et al. [8] adopted Ni–P electroless plating method to encapsulate the as-received CaF_2. It found that more CaF_2 powder was successfully retained in the coating after laser cladding process. Xu et al. [9] fabricated a MoS_2/TiC/Ni coating on the surface of 1045 low carbon steel substrate using a PRC-3 kW continuous wave CO_2 laser. The microstructure of the coatings is composed of multi-sulfide phases, including binary element sulfides and ternary element sulfides, Ni, TiC and Mo_2C. MoS_2 was decomposed during the cladding process. Wear testing results showed that the friction coefficient of the coating is lower than that of quenched 45 steel and weight loss is only one-sixth of that of 45 steel. The worn surface of the coating is clean and smooth (no noticeable groove and scratches) such that the microstructure of the coating can be clearly revealed.

Although some preventive methods were adopted, such as encapsulating the solid lubricant and optimizing the laser cladding process parameters, most of the solid lubricant decomposed and vaporized during laser cladding process and only a minor part of it remained in the coating. These problems limit the industrial application of laser clad self-lubricating coating.

In this paper, an in situ formed self-lubricating Cr_xS_y/Ni coating was fabricated on H13 steel by laser cladding using powder mixture of NiCrBSi+Ni/MoS_2 as a clad material. During the laser cladding process, MoS_2 decomposed and large quantity of Cr_xS_y lubricant was in situ formed in the coating. The in situ synthesis technology can effectively improve the interfacial compatibility between the lubricant and matrix. It can also overcome the technical obstacles in fabrication of self-lubricating coating, such as the oxidization, decomposition and vaporization of the lubricant.

The phase constituents and microstructure of the coating were analyzed in detail. To gain a deep and theoretical understanding of the phase transformation and microstructure evolution in the coating, the thermodynamics of the laser cladding process was simulated using the most developed Thermo-Calc software [10]. Combining with the calculated results and experimental data, the solidification process, precipitation behavior and reaction scheme in the coating were analyzed.

2. Experimental procedures

A cuboid sample of H13 steel with size of 50 mm × 20 mm × 20 mm was used as the substrate. The substrate was ground to a surface finish of Ra = 0.2 μm using abrasive paper and then cleaned with acetone. The powder mixture of Ni/MoS_2 (Ni coated MoS_2 powder) and NiCrBSi pre-alloyed powder in mass ratio of 1:2 was used as the clad material, NiCrBSi pre-alloyed powder with the composition of 17.0Cr, 3.5B, 4.0Si, 1.0C, < 12Fe, and balance Ni. The composition of Ni coated MoS_2 powder is 75Ni and 25MoS_2. The powder mixture was preplaced on the surface of substrate using an organic binder, to form a layer of 1.0 mm thickness.

Laser cladding was performed on a TJ-HL-T5000 CO_2 laser processing system. The focal length of the laser system is 315 mm. The energy of the laser beam has a Gaussian distribution arround the laser beam diameter. To optimize the processing parameters, a number of clad tracks were obtained by varying laser power P in the range of 1–4 kW, the scanning velocity V in the range of 3–10 mm/s and the laser beam diameter D in the range of 2–5 mm. The parameter selection criteria were based on the quality of the coating in terms of the amount of pores and cracks, the uniformity and dilution rate of the coating, and the formation of metallurgical bond at the interface. The optimal process parameters selected for laser cladding were laser power $P = 2$ kW, scanning velocity $V = 6$ mm/s and laser beam diameter $D = 3$ mm. To protect the melted pool from oxidation during the laser cladding process, argon gas shield with flux of 10 l/min was fed through a side nozzle. A single track was obtained for microstructural examinations, and several laser tracks with an overlapping ratio of 50% were obtained for XRD tests.

Phase constituent of the coating was analyzed on a Rigaku D/max 2500 PC X-ray diffractometer (XRD). The radiation source used was Cu Kα generated at acceleration voltage of 40 kV, scanning velocity 5°/min and current flow of 150 mA. The microstructure and phase composition of the coating were examined using a QUANTA 200 scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS).

3. Thermodynamic model

Commercially available Thermo-Calc software constructs a thermodynamic description of the alloy system based on modeling the Gibbs energy of each phase in the system as a function of temperature, pressure and constitution [11]. Once the Gibbs energy functions and the systematic database are available [12,13], phase diagrams and other thermodynamic properties can be calculated by applying standard thermodynamic relations according to the general principle of minimum Gibbs energy with the help of developed computer technology [14,15]. Thermo-calc software has become an important approach in understanding material properties and processes. It is usually used to solve different materials science problems in primary processes such as melting, alloying, casting, solidification, reheating and in other more product oriented areas such as heat treatment, annealing, surface treatments and sintering [16].

In the present paper, the thermodynamics (phase transformations and solidification process during the cladding process) of in situ formed Cr_xS_y/Ni coating on H13 steel was calculated by using Thermo-Calc software together with commercial thermo-chemical database TCNI5 (Ni-based Alloys' Database). In order to obtain feasible calculation results, the molten pool is assumed to be homogeneous during the laser cladding process. The initial calculation conditions were as follows: the system size 1 mol, the reference state 298.15 K and 10^5 Pa. During the laser cladding process, all the Mo and S elements came from the decomposition of MoS_2 compound. So the atomicity ratio of Mo to S in the coating was fixed as 1:2. The phase fraction, composition and transformation at various temperatures of the coating were calculated, and compared with the experimental results.

4. Results and discussion

4.1. Microstructure of the coating

Fig. 1 shows the cross-section macrograph of a single clad track. The coating is free from pores and cracks, with low dilution, homogeneous microstructure and good metallurgical bond to the substrate. The width of a single clad track is 3.8 mm and the maximal depth of the coating is 1.0 mm. Due to the Gaussian distribution of the laser beam, the energy at the center of laser beam is higher than that at the outside. During the laser cladding process, the temperature at the center of the single track was higher than that at both sides of the track. So the thickness at the