Vacuum 155 (2018) 23–28

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Formation of a titanium-carbide-dispersed hard coating on austenitic stainless steel by laser alloying with a light-transmitting resin

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ARTICLE INFO

Keywords:
Laser alloying
Stainless steel
Titanium carbide
Hard coating

ABSTRACT

Laser alloying is one of the most effective processes for improving surface properties such as wear resistance and corrosion resistance. Our group developed a laser-alloying process using a light-transmitting resin as a source for the carbon element. In this study we applied this process for the surface-hardening of austenitic stainless steels. Laser irradiation of a stainless steel sheet laminated with titanium foil and transparent adhesive tape obtained a laser-alloyed zone of about 5 μm in thickness. The thickness of the laser-alloyed zone was homogeneous. The laser-alloyed zone contained fine titanium carbide particles formed by a reaction between titanium and pyrolytic carbon stemmed from the resin. The surface hardness of the laser-alloyed zone increased up to 1200H V with increasing average laser power. We describe the laser-alloying process and an investigation of the microstructure of the laser-alloyed zone.

1. Introduction

Austenitic stainless steel 304 has become one of the most widely used materials in industrial fields such as chemical plants by virtue of its superior corrosion resistance, good cold formability, and excellent weldability. The hardness of the austenitic stainless steel, however, is only about 200H V, a level inadequate for uses requiring good wear resistance.

The surface-hardening process for improving the wear resistance of metal parts has been thoroughly researched. In applications with hard coatings such as PVD and CVD, the coating layer tends to adhere weakly to the base metal, which often results in delamination [1,2]. Thermal diffusion processes such as carburizing or nitriding are widely used for the surface-hardening of steels, but a passive film on a stainless steel surface makes it difficult to apply the conventional thermal diffusion process. A plasma process enables carburizing or nitriding of stainless steels, however, the formation of chromium compounds tend to decrease the corrosion resistance due to a lack of solute chromium content [3]. Recently, low temperature plasma treatments were studied to improve the surface hardness of stainless steels without degrading corrosion resistance [4–6]. However, these processes require long treatment time.

Laser alloying is an effective process for improving wear resistance [7,8]. The process is performed by melting the surface of a substrate with additional materials, mixing the components together, and rapidly solidifying the mixture. The advantages of laser alloying are good metallurgical bonding between the laser-alloyed zone and substrate, a fine microstructure due to the rapid cooling rate, a local treatment, and a very small heat-affected zone. In addition, various materials such as metals, ceramics, gas, and non-metallic materials, can be used as additional materials for laser alloying process. Hence, laser alloying can be used as surface carburizing, nitriding, and boronizing processes for improving surface properties of metal parts [9–12]. The method of laser alloying is also applicable to laser additive manufacturing for producing bulk-form metal matrix composites [13–15].

Titanium carbide is one of the hardest, most stable carbides, which makes it an effective reinforcement for improving wear properties [16]. Many researchers have reported on the laser-alloying process using titanium carbide [17–25]. When using powder as additional materials for the laser alloying process, inhomogeneity in the pre-placed powder thickness or powder scattering during laser irradiation makes it difficult to control the chemical composition of the laser-alloyed zone. Earlier our group developed a laser-alloying technique with a light-transmitting resin as a source for the carbon element [26,27]. The process yielded a thin and homogeneous laser-alloyed zone containing a high volume fraction of titanium carbides on the surface of a pure titanium substrate.

In most case, laser alloying processes have been carried out under vacuum or inert atmosphere in order to prevent oxidation. The advantage of the present laser alloying process using a light-transmitting resin as a carbon source is that the gas barrier effect of the resin layer eliminates any need for a shielding gas or atmosphere control chamber

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https://doi.org/10.1016/j.vacuum.2018.05.050
Received 9 April 2018; Received in revised form 28 May 2018; Accepted 28 May 2018
Available online 29 May 2018
0042-207X/

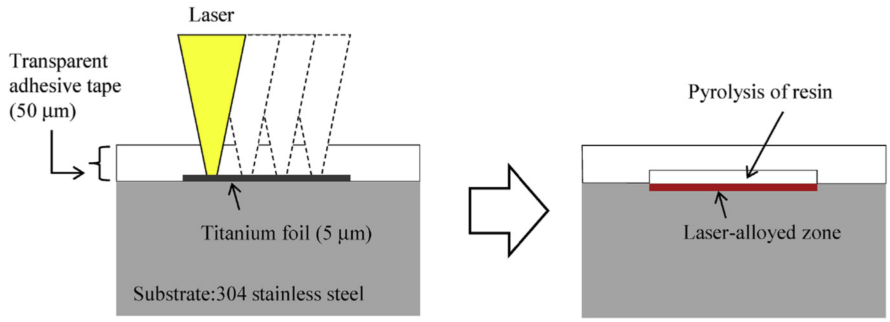

Fig. 1. Schematic illustration of the cross section of the specimen.

because alloying reaction is occurred at the interface of the substrate and the resin.

In this study we applied the same process to the surface-hardening of austenitic stainless steel. Instead of titanium carbide powder widely used in conventional laser alloying process, we used a titanium foil for the source of the titanium element, and a light-transmitting resin for the source of the carbon element, respectively. It seems that laser-irradiating a stainless steel substrate laminated with a titanium foil and a light-transmitting resin form a laser-alloyed zone containing titanium carbide by *in-situ* reaction between titanium and pyrolytic carbon in the molten pool. The microstructure and hardness properties of the laser-alloyed zone were studied.

2. Experimental procedure

A sheet of AISI 304 stainless steel (50 × 50 × 1 mm) was used as the substrate. The surface of the substrate was polished with SiC paper (P400) and cleaned with acetone. A 5 μm-thick sheet of pure titanium foil (99.6%, Nilaco) and a commercial transparent adhesive tape consisting of cellulose acetate film and acrylic adhesive (total thickness of about 50 μm) were laminated on the substrate in the manner shown in Fig. 1.

A nanosecond single-mode fiber laser (YLP-1-100-20-20) was focused to a spot diameter of 30 μm and scanned across the specimen surface with a galvano scanner. Table 1 shows the laser-alloying conditions. After laser irradiation, the transparent adhesive tape and titanium foil were removed and the specimen was ultrasonically cleaned with acetone.

The surface of the laser-alloyed zone was observed by an optical microscope (OM) and scanning electron microscope (SEM; S3400 N, Hitachi). The specimen was cut perpendicularly to the laser scanning direction and polished with SiC paper and Al_2O_3 suspensions. To reveal the interface of the laser-alloyed zone and parent metal, the specimen was electrochemically etched with a 10% $(COOH)_2$ solution.

The cross-sectional microstructure and chemical composition were studied using an OM, SEM/EDX (EDAX Genesis APEX2, AMETEK), and electron probe micro analyzer (EPMA; JXA-8530 F, JEOL). X-Ray diffraction with Cu Kα radiation (SmartLab, Rigaku) was performed for phase identification.

The hardness of the surface of the laser-alloyed zone was measured by a Vickers hardness tester with a load of 0.098 N.

Table 1
Laser irradiation conditions.

Wave length	1064 nm
Pulse width	100 ns
Spot diameter	30 μm
Frequency	200 kHz
Average power	9–11 W
Scanning speed	100 mm/s
Scanning pitch	15 μm

3. Results and discussion

3.1. Surface appearance and hardness of the laser-alloyed zone

The SEM images in Fig. 2 show the surfaces of laser-alloyed zones fabricated with different average laser powers. All of the surfaces shown were covered with the respective laser tracks at regular intervals. The surfaces of the laser-alloyed zones were relatively smooth. No cracks were observed in the laser-alloyed zone formed with an average laser power of 9 W (Fig. 2 (a)). As the average laser power rose, however, the amount of cracking rose, as well (Fig. 2 (b) and (c)). In the specimen irradiated with an average laser power of over 12 W, excessive heat input burned out the transparent adhesive tape. Fig. 3 shows the surface hardness of the laser-alloyed zone. The hardness of the non-laser treated stainless steel substrate is also given for comparison. The laser-alloyed zone was much harder than the stainless steel substrate, spanning a range between 800H V and 1200H V. The hardness value of the laser-alloyed zone rose as the average laser power increased.

3.2. Microstructure and phase identification

The optical micrograph in Fig. 4 (a) shows a cross section of a typical specimen with a laser-alloyed zone fabricated at an average laser power of 11 W. The laser-alloyed zone contained no voids and the thickness was relatively homogeneous. As shown in the surface observation by SEM (Fig. 2), cracks were observed in the cross section of the specimen. We examined the microstructure of the laser-alloyed zones and performed a phase analysis, mainly to ascertain the presence or absence of cracks.

Fig. 4 (b) and (c) show SEM back-scattered electron images of the laser-alloyed zone. The thickness of the laser-alloyed zone fabricated at an average laser power of 11 W (Fig. 4 (c)) was slightly larger than that of the laser-alloyed zone fabricated at an average laser power of 9 W (Fig. 4 (b)). The microstructure of the laser-alloyed zone fabricated at 9 W showed inhomogeneous contrast (Fig. 4 (b)), while that of the laser-alloyed zone fabricated at 11 W was relatively homogeneous (Fig. 4 (c)). In the laser-alloyed zone fabricated at 11 W, particles with diameters of several micrometers and particles with sub-micron diameters were dispersed in the laser-alloyed zone.

Fig. 5 shows elemental mapping images by EPMA corresponding to the area of the BSE images in Fig. 4. Both laser-alloyed zones contained the elements Ti, C, Fe, Cr, and Ni. The Ti and C stemmed from the alloying materials (i.e., titanium foil and pyrolysis products of the resin). The Fe, Cr, and Ni stemmed from the substrate material. Compared to the Fe, Cr, and Ni in the laser-alloyed zone fabricated at 9 W, those in the laser-alloyed zone fabricated at 11 W were more abundant and more homogeneously distributed. Carbon was detected from the dark contrast areas of the BSE images in Fig. 4, suggesting the presence of carbide particles in those areas. We can deduce, from these results, that the elemental distribution becomes relatively homogeneous when