Oxidation Resistance of a Hot-Die Steel (H13) with Al Coating and High Current Pulse Electron Beam Treatment

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ABSTRACT

A two-step surface treatment process has been developed, which combines arc deposition with High-Current Pulsed Electron Beam (HCPEB) post treatment. Arc deposition produced an Al-coating ~10 μm thick on H13. The coating was subsequently bombarded with HCPEB. Due to the rapid surface heating, melting and cooling, a part of the Al-coating was melted into the substrate surface, forming a mixed surface alloying and intermetallic layer. Experimental results revealed that the high temperature oxidation rate was reduced by a factor of 40 compared to the untreated steel. The mechanisms of the improvement in oxidation resistance were discussed according to the experimental results.

Key Words: H13 steel, High-Current Pulsed Electron Beam (HCPEB), Oxidation, Al-coating, Surface alloying
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1. INTRODUCTION

Oxidation is a major cause of failure for materials used under high temperature environment. To improve the oxidation resistance of steel materials, surface aluminizing is often used as one of the most economical and effective methods. There are a number of aluminizing techniques such as hot-dip aluminizing, powder aluminizing, vapor aluminizing and thermal spray /1/. However, these methods are either high-cost or inefficient; and the coatings often suffer from low adhesion between the coating layer and substrate.

Recently, high-energy beam surface modification of metallic materials has been actively studied /2,3,4,5,6,7,8/, which claims to be able to improve the surface service properties of structural materials significantly. Furthermore, there are some investigations on surface alloying and coating adhesion enhancements by means of beams mixing /5,6,7,8/. Among these techniques, High-Current Pulsed Electron Beam (HCPEB) is a technique that can apply high-density of energy on the material surface within a very short time. This high density of energy can produce fast melting and mixing followed by rapid solidification. Equipment simplicity and reliability give HCPEB technique great advantages over laser and ion beam treatment, and therefore potential industrial applications /3,5,6/.

HCPEB experiments have been conducted on a variety of coating-substrate systems, such as C-Al, TiN-Cr12MoV and Cr-Cr12MoV /7,8/. The results showed that a significant coating-substrate mixing process occurred during irradiation, consequently enhancing the

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mechanical properties such as micro-hardness and fretting wear resistance. The present paper reports the property enhancement of the hot-die steel (H13) that was coated by Al and followed by HCPEB treatment.

2. EXPERIMENTAL PROCEDURE

2.1. Equipment

Figure 1 is a schematic diagram of Nadezhda-2 HCPEB source, which can produce electron beams of energy (10~40 keV), high peak current density (10^2~10^3 A/cm^2), short pulse duration (~1 μs), and high efficiency with a pulse interval of 10 s. Electron beams are generated from an explosive emission graphite cathode. Spark plasma sources are placed evenly in a circle behind the anode, providing anode plasma that conducts the beam to the collector (target). An external magnetic field is applied to confine the beam. The energy density of the beam is decided by means of the accelerating voltage, magnetic field and anode-collector distance. More detailed information about the HCPEB system can be found from references /5,7/.

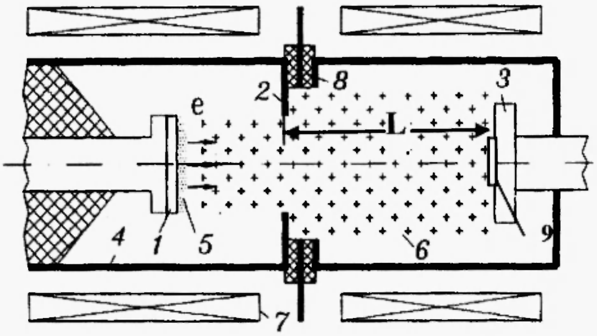

Fig. 1: Schematic diagram of HCPEB source using plasma-filled systems based on vacuum spark plasma. L: distance between anode and target (collector). 1: cathode, 2: anode, 3: collector, 4: vacuum chamber, 5: cathode plasma, 6: anode plasma, 7: solenoid, 8: spark plasma sources, and 9: specimen.

2.2. Samples preparation

H13 steel is a hot-die steel with a nominal composition of 4Cr5MoSiV (Table 1). It is widely used to shape Al and Cu alloys at working temperatures around 823-873 K (550-600°C). The high temperature oxidation resistance therefore is a basic requirement. Surface aluminizing and chromizing are two traditional methods to improve the oxidation resistance of H13 steel, but they are time-consuming processes. HCPEB was chosen to modify H13 due to its ability of surface alloying /5/ and enhanced diffusion /8,15/.

The H13 samples were machined into 20 × 10 × 2 mm shape, annealed at 1293 K (1020°C) for 0.5 hour (h), oil-quenched to room temperature and subsequently tempered at 883 K (610°C) for 2 h. The surfaces of the specimens were then polished with emery cloth to Ra ≈ 0.04 μm and followed by ultrasonic cleaning in acetone. A Bulat-6 type arc ion plating equipment was used to

Table 1

Chemical Composition of Steel H13

Elements	C	Si	Mn	Cr	Mo	V	S	P
Mass.%	0.32~0.45	0.8~1.2	0.2~0.5	4.75~5.5	1.1~1.75	0.8~1.2	<0.03	<0.03

Table 2

HCPEB Bombard Parameters

Samples		Voltage of acc. (KeV)	Energy density (J/cm^2)	Distance of source & target $L_{a\text{-}c}$ (mm)	Number of bombardments
Al-coated H13	1#	25	1	160	4
	2#	27	2	140	15

deposit Al films /9/. The processing parameters are listed below as the distance between the specimen and Al arc source is 400 mm; arc current $I_1 = I_2 = 90$ A; deposition time = ~1.5 h; bias $Us = -100$ V; and the vacuum pressure $P = 0.01$ Pa. These parameters produce an Al deposition of ~10 μm thick /8/. HCPEB was used to treat the Al-coated specimen (Table 2).

2.3. Oxidation test

Based on the working temperature range of H13 steel, 1023 K (750°C) was selected to perform the oxidation test in a vertical furnace. A quartz crucible was used to hold the specimens which included un-coated, Al-coated and Al-coated + HCPEB post-treated specimens. Total oxidation time was 20 h. After each cooling, an electronic balance with 0.1 mg accuracy was used to weigh the specimens. Before and after oxidation, selected specimens were analysed using a JSM-5600LV scanning electron microscope (SEM) with an energy dispersive spectroscope (EDS), and an X-ray diffractometer (XRD) with a Cu-K_α radiation source.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1 Surface morphology and composition analysis after HCPEB bombardment

Figure 2 shows the surface morphology of the specimens with Al-coating or HCPEB post-treatment. From Figure 2a it can be seen that the morphology of Al-coated layer shows a loose and flower-like structure with big particles on some areas – a typical morphology of arc ion plating film /9/. Since the structure of Al is very different from the substrate steel, and arc ion plating is a process of relatively low temperature deposition, adhesion between the coating and substrate was poor. In the sample after 4 bombardments of HCPEB it can be seen that some areas were slightly melted, while the majority of the surface was still uniform without apparent changes. Figure 2b shows the sample after 15 HCPEB bombardments. The Al film has melted almost completely as the result of bombardment and some areas of Al-coating were spalled away (e.g. marked box area). EDS analysis was conducted in the marked box area in Figure 2b, giving an Al content of 12 mass %, which shows the formation of a surface-alloying layer, although complete mixing may not be reached yet /10/. The corresponding XRD analysis shows that a new intermetallic phase–FeAl formed after HCPEB post-treatment (see Figure 6a). According to the previous studies, if Al contents reach the level of ~6 mass %, a continuous Al_2O_3 protective film will form during high-temperature oxidation /11, 14/, providing good oxidation resistance.

3.2 Oxidation results and discussions

The surface of Al-coated H13 specimen after

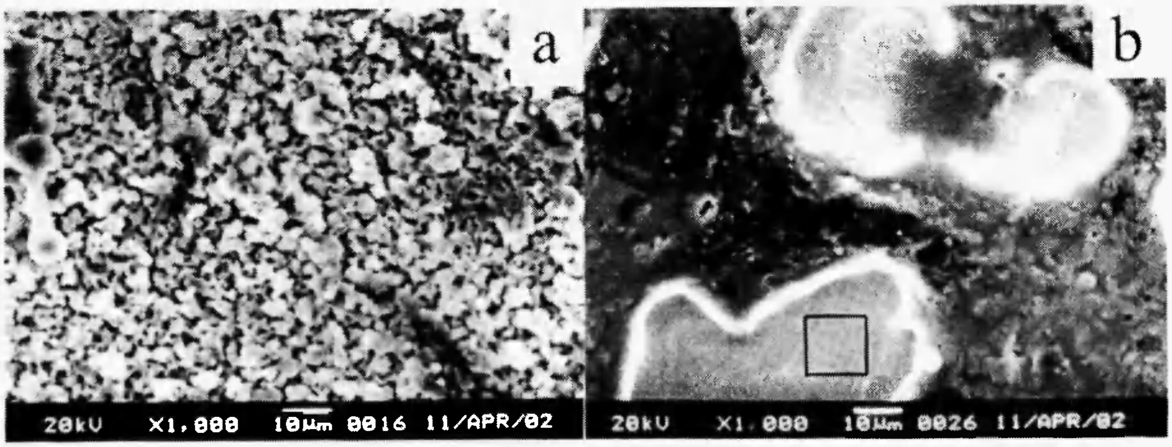

Fig. 2: Surface SEM morphologies of Al film: (a) Arc deposited Al film (non-bombarded) and (b) After 15 bombardments of HCPEB.

oxidation is shown in Fig. 3a. The morphology did not change much compared to the surface before oxidation, Fig. 2a. Referring to Fig. 3b, an oxide layer with small grains of ~ 1 μm formed after oxidation, came from the alloyed surface shown in Fig. 2b. There are no cracks or spallation evidence to be seen on the scale, demonstrating good high temperature oxidation resistance. Fig. 4 shows the oxidation kinetic curves of the specimens during 20 h exposure in air at 1023 K (750°C). The oxidation kinetics of H13 steel with Al deposition and deposition + HCPEB post-treatment follow an approximately parabolic rate law /12/, with a low mass gain of ~0.2 mg/cm^2, while the untreated H13 steel followed an approximately linear oxidation law, with a high mass gain of ~8 mg/cm^2 after 20 hours exposure, evidence of non-protective oxidation, whose reaction mainly depends on the chemical reaction /13/.

It should be noted that the oxidation mass gains were similarly low with or without HCPEB bombardment, indicating that the oxidation resistance of only Al deposited samples is already very good. From the mechanical property and practical application points of view, however, the arc deposited Al film is fairly loose, soft and easy to spall away. HCPEB bombardment mixed the surface layer, strengthened the surface, and is good for practical applications.

It can also be seen from Fig. 4b that the mass gain curves fluctuated during the first 6 hours exposure, perhaps due to the rough coating surfaces or partial scale spallation. It is common that a rough surface with

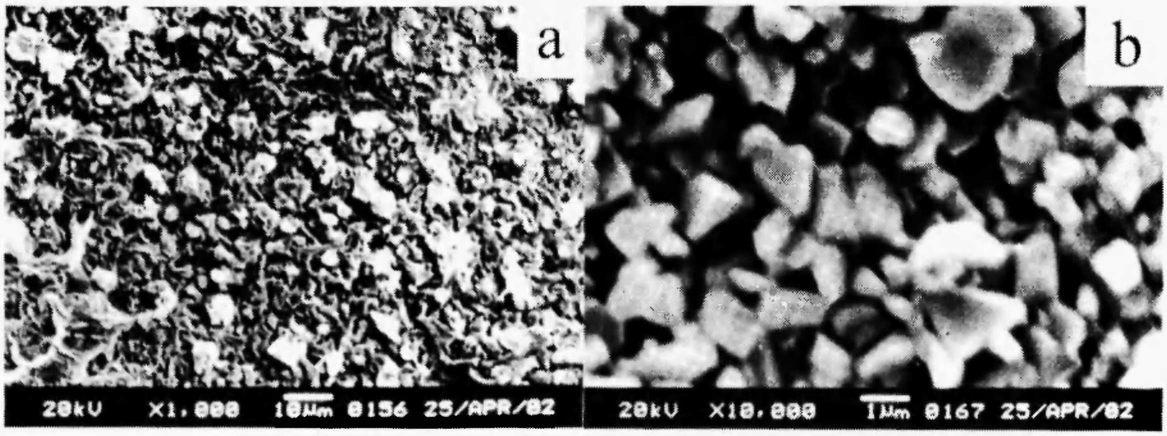

Fig. 3: Surface SEM morphologies of the specimens after oxidation at 1023 K (750°C) for 20h: (a) Al-coated, and (b) 15 times HCPEB treated.

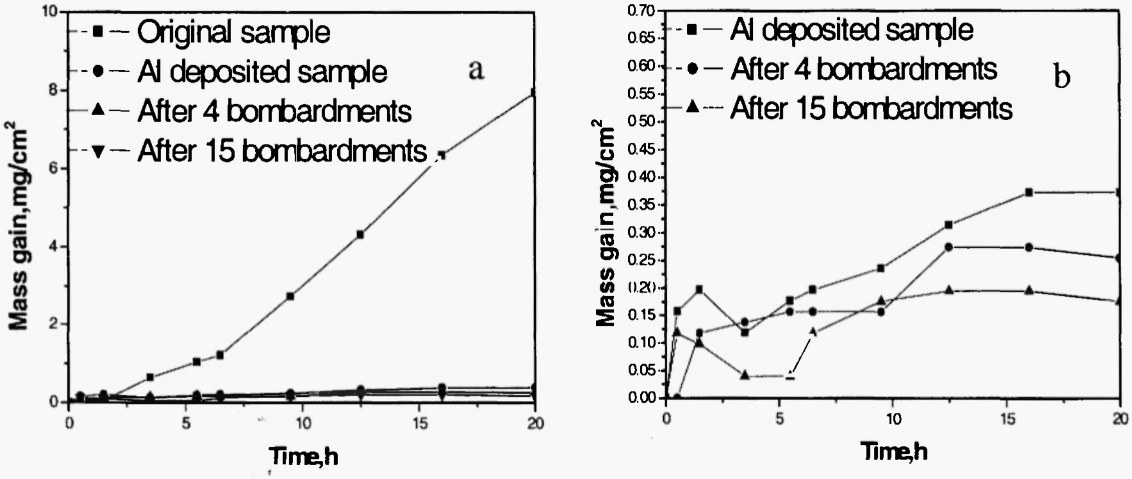

Fig. 4: Oxidation kinetic curves at 1023 K (750°C), 4b is an enlarged part of 4a.

high surface area shows a high initial oxidation rate. The oxidation rates slowed down and the curves became smoother after 6 hours oxidation, evidence of the formation of a protective oxide layer. Another possible influential factor is the carbon contamination on the surface after HCPEB bombardments /15/, where free carbon may be vaporized, resulting in a mass loss during the initial stage of oxidation, especially on the specimen with 15 bombardments of HCPEB.

Figure 5 is the XRD analysis of Al-coated H13 steel before and after oxidation testing. It was noted that the oxidation surface layer is mainly composed of two types of Al_2O_3, type I and type II Al_2O_3 /16,17/. The content of type I Al_2O_3 is higher than that of type II, and there is an apparent preferred orientation along the crystal plane (202) for type I Al_2O_3, while the deposited Al film before oxidation shows little preferred orientation. Fig. 6 is the XRD analysis of Al-coated H13 steel with 15

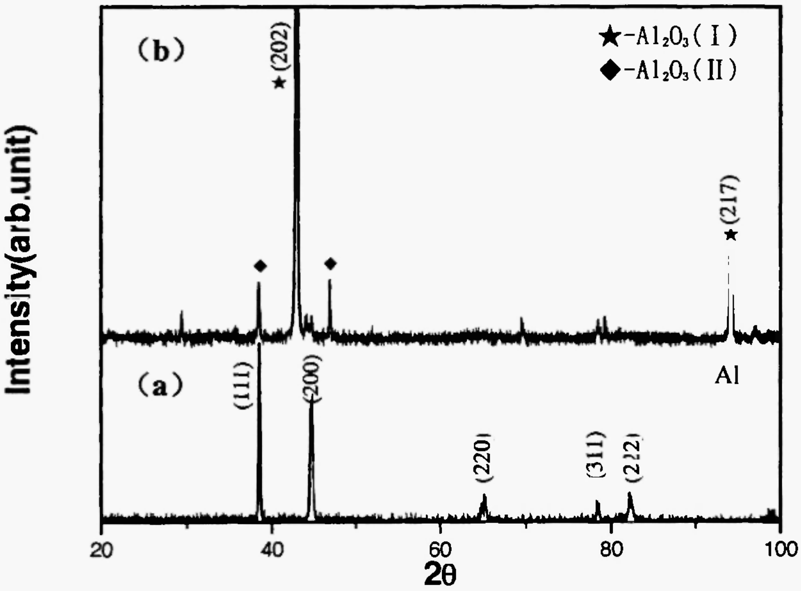

Fig. 5: XRD spectra of Al-coated H13 specimen: (a) before oxidation, and (b) after oxidation.

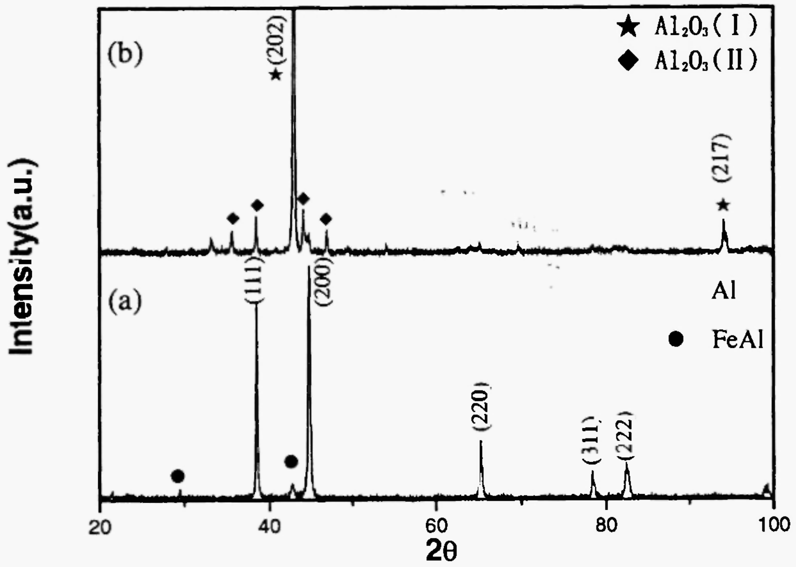

Fig. 6: XRD spectra of Al-coated H13 steel specimens with 15 bombardments of HCPEB: (a) before oxidation and (b) after oxidation.

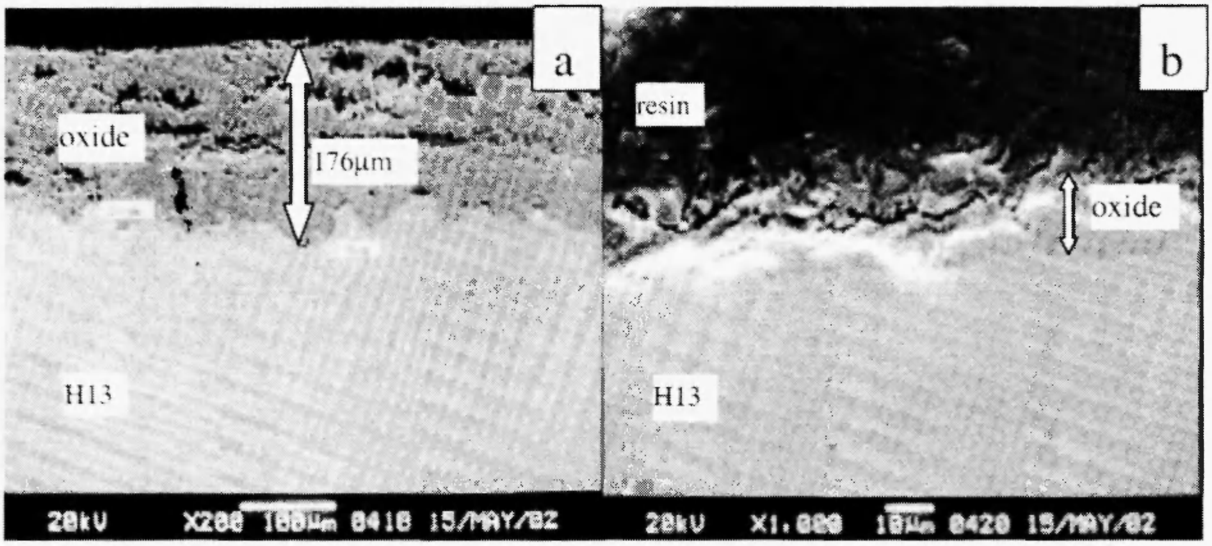

Fig. 7: Cross-sectional morphologies of the specimens oxidized at 1023 K (750°C): (a) H13 steel, and (b) Al-coated and 15 times HCPEB treated (sample 2#).

bombardments of HCPEB before and after oxidation testing, which also shows that the content of type 1 Al_2O_3 is dominant the oxidation products. Fig. 6a also demonstrates that an intermetallic compound – FeAl formed after HCPEB post-treatment, which may contribute to the formation of compact alumina as compared to the only Al-coated steel without HCPEB treatment. To understand the detailed oxidation mechanism, however, needs more study.

Figure 7 is the cross-sectional morphology of the oxidised specimens. It shows that the oxide layer formed on H13 steel is quite thick (~170 μm), and has a loose structure with many pores in the scale. The specimen with Al-coating and HCPEB post-treatment, however, produced a thin oxide layer of ~10 μm thick after 20 h oxidation (Fig. 7b), consistent with the low oxidation mass gain. The microstructure of the scale appears relatively compact; and no spallation can be seen after oxidation.

4. CONCLUSIONS

A new, two-step processing including Al deposition and High Current Pulsed Electron Beam post-treatment has been applied to a die steel surface. Oxidation tests were performed at 1023 K (750°C) in air to study the coating properties. The results indicated that the coatings contain aluminium and FeAl intermetallic compound, and has greatly improved the oxidation resistance of the steel. It is believed that the Al_2O_3–rich scales formed on the coated steel possess a compact microstructure, reduce the oxidation rate, and provide good oxidation resistance.

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