Original Article

Surface modification of A390 alloy with CaB₆ composite coating

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A390 alloy is widely used in piston production and owing to the adverse work conditions of piston, the demand for performance, especially surface performance of A390 alloy is very high. Grain refinement and Sr modification are widely used to improve the performance of A390 alloy; but this melt treatment for the improvement of surface properties is limited. In our study, in order to achieve excellent surface performance, a hard protective CaB₆ composite coating was built on the surface of A390 alloy by laser cladding. Results show that the in situ synthesized CaB₆/A390 composite coating exhibits ideal combination of good adhesion, high hardness and high abrasive resistance. Both of the surface and internal microstructure of A390 alloy can be modified and its performance can be improved remarkably owing to the formation of CaB₆ composite coating. The brinell hardness of the coating can reach 136.2 HB, increased by 24.7 % and the abrasive resistance of A390 alloy can be improved by 17.7 %.

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1. Introduction

As we all know, A390 alloy is widely used in piston production, due to its excellent casting performances, high specific strength and wear resistance [1–3]. However, the primary Si phase in Al-Si alloys without any treatment is coarse which can split Al matrix and be harmful to the mechanical properties of A390 alloy. So to eliminate the harmful effect of coarse primary Si phase in Al-Si alloys, primary Si particles must be modified [4]. It is widely accepted that evenly distributed fine primary Si is good for the mechanical properties and adding master alloy containing P can refine the primary Si which can improve its mechanical properties [4–7]. Besides, adding ceramic particles also is an effective method to enhance the mechanical properties of Al-Si alloys [8–10]. The content of Si in A390 alloy is 16%~18% and owing to the high content of Si, it must be effective to refine the primary Si much more smaller to further improve the mechanical properties. The Al melt treatment methods mentioned above refined the primary Si to 30 μm and it is hard to refine the primary Si to much smaller. However, for piston, its work condition is adverse. The refinement of primary Si and particles reinforced matrix are not enough for the present requirement. For the piston alloy performance, especially its surface performance, the requirement is demanding. So it is necessary to find a good method to refine the primary Si especially the zone near the surface. Nowadays, surface modification by building coatings is more and more widely used to improve the surface proper-
The types of coatings include SiC coating, Al2O3 coating, borides coating, etc. [14]. Borides coatings are widely used in aluminum alloys for structural applications, especially for structures exposed at high temperatures, for surface protection, and for wear-resistant parts used in a corrosive environment [15–21]. During the piston operation, poor work condition causes the surface continuing to wear arising from the failure. Building a hard protective borides coating with certain thickness and good combination on the surface of A390 alloy to improve its mechanical properties of the surface is a good method. A hard coating on A390 surface can reduce the damage to its work surface, because that the coating with high melting point, high hardness and good anti-oxidation stability can protect the matrix to some extent. The protection can improve reliability and service life of piston, which exhibits economic benefits to machinery industry.

Nowadays, metal borides have attracted much attention for various applications, such as reinforced particles, wear-resistant parts, high-temperature structural materials and light weight impact resistant armor material. Such as that TiB2 in form of thin films or coatings was used as hard materials [15,16]. [W,Ti,Cr]B3 coatings exhibit possess the ideal combination of good adhesion, sufficient plasticity, high hardness and high corrosion/erosion resistance. Moreover, borides coatings, such as ZrB2, CaB6, CrB2, B4C, NiB etc have been investigated for better performance [15–22]. Interesting coatings were produced by various groups, using nonmagnetic sputtering, dynamic ion mixing, electron beam evaporation or chemical vapor deposition. Calcium hex-borides (CaB6) is an alkaline-earth hex-bride which exhibits the properties of low density, high hardness and wear resistance, high melting point and corrosion resistance [22–25]. Owing to its excellent properties, CaB6 was chosen as protective coating of A390 alloy. Different from other borides particle coatings, the density of CaB6 is similar with the matrix which can ensure lightweight. During laser process, CaB6 particles diffused into A390 alloy and forming CaB6 composite coating on the surface of A390 alloy achieving good metallurgical combining between the matrix and the protection of CaB6 composite coating can improve the surface of A390 alloy. What's more, by this method, the microstructure of A390 alloy connected with the coating can also be modified, which can further improve its mechanical properties seriously. In this paper, in-situ CaB6 powders were coated on the surface of A390 alloy through laser cladding fabrication, forming a composite coating. Then the microstructure and mechanical properties of A390 alloy with the composite coating were studied in detail.

2. Material and methods

The substrate material, A390-T6 was cut into rectangular coupon of 10 × 10 × 40 mm3 dimensions. In-situ CaB6 with particle size < 2 μm was used as the pre-cursor powder [24]. The precursor powder was suspended in water soluble organic binder to form thick slurry and spray deposited using air spray gun onto a well-polished clean A390 substrate, then dried at room temperature (25 °C) to rid of the moisture before laser processing. A laser beam with wavelength of 1070 nm and beam spot of 0.6 mm was scanned at 60 mm/s linear speed on the sample surface to melt the entire precursor layer and part of the substrate material to form composite coating during laser processing, as shown in Fig. 1. The phase analysis of the coating was done by X-ray diffraction (XRD, Rigaku D/max-rB). Micro-structural characterization of the coatings was conducted in the cross section at a plane perpendicular to the laser processing direction. Samples for microstructure studies were analyzed by scanning electron microscope (SEM, JSM-6380LA) and field emission scanning electron microscope (FESEM, SU-70) with EDS. Brinell hardness was tested by the digital display brinell hardness tester and abrasive resistance was measured by using MM200 type wear testing machine. For the hardness test, the measurements were done using a steel ball of 10 mm diameter and load of 2.5 kN. The wear test was conducted for a total time of 40 min while the wear loss of each sample was recorded after every 10 min run. The applied load was 10 kg and rotate speed was 200 r/min.

3. Results

3.1. Characterization of the CaB6 composite coating

Fig. 2 shows the phase composition of (a) A390 alloy and (b) CaB6 composite coating on the surface of A390 alloy. It can be found that the main phases of A390 are α-Al, Si and Al2Cu.
For the composite coating, apart from the phases mentioned in A390 alloy, CaB$_6$ was the main phase. During the laser processing, the local temperature of the surface can reach 2000 K, the Al substrate can melt and then CaB$_6$ diffused into the substrate, forming CaB$_6$-A390 composite coating on the surface of A390 alloy.

Fig. 3 shows the optical micrograph of transverse cross section of the coating. At the macroscopic level, the alloy can be divided into three parts, marked as region A, B and C respectively and the corresponding microstructure was analyzed by FESEM. By comparing the micro structures, the size of primary Si exhibit gradient distribution from the surface to the inner. The coating layer thickness is about 1 mm which is dense and compact. In region A, the size of primary Si is small, with in 10 μm and they distribute uniformly in the Al matrix. The refinement of primary Si in region A may be caused by the high cooling rate. Because the scarce information about the evolution of microstructure along the cross-section, the microstructure of the composite coating marked as region A was studied in detail. By analyzing the microstructure (Fig. 4a and 4b), it can be found that some small black particles distribute near the primary Si and some even embedded in the primary Si. Combined with EDS analysis, the small particles were CaB$_6$ as shown in Fig. 4c and 4d. According to the Fick’s laws of diffusion, concentration gradient acts as the diffusion driving force. Thus the diffusion always spreads to the direction of low concentration [15]. In our study, owing to the concentration gradients of CaB$_6$ particles from the surface to the inner of A390 alloy, at high temperature CaB$_6$ particles diffused into the substrate, forming CaB$_6$ reinforced A390 composite microstructure. Results show that the composite coating is metallurgically bonded to the substrate and the

Fig. 2 – XRD pattern taken from the inner of (a) A390 and (b) free surface of CaB$_6$/A390 composite coating.

Fig. 3 – (a) Optical micrograph of transverse cross section of the coating and the microstructure of the alloys at different regions: (b) region A, (c) region B and (d) region C.
composite microstructure is fine and uniform. In terms of the second region B, it is a transition between region A and C, and this region consists of composite structure with small size of primary Si (5 μm) and large size of primary Si. The existence of region B achieved a good combination of substrate and the coating (as shown in Fig. 3c). Interestingly, the farther away from region A, the size of primary Si increased and until to region C, the primary Si kept stable within 30 μm. As for the third region C, primary Si with the size of 30 μm in the matrix is the dominant microstructure because of lower solidification rate. Rapid solidification process shows a marked enhancement of mechanical properties over the conventionally processed alloys through the extension of solid solubility limit, the refinement of microstructure and the dispersion of secondary phases [19–21]. By this method, not only the surface of A390 alloy can be strengthened but also the microstructure close to the surface of A390 alloy can be modified by CaB₆, which is better than other protective borides coatings.

### 3.2. Hardness and abrasive resistance of the composite coating

In order to study the influence of CaB₆ composite coating on the surface properties of A390 alloy, brinell hardness and abrasive resistance of the A390 alloy without coating and A390 with CaB₆ composite coating were tested, as shown in Fig. 5. According to the formula $HB = \frac{2P}{\pi D(D-d)}$, HB can be calculated. The brinell hardness of the A390 alloy is 109.2 HB, while with the composite coating, the brinell hardness can reach 136.2 HB, increased by 24.7 %. Besides, by analyzing the weight losses at different time, the wear weight loss of the A390 alloy was 33.3 mg at 40 min but with the composite coating, the wear weight loss is only 27.4 mg, decreased by 17.7 %. As mentioned above, the coating metallurgically combines with the substrate. The good hardness and abrasive resistance is attributed to the supersaturated solid solution and the grain refinement of primary Si. At the same time, the reinforcement of CaB₆ also makes a contribution to the improvement. Fig. 6a and 6b correspond to the worn surfaces of A390 and A390 with the protective coating respectively. By analyzing, the worn surface of A390 is relatively rough because of the presence of distinct grooves and craters, as shown in Fig. 6a. While, the worn surface of A390 with protective coating has a smooth appearance with few distinct grooves and craters owing to the indentation resistance offered by CaB₆ particles.

### 4. Discussion

Fig. 7 shows the crystal structure of Si and CaB₆. Both of them belong to cubic crystal structure. In order to study the effect of CaB₆ on the size of primary Si, the possible coherent interface of CaB₆ and Si was calculated, as shown in Table 1 and results show that the degree of dis-registry for interplanar distance of CaB₆ and Si is smaller than 5 %. The values imply good coherency between CaB₆ and Si. Due to this relationship, the nucleation and growth of Si will be inevitably influenced by
the CaB₆ particles in the melt, thus high cooling rate and CaB₆ additions can refine primary Si and modify the microstructure of A390 alloy. The factors influencing the hardness and wear resistance are complex and inter-related [25–28]. The uniform hard spots may inhibit the dislocation motion which can effectively improve the wear resistance of alloy. During the deformation, the dislocation should overcome the deformation resistance and the deformation resistance \( \tau \) can be calculated by the formula: \( \tau = \frac{G b \lambda}{2} \). Where \( G \) is the shear modulus of elasticity, \( b \) is the Burgers Vector and \( \lambda \) is the dislocation bypass spacing. It can be found that \( \tau \) is controlled by the dislocation bypass spacing. It is helpful to improve its hardness by reducing the grain size or increasing the volume fraction of the particles [28–30]. Compared with coarse primary Si, the dislocation bypass spacing among the refined primary Si can be much smaller. The resistance dislocation to overcome increased which can improve the carrying capacity of the alloy. Besides, the diffusion of CaB₆ to the substrate can also make contribution to the surface hardness of the alloy. CaB₆ particles distribute uniformly in the matrix, acted as hard spots, which can improve its hardness significantly. At the same time, hardness of the alloy can greatly affect its abrasive resistance.

In order to state the effect of protective of CaB₆ composite coating on the surface performance of A390 alloy, a schematic diagram was drawn as shown in Fig. 8. Without coating, abrasive particles wear the surface of A390 alloy obviously and the wear depth \( d_1 \) is deep, while with the protection of CaB₆ composite coating, the wear depth \( d_2 \) is much smaller than \( d_1 \).

### Table 1 – Parameters for the interatomic spacing misfit equation.

<table>
<thead>
<tr>
<th>Case</th>
<th>( d_{\text{in}} ) v ( \text{CaB}_6 )</th>
<th>( d_{\text{in}} ) v ( \text{Si} )</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((3 \ 1) \text{CaB}_6 \parallel (3 \ 3 \ 1) \text{Si})</td>
<td>1.2523</td>
<td>1.2457</td>
<td>0.527</td>
</tr>
<tr>
<td>((3 \ 2) \text{CaB}_6 \parallel (4 \ 2 \ 2) \text{Si})</td>
<td>1.1100</td>
<td>1.084</td>
<td>0.144</td>
</tr>
<tr>
<td>((4 \ 0) \text{CaB}_6 \parallel (5 \ 1 \ 1) \text{Si})</td>
<td>1.0384</td>
<td>1.0450</td>
<td>0.636</td>
</tr>
<tr>
<td>((4 \ 2 \ 1) \text{CaB}_6 \parallel (4 \ 4 \ 2) \text{Si})</td>
<td>0.9064</td>
<td>0.9050</td>
<td>0.154</td>
</tr>
<tr>
<td>((5 \ 1 \ 0) \text{CaB}_6 \parallel (6 \ 2 \ 2) \text{Si})</td>
<td>0.8146</td>
<td>0.8186</td>
<td>0.491</td>
</tr>
</tbody>
</table>
indicating a smaller contact area between abrasive wheel and surface of A390 alloy. A small contact area benefits the reduction of wear weight loss, ensuring good abrasion resistance. In conclusion, the well refined primary Si and uniform hard CaB₆ particles coordinating with each other and the formation of the composite microstructure can improve the surface performance of A390 alloy obviously.

5. Conclusion

In this paper, in order to achieve excellent surface performance to meet the performance requirements of piston materials, a hard protective CaB₆ composite coating was built on the surface of A390 by laser processing. For the composite coating, the main phases are α-Al, Si and Al₆Cu and CaB₆. Owing to the diffusion of CaB₆ and high cooling rate, not only the surface microstructure of A390 alloy but also the inner microstructure close to the surface can be modified and strengthened by forming the protective CaB₆ composite coating. By this surface modification, the size of primary Si near the surface can be refined to 5 μm which is much more smaller than those treated by traditional melt treatment process. The surface performance of A390 alloy strengthened by this composite coating can be improved obviously. The brinell hardness of the coating can reach 136.2 HB, increased by 24.7 % and the abrasive resistance of A390 alloy can be improved by 17.7 %.

Conflicts of interests

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

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REFERENCES


