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ARTICLE

High-temperature Sulfidation and Oxidation Behavior of Plasma-sprayed Al-Mo Coatings

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Abstract: Gas burner is the key component of coal-water slurry gasifier system. However, due to the sulfidation at high temperature, gas burner often fails in advance, which affects the stable operation of the system. In this work, Al-Mo coatings were deposited by plasma spraying with a Mo bonding layer. The sulfidation and oxidation behavior of the Al-Mo coatings was studied and compared with those of Mo coatings and Inconel 600 alloy at 973, 1073 and 1173 K. Results show that both the high-temperature sulfidation resistance and the high-temperature oxidation resistance of Al-Mo coatings are superior to those of Mo coatings. The high temperature sulfidation resistance of coatings is better than that of Inconel 600 alloy. Plasma-sprayed Al-Mo coatings with a Mo bonding layer are promising candidates for the corrosion protection of steels in a sulfur/oxide-rich atmosphere.

Key words: Al-Mo coating; plasma spraying; high temperature sulfidation

The coal gasification is one of the key techniques for clean utilization of coal[1]. As a core component of the coal-water slurry gasifier, the burner can atomize the coal-water slurry by high-velocity oxygen. But during the actual operation, some radial radioactive cracks often appear at the end of the burner, which has a significant influence on the production continuity and results in huge economic losses to the factory. It is generally considered that the radial radioactive cracks are mainly caused by high temperature sulfidation. In the meantime, the high temperature oxidation, erosive wear, thermal shock and stress concentration also have influences on the burner failure[2].

The high temperature corrosion of metals and alloys in a sulfur-containing atmosphere is usually much more severe than that in a pure oxidizing environment because common metal sulfides have a larger deviation from stoichiometry and a higher density of lattice defects than the corresponding oxides[3,4]. It is well known that refractory metals such as niobium, molybdenum and tantalum exhibit a high resistance to sulfide corrosion[5,6]. However, the oxidation resistance of these refractory metals is rather poor, due to the formation of volatile oxides or cracks in the oxide scale[7]. People pay more attention to the sulfidation of alloys because they are more commonly used materials, such as M(Fe,Co,Ni)Cr and MCrAl. It was shown that the sulfidation rates of binary iron-, nickel- and cobalt-base alloys containing niobium or molybdenum are several orders of magnitude higher than that of the corresponding refractory metals[8-10]. However, in high-temperature industrial environments with oxygen and sulfur vapour present, the conventional high-temperature corrosion-resistant alloys undergo rapid gaseous corrosion[11].

It has been pointed out that the Mo coatings prepared by cathodic arc deposition can protect the substrate from high temperature sulfidation attack owing to the compact molybdenum sulfide layer formed on the coating in the sulfidation environment[12]. It was also reported that sputter-deposited amorphous Al-Mo coatings can well protect high chromium steel substrates against high-temperature corrosion in sulfur vapor and oxygen at temperatures as high as 1273 K[13,14]. The high-temperature sulfidation resistance of

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Al-Mo coatings is higher than that of Mo coatings. Additionally, Al_2O_3 is formed on the Al-Mo coatings in a high temperature oxidizing environment, which can diminish the evaporation of the volatile molybdenum oxide, and the addition of aluminum improves the oxidation resistance of the Mo coatings.

Plasma spraying, a versatile coating technology with a great number of coating-substrate combinations, can satisfy the demand for new materials needed to work in severe environments[15]. It is also thought to be economical to deposit Al-Mo coatings for industrial applications. The present work aims to study the sulfidation and oxidation behaviors of plasma-sprayed Mo and Al-Mo coatings on Inconel 600 alloy, and explore the possibility of its application in gas burners.

1 Experiment

Al-Mo composite powder was synthesized by a mechanical alloying method. After accurate weighing, the Al and Mo powders (Al-27at%Mo, abbreviated as Al-Mo) were put into a stainless steel tank for ball milling (ND8-1L ball mill) with zirconia ceramic balls of 6 mm in diameter in an Ar atmosphere. The ball-to-powder mass ratio was 10:1. Stearic acid (1 wt%) was added to prevent the excessive sticking of the powder to the ball and the tank wall. After milling to 31 h, the mixed powders were transferred to a corundum crucible and annealed in a vacuum-tube- resistance furnace at 1273 K for 2 h. To obtain powders suitable for spraying, the sintered powders were milled again.

The Inconel 600 alloy was employed as a disc-shaped substrate with a thickness of 3 mm and a diameter of 16 mm. Commercial Mo powders and synthesized Al-Mo powders were deposited on a preheated substrate by plasma spraying (APS-2000, Beijing Aeronautical Technology Research Institute, 80 kW class). Argon gas was used as the primary plasma operating gas and hydrogen was selected as an auxiliary gas. During the spraying, the pressures of argon and hydrogen were fixed at 0.4 and 0.25 MPa, respectively. Argon gas was also used as the powder feed gas at a flow rate of 250 L/h. The plasma power was maintained at approximately 36 kW (600 A/60 V) and 30 kW (500 A/60 V) for the deposition of the Mo and Al-Mo coatings, respectively. Mo was also deposited as the bonding layer for the Al-Mo coating. The traverse speed of the spray gun was kept at 150 mm/s with a spaying distance of 12 cm for the Mo coating and 10 cm for the Al-Mo coating.

The sulfidation test was carried out in an $Ar\text{-}S_2$ atmosphere at a sulfur pressure of 1 kPa in a vacuum-tube-resistance furnace at 973, 1073 and 1173 K. The specimens were taken out several times for weighing until they were exposed up to 12 h. After each cycle, the mass gains were measured using an electronic balance with an accuracy of 10^{-5} g. The oxidation test was carried out in an air atmosphere in a muffle furnace. The phase composition of the powders and coatings was examined by X ray diffraction (XRD, D/MAX RIGAKU 2550 VB/PC) and analyzed by JADE5.0 MDI software. The morphology was observed by scanning electron microscopy (EVO MA15 ZEISS)

2 Results and Discussion

2.1 Powders and coatings

To form the Al-Mo coating, milled Al-27at%Mo composite powders were first synthesized and then heated to 1273 K for different periods of time in the vacuum-tube-resistance furnace. The intermetallic phase Al_8Mo_3 was formed after milling for 31 h and heat-treating for 2 h (Fig.1), which is expected to increase the sulfidation resistance at high temperatures. $Al_{3+x}Mo_{1-x}$ was also found in the powder. The microstructures of the as-received powder and the corresponding coating are shown in Fig.2. The particle size is not uniform, but mainly in the range of 60~100 μm. Every particle is bonded together by many tiny fragments. The flow ability of the powders is acceptable and meets the requirements of plasma spraying. The microstructure of the coatings is comparatively dense.

2.2 High-temperature sulfidation behavior of Mo and Al-Mo coatings

The morphologies of Inconel 600 and Mo and Al-Mo coatings after different high-temperature sulfidation processes are shown in Fig.3. It is found that the Inconel 600 alloy specimens are seriously corroded. At 973 and 1073 K, the morphology of all coated specimens is uniform and compact after sulfidation for 12 h without any visible cracks on the coating surface. However, a large part of the Mo coating was detached from the substrate after sulfidation at 1173 K for 8 h. A yellow corrosion product layer is formed on the Mo coating surface and the coating loses its integrity. If the corrosion test continues, the position of the molybdenum coating contacting with the corrosive medium includes not only the coating surface, but also the bottom surface of the coating and the surface of the rupture coating. The Inconel 600 alloy and

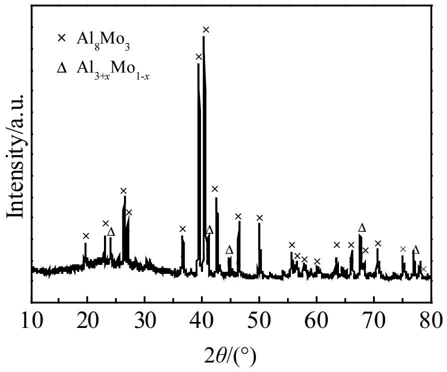

Fig.1 XRD pattern of the Al-27at%Mo powders milled for 31 h and heat treated at 1273 K for 2 h

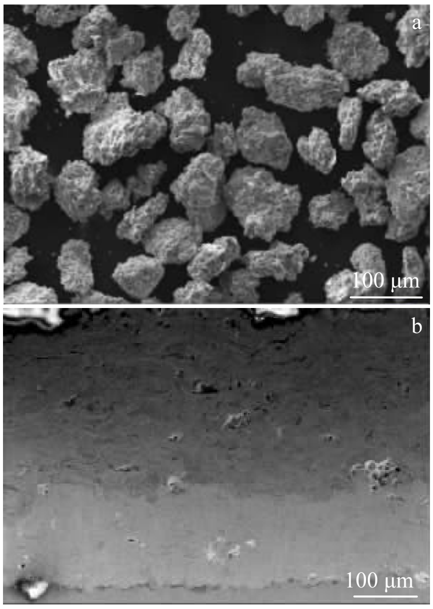

Fig.2 Microstructures of Al-Mo powders (a) and plasma sprayed Al-Mo coatings (b)

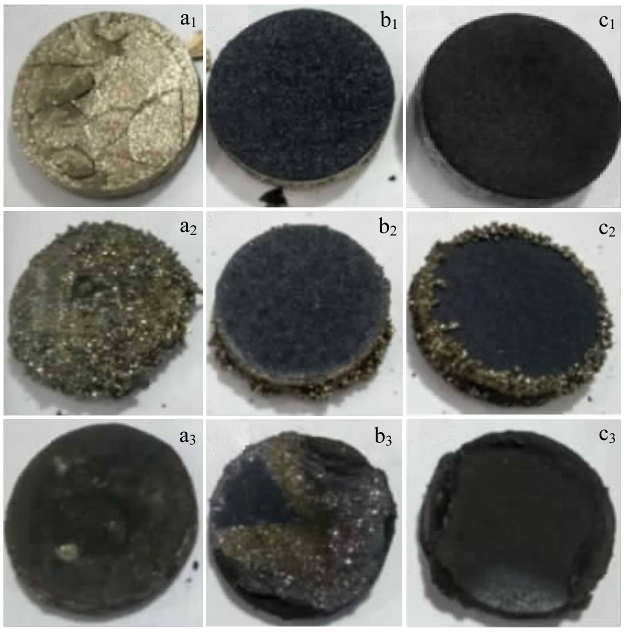

Fig.3 Morphologies of the Inconel 600 alloy (a), Mo coatings (b), and Al-Mo coatings (c) under different high temperature sulfidation conditions: (a$_1$, b$_1$, c$_1$) 973 K/12 h, (a$_2$, b$_2$, c$_2$) 1073 K/12 h, (a$_3$, c$_3$) 1173 K/12 h, (b$_3$) 1173 K/8 h

the Al-Mo coating only contact with the corrosive medium through the top surface. At this time, the corrosion contact area of the three materials in the present study is significantly different. The mass gain of these materials cannot be compared now. Therefore, the corrosion test of the Mo coating did not continued after 8 h. Although the Al-Mo coating was also separated from the substrate at the edge of the specimen after processing at 973 K for 12 h, most of the coating compactly bonded to the substrate after sulfidation. Further tests show that the Al-Mo coating can bond to substrate very well, even after sulfidation at 1173 K for 109 h. The cross-sectional microstructure of the coatings after sulfidation is shown in Fig.4. There are many large holes and long cracks in the Mo coating after sulfidation at 973 K for 12 h, even though its surface is relatively integrated. Comparatively, no obvious change in microstructure can be found for the Al-Mo coatings even after sulfidation at 1173 K for 109 h. A compact corrosion product layer forms on the Al-Mo coating, whose composition is Al$_8$Mo$_3$ and Al$_{13+x}$Mo$_{1-x}$ intermetallic compounds and small amounts of MoS$_2$ (Fig.5b). There are no sulfides consisting of Inconel 600 alloying elements (Fig.5a). Though the temperature is only 1073 K, the Inconel 600 alloy has reacted with the sulfur in the environment after 2 h. The reaction products of Fe$_9$Ni$_9$S$_4$ and Ni$_3$S$_2$ etc. are observed on the surface of the alloy from the XRD results. Due to the physical and chemical blocking of the Al-Mo coating, the corrosion of the substrate is prevented. Additionally, the Al-Mo coating can maintain its structural integrity much better than the Mo coating or the Inconel 600 alloy, and it possesses excellent performance in the high- temperature sulfidation environments.

The mass gain of the Inconel 600 alloy, Mo coatings and Al-Mo coatings after sulfidation at 973, 1073 and 1173 K are shown in Fig.6. The mass gains of the Inconel 600 alloy are much higher than that of the coated specimens because the corrosion products formed on the Inconel 600 alloy cannot protect the specimens from continuing corrosion. For the coated specimens, the mass gains of the Al-Mo coatings are lower than that of the Mo coatings. It can be seen that the Mo coatings and Al-Mo coatings prevent the sulfur from diffusing into the substrate at high temperatures, especially below 1073 K. It was reported that the low-melting-point Ni$_3$S$_2$ is formed on the Mo-coated Inconel 600 alloy, which promotes the rapid diffusion of both sulfur species and substrate elements via the edge of the Mo-coated alloy[16]. However, Ni$_3$S$_2$ has not been found on the Al-Mo coatings in the present investigation. Correspondingly, the sulfidation resistance for the Al-Mo coatings is much better than that of the Mo deposits. In addition, the sulfidation rate of bulk materials Mo and Al-Mo is about 5×10^{-12} and 4×10^{-14} $g^2\cdot cm^{-4}\cdot s^{-1}$, respectively[17]. The larger sulfidation rate of Mo shows the quick corrosion of Mo in the sulfur environment. We did not compare the rate of coatings with the corresponding bulk material, for the rate of coatings is not real through layer kinetics since the specimens has open edges. The corrosion of coatings could happen on the surface, also along the cracking or interface of the coating, which results in a porous microstructure of coatings compared with that of the as-sprayed ones. It can also be concluded

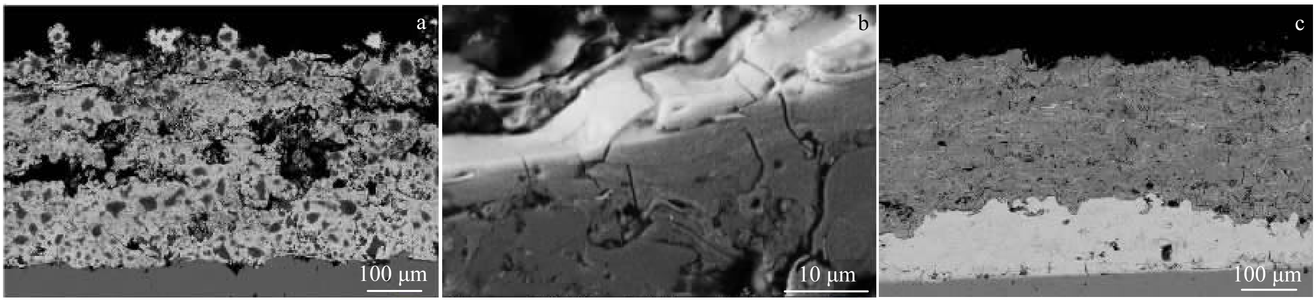

Fig.4 Microstructures of Al-Mo and Mo coatings after sulfidation: (a, b) Mo coating at 973 K/12 h and (c) Al-Mo coating at 1173 K/109 h

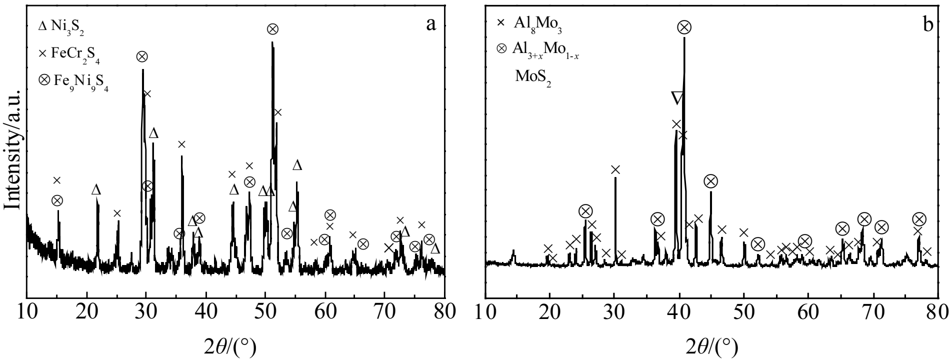

Fig.5 XRD patterns of Inconel 600 alloy after sulfidation at 1073 K for 8 h (a) and Al-Mo coating with a Mo bonding layer after sulfidation at 1173 K for 109 h (b)

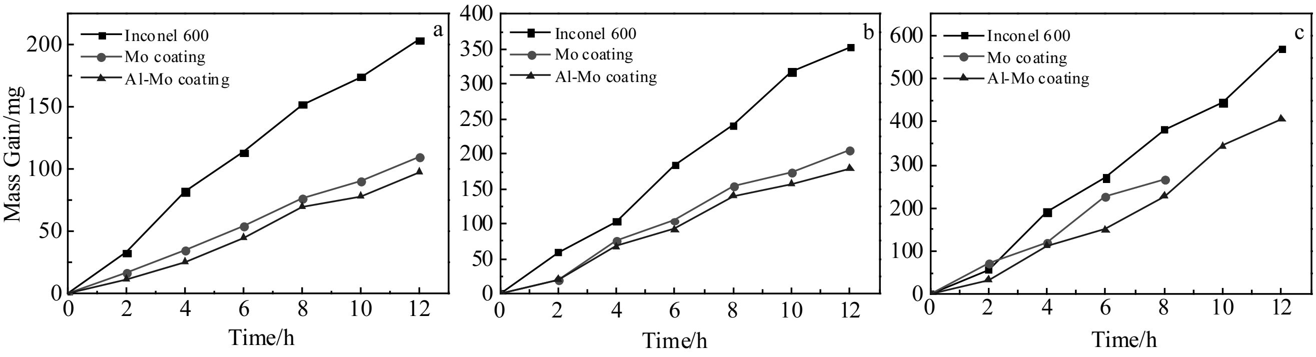

Fig.6 Mass gain of Al-Mo coatings, Mo coatings and Inconel 600 alloy with a Mo bonding layer at 973 K (a), 1073 K (b) and 1173 K (c) after the sulfidation

that the sulfidation rate of Mo coating is larger than that of the Al-Mo coating.

2.3 High temperature oxidation behavior of Mo and Al-Mo coatings

The sulfur in coal can cause the high temperature sulfur corrosion of the material. In addition, the oxygen concentration at the burner is high, and the material can oxidize in the high-temperature oxidation environment. In order to analyze the corrosion mechanism and corrosion resistance, the sulfur corrosion and oxygen corrosion are discussed separately. The high-temperature oxidation behavior was also investigated, and the results are shown in Fig.7. The Inconel 600 alloy shows high oxidation resistance at high temperatures and no visible corrosion failure could be observed on the surface. After oxidation at 973 K for 12 h in a muffle furnace, light yellow corrosion products are generated on the surface of the Mo coating. X-ray diffraction analysis shows that the Mo coating completely transforms to MoO_3 after oxidation at 973

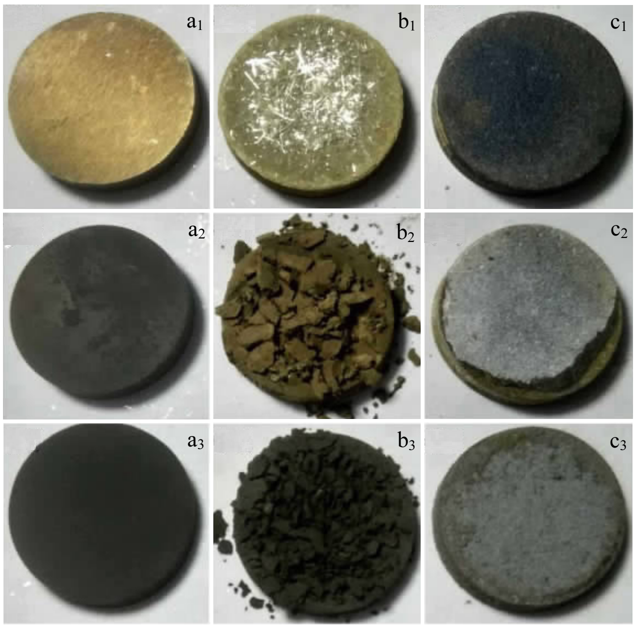

Fig.7 Morphologies of Inconel 600 (a), Mo coatings (b) and Al-Mo coatings (c) under different high-temperature oxidation conditions: (a_1,b_1,c_1) 973 K/12 h, (a_2,b_2,c_2) 1073 K/8 h, (a_3,b_3,c_3) 1173 K/2 h

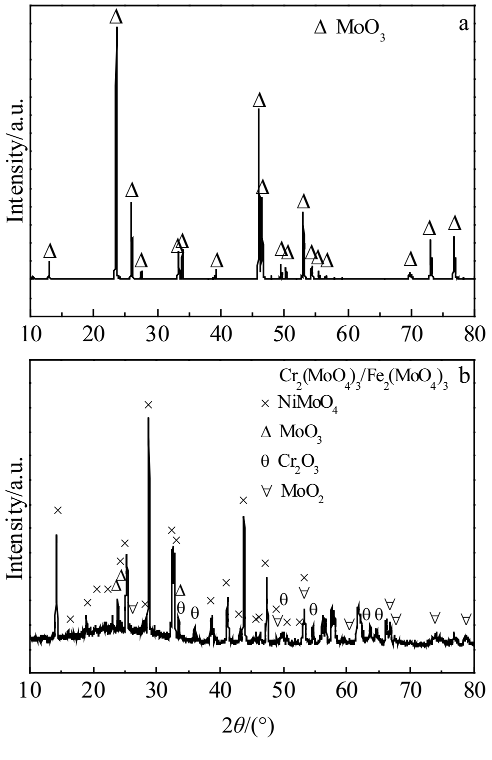

Fig.8 XRD patterns of Mo coatings after oxidation at 973 K for 12 h (a) and 1173 K for 2 h (b)

K for 12 h (Fig.8). However, as the temperature increases, the content of MoO_3 is obviously decreased due to the volatilization of the oxide. When the Mo coatings are put into the muffle furnace at 1073 K or 1173 K, massive smoke rises from the surface due to the evaporation of the volatile molybdenum oxide. The intact Mo coatings transform into powders when they are taken out. The product of substrate and oxide is also found on the surface of Mo coating at 1173 K, which indicates that the substrate is exposed to the environment. The Mo coatings cannot protect the specimen from high temperature oxidation. The morphology of the Al-Mo coating after oxidation at 973 K for 12 h is compact and integrated. X-ray diffraction analysis shows that the main phases of the Al-Mo coating after oxidation at 973 and 1073 K are still the original Al_8Mo_3 and $Al_{3+x}Mo_{1-x}$ intermetallic compound, without molybdenum oxides. As the temperature rises to 1173 K, alumina is the main phase of the Al-Mo coatings. The Al-Mo coating is separated from the substrate at the edge of the coating after processing at 1073 K for 8 h, but most of the coating still bonds with the substrate compactly.

The failure of components in the gasifier system can be attributed to sulfidation, oxidation and hot corrosion[1]. Correspondingly, the sulfidation and oxidation should be considered simultaneously. In the present investigation, the coatings possess good sulfidation and oxidation resistance compared with the Inconel 600 alloy. As for Al-Mo coatings, their high-temperature sulfidation and oxidation performances are superior to those of Mo coatings. Thus plasma-sprayed Al-Mo coatings are promising candidates for the corrosion protection of steels in sulfur/oxide-rich atmosphere.

3 Conclusions

1) The Al-Mo intermetallic compound was synthesized by a mechanical alloying method. Mo coatings and Al-Mo coatings with a Mo bonding layer were deposited by plasma spraying technique.

2) The high-temperature sulfidation and oxidation resistances are compared for Al-Mo coatings, Mo coatings and the Inconel 600 alloy. After sulfidation at high temperature, the alloy and Mo coatings are corroded seriously, while the Al-Mo coating maintains its integrity.

3) The sulfidation rate of the Al-Mo coating is the lowest in the present study, and its oxidation resistance is also better than that of the Mo coatings. Al-Mo coatings are promising candidates for the corrosion protection of steels in a sulfur/oxide-rich atmosphere.

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等离子喷涂 Al-Mo 涂层的高温硫化和氧化行为

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摘　要：烧嘴是水煤浆气化系统的重要部件。运行过程中的高温硫化经常导致烧嘴提前失效，进而影响设备的安全稳定运行。采用等离子喷涂方法制备了 Mo 为粘结层的 Al-Mo 涂层，测量其在 973 , 1073 和 1173 K 的硫化和氧化行为，并与 Mo 涂层和 Inconel 合金进行比较。结果表明，Al-Mo 涂层的高温硫化抗力和氧化抗力均优于 Mo 涂层，高温硫化抗力优于 Inconel 合金。该涂层的提出为喷嘴失效问题的解决提供了便捷、有效的技术方案。

关键词：等离子喷涂；Al-Mo 涂层；高温硫化

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