On the Oxidation Resistance of the Compound Fe-based Protective Coating by Supersonic Arc Spraying at 1123K

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ABSTRACT

The surface morphologies, chemical composition and the oxidation resistance of the compound Fe-based protective coating by supersonic arc spraying were investigated by SEM, EDS and cyclic oxidation weighing in the paper. The results show that the TiAlC coating is of the best oxidation resistance with mass gain of only 2.6621 mg/cm² after exposed for 100h at 1123K, while the LX88A coating is the worst anti-oxidation property with 76.6465 mg/cm². The HCrA-TiAlC, TiAlC-LX88A and TiAlC coatings show the similar performance. It is smooth and with some unmelted carbides particles on the surface of the coatings with many holes. The Fe-based coatings are mainly composed of Fe element with amount more than 50 wt.%, and the HCrA, TiAlC and their composite coatings are with about 20wt.%Cr. More than 8 wt.%Al can be detected in the TiAlC coating. More amounts of Al and Cr are contributing to improving the oxidation resistance. The thermodynamics of the preferential oxidation of the elements is discussed.

INTRODUCTION

Supersonic arc spraying is one of the most efficient types of surface engineering technology, which is utilized in many industrial fields to protect from the abrasion, corrosion, high temperature oxidation [1,2]. Many arc spraying coatings, deposited by metallic wires such as Ni-Cr(-Ti, Mo), NiCrAlY or cored wires filled with hard phase such as Cr/Al- oxides, carbides, et al, are extensively studied in the past decades [3,4]. The compound Fe-based coatings by supersonic arc spraying still has attracted increasing interest for their advantages in low cost, high spraying rate and high deposition efficiency among the thermal spraying coatings. The phase constitution depends on its chemical composition, influencing its performance in oxidation resistance, adhesion strength, hardness, lower density and porosity and so on [2]. For example, the anti-oxidation of the coating mainly depends on the level of Al and Cr...
elements and the characterization of their oxide films formed on the surface, while the wear resistance property lies on the amount and the distribution of the hard phase such as alumina oxides, carbides and chromic oxides \[4-7\].

Aiming to explore a new and applicable high temperature oxidation-resistant coating, the oxidation resistance of the newly independent researched and developed Fe-based coatings such as HCrA, TiAlC, LX88A and their composite coating deposited by supersonic arc spraying with cored wires filled with certain amount of chrome carbides, titanium-aluminum phases, and/or also small level of rare earth element are studied in this work.

**EXPERIMENTAL PROCEDURE**

The compound protective coatings were deposited on the #45 steel by SX-600 Supersonic Arc Spraying, and the substrate was fabricating into a cylindrical specimen with dimensions of Φ20 mm×30 mm. The parameters of the supersonic arc spraying technique are given in Table 1.

The cored wires were commercial LX88A, HCrA and TiAlC electrodes with Φ2mm in diameter. And the HCrA-TiAlC, HCrA-LX88A and TiAlC-LX88A coatings were composite ones that were prepared with two corresponding cored wires. The cored wires are with small amounts of Cr, carbides and chromic oxides, and Ti-Al intermetallic compound phases, and also very small level of rare earth element. The thicknesses of the coatings are more than 0.5mm.

The Kinetics of cyclic oxidation was conducted in the air furnace for designed heating and cooling time as an interval to 100h in total. The sample mass gain was measured by BT-25-S Balance after cooling to room temperature. The characterization of surface and the quantitative analysis of the coatings were carried out by a Field emission scanning electron microscope (FESEM, SU8020) equipped with Energy dispersive spectroscopy (EDS).

| TABLE 1. SUPersonic ARC SPRAYING PARAMETERS. |
|---------------------------------------------|
| Voltage/V | Current/A | Distance/mm | Air pressure/MPa | Wire feed rate/cm·min^{-1} |
|-----------|-----------|-------------|------------------|---------------------------|
| 32        | 180–220   | 150         | 0.5              | 60-80                     |

**RESULTS AND DISCUSSION**

The oxidation resistance of the coatings were distinct different among the Fe-based protective coatings exposed at 1123K in this paper. According to Table 2, it is shown that the LX88A coating got mass gain of 7.0642 mg/cm² after exposed for the first 1h, and the HCrA coating got the second highest increase of 4.7088 mg/cm². The third is HCrA-LX88A composite coating with 3.1526 mg/cm². The initial stage the TiAlC coating has already shown excellent oxidation resistance among the coatings. After exposed for 50h, the increasing weight of the LX88A coating has reached to 42.7823 mg/cm² while that is only 2.3697 mg/cm² for the TiAlC coating. The TiAlC coating has the best oxidation resistance for the lowest mass gain of only 2.6621 mg/cm² after exposed for 100h at 1123K, as shown in Fig. 1 and Table 2. The
LX88A coating owes the worst oxidation resistance with the highest weight gain of 76.6465 mg/cm\(^2\), which is more than 28 times to that of the TiAlC coating. Basing on the results, the HCrA-TiAlC, TiAlC-LX88A and TiAlC coatings show the same oxidation performance at 1123K as a whole.

![Figure 1. Kinetics curves of cyclic oxidation.](image)

The morphologies of the coatings are shown in Fig. 2. It is smooth and with some unmelted particles for the coatings. There are many fine particles distributing on the HCrA-TiAlC composite coating surface. Obviously, many holes in the coatings could be observed from the obtained images. The unmelted particles are main carbides such as Cr\(_2\)C\(_3\) and TiC, and the coatings are of typical lamellar structures as reported in our previous work\(^{[1,2]}\).

The chemical composition of the six as-deposited coatings in this work are measured and listed as Table 3. The HCrA coating is mainly composed of Fe and Cr elements that are 57.73wt.% and 21.52w.%, respectively. The level of Fe and Cr elements in the TiAlC coating is close with that of the HCrA coating, and the Al element is 8.28 wt.% while it is only 0.16wt.% in the former one. It is vastly good for improving the oxidation resistance of the coating. The Cr content of the HCrA-TiAlC coatings is also about 20.61 wt.%. For the LX88A coating, its main chemical composition is the Fe element as 78.08 wt.% and only about 2.50 wt.%Cr. There is certain content of the carbon element in the cored wires existing with carbides. Oxidation occurred to the as-deposited coatings during preparation. More serious oxidation happened to the composite coatings than the single coatings for the higher current in parameters.

| TABLE 2. MASS GAIN OF THE COATINGS WITH EXPOSED TIME AT 1123K (MG/CM\(^2\)). |
|---|---|---|---|---|---|---|---|
|       | 1   | 2   | 5   | 10  | 20  | 50  | 100 |
| HCrA   | 4.7088 | 5.7252 | 6.7909 | 7.7540 | 8.7952 | 10.6928 | 12.5201 |
| TiAlC  | 1.5388 | 1.8422 | 2.0340 | 2.0719 | 2.1522 | 2.3697 | 2.6621 |
| LX88A  | 7.0642 | 8.2642 | 11.3357 | 18.0207 | 21.7070 | 42.7823 | 76.6465 |
| HCrA-TiAlC | 2.7254 | 3.0206 | 3.7304 | 4.4256 | 4.8954 | 6.0365 | 6.7836 |
| HCrA-LX88A | 3.1526 | 3.9050 | 5.7600 | 6.3321 | 8.6235 | 18.1251 | 41.4189 |
| TiAlC-LX88A | 2.8310 | 3.0974 | 3.3561 | 3.8415 | 4.2759 | 4.8340 | 5.3471 |
Figure 2. Surface morphologies for the coatings (a) HCrA, (b) TiAlC, (c) LX88A, (d) HCrA-TiAlC, (e) HCrA-LX88A and (f) SXTiAlC-LX88A.

| Samples           | Fe  | Cr  | Al | O  | C  |
|-------------------|-----|-----|----|----|----|
| HCrA              | 57.73 | 21.52 | 0.16 | 12.67 | 7.7 |
| TiAlC             | 51.78 | 20.83 | 8.28 | 9.4 | 9.63 |
| LX88A             | 78.08 | 2.47 | 0 | 10.47 | 8.93 |
| HCrA-TiAlC        | 42.78 | 20.61 | 6.17 | 25.55 | 3.71 |
| HCrA-LX88A        | 67.75 | 7.29 | 0.29 | 19.47 | 5.2  |
| TiAlC-LX88A       | 61.67 | 12.3 | 6.31 | 16.76 | 2.96 |

The surface morphologies of the coatings after exposure at high temperature are shown in Fig. 4. Many oxides obviously grew on the surface of the coatings. There are huge cracks in the LX88A and the HCrA-LX88A composite coating (Fig. 4e). And there is compact and continuous oxide film on the TiAlC surface. Iron oxide phase can be detected from the coating surface from Table 4. According to Table 4, the oxides are mainly composed of Al$_2$O$_3$ and Cr$_2$O$_3$ for the TiAlC, HCrA-SXTiAlC, TiAlC-LX88A composited coatings after exposed to high temperature, which make them show excellent oxidation resistance. They show good anti-oxidation performance for more enough amount of Al and certain content of Cr element. Iron oxides are the main products on the LX88A and the HCrA-LX88A coatings surface. The spinel would form on the coatings because of two or more oxides existing at the same time when exposed to high temperature. The PBR (Pilling-Bedworth Rate, the volume rate of formation of corresponding metal oxides to the consuming metals) of the oxides or spinel are bigger than 2, resulting in great stress and crack owing to different coefficient of thermal expansion during heating or cooling. These lead to poor oxidation resistance for these coatings [5].
Figure 4. Surface morphologies for the coatings after exposed for 100h at 1123K (a) HCrA, (b) TiAlC, (c) LX88A, (d) HCrA-TiAlC, (e) HCrA-LX88A and (f) TiAlC-LX88A.

| TABLE 4. CHEMICAL COMPOSITIONS OF THE COATINGS AFTER EXPOSED FOR 100H AT 1123K (IN WT.%). |
|---------------------------------|-------|-------|-------|-------|
| Elements                        | Fe    | Cr    | O     | Al    |
| HCrA                           | 64.15 | 10.79 | 24.06 | 0     |
| TiAlC                          | 33.59 | 19.85 | 28.02 | 18.54 |
| LX88A                          | 72.56 | 1.75  | 25.26 | 0.25  |
| HCrA-SXTiAlC                   | 46.15 | 15.78 | 25.6  | 12.47 |
| HCrA-LX88A                     | 81.58 | 2.07  | 16.06 | 0.29  |
| TiAlC-LX88A                    | 40.41 | 9.80  | 26.13 | 23.66 |

The oxidation resistance of the coating depends on the chemical composition and the characterization such as surface morphology, and the stability of the oxide film formed on the surface. The Al element is the best element for improving the oxidation resistance with more content. And then is the Cr element. According to the theory of standard free energy of formation for the metallic oxide, the stability of the oxide under high temperature lies on how negative the value of standard free energy of formation.

From the reported $G^0$~T equilibrium diagram [8], the location of the $4/3\text{Al} + \text{O}_2 = 2/3\text{Al}_2\text{O}_3$ line locates the lowest in the equilibrium diagram, indicating that the Al element is preferential oxidized when exposed to the atmosphere with oxygen at high temperature. The $4/3\text{Fe} + \text{O}_2 = 2/3\text{Fe}_2\text{O}_3$, $2\text{Fe} + \text{O}_2 = 2\text{FeO}$ and $3/2\text{Fe} + \text{O}_2 = \text{Fe}_3\text{O}_4$ lines locate on the top of the equilibrium diagram, which show that they are the most unstable state at that temperature. That is to say that there is not sufficient protective effect when the Fe oxide film formed on the surface. The $4/3\text{Cr} + \text{O}_2 = 2/3\text{Cr}_2\text{O}_3$ line locates in middle of the diagram. Then the oxides of Fe and Cr can react with Al to form $\text{Al}_2\text{O}_3$. It can be illuminated by the value of standard free energy of formation. The $G^0$ of the Al, Cr and Fe oxides can be calculated and listed.
in Table 5. And the $G^0$ calculation is following the $G^0$~T related equation $^9$ as given in the Table. The spinel phases as FeAl$_2$O$_4$ and FeCr$_2$O$_4$ are also been calculated.

The $G^0$ of Al$_2$O$_3$ is the most negative among these oxides, illustrating that the Al$_2$O$_3$ phases is the most stable when oxidized. If the coating is exposed for long time at high temperature the Al element would be consumed exhausted, the Fe oxides and the spinel phases would form on the surface. It is poor to the oxidation resistance performance because many cracks will generate for the bigger PBR value and stress of the oxide films. From the data in Table 4 it is obvious that the TiAlC and the HCrA-SXTiAlC, TiAlC-LX88A composited coatings are still provided enough with Al and/or Cr elements. The continuous and compact protective the Al$_2$O$_3$ and/or Cr$_2$O$_3$ films grow on the surface of the coating.

| Oxides | Reaction | $G^0$~T Equation | $\Delta G^0$ /kJ |
|--------|----------|------------------|------------------|
| Al$_2$O$_3$ | $\frac{4}{3}$Al+O$_2$=2/3Al$_2$O$_3$ | $\Delta G^0 = -1120480 + 214.22T$ | -879.9 |
| Cr$_2$O$_3$ | $\frac{4}{3}$Cr+O$_2$=2/3 Cr$_2$O$_3$ | $\Delta G^0 = -746840 + 170.29T$ | -555.6 |
| Fe$_3$O$_4$ | $\frac{3}{2}$Fe+O$_2$=1/2Fe$_3$O$_4$ | $\Delta G^0 = -545590 + 156.48T$ | -369.8 |
| FeO | 2Fe+O$_2$=2FeO | $\Delta G^0 = -519230 + 125.1T$ | -378.7 |
| FeAl$_2$O$_4$ | FeO + Al$_2$O$_3$= FeAl$_2$O$_4$ | $\Delta G^0 = -860865 + 151.67T$ | -690.5 |
| FeCr$_2$O$_4$ | FeO + Cr$_2$O$_3$= FeCr$_2$O$_4$ | $\Delta G^0 = -487225 + 107.74T$ | -366.2 |

SUMMARY

The TiAlC coating shows the best oxidation resistance with mass gain of only 2.6621 mg/cm$^2$ after exposed for 100h at 1123K, while the LX88A coating is the worst with 76.6465 mg/cm$^2$. The HCrA-TiAlC, TiAlC-LX88A and TiAlC coatings show the similar oxidation performance at 1123K. It is indicated that the amounts of Al and Cr are very important to the oxidation resistance performance of the coating, which promotes the preferential oxidation and improve the anti-resistance property by formatting certain amount of continuous and compact Al$_2$O$_3$ and Cr$_2$O$_3$ films at the surface of the coating for their more thermodynamics stability at high temperature.

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