# Microstructural Study of the Interface between Aluminum Bronze Composite Coatings and Steel during Oxidation at 1173K

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## ABSTRACT

A composite coating system for oxidation resistance at elevated temperatures was composed of an inner layer of aluminum bronze and an outer layer of aluminum. When heated at 1173 K, aluminum melted and diffused inward into the inner layer. With aluminum and oxygen diffusing, oxides were formed in the pores in coatings where were then closed, resulting in blocking off the oxygen penetration. By observing and analyzing the interfacial microstructure of specimens tested at 1173 K for 1 hour, it was found that the diffusion zone and the oxide layer were located at the coatings/substrate interface and that the initial oxide layer consisted of Fe, Al, Cu and Mn. As test time proceeded, the oxide layer extended along the interface and became continuous after heating for 12 hours. The microstructural observation of the 30 hour-test specimen revealed that aluminum which came from the outer layer had diffused into the substrate and the interfacial oxide layer had been transformed almost completely into alumina. The change of interfacial microstructure did not degrade the coating adhesion. The composite coatings provided a good high temperature protection to the steel substrate.

**Key words:** Arc spray, Composite coatings, Oxide, Interfacial microstructure

## 1. INTRODUCTION

Coatings have historically been developed to provide protection against oxidation and hot corrosion. A wide variety of processes are used to apply coatings, although they rely on one of three general methods: physical vapor deposition, chemical vapor deposition and thermal spray. Among these processes, arc spray is one of the most convenient methods with characteristics of low cost, high deposition rate and easy operating. Therefore, there has been a growth of interest in this particular process.

It is generally thought that alumina-forming alloys have an excellent oxidation resistance. An alumina-rich protective film on the surface can provide an environmental protection to the base metal at elevated temperatures /1/. When aluminum is added to copper, it also enhances the oxidation resistance of the alloy. Aluminum bronzes are a family of copper-base alloys containing approximately 5% to 12% aluminum, some having additions of other elements. These alloys have excellent corrosion resistance under a wide range of service conditions /2/. Furthermore, a previous study on arc-sprayed aluminum bronze coatings in our laboratory revealed that metallurgical interaction between sprayed particles and steel substrate could occur and made it possible to produce arc-sprayed aluminum bronze coatings with high bond strength, which could strongly

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adhere to the smooth and clean surface of a steel substrate /3/. Thus, aluminum bronze is widely used as one of the important bond coating materials when sprayed by electric arc process /4/. Due to this excellent bond ability combined with their good resistance to oxidation, together with low cost and high deposition rate, these coatings have potential applications in high-temperature environments. However, the limited amount of aluminum in the coatings may be consumed during long-term service at high temperature. The present work has been developed to find a solution to this problem. Therefore, a multilayer architecture for oxidation resistance at elevated temperatures was designed, which was composed of an inner layer of aluminum bronze and an outer layer of aluminum. The primary investigation results indicated that the multilayer architecture was promising. The purpose of this study was to study the changes of the coatings/substrate interface at elevated temperature, while the oxidation behavior of the multilayer will be discussed in future papers.

## 2. EXPERIMENTAL

The substrate of all the specimens was made of mild steel. After being grit blasted, the specimens were sprayed with 0.6 mm-thick aluminum bronze coating and then an outer layer of aluminum of 0.1mm thick. 3-mm-diameter wires were used in the arc-spraying process and the chemical compositions of these materials are listed in Table 1. The parameters for the arc-spraying process are given in Table 2.

The isothermal oxidation tests were carried out at 1173 K in air at atmospheric pressure. The test temperature was held at 1173 K, and the specimens were removed from the furnace after 1 hour, 5 hours, 30 hours and 60 hours. The cross-section of the oxidized specimens were examined by using a scanning electron microscopy (SEM) and analyzed using an energy-dispersive X-ray spectrometer (EDS).

## 3 RESULTS AND DISCUSSION

### 3.1 As-sprayed coating microstructure

The microstructure of cross section of the coatings and interface is shown in Fig. 1. There are two different zones along the interface. One is a bonding zone between the coatings and the substrate and the other is an oxide layer which lies between the coatings and the substrate. The bonding zone plays a key role in the adhesion of the coating to the substrate. The structure of aluminum bronze coatings sprayed by arc process is layer-like and is composed of alloy droplets, oxides and some pore spaces. There are some oxide particles on the coating surface, inside the coatings and between the coatings and the substrate. The coatings have a layer-

**Table 1**

Chemical compositions of wires (mass fraction, %)

| wire | Al | Mn | Fe | Ni | Si | Cu |
|---|---|---|---|---|---|---|
| Al bronze | 8.61 | 2.10 | 0.079 | 0.28 | 0.069 | Bal. |
| Al | ⩾99.9 | -- | -- | -- | -- | -- |

**Table 2**

Arc spraying parameters

| parameter | material | |
|---|---|---|
| | bronze | aluminum |
| Arc voltage /V | 32 | 32 |
| Arc current /A | 220 | 200 |
| Air pressure /MPa | 0.5 | 0.5 |
| Substrate distance /mm | 150 | 150 |

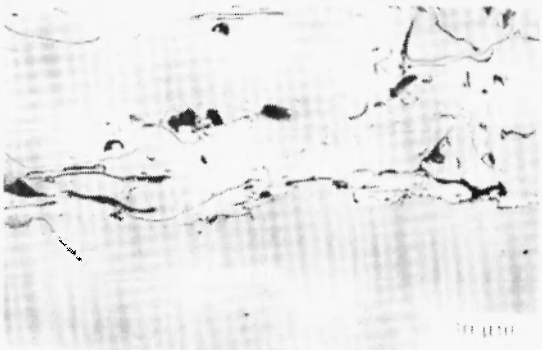

**Fig. 1:** SEM micrograph of the interface of coatings/substrate, as-sprayed

like structure because the droplets strike against substrate and become flat. According to thermodynamics, the formation of alumina is the most favored over those of other oxides. Because of the formation of alumina, a large amount of heat is generated and the droplets are heated during their flying until they strike against the base metal surface. The droplets become flat and the oxide film on the droplets breaks up and is conglomerated at the moment of the strike. It can be seen from the figure that there are some strip oxides which are in black in the coatings.

There are four kinds of alumina with different crystal structures, $\alpha$-$Al_2O_3$, $\gamma$-$Al_2O_3$, $\delta$-$Al_2O_3$ and $\theta$-$Al_2O_3$. With the exception of $\alpha$-$Al_2O_3$, the others are metastable forms. During spraying, the metal droplets are overheated and partly oxidized in air because the temperature of arc is above 5000 K /5/. Within about a tenth of a millisecond the temperature of particles rapidly drops to room temperature with a cooling rate of more than ten thousand degree centigrade per second /6/. Because of the high rate of transforming, a metastable phase, $\gamma$-$Al_2O_3$, is formed. The transition $\gamma$-$Al_2O_3$ grows predominantly by aluminum outward transport, while the $\alpha$-$Al_2O_3$ grows predominantly by oxygen inward transport. The growth rate of the former variety is about one order of magnitude faster than that of the latter /7, 8/. It was reported that $\gamma$-$Al_2O_3$ was formed during short time oxidation at 1173 K /9/. This process was also observed in our previous work using X-ray diffraction analysis.

In addition to the oxide, there are numerous pores in the arc-spray coatings. It is generally considered that pores in coatings limit the anti-oxidation performance of coatings /10/. The pores, a kind of defect, are much bigger in volume than defects in oxide or in metals. Unfortunately, some pores run through coatings and allow the penetration of oxygen, which results in oxidation inside the coatings. To apply the coatings to high temperature service the pores must be sealed in before or at the beginning of service. One potential solution to this problem is to take advantage of an outer aluminum layer that melts at service temperature. In the present experiment a thin aluminum layer was sprayed on the surface of bronze coatings, which provided a perfect adhesion to the outer layer. Figure 2 shows a cross section of the interface between the aluminum coating and aluminum bronze coating. The aluminum coatings (dark) lies over the aluminum bronze coating (light), while the outer layer is well adherent to inner layer.

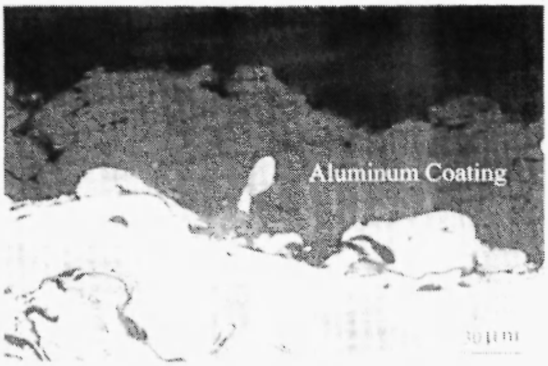

**Fig. 2:** SEM micrograph of the interface of aluminum coatings/aluminum bronze coatings

### 3.2 Interfacial microstructure after one-hour test

A micrograph of the cross-section of the composite coatings after heating at 1173 K for one hour, given in Fig. 3-a, shows the coating/substrate interface where there was the bonding zone before heating. After chemical etching, the diffusion zones are clearly seen in the substrate close to the interface. The diffusion zones are well bonded to the substrate and to the coatings. Figure 3-b is the X-ray image of Al, corresponding with Fig. 3-a, which shows also Al has diffused from the coating into the substrate. It is interesting to find that the

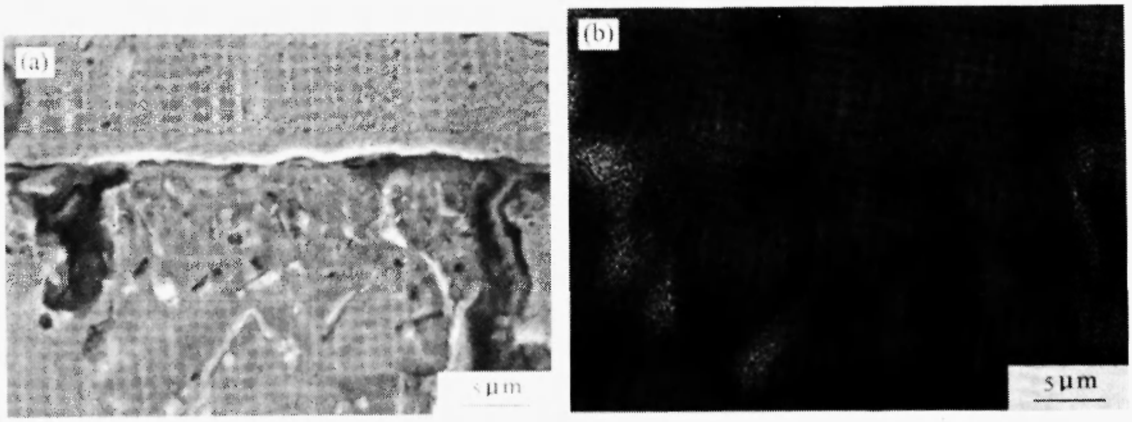

**Fig. 3:** SEM micrograph (a) and X-ray image of Al (b) of the diffusion zone of coatings/substrate of the specimen after testing for 1 hour

content of aluminum in this diffusion zone is more than that of the coating closed to the interface. It is supposed that an iron-aluminum intermetallic compound is formed in the zone. In general the diffusion mechanism is complex, since the amount of elements diffused does not only depend on the difference of composition between the two phases, but also on their structural compatibility.

The interfacial microstructure of the composite coatings/substrate does not differ from that of the specimens coated with a single aluminum bronze layer. There is not enough evidence to show that aluminum from the outer layer has reached the interface. At elevated temperatures, aluminum of outer layer melted. Part of it diffused inwards into the aluminum bronze coating, while the remaining fraction was combined with oxygen on the surface or in the pores, which acted also as diffusion paths for oxygen. The alumina film on the surface can play a role equal to that of preoxidation, acting as a barrier to the environment and restricting the initial rate of metal degradation. On the other hand, the alumina formed within the coating seals the pores due to a selective oxidation of aluminum, which involves a volume expansion /11/. Consequently, the oxide in the coating becomes a barrier to restrict the diffusion of oxygen and of metals, protecting the inner alloy from further oxidation.

### 3.3 Interfacial microstructure after five-hour test

As the heating time proceeds, the bonding zones become thinner and more oxides appear at the coating/substrate interface and also in the aluminum bronze coating. According to Wagner oxidation theory /11/, the oxidation rate is controlled by the diffusion of elements in the oxide scale. When all the pores in the coatings are closed, the penetration of oxygen becomes very difficult, leading to a sharp reduction of the oxidation rate.

A micrograph of a cross-section of the composite coatings after heating at 1173 K for five hours (Fig. 4) shows the microstructure of the coatings/substrate interface. An oxide layer has developed between the coating and the substrate and is well connected with each of them. The interfacial oxide layer is about one micron in thickness. The EDS results reveal that the oxide layer contains 27.90 % O, 26.88% Al, 1.32% Mn, 34.79% Fe, 8.22% Cu and 0.89% Si (all in mass %).

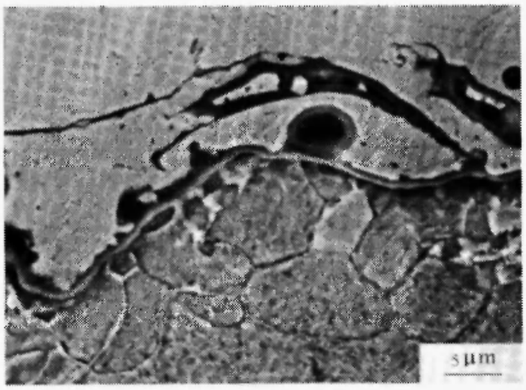

**Fig. 4:** SEM micrograph of the interfacial oxide of coatings/substrate, 5 hour test

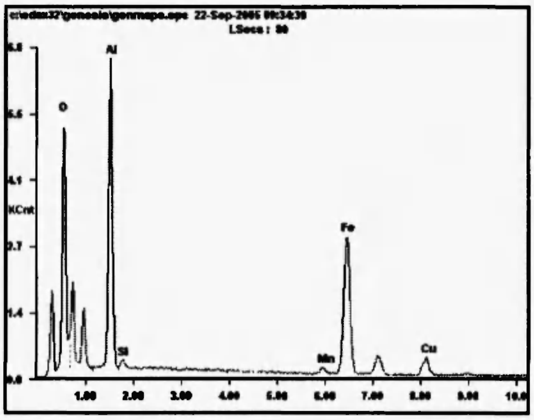

**Fig. 5:** EDS pattern of interfacial oxide in Fig. 4

The EDS spectrum of the interfacial oxide, as shown in Fig. 5, reveals that the chemical composition of the oxide corresponds approximately to the iron-aluminum spinel ($FeAl_2O_4$). During the early reaction stage, oxygen may reach the substrate and lead to a local oxidation due to the presence of some pores in the coating. It is easier for the oxide to be nucleated and grow up at the interface rather than at other places because the interface contains more defects. According to thermodynamics, when oxygen diffuses to the interface, aluminum should be preferentially oxidized with respect to the other metallic components. However, a double Fe-Al formed at the interface, apparently because the local oxygen pressure was sufficient to form this oxide. Fig. 6-a is the micrograph of the interfacial diffusion zone where content of aluminum has obviously decreased, due to aluminum having diffused further into steel substrate, as seen in Fig. 6-b.

### 3.4 Interfacial microstructures after thirty and sixty hours test

After 12-hour heating, the interfacial oxide layer became continuous, while after 24 hours aluminum from the outer layer reached the coatings/substrate interface. The microstructure of the coatings/substrate interfacial after heating for 30 hours, shown in Fig. 7, reveals that that some change has taken place in the substrate close to the interface. The composition was analyzed by EDS at the spots labeled "a", "b", "c", respectively, and is given in Table 3.

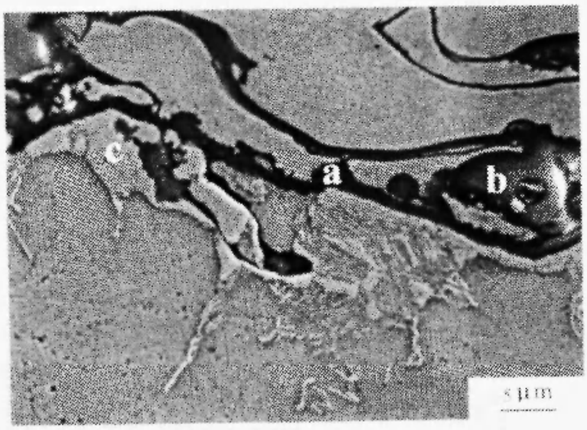

**Fig. 7:** SEM micrograph of the interface of coatings/substrate, 30 hour test

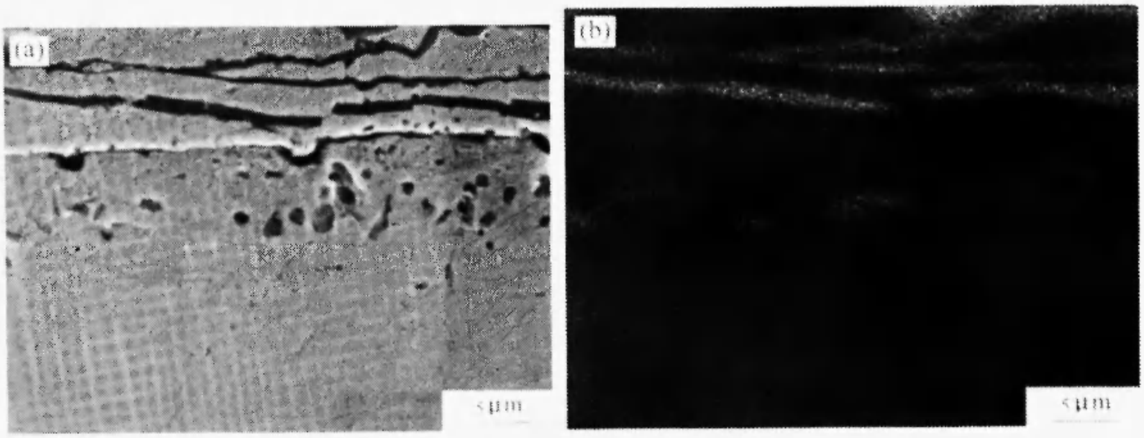

**Fig. 6:** SEM micrograph (a) and X-ray image of Al (b) of the diffusion zone of coatings/substrate of the specimen after testing for5 hour

**Table 3**
Elements detected by EDS at various locations in Fig. 7 (mass fraction, %)

| a | B | c |
|---|---|---|
| 37.68 | 45.67 | --- |
| 45.14 | 52.97 | 1.82 |
| 4.59 | --- | 1.13 |
| 7.75 | 0.41 | 93.70 |
| 4.85 | 0.95 | 3.35 |

After heating for 30 hours, the appearance and composition of the interfacial oxide (labeled "a" in Fig. 7) show some changes as compared with that formed on the specimen heated for 5 hours. In fact, after 30 hours the interfacial oxide between the coatings and substrate has become continuous, while its composition corresponds approximately to alumina. Aluminum coming from the outer layer has gradually reduced the oxides of iron and of the other elements in the interfacial oxide layer. With time, more aluminum diffused across the oxide layer and entered into the substrate, producing changes in its microstructure. The zone labeled "c" in Fig. 7 is a diffusion area where the content of Al, Cu, Mn is larger than the average in the substrate. The oxides formed in the arc-spray process, labeled "b" in Fig. 7, still keep their original appearance and composition.

The microstructure of a specimen exposed for 60 hours at 1173 K is shown in Fig. 8. As heating time increases, aluminum that entered into the substrate diffused continuously inwards, while its supply provided by the outer layer was decreasing, so that the aluminum content of the zone close to interface gradually decreased. As a result, the diffusion zones became thinner and smaller. Conversely, there was little change in the thickness of the interfacial oxide layer, indicating that the oxide had efficiently blocked off the diffusion of oxygen.

During service, the coatings degrade at two fronts, i.e. at the coating/gas-path interface and at the coating/substrate interface. For high temperature applications, the adhesion of the coatings is of the same importance as their antioxidation resistance. Although the structure of the coatings/substrate interface has changed considerably during exposure at 1173 K for 60 hours, the adhesion of the coating/substrate interface was not degraded. Tensile adhesion tests carried out for specimens heated for 1, 12 and 24 hr at 1173 K, respectively. In comparison, the measurements of the tensile bond strength of the heated specimens, which were mostly in the range from 25 to 30 MPa, were not less than those of the as-sprayed samples. In the view of composite theory, the interfacial products generated in chemical reactions can improve the joining between the metal matrix and the reinforcing phase /12/. The interfacial oxide layer grown between the coatings and the substrate produced chemical adhesion mechanism which joined the two sides quite efficiently as shown by the results of the adhesion tests.

**Fig. 8:** SEM micrograph of the interface of coatings/substrate, 60 hour test

## 4. CONCLUSIONS

During high temperature service, an outer aluminum layer present in the composite coating plays an important role for sealing the pores in the inner coating layer and for improving the oxidation resistance of the coating system. In an early stage of the heating test, both a diffusion zone and an oxide layer formed at the coatings/substrate interface. As the test time increased, the oxide layer extended along the interface and became continuous after heating for 12 hours. After 30-hour test, aluminum from the outer layer had diffused into the substrate and the interface oxide had been transformed into alumina. The interfacial oxide layer grown between the coatings and the substrate did not degrade the coating adhesion. Thus, it is believed that the composite coating system may be a potential candidate for protecting steel substrates from oxidation at high temperatures.

## REFERENCES

1. F. H. Scott, S. W. Green and N. J. Wood, *Oxidation of High-Temperature Intermetallics*, T. Grobstein (Ed.), TMS Pub., Cleveland, (1988), p.117-126.
2. R. J. T. Caney. *Australasian Engineer*, **46**, 54-69 (1954).
3. J.L.Wen and Z.L. Zhang, *11th International Thermal Spraying Conference* edited by Canada Welding Institute, Pergamon Press, Montreal, (1986), p.169-175.
4. Z.L. Zhang and Y.P. Hao, *National Thermal Spraying Conference*, Z. Wei (Ed.), China Thermal Spray Society, Shenyang, (1999), p.57-63.
5. K.A. Kowalsky, D.R. Marantz and R. Neiser, *13th International Thermal Spraying Conference*, C. C. Berndt (Ed.), ASM International, Orlando, (1992), p.337-342.
6. C. Moreau, P. Cielo, and M. Lamontagne, *13th International Thermal Spraying Conference*, C. C. Berndt (Ed.), ASM International, Orlando, (1992), p.761-766.
7. R. Klumpes, C.H. Maree and M. Schramm, *Materials Corrosion,* **47**, 619-624 (1996).
8. Y. Niu and P.Y. Hou, *Acta Metallurgica Sinica*, **39**, 1065-1070 (2003).
9. M. W. Brumm and H. J. Grabke, *Corrosion Science*, **33**, 1677-1690 (1992).
10. A.C. Rocha, F. Rizzo and C.L. Zeng, *Materials Research,* 7, 189-194 (2004).
11. M.S. Li, *High Temperature Corrosion of Metals,* edited by P. L. Li, Metallurgical Industry Press, Beijing, (2001), p.42-48
12. Y. S. Huang, J. L. Meng, *Materials Science & Engineering,* 17, 42-44 (1999).