High temperature oxidation resistance and microstructure change of aluminized coating on copper substrate

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Received 13 January 2014; accepted 28 May 2014

Abstract: The outermost coating with single phase Ni$_2$Al$_3$ was obtained on copper surface by electrodepositing nickel followed by slurry pack aluminizing at 800 °C for 12 h. The oxidation resistance and microstructure of the coating oxidized in ambient air at 1000 °C for 25−250 h were investigated using SEM, X-ray diffraction and optical microscope methods. The results show that the copper with single phase Ni$_2$Al$_3$ coating possesses the best high temperature oxidation resistance, and the mass gain of the coating is 1/15 that of pure copper and 1/2 that of nickel coating, respectively. The specimen surface after being oxidized for 25 h still comprises Ni$_2$Al$_3$ phase. However, when the time of oxidizing treatment increases to 50 h, the NiAl phase is formed. It is also found that the Ni$_2$Al$_3$ phase completely turns into NiAl phase after oxidizing treatment for 100 h and above. The NiAl coating shows excellent high temperature oxidation resistance when oxidation time is 250 h.

Key words: copper; Ni$_2$Al$_3$ coating; high temperature oxidation resistance; NiAl phase; pack aluminizing

1 Introduction

Due to the excellent electrical and thermal conductivity, copper is widely used as crystallizer in continuous casting and rolling. However, the poor resistance oxidation and wear resistance at high operating temperature limit its application [1,2].

In order to enhance the surface properties of pure copper, it is often needed to coat Ti, Si and Al on the copper surface. This may be achieved by diffusion of particular elements into the surface layers of copper in order to develop intermetallic type coatings. Therefore, lots of techniques have been studied to develop an efficient process to deposit coatings on copper or modify the chemical composition of its surface [3−5]. However, they are mainly focused on producing and characterizing the wear resistance of coatings. For instance, with the introduction of a nickel intermediate layer, a 0.13 mm thick Mo/Ni layer was obtained on copper by a two-step laser cladding of preplaced Ni and Mo layers. In this way, the wear resistance of copper could be largely improved [6]. A 1.5 mm nickel based alloy coating was deposited onto pure copper surface by laser cladding with coaxial powder feeding by ZHANG et al [7]. The results indicated that the average hardness of the coating was about HV 360, and the wear resistance of copper was significantly improved after cladding. Recently, Al and N have been introduced into copper by plasma immersion ion implantation and beam-line ion implantation by AN et al [8].

Among various coating processes used to improve the oxidation resistance, pack cementation is a relatively simple process to produce coatings on the substrate of complex geometry, which is widely used to deposit high temperature oxidation and corrosion resistance coatings on nickel-based superalloys and low-alloyed steels [9−14]. In recent years, several intermetallic compound coatings have been developed and successfully employed to copper surface with minimal wear in sliding and good oxidation properties [4].

To the best our knowledge, few information is available in literature concerning the oxidation resistance properties of copper after surface modification above 900 °C. The coating with the single phase Ni$_2$Al$_3$ was obtained on copper surface by electrodepositing nickel followed by slurry pack aluminizing at 800 °C for 12 h [15]. The aim of this work was to analyze the oxidation behavior and the structure of aluminized coating in ambient air at 1000 °C for 25, 50, 100, 150 and 250 h.

Foundation item: Projects (CKJB201205, QKJB201202, YJK.201307) supported by the Nanjing Institute of Technology, China

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DOI: 10.1016/S1003-6326(15)63594-4
2 Experimental

2.1 Materials and process

The plating electrolyte was a nickel sulfamate solution whose compositions are listed in Table 1 and the experimental process parameters are listed in Table 2. A commercial nickel plate with the size of 120 mm×80 mm×10 mm was used as the anode, and a copper plate with size of 12 mm×10 mm×2 mm was used as the cathode. The temperature of the electrolyte was maintained at room temperature. Cathode surface was ground with a series of Al₂O₃ paper up to 800-grit. They were ultrasonically cleaned in water bath, and then dipped in a water solution of 5% H₂SO₄ for 3 min, followed by cleaning in water and drying in air.

Table 1 Composition of electrolyte (g·L⁻¹)

<table>
<thead>
<tr>
<th>NiSO₄·6H₂O</th>
<th>H₃BO₃</th>
<th>NiCl₂·6H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>40</td>
<td>50</td>
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Table 2 Plating conditions

<table>
<thead>
<tr>
<th>pH</th>
<th>Current density/(mA·cm⁻²)</th>
<th>Plating time/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5–4.0</td>
<td>10</td>
<td>72</td>
</tr>
</tbody>
</table>

After electroplating, copper coated with nickel plating was firstly rinsed by water, and then cleaned ultrasonically in acetone. The slurry pack cementation powder mixtures mainly consisted of pure Al powder (70% as aluminizing source), NH₄Cl (5% as activator), albumen (egg white, as cohesive agent), and Al₂O₃ powder (20%) as an anti-sintering reagent which was inert and did not take place in the process reactions but only was used for balancing heat transfer and temperature distribution. After weighting and mixing, the slurry pack powder mixture was ground by hand using an alumina mortar and pestle thoroughly, then mixed with the cohesive agent albumen into slurry. The slurry was spread on the nickel coating thoroughly by hand, and then dried in a vacuum airer at 80 °C for 1 h. The samples were placed into an alumina crucible filled with alumina powder, then the crucible was put into the vacuum firing furnace which was washed by argon for three times, and then was full of argon with 1.25 MPa pressure to avoid oxidation. The furnace temperature was raised to a final depositing temperature of 800 °C at a rate of 10 °C/min and the holding time was 12 h. The furnace was then cooled to room temperature at its natural rate by switching off its power supply while maintaining the argon pressure. To remove the pack powder remaining on the surface of specimens after the pack aluminizing process, ultra-sonicated cleaning was conducted in acetone for 20 min, and then in deionized water for 20 min.

2.2 Oxidation tests

In order to assess the oxidation resistance of coating prepared by pack aluminizing at 800 °C for 12 h, isothermal oxidation tests were heat-treated in ambient air at 1000 °C for 25, 50, 100, 150 and 250 h, respectively. Each specimen was placed in a corundum crucible. Prior to the tests, the crucibles were heat treated at 1000 °C for 24 h. The crucibles were cooled down to room temperature in furnace and measured using an electronic balance with a resolution of 0.1 mg. The masses of the specimen and the crucible were recorded together, which means that the spalled scale, if any, was included in the kinetics curves.

2.3 Characterization of oxidized coating

Metallographic cross-sections of the oxidized coatings were prepared using standard procedures and etched using the etchant of HCl and HNO₃ in volume ratio of 3:1. The surface morphology and the distribution of elements in cross-sections of the oxidized specimens were analyzed using field-emission scanning electron microscopy (SIRON) associated with energy dispersive spectroscopy (EDS). Phase was identified by XD-3A X-ray diffractometer with Cu Kα radiation, λ=1.5804 and scan speed of 5 (°)/min. The microstructure of the cross-sections was observed by OLYMPUS-B202.

3 Results and discussion

3.1 Microstructure and concentration profiles of as-prepared coating

Figure 1(a) shows the structure of the cross-section of the coating formed by slurry pack cementation aluminizing process at 800 °C for 12 h. It can be seen that the surface copper consists of two layers: the outer layer is approximately 240 μm thick aluminized coating without obvious pores and the inner layer is about 300 μm thick Ni plating.

Figure 1(b) shows the SEM-EDS line-scanning profiles of element nickel and aluminum distribution across the aluminizing coating on the copper matrix. Figure 1(c) shows the optical micrograph of the etched cross-section of the aluminized coating. As shown in Fig. 1(b), the content of Al in the coating near the interface between Ni plating and aluminized coating decreases abruptly and that of Ni increases. EDS results show that the contents of Al at the surface and at the interface between Ni plating and aluminized coating are 62.3% and 64.4%, respectively, which indicates that there is a content gradient of Al from the surface layer to the inner layer of the aluminized coating. According to the binary phase diagram, Ni₂Al₃ phase can be formed after heating to 800 °C with the content of Al in the range of 59%–65% (mole fraction). During furnace cooling from 800 °C, the Ni₂Al₃ phase does not
Fig. 1 Cross-sectional morphology (a), content profiles of Ni and Al (b), optical image of Ni$_2$Al$_3$ (c), and XRD pattern (d) of coating prepared by slurry pack cementation at 800 °C for 12 h

transform. The XRD results indicate that the outmost layer of coating is a single phase Ni$_2$Al$_3$ intermetallic compound, as shown in Fig. 1(d), which is in agreement with the EDS results.

In the slurry pack cementation process, the Al metal powders at the treatment temperature react with the HCl vapors produced from dissociation of the activator (NH$_4$Cl), resulting in the formation of precursor vapors of aluminium chlorides, which would pass through the porous pack and reach the Ni plating layer surface. The aluminium chlorides are absorbed and decomposed and release the active atoms on the Ni plating surface, and during the subsequent solid-state diffusion, the active atoms react with the Ni plating, which results in the formation of the aluminium-containing coating on the sample surface. According to Refs. [12−14], the mechanism of the deposition of aluminium was mainly transferred by the disproportionate amount of lower valence chlorides at the substrate surface, followed by the subsequent solid-state inward diffusion of aluminium and outward diffusion of Ni.

3.2 Oxidation behavior of aluminized coating

Figure 2 shows the variations of mass gain vs time of the aluminized coating, copper and nickel coating during oxidation at 1000 °C for 25, 50, 100, 150 and 250 h, respectively. The results indicate that the mass gains of the aluminized coating and nickel coating are much lower than that of the copper matrix. The comparison of the oxidation behavior of nickel and aluminized coatings shows a lower mass gain for the latter. Scale growth on the pure copper follows parabolic law for the first 150 h. Since then, the oxidation rates become faster because the spallation of oxide scales exposes fresh surfaces of the metal. The oxidation of the aluminized coating and nickel coating does not obey the
parabolic growth law, they also show a similar trend during oxidation as shown in Fig. 2. After 250 h oxidation, the mass gain of pure copper is 148.313 mg/cm², whereas for Ni plating and aluminized coating it is 25.526 mg/cm² and 10.108 mg/cm², respectively.

3.3 Morphology and phases on surface of aluminized coatings after oxidation

Figure 3 shows the surface morphologies of the aluminized coating oxidized in ambient air at 1000 °C for 25 h and 250 h, respectively. It is found that a needle-like oxide is formed on the surface after oxidation of 25 h, as shown in Fig. 3(a). The size of oxides increases with the increase of the oxidation time, and no cracks and voids are observed, as shown in Fig. 3(b), which can effectively lower the diffusion ratio of O and Al atom through the oxides scale to form the oxides. This provides a good oxidation resistance for the substrate materials.

![Fig. 3](image)

The XRD patterns for the surfaces of the coatings after 1000 °C oxidation for different time are shown in Fig. 4. The phase on the surface of aluminized coating is a single phase Ni_2Al_3 intermetallic compound after oxidation for 25 h. At the early stage of oxidation, a needle-like shape oxide on the surface of the aluminized coating is formed after oxidation for 25 h (as shown in Fig. 3(a)), but X-ray diffraction cannot detect any oxides. This may be due to the fact that the thickness is rather small, exceeding the capability of the X-ray diffraction. When the oxidation time is up to 50 h, the coating surface consists of two phases: Al_2O_3 and Ni_2Al_3, as shown in Fig. 4(a). Further extending oxidation time to 100 h, the peaks of Ni_2Al_3 phase disappear and the peaks of NiAl phase appear, as shown in Fig. 4(b). After oxidation time from 100 to 250 h, the phases of the aluminized coating surfaces are still composed of Al_2O_3 and NiAl as shown in Fig. 4(b). On the surface of coating, Al depletion occurs in the coating near the interface between oxide and coating due to Al anion outward diffusion to the surface and reaction with oxygen at the gas/scale interface, which could be the formation of Al_2O_3 described by the reaction 4Ni_2Al_3+3O_2→8NiAl+2Al_2O_3. According to Ellingham-Richardson diagram, the free energies of formation of Al_2O_3 and NiO are −936 kJ/mol and −285 kJ/mol, respectively. From the thermodynamic point of view, the thermal stability of Al_2O_3 is much higher than that of NiO, which leads to selective oxidation to form Al_2O_3 scale at high temperature.

3.4 Constituent change in cross-sections of aluminized coatings after oxidation

Figures 5(a) and (b) show the microstructure and distribution of Al, Ni and O in cross-section of aluminized coating oxidized for 25 h, respectively. It can
be seen that the aluminized coating with a single phase \( \text{Ni}_2\text{Al}_3 \) (shown in Fig. 1(a)) has been changed into three-layer structure, which is composed of an outermost layer (1), an intermediate layer (2) and an inner layer (3). EDS patterns from the outermost layer and an intermediate layer show that the aluminized coating contains Al and Ni. The outermost layer contains 55.1%–58.9% Al (mole fraction), and the intermediate layer contains 50.5%–55.1% Al. According to the Ni–Al binary phase diagram, the outermost layer is \( \text{Ni}_2\text{Al}_3 \) phase and the intermediate layer is \( \text{NiAl} \) phase, respectively. When the oxidation time is up to 50 h, the thickness of the outermost layer decreases, and \( \text{Ni}_2\text{Al}_3 \) phase with 15 \( \mu \text{m} \) thickness still appears, which contains 53.5%–56.7% Al. The intermediate layer with the Al content between 48.5% and 53.5% is still \( \text{NiAl} \) phase. The dentritic structure grows with increasing the oxidation time. The microstructure of the inner layer remains unchanged with Al content in the range of 8.3%–48.5%, but the thickness is larger than that after oxidation 25 h, as shown in Fig. 6. Further extending the oxidation time to 250 h, the outermost layer remains to be a \( \text{NiAl} \) phase with an Al content in the range of 44.5%–52.68%, but cracks already present in the coating. It is observed that there are no voids and cracks in the intermediate layer with an Al content of 40.5%–44.5%. In the inner layer with an Al content of ~40.5%, voids are found at the coating/substrate interface. These voids may have been formed by phase transformation from \( \text{Ni}_2\text{Al}_3 \) to \( \text{NiAl} \), accompanied by a volume reduction. Using the molar volumes of \( \text{Ni}_2\text{Al}_3 \) (40.5 cm\(^3\)/mol) and \( \text{NiAl} \) (15.9 cm\(^3\)/mol), the volume reduction can be estimated to be about 21.5% theoretically. Accordingly, the relatively large reduction of volume due to the phase transformation could be the main cause of the void formation. In addition, many vacancies are left in the lattice of \( \text{NiAl} \) due to the Al anion outward diffusion. The vacancy congregates and grows with the increase of the oxidation time, and finally forms voids near the interface of \( \text{NiAl/Al}_2\text{O}_3 \) scale.

From the Ni–Al binary diagram, the \( \text{Ni}_2\text{Al}_3 \) phase region is narrow enough to easily transform to \( \text{NiAl} \) phase because of Al depletion. Due to the low melting point (1133 °C) and extreme brittleness of \( \text{Ni}_2\text{Al}_3 \) phase, it is not desirable to form a protective phase for high temperature application. It is possible to transform this brittle and low melting point \( \text{Ni}_2\text{Al}_3 \) phase into high melting point \( \text{NiAl} \) phase. There is an abrupt content change of Al at the interface between Ni plating and \( \text{Ni}_2\text{Al}_3 \) coating (as shown in Fig. 7(b)), which results in a

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**Fig. 5** Cross-sectional microstructure (a) and element content profiles of Ni, Al, O (b) for aluminized coating oxidized at 1000 °C for 25 h

**Fig. 6** Cross-sectional microstructure (a) and element content profiles of Ni, Al, O (b) for aluminized coating oxidized at 1000 °C for 50 h
Fig. 7 Cross-sectional microstructure (a) and element content profile of Ni, Al, O (b) for aluminized coating oxidized at 1000 °C for 250 h

diffusion couple between the nickel plating and Ni$_2$Al$_3$ coating. During the process of oxidation, the Al atoms in Ni$_2$Al$_3$ coating diffuse inwardly and the Ni atoms in nickel plating diffuse outwardly through the interface between Ni plating and Ni$_2$Al$_3$ coating. The interdiffusion leads to the decrease of the Al atom content in Ni$_2$Al$_3$ phase, and the increase of Ni atom content. Ni$_2$Al$_3$ phase near the interface transforms into NiAl phase described by the reaction Ni$_2$Al$_3$ + Ni $\rightarrow$ 3NiAl.

The good high temperature oxidation resistance of the Ni$_2$Al$_3$ coating is attributed to the high Al content in the coating layer that is beneficial in forming an Al$_2$O$_3$ scale. Furthermore, NiAl phase formed by Ni$_2$Al$_3$ phase by changes in the coating exhibits a better oxidation resistance at high temperature.

4 Conclusions

1) The coating formed on Ni plated copper substrate by the slurry pack cementation has a duplex layer structure (outermost Ni$_2$Al$_3$ and inner nickel plating). The outermost layer is a single Ni$_2$Al$_3$ phase with Al composition in the range of 59%–65%.

2) The coated copper is oxidized slowly without exfoliation of the protective Al$_2$O$_3$ scale, resulting in a mass gain of 10.108 mg/cm$^2$ after oxidation for 250 h at 1000 °C. The coating exhibits a better oxidation resistance. After being oxidized at 1000 °C for 25 h, the coating structure is still mainly Ni$_2$Al$_3$ phase; NiAl phase is presented after oxidation for 50 h. Finally, Ni$_2$Al$_3$ phase changes into NiAl phase wholly after being treated for 100 h or a longer time. Among them, NiAl phase in the outermost layer is Al-rich while NiAl in inner layer is Ni-rich.

References


铜基体上渗铝层的高温抗氧化性能和组织变化

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摘 要：以铜为基体，采用电镀镍和浆料包渗铝法，在 800 °C 渗铝 12 h 制备出组织为 Ni2Al3 的单相渗层。采用 SEM、XRD 和光学显微镜，研究在 1000 °C 下空气中氧化 25~250 h，Ni2Al3 濉层的高温抗氧化性能与组织转变行为。结果表明：Ni2Al3 濛层在 1000 °C 氧化 250 h 后，氧化增重分别为纯铜和镍镀层的 1/15 和 1/2。氧化时间在 25 h 内时，渗层表面仍有 Ni2Al3 相；氧化 50 h 后，出现 NiAl 相；当氧化时间增加到 100 h 时，Ni2Al3 相完全转变为 NiAl 相。当氧化到 250 h 时，渗层仍具有良好的抗高温氧化性能。

关键词：铜；Ni2Al3 相渗层；高温抗氧化性能；NiAl 相；包渗铅法

(Edited by Yun-bin HE)