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Sintered Cu Alloyed Stainless Steels and Their Corrosion Behavior

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Copper is an effective element to activate the sintering process of stainless steels and to enhance corrosion resistance of the sintered specimens. Ways of introducing Cu into stainless steel powders lead to different consequence in the microstructure and corrosion behavior of sintered Cu alloyed stainless steel. In the present work, two methods, mixing Cu with stainless steel powder and coating stainless steel powder with Cu by electroless plating, were introduced in order to investigate their influence on the sintered specimens. It was found that the sintered specimens from Cu-coated stainless steel powders (1-5 wt.%Cu) produce less porous surfaces with isolated pores than the specimens from mixed powders and the former have obviously high density and relatively even Cu distribution. Potentiodynamic polarization measurements indicate that Cu-electroless plating of 1-5 wt.%Cu improves the corrosion resistance of sintered stainless steel due to the lowering of passivation current density.

Keywords corrosion resistance, Cu-electroless plating, sintered stainless steel

1. Introduction

The demand for sintered stainless steels has notably increased due to their good mechanical properties, ease of fabrication, and the economic advantages (especially where large number of complex objects are involved) (Ref 1). However, in many applications, the corrosion resistance of the sintered parts is inferior to that of either cast or wrought stainless steel with the same chemical composition. It is well accepted that the corrosion resistance of sintered stainless steels depends on the interconnected porosity and the second phase, where Cr_2N and Cr_7C_3 are present in the grain boundaries (Ref 2). The interconnected porosity deteriorates corrosion resistance because it increases the area available for electrochemical reaction and inhibits the formation of passive films (Ref 3, 4).

The chemical activity of sintered stainless steels can be reduced by various techniques. These are mainly based on a reduction in the degree of porosity. For this case, the variables of the fabrication process such as sintering atmosphere, sintering temperature, and sintering time are being optimized, and the addition of alloying elements to the steels to increase corrosion resistance has been examined (Ref 5, 6).

Previous works reported that the addition of alloying elements, such as Cu, leads to a reduction in the interconnected open porosity due to the formation of a transient liquid phase and activates diffusion during sintering (Ref 6-8). The presence of the liquid phase produces a less porous surface with isolated pores, thus improving the corrosion resistance of sintered stainless steels. Most of these studies were focused on the corrosion behavior of sintered stainless steels that were sintered from elemental Cu-mixed stainless steel powders, while few publications dealt with the corrosion behavior of those that were fabricated by electroless Cu-plated stainless steel powders. Actually, ways of introducing Cu into stainless steel powders lead to different consequence in the microstructure and corrosion behavior of sintered Cu alloyed stainless steel. In the present work, two methods, mixing Cu with stainless steel powder and coating stainless steel powder with Cu by electroless plating, were introduced in order to investigate their influence on the sintered specimens. The effects of Cu-electroless plating on the microstructure and corrosion resistance of sintered stainless steel were investigated by using electronic probe analysis and electrochemical measurements.

2. Experimental Details

Water atomized AISI 316L stainless steel powders, supplied by Haining Feida Metallurgy Powder Co. Ltd., were used as the base materials in the study. For the ease of electroless plating, we chose the relatively coarse powders. The size of approximately 90% powders, per the supplier specifications was in the range of 75-150 μm and apparent density of the powders is 2.2 g/cm^3. The chemical composition provided by the product manufacturer is shown in Table 1.

Copper was introduced into the stainless steel powders in two ways. One is directly mixing the elemental Cu with stainless steel powders, the other coating Cu on the powders via electroless plating. The purity of copper powders supplied by Shanghai Institute of Fine Chemistry Technology is 99.5% and the particle size of powders is in the range of 35-50 μm.

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The electroless plating of Cu was conducted as follows. The stainless steel powders were activated using a proprietary process and then placed in an electrolyte containing copper sulfate and other chemicals at temperature of 70 °C and agitated the powders. After a period of reaction time, the copper-coated powders were separated, cleaned with water and alcohol, and dried at 70 °C. The thickness and concentration of copper on stainless powders were examined by SEM and chemical analysis. The Cu layer on the stainless steel particles is in the form of islands, the thickness of which is about 1 μm, and the concentration of Cu can be well controlled by the plating time.

Of all the test powders the Cu content was controlled at 1-5 wt.%. These treated powders then were compacted at a pressure of 600 MPa, rendering specimens of 10 mm in diameter and about 8 mm in height. No extra lubricants were applied during compaction. The green density of compacts is around 6.8 g/cm^3. The compacts were sintered in a vacuum furnace at 1150 °C, with vacuum pressure less than 0.13 Pa, for 60 min. The heating and cooling rate was controlled at 5 °C/min.

The density of all sintered specimens was measured by the water displacement method, and the copper distribution was examined by electronic probe analysis on the cross-section of the sintered specimens. For discussion, the sintered specimens obtained from the elemental Cu-mixed stainless steel powders is denoted as ECA, and the one from electroless Cu plated as ELCP.

A three-electrode cell system was used to perform electrochemical measurements. The working electrode was the specimen, the counter platinum and the reference a saturated calomel electrode (SCE). Prior to corrosion test the specimens were polished up to 600 grit, ultrasonically cleaned in acetone and dried at 150 °C for 2 h to prevent any liquid segregation in the open pores. The specimens were tested in 1N H_2SO_4 water solution at room temperature. Potentiodynamic polarization measurements were conducted at scanning rate of 1 mV/s.

Table 1 Chemical composition of AISI 316 L powder

Element	Cr	Ni	Si	Mn	Mo	C	S	Fe
wt.%	17.5	12.3	0.8	0.4	2.2	0.05	-	Bal

3. Results and Discussion

3.1 Microstructure Characterization

Figure 1 shows the influence of Cu-electroless plating on the morphology of sintered 316 L stainless steel containing 5 wt.%Cu. In comparison, a greater number and larger pores in ECA sintered specimens than those in ELCP are observed. The open porosity for both sinters is 1.7 and 1.3%, respectively. Those coarse pores found in the ECA specimens are in part due to formation of secondary pores from Cu particles. The liquid copper fills the micropores, and the number of pores is decreased while pores size is increased. The small pores in ELCP sintered specimens are due to the comparatively even distribution of copper in powder compacts.

The distribution of copper in ELCP and ECA sintered specimens was obtained by electronic probe microanalyses. The copper enriched zones in the sintered specimens are highlighted, and the copper lean ones dark as shown in Fig. 2. Obviously, Cu in ELCP sintered specimens diffused into stainless steel matrix more complete than that in the ECA. Moreover, more islands of copper are present in the grain boundary of the ECA than that of the ELCP. It follows that electroless Cu plating makes Cu much more uniformly distributed in the sintered specimens.

Variation of sintered density and porosity with copper content are given in Fig. 3 and Table 2. It was observed that the density of all ELCP sintered specimens containing 1-5 wt.%Cu was higher than that of ECA sintered specimens and the porosity of the former is lower. At a copper content of 1 wt.%, the density of both ELCP and ECA sintered specimens was increased as compared to that of sintered stainless steel without copper. This phenomenon is attributed to the fact that with small addition of copper, the amount of liquid phase was formed at the sintering temperature; the wetting and spreading of the liquid on the solid matrix was beneficial to rearrangement of stainless steel particles. Thus, there was an increase in sintered density when copper was added either in elemental form or coated. As the copper content was increased to 3 wt.%, a substantial improvement in the density of ELCP was obtained while the density of ECA was decreased. The density of ELCP sintered specimens reaches a value of about 7.14 g/cm^3 as compared to 6.94 g/cm^3 for the ECA. When copper content reaches 5 wt.%, the density of ECA sintered specimens decreased further. When copper is added to stainless steel in elemental form, a copper particle enclosed by several stainless steel particles after melting diffused to the stainless steel matrix

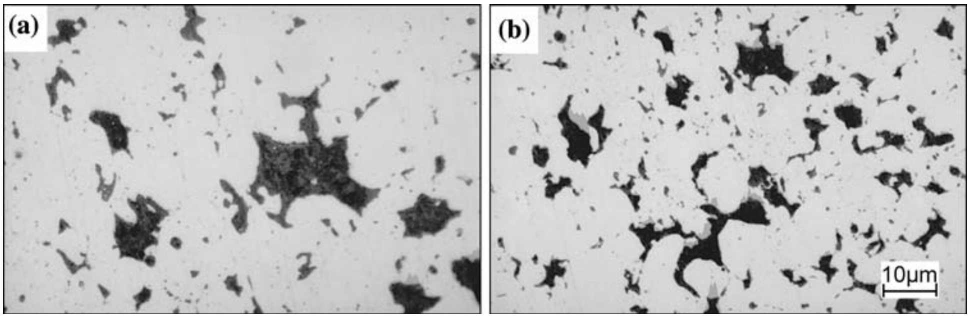

Fig. 1 Pores distribution of sintered 316 L stainless steels containing 5 wt.%Cu. (a) ECA sintered specimens and (b) ELCP sintered specimens (the open porosity of ECA and ELCP is 1.7 and 1.3%, respectively)

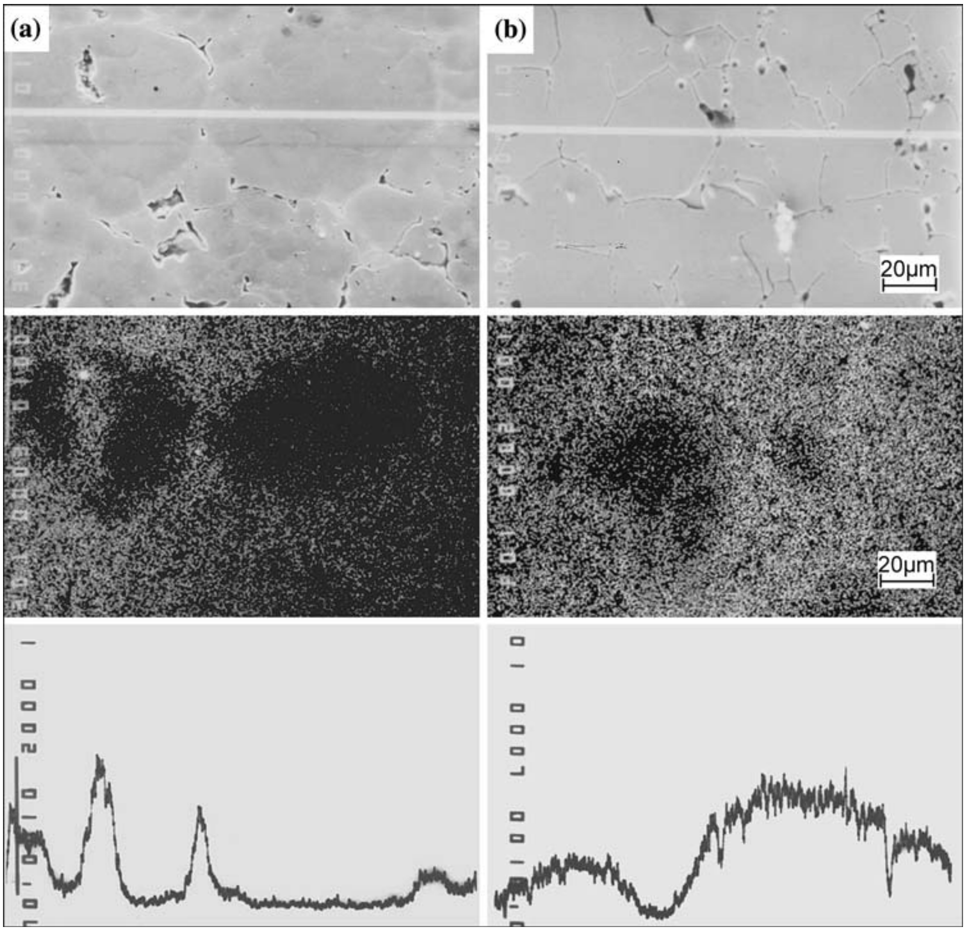

Fig. 2 Distribution of copper in (a) ECA and (b) ELCP sintered specimens obtained by electronic probe. The free copper areas in ECA and ELCP steels are 40 and 10%, respectively

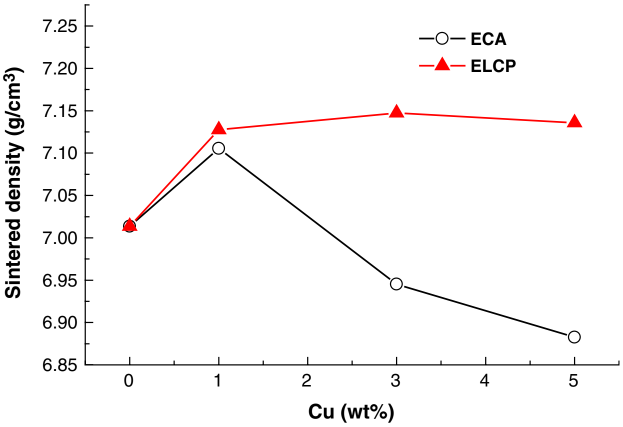

Fig. 3 Variation in the density of sintered stainless steels with Cu content, sintered for 1 h at 1150 °C in vacuum

and grain boundary and filled the micropores, resulting in a decrease in the number of pores but an increase in pore size. This assumption is confirmed by Choe (Ref 9). While copper is added by electroless plating, it is easier for the stainless steel particle encapsulated by liquid copper to rearrange, and therefore, to produce a reduction in porosity.

Table 2 Total porosity of ECA and ELCP specimens

		Porosity (%)			
Specimen	**Cu (wt.%)**	**0**	**1**	**3**	**5**
ECA		9.5	8.4	10.4	11.5
ELCP		9.5	8.1	7.8	8.2

Ways of introducing copper lead to obvious difference in Cu diffusion during the sintering process. For the compacts containing electroless plating Cu, the Cu diffused into the stainless steel powders and relatively evenly distributed as seen in Fig. 2. While in the compacts with addition of element Cu powder, the Cu diffusion was less even, and at the center of stainless steel particles almost no Cu atom was detected. During sintering, Cu-plated particles provide more chance for the Cu atom diffusion into stainless steel particles.

As we know, the solubility of copper in γ-iron is 8% at 1150 °C and the melting point of Cu is 1084 °C. In the case of ECA sintering at 1150 °C, copper melted and a small amount of copper dissolved in the outer layers of stainless steel particles. Much of the copper melt will penetrate along the stainless steel particles and/or penetrate into the stainless steel particle depending on the sintering duration. When copper gets

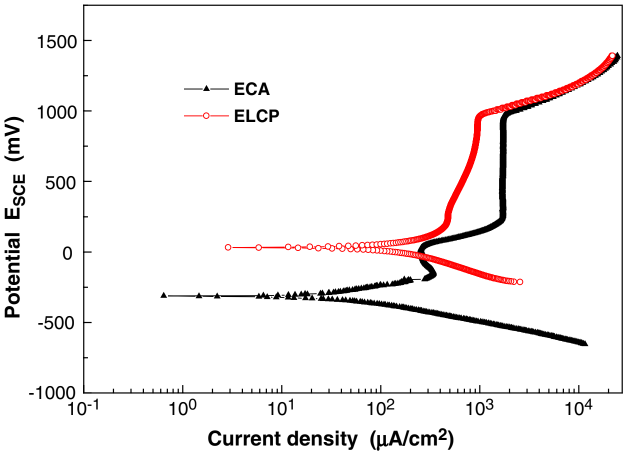

Fig. 4 Potentiodynamic polarization curves of the ELCP and ECA sintered specimens containing 3 wt.%Cu tested in 1N H_2SO_4

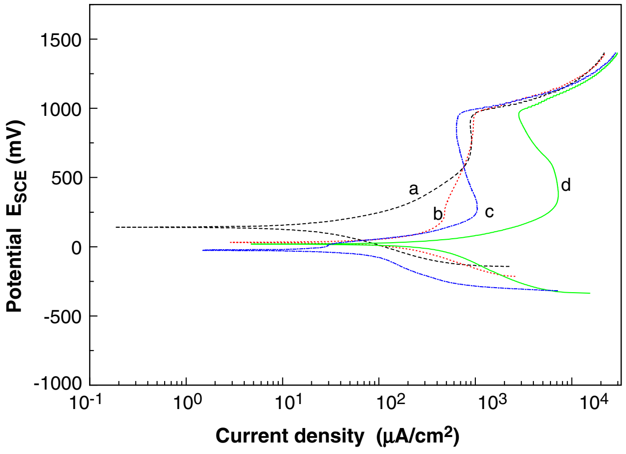

Fig. 5 Potentiodynamic polarization curves of as-sintered specimens tested in 1 N H_2SO_4. (a) ELCP containing 1 wt.%Cu; (b) ELCP containing 3 wt.%Cu; (c) ELCP containing 5 wt.%Cu; and (d) sintered stainless steel

redistributed, the space which copper originally occupied would become empty and a pore would form. Compared with the copper-coated particle, the element copper will leave larger pores because the thickness of copper layer is much thinner than the dimensions of copper particle and much of copper in the former case penetrates into stainless steel particles.

3.2 Corrosion Behavior

Figure 4 exhibits the difference in the corrosion resistance of ELCP and ECA sintered stainless steels. The ELCP sintered specimens sintered at 1150 °C show better electrochemical behavior that can be evidently seen by examining the value of passivation current density. These measures are justified by the microstructural characterization of the ELCP that showed lower porosity than that of the ECA; lower porosity involves a reduced surface for the dissolution. The ECA sintered specimens exhibited active-passive anodic transition with a clear active peak. This behavior is connected with the dissolution of free copper in acid solution (Ref 10). This result is well justified by considering the ECA microstructure that shows an amount of free copper in the samples sintered at 1150 °C.

Table 3 Passivation current density for ELCP specimens

Cu content (wt.%)	**0**	**1**	**3**	**5**
Passivation current density (μA/cm^2)	3.3×10^3	9.0×10^2	5.2×10^2 to 1.0×10^3	6.2×10^2

Figure 5 shows the anodic curves of ELCP sintered specimens with different amount of copper and Table 3 gives the corresponding passivation current density. It is observed that the passivation current density of all ELCP sintered specimens is lower than that of sintered stainless steel without copper. This result confirms the favorable influence of copper on the passivation of sintered stainless steel, due to the reduction in the interconnected porosity and the depolarization of the cathodic reaction (Ref 10, 11) as well as the reduction of total porosity (as seen in Table 2). The ELCP sintered specimens with 3 wt.%Cu exhibit a slightly better anodic passivation behavior with a passivation current density of 5.2×10^2 to 1.0×10^3 μA/cm^2, at the potential of +250 mV up to about +950 mV (SCE). The reason for the difference in the potential measured for the ELCP specimens lies most probably in the difference in the surface morphology. The ELCP specimen containing 3 wt.%Cu exhibits a more closed surface morphology compared to the other ELCP specimens. As such, an improved environmental behavior was obtained for the ELCP specimen with 3 wt.%Cu.

4. Conclusions

1. Electroless plating of Cu on 316 L stainless steel powders is beneficial to improving Cu distribution and reduction of porosity in the sintered steels.
2. All the sintered specimens from Cu-coated stainless steel powders (1-5 wt.%Cu) sintered at 1150 °C have higher density than those from mixed powders, and at copper content of 3 wt.%, a substantially improved density of the former sinter is obtained.
3. Cu-electroless plating of 1-5 wt.% improves the corrosion resistance of sintered stainless steel due to the lowering of passivation current density.

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