

The influence of copper addition on the corrosion performance of sintered AISI 304L stainless steel in sulfuric acid environment

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Abstract: The effect of copper addition on the corrosion behaviour of sintered 304L stainless steel in sulfuric acid solution has been investigated. Various additions of copper were used which corresponded to 2, 4, 8, 15 and 20 (wt.%). For comparison reasons, the sintered 304L stainless steel without copper was also studied. Open circuit potential measurements, potentiodynamic polarization curves and weight loss tests were used to evaluate the corrosion performance of the various sintered stainless steels studied. The results indicated that the corrosion characteristics at steady conditions were enhanced with the copper content. At high anodic potentials, however, the copper addition caused an increase in the critical current density for passivation and the current density at the passive region. The difficulty in reaching passivation also increased with the copper content in the sintered stainless steel.

1. INTRODUCTION

The demand for sintered steels has been continuously increasing due to the advantageous properties of these materials. The high surface area exposed to the environment, however, seriously affect their corrosion resistance. This problem has been well recognized and several works have been carried out to investigate the corrosion behaviour of sintered stainless steels in various environments (1-4). There is a general agreement that the corrosion resistance of sintered stainless steels is inferior to that of wrought stainless steels of similar composition(5). This has been attributed to the porosity, which is considered the main detrimental factor to the corrosion resistance, and consequently the presence of discontinuities in the passive films formed on sintered stainless steels(2-4).

In order to improve the corrosion resistance of sintered stainless steels various investigations have been performed. Some works studied the process parameters which affect the corrosion properties of the sintered materials(2,3), while others investigated the effect of alloying elements(6,7). Copper in additions up to 5 % has been reported as causing a significant improvement in the corrosion resistance of the steels which was attributed to the improved powders compressibility and consequently increased density(7).

The purpose of the present work is to evaluate the corrosion behaviour of sintered stainless steels with copper additions corresponding to 2, 4, 8, 15 and 20 (wt.%) in sulfuric acid media. The corrosion performance of the various sintered stainless steels is explained with reference to weight loss measurements and electrochemical studies.

2. EXPERIMENTAL

The 304L austenitic stainless steel powder used had an average particle size inferior to 150 μm , and the copper powder had an average particle size between 2 and 3 μm . The mixed powders were compacted at a pressure of 700 MPa in an uniaxial type press. Sintering was carried out at 1150 °C for 1 hour in a reducing 90 % N_2 / 10 % H_2 atmosphere. Chemical analysis was accomplished on all the specimens in order to determine the amount of absorbed nitrogen from the sintering atmosphere. The specimens microstructure was characterized by light and scanning electron microscopy (SEM).

The corrosion behaviour of the specimens was studied in 1N H₂SO₄ at room temperature by measuring the weight change, the variation of open circuit potential with time and potentiodynamic polarization studies. Specimens for the weight loss measurements were polished up to 600 mesh, ultrasonically cleaned in acetone and hot air dried. The surface of the specimens prior to the electrochemical tests were polished up to 1000 mesh. The polarization tests were carried out by using a PAR 273 scanning potentiostat. Polarization was from -600 mV (SCE) at a scan rate of 2 mV/s. The reproducibility of the results was verified by using 2 to 3 specimens of each type.

3. RESULTS AND DISCUSSION

The effect of the copper amount on nitrogen absorption from sintering atmosphere is shown in Table 1.

Table 1 Absorbed nitrogen content as a function of copper content in the steel

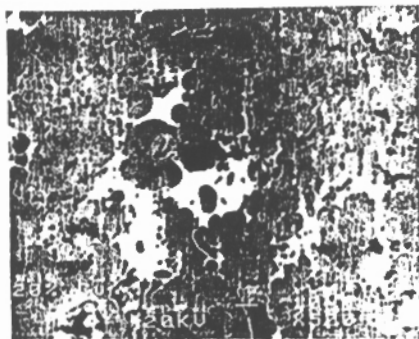
Cu (wt.%)	0	2	4	8	15	20
N (ppm)	6900	6200	5900	5300	4700	4100

It can be noticed that the addition of copper resulted in a reduction of absorbed nitrogen by the steel. These results confirm that copper does reduce the contamination of the steel and consequently decreases the tendency for chromium nitrides to precipitate.

SEM characterization of the samples revealed that the porosity morphology of the various specimens studied was irregular, particularly that corresponding to the large pores. Small pores, however, showed a round shape. The amount of the small and round pores seems to have increased for the specimens with higher copper contents as compared to lower copper content specimens, as shown in Fig. 1.



(a)



(b)

Fig. 1 SEM micrographs of the stainless steels with (a) 4 (wt. %) Cu (b) 20 (wt. %) Cu

Fig. 2 shows the SEM micrographs of the sintered stainless steels studied. It can be seen in this figure that for steels with copper contents up to 4 (wt.%), the copper is homogeneously distributed in the sintered steels. For the steels studied with higher copper amounts, 8, 15 and 20 (wt.%), the solubility limit is exceeded and copper precipitates.

The open-circuit potential, E_{corr} , of the various specimens tested decreased initially with exposure time and then after around 20 hours it became fairly constant. The shift into more active potentials indicates that the passive film is getting destroyed. At the steady state potentials the rate of metal dissolution is equal to the rate of the cathodic reaction, which in this case is the reduction of hydrogen. The potential at which the specimens stabilized was nobler for the steels with the highest copper contents.

Despite the criticism to weight loss tests when applied to porous materials, this test provides a comparison method of materials corrosion resistance in a certain environment. The weight loss data originated the curves shown in Fig. 3. The sintered stainless steels specimens without copper were severely attacked from the beginning of immersion. These specimens corroded during the exposure period up to total loss. The weight losses corresponding to the other specimens decreased with the copper content, and for the specimens containing 15 and 20 (wt.%) Cu the weight loss was negligible. This was confirmed by visual observation. The specimens corresponding to these two last steels still showed a metallic surface when the test was terminated after 330 hours immersion. In this work the weight loss method was very effective in comparing the corrosion resistance of the various specimens studied and the results produced by this method supported that originated by open circuit potential measurements.

The results suggest that the addition of copper increases the corrosion resistance of the sintered stainless steels at steady state potentials and this effect is enhanced by the amount of copper added.

In order to investigate the corrosion behaviour of the various specimens studied at conditions removed from the equilibrium, polarization studies were carried out. The results produced are presented in Fig. 4. The potentiodynamic polarization curves depict clear corrosion differences, at large polarization potentials, for the various sintered steels tested. The critical current densities, i_{crit} , and the passive current densities, i_{pass} , increased with the copper content in the steels, Fig. 5. The addition of copper to the sintered steels also shifted the active/passive potential towards the positive direction. These results imply that the passivation of the steels with copper occurs with greater difficulty as compared to the copper free steels. The possible reasons for this behaviour are the presence of copper precipitated on the surface and a greater number of fine pores in the specimens with large copper contents (Fig. 1). The fine pore sized specimens with heterogeneous surface composition will have more discontinuities in the passive film, and this makes passivation more difficult.

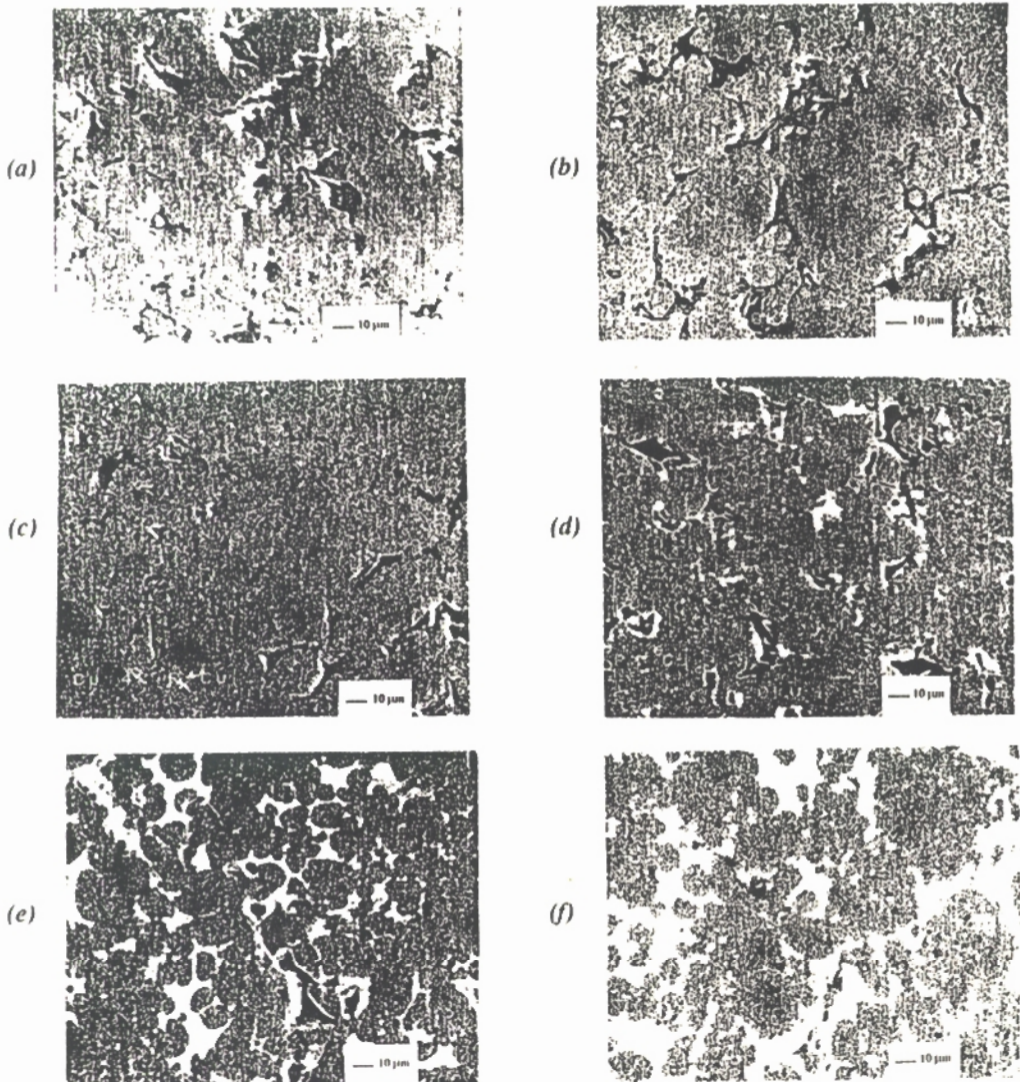


Fig. 2 SEM micrographs of the sintered stainless steels tested showing secondary electron image and Cu X-ray image. (a) 0% Cu, (b) 2% Cu, (c) 4% Cu, (d) 8% Cu, (e) 15% Cu, and (f) 20% Cu.

The increase in passive current density with the copper content in the steel might have been caused by copper incorporated in the passivating film. If this occurred an increase in the electronic conductivity of the passivating film would be expected. As a result the current density in the passive state would also increase.

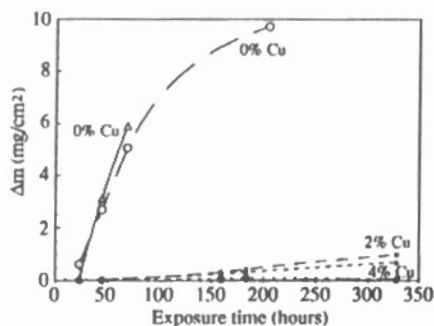


Fig. 3 Weight loss measurements as a function of exposure time for the sintered steels studied.

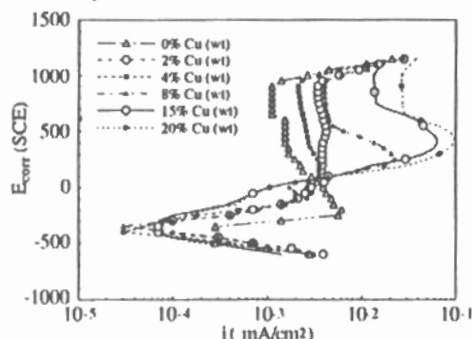
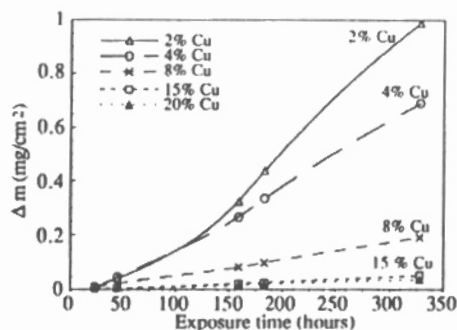


Fig. 4 Polarization curves of the sintered steels studied in 0.5 M H_2SO_4

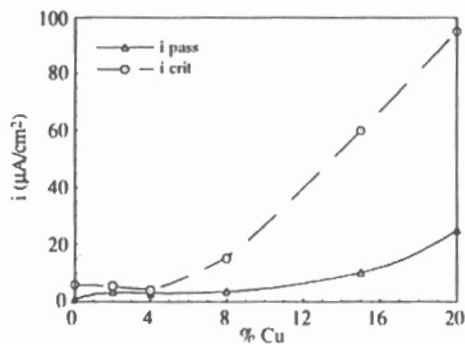


Fig. 5 Relation between i_{pass} and % Cu and between i_{crit} and % Cu.

4. CONCLUSIONS

The following conclusions can be drawn from the present investigations:

1. The addition of copper enhanced the corrosion behaviour of the sintered 304L stainless steel at stable conditions. This improvement in corrosion resistance increased with the copper content added.
2. A shift in the active-passive transition potential into more positive potentials was found for the specimens with copper added. Copper also caused an increase in the critical current densities for passivation. This greater difficulty in reaching passivation might have been caused by the presence of copper precipitates and fine pores in the specimens with higher copper contents.
3. Copper addition also caused an increase in passive current densities. This was likely caused by copper enrichment in the passive oxide layers.

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