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A new acid pickling process for copper alloys

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Abstract: The cleaning process of removing oxides on the surface of copper alloy sheets was investigated systematically. Through optimizing, a perfect process was selected that is fit for removing oxides on the surface. By acid pickling, all kinds of copper oxides are removed completely, furthermore, no poisonous gases are given out and a smooth and clean surface of copper alloys is obtained. At present, the process is applied successfully in the copper-processing industry.

Key words: copper alloy; surface processing; oxides of copper; acid pickling

Copper alloys with anti-causticity and plasticity have been found many important applications in many industries. However, in the rolling and machining process of copper and its alloys at high temperatures, as a result of oxidization, a layer of membrane (1-10 μm) made of all kinds of oxides is formed easily on the surface. It is shown by analysis that the oxide membrane can be divided into three layers. The outer layer is mainly made of CuO, the middle layer is made of Cu_2O, CuO and a little of Cu, and the inner layer is made of Cu_2O, Cu and a little of CuO. The present process of removing these layers is that copper with oxides on the surface is first pickled for about 1 h in about 25% H_2SO_4 solution at 70℃ [1], then pickled for 20 s in about 25% HNO_3 solution at room temperature [2]. Pickled in H_2SO_4 solution, CuO in the outer layer can be dissolved rapidly in hot sulphuric acid solution, but Cu_2O in the middle layer reacts easily as the following in acidic solution [3]:

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O,$$

and produced Cu is covered on the copper alloy surface. Because little copper can be dissolved in H_2SO_4 solution, the layer of copper keeps the other oxides of copper from being dissolved further, so oxides on the copper alloy surface can only be removed in part in hot H_2SO_4 solution. The copper alloy sheet is pickled further in about 20% HNO_3 solution to remove the remaining oxides. Although oxide membrane can be removed completely in HNO_3 solution, an amount of NO_x is formed when Cu and Cu_2O react with HNO_3. NO_x with toxicity pollutes environment and does harm to personal health; besides, there is a worse pickled effect in surface quality [4,5]. This paper aims to develop a new acid pickling process in which the above disadvantages can be all overcome.

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1 Experimental

The rolled copper alloy sheet was cut into a sample of 20 mm × 50 mm. The sample was pickled for about 1 h in 25% H_2SO_4 solution at a temperature higher than 70℃, then the sulfuric acid-pickled sample was put into a sulfuric acid solution containing various kinds of oxidizers such as $(NH_4)_2S_2O_8$, H_2O_2, $NaClO_3$ or other oxidizers containing catalyzers, smoothing and cleaning reagents at room temperature. After dipped into the solution for a given time, it was taken out and rinsed in water.

2 Results and discussion

2.1 Selection of acid

In a view of their low costs, HCl and H_2SO_4 were selected. It was shown that H_2SO_4 is an idea acid for dissolving copper oxides, but HCl is not selected as the agent to remove oxides on the copper alloy sheet surface, because of the following reaction:

$$Cu^+ + Cl^- = CuCl \downarrow.$$

Formed CuCl is not dissolved in water and covered on the copper alloy sheet surface, it affects seriously sheet surface quality.

2.2 Selection of oxidizer

To dissolve Cu covered on oxides, oxidizers had to be added in H_2SO_4 solution. Experiments were done on different kinks of oxidizers. Results showed as the following.

(1) $(NH_4)_2S_2O_8$ and H_2O_2 oxidizers.

Although $(NH_4)_2S_2O_8$ and H_2O_2 can be used as oxidizers for dissolving low-valence Cu, their oxidabilities are too strong to be adequate for removing Cu in oxides. Firstly, although Cu on oxides can be oxidized and dissolved, at the same time, excessive Cu in Cu alloys is also dissolved so as to have a great loss in Cu. Secondly, a lot of spots are formed on its surface as a result of uneven erosion so as to have a serious effect on end product surface quality. Thirdly, because of their low thermostabilities, a lot of $(NH_4)_2S_2O_8$ and H_2O_2 are decomposed at a temperature more than 40 ℃ [6]. Eventually, the great amount of oxidizer consumption results in the great increase in acid pickling cost.

(2) $NaClO_3$ oxidizer.

The oxidability of $NaClO_3$ is adequate for oxidizing low-valence Cu. It can remove rapidly Cu on oxides, but it has many disadvantages. Firstly, it reacts chemically with Cu to form a layer of CuCl deposits covered on the Cu alloy sheet surface. It is hard to remove the CuCl deposit film from the surface in other reagents such as NH_3 solution. Involved reactions are shown as the following:

$$6NaClO_3 + 17Cu + 18H_2SO_4 = 3Na_2SO_4 + 2CuCl\downarrow + 15CuSO_4 + 2Cl_2\uparrow + 18H_2O \quad (1)$$

$$2NaClO_3 + 7Cu + 6H_2SO_4 = Na_2SO_4 + 2CuCl\downarrow + 5CuSO_4 + 6H_2O \quad (2)$$

The result of SEM analysis is shown as **figure 1**.

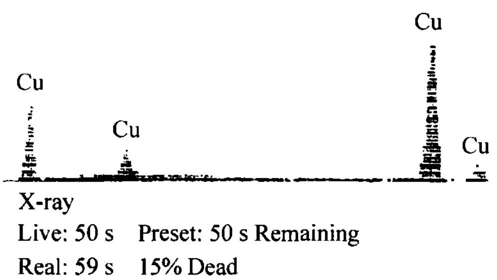

Figure 1 XPS pattern of the surface pickled in H_2SO_4 solution containing $NaClO_3$.

Secondly, in the two following reactions:

$$ClO_3^- + 6H^+ + 5e = \frac{1}{2}Cl_2 + 3H_2O, \ \varepsilon^\circ = 1.47 \text{ V} \quad (3)$$

$$ClO_3^- + 6H^+ + 6e = Cl^- + 3H_2O, \ \varepsilon^\circ = 1.45 \text{ V} \quad (4)$$

the values of ε° are very close to each other, so ClO_3^- can be deoxidized into Cl_2 and Cl^- simultaneously or respectively at a certain acidity. Because acidity has a greater effect on reaction (3) than reaction (4), ClO_3^- can only be deoxidized into Cl_2 at a higher acidity, deoxidized into Cl_2 and Cl^- simultaneously at a middle acidity, and only at a lower acidity can ClO_3^- be deoxidized into Cl^-. To keep toxic Cl_2 from forming, it is necessary to control a lower acidity in the solution containing oxidizer $NaClO_3$, but the low acidity affects conversely pickling rate and effects.

Eventually, formed Cl_2 is a kind of toxic and stimulant gas, it harms to surrounding environment and personal health.

(3) $Na_2Cr_2O_7$ oxidizer.

$Na_2Cr_2O_7$ oxidizer can oxidize CuO into Cu^{2+}, but its oxidization rate is so slow that it takes 30-40 min to remove CuO on oxides and low-valence oxides from the copper alloy sheet surface at room temperature. Even though at a higher temperature such as 60℃, its oxidization rate increases a little. In addition, the pickled Cu alloy sheet is also poor in surface quality. To improve oxidization rate and pickled quality, such additives as catalyzers, smoothing and cleaning reagents are added. After the given additives are added, many performances are improved more or less. Firstly, the rate of oxidization of CuO and low-valence Cu by $Na_2Cr_2O_7$ increases obviously, the pickled time is reduced from 30-40 min to about 10-15 s. Secondly, the surface quality improves evidently. The comparison between different results is shown in **figure 2**. It is obviously found out from the pickled results in figure 2 that the specimen pickled in H_2SO_4 solution containg $Na_2Cr_2O_7$ and catalyzer AB is much better than the specimen pickled in HNO_3 solution in pickled surface quality. Eventually, the loss in copper-based materials is less for pickling in the solution containing $Na_2Cr_2O_7$ and catalyzer AB than that for pickling in HNO_3 solution. The former loss is about 0.5%-0.8% and the later is 1.0%-1.5%. Related reactions are as follows.

In the absence of catalyzers, Cu can react with $Na_2Cr_2O_7$:

$$3Cu + Na_2Cr_2O_7 + 7H_2SO_4 = 3CuSO_4 + Na_2SO_4 + 7H_2O + Cr_2(SO_4)_3.$$

In the presence of the catalyzer AB, Cu can react with $Na_2Cr_2O_7$:

$$Na_2Cr_2O_7 + 7H_2SO_4 + 6Cu + 6AB = 6CuB + Na_2SO_4 + 3A_2SO_4 + Cr_2(SO_4)_3 + 7H_2O,$$

$$6CuB + Na_2Cr_2O_7 + 7H_2SO_4 = 6CuSO_4 + Na_2SO_4 + 2CrB_3 + 7H_2O,$$

$$2CrB_3 + 3A_2SO_4 = Cr_2(SO4)_3 + 6AB.$$

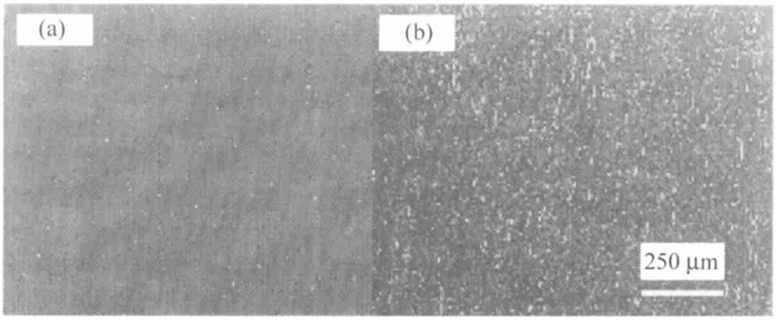

Figure 2 SEM microphotograghs of the pickled surfaces for copper alloy specimens. (a) The specimen pickled in H_2SO_4 solution containing $Na_2Cr_2O_7$ and catalyzer; (b) the specimen pickled in HNO_3 solution.

3 Conclusions

(1) $(NH_4)_2S_2O_8$, H_2O_2 and $NaClO_3$ can not be used as oxidizers for acid pickling of oxides on the copper alloy surface.

(2) In the absence of catalyzers, $Na_2Cr_2O_7$ reacts slowly with Cu and poor pickled surface quality is obtained.

(3) In the presence of the catalyzer AB, Cu reacts quickly with $Na_2Cr_2O_7$ and good pickled surface quality is achieved.

(4) No toxic and harmful gases are produced in the new process, thus it can meet the demands of environmental protection and production simultaneously.

(5) The cleaning process improves greatly the product quality of Cu alloy sheets.

(6) The cleaning process reduces the loss of copper-based materials from 1.0%-1.5% to 0.5%-0.8%.

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