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Selection of Stainless Steel for Cathode Plate in Hydrometallurgical Process

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Abstract

Recently, the hydrometallurgy for metal refining is getting more and more popularin China. During a traditional hydrometallurgical process sulphuric acid is often used. In many cases, the working conditions in the solvent extraction and electro winning processes could be very tough for the commonly used material of different equipment and components, such as, austenitic stainless steels of 304/304L and 316L. In a copper refinery, a permanent cathode plate made of 316L was taken out of production due to heavy corrosion. The samples from the corroded plate were investigated thoroughly, possible reasons were pointed out and new material was suggested in this work. It is expected this research could help the copper refineries and Sanmen Sanyou to select the proper cathode plates in complicated working conditions.

Keywords

Mining, Pitting Corrosion, Cathode Plate, Hydrometallurgy, Copper Refining

1. Introduction

The demands for copper have been increasing largely in China during the recent decades. Traditionally, pyrometallurgy is the dominated process for copper production in China. The majority of copper come from pyrometallurigical process. However, the resources on the earth are limited and high grade traditional ores are reducing rapidly. Therefore, the hydrometallurgy for metal refining is getting more and more popular, including in China. A traditional hydrometallurgical process includes leaching, solution concentration & purification and metal recovery. As sulphuric acid is often used, the working conditions in the solvent extraction and electrowinning processes vary largely and can be very tough for the commonly used material of different equipment and components. By tradition, austenitic stainless steels, such as 304/304 L, 316 L, 317 L and 904 L, have been used for hydrometallurgical processes. With the recent development of the processes, with higher temperature and complicated composition of solvent, several failures cases of stainless steel used have been reported. In the recent years, more stainless steels, such as duplex stainless steels, have been introduced into hydrometallurgical applications. Based on the experiences from daily operation, working environment varies large between different copper refineries, even the process principle is the same. This will affect the material selection as well the performance of the equipment.

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In a normal electrowinning process, the copper is refined by electrolysis. The anodes cast from processed blister copper are placed into an aqueous solution of 3% - 4% copper sulfate and 10% - 16% sulfuric acid. Cathodes are thin rolled sheets of highly pure copper in the early days. Recently, reusable stainless steel starting sheets have been used as permanent cathode plates with many benefits. The most common grade used is 316 L with 2B surface finish and typical thickness is 3.25 mm. At the anode, copper and less noble metals dissolve. More noble metals such as silver, gold, selenium, and tellurium settle to the bottom of the cell as anode slime, which forms a salable byproduct. Copperions migrate through the electrolyte to the cathode. At the cathode, copper metal plates out, but less noble constituents such as arsenic and zinc remain in solution unless a higher voltage is used. The total reactions [1] are:

$$\text{At the anode:}\quad \mathrm{Cu}\left(\mathrm{s}\right) \rightarrow \mathrm{Cu}^{2+}_{(\mathrm{aq})} + 2\mathrm{e}^-$$

$$\text{At the cathode:}\quad \mathrm{Cu}^{2+}_{(\mathrm{aq})} + 2\mathrm{e}^- \rightarrow \mathrm{Cu}\left(\mathrm{s}\right)$$

The principle for a typical copper refining process is shown in **Figure 1(a)**, and stainless steel permanent cathode plate is shown in **Figure 1(b)**.

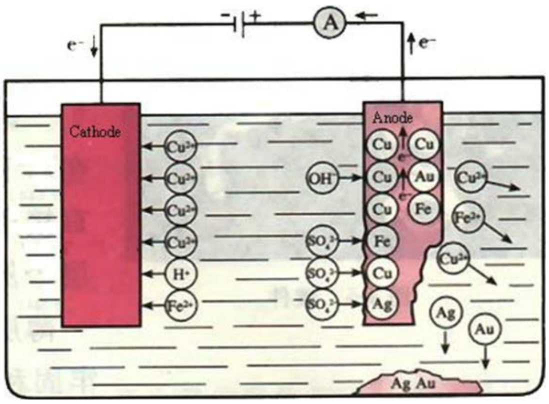
Typical composition of electrolytic solution are: $CuSO_4$, H_2SO_4, H_2O and reaction agent. Cl^- ions could also be added via reaction agents. The concentration of H_2SO_4 varies between 100 and 220 g/L. When the electric density is 300 A/m^2 and temperature 60˚C - 65˚C, the concentration of H_2SO_4 is about 180 g/L [1]. These process parameters could affect the performance of stainless steel cathode plates. Corrosion in different degree could occur accordingly.

Sanmen Sanyou Technology Inc is a leading company supplying different equipment to the hydrometallurgical industry in China. As one of the first Chinese companies producing stainless steel cathode plates, Sanmen Sanyou has made a lot of effort on developing the cathode plate technology, and studying the actual problems in copper refineries to improve product performance. Recently, one of their customers had reported a failure case. Together with the technical & quality department, the failed cathode plate was studied thoroughly and the case is described in this paper. The reasons for the failure are given and more suitable stainless steels are suggested.

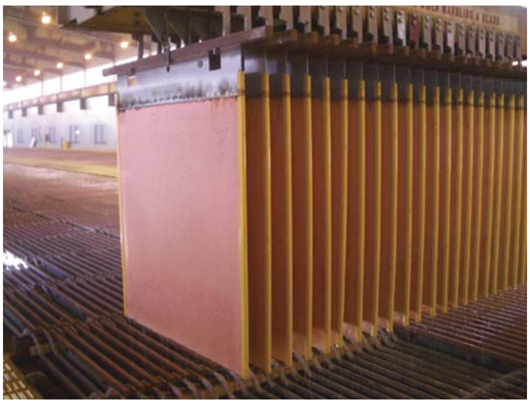
2. Samples Investigated [2]

From the copper refinery, several samples were received, see **Figure 1** below. As can be seen, both sides of the cathode plate were heavily corroded.

In total, a part of a cathode plate, see **Figure 2**, with a size of approximately 250 × 130 mm was collected. The surface of the steel was 2B surface finish. Six small pieces of copper where one side is greenish see **Figure 3**, with the largest size of 70 × 50 mm. The thickness of the homogeneous copper was approximately 2 mm while the total thickness was approximately 5 mm. Two small plastic bags with corrosion products from the cathode plate; see **Figure 4**.

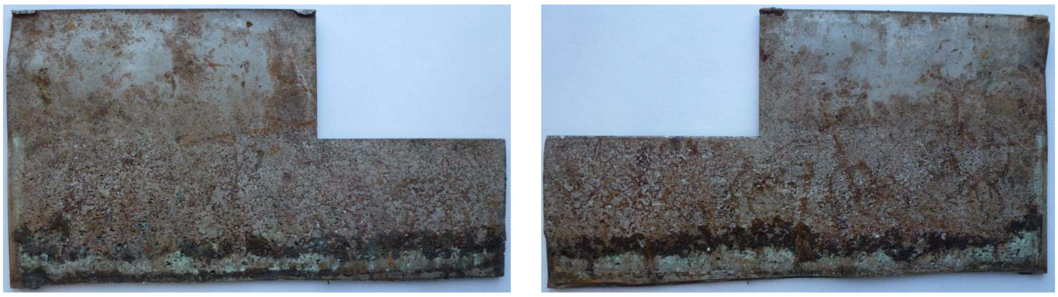


(a)



(b)

Figure 1. Principle for copper refining process and cathode plate. (a) Electrolytic copper refining process; (b) Stainless steel permanent cathode plates.



(a) (b)

Figure 2. The corroded permanent cathode plate was gathered. (a) One side of the plate; (b) Another side of the plate.

Figure 3. Sample from the copper refinery with copper and corroded products.

Figure 4. Some corrosion products gathered from the cathode plate and its surrounding.

3. Investigation

All the samples gathered were investigated by different methods.

By visual examination, the cathode plate was examined in a Light Optical Microscope (LOM).

Chemical composition of the cathode plate was verified by X-ray fluorescence using an X-MET 3000TX instrument, in order to identify the steel grade.

Metallographic examination of the cathode plate was carried out and the microstructure of the cathode plate was examined in a light optical microscope after etching.

Several small pieces of samples and the content in the plastic bags were examined in a scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) for analyzing the chemical content, in order to identify the nature of corrosion.

4. Results

Metallographic examinations on the cross sections of the cathode plate were carried out. The microstructure of the cathode plate shows a normal structure for 316 L with a typical grain sizes, see **Figure 5**. However, some shallows of intergranular attacks in the grain boundaries could also be seen, indicating one of type corrosion attacks occurred during the operation.

Under Light Optical Microscope, a lot of pitting corrosion attack is found, see **Figure 6**. The measured depth of the pitting attack is about 1.3 mm, although it is difficult to find out the deepest attack places. As shown in **Figure 2**, most pitting attacks are present in the areas which are the border lines of the electrolytic solution. Some of pitting attacks are also in the areas just above the solution level line.

The chemical composition of the cathode plate was determined by SEM. The result from this investigation showed no deviation from the expected chemical composition, confirming the grade to be 316/316 L.

Samples shown in the **Figure 3** and **Figure 4** were analyzed by SEM-EDS. The chemical compositions from different parts on several of the small copper pieces were measured. The results of chemical composition analysis are shown in **Table 1** and **Table 2**, respectively.

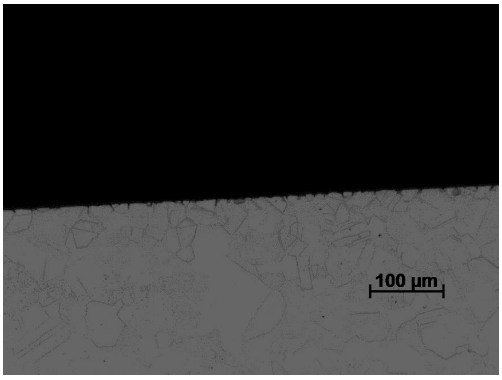


Figure 5. Microstructures on the cross section of the cathode plate.

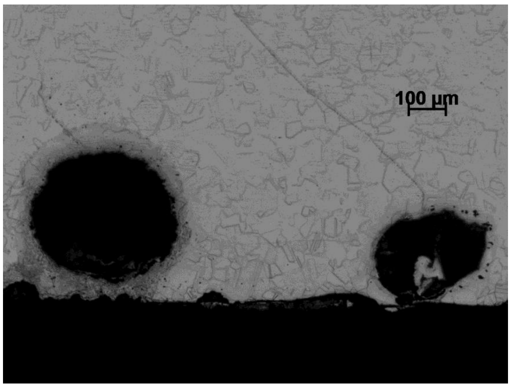


Figure 6. Microstructures on the cross section of the cathode plate.

Table 1. Chemical analysis from samples shown in **Figure 3**.

Analysis	C	O	S	Cl	Cu
Average	5.81	28.40	3.96	6.41	55.30

Table 2. Chemical analysis from samples shown in **Figure 4**.

Analysis	C	O	Al	Si	S	Cl	Cr	Fe	Ni	Cu
Average	9.97	46.64	0.79	0.12	4.91	4.07	6.30	26.93	0.68	0.70

As shown in **Table 1**, a lot of Cu and Cl were found. The high content of Cu, O and Cl indicate that the analyzed parts and/or areas may consist of $CuCl_2 + 2H_2O$. This kind of component is normally known to have a green-blue color.

Table 2 shows high concentrations of O, Cl and Fe. The elements of Cr, Fe and Ni analyzed come most certainly from the stainless steel. The concentrations of these elements indicate that the analyzed areas in **Figure 4** are corrosion products. The presence of chlorides in the corrosion products explains why the corrosion experienced was pitting corrosion.

5. Alternative Stainless Steels

Table 3 shows chemical analysis of two other stainless steels apart from the 316 L used in this case: 904 L and 2205. 904 L is an austenitic stainless steel—the same type as 316 L. The only difference is higher contents of Cr, Ni and Mo, compared to 316 L. 2205 is a duplex stainless steel, which contains higher content of Cr and Mo, but lower Ni-content, compared to 316 L.

Due to the differences in the chemical composition, the resistances to pitting corrosion are also different, which can be shown by the PRE values. The higher PRE value is, the higher resistance to pitting corrosion. As shown in the **Table 3**, both 904 L and 2205 have higher PRE value than 316 L [3].

The pitting resistance of a stainless steel can also be determined by corrosion test. One of tests had been carried out according to ASTM G150—a commonly used and standardized corrosion testing method. The result is given in the **Figure 7**. CPT means critical pitting temperature. Steel grade with higher CPT value has also higher pitting corrosion resistance. As can be seen in the **Figure 7**, both 904 L and 2205 have higher resistance to pitting corrosion than 316 L, while 904 L has the highest CPT value among the three grades.

6. Discussions and Conclusion

The production of copper by the electrowinning process is done in an electrolyte containing mainly sulphuric acid and copper sulphate. However, the electrolyte also contains chloride ions, as shown in this case. During the process, the copper ions from the electrolyte are reduced to metallic copper which precipitates onto the cathode plate. Stainless steel of 316/316 L is commonly used for the cathode plates, based on the development in the last decade. The electrolyte can be very aggressive for many stainless steel grades. As the investigated in this case, cathode plate made of 316 L had severe corrosion attacks such as pitting corrosion. One of reasons could be that

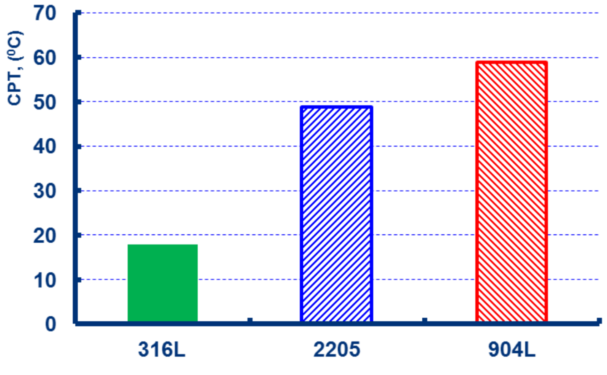


Figure 7. Microstructures on the cross section of the cathode plate.

Table 3. Typical chemical composition for other stainless steels.

Grades	C	Cr	Ni	Mo	N	Other	PRE
316 L	0.02	17.2	10.1	2.1	-	-	24
904 L	0.01	20.0	25.0	4.3	-	1.5Cu	34
2205	0.02	22.0	5.3	3.1	0.17	-	35

PRE = %Cr + 3.3 × %Mo + 16 × %N.

the cathode plate has been left in the electrolyte with the direct current switched off. This leads to corrosion on the cathode plate. The corrosion starts in the areas such as copper on the cathode plate, the cathode plate above the electrolyte line as well as above the copper layer. The aggressiveness of the electrolyte varies depending on the actual composition of the electrolyte. The relatively high content of Cl indicates that the working condition is so severe that it is too tough for 316 L so that pitting corrosion could occur.

For a refinery with such working condition, stainless steel cathode made of 316 L will have shorter life time due to the corrosion. A better choice of cathode plate material would be 904 L and 2205, as both have higher corrosion resistance. The final selection will depend on the actual situation, fabrication as well as economic considerations.

Sanmen Sanyou Technology Inc has been concentrating on many detail R & D works of raw material selection for cathode plates, based on these experiences, both 904L and 2205 can be used as cathode plate. However, due to the high strength of 2205, special equipment and production process is needed. With the newly invested equipment, Sanmen Sanyou has developed a route for using high strength material and produced duplex stainless steel cathode plate successfully. As the references have been achieved in China already, the final material selection shall depend on the actual situation as well as long term experience of fabrication.

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