Acid Pickling Process of Titanium alloys and its Investigation of intergranular corrosion and Pitting corrosion

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Abstract. Before fluorescence detection of Titanium alloy components, acid pickling in HF-HNO3 solutions is always required in order to remove the superficial oxides of the components. According to the relative CPS document, the conditions for Titanium alloy pickling are HF arranged below 90g/L, HNO3 300-450g/L and at ambient temperature. In this paper, the corrosion rate of the acid pickling process of TC4 alloy was investigated using the acid solutions with variable HF、Titanium contents and fixed HNO3 content of 375g/L at different temperatures. In addition, the intergranular corrosion and pitting corrosion of the TC4 alloys after pickling under different conditions were conducted. The effects of HF and HNO3 on the intergranular corrosion and pitting corrosion were discussed.

Introduction

Due to their high specific strength, excellent corrosion resistance and welding properties, titanium alloys are widely used in industries [1,2]. Fluorescence detection of Titanium alloy components has become a usual method to examine their quality. Before the fluorescence detection, acid pickling is the most important process in order to remove the superficial oxides of the components.

Acid pickling of the Titanium alloys are widely investigated at home and abroad [3,4]. Rudy[4] reported the effects of HF、HNO_3、H_2SO_4 and H_3PO_4 on the surface microstructure, roughness and hydrogen content of the titanium alloys after acid pickling in detail. Ogawa et al [5] found that, when the titanium alloy was immersed in HF solutions, it contained more hydrogen as the time increases. Besides, the hydrogen concentration in the alloy increased with the HF content in the pickling solution [6]. Vermesse et. al.[7] concluded that the surface quality and fatigure properties of the Ti-6Al-4V alloy can meet the requirements of the aviation industry when the acid pickling solutions contain HNO_3 below 20% and HF below 2.5%.

According to the relative CPS document, the conditions for Titanium alloy pickling are HF arranged below 90g/L, HNO_3 300-450g/L and at ambient temperature. The document is relatively simple and always causes troubles when the acid pickling conditions changes for the removal amount is fixed, while the corrosion rate is variable.

In this paper, the corrosion rate of the acid pickling process of TC4 alloy was investigated using the acid solutions with variable HF、Titanium contents and fixed HNO_3 content of 375g/L at 10^oC、20^oC 、30^oC and 38^oC temperatures. Besides, the intergranular corrosion and pitting corrosion of the TC4 alloys after pickling under different conditions were conducted. The effects of HF and HNO_3 on the intergranular corrosion and pitting corrosion were also discussed.

Experimental

Calculation of corrosion rate. The TC4 samples are about 51mm×51mm×3mm, and the immersion time is 15 min. Before and after the acid pickling, the weight, size and thickness values of the samples are strictly measured by electronic balance, vernier caliper and micrometer caliper, respectively. The corrosion rate of the samples can be calculated by the following formula.

$$V = \frac{4(m_1 - m_2)v}{A * m_1}$$

That is, V: corrosion rate, mm/side/h; m_1: original weight, g; m_2: weight after pickling, g; v: original volume of the sample, mm^3; A total original surface area, mm^2.

Acid pickling process. The acid pickling solutions are prepared using analytical reagent HF、HNO_3 、 H_2TiF_6 and purified water, and the solutions contain fixed HNO_3 content of 375g/L, fixed Titanium content of 5 or 15g/L，variable HF content arranged 20-50g/L. The total volume of the acid solution is 2L. The pickling experiments were conducted at 10^oC、20^oC 、30^oC and 38^oC temperatures. For insurance, the solutions are set in water bath of the constant temperature freezer.

Intergranular corrosion and pitting corrosion. Polished samples are prepared to conduct the intergranular corrosion and pitting corrosion tests. The corrosion depths of the samples were about 12 m and corrosion conditions is listed in Table 1. The cross-sectional morphologies of the tested samples were observed by a XJP-6A optical microscope at the magnification of 600.

Table 1 The conditions of intergranular corrosion and pitting corrosion

Experiment serial number	Acid pickling conditions /(g/L)			temperature/℃
	Ti	HF	HNO_3	
1	10	30	450	10
2	10	30	300	10
3	10	90	300	10
4	10	90	300	38
5	10	30	300	38
6	10	90	450	38

Results and discussion

The corrosion rate of the TC4 alloy at different conditions are shown in Fig.1.

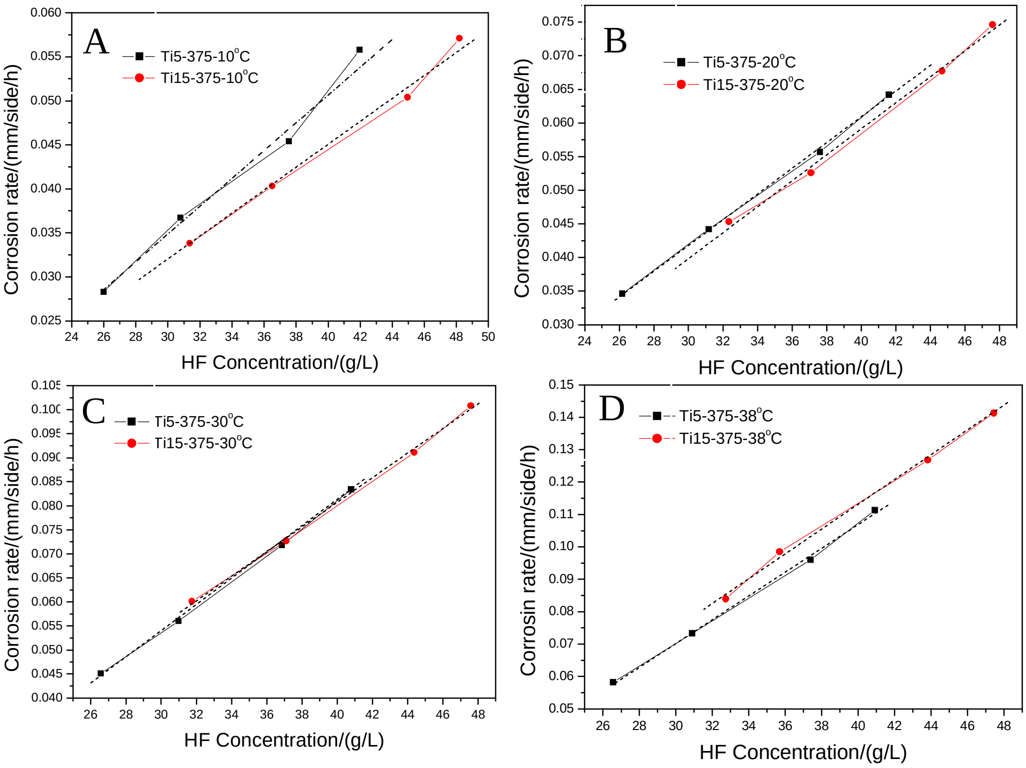

Fig.1 the corrosion rates of TC4 alloy under different conditions. A:10°C; B:20°C; C:30°C; D:38°C

From Fig.1, it can be seen that, with the temperature and HF concentration increased, the corrosion rate increased. The HNO_3 content in the solutions also has influence on the corrosion rate. At low temperature, the corrosion rate of the solution with 15 g/L Ti ions is much smaller than that of containing 5 g/L, as seen in Fig.1A. While, with temperature increased, the difference of corrosion rate between them became narrower, seeing in Fig1B and C. When the corrosion temperature was 38 °C as shown in Fig.1D, the corrosion rate of the solution with 15 g/L Ti ions is apparently higher than that of containing 5 g/L. This phenomenon may be ascribed to the passivation effects of HNO_3, which is much more intensive at low temperature than at high temperature.

The typical intergranular corrosion and pitting corrosion morphologies after are shown in Fig.2, and the summaries of the values of intergranular and pitting corrosion are shown inTable.2.

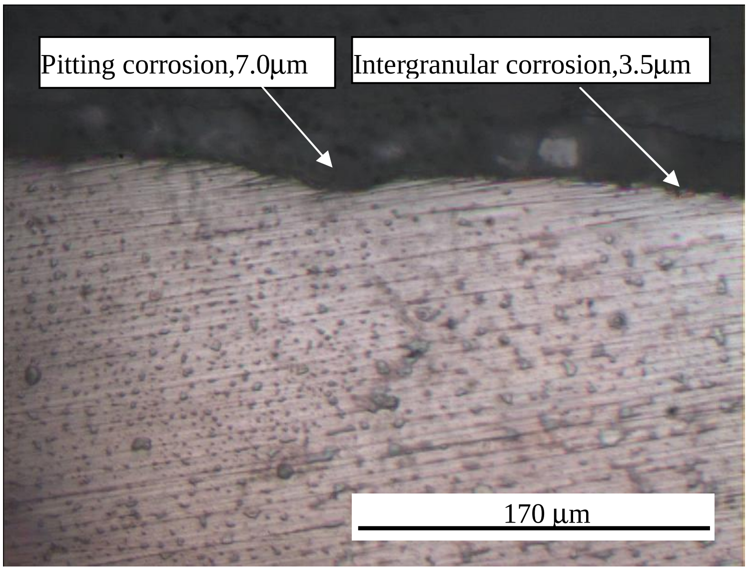

Fig.2 Typical intergranular corrosion and pitting corrosion of the TC4 alloy after pickling

It can be found from Table.2 that, at low temperature, the average intergranular corrosion depth decreased from 7.2 to 3.5μm as the HNO_3 concentration increased from 300 to 450g/L. As the HF concentration increased, the average pitting corrosion depth slightly increased. The effects of HNO_3 and HF can also be found for pickling at 38°C.It may be summarized the HNO_3 can restrain the growth of intergranular corrosion, while the HF promote the pitting corrosion during acid pickling.

Table.2 Results of intergranular corrosion and pitting corrosion

Experiment serial number	Acid pickling conditions /(g/L)			Temper-ature/℃	A:Intergranular corrosion depth/μm	Average of A/μm	B:Pitting corrosion depth/μm	Average of B/μm
	Ti	HF	HNO_3					
1	10	30	450	10	3.8, 2.2, 2.8, 5.0	3.5	5.9, 8.8, 6.0, 7.3, 10.7	7.7
2	10	30	300	10	8.6, 5.8, 5.2, 7.5, 6.6, 7.6, 9.2	7.2	4.3, 3.9	4.1
3	10	90	300	10	4.3, 3.6, 3.5, 6.0	4.4	6.1, 7.0, 4.5, 2.9	5.1
4	10	90	300	38	5.7, 7.4, 5.6, 4.8, 6.7, 9.2, 10.5	7.1	9.4, 11.1, 6.7, 18.1, 10.7	11.2
5	10	30	300	38	5.0, 6.6	5.8	3.4, 3.7, 5.1, 4.1	4.1
6	10	90	450	38	6.3, 4.3	5.3	5.6, 3.5, 2.2, 3.4, 9.4, 6.7	5.1

Conclusion

HF can promote the acid pickling rate apparently, while the effects of HNO_3 and Ti are opposite. The passivation effects of HNO_3 decreases as the pickling temperature increases.

HNO_3 can restrain the growth of intergranular corrosion, while the HF promote the pitting corrosion during acid pickling.

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