THE EFFECT OF IRON CONTENT ON THE CORROSION BEHAVIOR OF TITANIUM IN SULPHURIC ACID MEDIUM

Li Zuochen, Wu Qingzhi and Liu Hongyi

Baoji Non-ferrous Metal Research Institute,China

Xin Xiangjie, Jin Zhaofa, Liu Huatang and Zhou Jinyi

Hefei Universal Machinery Research Institute,China

Introduction

There already have been some reports about the effect of iron and surface iron contamination on the corrosion behavior of titanium(1-5). However, there still are some unclear points about this problem, especially those about the relation between the effect of iron and iron contamination on the corrosion behavior of titanium and the property of oxidation-reduction of the solution have not been clarified.

The object of this study is to research the general rule of the effect of iron content in titanium, surface contamination of iron, welding thermal cycle and anodization treatment on corrosion behavior of titanium in sulpharic solution containing potassium chromate and cathode hydrogenation, and to provide the criterion for the design and manufacture of chemical engineering equipment made of titanium.

Experiment conditions

Six kinds of titanium with different iron contents were prepared with magnesium-reduction sponge titanium and electrolysed pure iron.

The chemical compositions of the ingots are shown in table 1.

Table 1. The chemical composition of the ingots

Specimens No.	The chemical compositions (wt%)					
	Fe	Si	N	C	H	Ti
1	0.035	0.20	0.019	0.018	0.0018	Bal.
2	0.075	0.20	0.021	0.018	0.0012	Bal.
3	0.127	0.20	0.022	0.018	0.0016	Bal.
4	0.223	0.20	0.022	0.021	0.0020	Bal.
5	0.329	0.20	0.024	0.014	0.0012	Bal.
6	0.392	0.20	0.019	0.012	0.0010	Bal.

The size of specimen of parent material was 25 x 25 x 2mm. The size of welding specimen was 15 x 15 x 2mm. The iron contamination on the surfaces was carried out by means of surface scratching with a tool made of iron or by using resistance-spot welding to melt and attach a little amount of iron onto the surface. Some specimens were anodized in 10% $(NH_4)_2SO_4$ solution for 72 hours. D.C. voltage so used is 25 V.

The corrosion experiment is carried out in 40% H_2SO_4 solution at 60 ℃, potassium chromate was used to adjust the property of oxidation-reduction of the solution.

Before corrosion test the specimens were ground with No.700 water proof emery papers degreased with acetone, boiled in deionized water and baked.The corrosion solution was prepared with chemically pure sulphuric acid and deionized water. The amount of the solution was 25 - 30 ml/cm^2. The solution are not changed during the corrosion test .

Experimental result

1. The effect of iron content in titanium

In 40% H_2SO_4 solution at 60°C, the effect of the content of potassium chromate in the solution on corrosion rate is shown in Fig.1. It can be seen from the figure that the corrosion rates of the six kinds of specimens increase at the beginning with increasing of the concentration of potassium chromate in sulphuric acid solution. When the concentration of potassium chromate is increased to 0.00015 M, the corrosion rates of the all six kinds of specimens are up to their maximum value. When the concentration of potassium chromate increases and reaches 0.00023 M, the corrosion rates of No.1-4 specimens decrease rapidly and the specimens come into passivation. At the same time, the corrosion rates of No.5 and No.6 specimens are up to 13.2 g/M^2.hr. and 14.6 g/M^2.hr. respectively. When the concentration of potassium chromate increases further to 0.00035 M and 0.00040 M, No,5 and No.6 specimens also come to passivation respectively.

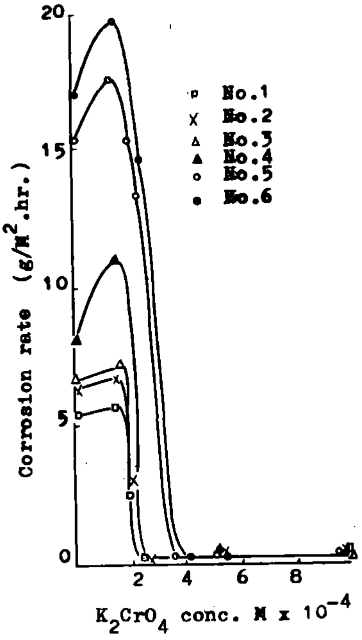

Fig. 1

The effect of the added amount of K_2CrO_4 on the corrosion rate of titanium specimens with different iron contents.

(60°C, 40% H_2SO_4, for 2 hrs.)

The curves in Fig.2 show the relation between hydrogen content and iron content of the specimens. It can be seen from this figure that the hydrogen absorption increases with increasing of iron content. When the added amount of K_2CrO_4 is increased to 0.00023 M, as No.1-4 specimens cometo passivation, their hydrogen absorption is stopped. When the concentration on K_2CrO_4 is up to 0.00040 M, all the specimens come to passivation and their hydrogen contents are close to the original values.

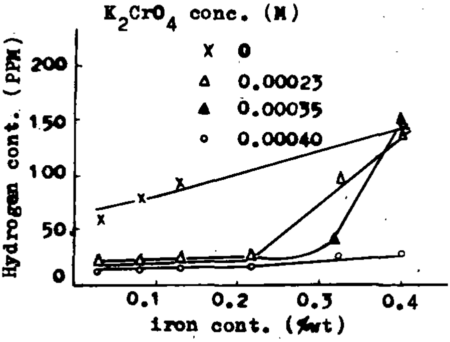

Fig.2

The relation between the amount of hydrogen absorption of titanium and the iron contents of specimens in 60°C, 40% H_2SO_4 solution containing K_2CrO_4 for 2 hrs..

2. The effect of welding thermal cycle

In table 2, the changes of corrosion rate of the specimens of parent materials and welded specimens are listed.

Table 2. The comparesion of corrosion rates between specimens of parent materials and welded specimens in 60°C,40% H_2SO_4 solution

(g/M^2.hr.)

The added amount of K_2CrO_4 (M)	No.1		No.2		No.3		No.5	
	parent material	welding	parent material	welding	parent material	welding	parent material	welding
0	5.6	9.8	6.0	10.0	6.8	9.1	14.2	12.3
0.0005	-	-	-	0.0	0.0	0.0	0.0	5.0

The table shows that the corrosion rate of welded specimens is higher than that of parent material except No.5 specimen. It can also be seen that when 0.0005 M of K_2CrO_4 are added to the solution, the corrosion rates of both parent materials and welded specimens of No.2 and No.3 decrease to zero, that is, the specimens come to passivation. The corrosion rate of No.5 specimen decreases from 12.3 g/M^2.hr. to 5.0 g/M^2.hr..

Table 3 shows the hydrogen content of the specimens after being corroded. In the H_2SO_4 solution without K_2CrO_4 the hydrogen absorption of No.2 and No.3 specimens is not obvious, but that of No.5 specimen with higher iron content is most serious, pqrticularly in the heat affected zone, where the amount of hydrogen absorption is as high as 290 PPM. In the H_2SO_4 solution containing 0.0005M of K_2CrO_4, No.2 and No.3 specimens come to passivation, and the amount of hydrogen absorption of No.5 specimen has decreased obviously.

Table 3. The hydrogen content of welded specimens.(ppm)
60°C, 40% H_2SO_4, for 2 hrs.

The added amount of K_2CrO_4(M)	No.2			No.3			No.5		
	A	B		A	B		A	B	
		C	D		C	D		C	D
0	76	66	62		66	60	104	110	290
0.0005	16	22	18	24	25	25	24	50	76

Notes: A stands for parent material.
B stands for welding.
C stands for weld.
D stands for heat-affected zone.

3. The effect of the surface condition of specimens.

Fig.3 shows the curves of corrosion rate of anodized specimens with different iron content in H_2SO_4 solution. It can be seen from this figure that the corrosion rate of specimens are very low within two hours'test. However, the corrosion rate has increased significantly for 24 hrs. test.

The critical concentration of K_2CrO_4 needed for the passivation of anodized specimens has decreased slightly. All the specimens can be passivated by adding 0.00020M of K_2CrO_4 in 60°C, 40% H_2SO_4 (for 2 hrs.).

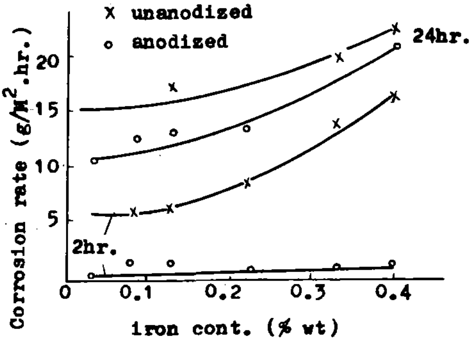

Fig.3

The effect of anodization on corrosion rate of the specimens in 60°C, 40% H_2SO_4.

The hydrogen contents of No.2 and No.4 specimens after being tested for different time are listed in table 4. It can be seen from this table that anodization can decrease the hydrogen content of specimens within short testing time. However, with the increase of the testing time, the hydrogen content of the anodized specimens is close to that of unaodized specimens.

Table 4. The effect of anodization on the amount of hydrogen absorption 60^{o}C, 40% H_2SO_4, (ppm)

testing time (hr.)	No.2		No.4	
	unanodized	anodized	unanodized	anodized
2	87	30	60	19
4		57	100	58
8			110	120
24	92	72		

The corrosion rate of contaminated specimens are listed in table 5. The iron contamination on surface can make the corrosion rate and the amount of hydrogen absorption of the specimens with various iron contents increase. (The metalographic structure are shown in Fig.4). It can also be seen from the table that the critical concentration of K_2CrO_4 needed for the passivation of the contaminated specimens in H_2SO_4 solution has increased. However, if only there is sufficient oxidizer in the solution, contaminated specimens can also be passivated and hydfogen absorption will also be lightened. The hydrogen content and the corrosion rate of anodized specimens after being contaminated decrease obviously. The corrosion rates of No.1 and No.6 specimens decrease from 11.7 g/M^2.hr. and 20.7 g/M^2.hr. to 0.6 g/M^2.hr. and 1.3 g/M^2.hr. respectovely. Their hydrogen contents are close to the original data.

(500 X) uncontaminated

(500 X) contaminated

Fig. 4. The metallographic structure after being corroded in 60^{o}C, 40% H_2SO_4, for 2 hours

Table 5. The corrosion rates of contamination specimens in 60^{o}C, 40% H_2SO_4 solution for 2 hrs. (g/M^2.hr.)

The content of K_2CrO_4 in solution (M)	No.1	No.2	No.3	No.4	No.5	No.6
0	11.7	11.2	10.4	12.3	-	20.7
0.00030	14.5	13.9	11.8	-	-	24.4
0.00040	15.4		11.8	-	-	21.7
0.00050	0.4	0.5	11.8	-	-	-
0.001	0.2	0.5	0.0	0.1	11.4	-
0.002	-	-	-	-	0.4	0.1

4. The selective corrosion of iron

In order to make sure whether there is selective corrosion of iron, the concentration of the ions of titanium and iron in the solutions after being tested has been analysed. The result is listed in table 6. It can be clearly seen from this table that the iron in titanium has been subjected to selective corrosion.

Table 6. The metallic ion content in solution after being corroded

specimen No.	iron content in specimen (wt%)	testing time (hr.)	the analysis values of ions in solution (g/l)		$\frac{\text{Fe ion}}{\text{(Fe+Ti) ion}}$ (%)
			Fe ion	Ti ion	
No.1	0.035	4	0.0006	0.1100	0.5
		8	0.0016	0.4800	0.33
		24	0.0015	1.2800	0.12
No.2	0.075	4	0.0009	0.1160	0.8
		8	0.0007	0.3120	0.22
		24	0.0022	1.6000	0.14
No.3	0.127	4	0.0008	0.1260	0.6
		8	0.0010	0.3680	0.27
		24	0.0031	1.6200	0.19
No.6	0.392	4	0.0022	0.1700	1.3
		8	0.0033	0.3920	0.84
		24	0.0081	1.8700	0.43

Discussion

1. The effect of the addition of K_2CrO_4 on the corrosion course of titanium in sulphuric acid medium.

K_2CrO_4 is used as either an inhibitor of anode or an accelerator of cathode in H_2SO_4. The effect of K_2CrO_4 on the corrosion process of titanium depends on its added amount.

The main electrode process of titanium in 60°C, 40% H_2SO_4 solution is as follows:

anodic reaction: $Ti \rightarrow Ti^{+3} + 3e$ ....(1)

cathodic reaction: $H^+ + e \rightarrow H$ ....(2)

A part of atomic hydrogen generated from cathodic reaction penetrates in to the metal, and another part combines into hydrogen molecules and escapes.

The electrode process may become complex after K_2CrO_4 has been added, and several new reaction processes may occur:

anodic reaction: $Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e$ .....(3)

cathodic reaction: $\underset{\text{(yellow)}}{Cr^{+6}} + 3e \rightarrow \underset{\text{(green)}}{Cr^{+3}}$ ....(4)

If the added amount of K_2CrO_4 is extremely small (< 0.00015 M), then the corrosion potential of the specimens is very low (-760 mv) and the reaction shown in equation (3) can not occur. The cathodic depolarization of Cr^{+6} controls the corrosion course strongly. This makes the reaction shown in equation (1) and (2) speed up. The corrosion rate reaches a peak value as shown in Fig.1. In the experiment, it can be observed that the yellow colour disappears rapidly after the reaction begins and there appears characteristic violet of Ti^{+3}, that is, titanium has been subjected to serious corrosion.

While the content of K_2CrO_4 in the solution increases gradually but it is still not sufficient to make the specimens passivate, the oxidizing ability of the solution increases correspondently. Because of this increase, though the reaction shown by equation (3) may not occur, the reactions shown by equations (1) and (2) are inhibited, thus the reaction rates have slowed down and there appear the reduction of the corrosion rate and the decrease of the amount of hydrogen absorption (see Fig.1 and 2). When sufficient amount of K_2CrO_4 is contained in the solution, the oxidizing ability of the solution increases remarkably, then the reaction shown by equation (3) occurs, a dense and stable oxidic film will form on the surface of titanium, the specimens will come to passivation and hydrogen absorption will stop consequently.

2. The effect of iron on corrosion behavior of titanium

The solubility of iron in α- Ti is extremely low. It is considered that its solubility is 0.05 - 0.10% (wt%) at room temperature. The iron content in commercial titanium of ten exceeds this solubility limit. In usual cooling condition, eutectoid transformation does not occur in commercial titanium but supersaturated solid solution is obtained. ß-phase can be decomposed and Ti-Fe phase can be precipitated in certain conditions. With the increase of the iron content in titanium, the amount of residual ß-phase increases, therefore the corrosion rate increases.

The degree of the effect of iron content in titanium on its crrosion behavior has close relation to the oxidation-reduction characteristics of sulphuric solution with K_2CrO_4.

When the solution is strongly reductive, the surface film is very unstable. With the increase of the iron content in titanium, the corrosion resistance of α-phase decreases and the occurrence of the second phase makes its corrosion resistance decrease further. Therefore, the corrosion rate of titanium increases with increasing of iron content.

When the reductive ability of the solution weakens and that of oxidization grows, the stability of the surface film increases [5]. The lower the iron content in the specimens is, the faster the stability of the surface film increases and so the corrosion rate and the amount of the hydrogen absorption decrease correspondingly. When the amount of added K_2CrO_4 in 60°C, 40% H_2SO_4 solution is less than 0.00023M, the corrosion rate and the hydrogen absorption of titanium may vary according to above rule.

When the oxidization of the solution increases further, the passsivation occurs first on the specimens of titanium with lower iron content. For example, when 0.00023M of K_2CrO_4 is added, the passivation occurs on the specimens No.1 to No.4, however, the corrosion rate of the specimens No.5 and No.6 with higher iron content is still very high. The reason for this is that when the iron content in specimens is higher, there are more ß -phase residue and TiFe-phase precipitated in the specimens, and they have damaged the uniformity of the surface film and decreased its stability. Therefore the specimens of titanium with higher iron content are still in activating state.

When the solution shows strong oxidizing ability that is, when the concentrations of K_2CrO_4 is increased to 0.00035M and 0.00040M respectively, all the specimens of No.5 and No.6 with higher iron content come to passivation and both corrosion and hydrogen absorption tend to stop.

3. The effect of iron contamination and welding thermal cycle.

It is not difficult to note from the data listed in tables 2 & 5, that iron contamination and welding thermal cycle have speeded up the corrosion and cathode hydrogenation of titanium and also made critical concentration of K_2CrO_4 needed for the passivation of the specimens increase remarkably.

The passivation of titanium depends on the existence of surface oxide film. If the oxide film of titanium can exist stably in medium, then it is corrosion-resistant. Surface contamination can not only make oxide film to be subjected to local damage and provide a convenient path for the penetration of hydrogen, but can also make the electrode potential of whole metal decrease to below the hydrogen precipitation potential. Hydrogen can precipitate even if it is in moderate oxidizing conditions. The existence of iron at contaminated part can also make the potential of near by titanium decrease and make the titanium dissolve, more hydrogen is therefore released.

Welding thermal cycle has changed the size and distribution of residual ß -phase, led to the concentration of ß -phase, the occurrence of acicular structure and formation of serious local corrosion. The more the iron content in specimen, the more the acicular ß -phase, and thus the more serious the corrosion. The iron contamination in welds leads melted iron to enter into titanium easily. Therefore, more quantity of acicular ß -phase of rich iron appears. Therefore the iron contamination in welds and heat affected zone is more harmful.

Iron contamination and welding thermal cycle may increase the corrosion rate and cathode hydrogenation of titanium. However, it must be pointed out that with the variation of oxidation condition of solution, that is, when sufficient oxidant is contained in solution, the effect of contamination and welding thermal cycle may decrease, even may be eliminated completely. The treatment of anodination has the similar effect. This result has important guiding significance for the application of titanium in the chemical industry.

Conclusions

1. The effect of the iron content in titanium on its corrosion property is closely related to the oxidation-reduction characteristics of the solution, that is, in 60°C, 40% H_2SO_4 solution:

When the concentration of K_2CrO_4 is less than 0.00023M, the corrosion-resistance of titanium decreases with the increase of its iron content.

When the concentration of K_2CrO_4 is up to or more than 0.00040, the corrosion resistance of titanium has no relation to the iron content of the specimens tested in the experiment.

2. Welding thermal cycle and iron contamination on surface have decreased the corrosion-resistance of titanium. The more the iron content in titanium, the more obvious the effect. This kind of harmful effect can be lightened and eliminated by increasing the oxidizing ability of solution.

3. Anodization treatment may lighten harmful effect brought about by surface iron contamination, but it can not be taken as an essential method to improve the corrosion-resestance of titanium in reductive medium.

4. Iron as impurity in titanium is susceptible to selective corrosion in 40% H_2SO_4 at 60°C.

References

1. B.S. CP. 3003 (1970).
2. B.S. patent, 19255/66.
3. J.B. Cotton, J.G Hines: The Science Technology and Application of Titanium p. 155, 1970.
4. S.F. Vajenin, O.M. Shapovalova, N.A. Pampushko: Titanium Science and Technology 4 (1973), 2373.
5. T.J. Murphy: The Science Technology and Application of Titanium, Pergamon 1970, 217.