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Influence of chemical composition and temperature on the passivation of some stainless steels and nickel-based alloys in sulphuric acid

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The critical current densities for passivation of a number of industrial stainless steels and nickel-based alloys have been measured in 20% H_2SO_4 at temperatures from 30 to 103° C (boiling). The critical current decreases – and then the aptitude for passivation increases – as the chromium and molybdenum contents of the alloys are increased; molybdenum was about three times as effective as chromium. Increasing the temperature extends the range of active dissolution of the alloys and markedly increases the critical current density for passivation. The effect is least severe for the alloys of high Cr and Mo content, but even for these, spontaneous passivation does not take place above 50° C. The logarithm of the active current density varies linearly with the reciprocal of absolute temperature over limited ranges. Apparent activation energies have been measured and proposals for the rate-determining factors in the mechanisms are outlined on the basis of these measurements.

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1. Introduction

Sulphuric acid is the most widely used inorganic acid and consequently the corrosive medium mostly encountered in chemical and hydrometallurgical processing. The need to conserve essential raw material raises problems of corrosion resistance in this environment.

The selection of a corrosion-resistant alloy appears easy when chemical environment are well known and reproducible. This is more difficult when processing conditions are new or variable. The behaviour of alloys is often indicated by iso-corrosion charts which have been compiled from immersion tests. In electrochemical studies, the critical anodic current density i_c may be used to predict or compare the corrosion susceptibility for alloys exhibiting active–passive transitions. An alloy with a small critical anodic current density will spontaneously passivate and corrode at insignificant rates, even in weak oxidizing environments [1].

In the present study, the passivation aptitude of some industrial stainless iron and nickel-based alloys containing chromium and sometimes molybdenum and copper has been determined in hot aqueous 20% H_2SO_4. In higher acid concentrations, the usual stainless steels have only a poor corrosion resistance. The aim of this systematic study is to provide a selection guide based on the tendency to passivate of active–passive alloys commonly used in a sulphuric acid environment.

2. Experimental

The materials for testing were obtained from available industrial samples: 1–3 mm mill annealed sheet. The average compositions of specimens are given in Table 1. Samples were mounted in a Teflon holder and the resulting surface area of the exposed face was 1 cm^2. This surface was wet ground with 600 silicon-carbide paper.

The test solution was prepared by diluting concentrated H_2SO_4 (R.P. Prolabo) with distilled

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Table 1. Chemical composition (wt%) of tested alloys

Reference number	*Alloy*	*Fe*	*Ni*	*Cr*	*Mo*	*Cu*	*Co*	*C*	*W*	*Ta + Nb*	*Ti*
1	Orion[a]	76		26	1			0.002			
2	Ferralium[b]	65	5	25	2	3					
3	7-Mo[c] (AISI 329)	64–72	2.5–5	23–28	1.5–2.5			⩽ 0.2			
4	Uranus 50[a]	65	7–9	20–22	2.2–2.8	1–2		⩽ 0.06			
5	NS 22 S[d] (AISI 304 L)	71	10	18				⩽ 0.03			
6	ICL 164BC[d] (AISI 316 L)	72	12	17	2.2			0.03			
7	NSCD[d]	60	16	17.5	⩾ 5	3		⩽ 0.03			
8	Uranus 65[a]	54	20	25				⩽ 0.03		0.20	
9	Multimet[e]	29	19–21	20–22.5	2.5–3.5		20	0.08–0.16	2–3	0.75–1.25	
10	Uranus B6[a]	52	24–27	19–22	4–4.8	1–2		⩽ 0.02			
11	MIO 20[f]	44	28–30	19–21	2	3					
12	Incoloy 800[g]	45	30–35	19–23		⩽ 0.75		⩽ 0.1			0.15–0.60
13	Incoloy 825[g]	30	38–46	19.5–23.5	2.5–3.5	1.5–3		⩽ 0.05			0.6–1.2
14	Hastelloy G[e]	18–21	44	22.2	6.5	2	⩽ 2.5	⩽ 0.05	⩽ 1	2.1	
15	Hastelloy F[e]	20	46	22	6.5		⩽ 2.5	⩽ 0.05	⩽ 1	2.1	
16	Hastelloy X[e]	18.5	47	22	9		1.5	0.1	0.6		
17	Hastelloy C[e]	5	54	16	16		⩽ 2.5	⩽ 0.08	4		
18	Hastelloy C 276[e]	5	54	16	16			0.01	4		
19	Inconel 625[g]	2.5	60.5	21.5	9		⩽ 1	⩽ 0.1		3.15–4.15	
20	Hastelloy N[e]	5	69.5	7	16.5			0.06			
21	Inconel 600[g]	8	75	15.5				0.05			
22	Nickel 200[g]	0.2	99.2			0.13		0.08			

TRADEMARKS

[a] Creusot-Loire (France)
[b] Langley Alloys (Great Britain)
[c] Carpenter (USA)
[d] Ugine (France)
[e] Cabot (USA)
[f] Metaux Inoxydable Ouvrés (France)
[g] Wiggin (Great Britain)

water and was purged with oxygen-free high-purity nitrogen prior to each polarization test. The platinum auxiliary electrode was separated from the working electrolyte (500 cm^3) by a glass sinter to prevent oxygen contamination. The cell was equipped with a jacket for the circulation of a thermostating fluid. The test solution was stirred with nitrogen continuously.

The reference electrode Hg/Hg_2SO_4 (saturated K_2SO_4) was immersed in a bridge which contained some of the electrolyte at 25° C. Polarization curves were carried out by potentiodynamic scanning towards noble direction (450 mV h^{-1}) from a cathodic potential corresponding to a 100 mA cm^{-2} current density. All potentials reported were expressed with respect to the standard hydrogen electrode (SHE).

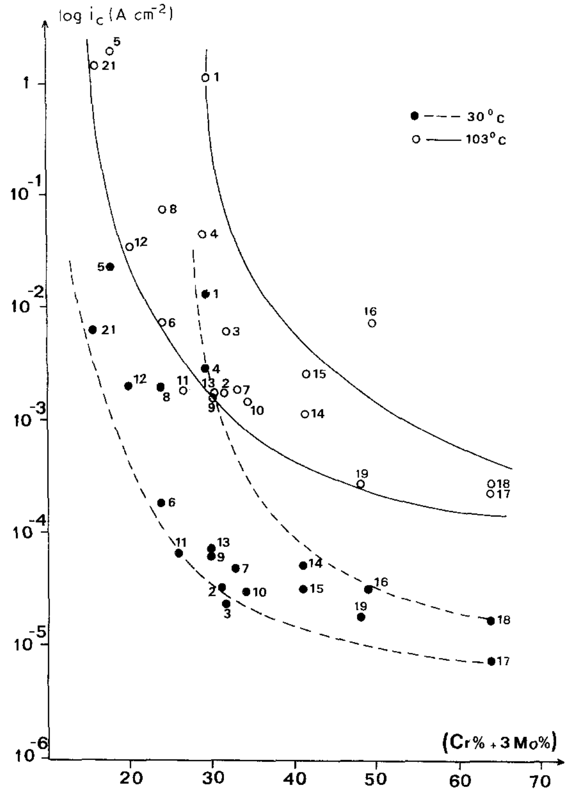

Fig. 1. Effect of chromium and molybdenum contents on the critical anodic current density at 30 and 103° C.

3. Effect of alloy chemical composition

The variation of critical current densities with the Cr and Mo contents is shown in Fig. 1, for several industrial alloys at 30° C and in boiling 20% H_2SO_4 solutions.

An increase in chromium content always improves the tendency to passivate [2, 3]. The beneficial effect of chromium in 20% H_2SO_4 is apparent for both iron- and nickel-based alloys. Thus, Uranus 65 alloy (25% Cr) has a lower critical current density than the other austenitic Fe–Ni–Cr stainless steels, for example Incoloy 800 (21% Cr) and NS 22 S (18% Cr). The same effect is observed with the duplex austenitic-ferritic alloys Carpenter 7-Mo and Ferralium [4] which have higher chromium content than Uranus 50 alloy. Moreover, the polarization curve of Hastelloy N alloy does not demonstrate an active–passive transition. Passivation of Ni–Mo–Cr alloys indeed requires a high chromium content [5].

Nickel also contributes to the decrease in the critical current density of chromium stainless steels [6]. Thus, with regard to Uranus 50 (8%) Ni), ICL 164 BC alloy (12% Ni) shows a better passivation tendency. Yet, the Inconel 600 nickel-base alloy is characterized by an active current peak between that of the NS 22 S and Incoloy 800 iron-base alloys, because of their higher chromium contents.

Molybdenum addition makes passivation more likely in H_2SO_4 as well as in HCl solutions [7–10]. This is illustrated by a decrease of the active peaks for the ICL 164 BC alloy compared with that of the Fe–Cr–Ni alloys studied, and especially the NS 22 S alloy. In spite of the presence of the nickel, the NS 22 S alloy without molybdenum is found to have higher i_c values than the 26 Cr–1 Mo alloy. An improvement in passivation performance of ferritic alloys should be expected by increasing chromium and molybdenum contents.

The Hastelloy C 276 and Inconel 625 alloys have the lowest critical current density at 103° C, i.e. the greatest tendency to passivate. The high chromium content of Inconel 625 is balanced by its low molybdenum content. The Carpenter 7-Mo and Ferralium alloys easily passivate but only at 30° C.

Polarization curves of austenitic alloys containing copper also indicate a marked tendency to passivate at 30° C, including those with higher iron contents. At this temperature the small difference between critical current densities seems to be related to the beneficial effect of chromium and molybdenum and to the rather deleterious effect

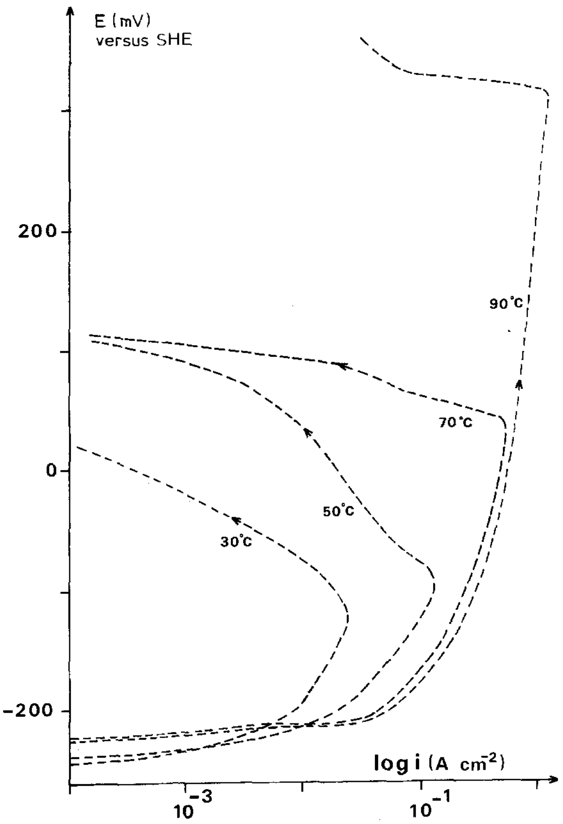

Fig. 2. Effect of temperature on the anodic polarization of NS 225 alloy (18 Cr–10 Ni).

of stabilized carbon. The passivation of the Multimet (20% Co) alloy is found to approximate the Fe–Ni–Cr–Mo–Cu alloys at any temperature.

This study shows that both chromium and molybdenum greatly reduce the critical current density for passivation of iron- and nickel-base alloys. The effect of molybdenum appears much more efficient than that of chromium except for the Hastelloy N alloy. Fig. 1 shows the synergic effect of chromium and molybdenum on the critical current density for passivation. According to the results, i_c decreases regularly with these additions for the alloys studied.

4. Effect of temperature

The electrochemical parameters are affected by temperature. The anodic peak for alloys which are not readily passivated, such as NS 22S, exhibits a pronounced broadening at higher temperatures (Fig. 2). The critical anodic current density increases depending on the chemical composition of the alloy. When the temperature increases from 30 to 103° C (Fig. 1), the critical current density is, on average, 50 times higher. But, depending on the alloy composition, the i_c increasing factor may be: (a) comparatively low: 14 for Incoloy 800 and Uranus 50, or (b) very high: 150 for Carpenter 7-Mo, 250 for Hastelloy X. Hence many alloys no longer show spontaneous passivation when the temperature increase is above 30° C, their i_c values exceeding 10^{-4} A cm^{-2}.

At a constant potential E, within the anodic peak potential range but at a value which depends on the alloy composition, the variation of the dissolution current in the active state fits an Arrhenius law:

$$i_E = A \exp(-Q/RT).$$

Figs. 3 to 5 show the plots of log i_E versus the reciprocal of the absolute temperature. For the various alloys, the apparent activation energies, Q, determined from the slope of the best fit of the log i_E variation are indicated on the curves.

A review of the literature on the temperature dependence of the parameters that characterize the anodic polarization curve failed to disclose much information for the interpretation of this dependence [11]. Most studies of the temperature effect only discuss the polarization curves. It was postulated, however, [12], that the corrosion process may be preferentially controlled by diffusion rather than by a charge transfer process when the Q value of the apparent activation energy is markedly lower than 14 kcal mol^{-1}. Hence, nickel dissolution ($Q \simeq 6.0$ kcal mol^{-1}) should be associated with a diffusion through a layer of nickel sulphate [13]. In some cases, deviation from the Arrhenius law may be assigned to different processes, the importance of which changes with temperature. The prevalence of a diffusion process is also observed for NS 22 S and Orion 26-1 alloys at high temperatures. For most other alloys, dissolution seems to be at least partially controlled by diffusion in the low temperature range.

Examination of Fig. 2 shows that the activity peak occurs in a potential range which is strongly temperature dependent, at least for the NS 22S alloy. One should, therefore, be careful in attempting to derive an actual reaction mechanism from any apparent activation energy.

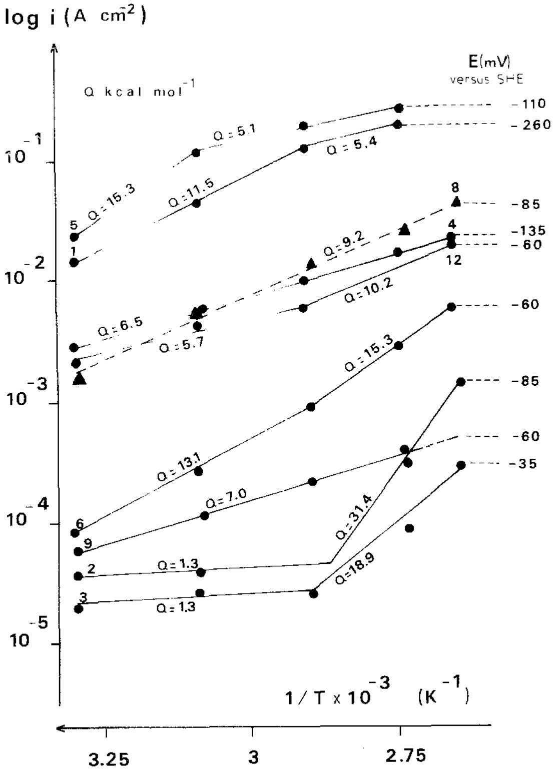

Fig. 3. Arrhenius plot for some iron-based alloys.

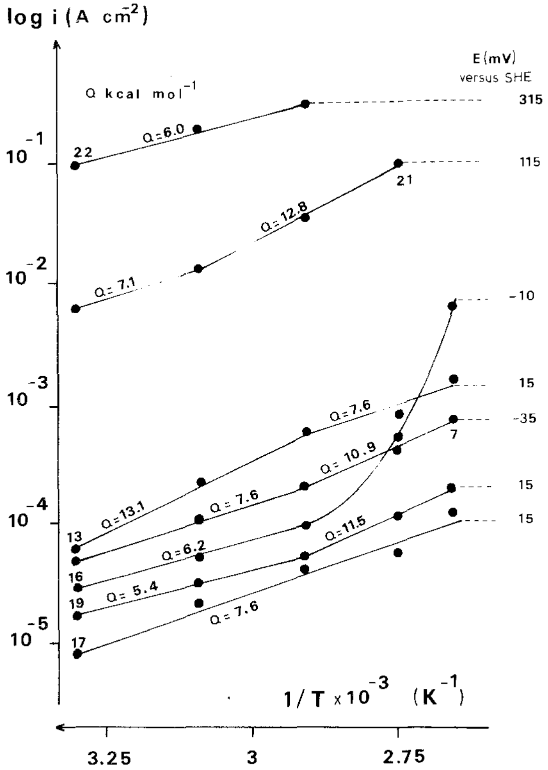

Fig. 4. Arrhenius plot for some nickel-based alloys and one stainless steel NS 22S [7].

In this comparative study undertaken with industrial alloys, the real content of the main alloying elements deviates more or less from that indicated by the alloy nominal composition. This fact may influence the results. The contribution of other factors like minor alloying elements (C, Si, Ti, Nb, Ta, W . . .) and tramp elements (N, S, P, As, etc) to the tendency to passivate should also be taken into account. Indeed it is known that, for instance, sulphur [14] and niobium [4] used as stabilizing elements, appear to increase the active current peak. Moreover, grain-boundary precipitates (M_6C in Hastelloys X, C, G, F), surface coverage with sulphate ions and the presence of sulphide ions and NiS [15] may also affect the anodic behaviour in the active region.

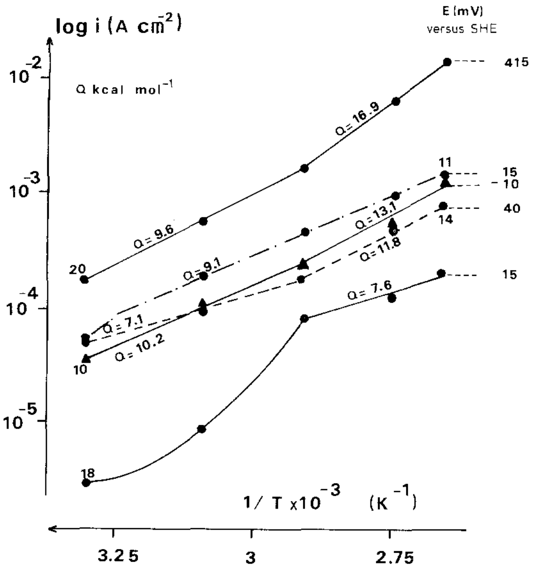

Fig. 5. Arrhenius plot for some Fe–Cr–Ni–Mo–Cu and Ni–Cr–Mo alloys.

5. Conclusions

The study of the critical anodic current densities of various iron- and nickel-base industrial alloys reveals that variations of chromium and molybdenum contents are critical in the H_2SO_4 20%

solution. The critical current decreases markedly with the simultaneous increase in Cr and Mo content. The deleterious effect of temperature on this reduction depends on the alloy composition.

Austenitic-ferritic steels with 25% Cr and 2% Mo (Ferralium, Carpenter 7-Mo) which are readily passivated at temperatures under 70° C, are subject to quick degradation of their passivation ability at higher temperatures. Nickel-base alloys with high chromium and molybdenum contents, exhibit the lowest i_c values at temperatures near the boiling point of the acid.

In some cases, the low values of apparent activation energy associated with active current densities indicate that diffusion processes play a significant role.

This comparative study could reduce the number of tests necessary to solve some corrosion problems.

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