ANODE DISSOLUTION CHARACTERISTICS OF STAINLESS STEELS STABILIZED WITH TITANIUM

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Maximum current density values J_M measured on the polarization curves of austenitic stainless steels stabilized with titanium are proportional to the amount of titanium carbides present in their structure. The polarization curve makes it possible to draw conclusions as to the behaviour of this kind of steels in the oxidizing media and to the corrosion effects occurring primarily in concentrated nitric acid. The measurement of J_M is indirectly associated also with measuring the content of carbon bound to titanium, and hence also of free carbon.

In oxidizing media, the sensitivity to general and pitting corrosions is higher for austenitic stainless steels stabilized with titanium than for the steels stabilized with niobium, or low-carbon steels without stabilizing elements[1]. In addition, differences in the behaviour of steels stabilized with titanium or niobium with respect to the knife-line corrosion of their welded joints have been observed. The steels stabilized with titanium, overheated to 1300—1300°C, without subsequent sensitization at critical temperatures 500—900°C particularly incline to this kind of corrosion in oxidizing media or in the electrolytic dissolution in the upper potential region of passivity, i.e. near the transpassivity. Thus the interest in the investigation of electrochemical properties of steels stabilized with titanium and niobium, as well as in the properties of titanium and niobium carbides[2-10], may be explained.

The previous study showed that titanium carbides were considerably more strongly attacked in 2·5M-H_2SO_4 solution at potentials above 0·6 V than niobium carbides[9,10]; moreover, in boiling 65% HNO_3, titanium carbides only are corroded, while on niobium carbides a firmly adhered protective layer is being produced[8,10]. For that reason, the steels stabilized with niobium are negligibly sensitive to the knife-line corrosion in oxidizing media, in spite of dendritic niobium carbides at the grains interface under overheating being formed, similarly as in the steels with titanium[9].

In this paper, attention has been primarily paid to making more precise the effect of titanium carbides on the anode dissolution of steels stabilized with titanium.

EXPERIMENTAL

Austenitic stainless steels of various carbon and titanium contents, stabilized with titanium (Table I), which were subjected to several types of heat treatment, have been studied. Steel No 1 does not contain any titanium and serves for comparative experiments. The steels were first treated by the dissolution annealing at 1150°C (20 min, water), followed by 20 min annealing

at the temperatures of 750—1350°C and quenching in water. These heat treatments, similarly as selection of the steels itself aimed at changing the content of carbides in their structure.

After a mechanical and electrolytical polishing, the samples were re-polished using diamond and on an area of 0·5 cm^2, defined by a teflon device, potentiodynamic polarization curve was taken from the sample surface. Aqueous H_2SO_4 and 65% HNO_3 were used in terms of electrolytes. In the former case, mercuric and potassium sulphates were used for the reference electrode, in the latter case the calomel electrode with potassium chloride, and the potassium nitrate bridge were employed. The potential values are coverted to the hydrogen scale (E_H). The polarization curves were achieved potentiodynamically by means of a potentiostat, logarithmator, electronic millivoltmeter (Tacussel), and XY coordinatograph (Sefram). This arrangement made it possible to record polarization curves of the increasing as well as decreasing potential, this fact being significant in view of the reproducibility of the experiments. The counter-electrode made of platinum was separated from the sample by a glass diaphragm.

RESULTS

The polarization curves of the steels tested were recorded, the concentration of electrolyte, temperature, and rate of polarization being changed. These curves confirmed that titanium carbides sensitively modify the anode behaviour of the stainless steel. The polarization curves of steels 1 and 4 are as an example graphically presented
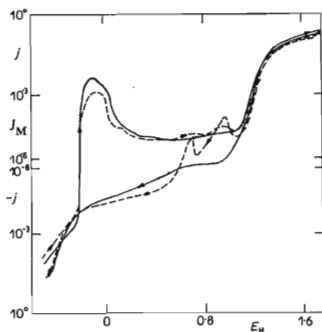

FIG. 1

Polarization Curve Recorded at a Rate of 9 V/h with Increasing and Decreasing Potential E_H (V) in the 2·5M-H_2SO_4 Solution at 70°C under Bubbling N_2 through

Full line steel 1 nonstabilized; dashed line steel 4 stabilized. Current density j in A/0·5 cm^2.
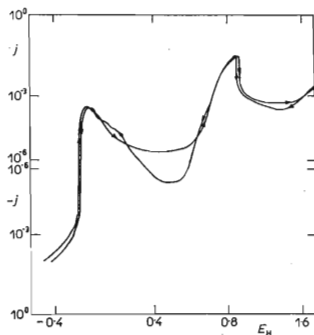
FIG. 2

Polarization Curve of Titanium Carbide Prepared by Powder Metallurgy

The same conditions as for Fig. 1.

in Fig. 1. The current density relates to 0·5 cm², *i.e.* to the area which was in contact with the electrolyte. Steel No 4 containing 0·65% of titanium markedly differs from steel No 1 without titanium by two current maxima at potentials near 700 and 1 000 mV. These maxima are particularly distinct for the decreasing potential.

TABLE I

Composition of the Steels Tested

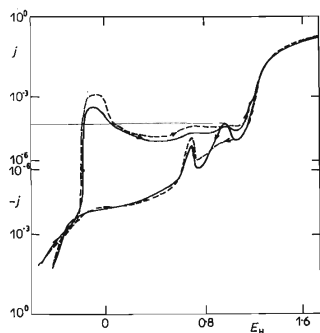| Steel	C	Mn	Si	S	P	Ni	Cr	Ti	Al	N_2	Nb
1	0·069	0·41	0·42	0·019	0·013	12·2	18·3	—	—	—	—
2	0·022	0·45	0·30	0·020	0·015	12·1	17·8	0·11	0·021	0·035	<0·003
3	0·035	0·48	0·28	0·015	0·018	12·0	18·0	0·21	0·043	0·025	<0·003
4	0·068	0·48	0·30	0·015	0·016	12·0	18·0	0·65	0·153	0·011	<0·003
5	0·088	0·52	0·34	0·019	0·016	12·0	17·8	0·83	0·174	0·015	<0·003
6	0·185	0·56	0·34	0·019	0·017	12·0	17·8	1·86	0·269	0·007	<0·003

Fig. 3

Effect of Temperature of the Dissolution Annealing on Nature of the Polarization Curves of Stabilized Steel (steel 4); Electrolyte 2·5M-H_2SO_4 at 70°C

Full line 1 200°C (20 min, water), dashed line 1 350°C (20 min, water). Current density in A/0·5 cm².
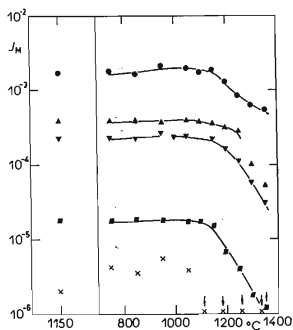

Fig. 4

Plot of Current Density J_M (A/cm²) against Temperature of Annealing after Preceding Dissolution Annealing for a Period of 20 min at 1 150°C

Steel 2 ×, 3 ■, 4 ▼, 5 ▲, 6 ●. Electrolyte 2·5M-H_2SO_4 at 70°C under bubbling N_2 through.

The current maximum at potentials near 1000 mV corresponds quite unambiguously to the preferential attack against titanium carbide. The polarization curve of titanium carbide, namely, exhibits in the same solution 2 potential regions of the anode dissolution[9]. In Fig. 2, an example of the polarization curve achieved with titanium carbide prepared by powder metallurgy is presented. The first region of dissolution $(-200$ to $+300$ mV$)$ occurs at activity potentials of the stainless steels; after passivation of titanium carbide, the second region of dissolution appears between 700 and 1000 mV. At yet higher potentials, titanium carbide is again passivated before it begins to be strongly dissolved at high anode potentials. The maximum observed at 1000 mV for the steels tested is in very good accordance with that found for titanium carbide. Rapid rise in current density for steels containing titanium or without titanium (Fig. 1) is above 1100 mV associated with transpassivity of steels, for in this potentials region titanium carbide is again passivated. Comparison of Fig. 1 and 2 shows that by keeping the steels at potentials above 1100 mV, a preferential attack against the basic solid solution and enrichment of the surface with titanium
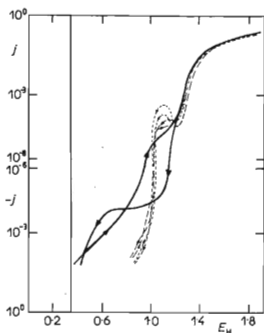

FIG. 5

Polarization Curves Recorded at a Rate of 9 V/h with Increasing and Decreasing Potential E_H (V) in 65% HNO_3 Solution at 70°C and under Bubbling Air through

Full line steel No 1 nonstabilized, annealed at 1150°C, dotted line No 4 stabilized with titanium at 1150°C, dashed line No 4 stabilized with titanium at 1250°C, always (20 min, water). Current density j in A/0·5 cm².
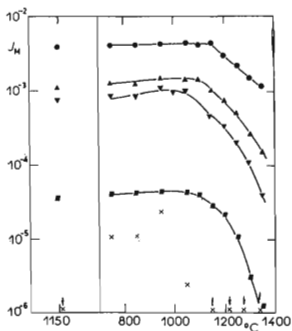
FIG. 6

Plot of Current Density J_M (A/cm²) against Temperature of Annealing the Steels as in Fig. 4

With steels No 2 and 3 the values lower than 10^{-6} A/cm² were measured starting with the temperature of 1150°C and 1350°C, respectively. Electrolyte 14·4M-HNO_3 at 70°C under bubbling air through.

carbides takes place. It can be explained in this way, why maximum at 1 000 mV is considerably more distinct within recording the curve with the decreasing potential from the transpassivity region. The same holds also for the second, lower maximum at potentials near 700 mV, which can be assigned to the preferential dissolution of another phase; the recent research proved the phases responsible for this maximum to be titanium sulphides[11,15].

Preliminary study of the effect of conditions, under which the polarization curves are recorded, showed that the maximum connected with the dissolution of titanium carbides is most distinct when using 2·5M-H_2SO_4 solution at 70°C and at the polarization rate of 9 V/h. These conditions are a compromise between the anode dissolution characteristics typical for the stainless nonstabilized steel and for the given dissolution of titanium carbides[10].

The polarization curves of the stabilized steels subjected to annealing within 750 to 1 350°C make it possible to follow lowering of the content of titanium carbides in the structure of steels with the increasing temperature (Fig. 3). The last treatment removes maximum at 1 000 mV in the polarization curve when recording at the increasing potential, and feeble is also maximum, if recording at the decreasing potential is carried out. From the measurements of the current density at the maximum of the polarization curve, J_M, under record with the decreasing potential, we can draw a conclusion as to the amount of titanium carbides in the structure of steel.

The change of J_M as dependent upon the temperature of annealing and composition of the steels studied may be evaluated on the basis of Fig. 4; the J_M values were obtained from the curves recorded at the decreasing potential at a rate of 9 V/h in 2·5M-H_2SO_4 and at 70°C. It is evident that the J_M value is primarily a function of the carbon and titanium contents and hence of the titanium carbides in steels. It must be mentioned that the polarization curves corresponding to steels with 0·11% and 0·21% of titanium have no distinct maximum near 1 000 mV. The current density values at the potential of 1 000 mV are for these steels plotted in Fig. 4. Within the whole range of the annealing temperatures studied, the J_M values, 100 times enhanced, can be observed for the steel of 1·26% titanium. For the given carbon and titanium contents, enhancement of the annealing temperature within 750 to 1 350°C provides changes much smaller, but very significant and dependent on the level of their contents. Thus for the steel with 1·26% of titanium, J_M doubly decreases with the rising temperature within the given range of annealing, while for the steel having 0·21% of titanium J_M decreases ten times.

Fig. 5 presents the polarization curves and results obtained by the measurements in 14·4M-HNO_3 at 70°C. The polarization curves of the steels tested have above 1 000 mV analogous course as in the sulphuric acid solution. Current density value J_M is in nitric acid approximately 2 to 3 times higher. In Fig. 6, the plot of J_M on the temperature of annealing and composition of the steels studied is graphically presented. Fig. 6 and Fig. 4 show consistent relations, and more significant dissolution

of titanium carbides in the solid solution may be considered from the temperature of 1 100°C upwards. The measurement of J_M is indirectly associated also with the determination of the content of carbon bound to titanium, and hence also of free carbon. The results suitably complete the measurement of the changes in the region of secondary passivity as dependent on the carbon content in the solid solution[12-14].

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