

The Corrosion and Electrochemical Behaviour of Ductile Chromium Alloys

BENEFICIAL EFFECTS OF PLATINUM GROUP METAL ADDITIONS

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Until recently the brittleness of chromium and its alloys has limited their use in applications which require a high resistance to corrosion in oxidising environments. Now, minor additions of selected metals can produce alloys with satisfactory low temperature ductility and workability, but even these alloys are susceptible to corrosion in non-oxidising environments. Passivation and corrosion resistance in such conditions can be increased by cathodic additions of noble metals; this paper reports a study of the effects of such additions on the corrosion and electrochemical behaviour of ductile chromium alloys in non-oxidising environments.

The high corrosion resistance of chromium and its alloys in oxidising environments makes them promising construction materials for use in chemical, oil refining and other industries. Formerly their employment has been limited by their brittleness but in recent years minor additions of several metals have been made to chromium to produce alloys with adequate low temperature ductility and workability (1, 2). However, the extra opportunities created by these new alloys are still limited by the fact that chromium alloys are generally susceptible to corrosion in non-oxidising media such as hydrochloric and sulphuric acid solutions. It has already been shown (3, 4, 5) that the tendency to passivation, and the corrosion resistance of chromium in a non-oxidising acid environment, can be increased by alloying with certain noble metals. A more detailed study of the electrochemical behaviour of these alloys and its effect on their corrosion has now been made.

Ductile alloys with 0.1 to 0.4 weight per cent of ruthenium, osmium, or iridium or up to 1 per cent of rhenium were prepared at the

Institute of Problems of Materials Science, Academy of Science of the Ukraine, Kiev. Their corrosion and electrochemical behaviour was studied in sulphuric acid of strengths ranging from 5 to 60 per cent and at temperatures from 25 to 100°C. The test specimens were in the form of cylinders pressed into Teflon holders so as to leave one end of the cylinder exposed to the electrolyte. The alloy surface was prepared for corrosion tests by polishing with carborundum paper and degreasing with acetone, prepared specimens were kept in a desiccator for three hours prior to testing. Metal losses were determined by accurate weighing. Electrochemical tests were carried out on freshly polished samples; in all tests free access air was allowed.

The data obtained in these tests are presented diagrammatically in Figure 1 as a function of temperature and sulphuric acid concentration. Boundary lines separating regions of active corrosion from regions where passivation occurs are shown for each alloy. Below and to the left of a line the passive oxide film is stable; above and to the right

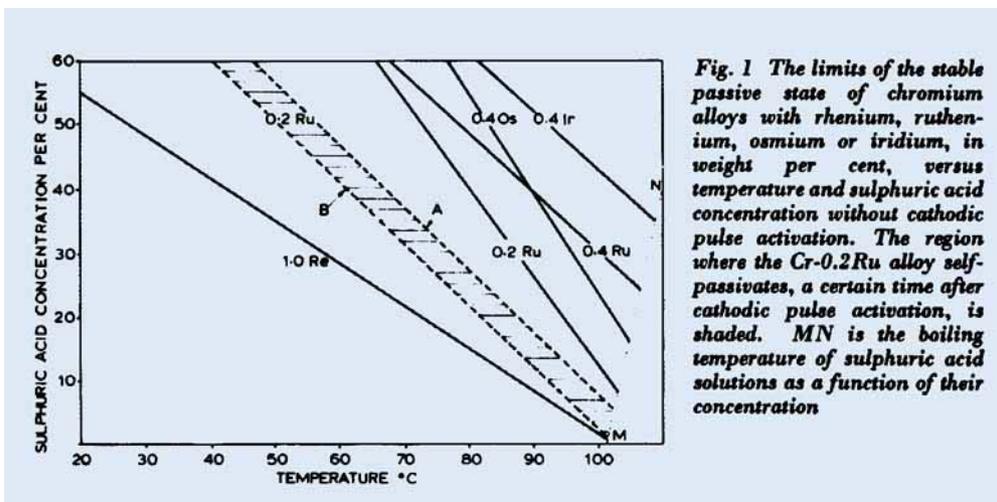


Fig. 1 The limits of the stable passive state of chromium alloys with rhenium, ruthenium, osmium or iridium, in weight per cent, versus temperature and sulphuric acid concentration without cathodic pulse activation. The region where the Cr-0.2Ru alloy self-passivates, a certain time after cathodic pulse activation, is shaded. MN is the boiling temperature of sulphuric acid solutions as a function of their concentration

the alloy dissolves readily. The chromium-rhenium alloy has the smallest range of conditions under which the alloy remains passive, and the chromium-iridium alloy has the largest. The stability of the passive film is increased by increasing the noble metal concentration, as shown in Figure 1, for alloys with 0.2 and 0.4 per cent of ruthenium. Below and to the left of the dotted line A the alloy with 0.2 per cent ruthenium self-passivates even after it has been cathodically activated by the application of a potential of -0.175 volt for 10 seconds. In the shaded region between the dotted lines A and B this alloy remains active for a time after the cathodic treatment. However, below and to the left of line B passivation is immediate when the cathodic potential is removed.

The rates of dissolution of the chromium alloys containing ruthenium, osmium and iridium, were measured at various temperatures and sulphuric acid concentrations where the alloys were in the stable passive state. For each alloy similar corrosion rates were obtained under all the test conditions, as shown in Table I. A sample of chromium tested under the same conditions corroded rapidly and the rate of corrosion only began to decrease in the test with 60 per cent acid, this strength of sulphuric acid being appreciably oxidising. The noble metal alloys remained

passive in all the tests; their corrosion resistance was several orders of magnitude higher than that of chromium, and increased in the order osmium, ruthenium, iridium. The rate of corrosion was also reduced by increasing

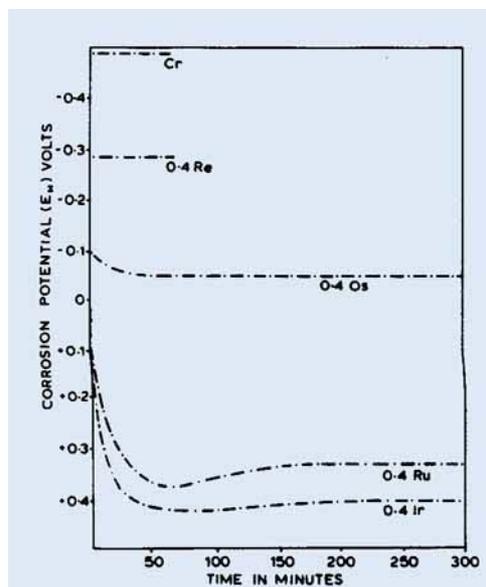


Fig. 2 The time dependence of corrosion potential, E_H , for chromium and its alloys with 0.4 weight per cent osmium, ruthenium, iridium and rhenium, in boiling 5 per cent sulphuric acid

Sulphuric acid concentration per cent	Temperature °C	Pure chromium (standard)	Corrosion rate, mm per year*					
			Alloying element, and amount in weight per cent					
			Ruthenium				Osmium	Iridium
0.1	0.2	0.3	0.4	0.4	0.4			
5	102	1420	0.671	0.35	0.253	0.179	0.427	0.06
20	90	1430	0.104	0.045	0.034	0.018	0.04	0.01
30	80	1100	0.061	0.031	0.024	0.012	0.05	0.01
50	70	1300	1.58	0.865	0.56	0.41	0.635	0.025
60	60	155	0.134	0.056	0.039	0.031	0.085	0.01

*Chromium was tested for 20 minutes, the alloys for 5 hours.

of the noble metal concentration of the alloy.

Corrosion tests made in boiling 5 per cent sulphuric acid, as reported in Table II, showed that corrosion rates for the passive noble metal alloys were virtually unchanged with time. Figure 2 shows the corrosion potentials measured against the standard hydrogen electrode. For all the alloys the potentials became constant after 5 hours in boiling 5 per cent sulphuric acid. The potentials for the ruthenium, osmium and iridium alloys remained in the passive region throughout the experiment. However the osmium alloy potential was close to zero volts

and, as expected, the corrosion rate was higher than for the ruthenium and iridium containing alloys. Chromium itself, and an alloy containing rhenium, showed negative corrosion potentials and thus they were actively corroded under these test conditions. In conditions corresponding to the shaded region in Figure 1 the alloy with 0.2 per cent ruthenium showed special behaviour. After the termination of the cathodic prepulse, which consisted of -0.175 volt applied for 10, 15 or 20 seconds, the corrosion potential was at first positive, corresponding to regions b_1 , b_2 and b_3 , respectively, in Figure 3. The

Duration of tests, hours	Corrosion rate, mm per year							
	Alloying element, and amount in weight per cent							
	Ruthenium				Osmium			Iridium
0.1	0.2	0.3	0.4	0.1	0.2	0.4	0.4	
1	0.64	0.45	0.33	0.24	0.78	0.68	0.57	0.06
5	0.67	0.35	0.25	0.18	1.10	0.52	0.43	0.06
10	0.73	0.29	0.22	0.16	1.12	0.55	0.40	0.04
15	0.78	0.28	0.18	0.15	1.18	0.56	0.36	0.05
20	0.82	0.28	0.20	0.15	1.22	0.55	0.40	0.06

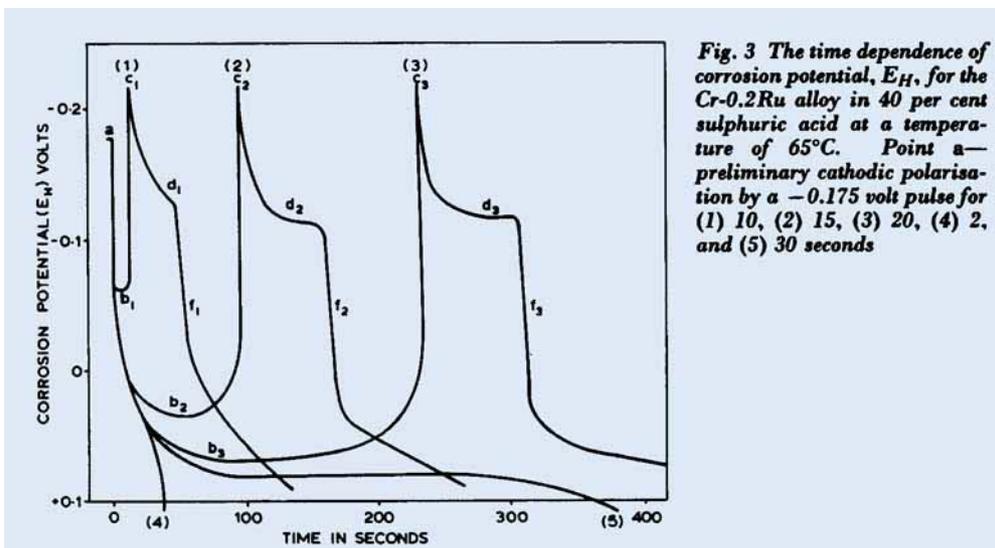


Fig. 3 The time dependence of corrosion potential, E_H , for the Cr-0.2Ru alloy in 40 per cent sulphuric acid at a temperature of 65°C. Point a—preliminary cathodic polarisation by a -0.175 volt pulse for (1) 10, (2) 15, (3) 20, (4) 2, and (5) 30 seconds

potential then fell to reach the active dissolution potential— c_1 , c_2 , c_3 in Figure 3—and then rose again to form a plateau— d_1 , d_2 , d_3 . Next the potential moved steeply, as indicated by f_1 , f_2 and f_3 , to the passive region where each alloy eventually attained a stationary potential of about +0.6 volt.

The first positive regions on these potential-time curves is due to saturation of the noble metal component, ruthenium, with atomic hydrogen during the cathodic pre-treatment. Hydrogen is adsorbed by surface atoms or aggregates of atoms of the noble metal which have a low hydrogen overvoltage. After the cathodic pulse, the potential rises to approach that of the reversible hydrogen electrode—points b. However, if only small amounts of hydrogen are involved, desorption will prevent this potential being reached— b_1 and b_2 . With sufficient adsorbed hydrogen the alloy does, in fact, reach the hydrogen potential, which in an acid environment at a hydrogen partial pressure less than one atmosphere may be calculated to be rather greater than zero volts (6).

After desorption of hydrogen the alloy surface activates, its potential rapidly decreasing from b to c. Increasing the cathodic polarisation time from 10 to 20 seconds

causes the b loop to expand by a greater amount than expected. The reason is an increase of the noble metal component on the surface of the alloy during polarisation (7). If the alloy was polarised by short pulses, of two seconds duration or less, activation was incomplete and passivation was immediate after the pulse, as is shown by curve 4 in Figure 3. Pulses of 30 seconds or longer resulted in an appreciable accumulation of ruthenium on the alloy surface and the self-passivation occurred sooner after prepolarisation. In this case, after hydrogen desorption the activation peak was not observed, as shown by curve 5 in Figure 3. In experiments where the polarisation time was kept constant at 10 seconds and the cathodic potential was varied from -0.13 to -0.25 volt the potential-time curves obtained for the same 0.2 per cent alloy were similar to those in Figure 3. Pulses less negative than -0.13 volt did not activate the alloy since they are within the self-passivation region.

The effect of the ruthenium concentration of the alloy on the potential-time curves was also studied in 40 per cent sulphuric acid at 65°C. A cathodic prepulse of -0.175 volt for 10 seconds was used and the results are shown in Figure 4. Under these conditions

chromium activation took place immediately without the prepulse. The 0.1 per cent ruthenium alloy reached the active dissolution potential in about 30 seconds without polarisation. Then, due to ruthenium accumulation on the surface, the potential became more positive but the alloy did not completely passivate. The 0.2 per cent alloy activated only after polarisation, and then self-passivated after being active for a short time. The 0.3 and 0.4 per cent alloys immediately re-passivated after the polarising pulse.

Minor amounts of chloride ions, 5 to 10 milligrams per litre, in the sulphuric acid solutions reduced the region of passivation stability for the 0.1 to 0.4 per cent ruthenium alloys, as shown in Figure 4. The addition of 10 milligrams of chloride ions per litre of 40 per cent sulphuric acid at 65°C promoted activation of the 0.3 per cent alloy; and 20 milligrams per litre was sufficient to activate the 0.4 per cent alloy and to prevent self-passivation of the 0.2 per cent alloy.

Accumulation of the noble metal on the surface of the 0.1 to 0.4 per cent ruthenium alloys during active dissolution is indicated by the current-time curves obtained during cathodic polarisation at a constant potential of -0.175 volt. Changes in the size and direction of this current, as shown in Figure 5, reflect the kinetics of the electrochemical process. The oxide film on unalloyed chromium dissolved completely in 25 seconds. For alloys with 0.1 to 0.3 per cent ruthenium the current was cathodic initially, then it decreased rapidly and became anodic. After reaching an anodic maximum it decreased, eventually becoming cathodic again and finally reaching a constant value in the cathodic region. With increasing ruthenium content the anodic current appeared later and disappeared earlier; at the same time its maximum value decreased and occurred earlier and the stationary value of the final cathodic current increased.

These trends may be explained as follows. On immersion of the alloys in the solution the anodic dissolution of chromium is hampered

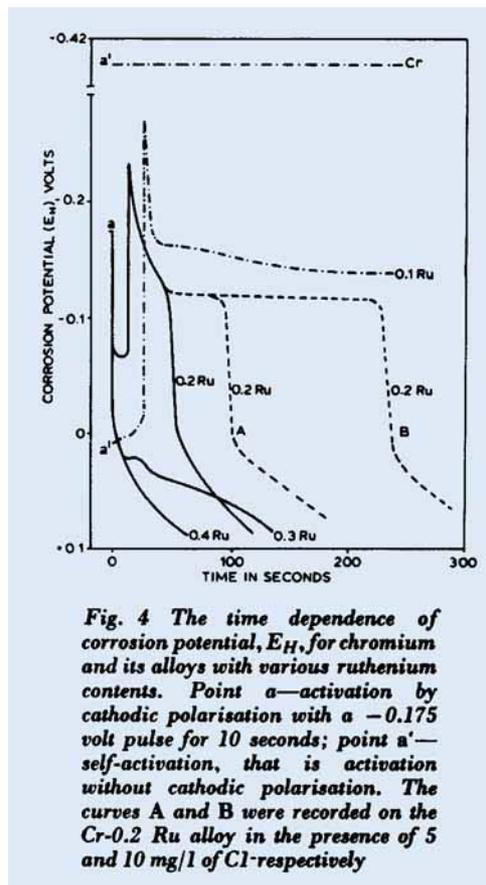


Fig. 4 The time dependence of corrosion potential, E_H , for chromium and its alloys with various ruthenium contents. Point a—activation by cathodic polarisation with a -0.175 volt pulse for 10 seconds; point a'—self-activation, that is activation without cathodic polarisation. The curves A and B were recorded on the Cr-0.2 Ru alloy in the presence of 5 and 10 mg/l of Cl⁻ respectively

by the passive atmospheric oxide film. At the same time, reduction of the hydrogen can occur on the noble metal causing a cathodic current. During activation the anodic process exceeds the cathodic, and the overall current is anodic. Dissolution of the alloy enriches the surface in ruthenium and the cathodic current rises to exceed the anodic current. The cathodic process is more efficient when the alloy has a higher ruthenium content initially, and the alloy with 0.4 per cent ruthenium shows a continuous increase of the cathodic current from the beginning of the test.

Weight loss measurements were included in the current-time curve experiments to determine corrosion as a function of time. As shown in the small graph inserted in Figure 5,

Table III				
The Effect of Time on the Accumulation of Ruthenium on the Surface of Alloys During their Dissolution by Cathodic Polarisation (-0.175 V) in 40 Per Cent Sulphuric Acid at a Temperature of 65°C				
Polarisation time, seconds	Accumulation, expressed as atomic layers of ruthenium*			
	Ruthenium content of the alloy, in weight per cent			
	0.1	0.2	0.3	0.4
50	2.6	2.8	2.9	2.2
100	5.2	5.7	5.7	4.3
200	10.8	11.3	11.5	8.8

*It is assumed that all the ruthenium released by dissolution of the chromium from the alloy remains at the surface.

the rate of dissolution of the alloys decreased with increasing ruthenium content, but the corrosion rates were constant for each alloy, the corrosion curves being straight lines passing through the origin. This leads to the conclusion that the ruthenium in the alloy

slows the anodic dissolution of chromium, whereas the accumulation of ruthenium on the surface has no such effect.

This increase in ruthenium content on the surface of the alloys during chromium dissolution has been calculated from the weight

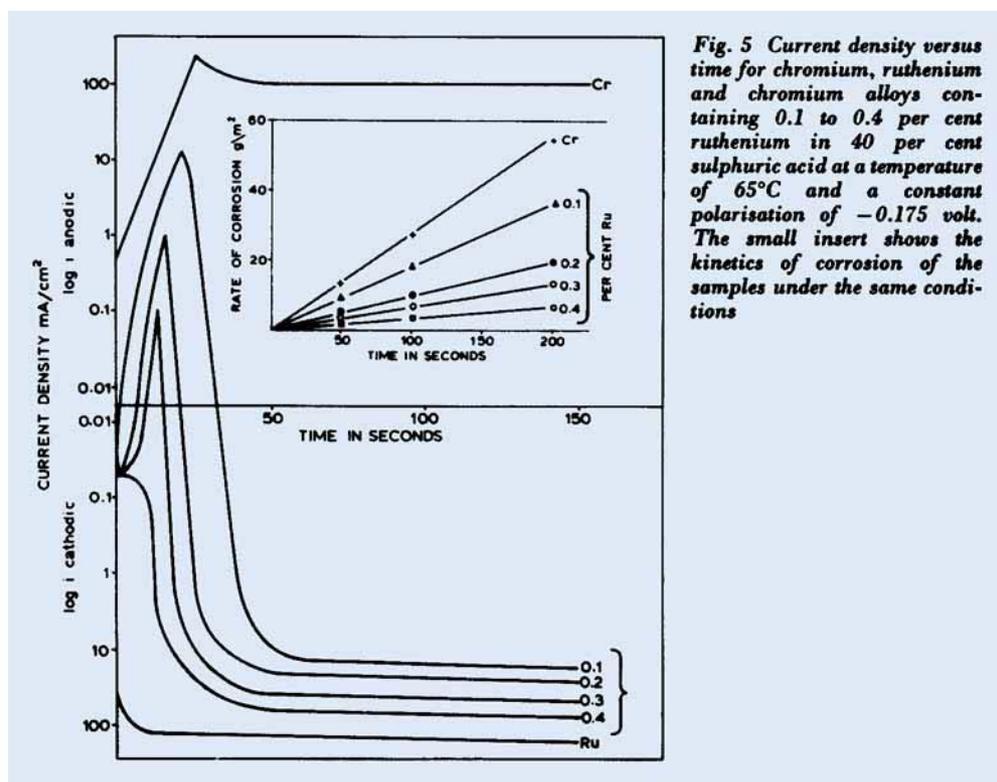


Fig. 5 Current density versus time for chromium, ruthenium and chromium alloys containing 0.1 to 0.4 per cent ruthenium in 40 per cent sulphuric acid at a temperature of 65°C and a constant polarisation of -0.175 volt. The small insert shows the kinetics of corrosion of the samples under the same conditions

losses and is shown in Table III. It has been assumed that all the ruthenium released by dissolution of the chromium remains on the surface of the alloy. As expected, the table shows that the ruthenium accumulated is proportional to the active dissolution time. It is not, however, proportional to the ruthenium content of the alloy in the range being considered because of the greater corrosion resistance of the richer alloys. This may reduce the amount of ruthenium accumulating on the surface of a rich alloy to a lower value than is observed for the less noble alloys.

Previously it has been shown (8, 9) that the noble metal forms separate islets on the surface of the alloy rather than a homogeneous layer. The surface coverage by such microcrystals is not high and we have estimated a value less than one per cent of the total surface. It can thus be understood why the noble metal does not affect the kinetics of active dissolution of the alloys.

Conclusions

It has been shown that ductile chromium alloys with additions of 0.1 to 0.4 per cent of osmium, ruthenium or iridium are stably passive for a wide range of temperatures and sulphuric acid concentrations, and they display high corrosion resistance.

In addition the self-passivation region for a particular alloy composition, and the tendency to repassivate, is reduced by the presence of chloride ions.

Finally, the rate of dissolution of chromium-ruthenium alloys in the active state decreases with increasing ruthenium content in the alloy. Ruthenium accumulating on the surface of the alloy during the corrosion process has no appreciable effect on the anodic dissolution process but does play a major role in shifting the corrosion potential positively, and thus in making the alloy passive and corrosion resistant.

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Advances in Platinum Metallurgy in Russia

Physical Metallurgy of the Platinum Metals BY E. M. SAVITSKII, V. P. POLYAKOVA, N. B. GORINA AND N. R. ROSHAN, Mir Publishers, Moscow, 1979, 395 pages, available from Pergamon Press, £20

Some three years ago a book under the above title was published in Russian and briefly reviewed in this journal (*Platinum Metals Rev.*, 1976, **20**, (3), 99). An English version, revised from the earlier edition and translated by I. V. Savin, is now available.

The volume is again contributed by four leading workers in the laboratories of the

A. A. Baikov Institute of Metallurgy of the U.S.S.R. Academy of Sciences and deals fully with the physical metallurgy and metal physics of the platinum metals, with a number of tables of reference data of use to industrial users and research workers.

A number of additional references have also been included in this second edition.