



Title	SOME PECULIARITIES OF THE CORROSION AND ELECTROCHEMICAL BEHAVIOUR OF ALLOYS
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 22(2), 73-81
Issue Date	1975-08
Doc URL	http://hdl.handle.net/2115/24969
Type	bulletin (article)
File Information	22(2)_P73-81.pdf



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SOME PECULIARITIES OF THE CORROSION AND ELECTROCHEMICAL BEHAVIOUR OF ALLOYS^{**}

By

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(Received October 5, 1974)

The supposition has been repeatedly expressed in literature that many of the peculiarities of the corrosion behaviour of alloys could be connected with the selective dissolution of their individual components. With this in mind, researchers have lately concentrated on the dissolution of the individual components of alloys, as well as the formation of surface layers enriched by components that are more corrosionresistant in the given conditions. But right up to the last few years such research was often complicated by the absence of reliable methods for the direct determination of very low dissolution rates, and the changes in the chemical composition of very thin surface layers. The absence of such methods practically completely ruled out any possibility of determining the kinetics of the selective dissolution of alloy components when they corroded at very low rates. It was for this reason, for instance, that until lately there was practically no data in literature on the selective dissolution of alloy components in the passive state.

The situation has, however, changed very greatly in recent years. Very wide opportunities were opened for determining low rates of corrosion, of alloys and especially of the individual components by the gamma spectroscopic methods developed in our institute which are highly sensitive and selective. These methods permit the simultaneous determination in the dissolution products of 5-6 alloy components ; for individual components the sensitivity proved sufficient to register reliably the transition into the solution of hundredths and even thousandths of parts of the monoatomic layer.

X-ray microanalysers have begun to be used successfully in recent years for determining the changes in the chemical composition of thin layers ($\geq 1 \text{ mcm}$), while the use of Auger spectroscopy and electron spectroscopy looks most promising for the analysis of even thinner layers (right up to monoatom).

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^{**) This paper was read at the JAPAN-Soviet Symposium on Electrochemistry in Sapporo.}

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The very first investigations conducted by these methods showed these methods to be very fruitful. I shall illustrate this on the results obtained recently in our laboratory when studying the anodic dissolution of the binary alloy Fe-28% Cr. The experiments were conducted with samples that had undergone homogenising thermo treatment, which ruled out the presence of zones whose chemical composition could have differed from that of the solid solution, and which also reduced to a minimum the presence of phase structure components. The gamma-spectroscopic method was used to determine the dissolution rate of the alloy as a whole and each of components separately at different potentials corresponding to the regions of transition from the active to the passive state, passivation and overpassivation.

The results are given on Fig. 1 which shows in dependence on the time: in the upper part the dissolution rate of the alloy itself (curve 1) and its components: iron (curve 2) and chromium (curve 3), and in the

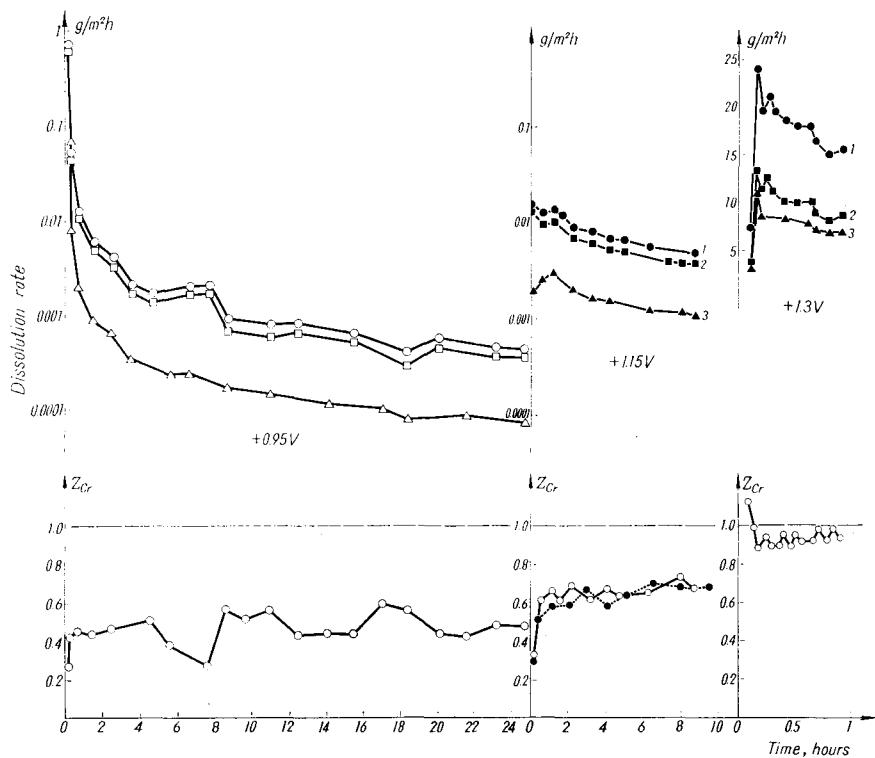


Fig. 1. Time Behavior of total and partial dissolution rates of Fe-28% Cr alloy and also of the selective dissolution coefficient (Z_{Cr}) in 1 N H_2SO_4 , 40°C different potentials.

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lower part—the selectivity coefficient for chromium, indicating how many times the chrome to iron concentration ratio in the dissolution products differs from the same ratio in the alloy.

It can be seen that when the sample is kept at a constant potential, this is usually accompanied by a sharp decrease both in the overall dissolution rate of the alloy and in the partial dissolution rates of its components, especially at the initial stage of the alloy's contact with the solution.

In the passive region the dissolution of the alloy proceeds with the preferential transition of iron into the solution, and its partial dissolution rate is higher than the dissolution rate of chromium by about one order of magnitude and almost wholly determines the overall dissolution rate of the alloy. This determines the low value of the selectivity coefficient Z_{Cr} for chromium, which is particularly low in the initial period corresponding to the high non-stationary dissolution rates of the alloy. The subsequent transition to a stationary dissolution regime is accompanied by a certain increase in Z_{Cr} , however, in these conditions too its value remains substantially less than one, contrary to the views of some researchers. Like the dissolution rate of the alloy, the value of Z_{Cr} does not remain strictly constant, but the observed deviations from the medium value both towards lower and higher values cannot be attributed to inaccurate measurements.

A curve was plotted on the basis of these measurements (Fig. 2) characterising the dependence on the potential of the average values of the selectivity coefficient for chromium corresponding to the established stationary regimes of dissolution. It can be seen that only in the active state region does the value of Z_{Cr} somewhat exceed one. When the alloy passes into the passive state Z_{Cr} at first falls sharply and then decreases smoothly and at the potential 0.75 V, corresponding to the end of the passive region, it achieves a minimal value equal to 0.1. As the potential increases further, Z_{Cr} rises and at the potential 1.3 V, corresponding to already fairly high dissolution rates of the alloy, it comes close to 1.

This data shows that in a wide range of potentials corresponding to the passive region, the region of transition from the active to the passive state and, partially, to the region of overpassivation, the dissolution of the alloy proceeds with the predominant transition into the solution of iron and only in the active state region is there any selective dissolution of chromium.

A comparison of curves 4 and 5 with curves 1 and 3 on Fig. 2 shows the existence of a certain correspondence between the selective dissolution of the solid solution and the corrosion-electrochemical characteristics of its components. That component undergoes selective dissolution whose disso-

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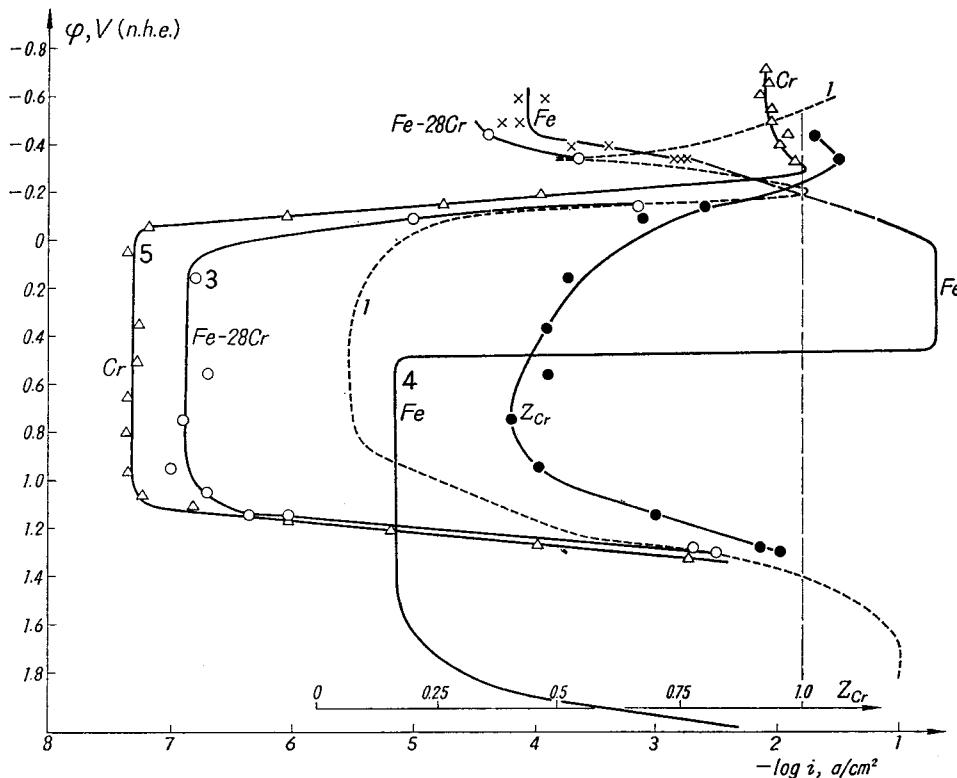


Fig. 2. Comparison of corrosion-electrochemical properties for iron, chromium and Fe-28% Cr alloy in 1N H_2SO_4 at 40°C.
1-cathodic and anodic potentiodynamic curves.

lution rate in its individual state at the given potential is substantially greater than the dissolution rate of the other component. Or, in other words, the selective dissolution of a component of a solid solution is observed in that region of potentials where its individual dissolution rate is greater than that of the other component. The correctness of this conclusion for solid solutions with a comparatively high content of components is indisputable. However, to what extent it can be applied to regions of very low (additive) concentrations remains unclear and requires a special check.

An x-ray micro-analyser MS-46 (produced by Kamek) was used for the direct observation of changes in the chemical composition of the alloy surface in the process of dissolution. The electronic beam of the analyser penetrated to a depth of 1 mm. Consequently, in sensitivity this method cedes place substantially to gammaspectrometric methods, since it permits

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observation of changes in comparatively thick surface layers, which as during the dissolution of the alloy in the passive state cannot be formed in a reasonable space of time. In view of this the studied alloy samples were kept for a long time at potentials corresponding to the beginning of the region of over-passivation. In these conditions the dissolution rate of the alloy is already considerable, and selectivity effects are still noticeable.

Fig. 3 and 4 show the obtained results in the form of characteristics of the x-ray spectrums of the two elements determined in one and the

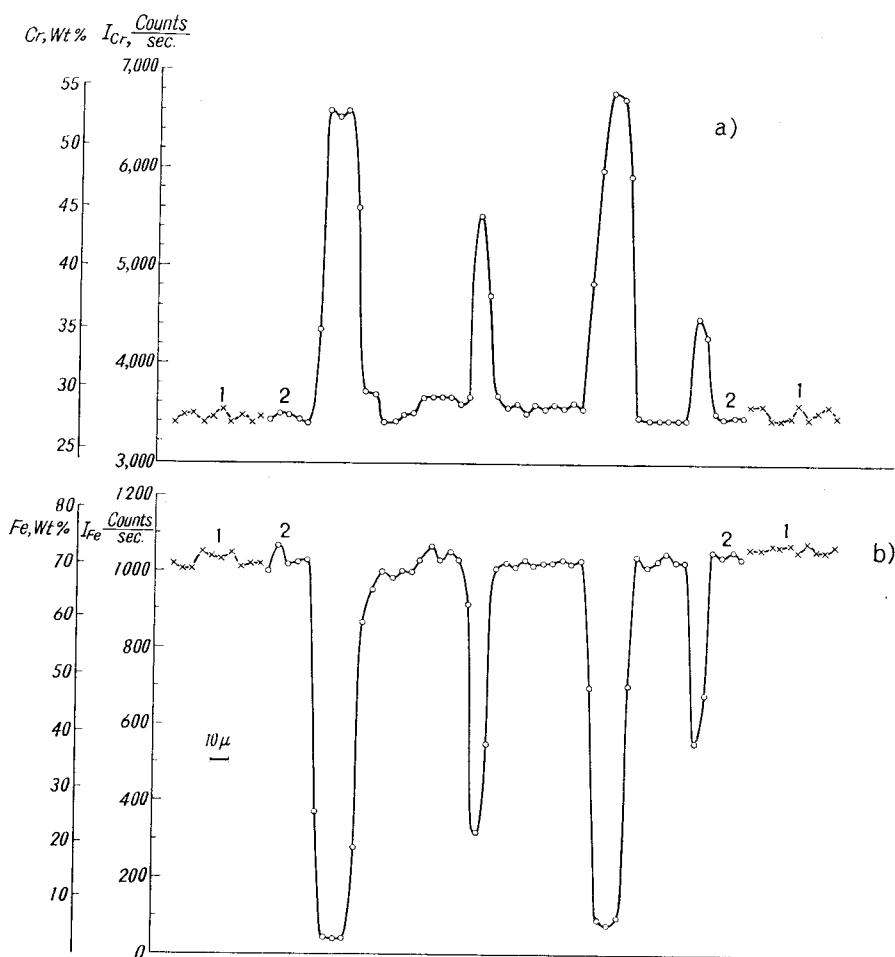


Fig. 3. Content of the chromium (a) and iron (b) in the surface layer of Fe-28% Cr alloy before (1) and after (2) its dissolution (28 hours) in 1 N H_2SO_4 , 40°C at 1.15 V.

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same point of the surface when scanned by an electronic beam along the chosen direction.

Also given is the scale of the percentage content of the element calculated from the standard sample.

It can be seen from Fig. 3 that when the alloy is kept for a long time in these conditions, it leads to the enrichment of its surface by chromium and the impoverishment in iron. But this change in composition does not take place throughout the surface, only on comparatively small sections. It

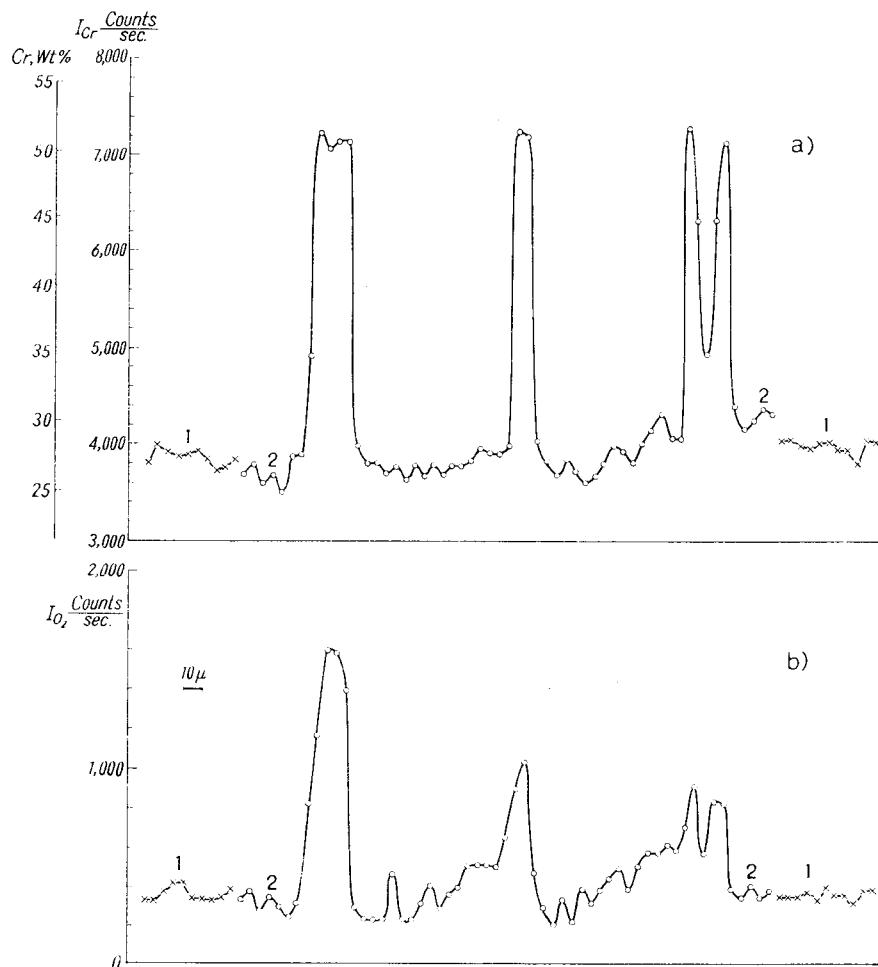


Fig. 4. Content of the chromium (a) and oxygen (b) in the surface layer of Fe-28% Cr alloy before (1) and after (2) its dissolution (28 hours) in 1N H₂SO₄, 40°C at 1.15 V.

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is highly important that for each maximum intensity of chromium there is a corresponding intensity of oxygen (Fig. 4). This last indicates that the excess chromium observed on the surface is directly linked with the oxygen.

On the rest of the surface of the alloy a small increase in the content of chromium could be observed only in separate cases. This is apparently due to the fact that on the main surface the layer of changed chemical composition formed was of a thickness much less deep than the beam of the microanalyser penetrated.

When explaining the mechanism of selective dissolution, the view is often propounded that in effect both components of the alloy dissolve at rates proportional to their content in the alloy, and the selectivity is the result of the reverse electrochemical deposition on the alloy surface of its electropositive component.

In the case examined such a mechanism is thermodynamically impossible, since the experiments were conducted at potentials much more positive than the potentials of the reduction of the chromium and iron ions.

The results obtained agree well with another mechanism known as the mechanism of volume diffusion. In this case it is believed that what dissolves is only or predominantly the less stable component and that the surface layer of the alloy is enriched not only by the more stable component, with the participation of which the corrosion-resistant structure is formed, but also by the vacancies in the crystal lattice thanks to which the diffusion coefficient in the surface layers can greatly surpass the diffusion coefficient in the bulk. When a stationary regime is achieved, selective dissolution can be maintained by the diffusion of the less stable component from the bulk to the surface and the more stable from the surface layer to the bulk. It was shown in the work of Pickering and Wagner that with the constant generation of vacancies through this mechanism considerable dissolution rates can be kept up even at usual temperatures.

From this data it follows that the selective dissolution of alloys is characterised by a number of features which, to judge from everything are of great importance for understanding the mechanism of its influence on the corrosion stability of alloys.

The first peculiarity, as already noted above, is the sharp drop in the dissolution rate of the alloy and in the partial dissolution rates of each of its components at the initial period when the sample is kept at a constant potential. There are grounds for supposing that this effect is largely due to the enrichment of the surface by the more stable component. If that is the case, then it follows from the data given that in the process of

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corrosion a layer could be formed on the surface of the alloy through selective dissolution which in its stability greatly surpasses the corrosion stability of the surface layer of the initial composition.

The second peculiarity is the uneven enrichment of the surface by chromium, which undoubtedly testifies to the unequal dissolution of the surface when its stationary state is formed. This conclusion was confirmed by a direct examination of the samples after dissolution by means of optical and electron solution microscopes. It was established that dissolution usually begins near the inclusions, and then can spread to the borders and separate sections of the body of the grain. As was shown in our laboratory in certain conditions the rate of local dissolution of stainless steel at the inclusions was so high, that cavities of the pit type were formed in these places. This result agrees well with the data obtained in recent years by various researchers when studying the nature of centres of pitting formation in chloride and other solutions with de-passivated anions. It was shown in these works that on non-sensitized stainless steels were formed predominantly on the border of the metal and non-metallic inclusions. It was recently shown at our institute, using methods of x-ray microanalysis and scanning electronic microscopy, that non-metallic inclusions are the preferable centres of pitting formation not only in non-sensitized austenitic steels of various composition (chrome-nickel, chrome-nickel-silicon, chrome-nickel-molybden), but also in alloys of nickel-chrome, titanium and even platinum.

Two important conclusions follow from this. First, that in the process of corrosion selective dissolution ensures the healing of weak sections, as if placing on them strong patches. The second and more general conclusion is that the weak sections of the surface are the borders of the metal and non-metallic inclusions, and possibly, the points where these borders intersect the borders of the grain. The high corrosion activity of the borders of the inclusions is, apparently, due to the high degree of defectivity and pollution of the crystal lattice of the metal near the inclusion, and in cases of sulphide inclusions, also to the catalytic action of the sulphide ions formed during the dissolution of the inclusions. As the research conducted at our institute has shown, in certain conditions the influence of non-metallic inclusions can supersede the influence of the alloying elements. It is known, for instance, that alloying with silicon, which dissolves in austenite, heightens the steel's stability to pitting corrosion. But it has also been established that it is polluted with inclusions of SiO_2 when the silicon is introduced into the steel then in certain conditions heavy pitting can develop on these inclusions, with the stability of chrome-nickel-silicon becoming much less

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than that of chrome-nickel.

The third peculiarity is the existence of periodic oscillation of the dissolution rates of steel and its individual components in time. An analysis of all the results taken together showed that this oscillation is not connected with inaccurate measurements, but is indeed a feature of the dissolution of steel. There are grounds for believing that the cause of the oscillation is the spontaneous local activation of separate sections of the alloy surface and their subsequent re-passivation in keeping with the mechanism of selective dissolution. The activation could be due to different causes, including the uncovering of new inclusions with a pile-up of dislocations in the adjacent layers of the metal, and the violation of the passivating layer as a result of the internal stresses.

These and certain other data obtained in the past few years show convincingly that the former conventional idea of the passivating layer as a static formation is incorrect. In reality this layer is an extremely dynamic formation in which local violations arise almost constantly and cause flare-ups of the dissolution rate. This was demonstrated very well by Sukhotin, who with the help of a little inertial instrument showed that the stationary dissolution rate of passive iron at a constant potential does not remain strictly constant, as is shown by a conventional instrument, but it oscillates constantly around a certain value.

Depending on the conditions, active sections of the surface can either be repassivated or can become the centre of pitting formation.