ELECTROCHEMICAL AND CORROSION BEHAVIOR OF CHROMIUM-PLATED STEEL SHEET IN CONNECTION WITH ITS USE IN THE CANNING INDUSTRY

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UDC 620.198

The radiochemical method was used to find the partial speeds of iron and chromium passage from chromium-plated sheet (with and without a lacquer coating) into various canned goods and solutions simulating them. The results were compared with polarization measurements on iron, chromium, and chromium-plated sheet. It was shown that the corrosion and electrochemical behavior of chromium-plated sheet could be described on the basis of the appropriate characteristics of the individual iron and chromium. An analysis was made of the effect of certain parameters on the corrosion resistance of chromium-plated sheet in connection with its use in the canning industry.

Due to the scarcity of tin, a demand has arisen in the canning industry to replace tinplate by chromium-plated sheet. The latter is steel strip with an electrolytic chromium deposit 0.03-0.05 μ thick on its surface.

There are no systematic data on the corrosion resistance of such sheet. All that is known is that its resistance can be guaranteed only after an additional coating of lacquer, and that apparently applies only to a limited number of corrosive media.

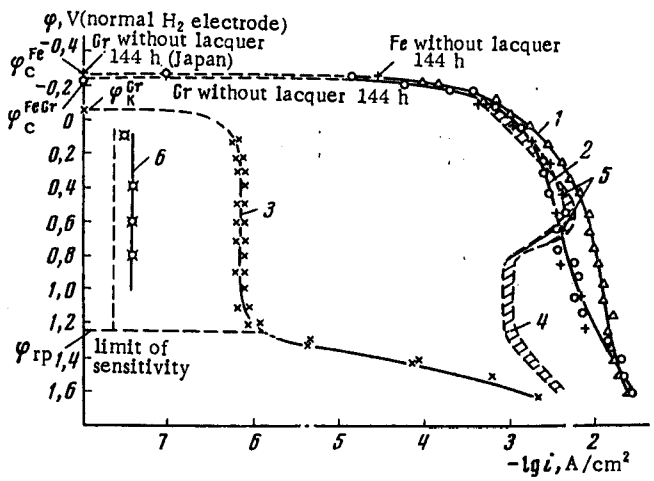

Fig. 1. Anodic polarization curves in 2.5% malic acid solution: 1) steel base; 2) chromium-plated sheet; 3) chromium; 4) Japanese chromium-plated sheet; points 5 and 6 are the analytically determined speeds of solution of iron (in 20 min) and chromium (in 10 h) respectively.

L. Ya. Karpov Physicochemical Scientific-Research Institute. Translated from Zashchita Metallov Vol. 10, No. 6, pp. 648-654, November-December, 1974. Original article submitted November 27, 1973.

TABLE 1. Partial Speeds of Passage into Solution of Iron (i_{Fe}) and Chromium (i_{Cr}) from Chromium-Plated Sheet (Calculated on the Apparent Surface)

test pieces	Unlacquered test pieces: duration of experiment	i_{Fe} A/cm²	i_{Fe} g/cm²·h	i_{Cr} A/cm²	i_{Cr} g/cm²·h	Lacquered test pieces: duration of experiment	i_{Fe} A/cm²	i_{Fe} g/cm²·h	i_{Cr} A/cm²	i_{Cr} g/cm²·h
2.5% malic acid solution										
TsNIIChM	144	$2\cdot10^{-5}$	$2{,}1\cdot10^{-5}$	$1\cdot10^{-7}$	$6{,}4\cdot10^{-6}$	360	$2{,}5\cdot10^{-6}$	$2{,}6\cdot10^{-6}$	$5\cdot10^{-6}$	$3{,}2\cdot10^{-6}$
Japanese (with oxide film)	144	$1\cdot10^{-5}$	$1{,}0\cdot10^{-5}$	less than $1{,}6\cdot10^{-8}$	less than $1{,}00\cdot10^{-6}$	360	$9{,}4\cdot10^{-7}$	$9{,}6\cdot10^{-7}$	less than $1\cdot10^{-6}$	less than $6{,}4\cdot10^{-10}$
TsNIIChM with oxide film	—	—	—	—	—	360	$2{,}5\cdot10^{-6}$	$2{,}6\cdot10^{-6}$	less than $1\cdot10^{-6}$	less than $6{,}4\cdot10^{-10}$
3% sodium chloride solution										
TsNIIChM	—	—	—	—	—	360	$4{,}4\cdot10^{-6}$ $4{,}6\cdot10^{-6}$		$2{,}8\cdot10^{-6}$	$1{,}8\cdot10^{-6}$

Abroad the chromium-plated sheet is given a supplementary treatment in chromate solutions prior to lacquering, which gives better lacquer adhesion and increases the corrosion resistance of the lacquered material [1]. Sheet of this type has been used for containers for beer, aerated beverages, tobacco, perfumery, and confectionery products, bulk food products, and for all kinds of non-food packaging.

The chromium-plated sheet produced in the experimental unit at the Lys'va Metallurgical Plant has a chromium coating 0.03-0.05 μ thick and a lacquer coating about 8-9 μ thick.

In addition to statements that chromium-plated sheet could be widely used for the most varied types of canned goods [2], fears have been expressed as to the possible passage of chromium into the canned goods, causing their organoleptic characteristics (color and taste) to deteriorate.

We studied the corrosion and electrochemical behavior of chromium-plated sheet in certain model media simulating the basic forms of canned product, and also in a number of actual canned products. The methods used were the potentiostatic method of polarization measurements [3] and the radiometric method of determining the partial speeds of solution of iron and chromium [4] during the corrosion and anodic solution of the chromium-plated sheet. The subjects of study were samples of sheet from the Lys'va Plant and samples manufactured at the Central Scientific Research Institute of Ferrous Metallurgy (TsNIIChM) with the same coating thickness.

The Lys'va sheet, thickness 0.28-0.3 mm, was used for the polarization measurements, and the TsNIIChM sheet, thickness 0.05 mm, for the radiometric studies.

Polarization measurements were made on sheet without lacquer, and also (for comparison) on grade 08 KP steel strip samples from the Zaporozh'e Steel Plant and on chromium manufactured by vacuum melting at TsNIIChM (carbon content 0.02%).

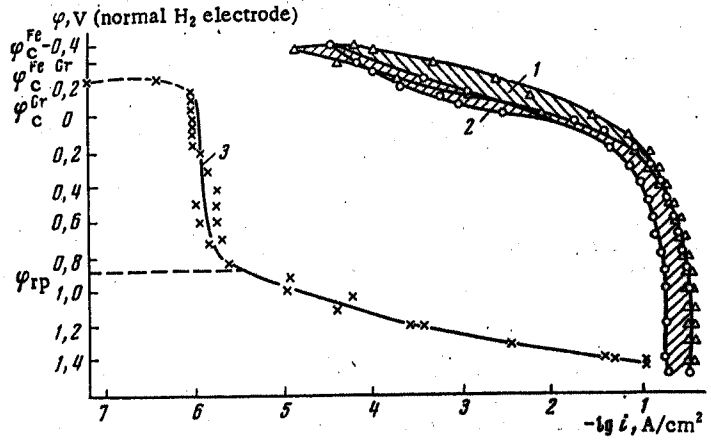

Fig. 2. Anodic polarization curves in 3% NaCl solution: 1) steel base; 2) chromium-plated sheet; 3) chromium.

TABLE 2. Corrosion Resistance of Lacquered Chromium-Plated Sheet (without oxidation) in Actual Canned Goods

Canned goods	Corrosion speed, g/cm²·h		Accumulation of Cr in goods, mg/kg·year	
	iron	chromium	can No. 3	SKO-1-82-500
30% tomato paste	$1 \cdot 10^{-6}$	less than $5{,}1 \cdot 10^{-10}$	less than 4,5	less than 0,45
Green peas	$1 \cdot 10^{-8}$	less than $6{,}4 \cdot 10^{-11}$	less than 0,56	less than 0,056
Pumpkin paste	$2 \cdot 10^{-7}$	less than $2{,}5 \cdot 10^{-10}$	less than 2,2	less than 0,22
Braised beef	$1 \cdot 10^{-7}$	less than $1{,}6 \cdot 10^{-10}$	less than 1,4	less than 0,14

The partial speeds of solution of iron and chromium from the chromium-plated sheet were measured both with and without a lacquer coating. Japanese chromium-plated sheet with an oxide film (with and without lacquer) was compared with oxidized chromium-plated sheet coated with lacquer manufactured at TsNIIChM.

The model media used were solutions of 3% NaCl, 3% CH_3COOH, 2.5% malic acid, and a mixture of 1.5% lactic acid with 1.5% sodium chloride, prepared with double-distilled water. The actual canned products used for the corrosion tests were 30% tomato paste, green peas, pumpkin paste, and braised beef. Tomato juice and the liquid from green peas and pickled vegetables were used for the polarization measurements.

The object of the work was to determine the role of the chromium coating in the corrosion process, to find the speed of corrosion of chromium-plated sheet in various canned products (with separate determination of the speeds of passage of iron and chromium into the products), and to ascertain the valence of the chromium passing into the canned products (the latter is vital, because of the toxicity of hexavalent chromium compounds). The polarization measurements were made in a three-electrode cell with separated cathode and anode spaces, at room temperatures and in solutions deaerated with argon.

The anodic polarization curves for chromium-plated sheet, iron, and chromium in various model media, plotted at a speed of 3 V/h (for potentials on the negative side of 0.5 V*) and at 6 V/h (for more positive potentials), are compared in Figs. 1-4. In the case of iron and chromium-plated sheet, this speed of polarization curve plotting corresponds to steady results. The polarization curves for chromium plotted under these conditions are not steady (the anodic currents in the chromium passive state region decrease in time).

*All potentials are given relative to a normal hydrogen electrode.

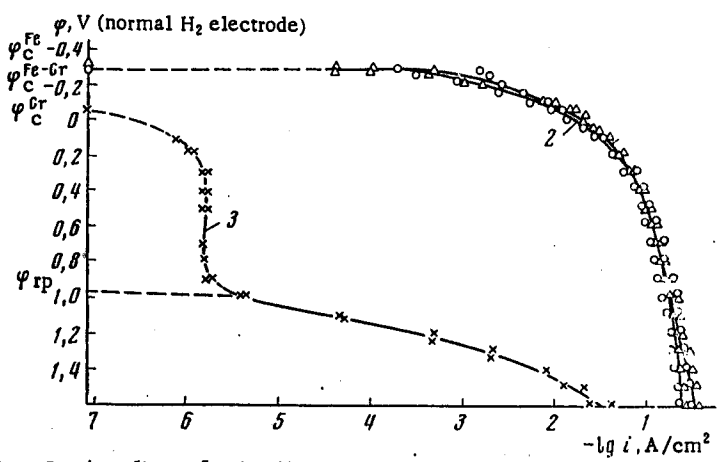

Fig. 3. Anodic polarization curves in a solution of 1.5% NaCl + 1.5% lactic acid: 1) steel base; 2) chromium-plated sheet; 3) chromium.

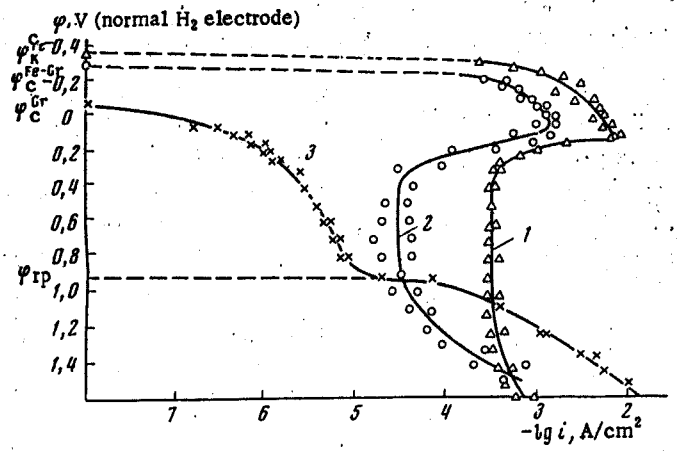

Fig. 4. Anodic polarization curves in 3% CH_3COOH solution: 1) steel base; 2) chromium-plated sheet; 3) chromium.

The polarization curves for chromium-plated sheet and iron (Figs. 1-4) are comparatively close to each other and differ perceptibly from the polarization curves for chromium. The maximum difference in the speed of anodic solution of iron and chromium-plated sheet is about half an order of magnitude. In malic acid (Fig. 1) the chromium-plated sheet dissolves at all potentials twice as slowly on average as iron. In the solutions containing sodium chloride and malic acid, the polarization curves lack passivation regions of current drop (a passivation region is apparent only on Japanese chromium-plated sheet in malic acid [Fig. 1, curve 4]). In acetic acid, iron and chromium-plated sheet are more readily passivated than in other solutions: the passivation potential is 0.125 ± 0.025 V, which is approximately 400 mV more negative than the known passivation potential for iron in sulfuric acid of the same acidity.

Comparison of the anodic polarization curves with the results of analytical determination of partial speeds of iron and chromium passage into solution from chromium-plated sheet leads to the assumption that the experimentally found anodic currents for chromium-plated sheet at potentials on the negative side of 1.0 V* correspond practically completely to the speeds of solution of iron. The speeds of solution of iron (Fig. 1) as found by the radiometric method (by reference to solution radioactivity after a neutron-irradiated

*The electrochemical behavior of chromium-plated sheet at more positive potentials will be examined further on in the article.

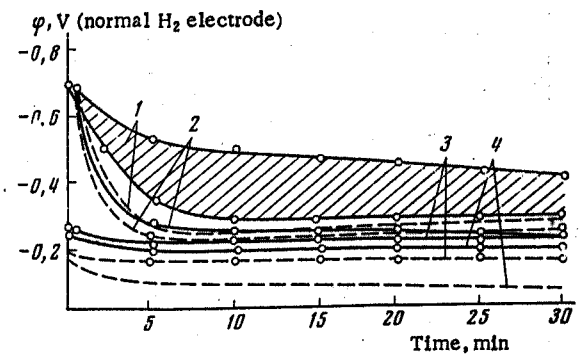

Fig. 5. Corrosion potential of chromium-plated sheet in various solutions: 1) 3% NaCl; 2) 1.5% lactic acid + 1.5% NaCl; 3) 3% CH_3COOH; 4) 2.5% malic acid without O_2, - - -) with O_2.

test piece has dissolved under controlled conditions) practically coincide with those calculated from the results of polarization measurements. According to the radiometric data, chromium dissolves at these potentials at incommensurably lower speeds.*

The analysis of the results of polarization and radiometric measurements for iron, chromium, and chromium-plated sheet has led to the conclusion that the corrosion resistance of unlacquered chromium-plated sheet in any medium can be assessed by the resistance in that medium of the individual metals (iron and chromium), taking account of the potential being established and the porosity of the chromium coating.

The closeness of the polarization curves measured on chromium-plated sheet in actual canned goods to the curves for the corresponding simulated solutions makes it possible to extend the conclusions based on the data in Figs. 1–4 to actual systems.

In accordance with the conclusions drawn above, in order to predict the corrosion resistance of chromium-plated sheet it is essential to know the corrosion potential in the medium prescribed. These potentials have been measured in various deaerated and naturally aerated solutions. Having regard to the pH of the solutions examined and the known passivation potentials for chromium, one may conclude on the basis of the results obtained (Fig. 5) that at the corrosion potential the chromium from the plated sheet dissolves in the passive state. This is confirmed by the experiments in malic acid (duration 144 h). As can be seen from Fig. 1, at the corrosion potential (φ_c) in this case the corrosion speed of chromium-plated sheet in terms of chromium is $1 \cdot 10^{-7}$ A/cm^2, which does indeed correspond to the solution of passive chromium. In these circumstances the corrosion speed in terms of iron is $2.0 \cdot 10^{-5}$ A/cm^2, as might have been expected, in accordance with the polarization curve for iron.

Since the corrosion potentials for chromium-plated sheet in all the solutions studied are substantially negative of the repassivation potentials (φ_{rp}) for chromium (Figs 1–4), an important conclusion can be drawn from the results obtained: under actual conditions the passage of chromium from chromium-plated sheet into canned goods in the form of hexavalent chromium compounds is impossible.

The speed of chromium passage into solution increases perceptibly at potentials on the positive side of 1.25 V, so that at these potentials the anodic current measured on chromium-plated sheet may in the particular case be determined by the speed of solution not of iron, but of chromium. For example, this occurs when chromium-plated sheet dissolves in acetic acid at potentials on the positive side of 1.0 V (Fig. 4).

Analysis of the polarization curves (Figs. 2–4) leads to the conclusion that the corrosion speeds for chromium-plated sheet have fairly high values for the other solutions studied, as for malic acid. This prevents the practical use of the sheet without supplementary protection. Tables 1 and 2 give data obtained by us on the corrosion resistance of chromium-plated sheet in certain simulated and actual canned goods after supplementary protection of the sheet with a combined coating (lacquer ÉP-547 and FL-559) applied and dried according to the conditions indicated in the process instructions, including preliminary surface oxidation. The data in Tables 1 and 2 were obtained by the radiometric method, and in the case of chromium are limited in a number of cases to indicating the upper boundary of the speed of solution, for the reasons given above. For purposes of comparison, Table 1 also gives the speeds of passage of iron and chromium into solution from chromium-plated sheet without a lacquer coating (in the case of TsNIIChM sheet these data correspond to the points for φ_c in Fig. 1).

It is demonstrated (Table 1) that when chromium-plated sheet without a lacquer coating corrodes in malic acid solution, the speed of passage of iron into solution is 200 times greater than the speed of chromium solution.

*The problems connected with the sensitivity of the radiometric method in application to the study of corrosion resistance in chromium-plated sheet were examined by us in detail in [5]. Here we confine ourselves to pointing out that sensitivity as regards chromium depends on the co-presence of iron in the solution, decreasing as its concentration increases. Due to the high speed of iron solution in anodic polarization in malic acid, the sensitivity of the method as regards chromium for experiments of 10 h duration (test-piece surface 0.75 cm^2) corresponds in electrical units to a speed of solution of $5.9 \cdot 10^{-8}$ A/cm^2 (broken straight line in Fig. 1). The chromium solution speeds found experimentally are at the limit of sensitivity of the method (Fig. 1,6). The deviation of these points from the anodic currents on the polarization curve for chromium (Fig. 1,3) is due to the unsteadiness of the curve.

The ratio of iron and chromium speeds of passage into solution is perceptibly reduced as a result of lacquering the sheet. Oxidation of the chromium-plated sheet surface, with or without subsequent lacquering, leads to a reduction in chromium solution speed. The absolute speeds of solution of iron and chromium are reduced by one order of magnitude after lacquering, but still remain fairly high.

To find the speeds of iron and chromium corrosion in canned goods (Table 2), samples of the sheet were placed in test tubes containing the goods (the ratio of test-piece surface to volume of canned goods corresponded to can No. 3, GOST 5981-71), the tubes were sealed, sterilized in a glycerin bath using accepted conditions of sterilization and stored for 3 months at room temperature and 3 months at 55°. In these circumstances the speed of iron passage into the canned products was greatest in the case of tomato paste and least in the case of green peas. The speed of chromium solution could not be ascertained by the method used.*

CONCLUSIONS

1. The patterns of solution of iron and chromium from chromium-plated sheet in solutions simulating basic canned goods remain the same as for the individual iron and chromium.

2. Having regard to the high speed of iron corrosion in unlacquered chromium-plated sheet in the solutions studied, the practical use of lacquered sheet in the canning industry demands strict checking of the integrity of the lacquer coating.

3. The speed of iron and chromium corrosion in chromium-plated sheet is reduced by approximately one order of magnitude when a lacquer coating is applied.

4. When unlacquered and lacquered chromium-plated sheet corrodes in the solutions tested, the speed of iron passage into solution is greater than that of chromium by 2-3 orders of magnitude.

5. Application of an oxide film to the sheet surface leads to a reduction in the speed of chromium corrosion in both lacquered and unlacquered sheets.

6. Under actual conditions of passage into canned goods from chromium-plated sheet of chromium in the form of hexavalent compounds is impossible.

The authors wish to express their gratitude to Ya. M. Kolotyrkin for his assistance in formulating the problems for study and valuable advice during the discussion of the results. The authors also thank M. A. Dembrovskii and A. I. Sherstyannikov for their part in making the radiometric measurements, and the staff of the TsNIIChM tinplate laboratory for making the ultrathin chromium-plated sheet test pieces.

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*A special study with application of radioactive chromium to inactive iron is necessary for this.