While the physical properties of the carbide Cr$_{23}$C$_6$ have already been extensively investigated [1, 2], there are virtually no data on the properties of the iron-chromium carbides (Cr, Fe)$_{23}$C$_6$, although many authors [3, 4] attribute the susceptibility to intergranular corrosion of chromium-nickel steels and alloys to the precipitation of these carbides at the grain boundaries during heat treatment. A knowledge of the physical properties of the carbides and of the laws governing their variation for various compositions within their homogeneity region is indispensable for the study of the mechanism of intergranular corrosion and for the exploration of ways of formulating new constructional materials capable of resisting intergranular attack.

In the present work, a study was made of the electrical resistivity and microhardness of the iron-chromium carbides (Cr, Fe)$_{23}$C$_6$ at room temperature as a function of their iron content. Carbide specimens had been prepared previously by the method of alloying single-phase Cr$_{23}$C$_6$ carbide powder with carbonyl iron [5]. The chemical compositions of the carbides investigated are listed in Table 1. The microhardness was measured by the standard technique [6] with a PMT-3 tester under a load of 50 g, and the electrical resistivity by a probe method [7], using a U-202 apparatus at a stable sensitivity of not less than $10^{-6}$ Ω. The reproducibility of results was evaluated from experimental error on the basis of 10 measurements. Figure 1 shows that the microhardness of the complex carbides linearly decreases with rise in iron concentration.

To describe experimental data on the conductivity of the carbide (Cr, Fe)$_{23}$C$_6$ as a function of pore concentration, a comparative examination was made of several analytical generalized conductivity formulas [8, 9] (see Fig. 2). Taking the conductivity of the pores to be zero, the analytical expressions for conductivity were transformed into expressions for electrical resistivity ($\rho$),

$$\rho = \rho_0 \left( \frac{1 + 0.5I}{1 - I} \right),$$

(1)

$$\rho = \rho_0 \left( \frac{1 + I}{1 - I} \right),$$

(2)

$$\rho = \rho_0 \frac{1}{(1 - I)\sqrt{I}}.$$

(3)

Curve 2 in Fig. 2 was plotted using the formula [10]

$$\rho = \rho_0 \frac{1 + 6I^2}{1 - I},$$

(4)

and curve 3, using Odelevskii’s formula

$$\rho = \rho_0 \frac{2}{2 - 3I^2}.$$

(5)
TABLE 1. Chemical Compositions of Iron—Chromium Carbides

<table>
<thead>
<tr>
<th>Carbide formula</th>
<th>Composition, wt.%</th>
<th>Cr/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂₃Fe₈C₆</td>
<td>Cr</td>
<td>Fe</td>
</tr>
<tr>
<td>Cr₁₆.₉Fe₆.₁C₆</td>
<td>67,81</td>
<td>26,42</td>
</tr>
<tr>
<td>Cr₁₆.₉Fe₆.₁C₆</td>
<td>66,97</td>
<td>27,12</td>
</tr>
<tr>
<td>Cr₂₃Fe₈C₆</td>
<td>64,15</td>
<td>34,37</td>
</tr>
</tbody>
</table>

There is disagreement between the theoretical plots of Eqs. (2) and (4) and experimental points. At low porosity (\(\Pi < 6\%\)), a good correlation is observed between the theoretical and experimental values of \(\rho\) obtained from Eqs. (1), (3), and (5). The relationship between porosity and experimental values of \(\rho\) (at \(\Pi > 6\%\)) is satisfactorily represented by curve 4, constructed with the aid of Eq. (3).

The variation of \(\rho\) as a function of porosity for \((\text{Cr}, \text{Fe})_{23}\text{C}_6\) carbides of various compositions is represented by curves 2-4 in Fig. 3. The equidistant position of these curves is evidence of the existence of some common laws governing the relationship between \(\Pi\) and \(\rho\) for different carbides. Equation (3) was used to determine the values of \(\rho_0\) for the alloyed carbides investigated (Fig. 4).

The alloying of single-phase \(\text{Cr}_{23}\text{C}_6\) carbides with iron lowers their electrical resistivity. As a result of mathematical processing, experimental data yielded the following empirical relationship between the electrical resistivity of alloyed \((\text{Cr}, \text{Fe})_{23}\text{C}_6\) carbides and the carbides and the volume percentage of iron:

\[
\rho(\%\text{Fe}) = \rho_0 + 1.25 \%\text{Fe}, \quad [\mu\Omega \cdot \text{cm}],
\]

where \(\rho_0\) is the electrical resistivity of the carbide \(\text{Cr}_{23}\text{C}_6\), \(\rho(\%\text{Fe})\) the electrical resistivity of the alloyed carbide \((\text{Cr}, \text{Fe})_{23}\text{C}_6\), and \(\%\text{Fe}\) the volume percentage of iron in the carbide \((\text{Cr}, \text{Fe})_{23}\text{C}_6\). The electrical resistivity and microhardness of \((\text{Cr}, \text{Fe})_{23}\text{C}_6\) carbides depends on the degree of alloying with iron, the character of the relationship being linked with changes in the electronic structure of refractory compounds. The carbide \(\text{Cr}_{23}\text{C}_6\) is capable of dissolving up to 35 wt.% iron. When some of the chromium is replaced by iron atoms, the latter preferentially occupy some points of the cubic lattice [11]. Iron implanted in the crystal lattice of the carbide consolidates the stable d⁵ configurations of the localized valency electrons. A higher degree of valency electron localization reduces the probability of scattering of conduction electrons on lattice points [12]. When the amount of iron in the carbide lattice increases, the concentration of collectivized electrons rises. This appears to be the main reason why the electrical resistivity of the carbide \(\text{Cr}_{23}\text{C}_6\) decreases as a result of alloying with iron.

The microhardness of carbides is determined by the statistical weight of stable sp³ configurations and the proportion of collectivized electrons [13]. During the alloying of the carbide with iron, the fraction of valency electrons transferred to carbon for the formation of sp³ configurations diminishes. As a result, with rise in iron content the microhardness of the complex carbide \((\text{Cr}, \text{Fe})_{23}\text{C}_6\) linearly decreases.