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Abstract

Full Text

PHYSICAL CHEMISTRY

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THERMOELECTRIC PROPERTIES OF CHROMIUM SILICIDES

(Presented by Academician I. P. Bardin on 6 VIII 1956)

The study of the electrical and thermoelectrical properties of chromium alloys with silicon is of interest in connection with the search for materials possessing semiconductor properties.

Chromium forms a number of chemical compounds with silicon. The composition has been established and the crystal structure has been studied for the compounds: CrSi_2 , CrSi , and Cr_3Si ⁽¹⁾. There are data on the existence of silicides of the compositions Cr_2Si ⁽²⁾ and Cr_3Si_2 ^(2, 3). On the basis of a study of the phase diagram by methods of X-ray diffraction and microstructural analyses, we did not detect the latter two compounds, and only one intermediate phase between the compounds CrSi and Cr_3Si , of composition Cr_5Si_3 , was established.

Information on the thermoelectrical properties of chromium silicides is lacking, and that on the electrical properties is very limited. In work ⁽³⁾, data are given on the specific electrical resistance of chromium-silicon alloys. The authors used silicon containing up to 1.3% metallic impurities; therefore, these data cannot characterize the electrical properties of individual silicides.

Fig. 1. Thermoelectromotive force α (a) and specific electrical conductivity σ (b) of silicon alloys with chromium.

We studied the electrical and thermoelectrical properties both of individual silicides and of heterophase alloys rich in silicon.

The alloys were melted in quartz crucibles under a flux—barium chloride—in a high-frequency furnace. The starting materials were electrolytically refined chromium and silicon of 99.8% purity. Homogenizing annealing was carried out at 1100° for four days in vacuum, followed by quenching in water. The

phase composition of the chromium silicides was established by methods of X-ray diffraction and microstructural analyses. The properties were measured by the compensation method using a PPTV-1 potentiometer. The thermoelectromotive force was measured in a couple with copper.

The alloy of composition Cr_5Si_3 , after melting, was porous; therefore it was ground, pressed, and sintered, after which its properties were studied.

The results of the measurements are presented in Fig. 1. The electrical conductivity of alloys in the heterophase region from 0 to 40 wt.% Cr increases only slightly with increasing chromium content and for the compound CrSi_2 is about $150 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$. Upon the appearance of CrSi silicide in the alloys (at

concentration of chromium exceeds 48 wt.%) the electrical conductivity of the alloys rises sharply, reaching, at 65 wt.% Cr, a maximum value of $4000 \text{ } \Omega^{-1} \cdot \text{cm}^{-1}$.

The thermoelectromotive force of the alloys also changes with composition. At low chromium concentrations the thermoe.m.f. of the alloys falls to zero, then changes sign, increases as the chromium content rises, and reaches the maximum positive value in alloys near the composition of the compound CrSi_2 . In the composition range bounded by the silicides CrSi_2 – CrSi , the thermoe.m.f. falls to $-12 \cdot 10^{-3} \text{ mV/deg}$.

Table 1

Compound	CrSi_2	CSi	Cr_5Si_3	Cr_3Si
Composition, wt.% Cr	47.5	65.0	75.4	84.0
$\sigma \text{ } \Omega^{-1} \cdot \text{cm}^{-1}$	150	4000	1500	22 000
$\alpha \cdot 10^{-3} \text{ mV/deg}$	+90	-12	-2	-

The thermoelectromotive force and electrical conductivity of the silicide CrSi_2 do not depend on heat treatment.

Table 1 gives data on the electrical conductivity and thermoe.m.f. of individual silicides.

It is seen from Table 1 that only the compound CrSi_2 , in the magnitude of its thermoe.m.f. and electrical conductivity, can be assigned to compounds of the semiconductor type; therefore, for it a study was carried out of the dependence of electrical conductivity and thermoe.m.f. (in the temperature range from 20 to 600°) (see Figs. 2, 3, 4).

From the curve of the change of σ with temperature (Fig. 2, b) it is seen that up to 400° the electrical conductivity of CrSi_2 decreases somewhat. However,

with a further increase in temperature an increase in electrical conductivity is observed, which confirms the semiconductor properties of the compound CrSi_2 .

Fig. 2. Dependence of the thermoelectromotive force α (a) and the specific electrical conductivity σ (b) of the compound CrSi_2 .

Figure 3 gives the logarithmic dependence of electrical conductivity on temperature, from which it follows that at low and high temperatures the conductivity has a different character. Up to 400° the electrical conductivity of the substance is determined mainly by the current carriers of impurities; at higher temperatures it is effected predominantly by the current carriers of the main substance. The increase of electrical conductivity with temperature in the region of intrinsic conductivity occurs according to an exponential law and is expressed on the graph by a straight line. The width of the forbidden band of this silicide can be determined from the value of the tangent of the angle of inclination of the straight line to the abscissa axis. It is 1.3 eV,

$$\Delta E_{\text{CrSi}_2} \simeq 2.2 \cdot 10^{-12} \text{ erg} \simeq 113 \text{ eV}.$$

Fig. 3. Dependence of $\ln \sigma$ on $1/T_{abs}$ for the compound CrSi_2 .

Figure 3 also shows the temperature dependence of α . The thermoelectromotive force in the region of impurity conductivity increases with temperature from $90 \cdot 10^{-3}$ to $140 \cdot 10^{-3}$ mV/deg. Upon transition to the region of intrinsic conductivity it falls to $80 \cdot 10^{-3}$ mV/deg at 610° . The character of the change of the thermoelectromotive force with temperature corresponds to the regularity derived for electron and hole semiconductors (⁴).

Thus, the study of the electrical and thermoelectric properties of chromium silicides has shown that the compounds Cr_3Si , Cr_5Si_3 , and CrSi are characterized by a metallic type of conductivity; the compound CrSi_2 is a semiconductor with an activation energy of about 1.3 eV.

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