INVESTIGATION OF THE ELECTROPHYSICAL PROPERTIES
OF ALLOYS BASED ON SEMICONDUCTOR DISILICIDES OF
CHROMIUM AND MANGANESE

L. D. Dudkin and E. S. Kuznetsova

The A. A. Baikov Institute of Metallurgy, Academy of Sciences, USSR

Translated from Poroshkovaya Metallurgiya, No. 6 (12), pp. 20-31, November-December, 1962

Original article submitted April 14, 1962

The production of high-temperature semiconductor materials is a very important problem. Semiconductor disilicides of chromium and manganese can play a substantial role in resolving the problem since they possess high thermal and corrosion resistance.

However, these compounds have not been thoroughly studied and some of the data on the subject [1-13] are contradictory.
Review of the literature. According to paper [1] CrSi$_2$ fuses with an open maximum at 1550 ± 20°C, is resistant to the action of aggressive reagents and does not oxidize in air at temperatures up to about 1100° [4,5]. The homogeneous region of this compound lies in the range CrSi$_{1.99}$-CrSi$_{2.25}$ [7]. Data of different authors on the width of the prohibited zone vary in quite wide limits: about 1.1 eV [10], 0.3-0.4 eV [7], 0.1 eV [8].

The state diagram for the system Mn-Si was studied in papers [1, 11, 12] according to which the compound MnSi$_2$ is formed by the reaction

\[ \text{HC} + \text{MnSi} \rightleftharpoons \text{MnSi}_2 \]

at about 1155°, or by the reaction

\[ \text{HC} + \text{Si} \rightleftharpoons \text{MnSi}_2 \]

at 1144°.

According to paper [8] manganese disilicide at room temperature has a coefficient of thermo-emf of the order of +80 - 120 μV/deg depending on the purity of the original materials) with an electric conductivity of 300-400 Ω$^{-1}$·cm$^{-1}$. With an increase in temperature, the electric conductivity falls, and the thermo-emf rises.

In the paper [13] the electrical properties of alloys in the system Mn-Si in the range 20-80 atomic % Si were also investigated and a conclusion was drawn on the existence of a new compound, Mn$_2$Si$_4$, in the Mn$_2$Si-MnSi$_2$ region. However, this conclusion was not quite correct, since the author did not control the phase composition of the alloys and their equilibrium.

Raw Materials, Methods of Making and Studying the Alloys

1. The starting materials were electrolytic refined chromium (99.9%) silicon, obtained by the Beckett method (99.99%) and electrolytic manganese prefused twice in a vacuum, containing traces of Al, Si, Cu and less than 0.001% Pb, Mo, Ti and Co according to spectral analysis.

2. Specimens based on CrSi$_2$ were prepared by a method developed by the authors involving the fusion of the raw materials in evacuated quartz ampoules. In view of the relatively low elasticity of the vapors of Cr and Si at the alloying temperature of disilicide (1.7 and 0.25 mm Hg pressure, respectively [14]) it may be expected that significant deviations in the composition of the specimens from the original composition will result.

To create a temperature gradient over the cross section of the walls of the quartz ampoule, use was made of high-frequency heating of the batch using a water-cooled quartz "jacket." So that the specimens would be dense and not develop shrinkage cavities, we used the method of controlled crystallization which was done by slowly raising the inductor thus ensuring a gradual lifting of the crystallization front from bottom to top. In addition, to densify the specimens by grinding the grains and to avoid the development of liquidation over the length of the ingot (blank), several of them were used for vibration mixing of the melt at a frequency of 100 cps.

Cylindrical specimens for investigating the properties were made from preliminarily alloyed materials (same equipment), but in wider ampoules and without controlled crystallization. The weight of the specimens during alloying varied by about 0.2%. If we consider the closeness of the elasticity values of vapors of Cr and Si at the alloying temperature of the specimens, then it is possible to assume the variation in the composition of the alloy from the starting batch composition to be insignificant.

Cast specimens were annealed in quartz ampoules with argon according to the following schedule: 800° - 12 h; 900° - 12 h; 1000° - 24 h; 1100° - 24 h. The specimens were cooled with the furnace.

3. To make alloys of Mn-Si the starting components were alloyed in evacuated quartz ampoules using high-frequency heating. Later, to obtain specimens of the required dimensions, the resulting alloy was placed in a quartz ampoule of the necessary diameter and remelted in a resistance furnace. After carefully mixing of the alloy, it was cooled in air.

The identical conditions of preparing the alloys and the small reduction in weight of the specimens (about 0.2%) compared with the weight of the starting batch means that the variation in composition from the calculated composition can be considered to be insignificant.