COEFFICIENTS OF THERMAL EXPANSION OF CHROMIUM DISILICIDE AND ITS SOLID SOLUTIONS WITH TiSi₂ AND VSi₂

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The higher chromium silicide has been the subject of numerous investigations, mainly because of its good oxidation resistance and semiconducting properties at elevated temperatures. However, although much information on various physical properties of CrSi₂ is now available, the thermal characteristics of this silicide have so far been investigated only very superficially. It is only recently that some investigations of its specific heat and enthalpy have been reported in the literature. Even less information has been published on the thermal expansion characteristics of CrSi₂, although their knowledge is indispensable for analyzing the operating conditions of parts made of this material and for evaluating the characteristics of interatomic reaction in its lattice.

Thus, Davydov [1] has reported the results of investigations conducted on ten polycrystalline alloys prepared from commercially pure chromium and silicon (containing between 0 and 100% Si), at temperatures from 20 to 1000°C. Data have been included on the coefficients of thermal expansion (α) of two specimens with compositions (~49.6 and 54.8 wt.% Si) close to that of the stoichiometric disilicide (~51.9% Si). From the experimental results of Davydov it follows, firstly, that α strongly depends on alloy composition and, secondly, that α rapidly increases with rise in temperature (Fig. 1). Entirely different results were obtained by Verkhorobin and Matyushenko [2], whose x-ray diffraction investigation was carried out on purer substances. In particular, these authors came to the conclusion that the interplanar spacings in the chromium disilicide lattice linearly increase with rise in temperature and the coefficient of thermal expansion along the a and c axes are: αa = 9.2 × 10⁻⁶ and αc = 7.4 × 10⁻⁶ 1/°C.

The causes of such substantial differences in the results of these investigations are not clear. It may be that the discrepancies are partly due to the use of more impure (and two phase) substances in [1], as well as to some errors in experimental technique, whose nature would be difficult to establish.

The authors have been unable to discover any other information on the thermal expansion of CrSi₂. Similarly, no such information is available on the properties of solid solutions of this silicide. In this connection, an investigation was undertaken with the aim of determining the coefficients of thermal expansion of both single phase chromium disilicide (within its homogeneity limits) [3, 4], and its solid solutions with TiSi₂ and VSi₂.

Specimen Testing Techniques

A dilatometric study of the thermal expansion of the alloys (between 20 and 900°C) was conducted, using a Chevenard instrument, by the differential technique with photographic recording. A Pyres (Ni - Cr - W) alloy was used as a reference standard. The following formula was employed for calculating α:

\[ \alpha = \alpha_f + K_s K_f (\alpha_f - \alpha_q) \frac{dy}{dt}. \]

where \( \alpha, \alpha_r, \) and \( \alpha_q \) are the coefficients of expansion of the specimen, the reference standard, and quartz, respectively; \( K_1 \cdot K_2^{-1} = 0.501 \) is the ratio of the magnification coefficients along the dilatogram axes; \( \frac{dy}{dt} \) is the tangent of the slope of the dilatogram at a given temperature.

In addition, values of \( \alpha \) were determined also by the x-ray diffraction technique. The lattice parameters (a and c) of specimens of elevated temperatures were measured by means of a bracket type attachment mounted on a URS-50I diffraction apparatus. Photography was performed in chromium K\( \alpha \) radiation. Special attention was paid to temperature stabilization, as a result of which temperature fluctuations in the measurement of each pair of parameters (a and c) did not exceed 1 deg C. The results obtained were corrected on the basis of data yielded by photographs of a reference standard (a massive nickel specimen).

The starting materials for the preparation of alloys were refined electrolytic chromium (\( > 99.98\% \) Cr), titanium (\( > 99.95\% \) Ti), and vanadium (\( > 99.65\% \) V), as well as crystalline silicon (\( > 99.997\% \) Si). Appropriate weighed batches of the components were melted together in an MVP-3M high frequency furnace with a purified argon atmosphere (\( P_{Ar} = 100 \) mm Hg), using alundum crucibles.

Cylindrical specimens (50 mm long) for the dilatometric investigations were prepared by sucking up the molten materials into quartz capillary tubes of about 3 mm in diameter. Before testing, the specimens were subjected to homogenizing annealing for 100 h at 1100°C.

In the study of thermal expansion by the x-ray diffraction technique, use was made of pressed tablets sintered in a vacuum for 20 h at 1100°C.

This procedure was employed for obtaining three chromium disilicide specimens of various compositions, as well as specimens of the solid solutions \( \text{Cr}_1-x\text{V}_x\text{Si}_2 \) (0.0 \( \leq x \leq 1.0 \)) and \( \text{Cr}_1-x\text{Ti}_x\text{Si}_2 \) (0.0 \( \leq x \leq 0.8 \)). The metallographic and x-ray diffraction examinations established that, after homogenizing, all the alloys had a single-phase structure.

**TEST RESULTS AND DISCUSSION**

1. \( \text{Cr}_{1+x}\text{Si}_{2-x} \). By processing the dilatograms of the chromium-disilicide specimens of various compositions, it was possible to calculate the mean coefficients of thermal expansion of this material, \( \bar{\alpha} = \frac{1}{3}(2\alpha_r + \alpha_q) \). The results obtained in this manner, together with data of other investigators [1, 2], are presented in Fig. 1.

The figure shows, in the first place, that the results obtained by various authors at low test temperatures (~100°C) are in satisfactory agreement. Further, it was established that, as indicated by Davydov [1], \( \bar{\alpha} \) rapidly increases with rising chromium content of the alloys. Here, a relatively marked change in \( \bar{\alpha} \) is observed on transition from single phase \( \text{Cr}_{1+2}\text{Si}_{2-x} \) specimens to two phase materials [1] containing either monosilicide (49.66% Si) or silicon (54.84% Si) precipitates. Finally, in agreement with the results of Davydov [1] but contrary to those of Verkhorebin and Matyushenko [2], it was found that the coefficient of thermal expansion of chromium disilicide is very strongly affected by temperature. However, contrary to Davydov's assertion that \( \bar{\alpha} \) increases in a steady manner with rise in temperature, our results indicate that the relationship is more complex, its characteristics being exhibited particularly clearly by the stoichiometric specimen (\( \text{CrSi}_2 \)). Its \( \bar{\alpha}(T) \) polytherm exhibits two characteristic extreme points, a maximum near \( t_1 = 300°C \) and a minimum at about \( t_2 = 600°C \). Otherwise, it should be noted that the position of the former depends not only on composition, but also on conditions of alloy preparation. Experiments have demonstrated that values of \( t_1 \) for different specimens, even originating from the same heat, can vary from 300 to 400°C. These variations may possibly be due to differences in the extent of texturization and grain size, slight fluctuations in chemical composition, etc. The last of these factors, which is essentially caused by some vaporization of the components and segregation processes, is particularly significant. In fact, as can be seen from Fig. 1, even a small change in alloy composition (~0.2%) substantially alters the value of \( t_1 \).

The results of the x-ray diffraction studies of stoichiometric chromium disilicide (see Fig. 1) are qualitatively consistent with these data. They emphasize the complex and nonuniform character of the relationship between the mean coefficient of thermal expansion of \( \text{CrSi}_2 \) and temperature. This characteristic is somewhat unexpected. In fact, it is known that, in accordance with Grützig's law, the ratio of specific heat \( C_p \) to the coefficient of thermal expansion \( \alpha \) is independent of temperature. The same follows from the relationship \( |W_\alpha| = 1.5 C_p/\alpha \), where \( W_\alpha \) is the energy of one gram-atom at 0 K, established by Shmerts [6]. From this it follows that the character of the temperature dependences of \( \alpha \) and \( C_p \) should be identical. This, however, does not apply to chromium disilicide, whose specific heat increases in a steady manner with...