FEATURES OF FORMATION OF SOLID SOLUTIONS OF TRANSITION-METAL DISILICIDES DEPENDING ON THE MECHANISM OF THE SOLID-PHASE REACTION

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Numerous results of investigations on mechanosynthesis processes of group IV-VI transition-metal disilicides, performed by the authors and foreign researchers showed that, depending on the value of the exothermic effect of the reaction, the interaction proceeds by two mechanisms: the mechanism of solid-phase diffusion (SD) or mechanism of mechanically stimulated reactions (MSR), which determines the approach to the synthesis of nanopowders: mechanosynthesis or low-temperature synthesis of preliminarily mechanoactivated reaction mixtures.

Our previous investigations showed that the formation of $MoSi_2$ during high-energy mechanotreatment proceeds by the MSR mechanism, whereas the formation of $CrSi_2$ occurs by the SD mechanism, and the preparation of a homogeneous product requires long treatment (for more than 200 h). The aim of the present work us to investigate the possibilities of preparation of nanosized powders of solid solutions based on chromium disilicide or molybdenum disilicide in the process of low-temperature synthesis of mechanoactivated reaction mixtures. The high-energy mechanotreatment of reaction mixtures was performed in an AIR-0,015 planetary mill under identical conditions, namely, a powder to balls mass ratio of 1:10, treatment time of 90 min, rotation speed of 1370 rpm, in an argon atmosphere. The regularities of formation of solid solutions in the process of solid-phase interaction of activated mixtures were studied in the temperature range 300–1000 °C in vacuum. The control of reaction products in all stages was performed by X-ray analysis and electron microscopy.

It was established that the activated reaction mixtures for the preparation of solid solutions based on chromium disilicide $(Cr,Me)Si_2$, where Me is Ti and Ta, are mixtures of Si, initial metals, and nuclei of individual disilicides. The formation of solid solutions $(Cr,Ti)Si_2$ and $(Cr,Ta)Si_2$ during treatment proceeds through intermediate stages of formation of individual silicide phases from lower silicides to higher silicides with their following homogenization, which requires long isothermal hold. It was established that preliminary mechanoactivation under the conditions of the experiment does not influence the regularities of the solid-phase synthesis, but leads to a decrease in the initial and final temperature of the solid-phase interaction by 200–300 °C as compared with those for micron powders. As a result of the low-temperature synthesis, we obtained nanostructured powders of solid solutions with a coherent-scattering region (CSR) of about ~ 200 nm.

In the case of solid solutions based on molybdenum disilicide $(Mo,Me)Si_2$, where Me is Cr and Nb, according to the X–ray analysis data, already in the process of mechanoactivation, solid solutions based on the α-$MoSi_2$ tetragonal modification (which make up about 50–60 %) form. Along with these solid solutions, the activated mixtures contain also Mo and Si in the roentgen-amorphous state.

According to the X-ray analysis data of the solid-phase interaction products, in the process of heat treatment, the formation of solid solutions is observed in the temperature range 700–800 °C. The CSR of the obtained powders is 40–70 nm. The absence of lower silicide phases in the temperature range 400–600 °C and an insignificant rate of formation of solid solutions (30 min) indicate that the reaction proceeds in the pseudo-self-propagating high-temperature synthesis regime.

According to the electron microscopy data, the synthesized solid-solution powder consists of agglomerates of polycrystalline particles with a size $\leq$100 nm.

The performed investigation showed the difference between the mechanisms of formation of solid solutions, which is connected with the chemical nature of compounds and the value of the exothermic effect of the reaction.