SYNTHESIS OF DISPERSED POWDERS, CRYSTALS, AND COATINGS OF CHROMIUM SILICIDES, AND THEIR OXIDATION RESISTANCE

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Electrochemical synthesis of chromium silicides was carried out in the NaCl-NaF-K_2CrO_4-K_2SiF_6 melt.Voltammetric curves showed waves of electroreduction of oxyfluoride complexes of chromium and silicon at significantly different potentials, -(0.7-0.9) V and -(1.6-1.9) V, respectively.Chromium was deposited in the form of oxide and reduced by silicon directly at the cathode.Thermodynamic calculation of reactions of reduction of chromium oxide by silicon to form silicides of different composition showed that, at 900°C, the most thermodynamically favorable reaction is formation of silicides Cr_3Si and $CrSi_2$.

Depending on the electrolysis parameters, both individual phases of Cr_2O_3, Cr_3Si, $CrSi_2$, and mixtures thereof.The process has been optimized for highest silicide $CrSi_2$ obtaining.Chromium disilicide yield was 0.2-0.3 g/A·h.

Crystals of chromium silicide were synthesized from pure components in metal melt.To reduce the synthesis temperature, molten mixture Sn-Zn (1:10) was used as a solvent, into which a mixture of Cr i Si was placed in a ratio corresponding to the stoichiometry of the desired product.The resulting product was examined by scanning electron microscopy and X-ray analysis methods.Needle-shaped crystals were formed which were aggregated with each other to the some extent.Average crystals size was as follows: 200 mm long and 15-20 microns in diameter.X-ray phase analysis confirmed the hexagonal structure of disilicide crystals; crystal lattice parameters were also determined.Impurities of Sn and Zn were not detected; yet small amount of CrSi phase was found.

For obtaining of coatings of chromium disilicide, method of current-free deposition of silicon onto the surface of chromium was used from halide melts of the following composition, mol. %: NaCl - 36.58, KCl - 36.85, NaF - 21.95, Na_2SiF_6 - 4.89, Si - 21.85.When Na_2SiF_6 and Si powder were added to chloride salts mixture, reproportioning reactions between Si and Si^{4+} occur at the surface of the metal substrate (Cr) Silicon formed from Si^{+2} diffuses into the metal and forms an alloy with the metal substrate.Formation of chromium disilicide occurs according to the following reaction:

$$Cr + 4SiF_6^{4-} = CrSi_2 + 2SiF_6^{2-} + 12F^-$$

$$CrSi_2 + Cr\ (plate) = Cr\text{-}Si\ (layer)$$

The latter is caused by the difference of the thermodynamic activity of elemental silicon and silicon within the composition of the silicide layer.Growth constant of coating for this reaction was found to be equal to 147□10^{-16} m^2/s and is caused by diffusion in the Cr-Si system.

Using characteristic radiation of chromium and silicon, cross-section was divided into three zones, namely chrome substrate (1), Kirkendall zone (2), and silicide layer (3), being different by the ratio of chromium and silicon in their composition. Using characteristic radiation of silicon, it was shown that the substrate consisted of chromium only and scarcely contained silicon. Zone Kirkendall (2) was of intermediate composition between the metal substrate and the silicide layer which may correspond to the composition of CrSi silicide and was < 25 μm thick.The results of X-ray phase analysis confirmed that the resulting coating corresponds to $CrSi_2$ composition.

Oxidation stability of obtained samples was determined by methods of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in air at temperature up to 1000 °C. Up to 600 °C, samples were not oxidized. Nanopowders started to oxidize at about 800 °C, and crystals and coatings - at about 700 °C, which may be due to particle size and morphology of samples, as well as due to method of the product obtaining.

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