A MICROMECHANISTIC CRITERION FOR CHANGEOVER OF INTERACTION MECHANISMS DURING SHS OF REFRACTORY INTERSTITIAL PHASES (CARBIDES, NITRIDES)

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Self-propagating high-temperature synthesis (SHS) has acquired a wide use as a versatile cost-effective method for producing a wide range of refractory compounds such as carbides, nitrides, borides, intermetallics, and composite materials which possess a fine-grain structure and superior properties. Recent experimental studies have revealed the non-equilibrium nature of phase and the structure formation during SHS [1,2], which is typically ascribed to extreme conditions in SHS waves such as (i) high heating rate up to 106 K/s, (ii) steep temperature gradient up to 105 K/cm, and (iii) fast accomplishment of interaction, about 1 s.

The main drawback of SHS is the impossibility of controlling transformations in the SHS wave in situ after a specimen is ignited; the product structure can only be influenced by varying the composition of the charge mixture and initial temperature. Development of controllable SHS processes is a complex task which can be solved only through elaboration of mathematical models adequately describing intricate physical and chemical phenomena inherent in SHS. Recently it has been demonstrated that the existing kinetic models can neither provide an adequate description of the experimentally observed non-equilibrium phenomena in SHS nor the peculiarities of phase and structure formation, and a non-equilibrium concept for modeling SHS has been proposed [3]. Also, a micromechanistic criterion has been derived [3] to determine the conditions for cracking of a thin film of a primary product (e.g., TiC_x) forming on the surface of a metal particle (here Ti) due to solid-state interdiffusion upon heating in the SHS wave until the melting temperature of the metal is attained. Then the molten metal spreads and engulfs non-metallic particles (here carbon), and after that only the non-equilibrium dissolution-precipitation mechanism of structure formation can operate in SHS.

In this work, the obtained criterion is used for constructing a diagram describing the phase and structure formation mechanisms for high-temperature interaction of a metallic and non-metallic reactants in the non-isothermal conditions at different heating rates. A diagram for the formation of titanium carbide is built using realistic parameter values determined independently, viz. chemical diffusion coefficients for the growth of TiC in Ti-C diffusion couples, which are known in literature. It is demonstrated that at high heating rates corresponding to SHS in the wave propagation mode (above 10^4 K/s) only the substantially non-equilibrium dissolution-precipitation mechanism can operate. At slower heating rates and small particle size of the metallic reactant (Ti) the quasi-equilibrium mechanism of phase and structure formation can take place where the rate-controlling stage is solid-state diffusion across the refractory product layer (TiC) which grows on the surface of the metallic particle, thus separating the starting reactants (solid or liquid Ti and solid C). In this situation, the molten metal cannot break the outer spherical shell of the refractory product (here TiC) and thus the melt spreading does not occur; the interaction proceeds in the "slow" (solid-state diffusion-controlled) mode since the diffusion coefficient in this layer is low.

The diagram clearly demonstrates a difference in the structure formation mechanisms between SHS and traditional furnace synthesis of the same compound (TiC). Similar diagrams can be calculated for SHS of other refractory interstitial compounds such as carbides, nitrides, certain borides, etc.

Earlier, the diagram of interaction mechanisms for SHS in the Ti-N system has been built taking into account the nitrogen pressure and kinetics of nitrogen adsorption by titanium particles during gas flow through a porous pellet in the SHS wave front [4]. Combination of these two diagrams can be used for predicting the interaction route and, hence, the microstructure of the synthesized product.

References

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