

Interaction Kinetics In SHS: Is the Quasi-Equilibrium Solid-State Diffusion Model Valid?

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ABSTRACT

A consistent analysis of the SHS kinetics based on the quasi-equilibrium solid-state diffusion model (the non-isothermal diffusion-type Stefan problem) is performed on the example of the Ti-C system using both experimental parameters of the SHS wave and known diffusion data for the product phase, TiC. A micromechanistic criterion for the changeover of interaction routes due to melting and spreading of the metallic reactant is derived. Calculations reveal that the diffusion-controlled growth kinetics (the so-called "emptying-core mechanism") cannot provide the heat release necessary for sustaining SHS, and the product porosity will substantially differ from experimental observations. Further, a quasi-equilibrium dissolution-precipitation model (the so-called "shrinking-core mechanism"), where a solid nonmetal particle (C) dissolves in the molten metal (Ti) due to diffusion across a thin product film (TiC) whose thickness remains constant, is analyzed. It is shown that with realistic diffusion data this mechanism loses its physical meaning: the film thickness must be below the critical nucleus size. It is demonstrated that this quasi-equilibrium concept is not applicable to modeling the SHS of refractory interstitial compounds. As an alternative, a qualitative nonequilibrium dissolution-precipitation concept is proposed which agrees with the experimental results of the structure of SHS products known in literature.