Innovative Processing and Synthesis of Ceramics, Glasses, and Composites IV

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Innovative Processing and Synthesis of Ceramics, Glasses, and Composites IV

Proceedings of the Innovative Processing and Synthesis of Ceramics, Glasses, and Composites symposium at the 102nd Annual Meeting of The American Ceramic Society, St. Louis, Missouri, April 29–May 3, 2000.

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COVER PHOTO: "SEM micrograph of α-alumina powder made by combustion synthesis," is courtesy of Melissa V. Collins, Deidre A. Hirschfeld, and Lauren E. Shea, and appears as figure 2 in their paper "Effects of Processing Parameters on Properties of Alumina Formed by Combustion Synthesis," which begins on page 83.

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Preface

An international symposium, "Innovative Processing and Synthesis of Ceramics, Glasses, and Composites" was held during the 102nd Annual Meeting of The American Ceramic Society in St. Louis, Missouri, April 30–May 3, 2000. The purpose of this symposium was to provide an international forum for scientists, engineers, and technologists to discuss and exchange ideas, information, and technology on advanced methods and approaches for processing and synthesis of ceramics, glasses, and composites. A total of 120 papers, including nine invited talks, were presented in the form of oral and poster presentations, indicating continued interest in the scientifically and technologically important field of ceramic processing. Authors from 21 countries (Brazil, Belgium, Canada, China, Egypt, France, Germany, India, Italy, Japan, Korea, Mexico, Norway, Russia, Slovenia, Spain, Sweden, Taiwan, Thailand, United Kingdom, and the United States) participated. The speakers represented universities, industry, and government research laboratories.

These proceedings contain contributions on various aspects of synthesis and processing of ceramics, glasses, and composites that were discussed at the symposium. Fifty-four papers describing the latest developments in the areas of reaction forming, combustion synthesis, plasma processing, rapid prototyping and laminated object manufacturing, electrophoresis, freeze drying, polymer processing, sintering, joining and bonding, nanotechnology, processing of composites, porous ceramics, electronic ceramics, functionally graded materials, coatings and membranes, thin films, modeling and simulation, and characterization, etc. are included in this volume. Each manuscript was peer-reviewed using The American Ceramic Society review process.

The editors wish to extend their gratitude and appreciation to all the authors for their cooperation and contributions, to all the participants and session chairs for their time and efforts, and to all the reviewers for their useful comments and suggestions. Financial support of The American Ceramic Society is gratefully acknowledged. Thanks are due to the staff of the meetings and publications departments of The American Ceramic Society for their invaluable assistance.

It is our earnest hope that this volume will serve as a valuable reference for the researchers as well as the technologists interested in innovative approaches for synthesis and processing of ceramics, glasses, and composites.

Narottam P. Bansal

J.P. Singh

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REACTIVE SYNTHESIS AND FORMING OF TRANSITION METAL SILICIDES

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ABSTRACT

Solid-state synthesis and forming of silicides from metal – silicon powder mixture is summarized with two reaction models: nucleation-controlled and diffusion-controlled reactions. Transition metal – silicon systems are employed to experimentally describe fundamental features of these models. Former reaction mechanism is characterized by fast-rate reaction starting from locally formed embryos. In the latter reaction mechanism, reaction rate becomes slow and continuous often together with formation of intermediate or meta-stable phases. This reaction model enables us to make solid-state processing design for formation of functional silicide materials.

INTRODUCTION

Refractory metal silicides such as $MoSi_2$ or $NbSi_2$ have been keenly studied as a promising structural intermetallic compound to be working at the elevated temperature [1]. Typical example is a $MoSi_2$; high melting point and intrinsic heat and oxidation resistance due to formation of SiO_2 surface layer as a protect to matrix materials. In order to increase its ductility and toughness at the ambient temperature, there have been proposed various ideas and processings: application of P/M approach from $MoSi_2$ and $NbSi_2$ mixture [2], formation of a solid solution by addition of WSi_2 [3], composite materials with SiC particles or whiskers [4,5], or toughening with addition of niobium [6]. The conventional processing such as solidification and melting or P/M (Powder Metallurgy) approach is difficult to make near-net shaping of these silicides since relatively high temperature is necessary for melting, homogenizing or sintering. The fabricated specimens suffer from lack of endurance in mechanical testing mainly because of low density, residual defects, grain growth or microstructure coarsening. Solid-state synthesis is found to be effective to reduce the critical temperature to commence reaction

into silicides and to make net-shaping and microstructure control simultaneously. In particular, this type of approach is favored by formation of di-silicides from the refined metal and silicon powder mixture [7-9].

Recently, various functional silicide materials are high-lighted in applications. Typical example can be seen in Mg-Si or Ni-Si systems. Both constituents in Mg-Si system have different melting temperature and vaporizing pressure so that solid-state synthesis is effective to make synthesis of n-type semi-conducting thermoelectric material of Mg_2Si. $NiSi_2$ is relatively easy to synthesize but difficult to control microstructure, phase and residual silicon, aiming for secondary-battery materials.

In the present paper, transition metal and silicon systems are employed to experimentally discuss the solid-state reaction models, aiming for construction of design knowledge-base of solid-state processing into silicides. First, two solid-state reaction mechanism models are proposed with reference to silicide formation in thin films. One is a nucleation-controlled reaction, where local embryo or nuclei is first formed by enhancement of free energy among interface between two constituents and local reactions are cascaded into global reaction in a short duration. The other is a diffusion-controlled reaction, where mixture powders are gradually reacted to intermediate or meta-stable phase and further reacted to final di-silicides in longer duration. Nine transition metal – silicon systems are first categorized into two groups, and, this knowledge is applied to synthesis design in Mg-Si and Ni-Si systems.

DESIGN BASE FOR SOLID-STATE SYNTHESIS

In the conventional material processing, the phase diagram and the equilibrium thermo-dynamics become a map and a compass in every aspect of material processing. However, both melting – solidification method and P/M approach are in vain to make synthesis and forming of engineering silicides, having endurable properties in practice. Consider how to improve the ductility and toughness of $MoSi_2$ at the ambient temperature. Formation of its composites with ceramics or other metals can be only made by the solid-state synthesis [4-9]. Grain size reduction can be expected on the route of solid-state synthesis. In this approach, however, non-equilibrium phase or activated microstructure have a significant role in processing. Then, there are little directions or common knowledge to construct material processing design in selection of various routes. Let us propose here a reaction mechanism model to classify various reactions from elemental powder mixture into silicides with use of fundamental data of silicide reactions.

The first item is a reaction datum with respect to its type, the structure of synthesized silicides or melting point, as listed in Table I from various data sources [10-15]. As had been reported in elsewhere [10], the silicon melts are active to make reactions even with refractory metals above its melting point, resulting in a congruent reaction into disilicides in most cases. SHS (Self-Heating Synthesis) utilizes this enhancement of reactivity between the solid transition or refractory metals and silicon melts.

Table I. Reaction from elemental mixture to transition metal di-silicides.

Transition Element	Type of reaction	Onset Temperature (K)	Structure of synthesized silicides
Ti	Congruent	- 1770	Orthorhombic
V	Congruent	- 1950	Hexagonal
Cr	Congruent	- 1750	Hexagonal
Zr	Peritectic	- 1900	Orthorhombic
Nb	Congruent	- 2200	Hexagonal
Mo	Congruent	- 2300	Tetragonal Hexagonal
Hf	Peritectic	- 2200	Orthorhombic
Ta	Congruent	- 2300	Hexagonal
W	Congruent	- 2600	Tetragonal Hexagonal

Note 1) Among these transition metal silicides, di-silicide becomes more unstable than mono-silicide or tri-silicide.

Note 2) Crystalline structure can be sometimes changed by reaction temperature.

The second item is the enthalpy of formation in metal – silicon system. Table II lists the reference data of the enthalpy of di-silicide formation in the nine transition – silicon systems [10]. In most of systems, the formation energy exceeds over 100 kJ/mol; then, if the sustainability of reaction into di-silicide is mainly governed by this formation energy, most of di-silicide formation could become easily enhanced to fast-rate reaction or explosive reaction as seen in SHS where reactivity is mainly sustained by the formation energy [16]. To be noted, among nine systems, zirconium – silicon system has the highest formation energy. Sometimes, formation energy of mono-silicide or other compounds becomes higher than that for di-silicides.

Table II. Formation energy in the metal – silicon system.

Transition element	Formation energy (kJ/mole)
Ti	133
V	125
Cr	90
Zr	160
Nb	125
Mo	135
Hf	143 for HfSi; 227 for $HfSi_3$ *
Ta	125
W	100 *2

*) No data are available for $HfSi_2$.

*2)Scattered data are reported in literature.