Powder Technology 288 (2016) 191–201

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Effect of precursor fraction on silicide nanopowder growth under thermal plasma conditions: A computational study

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ARTICLE INFO

Article history:
Received 12 March 2015
Received in revised form 28 October 2015
Accepted 1 November 2015
Available online 2 November 2015

Keywords:
Nanopowder
Thermal plasma
Silicide
Modeling
Co-condensation

ABSTRACT

Computational study is carried out to clarify the growth mechanisms and the effects of the silicon fraction in precursor on the fabricated nanopowders for metal–silicon binary systems (Co–Si, Mo–Si, and Ti–Si systems) under a thermal plasma condition, using a model that can simulate the collective and simultaneous combined processes of binary homogeneous nucleation, binary heterogeneous co-condensation, and coagulation among nanoparticles with different compositions as well as solidification temperature depression. Those three systems that have different ratios of the materials' saturation pressures show different growth behaviors and mature states of the nanopowders. Furthermore, parametric studies indicate that the majority of the fabricated nanoparticles have the silicon content identical to the initial precursor's silicon fraction. Because the solidification temperature depends on the silicon content in the material, the yield and size of the nanopowder are also affected indirectly by the precursor's silicon fraction.

1. Introduction

Nanopowder has attracted interests of scientists and engineers because it exhibits unique capabilities that differ greatly from those of bulk materials or powders composed of larger particles [1]. In particular, the nanopowders composed of binary alloy nanoparticles are expected as potentially useful materials [2]. However, because those raw materials usually have high melting points or boiling points, high-rate fabrication of binary alloy nanopowders is almost impossible using conventional methods such as liquid-phase deposition or grinding techniques. Even combustion processes are ineffectual because the combustion flame cannot reach sufficiently high temperatures to vaporize the raw materials; furthermore, the oxidation atmosphere for combustion causes unfavorable production of contaminants.

Meanwhile, thermal plasmas have been utilized for the effectual fabrication of binary alloy nanopowders [3–8] because thermal plasmas offer several distinctive advantages: high enthalpy, high chemical reactivity, variable properties, and steep temperature gradients. Additionally, thermofluid fields such as temperature and velocity are controllable using external electromagnetic fields [9–11].

Thermal plasma fabrication of binary alloy nanopowders involves vaporization of the raw materials and the subsequent conversion of the binary vapors into numerous nanoparticles by virtue of the high enthalpy and a high cooling rate of thermal plasma. However, the growth of a nanopowder in a binary system is tremendously complicated because such a nanopowder grows in a few tens of milliseconds through collective and simultaneous processes of binary homogenous nucleation, binary heterogeneous condensation of two-component vapors, and coagulation among nanoparticles with different compositions. Therefore, in addition to the high demand in industry, although the morphology of binary alloy nanopowders is of great interest from the scientific viewpoint of physics and chemistry as well as engineering, the growth mechanism remains poorly understood. This is true because it is impossible to observe every process using experimental approaches directly; only the characteristics of the final products can be evaluated.

On the other hand, theoretical and numerical approaches can clarify the growth mechanism and to predict the profile of the nanopowder that will be fabricated. However, fundamental schemes such as molecular dynamics (MD) calculation cannot simulate the whole growth process from nucleation until a nanopowder completes their growth because of computational resource limitations [12]. Meanwhile, in place of such schemes, which require a heavy computational load, models based on aerosol dynamics have been used to simulate the whole process of a nanopowder's collective growth. Nevertheless, most models are applicable only to unary systems [13–19].

Only a few models were developed on the basis of aerosol dynamics for the thermal plasma fabrication of nanopowder involving co-condensations of binary material vapors [7,20,21]. However, those models had to adopt several oversimplifications to obtain even simple numerical solutions; furthermore, the solutions were only mean values. We therefore developed a unique solution algorithm to analyze nanopowder growths numerically in binary systems [22–24]. That model can not only express any profile of particle size–composition

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http://dx.doi.org/10.1016/j.powtec.2015.11.005
0032-5910/

distribution (PSCD) of a nanopowder but also simulate the whole growth process of a binary alloy nanopowder even with widely-ranging sizes from sub-nanometers to a few hundred nanometers.

This study especially examines nanopowders composed of metal–silicide nanoparticles, which are silicon-based intermetallic compounds that have been fabricated for extremely small electronic and mechanical applications such as solar-controlled windows, electromagnetic shielding, and contact materials in microelectronics. Using that model, numerical calculations are demonstrated to clarify the detailed growth mechanisms and the effect of the silicon fraction in precursor on the fabricated nanopowder for three representative binary systems (Co–Si, Mo–Si, and Ti–Si systems) because these three systems typically have different saturation pressure ratios between the metal and silicon.

2. Target process and computational conditions

The target process of this study is thermal plasma fabrication of nanopowders that consist of metal–silicide nanoparticles, regarded as a vapor-phase synthesis in binary systems. Fig. 1 shows a schematic illustration of nanopowder fabrication using an induction thermal plasma (ITP). The precursor raw materials are injected into a plasma and vaporized in the high-enthalpy field of the plasma. The metal vapor and silicon vapor are transported with the flow to the plasma's tail at which the temperature drastically decreases. Consequently, either or both of the material vapors become supersaturated, which engenders homogeneous nucleation. Because it is a binary system, nuclei composed of the metal atoms and silicon atoms are generated (binary nucleation). Immediately, the binary material vapors co-condense heterogeneously on the nuclei (binary condensation). This is the fundamental growth of metal–silicide nanoparticles. Additionally, during their growth, the nanoparticles mutually collide and merge into larger nanoparticles (coagulation). These three processes progress collectively and simultaneously. Therefore, the nanopowders composed of such binary-compound nanoparticles have varieties of sizes and compositions.

The computational conditions are set to be identical to the experiments [6,7]. Fig. 2 shows the bulk gas profiles of the temperature, density and velocity which were obtained numerically by the electromagnetic fluid dynamics approach [7] for the cooling region in Fig. 1. The temperature and the velocity decrease monotonically, whereas the density increases. The precursor of a metal (Co, Mo, or Ti) and silicon (Si) are supplied as the raw materials at the total feed rate of 0.1 g min^{-1}. Our previous numerical study confirmed that the raw materials were completely vaporized in the plasma operated at the flow rate of 34.0 slm [7]. This feed rate is equivalent to 0.17% of the mass ratio to the injected argon gas. This can thereby be regarded as a dilute condition in which the effect of the raw material on the flow field is negligible.

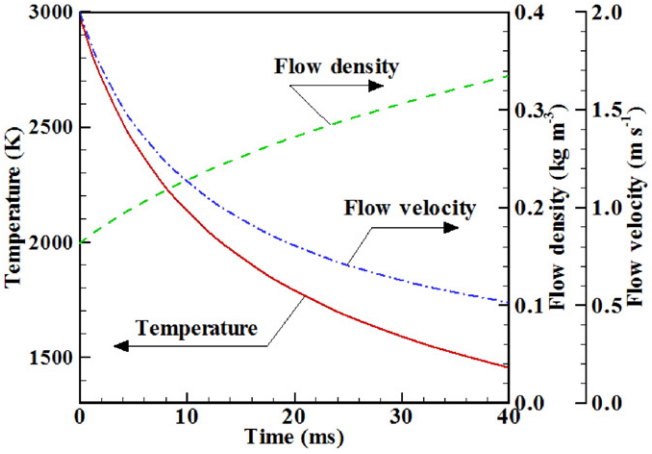

Fig. 2. Time dependence of temperature, flow velocity and mass density of the background gas.

Fig. 3 depicts the corresponding time variations of the saturation pressures for Co, Mo, Ti, and Si. The data of the saturation pressures were obtained as functions of temperature [25]. Because the temperature decreases, the saturation pressures also decrease. The saturation pressure is an important material property for a nanopowder growth, even in a unary system. In binary systems, the saturation pressure ratios of the metals to silicon (Co/Si = 10^{+1}, Mo/Si = 10^{-5}–10^{-3}, Ti/Si = 10^{-1}–10^{0}) will affect the nanopowder growths significantly. The other material properties of the metals and silicon are also obtained from Reference [25].

In this study, the computations are performed for four cases with the different material combinations and different initial silicon fractions in a precursor as controlled parameters, as summarized in Table 1. As implied in Fig. 2, the temperature decreases at the rate from 1.5×10^5 to 1.0×10^4 K s^{-1} as time passes. Corresponding to that cooling rate, the computation is carried out with the time increment Δt increasing from 5.0×10^{-6} to 2.0×10^{-5} s which provides sufficient resolution for the present condition.

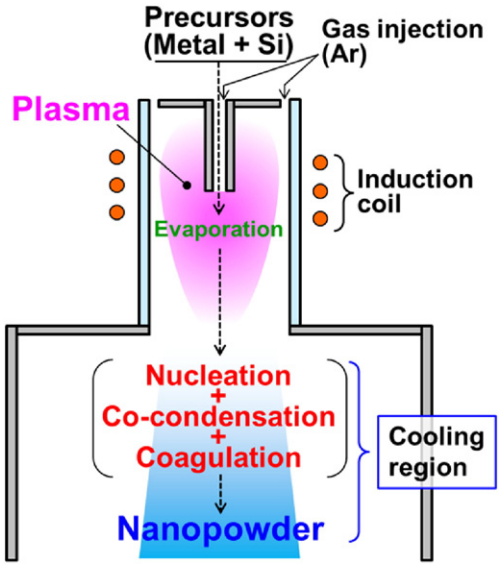

Fig. 1. Schematic of nanopowder fabrication using an ITP.

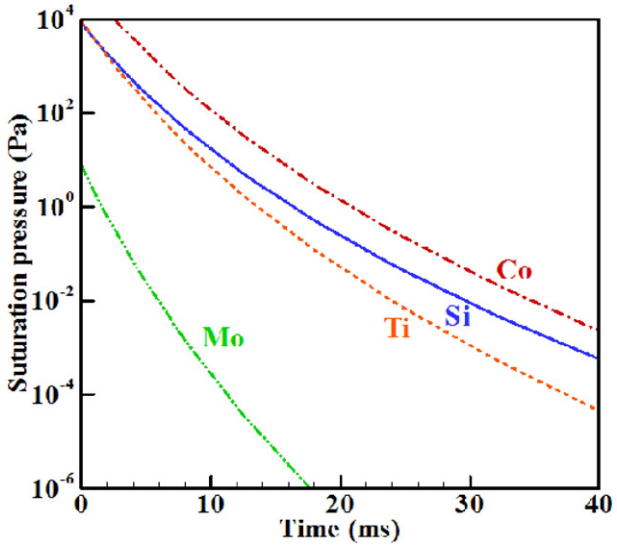

Fig. 3. Saturation pressures of the metals and silicon. The temperature-dependence data were obtained from Reference [25].