ผลของโลหะที่มีต่อกระบวนการไนไตรเดชันของซิลิคอนและสมบัติทางกลของชิ้นงานซิลิคอนไนไตรด์

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EFFECTS OF METALS ON THE NITRIDATION OF SILICON AND MECHANICAL PROPERTIES OF SILICON NITRIDE PRODUCTS

Miss Tananya Vongthavorn

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ธนัญญา วงษ์ถาวร: ผลของโลหะที่มีต่อกระบวนการไนไตรเดชันของซิลิคอนและสมบัติทางกลของชิ้นงานซิลิคอนไนไตรด์ (EFFECTS OF METALS ON THE NITRIDATION OF SILICON AND MECHANICAL PROPERTIES OF SILICON NITRIDE PRODUCTS) อ. ที่ปรึกษา: ดร.วรงค์ ปวราจารย์, อ. ที่ปรึกษาร่วม: ศ.ดร. ชิเกตากะ วาดะ, 107 หน้า. ISBN 974-17-5103-6

กระบวนการไนไตรเดชันของซิลิคอนเป็นกระบวนการหนึ่งที่ใช้ในการผลิตซิลิคอนไนไตรด์ในเชิงอุตสาหกรรม ถึงแม้ว่าวิธีนี้จะมีต้นทุนการผลิตที่ต่ำ แต่ซิลิคอนไนไตรด์ที่ได้มีเฟสอัลฟา ซึ่งเป็นเฟสที่ต้องการในปริมาณเพียง 92% เท่านั้น ซึ่งถือว่าเป็นสัดส่วนที่ค่อนข้างต่ำ งานวิจัยนี้ได้ทำการศึกษาอิทธิพลของโลหะที่ใช้ทั่วไปในการขึ้นรูปซิลิคอนไนไตรด์ เพื่อใช้ในการเร่งกระบวนการไนไตรเดชันของซิลิคอน โลหะที่ใช้ในงานวิจัยนี้ได้แก่ แคลเซียม ซีเรียม ลูทิเทียม แมกนีเซียม อิทเทอเบียม และอิทเทรียม โดยเติมลงไปในช่วงปริมาณ 0.125-2% โดยมวล จากนั้นนำไปทำปฏิกิริยาไนไตรเดชันที่อุณหภูมิในช่วง 1300-1390°C เป็นเวลา 3 ชม. จากการศึกษาพบว่าปริมาณของเฟสอัลฟาในซิลิคอนไนไตรด์เพิ่มขึ้นอย่างเห็นได้ชัด เมื่อเติมแคลเซียม อิทเทอเบียม หรือ อิทเทรียม ลงไปในซิลิคอนและทำการไนไตรเดชันที่อุณหภูมิ 1300°C เป็นเวลา 1 ชม. แล้วจึงเพิ่มเป็น 1390°C อีก 2 ชม. โดยซิลิคอนไนไตรด์ที่ได้จากการเติมแคลเซียมเพียง 0.125% มีค่าคอนเวอร์ชันจากซิลิคอนไปเป็นซิลิคอนไนไตรด์และปริมาณเฟสอัลฟาสูงเกือบ 100% ในขณะที่ซิลิคอนไนไตรด์ที่ได้จากการเติมอิทเทอเบียม 1% หรือ อิทเทรียม 2% มีค่าคอนเวอร์ชันและปริมาณเฟสอัลฟามากกว่า 97% จากผลการวิจัยพบว่าการใช้โปรแกรมอุณหภูมิจาก 1300°C เป็นเวลา 1 ชม. แล้วจึงเพิ่มเป็น 1390°C อีก 2 ชม.นั้น สามารถเร่งปฏิกิริยาไนไตรเดชันให้ได้ค่าคอนเวอร์ชันเข้าสู่ 100% โดยที่ปริมาณเฟสอัลฟายังคงอยู่ในระดับสูง นอกจากนี้ยังพบว่าการเติมแมกนีเซียม 2% ลงไปในซิลิคอนและทำการไนไตรเดชันที่อุณหภูมิ 1390°C เป็นเวลา 3 ชม. ช่วยเพิ่มความสามารถในการไนไตรเดชันของซิลิคอนได้ นอกจากนี้ยังศึกษาผลของโลหะเหล่านี้ที่มีต่อสมบัติทั้งทางกายภาพและทางกลของชิ้นงานซิลิคอนไนไตรด์ โดยนำผงซิลิคอนไนไตรด์ที่ได้จากสภาวะที่ดีที่สุดของแต่ละโลหะมาทำการขึ้นรูปและเผาที่อุณหภูมิ 1750°C เป็นเวลา 2 ชม. ภายใต้ความดัน 1 MPa ของไนโตรเจน จากการศึกษาพบว่า โลหะที่ตกค้างอยู่ในชิ้นงานนั้นส่งผลเพียงเล็กน้อยต่อสมบัติทางกายภาพและทางกลของชิ้นงาน ค่าของสมบัติทางกายภาพและทางกลของชิ้นงานซิลิคอนไนไตรด์ที่ได้รับผลกระทบจากโลหะที่ตกค้างนั้นยังคงอยู่ในช่วงที่ยอมรับได้ในการนำไปใช้งาน

ภาควิชา....วิศวกรรมเคมี.............. ลายมือชื่อนิสิต..

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##4570346221: MAJOR CHEMICAL ENGINEERING
KEY WORD: SILICON NITRIDE / DIRECT NITRIDATION / CATALYSTS / SINTERING ADDITIVES / PHYSICAL PROPERTIES

TANANYA VONGTHAVORN: EFFECTS OF METALS ON THE NITRIDATION OF SILICON AND MECHANICAL PROPERTIES OF SILICON NITRIDE PRODUCTS. THESIS ADVISOR: VARONG PAVARAJARN, Ph.D., THESIS COADVISOR: PROF. SHIGETAKA WADA, Ph.D., 107 pp. ISBN 974-17-5103-6.

The direct nitridation of silicon has been recognized as one of the methods for mass-production of silicon nitride. Although this process is considered low-cost, the product obtained usually contains only approximately 92% of desired phase of silicon nitride, α-phase, which is considered as moderately low value. In this study, catalytic effects of common elements, which are employed in the process of sintering silicon nitride, on the direct nitridation of silicon were investigated. Silicon granules impregnated with 0.125-2.0% by mass of calcium, cerium, lutetium, magnesium, ytterbium or yttrium were nitrided in a tubular flow reactor operated at temperature in the range of 1300-1390°C for 3 hours. Significant enhancement in selectivity of α-silicon nitride formation is observed when calcium, ytterbium or yttrium is incorporated with the nitridation using a stepwised increase in temperature from 1300°C to 1390°C. The silicon nitride product from the nitridation of 0.125% calcium impregnated silicon can achieve the overall conversion and the fraction of α-phase towards 100%, while 1% ytterbium or 2% yttrium addition can reach the overall conversion as well as the α-phase content over 97%. It is also found that a stepwised increase in temperature operation can accelerate the overall conversion of the nitridation toward 100% while maintaining high content of α-silicon nitride. Moreover, 2% magnesium addition also enhances the nitridation if the reaction temperature is 1390°C. Besides the investigation of catalytic effects of metals, the effects of their residual on the microstructure and the physical as well as the mechanical properties of silicon nitride articles were also investigated. The silicon nitride powders from the best condition of each metal were selected to fabricate into the specimen and sintered in furnace at 1750°C for 2 hours under N_2 pressure of 1 MPa. It is found that residual metal contained in silicon nitride powder slightly affects the properties of silicon nitride articles. However, the physical and mechanical properties of silicon nitride article obtained still in the acceptable range for many applications.

Department...Chemical Engineering…..	Student's signature……………………....
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CHAPTER I

INTRODUCTION

Silicon nitride (Si_3N_4) is one of the most promising structural materials for high-temperature and high mechanical stress applications because of its excellent properties such as high strength retention at elevated temperature, good thermal shock resistance due to low thermal expansion coefficient, high-temperature deformation resistance as well as high corrosion resistance [Hirosaki, 2002]. It has much higher creep resistance than metals and its thermal shock resistance is much better than other ceramics. It can withstand erosion from many molten metals, including molten aluminum. For these good properties, technology of silicon nitride materials has been studied intensively for more than 40 years in order to use silicon nitride instead of stainless steel or nickel-based alloy which is inferior in both properties and life-time.

The applications of silicon nitride depend on its high temperature strength, good thermal shock resistance and chemical inertness. Reports of the use of silicon nitride as a refractory material appeared in the early 1950s. At that time, it was produced by the carbothermal reduction of silicon oxide (SiO_2) in the presence of nitrogen or by the direct nitridation of silicon. Its applications included a bonding phase for silicon carbide and oxide refractories, a mold wash resisting attack by molten nonferrous metals, and a thermocouple sheath material withstanding more than 50 cycles of rapid (10 s) heating to 1371°C, which was more than 4 times better than an equivalent aluminum oxide (Al_2O_3) article [Collins and Gerby, 1955]. Silicon nitride was also used as high-temperature and unlubricated rollers and ball bearing in applications such as in oil drilling with abrasive environments, sterilizable and unlubricated dental drills, and vacuum pumps [Datton and Drobeck, 1986] because of its high-wear resistance, low friction and high stiffness.

The development of silicon nitride ceramics as potential high-temperature structural engine materials markedly accelerated in the early 1960s. It was the outcome of a deliberate and structured search for new materials with good high-temperature properties, of which resistance to thermal shock was the most important.

It led to the development and successful testing of a wide range of silicon nitride components piston and gas turbine for internal combustion engines. Moreover, the low specific density of silicon nitride turbocharger improves the response of the engine during acceleration when comparing with the heavier metal parts. The nozzles of certain rockets have already been prepared by using silicon nitride [Tsuruto*, et al.*, 1990]. These applications are not the very-high-temperature applications originally envisaged, but rely on the low density (mass and inertia) of the silicon nitride component coupled with high strength and toughness required to withstand impact damaged.

In the past 30 years, during which most of the considerable development work on silicon nitride has been conducted primarily in the ceramics and electronics communities, many different aspects have been explored. Current development concerns further introduction of silicon nitride components to diesel and spark-ignited engines in locations where low mass and improved wear resistance are required, such as exhaust valves, valve spring retainers, bucket tappets, stator blades, valve springs and rocker arm pads [Wotting*, et al.*, 1996].

Silicon nitride exists as amorphous and crystalline forms. Two well-known crystal structures of silicon nitride are designated as α-phase and β-phase, both appearing to be hexagonal [Turkdogan*, et al.*, 1958; Wang*, et al.*, 1996]. β-silicon nitride is more desirable for high-temperature engineering applications because of its high temperature strength and excellent thermal shock resistance [Lange, 1979]. However, silicon nitride ceramics are commonly fabricated from α-silicon nitride powder rather than from β-silicon nitride powder because densification and sintering of α-silicon nitride powder is much easier than sintering of β powder [Hirosaki*, et al.*, 1994; Mitomo and Uenosono, 1991]. The fabrication of β-silicon nitride parts usually starts from α-silicon nitride powder mixed with sintering additives. The mixture is then shaped into a desired component and sintered at high temperatures (1700-1800°C). During sintering process, the transformation of α-phase to β-phase occurs, providing desirable microstructure having high mechanical and thermal strength [Ault and Yeckley, 1994; Lange, 1979]. Thus, α-silicon nitride powder is the important starting materials for making silicon nitride components. A high content of α-form, usually higher than 95%, is often desired.

The direct nitridation of silicon is one of the most commonly used process to produce silicon nitride powder. It is one of commercial methods for mass-production of silicon nitride containing predominantly α-form. It is an inexpensive option for applications in which metal impurities contained in the product, silicon nitride, can be tolerated. However, the important disadvantage of this process is the quality of the product. Silicon nitride powder produced from the direct nitridation process usually contains about 92% of α-silicon nitride [Segal, 1985], which is considered as moderately low quality powder. On the contrary, very pure silicon nitride with a high content of α-form (> 95%) can be prepared from much more expensive method, the diimide process [Ault and Yeckley, 1994]. Therefore, it is desired to increase the content of α-silicon nitride in the product from the direct nitridation of silicon.

It has been known that transition metals contained in silicon as impurities regulate kinetics of its nitridation as well as the phase formation [Boyer and Moulson, 1978; Jennings, 1983; Lin, 1977; Pavarajarn and Kimura, 2001; Pigeon, *et al.*, 1993]. Many researchers have studied the effects of several transition metals on the nitridation of silicon by intentionally adding metals into silicon before the nitridation. However, metals investigated in the past are not elements commonly used in silicon nitride processing operation and the impact of metal residual on physical and mechanical properties of the silicon nitride articles has not been reported. Since sintering additives are always used in fabrication of articles from silicon nitride powder, yet no report on catalytic effects of additives on the nitridation of silicon has been done, it is the objective of this work to investigate the enhancement of the direct nitridation of silicon from elements in common sintering additives, e.g. calcium, cerium, lutetium, magnesium, ytterbium and yttrium.

As mentioned above, the main purpose of this research is to investigate the catalytic effects of metals, used as common sintering additives, on the nitridation of silicon and observe the effects of their residual in the silicon nitride product from the direct nitridation process on its microstructure as well as physical and mechanical properties. The scopes of this study are as follows:

1. Silicon nitride powders are synthesized via the direct nitridation of silicon process. Both reaction temperature and amount of metal are varied to determine the appropriate conditions and content of each metal that result in a high overall conversion and high content of α-phase in the product. Values of metal content and temperature investigated are in the range of 0.125-2.0% by mass, and 1300 to 1390°C, respectively.

2. The silicon nitride products are characterized by using powder X-ray diffraction (XRD) for crystalline phase analysis, both qualitatively and quantitatively. Mass fractions of each phase as well as the conversion from silicon to each α- and β-silicon nitride are calculated from the integrated intensity of various peaks of silicon, α- and β-silicon nitride [Jovanovic and Kimura, 1994].

3. The silicon nitride articles are fabricated by gas-pressure sintering method. The synthesized silicon nitride powder is mixed with alumina (Al_2O_3) and yttria (Y_2O_3) as sintering additives. The mixed powder is pressed to form the testing specimen, and then sintered in a furnace at high temperature under pressure of nitrogen.

4. Effects of metal residual on properties of silicon nitride product are investigated as the following:
   - Bulk density is measured by Archimede's method.
   - Phase identification is performed by X-ray diffraction.
   - Fracture toughness and hardness are evaluated by using Vickers indenter.
   - Grain morphology and fracture surfaces observations are performed by using a scanning electron microscope (SEM).

This work is intended to improve quality of silicon nitride powders synthesized from an economical process without deterioration of mechanical properties of products.

This thesis is divided into five parts. The first three parts describe general information about the study, while the following two parts emphasis the results and discussion observed from the present study. The background and scope of the study are presented in Chapter I. Chapter II consists of the theory and literature survey, while the experimental systems and procedures used in this study are shown in Chapter III. The experimental results, including an expanded discussion, are given in Chapter IV. Finally, in the last chapter, the overall conclusion from the results and some recommendations for future work are presented.

CHAPTER II

THEORY AND LITERATURE SURVEY

2.1 Crystal Structure of Silicon Nitride

It has been generally accepted that there are two forms of crystalline silicon nitride, designated as α- and β-forms. Although the third polymorph of silicon nitride, designated as c-Si_3N_4, was recently discovered [Zerr, *et al.*, 1999], it had to be synthesized under extremely high pressure (15 GPa) and extremely high temperature (2200 K), yet the amount obtained was very small. Thus, this work will focus mainly on the more common polymorph, α- and β-forms.

Detailed X-ray diffractometry (XRD) examinations in the mid-1950s have proved that the crystal structure of both α and β polymorphs are hexagonal [Turkdogan, *et al.*, 1958]. However, their respective structural dimensions are different. There is a wide spread in the reported lattice parameters or unit cell dimensions for the two phases. Values for the α-phase have ranged from 0.7748-0.7818 nm for *a* and from 0.5591-0.5628 nm for *c*, while the axial ratios *c/a* are reasonably constant [Wang, *et al.*, 1996]. The lattice parameters for the β-phase have been reported in the range from 0.7595-0.7608 nm for *a* and from 0.2900-0.2911 nm for *c* [Wang, *et al.*, 1996]. It can be seen that the *c*-axis dimension of the unit cell of the α-phase is approximately twice that of β-phase.

In both the forms, the basic building unit is the silicon-nitrogen tetrahedron in which a silicon atom lies at the center of a tetrahedron, and four nitrogen atoms at each corner. Each nitrogen atom is shared among three tetrahedra so that each silicon atom has four nitrogen atoms as nearest neighbors [Ruddlesden and Popper, 1958]. The structures also can be regarded as puckered eight-membered rings of alternating silicon and nitrogen atoms. Basal planes are formed by the joining of six of these rings forming a larger central void encapsulated by six silicon atoms. Stacking of the basal planes forms the structure of β-phase, as shown in Figure 2.1. The large void between the hexagonal arrangement of atoms is continuous through the β-phase lattice forming a c-axis channel that has an equivalent cylindrical radius of 1.5 Å. Theoretically, it may enable large atoms to diffuse readily through the lattice [Thompson and Pratt, 1967].

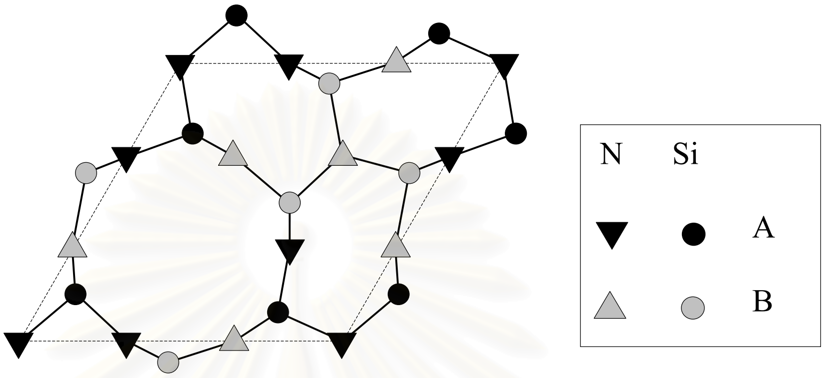

Figure 2.1 β-Si_3N_4 unit cell: the structure of β-Si_3N_4 can be described as a stacking of Si-N layers in …ABAB… sequence.

The structure of α-Si_3N_4 was determined to be closely related to that of β-Si_3N_4, consisting of alternate basal layers of β-Si_3N_4 and its mirror image, as shown in Figure 2.2. Because of the operation of a c-glide plane, the continuous voids are interrupted to form a series of large interstices, which are roughly spherical in shape with a radius of approximately 1.5 Å, linked by tunnels having a radius of 0.7 Å. Consequently, large foreign atoms or molecules could be trapped within the lattice while small ones, such as oxygen, will be able to diffuse within the lattice [Thompson and Pratt, 1967].

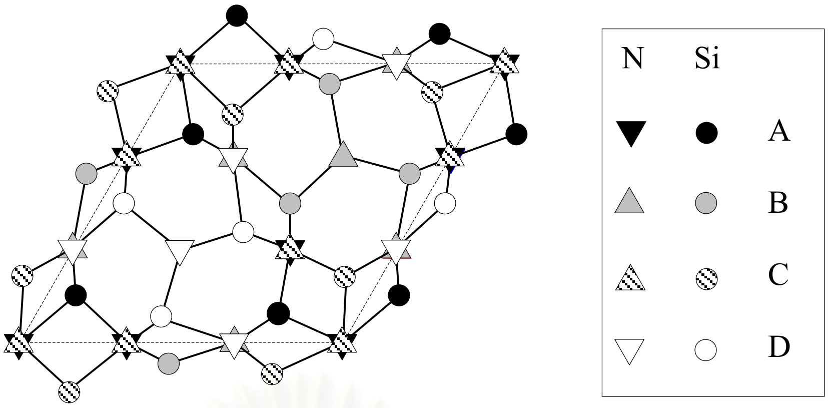

Figure 2.2 α-Si_3N_4 unit cell: the structure of α-Si_3N_4 can be described as a stacking of Si-N layers in …ABCDABCD… sequence.

The α to β transformation of silicon nitride is commonly observed during the sintering process, at temperature exceeding 1500°C. It has been suggested that the transformation is a reconstructive transformation involving breaking reforming of six Si-N bonds in each unit cell, with a change in the position of one nitrogen and a small displacement of neighboring atoms [Messier, *et al.*, 1978; Thompson and Pratt, 1967]. Because the difference between the Gibbs function of formation of β-Si_3N_4 and that of α-Si_3N_4 is small ($\approx$30 kJ/mol at 25 °C) and the activation energy is high, the process apparently can occur only in the presence of a liquid phase, which is believed to lower the transformation activation energy [Messier, *et al.*, 1978; Suematsu, *et al.*, 1997]. The reverse β to α transformation has never been observed experimentally, but it has been expected to be too slow to be detected at temperatures < 1400 °C [Jennings, 1983; Riley, 2000].

Silicon nitride does not melt but dissociates into silicon and nitrogen, with the nitrogen dissociation pressure reaching 1 bar (10^5 Pa) at about 1880 °C [Riley, 2000].

2.2 Commercial Techniques for Mass-Producing Silicon Nitride Powder

Silicon nitride is not found in nature, but can be synthesized by a number of different techniques. For industrial production of silicon nitride powder, silicon, silica (SiO_2) and silicon tetrachloride ($SiCl_4$) are the three commonly used starting materials because they are available in high purity on an economic basis or can be easily purified.

There are three typical methods which have already been used for producing silicon nitride on a commercial scale [Dijen, *et al.*, 1994; Yamada, 1993]. Their final products are different in quality as well as the production cost.

2.2.1 Carbothermal reduction of silica under nitrogen

The carbothermal reduction of silica powder under nitrogen was earliest used method for silicon nitride production [Riley, 2000].

In the presence of carbon and nitrogen, fine silica powder reacts according to the overall equation [Segal, 1985]:

$$3\,SiO_2\,(s) + 6\,C\,(s) + 2\,N_2\,(g) \leftrightarrow Si_3N_4\,(s) + 6\,CO\,(g) \tag{2.1}$$

Fine α-silicon nitride powder can be produced directly by using very fine silica. The reaction is usually performed at temperature in the range of 1200-1450°C, depending on the reactivity of raw materials. Since an excess amount of carbon is required for full transformation of silica to silicon nitride, some free carbon can remain in the nitrided powder. By annealing this powder in air, the remaining carbon can be partially oxidized, but so is the silicon nitride. Consequently, the product powder produced by this method often suffers from purity problem associated with residual carbon and oxygen content. The content of α-silicon nitride obtained from this process is at most 88%.

2.2.2 High-temperature decomposition of silicon diimide

This process could be described as a two-step process. The first step is the liquid phase reaction between silicon tetrachloride and ammonia at room temperature, as follows:

$$SiCl_4\,(l) + 6\,NH_3\,(l) \leftrightarrow Si(NH)_2\,(s) + 4\,NH_4Cl\,(s) \qquad (2.2)$$

In principle, the liquid phase reaction of silicon tetrachloride with ammonia can be performed in three different ways: (a) liquid $SiCl_4$ with liquid NH_3, (b) gaseous $SiCl_4$ with liquid NH_3 and (c) liquid $SiCl_4$ and gaseous NH_3. In all three cases, fine silicon diimide and ammonium chloride particles are formed. The ammonium chloride can be removed by series of washing with liquid ammonia.

After removing the ammonium chloride, the silicon diimide is given a polymerization via heat treatment in nitrogen or ammonia [Yamada, 1993]. The polymer is then pyrolized at 1100°C in nitrogen to produce amorphous silicon nitride. Subsequent heat treatment at temperature higher than 1430°C initiates conversion of amorphous product into α-crystalline form, which may be represented by an overall stoichiometric equation as:

$$3\,Si(NH)_2\,(s) \leftrightarrow Si_3N_4\,(s) + N_2\,(g) + 3\,H_2\,(g) \qquad (2.3)$$

Since reactants are liquids or gases, very pure silicon nitride with a high content of α-form (> 95%) can be prepared [Ault and Yeckley, 1994]. However, the production cost is high due to complexities of the process and extensive efforts to purify the intermediate silicon diimide.

2.2.3 Direct nitridation of silicon

The direct nitridation of silicon is one of the most commonly used process in the production of α-silicon nitride [Cambier and Leriche, 1990]. The process is based on contacting elemental silicon with nitrogen at temperature in the range of 1200-1400°C. Although the true mechanism is unknown, the overall reaction of this process can be represented by the following equation:

$$3\,Si\,(s) + 2\,N_2\,(g) \leftrightarrow Si_3N_4\,(s) \qquad (2.4)$$

The reaction is highly exothermic. Extreme care must be taken to prevent temperature run-away, which results in melting of silicon particles. β-Si_3N_4 is found in greater abundance when the reaction is carried out at temperature near the melting point of silicon, 1410°C [Jennings, 1983].

The direct nitridation process is more complicated than Equation (2.4) implies. Several models have been proposed to describe the nitridation of silicon [Atkinson, *et al.*, 1973; Jennings, 1983; Pigeon and Varma, 1993; Varma, *et al.*, 1991], but there is no general agreement regarding the mechanism of the nitridation.

The production cost for this process is low, compared to other processes mentioned earlier, since the process is one simple step using inexpensive reactants. This process is an inexpensive option for the applications in which metal impurities, originating from silicon, contained in the product silicon nitride can be tolerated. It has been reported that the commercial product obtained by this method normally contains 92% α-form [Segal, 1985].

2.2.4 Reactions of vapor-phase species

In principle, the reactions of vapor-phase species, which can be obtained in a very pure state, should yield equally high-purity silicon nitride powders. Later attempts to produce nanosized powders use CO_2 laser and plasma-energized reactions of silane and ammonia [Riley, 2000]:

$$3\,SiH_4\,(g) + 4\,NH_3\,(g) \leftrightarrow Si_3N_4\,(s) + 12\,H_2\,(g) \qquad (2.5)$$

Particle sizes of the amorphous product are typically 10-25 nm, from which equiaxed α-Si_3N_4 is produced by crystallization at 1400°C [Cannon, *et al.*, 1982]. Production rates are, however, very slow, and the commercial viability of this method seems questionable [Bauer, *et al.*, 1991; Lange, *et al.*, 1991].

Each form of powder has its own characteristics and trace impurities. Comparative reviews made of production methods and general powder properties have established that the wide differences in silicon nitride densification behavior are related to powder characteristics, of which α-Si_3N_4 content, ultimate crystallite size, and oxygen content are important factors [Vandeneede, *et al.*, 1986].

2.3 Effects of Metals in Silicon on the Direct Nitridation Process

There are many reaction variables involved in the direct nitridation process, such as reaction time, temperature, heating rate, particle characteristics, and reactant gas composition. Their influences on the microstructure, phase development, and reaction rates have been extensively examined by a number of different researchers [Atkinson and Moulson, 1976; Jennings, 1983]. Determining the dependence of each process variable is complicated by the mutual interactions among them.

It has been known that transition metals contained in silicon as impurities regulate both kinetics of its nitridation and the phase transformation [Boyer and Moulson, 1978; Cofer and Lewis, 1994; Huttinger and Pieschnick, 1994; Jennings, 1983; Lin, 1977; Lin, 1975; Mitomo, 1977; Moulson, 1979; Mukerji and Biswas, 1981; Pigeon, *et al.*, 1993; Sanyal, *et al.*, 1991]. Many researchers have studied the effects of several transition metals on the nitridation of silicon by intentionally adding metals into silicon before the nitridation. Aluminum, titanium, hafnium, zirconium and chromium are known as metals that accelerate the growth of β-silicon nitride [Cofer and Lewis, 1994; Lin, 1977; Mitomo, 1977; Mukerji and Biswas, 1981; Pigeon, *et al.*, 1993]. Calcium is known to promote the development of α-silicon nitride [Pigeon, *et al.*, 1993]. It has been found that an addition of calcium as small as 0.125% by mass could achieve an approximately 99% overall conversion with 100% α-phase [Pavarajarn and Kimura, 2001]. Copper is recently studied for the aid of silicon nitride production [Deckwerth and Russel, 1994]. It was found that copper promoted not only the nitridation but the formation of α-silicon nitride at 1200°C, but enhanced the β-phase formation at higher temperatures [Pavarajarn and Kimura, 2001]. Iron is the metal that has been studied most frequently, since it is the most common metal impurity in commercially available silicon powders. It has been suggested that iron appears to inhibit the α-silicon nitride formation while favors the growth of β-silicon nitride as the iron-rich region forms a liquid below 1350°C

[Campos-Loriz and Riley, 1978; Mukerji and Biswas, 1981]. With an increase in amount of iron in silicon, the content of β-silicon nitride obtained after nitridation of silicon becomes as high as double the content of β-phase in the product from bare silicon at 1300°C [Pavarajarn and Kimura, 2001]. Effects of yttrium on the direct nitridation of silicon has been recently reported. It has been found that an addition of yttrium 2% by mass leads to the overall conversion over 98% with α-phase content about 97% [Pavarajarn and Kimura, 2001]. Moreover, since yttrium is often added during the process of sintering silicon nitride, the effect of yttrium residue in silicon nitride product should be minimized.

By studying the effects of various transition metals on the nitridation of silicon, a higher content of α-silicon nitride could be achieved by adding small amount of metals in the raw material, silicon, before nitridation, and this could enhance the formation of α-phase or suppress the formation of β-phase.

In this work, besides the effect of calcium and yttrium, the effect of cerium, magnesium, lutetium and ytterbium are also subjected to be studied, since they have been reported to be used during the process of sintering silicon nitride [Dai, *et al.*, 2003; Guo, *et al.*, 2003; Guo, *et al.*, 2001; Haitao, *et al.*, 2001; Lu and Huang, 2001; Yang, *et al.*, 1998], while no result regarding the catalytic effect of them on the nitridation of silicon has been reported.

2.4 General Methods for Forming Silicon Nitride Ceramics

Most traditional and technical ceramic products are manufactured by compacting powders or particles into shapes which are subsequently heated to a temperature that is high enough to bond particles together. The basic steps of the ceramic processing via the agglomeration of particles consist of material preparation, forming or casting, and thermal treatment.

There are four major processing methods that have been developed for silicon nitride [Smith, 1996]:

2.4.1 Reaction-Bonded Silicon Nitride (RBSN)

In reaction-bonded silicon nitride, a compact of silicon powder with sintering additives is heated in nitrogen atmosphere (1 atm) at 1200-1400°C. During nitridation, simultaneous bonding or sintering of the product nitride occurs. The ability to produce complex-shaped components without the need for time-consuming and expensive finishing operations is a major advantage of this method. However, the product obtained is porous (25-35%) with lowest strength, when comparing with the other methods [Riley, 2000; Smith, 1996].

2.4.2 Hot-Pressed Silicon Nitride (HPSN)

In this process, silicon nitride ceramic parts of high density and improved mechanical properties are produced by combining the uniaxial pressing and firing (sintering) operations [Smith, 1996]. By this method, silicon nitride powder with sintering additives is pressed and sintered in a refractory die under high pressure and high temperature at 15-30 MPa and 1650-1850°C, respectively [Hampshire, 1994]. The additives react with the silicon nitride starting powder and its silica surface layer to create a grain boundary oxynitride whose characteristics control the bonding process at high temperatures [Smith, 1996]. The industrial use of uniaxial hot pressing is limited, because its productivity is relatively low and the die maintenance is expensive [Reed, 1989]. Nevertheless, the advantage of this method is that the high temperature strength material is obtained [Hampshire, 1994].

2.4.3 Hot-Isostatic-Pressed Silicon Nitride (HIP-SN)

In this process, the mixture of silicon nitride powder and sintering additives is loaded into a glass ampoule that is inside a chamber of hydraulic fluid to which high pressure uniformly in all directions and high temperature are applied at 50-250 MPa and 500-1800°C, respectively [Koizumi and Nishihara, 1987]. The compact is sintered to achieve the required properties and microstructure. The ability to produce complex-shaped and high temperature components is a major advantage, but very expensive finishing operations are often needed [Hampshire, 1994].

2.4.4 Sintered Silicon Nitride (SSN)

Sintering is the process by which a powder compact is transformed to a strong dense ceramic body upon heating. It can occur in the presence or absence of a liquid phase. In the former case, it is called liquid-phase sintering, where the compositions and firing temperatures are chosen such that some liquid is formed during processing. Liquid-phase sintering of ceramics is of major commercial importance since a majority of ceramic products, such as silicon nitride, are fabricated via this route [Barsoum, 1977].

General liquid-phase sintering system densifies in three overlapping stages that composed of particle rearrangement, solution-reprecipitation and solid-state sintering [Barsoum, 1977; German, 1985]. With liquid formation, there is rapid initial densification due to the capillary force exerted by the wetting liquid on the solid particles. When this densification slows down, solubility and diffusivity effects become dominant. A general attribute of solution-reprecipitation processes is microstructural coarsening. Material is transported from the small grains to the large grains by diffusion. This stage is not only contributed to grain coarsening, but also to densification. The last stage is referred to solid state controlled sintering. Densification in this stage is slow because of the existence of a solid skeleton. Processes dominant in this stage are also active throughout the entire liquid-phase sintering cycle, however, because of the slow nature, solid state sintering is not of significance until late in the sintering cycle [German, 1985].

However, it is difficult to densify pure silicon nitride into useful high strength ceramics due to its high covalent nature of bonding (approximately 70%), but metal oxides and rare-earth oxides have been found to be effective sintering additives for silicon nitride [German, 1985; Hirosaki, *et al.*, 1988; Wang, *et al.*, 1998]. In general, these oxide additives promote densification by liquid-phase sintering mechanism. Oxide additives such as CeO_2, La_2O_3, Sm_2O_3, Y_2O_3, Al_2O_3 and MgO are used as sintering additives, especially for Y_2O_3 and Al_2O_3 system. It is the most popular oxide additives for silicon nitride ceramics [Lange, 1973; Yang, *et al.*, 2000].

The liquid-phase sintering mechanism of silicon nitride with oxide additives is shown in Figure 2.3. As seen in the figure, α-silicon nitride dissolves in glassy phase that resulted from additives and silica (SiO_2). Then, the transformation of α- to β-phase occurs, following by grain growth of the precipitated β-silicon nitride into rod like grains [Wotting and Ziegler, 1986; Xu, *et al.*, 2002]. The overall reaction of this process can be represented by the following equation [Hampshire, 1994]:

$$\alpha\text{-}Si_3N_4\ (+\ SiO_2)\ +\ M_xO_y\ \rightarrow\ \beta\text{-}Si_3N_4\ +\ \text{M-Si-O-N phase} \qquad (2.6)$$

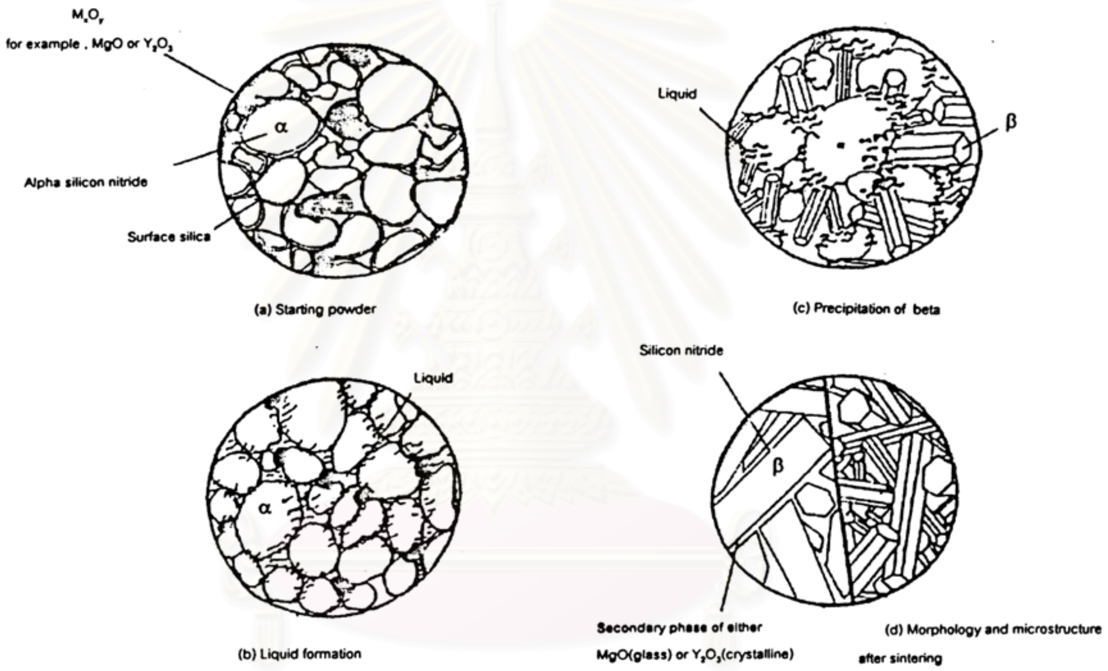

Figure 2.3 Schematic of liquid-phase sintering of silicon nitride with oxide additives [Hampshire, 1994].

Behaviors of nucleation and phase transformation are affected by mass transport through the glassy phase during the liquid phase sintering. When the sintering temperature is increased, the liquid phase composition changes into an oxynitride by preferred dissolution of α-silicon nitride, which leads to re-precipitation of β-silicon nitride. High viscosity of melted oxynitride reduces the nucleation rate of β-silicon nitride, which provides grains with high aspect ratio. This improves good mechanical properties of the sintered products [Xu, *et al.*, 2002].

By this method, the silicon nitride powder mixed with sintering additives is form into desired shape, and then sintered in the furnace at 1700-1800°C under nitrogen atmosphere. If the pressure is atmospheric pressure, the process is called “Pressureless sintering”, but when the pressure is more than 1 atm, it is called “Gas pressure sintering”. Sintering process is a cost-effective method to produce silicon nitride ceramics in mass-production. However, the density of the product obtained is relatively low, comparing to that from HPSN or HIP-SN [Hampshire, 1994]. Thus, many researchers have studied the effects of sintering additives on the sintering process in order to improve properties of material obtained.

In this work, the metal-doped silicon nitride powder mixed with yttria and alumina, which are employed as sintering additives, is form into disc-shaped specimen by compression. Then, it is sintered using gas-pressure sintering under nitrogen atmosphere in the furnace, in order to investigate the effects of metal residual on microstructure as well as physical and mechanical properties of the silicon nitride product.

CHAPTER III

EXPERIMENTAL

This chapter describes the experimental systems and procedures used in this study. The chapter is divided into two parts, i.e., synthesis of silicon nitride powders and formation of silicon nitride articles. The chemicals, apparatus and procedures for the synthesis of silicon nitride powders are explained in section 3.1 and those for the formation of silicon nitride articles are given in section 3.2.

3.1 Synthesis of Silicon Nitride Powders

3.1.1 Raw material and chemicals

Silicon raw material used in this work composes of fine silicon grains which are partially sintered into larger porous granules. These particles were prepared by Shin-Etsu Chemical Company, Ltd. from silicon grains of 2 μm in average size, granulated and briefly sintered to become slightly cemented together about 300 μm average-sized. The specifications of the silicon raw material used are given in Table 3.1. All other physical properties of the granules should be referred to elsewhere [Jovanovic, *et al.*, 1994].

Table 3.1 Specifications of silicon raw material

Trace impurities (% by mass)*					BET area** (m^2/g)
Fe	Al	Ca	C	O	
0.08	0.10	0.02	0.02	0.51	1.81
source: *Shin-Etsu Chemical Company Ltd.; **Micromeritics ASAP 2000					

List of chemicals used in the experiments are shown in Table 3.2

Table 3.2 Details of chemical reagents used for raw material preparation

Chemical	Formula	Grade	Source
Calcium nitrate tetrahydrate	$Ca(NO_3)_2 \cdot 4H_2O$	min. 99.0%	Sigma-Aldrich Chemical Co., U.S.A.
Cerium (III) nitrate hexahydrate	$Ce(NO_3)_3 \cdot 6H_2O$	99.0%	Fluka Chemika, Switzerland
Lutetium (III) nitrate hydrate	$Lu(NO_3)_3 \cdot xH_2O$	99.999%	Sigma-Aldrich Chemical Co., U.S.A.
Magnesium nitrate hexahydrate	$Mg(NO_3)_2 \cdot 6H_2O$	99.0%	Sigma-Aldrich Chemical Co., U.S.A.
Ytterbium (III) nitrate pentahydrate	$Yb(NO_3)_3 \cdot 5H_2O$	99.9%	Sigma-Aldrich Chemical Co., U.S.A.
Yttrium nitrate hexahydrate	$Y(NO_3)_3 \cdot 6H_2O$	99.9%	Sigma-Aldrich Chemical Co., U.S.A.
Methyl alcohol	CH_3OH	min. 99.9%	Carlo Erba Reagenti, Australia

3.1.2 Raw material preparation procedures

In this section, the catalytic effects of metals on the nitridation of silicon were investigated by intentionally adding small amount of metals into the silicon raw material. Metals used in this work are calcium, cerium, lutetium, magnesium, ytterbium and yttrium, respectively.

For samples preparation, silicon granules of about 10 g were immersed in 30 ml solution of metal-nitrate compound in methanol under continuous agitation by using an ultrasonic bath. After all methanol was naturally evaporated at room temperature, the samples were then put in an oven at 110°C for 24 hours to ensure the elimination of all possibly remaining methanol and moisture. The amount of each metal-nitrate compound dissolved in methanol was adjusted so that a desired level of metal impregnation was achieved after the decomposition and reduction of the nitrate compound at high temperature before the silicon-nitridation reaction. The final contents of each metal were adjusted to be 0.125, 0.45, 1.00 and 2.00 percent by mass, respectively.

3.1.3 Experimental apparatus for silicon nitride powder synthesis

The synthesis of silicon nitride powders was performed in a horizontal tubular flow reactor as shown in Figure 3.1. The reaction was carried out in an alumina tube (49 mm inside diameter × 1200 mm long) placed inside a furnace (Carbolite-STF 15/--/180). The operation was performed under atmospheric pressure.

3.1.4 Silicon nitride powder synthesis procedures

For each run, about 0.5 g of sample granules was put into an alumina tray (25 mm×15 mm×5 mm deep). Then, three alumina trays of different samples were placed next to each other in the uniform temperature zone of the reactor. The thickness of particles layer in each tray was about 2-3 mm to avoid any mass and heat transfer effects from intruding in the nitridation. Samples were then heated to a predetermined temperature, in the range of 1300-1390°C, at the rate of 10°C/min, under the continuous flow of argon. After the system had reached the prescribed temperature, the sample granules were pretreated by replacing the argon with a mixture containing 90% argon and 10% hydrogen for 1 hour to remove any surface oxide on silicon as well as to convert metal nitrates impregnated into reduced metals [Pavarajarn and Kimura, 2003].

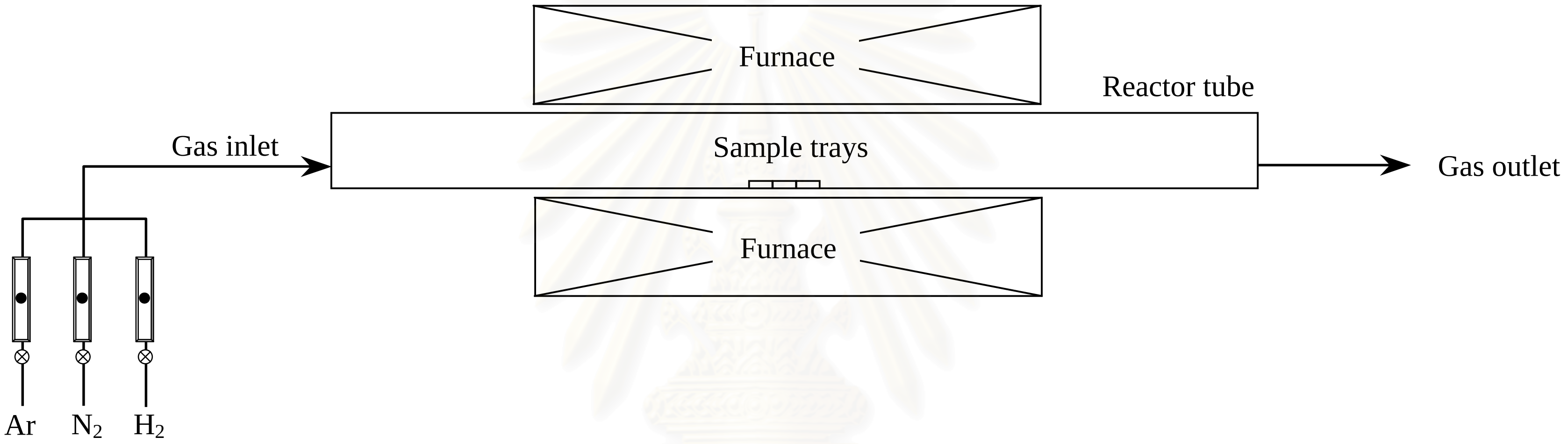

Figure 3.1 Schematic diagram of the tubular flow reactor system

After the pretreatment, the nitridation was initiated by supplying a gas mixture of 90% nitrogen and 10% hydrogen. Hydrogen was always added in the feed to enhance the nitridation of silicon by preventing the formation of the protective layer that retarded the progress of the reaction [Jovanovic, *et al.*, 1994; Pavarajarn and Kimura, 2003]. The flow rate of the reactant gas mixture was fixed at 4.28 l/min (measured at room temperature), which was high enough to eliminate the gas-film mass-transfer resistance [Pavarajarn and Kimura, 2001]. The nitridation was done for 3 hours, since it has been reported that the nitridation of silicon granules reached a stage of very slow progress in about 3 hours [Jovanovic, *et al.*, 1994].

In the programmed temperature operation, the nitridation reaction was carried out at 1300°C for one hour and then at 1390°C for two hours, as suggested elsewhere [Jovanovic, *et al.*, 1994]. It took about 9 minutes to raise the reaction temperature. During this transitional period, the feed of reactant gas was maintained unchanged.

3.1.5 The analysis of products

The silicon/α-, β-silicon nitride phase composition of nitridation products were determined by powder X-ray diffraction (XRD) using a SIEMENS D5000 diffractometers with CuK_α radiation. Each sample was scanned in the range of 2θ = 26-38° with a step size of $2\theta = 0.01°$. Peak areas, background noise, and separation of overlapped peaks were determined by fitting the diffraction patterns using the Pseudo-Voight function [McCusker, *et al.*, 1999] in the Xfit-Koalariet software package from the Collaborative Computational Project number 14 (CCP14). Then, the mass fraction of each phase as well as the conversion from silicon to α- and β-silicon nitride were calculated from the method proposed by Jovanovic and Kimura [1994], using the integrated intensity of (111) peak of Si, the integrated intensities of (102), (210) and (201) peaks of α-silicon nitride and those of (101) and (210) peaks of β-silicon nitride, as follows:

$$\frac{I_\alpha(102) + I_\alpha(210)}{I_\beta(101) + I_\beta(210)} = K_{\alpha/\beta}\frac{W_\alpha}{W_\beta} \qquad (3.1)$$

$$\frac{I_{Si}(111)}{I_{\alpha}(201)} = K_{Si/\alpha}\frac{W_{Si}}{W_{\alpha}} \tag{3.2}$$

and $$W_{\alpha} + W_{\beta} + W_{Si} = 1 \tag{3.3}$$

where $I_{\delta}(hkl)$ signifies the integrated intensity of the *hkl* reflection of phase δ, and W_{δ} is the mass fraction of corresponding phase δ in a mixture. The linear regression calibration constants, $K_{\alpha/\beta}$ and $K_{Si/\alpha}$ were evaluated to be 0.647 and 5.53 respectively [Jovanovic and Kimura, 1994].

From measured mass composition, the overall conversion of silicon, *X*, was calculated as:

$$X = \frac{1 - W_{Si}}{1 + \left(\frac{M_{SN}}{3M_{Si}} - 1\right)W_{Si}} \tag{3.4}$$

where M_{SN} and M_{Si} are the molar masses of silicon nitride and silicon, and $(M_{SN} / 3M_{Si})$-1 = 0.665 is a converting factor.

Thus, the mass fractional yields of α-silicon nitride, X_{α}, and β-silicon nitride, X_{β}, were calculated as:

$$X_{\alpha} = \frac{1 - W_{Si}}{1 + 0.665W_{Si}}\left(\frac{W_{\alpha}}{W_{\alpha} + W_{\beta}}\right) \tag{3.5}$$

and $$X_{\beta} = \frac{1 - W_{Si}}{1 + 0.665W_{Si}}\left(\frac{W_{\beta}}{W_{\alpha} + W_{\beta}}\right) \tag{3.6}$$

The overall conversion of silicon, *X*, is therefore the sum of the mass fractional yields of α- and β-silicon nitride:

$$X = X_{\alpha} + X_{\beta} \tag{3.7}$$

An example of X-ray diffraction pattern of synthesized product and the calculation are given in Appendix A.

In addition to the phase composition determination, grain morphology and surface of silicon nitride granules were also examined by using scanning electron microscope (SEM) (JSM-6400, JEOL Co., Ltd.) at the Scientific and Technological Research Equipment Center, Chulalongkorn University (STREC).

3.2 Formation of Silicon Nitride Articles

3.2.1 Sample preparation procedures

Besides the investigation of catalytic effects of metal, the effects of metal residual on the microstructure and the mechanical properties of silicon nitride articles were also investigated. In order to fabricate the silicon nitride specimen, chemical reagents as shown in Table 3.3 were employed.

Table 3.3 Chemical reagents used for preparation of silicon nitride articles

Chemical	Formula	Grade	Source
Aluminum oxide	Al_2O_3	TD-MA	Taimei Chemicals, Japan
Yttrium oxide	Y_2O_3	NR Grade	Daiichikigenso, Japan
n-Propanol	$C_2H_5CH_2OH$	min. 96.0%	UNILAB Reagent, Australia

For each sample, the synthesized silicon nitride granules, about 0.7 g, were first ground into powder by using an alumina mortar and pestle for 20 minutes. Then, the powder was mixed with Al_2O_3 and Y_2O_3, as sintering additives, in the same mortar for 30 minutes by using n-propanol as a mixing medium. The weight ratio of the Si_3N_4:Al_2O_3:Y_2O_3 mixture was fixed at 90:5:5 [Chaiyapuck, 2003]. After that, the mixed powder was dried in an oven at 110°C for 12 hours to eliminate all n-propanol and consequently ground in the alumina mortar for 5 minutes. Finally, the powder was die-pressed uniaxially at 20 MPa to form a disc-shaped article, called green compact which was 12 mm in diameter and 3 mm thick.

The green compact was subsequently put in a boron nitride crucible and sintered in a graphite gas-sintering furnace (Hi-Multi 5000, FVPHP-R-5, Fuji Electric Co., Ltd., Tokyo, Japan) at 1750°C for 2 hours under pressure of 1 MPa in N_2 atmosphere. It was suggested that this sintering condition can result in sintered bodies with more than 98% of theoretical density [Chaiyapuck, 2003].

3.2.2 Characterization of silicon nitride articles

The characterization of sintered articles is described in this section. The effects of metal residual on the physical and mechanical properties as well as microstructure were investigated by various techniques, as follow:

Bulk density of sintered specimens was measured by the Archimede’s method, according to ASTM-C830-93-1996 standard. The specimens were first dried in an oven at 110°C for 2 hours and subsequently determined the dry weight (*D*) in grams. Then, the specimens were placed in a vacuum vessel for 30 minutes and consequently poured water into the vessel, maintained the vacuum for 30 minutes. Weight of the saturated specimens were measured as the saturated weight (*W*), in grams. Next, the specimens were suspended from one arm of the balance in a loop or a halter made from copper wire and the suspended weight (*S*) of specimens in water was measured. Noted that the balance should be previously counter-balanced with the wire and immersed in water to the same depth as when the specimens were placed. Finally, these measured values were used in the calculation as follows:

$$B.D. = \left(\frac{D}{W - S}\right) \times \rho_w \qquad (3.8)$$

where $B.D.$ represents bulk density (g/cm^3), and ρ_w is the density of water (g/cm^3).

Relative density was also calculated based on theoretical density derived from each individual constituent and its content:

$$R.D. = (\frac{B.D.}{T.D.}) \times 100 \tag{3.9}$$

where $R.D.$ and $T.D.$ represent relative density (%) and theoretical density (g/cm^3), respectively. The theoretical density was calculated as:

$$\begin{aligned} T.D. = {} & (\text{weight fraction of } Si_3N_4 \times \text{density of } Si_3N_4) + (\text{weight fraction of metal} \\ & \times \text{density of metal}) + (\text{weight fraction of } Al_2O_3 \times \text{density of } Al_2O_3) + \\ & (\text{weight fraction of } Y_2O_3 \times \text{density of } Y_2O_3) \end{aligned} \tag{3.10}$$

The example of calculation is given in Appendix B.

It has been known that phase transformation from α- to β-silicon nitride is an important factor for microstructure of the final article [Tsuge, *et al.*, 1975; Wotting and Ziegler, 1986]. Therefore, phase identification of the sintered articles was confirmed by using X-ray diffraction (SIEMENS D5000). The samples were scanned from 10 to 80° with a step size of 0.04° and from 26 to 38° with the step size of 0.01°.

For mechanical properties measurement, sintered specimens were first polished with SiC paper (grid No. 240, 800 and 1200) and 1-μm diamond polishing paste before the fracture toughness and the hardness determination. The fracture toughness was determined by measuring an indentation crack size from the load of 98 N of a Vickers indenter (Zwick 3212, Zwick GmbH & Co.) for 15 second in air at room temperature according to JIS-R1610-1991 standard. The corresponding diagonal length of the indentation and crack size measured by using an optical microscope (BX60MF5, OLYMPUS OPTICAL Co., Ltd., Japan), as shown in Figure 3.2, are used to calculate the Vickers hardness and fracture toughness.

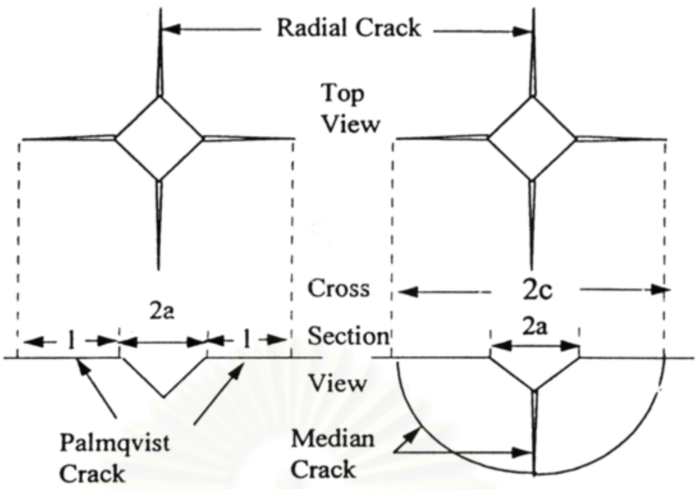

Figure 3.2 Drawing of Vickers indentation [Hill, *et al.*, 1998]

The Vickers hardness, H_v, was calculated by using the following equation:

$$H_v = 1.8544 \times \frac{P}{(2a)^2} \tag{3.11}$$

where P is the indentation load (kg), and $2a$ is the diagonal of indentation (mm). The fracture toughness, K_{1C}, was calculated as:

$$K_{1C} = 0.018 \times \left(\frac{E}{H_v}\right)^{1/2} \left(\frac{P}{c^{3/2}}\right) \tag{3.12}$$

or

$$K_{1C} = 0.026 \times \frac{E^{1/2} P^{1/2} a}{c^{3/2}} \tag{3.13}$$

where E is the Young's modulus (GPa), and c is crack length (mm). Examples of indentation and its calculation are shown in Appendix C.

All fracture toughness and hardness measurements were done at STREC.

Finally, the grain morphology and the microstructure of fracture surfaces were investigated by using a JSM-6400 (JEOL Co., Ltd.) scanning electron microscope (SEM) at STREC.

CHAPTER IV

RESULTS AND DISCUSSION

The main purpose of this study is to investigate catalytic effects of metals, commonly used as sintering additives, on the nitridation of silicon and to observe the effects of their residual on the microstructure as well as physical and mechanical properties. This chapter is divided into three sections. The preliminary experiments are firstly discussed in section 4.1. Results and discussion for the synthesis of silicon nitride powder are given in section 4.2, while those for the properties of silicon nitride articles are presented in the last section.

4.1 Preliminary Experiments

4.1.1 Verification of the impregnation

The metal content in selected impregnated silicon raw materials were analyzed by atomic absorption spectroscopy (AAS) at Thailand Institute of Science and Technology Research, Bangkok, Thailand. The results are shown in Table 4.1

Table 4.1 The measured metal content in the selected impregnated silicon

Sample	Impregnated metal content, [%]	Metal content detected by AAS, [%]
Calcium impregnated silicon	0.125	0.38
	2.0	1.80
Magnesium impregnated silicon	0.125	0.20
	2.0	1.70

As shown in Table 4.1, the content of impregnated metals are in the neighbor of those detected from AAS. It should be noted that the higher the metal content, the lower the error detected. Significant errors detected from the samples with lower metal content might be the result from sample digestion procedure for AAS measurement. Although there are some errors, this is an important evidence to confirm that the metals from the impregnation are still contained in silicon raw material. However, the metal content in silicon nitride product can not be analyzed because the complete digestion of silicon nitride is very difficult.

4.1.2 Consistency and reproducibility of results

Bare silicon granules were put in the most upstream sample tray for every experiment as a control sample. The conversion of the control sample in each run was recorded to observe the consistency of the experiments. As shown in Figures 4.1-4.3, the results of experiments under the same operating conditions are generally consistent.

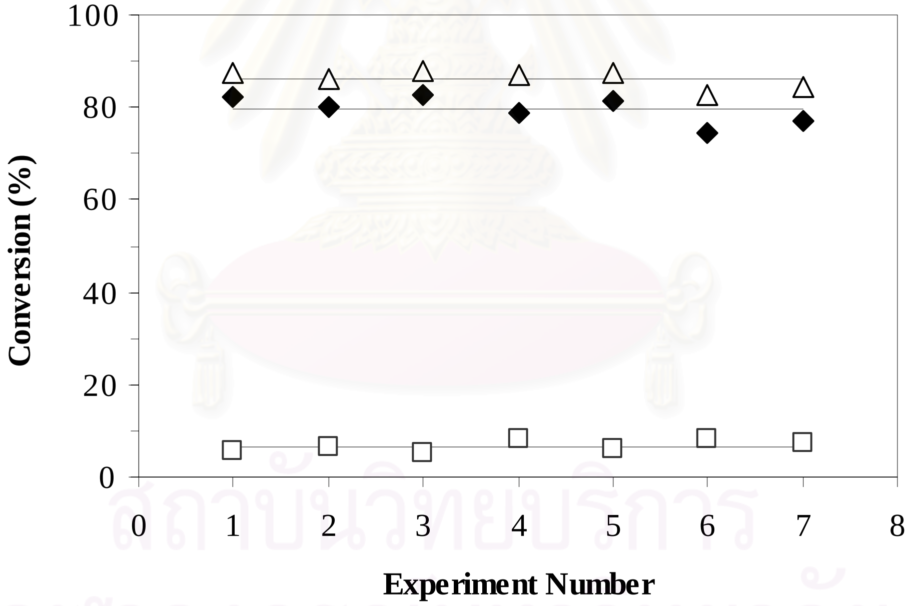

Figure 4.1 Conversions of control samples from nitridation at 1300°C: (△) – overall conversion; (◆) – conversion of silicon into α-Si_3N_4; (□) - conversion of silicon into β-Si_3N_4; (—) – average values.

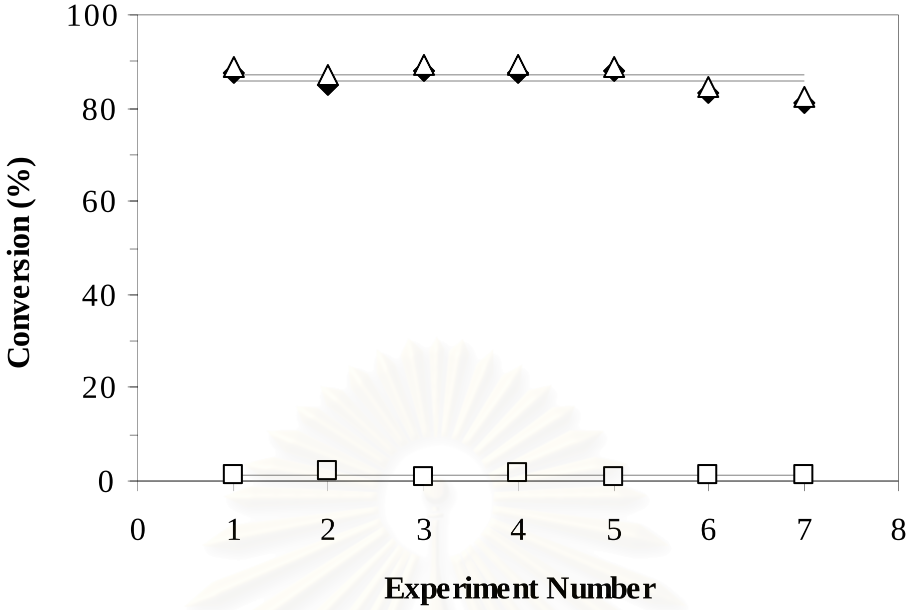

Figure 4.2 Conversions of control samples from nitridation at 1390°C: (△) – overall conversion; (◆) – conversion of silicon into α-Si_3N_4; (□) - conversion of silicon into β-Si_3N_4; (—) – average values.

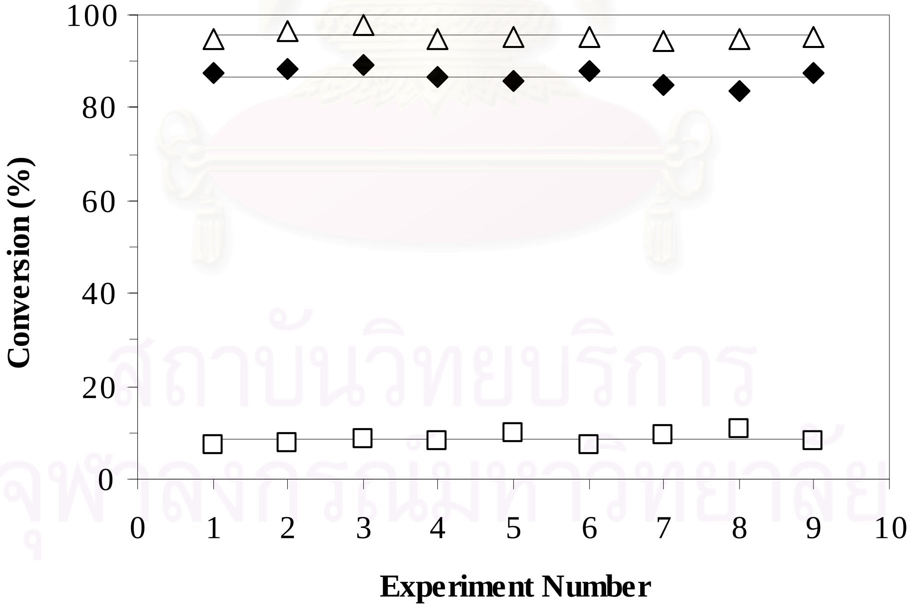

Figure 4.3 Conversions of control samples from nitridation using stepwised increase in temperature: (△) – overall conversion; (◆) – conversion of silicon into α-Si_3N_4; (□) - conversion of silicon into β-Si_3N_4; (—) – average values.

The reproducibility for sample preparations was also confirmed. The samples impregnated metals from different batches yielded roughly the same conversion, as presented in Table 4.2.

Table 4.2 Conversions observed from different sample-preparation batches:

(a) Nitridation of various silicon granules at 1300°C.

Sample	Batch I			Batch II		
	Yield of α-phase, [%]	Yield of β-phase, [%]	Overall conversion, [%]	Yield of α-phase, [%]	Yield of β-phase, [%]	Overall conversion, [%]
Bare Si	84.98	5.69	90.67	84.61	5.00	89.61
0.125% Mg added	80.99	6.27	87.26	82.59	5.57	88.16
2% Mg added	60.06	3.13	63.19	62.76	3.67	66.43

(b) Nitridation of various silicon powders using stepwised increase in temperature.

Sample	Batch I			Batch II		
	Yield of α-phase, [%]	Yield of β-phase, [%]	Overall conversion, [%]	Yield of α-phase, [%]	Yield of β-phase, [%]	Overall conversion, [%]
Bare Si	98.57	1.14	99.71	98.85	0.86	99.72
0.125% Ca added	98.43	0.73	99.16	98.13	0.80	98.93
1% Yb added	98.09	0.51	98.60	98.16	0.46	98.66

4.2 Synthesis of Silicon Nitride Powder

4.2.1 The direct nitridation at constant temperature

The propose of this work is to achieve high content of α-silicon nitride in the product from the direct nitridation of silicon. As mentioned earlier, one of the most apparent factors that affects α-/β-phase composition of the product from the direct nitridation is the presence of metals in silicon. The effects of various transition metals on the nitridation of silicon are investigated.

It has been known that the overall conversion of the direct nitridation at temperature lower than 1300°C is unacceptably low and the temperature near 1400°C would result in melting of the silicon raw materials [Jovanovic, 1998]. Moreover, the extent of the nitridation at temperature in the range of 1300 to 1370°C are roughly constant [Pavarajarn and Kimura, 2001]. Therefore, in this study, the nitridation was conducted only at 1300 and 1390°C by using a tubular flow reactor. It was operated for 3 hours with the stream of 90% nitrogen with 10% hydrogen, after 1 hour of pretreatment in a stream of 90% argon with 10% hydrogen at the same temperature as the reaction temperature. Some researchers used ammonia as the nitrogen source, but the reactant was silicon hydrides produced by reacting silicon powder with hydrogen [Huttinger and Pieschnick, 1994]. However, the nitridation of silicon by using ammonia has not been reported. The results regarding the effects of metal on the overall conversion and fraction of α- and β-phase of the direct nitridation at constant temperature are described below.

The effects of various metals on the overall conversion of silicon to silicon nitride, at 1300 and 1390°C are presented in Figure 4.4. It can be observed that the overall conversions at 1300ºC are generally decreased when a metal is added to the silicon raw material. The higher the metal content, the lower the overall conversion, with exception of an addition of small amount of calcium which enhances the conversion of silicon to silicon nitride. When the reaction temperature is raised to 1390ºC, the overall conversion is slightly increased with the same trend as at 1300°C. This observation levels off or increases when the amount of calcium, cerium, lutetium or magnesium is higher than 1%, except for yttrium. Moreover, the results from ytterbium impregnated silicon show that it does not significantly influence the progress of silicon nitridation at both temperatures.

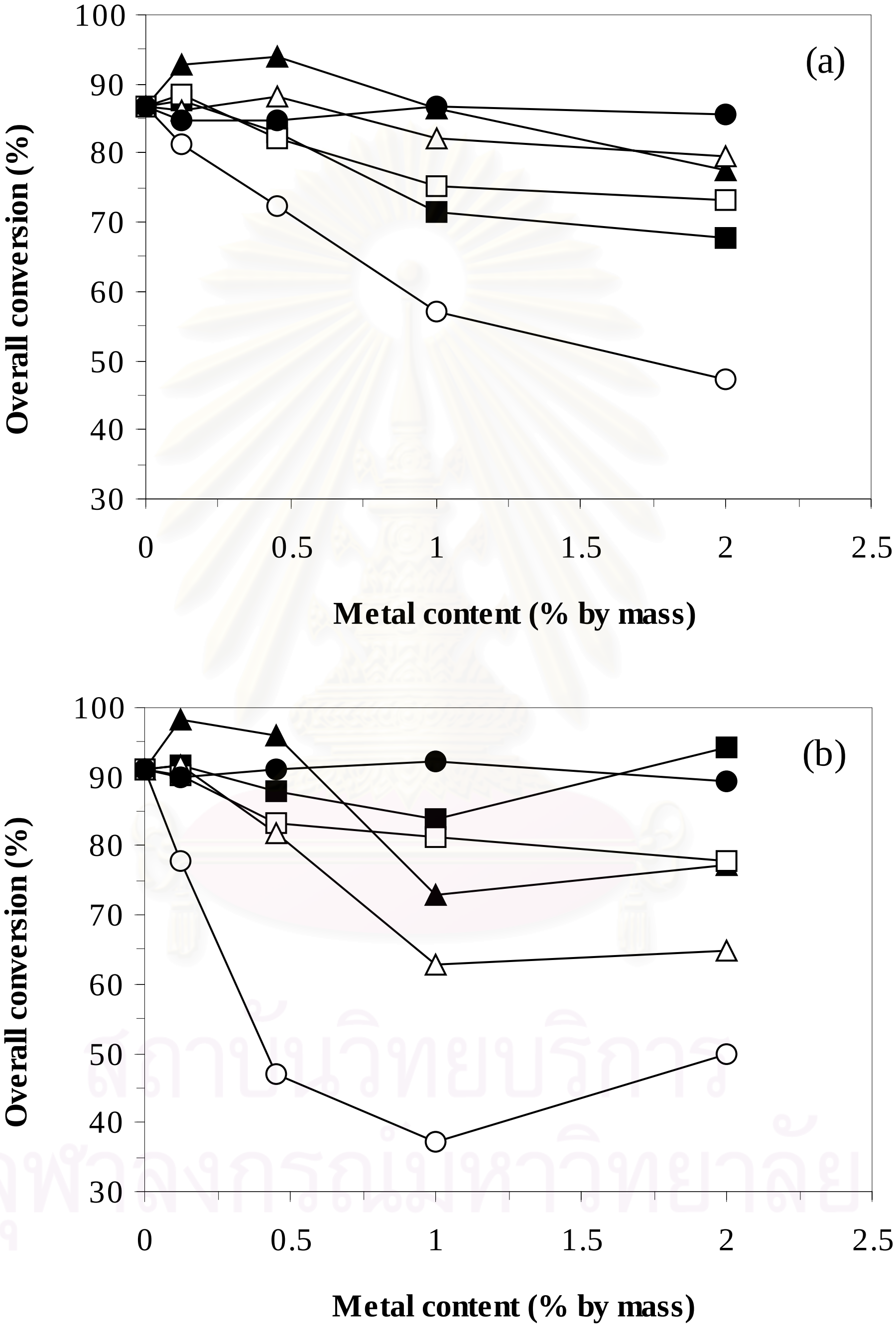

Figure 4.4 Comparison of the overall conversions from the direct nitridation of silicon impregnated with various kind of metal at constant temperature; (a) 1300°C, and (b) 1390°C: (▲) – calcium; (○) – cerium; (△) – lutetium; (■) – magnesium; (●) – ytterbium; (□) – yttrium.

The effects of each metal on the fraction of α- and β-phase in the product are presented as follows:

4.2.1.1 Addition of Calcium

Calcium is investigated in this work because it has been found to be effective in term of enhancing the formation of α-silicon nitride [Pigeon, *et al.*, 1993]. Results of the nitridation of calcium impregnated silicon at 1300 and 1390°C are shown in Figure 4.5. They indicate that an addition of a small amount of calcium, as low as 0.125%, significantly enhances the formation of α-phase in silicon nitride product and suppresses fraction of β-phase at both temperatures. This tendency is consistent with previous work [Pavarajarn and Kimura, 2001].

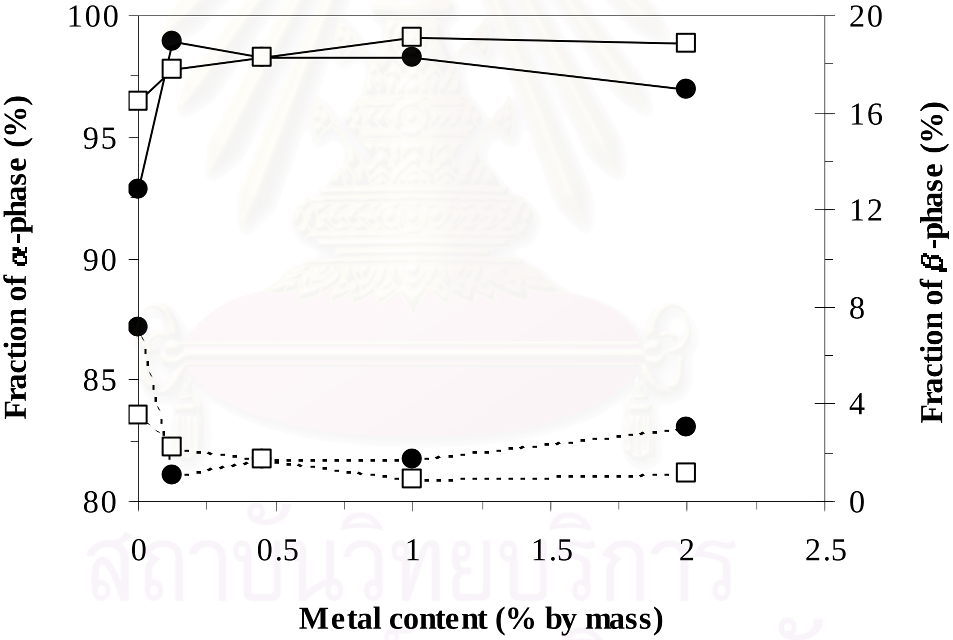

Figure 4.5 Fraction of α- and β-phase in silicon nitride product obtained by the direct nitridation of calcium impregnated silicon.
(●) – nitridation at 1300°C; (□) – nitridation at 1390°C;
(—) – fraction of α-phase; (--) – fraction of β-phase

Especially for 1300°C, the fraction of α-phase in silicon nitride product obtained from 0.125% calcium impregnated silicon is markedly increased more than

6% in addition to those from bare silicon, while the content of β-phase is clearly decreased as low as 85% of those from bare silicon. However, the enhancement in the fraction of α-phase decreases when the content of calcium is higher than 0.45%. This phenomenon is not observed from the nitridation at 1390°C.

At 1390°C, when the amount of calcium is low, the fraction of α-phase obtained is slightly increased, comparing to that obtained from bare silicon. This observed enhancement increases with amount of calcium added, but levels off at high calcium content. It is also observed that the formation of α-phase at 1390°C is slightly higher than those from 1300°C.

4.2.1.2 Addition of Cerium

Figure 4.6 shows the effect of cerium on the nitridation of silicon at 1300 and 1390°C. As shown in figure, for the nitridation at 1300°C, the slightly increased of α-phase content in silicon nitride product is found in all composition of cerium. But for 1390°C, it seems that cerium generally suppresses fraction of α-phase. The higher the cerium content, the lower the fraction of α-phase. The nitridation of 2% cerium impregnated silicon at 1390°C results in only 49.9% overall conversion with 79.6% α-phase content.

However, it is found that the fraction of α-phase obtained from 0.45% cerium added is slightly higher than bare silicon. This result can be observed from both temperatures. In addition to the fraction of α-phase, the formation of β-phase from 0.45% cerium impregnated is lower than that from bare silicon, especially at 1390°C which results only 1% β-phase. Conversely, at 1390°C, the content of β-silicon nitride obtained from 2% cerium addition becomes as high as six times the content of β-phase in the product from bare silicon.

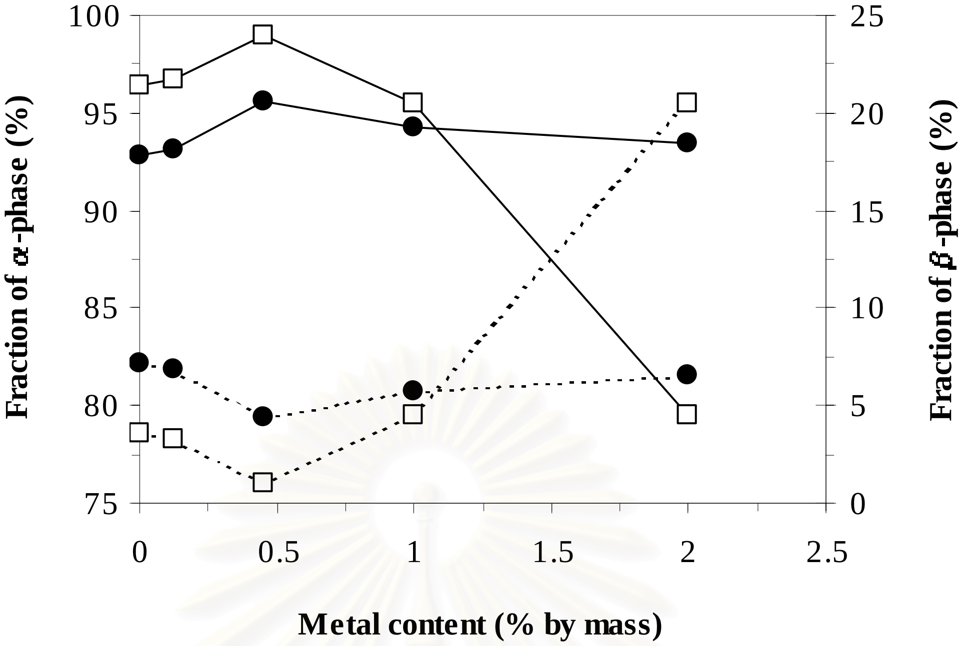

Figure 4.6 Fraction of α- and β-phase in silicon nitride product obtained by the direct nitridation of cerium impregnated silicon
(●) – nitridation at 1300°C; (□) – nitridation at 1390°C;
(—) – fraction of α-phase; (--) – fraction of β-phase

4.2.1.3 Addition of Lutetium

Results of the nitridation of lutetium impregnated silicon is shown in Figure 4.7. It indicates that lutetium tends to enhance the formation of α-phase at both temperatures. The higher the lutetium content, the higher the fraction of α-phase. Especially at 1390°C, the α-phase content achieved reaches 100% while the formation of β-phase is suppressed to 0% when the amount of lutetium added is 1% or higher.

The same tendency is also observed from the nitridation at 1300°C with lower α-phase content and higher for β-phase than those from 1390°C.

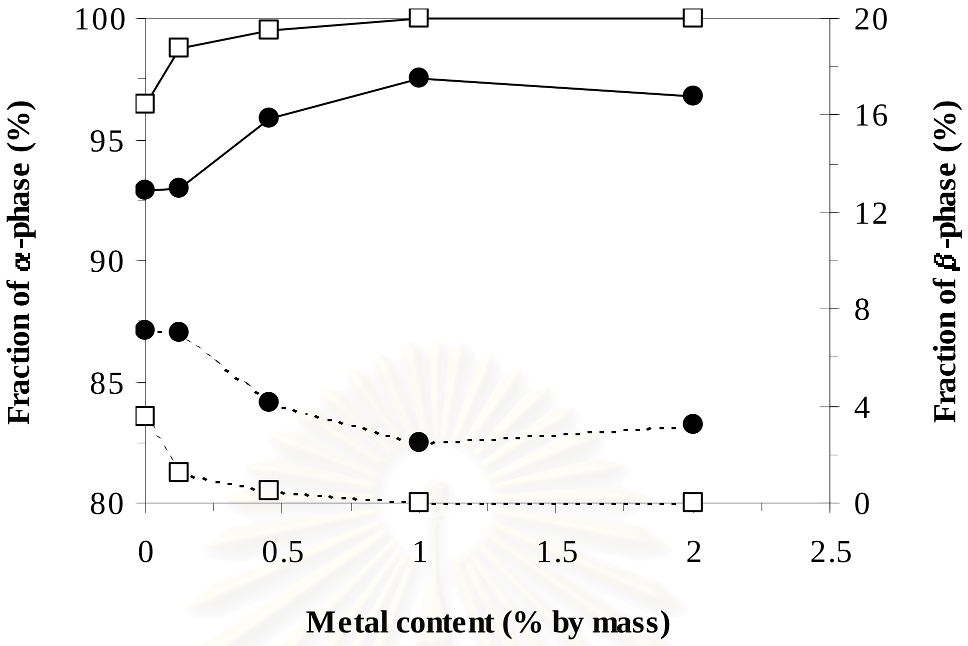

Figure 4.7 Fraction of α- and β-phase in silicon nitride product obtained by the direct nitridation of lutetium impregnated silicon
(●) – nitridation at 1300°C; (□) – nitridation at 1390°C;
(—) – fraction of α-phase; (--) – fraction of β-phase

4.2.1.4 Addition of Magnesium

The effect of magnesium impregnated on the nitridation of silicon is presented in Figure 4.8. It can be observed that magnesium does not influence the progress of silicon nitridation at both temperatures. As shown in the figure, the fraction of α- and β-phase obtained from silicon impregnated with magnesium are roughly the same as those from bare silicon, regardless the amount of magnesium added. Although, addition of magnesium does not affect the content of α- or β-phase in the silicon nitride product, the overall conversion is effected by magnesium content, as mentioned earlier.

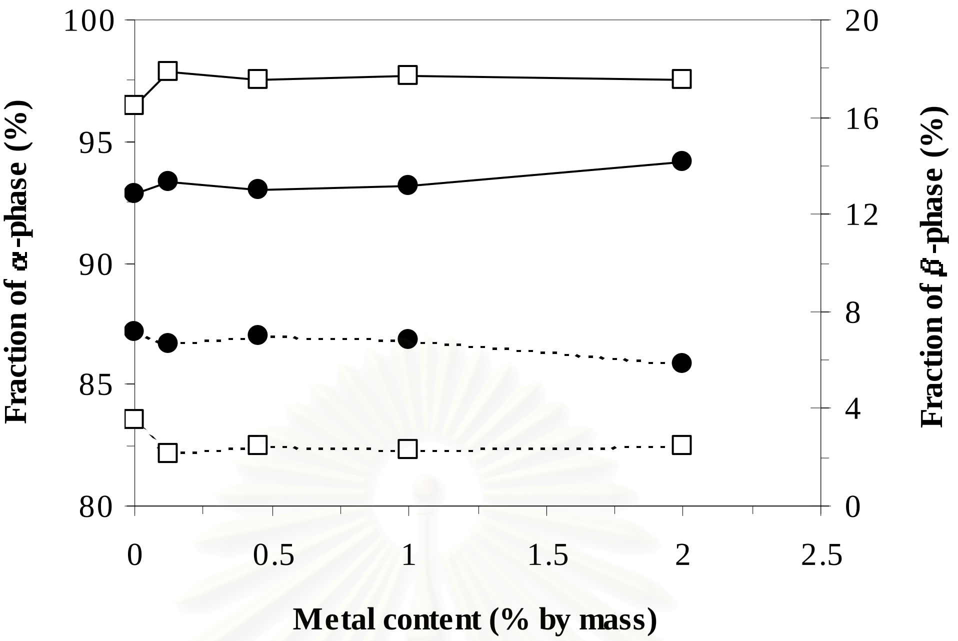

Figure 4.8 Fraction of α- and β-phase in silicon nitride product obtained by the direct nitridation of magnesium impregnated silicon
(●) – nitridation at 1300°C; (□) – nitridation at 1390°C;
(—) – fraction of α-phase; (--) – fraction of β-phase

4.2.1.5 Addition of Ytterbium

Figure 4.9 shows the effect of ytterbium on the nitridation of silicon at 1300 and 1390°C. It is found that at 1300°C, the fraction of α-phase significantly increases with the ytterbium content. Especially for 2% ytterbium addition, the α-phase content increases towards 100% and also suppresses the fraction of β-phase by 91% of the value obtained from bare silicon. The nitridation at 1390°C also results in the same trend, but the value of α-phase content achieves nearly 100% when amount of ytterbium as small as 0.125% is added to silicon. Moreover, similar to calcium and lutetium, the formation of β-phase at 1390°C is suppressed to very low level comparing to those from 1300°C.

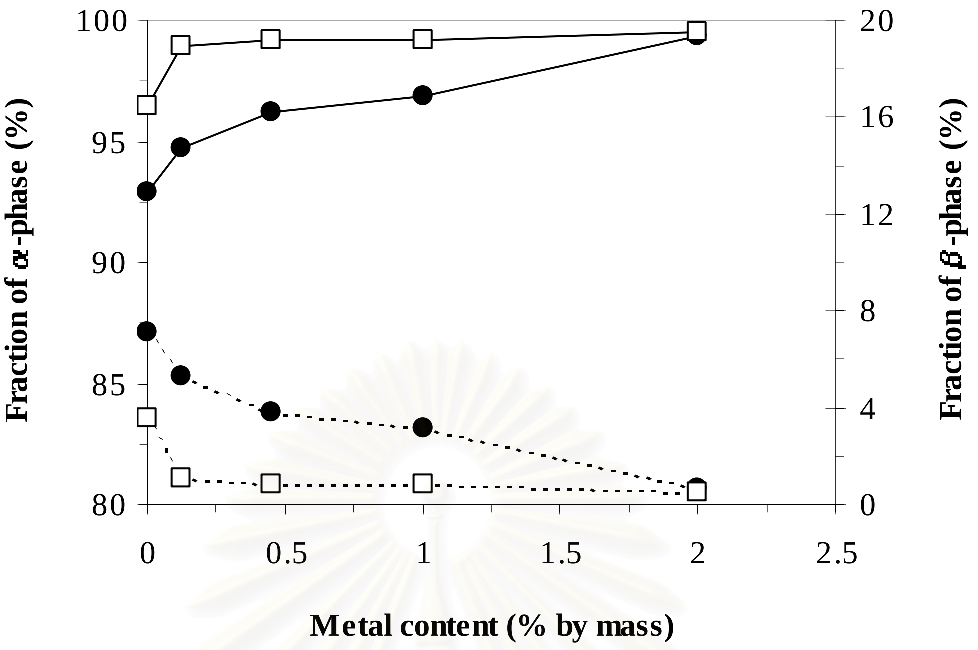

Figure 4.9 Fraction of α- and β-phase in silicon nitride product obtained by the direct nitridation of ytterbium impregnated silicon
(●) – nitridation at 1300°C; (□) – nitridation at 1390°C;
(—) – fraction of α-phase; (--) – fraction of β-phase

4.2.1.6 Addition of Yttrium

The effect of yttrium on the nitridation of silicon is very similar to those of ytterbium. Figure 4.10 indicates that yttrium is another metal that suppresses the β-silicon nitride formation. β-phase is hardly detected by XRD since it becomes as low as almost zero when silicon granules impregnated with 1% yttrium or higher was nitrided at 1390°C.

Fractions of α-phase from the nitridation at both temperatures increase with the yttrium content. The content of α-phase obtained from the reaction at 1390°C is higher than those from 1300°C, especially for 2% yttrium addition which promotes the formation of α-silicon nitride toward 100%.

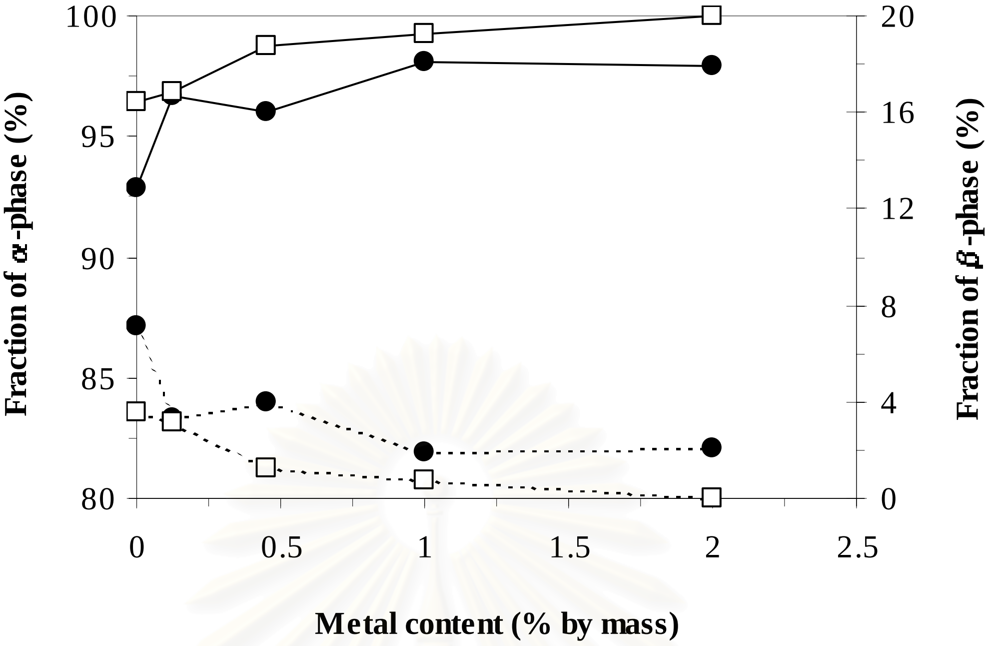

Figure 4.10 Fraction of α- and β-phase in silicon nitride product obtained by the direct nitridation of yttrium impregnated silicon
(●) – nitridation at 1300°C; (□) – nitridation at 1390°C;
(—) – fraction of α-phase; (--) – fraction of β-phase

Comparison for the effects of all metals investigated on the direct nitridation, in term of the fraction of α-phase, at both 1300 and 1390°C are presented in Figure 4.11 (a) and (b), respectively.

As mentioned in the prior chapter, the content of α-phase in silicon nitride higher than 95% is often desired. According to Figure 4.11, it is shown that the nitridation of silicon impregnated with almost all metals investigated at both temperatures can achieve the fraction of α-phase higher than 95%, with exception of the whole series of magnesium at 1300°C, high cerium content at both temperatures and low content of lutetium and ytterbium at 1300°C. It is clearly evident that an addition of some metals to the silicon before the nitridation can enhance the selectivity of α-silicon nitride formation. The obtained results agree with the report from literature that the characteristics of individual metals dominate the formation of α- or β-silicon nitride [Pavarajarn and Kimura, 2001].

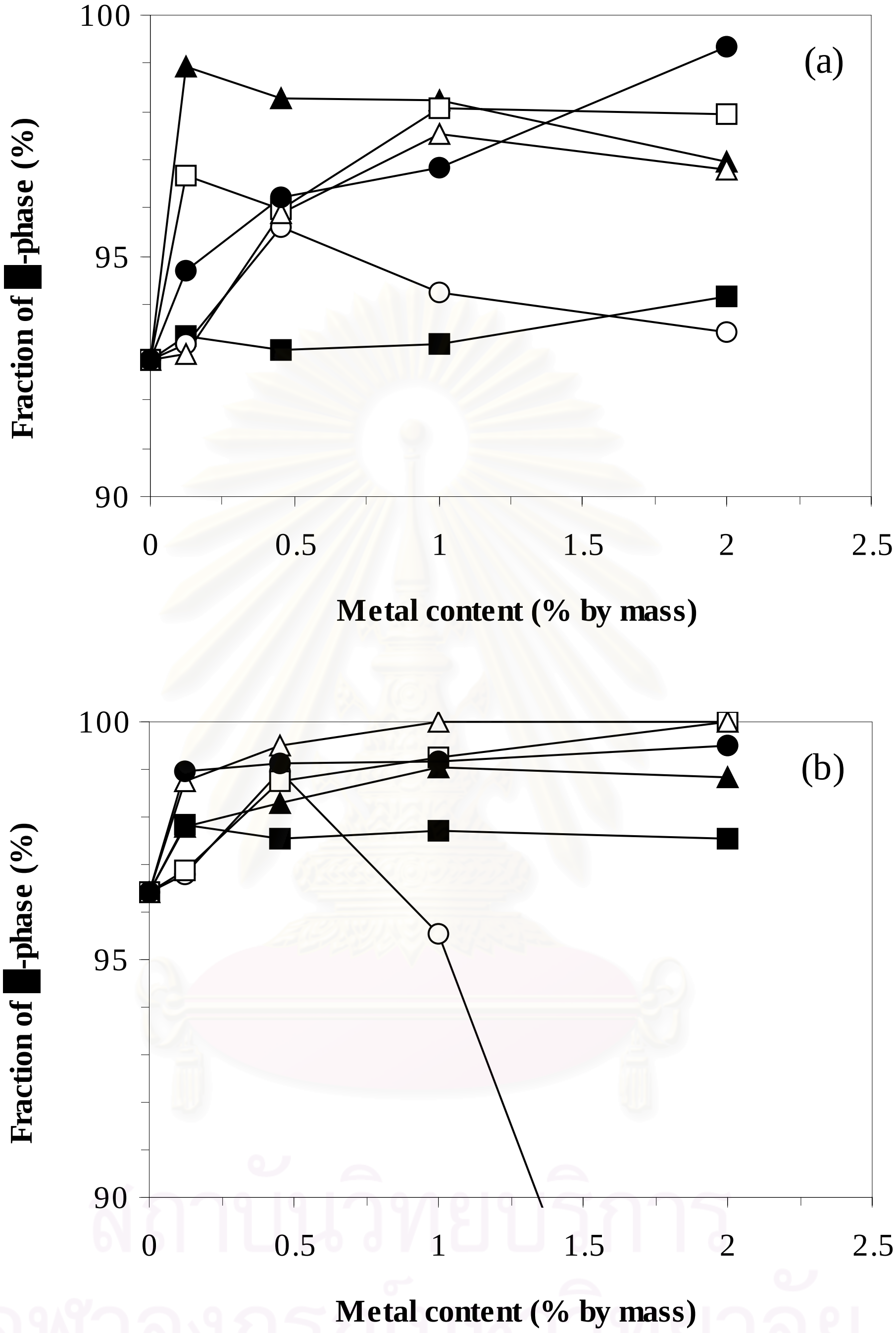

Figure 4.11 Comparison of the fraction of α-phase from the direct nitridation of silicon impregnated with various kind of metals at constant temperature; (a) 1300°C, and (b) 1390°C: (▲) – calcium; (○) – cerium; (△) – lutetium; (■) – magnesium; (●) – ytterbium; (□) – yttrium.

It should be noted that the product from the nitridation of bare silicon at 1390°C contains more than 95% of α-phase. Nevertheless, the enhancement of each metal on the formation of α-silicon nitride is also more than those from bare silicon. Although the nitridation at 1300°C gives lower fraction of α-phase than those from 1390°C, the reaction temperature of 1300°C is preferable for the direct nitridation of silicon since it is not too close to the melting point of silicon. Therefore, the agglomeration of product can be avoided.

However, as reported earlier, the overall conversion of the direct nitridation at both temperatures are generally decreased with the metal content. At this point, it should be mentioned that the success of employing metals to enhance α-phase content and suppress formation of β-phase is not complete. The problem is needed to be solved in order to increase the overall conversion of the silicon nitride product from the direct nitridation of silicon. This issue will be discussed in the following section.

4.2.2 The direct nitridation using stepwised increase in temperature

The results presented in the above section confirm the enhancement of the direct nitridation by the addition of some metals into silicon raw materials. However, the main problem lies on the fact that the achievable overall conversion of silicon is not high enough. The overall conversions achieved from metal-impregnated silicon granules are usually lower than that achieved by using bare silicon. This problem can be overcame by using a step-wise increase in the reaction temperature from 1300°C to 1390°C, as suggested elsewhere [Jovanovic, *et al.*, 1994]. In order to avoid the agglomeration of silicon, the nitridation was initially carried out at 1300°C for one hour to build up silicon nitride shell covered silicon surface. Then, the temperature was raised at the rate of 10°C/min to 1390°C where the system was held at this temperature for two hours in order to complete the nitridation of silicon. The results of the operation with programmed temperature are shown in Figure 4.12 to 4.14, respectively.

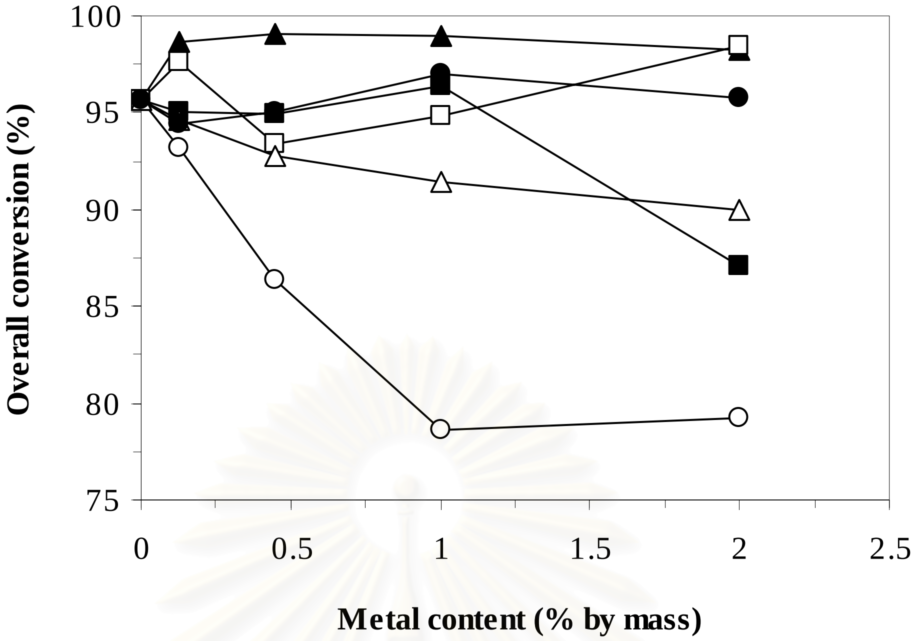

Figure 4.12 Comparison of the overall conversion from the direct nitridation of silicon impregnated with various kinds of metal using stepwised increase in temperature: (▲) – calcium; (○) – cerium; (△) – lutetium; (■) – magnesium; (●) – ytterbium; (□) – yttrium.

Figure 4.12 clearly illustrates significant improvement in the overall conversion achieved by using the programmed temperature operations, comparing to the nitridation at constant temperature shown in Figure 4.4. Especially for the nitridation of silicon impregnated with calcium, it yields the overall conversion that is almost 100% for all composition investigated. It can be concluded that this operation is effective for achieving high overall conversion within short time.

Moreover, the fraction of α-form in the product remains at relatively high level, as shown in Figure 4.13, especially when calcium, ytterbium or yttrium is used.

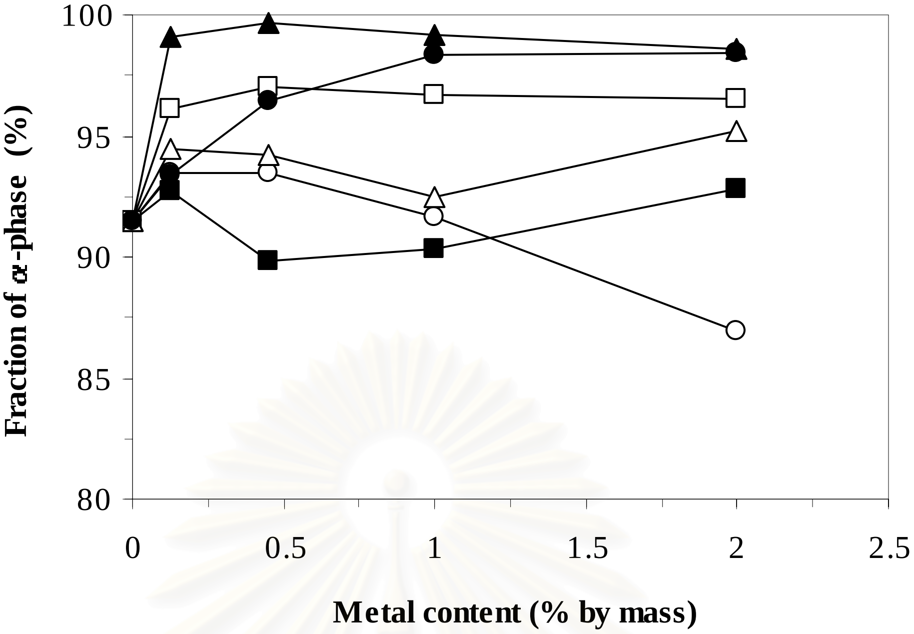

Figure 4.13 Comparison of the fraction of α-phase from the direct nitridation of silicon impregnated with various kinds of metal using stepwised increase in temperature: (▲) – calcium; (○) – cerium; (△) – lutetium; (■) – magnesium; (●) – ytterbium; (□) – yttrium.

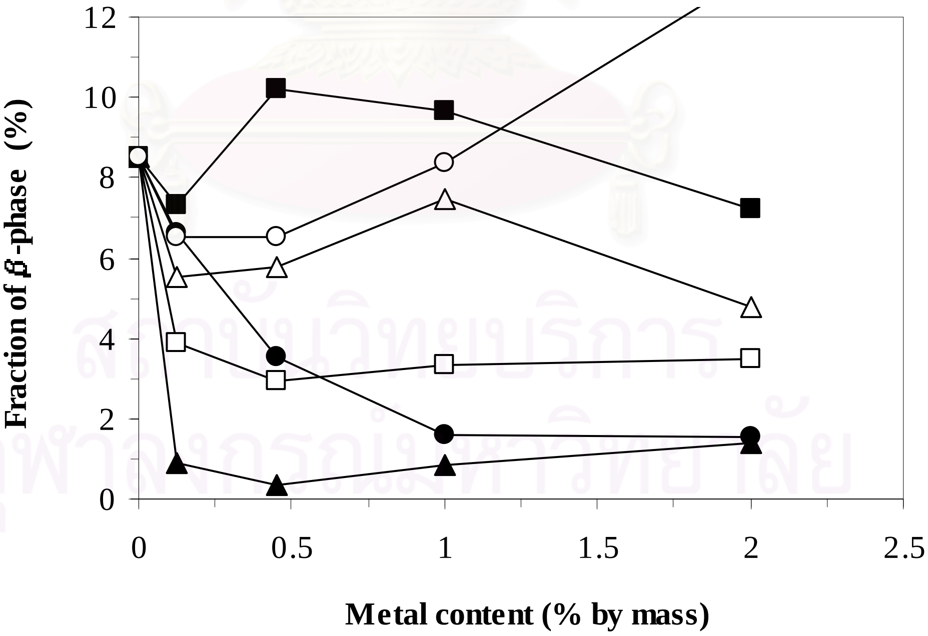

Figure 4.14 Comparison of the fraction of β-phase from the direct nitridation of silicon impregnated with various kinds of metal using stepwised increase in temperature: (▲) – calcium; (○) – cerium; (△) – lutetium; (■) – magnesium; (●) – ytterbium; (□) – yttrium.

The content of α-phase obtained from calcium impregnated silicon reaches 100% with only small amount of calcium added and remains at high level in all calcium compositions. A significantly improved α-phase content about 98% is achieved by 1% ytterbium or higher, while more than 0.45% of yttrium is needed to get about 97% α-phase content. In addition to the enhancement of the nitridation, as shown in Figure 4.14, the formation of β-phase in silicon nitride product is also suppressed when silicon is impregnated with small amount of calcium. It prominently decreases over 90%, comparing with the result obtained from bare silicon. This effect is also observed in 1% ytterbium or 0.45% yttrium addition. For cerium, lutetium and magnesium impregnated silicon, the content of β-phase tends to increase, comparing to the result from the direct nitridation at constant temperatures.

4.2.3 Summary for catalytic effects of metals on the direct nitridation of silicon

The overall conversion and the fraction of β-phase in the nitrided product from all nitridation conditions are plotted together to clearly verify the best condition to get highest α-silicon nitride for each metal. Noted that the fraction of β-phase is directly related to the fraction of α-phase. Figures 4.15 and 4.16 indicate that, among the metals investigated, only cerium enhances neither the overall conversion nor the fraction of α-silicon nitride in the product. It seems that cerium retards the nitridation of silicon, especially at 1390°C. On the contrary, lutetium and magnesium have shown a significant enhancement of the nitridation at 1390°C. The nitridation of silicon with an addition of 0.125% lutetium at 1390°C yields high overall conversion with α-phase content higher than 98% while 2% magnesium can result in over 94% overall conversion with an α-phase content about 97%.

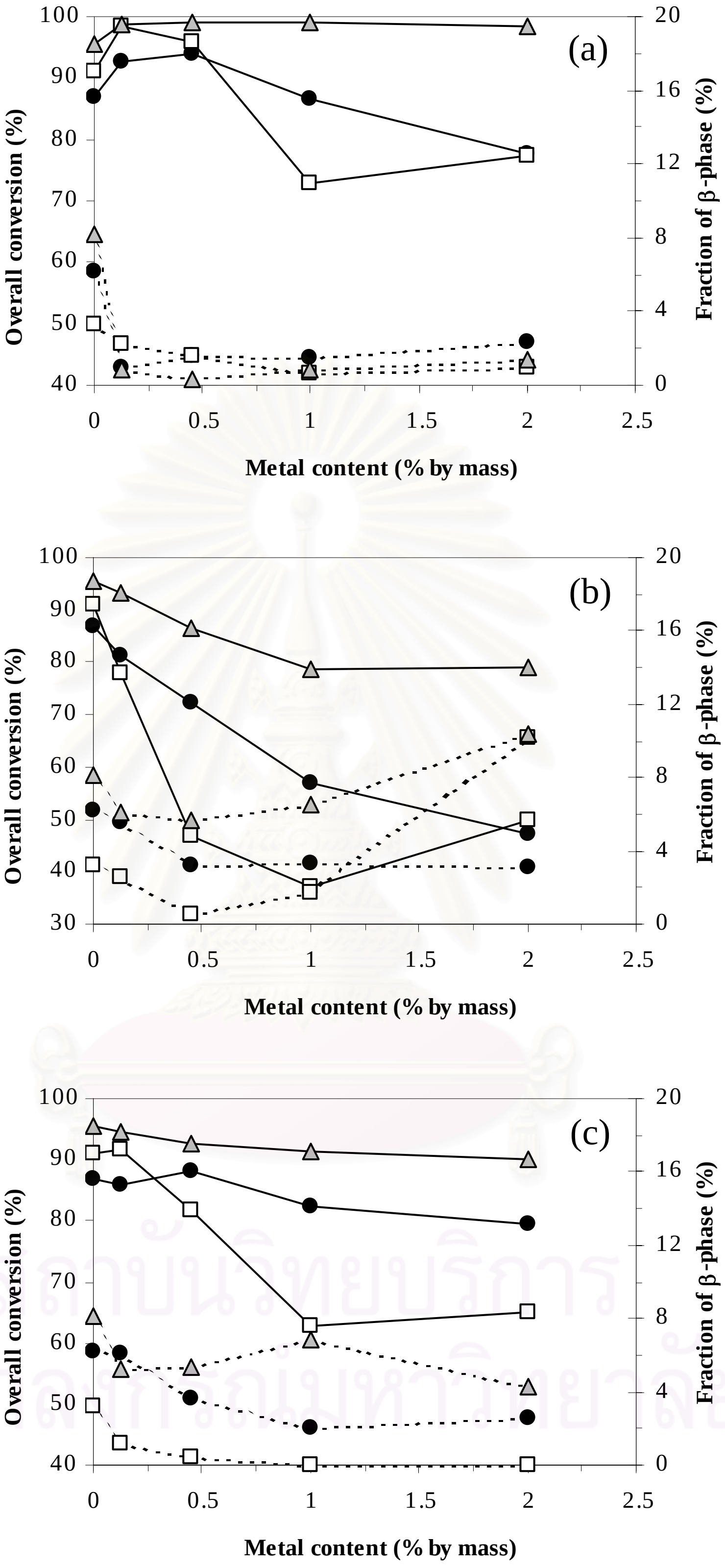

Figure 4.15 Nitridation of metal impregnated silicon; (a) calcium, (b) cerium, and (c) lutetium: (●) – nitridation at 1300°C; (□) – nitridation at 1390°C; (▲) – nitridation using stepwised increase in temperature; (—) – overall conversion; (--) – fraction of β-phase in silicon nitride product

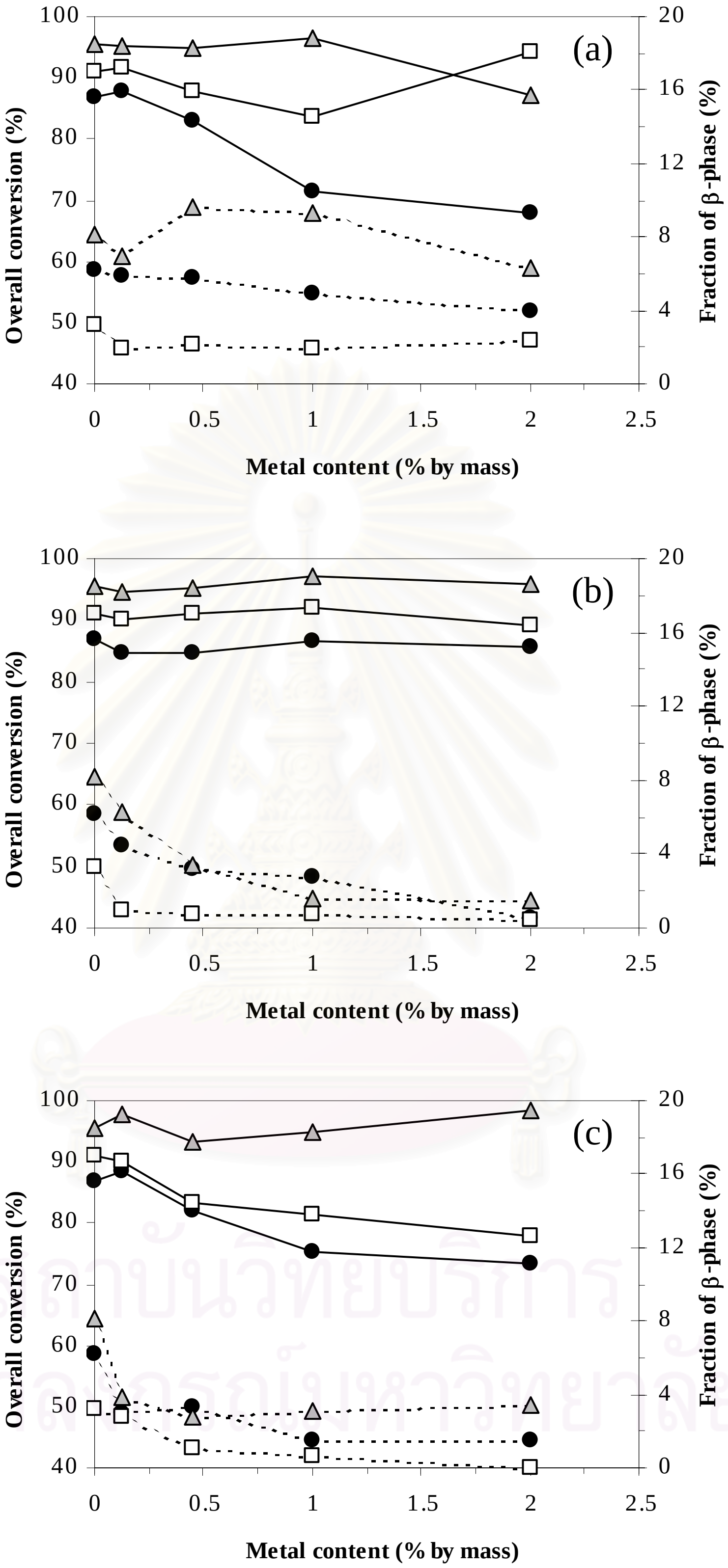

Figure 4.16 Nitridation of metal impregnated silicon; (a) magnesium, (b) ytterbium, and (c) yttrium: (●) – nitridation at 1300°C; (□) – nitridation at 1390°C; (▲) – nitridation using stepwised increase in temperature; (—) – overall conversion; (--) – fraction of β-phase in silicon nitride product

According to these figures, it shows that calcium is the best metal to accelerate the nitridation of silicon. The silicon nitride produced from the nitridation of 0.125% calcium impregnated silicon by using stepwised increase in temperature from 1300 to 1390°C can achieve the overall conversion and the fraction of α-phase both toward 100%. Ytterbium and yttrium also enhance the nitridation at this condition. The products from 1% ytterbium or 2% yttrium can reach the overall conversion as well as the α-phase content over 97%.

As reported earlier, various metals show different catalytic effects on the α- and β-silicon nitride formation. Although many hypotheses were proposed to describe the enhancement of α- or β-phase formation in silicon nitride, there was no general agreement concerning the exact mechanism of the formation of α- and β-silicon nitride.

It has been known that silicon is hardly nitrided with nitrogen in the absence of hydrogen [Boyer and Moulson, 1978; Lin, 1977; Maalmi and Varma, 1996]. An addition of hydrogen to nitrogen increases the rate of nitridation particularly at low temperature and allows high conversion of silicon to silicon nitride in a short time [Barsoum, *et al.*, 1991; Jennings, 1983; Jovanovic, *et al.*, 1994; Maalmi and Varma, 1996; Rahaman and Moulson, 1984]. In this work, hydrogen was always supplying into the reactor at the concentration of 10 vol. % to prevent the formation of the protective layer which retarded the progress of the reaction. This layer composed of silicon dioxide, silicon oxynitride, or a mixture of these two, from forming via the reaction of silicon with impurity oxygen contained in the nitrogen. The protective layer which had once formed in the absence of hydrogen hindered the subsequent nitridation even in the presence of hydrogen [Pavarajarn and Kimura, 2003].

The nitridation takes place at high temperature, in the range of 1200-1400°C. At this temperature, hydrogen can dissociate into ions. These ions are suspected to involve in the reaction, according to the fact that silicon can be passivated by hydrogen [Jackson, 1991]. It is implied that the mechanism of the nitridation may involve electrons or protons transfer within reactants. As discussed earlier, some metals can enhance the nitridation of silicon, in terms of overall conversion as well as formation of α-phase. Thus, it is suggestive to consider the standard reduction potentials of each metal investigated, i.e. an ability to donate or receive electron of each metal as presented in Table 4.3. According to the table, the metals in section A are investigated in this work while those in section B have been investigated in the literatures [Pavarajarn and Kimura, 2001].

Table 4.3 Standard reduction potentials at 25°C [Shriver, *et al.*, 2001]

Half-reaction	Enhance α-Si_3N_4	E° (V)
(A)		
Ca^{2+} (aq) + $2e^-$ ↔ Ca (s)	✓	-2.87
Ce^{3+} (aq) + $3e^-$ ↔ Ce (s)	×	-2.34
Lu^{3+} (aq) + $3e^-$ ↔ Lu (s)	✓	-2.30
Mg^{2+} (aq) + $2e^-$ ↔ Mg (s)	✓	-2.36
Yb^{3+} (aq) + $3e^-$ ↔ Yb (s)	✓	-2.22
Y^{3+} (aq) + $3e^-$ ↔ Y (s)	✓	-2.37
(B)		
Ag^{+} (aq) + e^- ↔ Ag (s)	–	+0.80
Cr^{3+} (aq) + $3e^-$ ↔ Cr (s)	×	-0.74
Cu^{2+} (aq) + $2e^-$ ↔ Cu (s)	×	+0.34
Fe^{3+} (aq) + $3e^-$ ↔ Fe (s)	×	-0.04
Pd^{2+} (aq) + $2e^-$ ↔ Pd (s)	–	+0.92

✓: enhance formation of α-Si_3N_4

×: enhance formation of β-Si_3N_4

– : enhance neither α- nor β-Si_3N_4

It should be noted that E° of metal in section A, which enhances the formation of α-phase, is a high negative value. While metal that does not promote α-phase formation has E° that is positive value or very close to 0. This implies that metal having the tendency to give up electron much more easily than hydrogen tends to enhance the nitridation toward α-silicon nitride. This observation can be applied to all metals investigated, both in this work and in literature, except for cerium. The standard reduction potential of cerium is in the same range of other metals that enhance α-phase but cerium retards the nitridation. This contrary behavior has to be studied in further detail to verify the reason of this result.

Although the actual role of all metals investigated on the nitridation has not been clarified yet, this observation may be useful for further study in the future.

4.2.4 Effects of reaction temperature

Although the effects of various metals dominantly influence the enhancement of the nitridation as well as the formation of α-phase, the effects of the nitridation temperature is also discussed. Scanning electron microscope (SEM) is used to observe surface morphology of silicon nitride product obtained from all reaction temperatures. The results are shown in Figures 4.17 to 4.24, respectively.

The overall observation of SEM pictures indicate that the silicon nitride product obtained from the nitridation at 1300°C has similar surface morphology as those obtained from stepwised increase in temperature from 1300 to 1390°C. The surface of the silicon nitride particle is covered by lots of long fibers which have diameter in submicron range. Although the exact mechanism has not been clarified, the presence of fibers has confirmed that the nitridation involves in the reaction in gas phase which results in fiber growth. On the other hand, morphology of surface of particle obtained from the nitridation at 1390°C is clearly different than the others. The bush-like grains was observed on the surface of the particle. This feature, which suggested the growth of silicon nitride grains in the presence of liquid phase, was found in all products obtained from the nitridation at 1390°C, regardless of type of metal impregnated. Nevertheless, the shape of silicon nitride grains observed varied according to type of metal impregnated, especially yttrium.

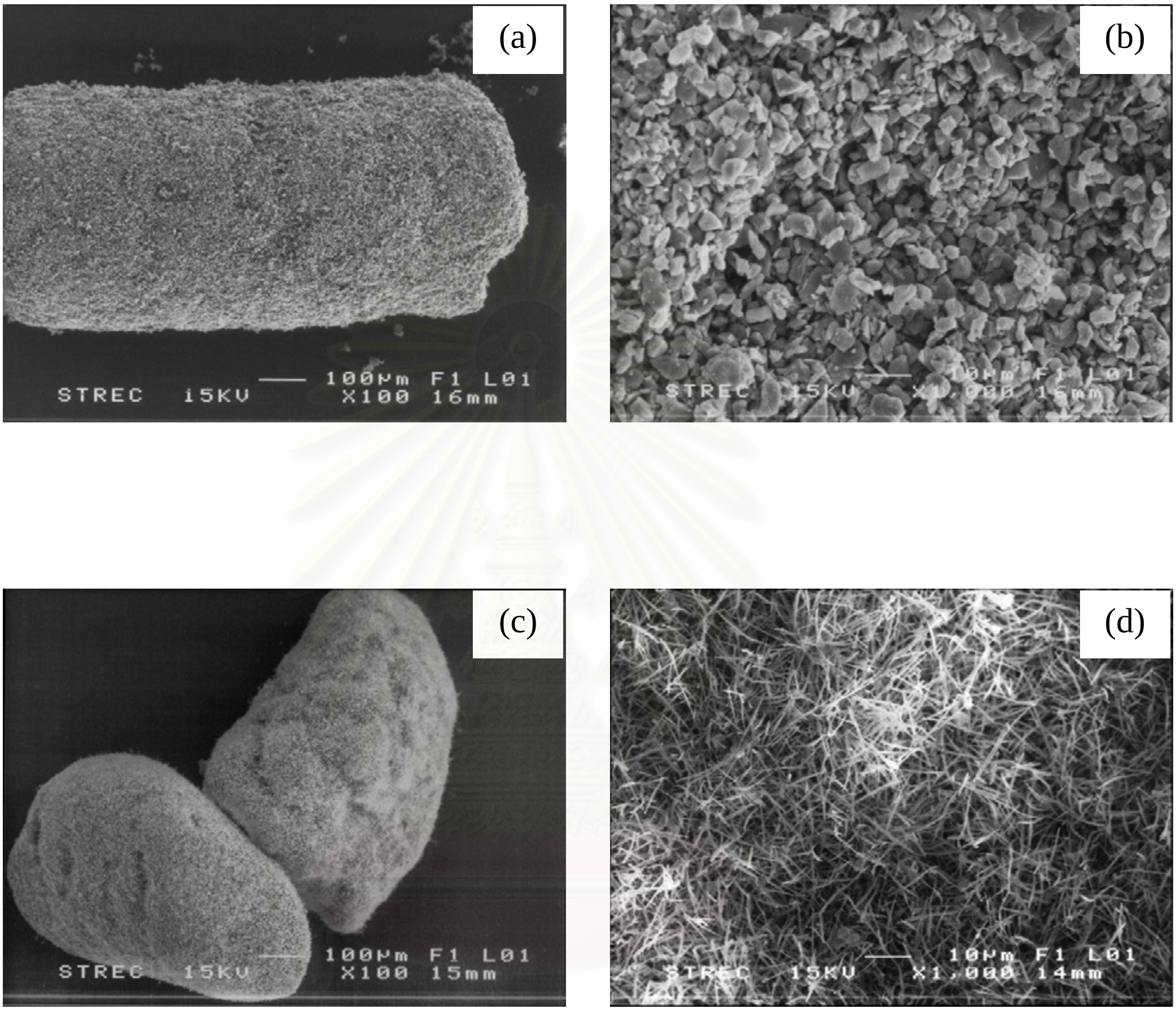

Figure 4.17 SEM micrograph of silicon raw material and silicon nitride product: (a) low magnification image of Si granule; (b) surface of Si granule; (c) low magnification image of silicon nitride product obtained from the nitridation of bare silicon by using stepwised increase in temperature; (d) surface of silicon nitride product

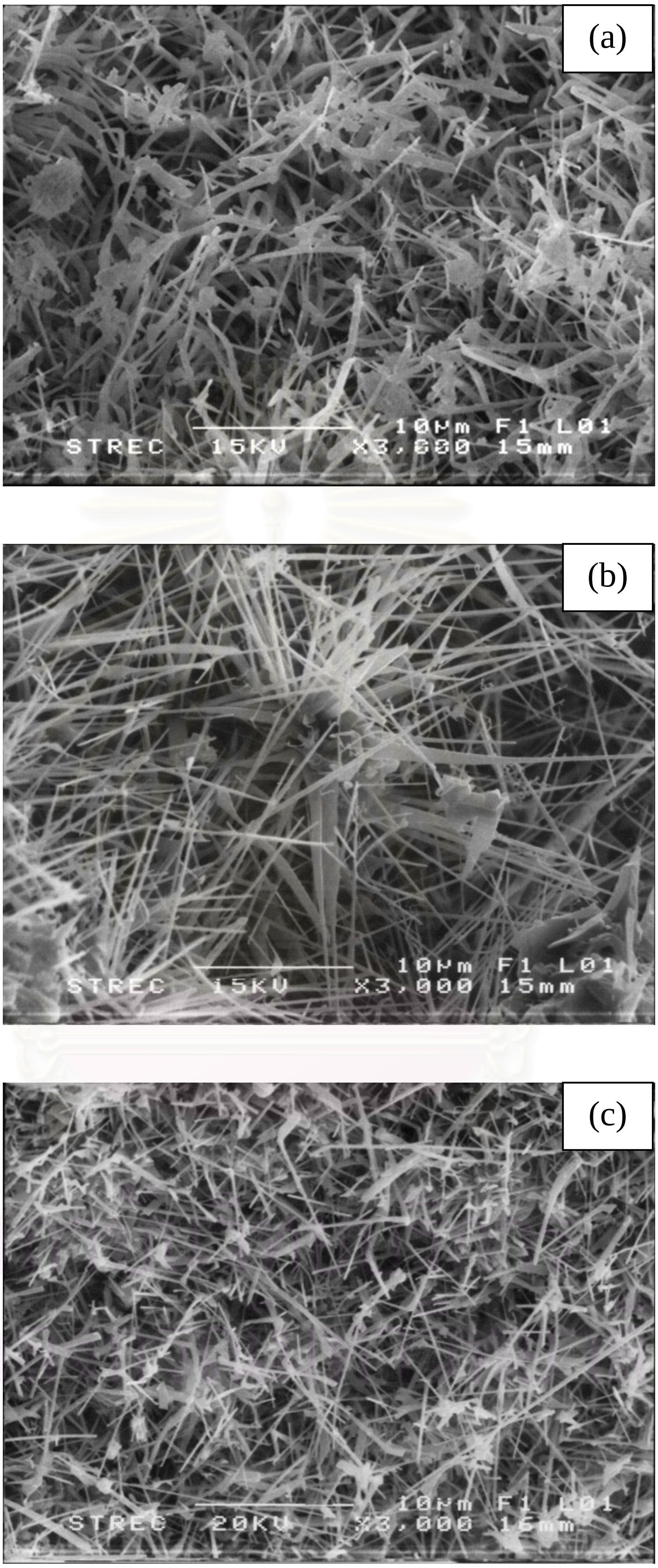

Figure 4.18 SEM micrograph of surface of bare silicon nitride granules obtained from: (a) nitridation at 1300°C; (b) nitridation at 1390°C; (c) nitridation by using stepwised increase in temperature

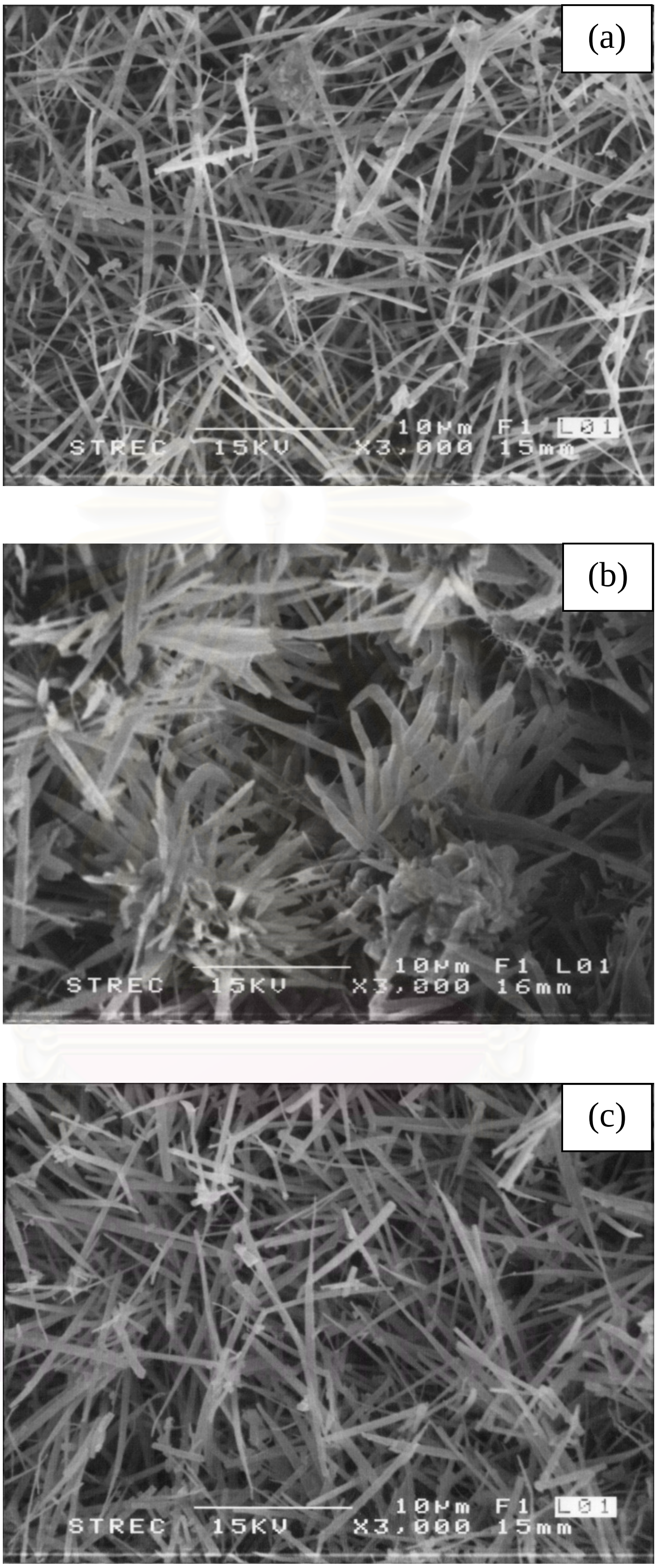

Figure 4.19 SEM micrograph of surface of 1% calcium-doped silicon nitride granules obtained from: (a) nitridation at 1300°C; (b) nitridation at 1390°C; (c) nitridation by using stepwised increase in temperature

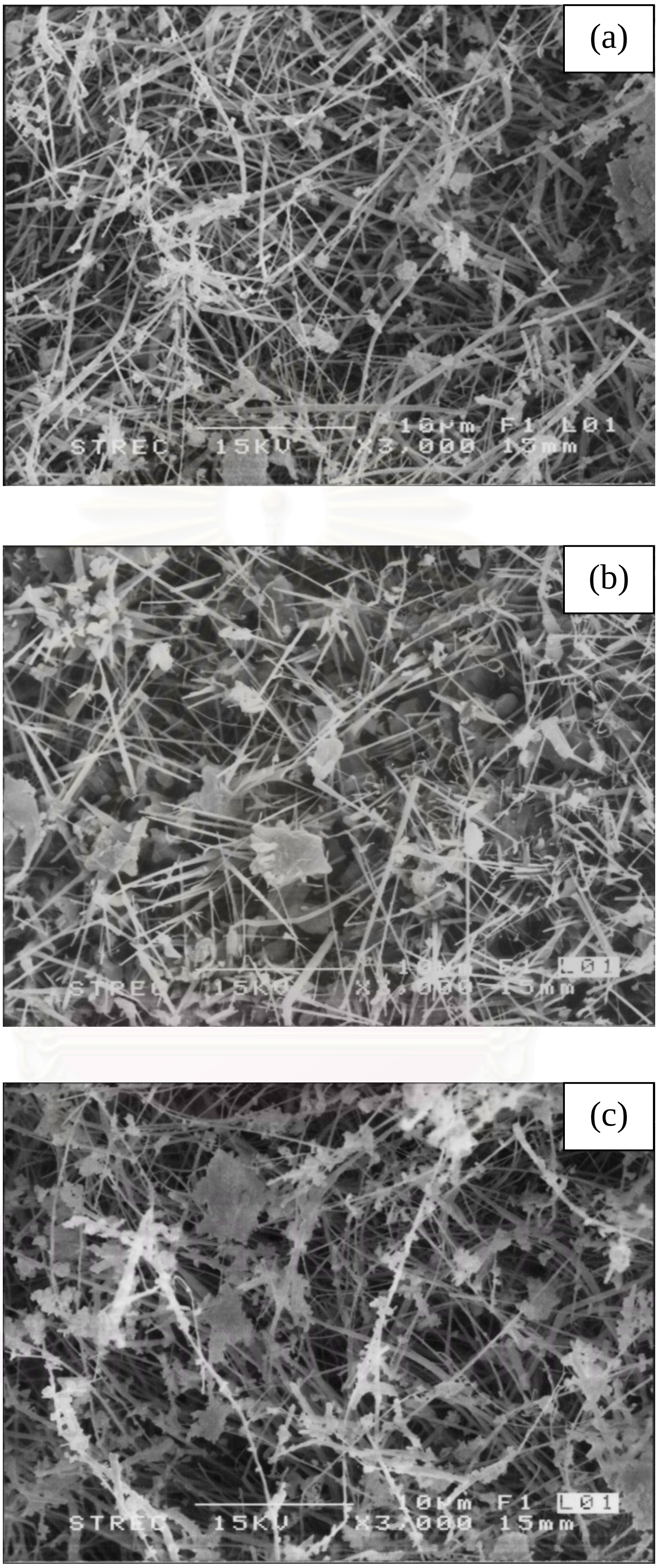

Figure 4.20 SEM micrograph of surface of 0.45% cerium-doped silicon nitride granules obtained from: (a) nitridation at 1300°C; (b) nitridation at 1390°C; (c) nitridation by using stepwised increase in temperature

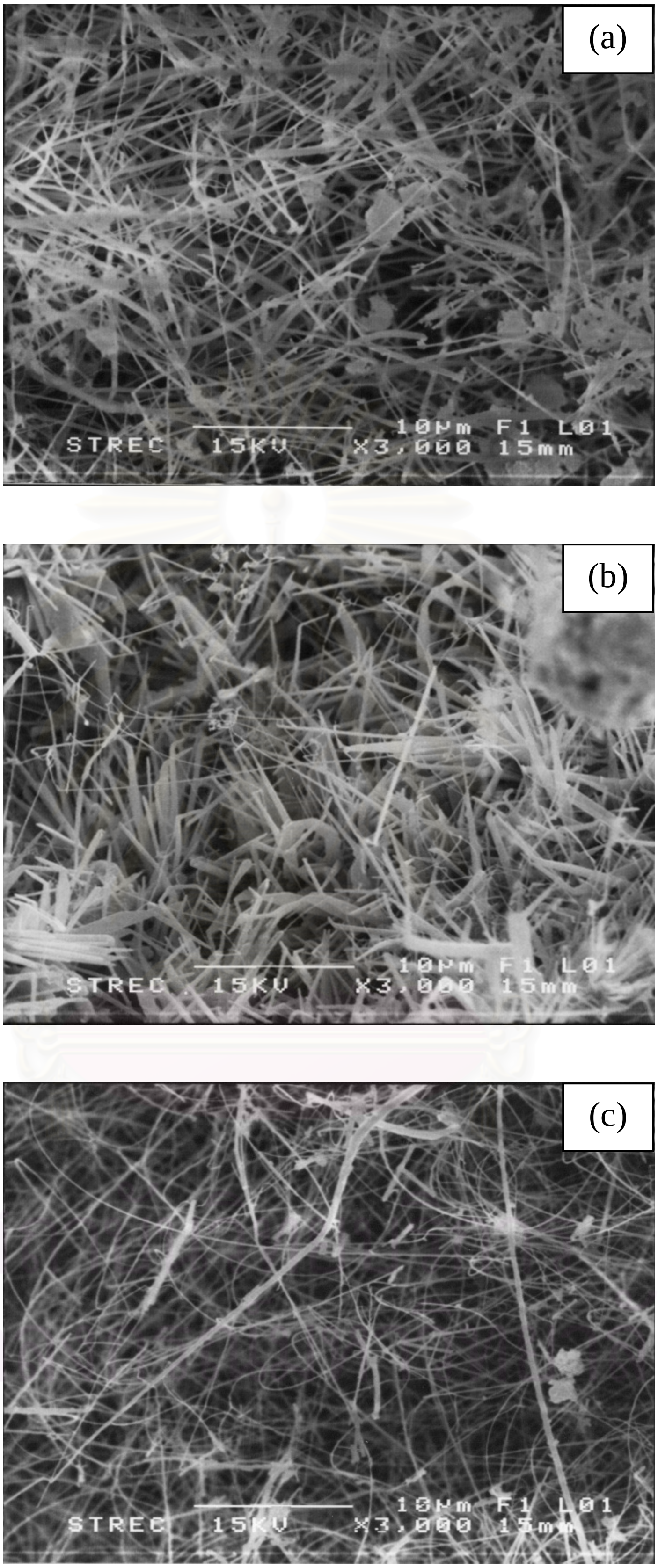

Figure 4.21 SEM micrograph of surface of 2% lutetium-doped silicon nitride granules obtained from: (a) nitridation at 1300°C; (b) nitridation at 1390°C; (c) nitridation by using stepwised increase in temperature

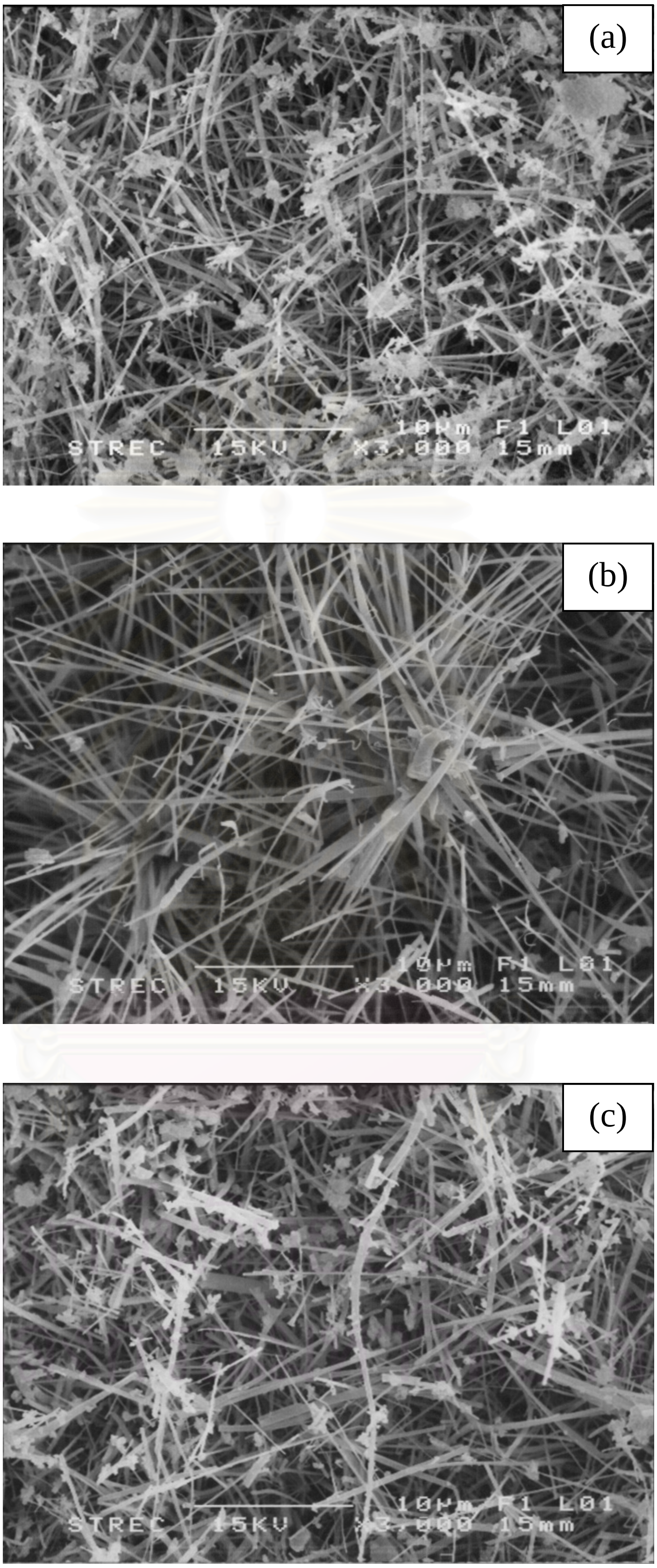

Figure 4.22 SEM micrograph of surface of 0.125% magnesium-doped silicon nitride granules obtained from: (a) nitridation at 1300°C; (b) nitridation at 1390°C; (c) nitridation by using stepwised increase in temperature

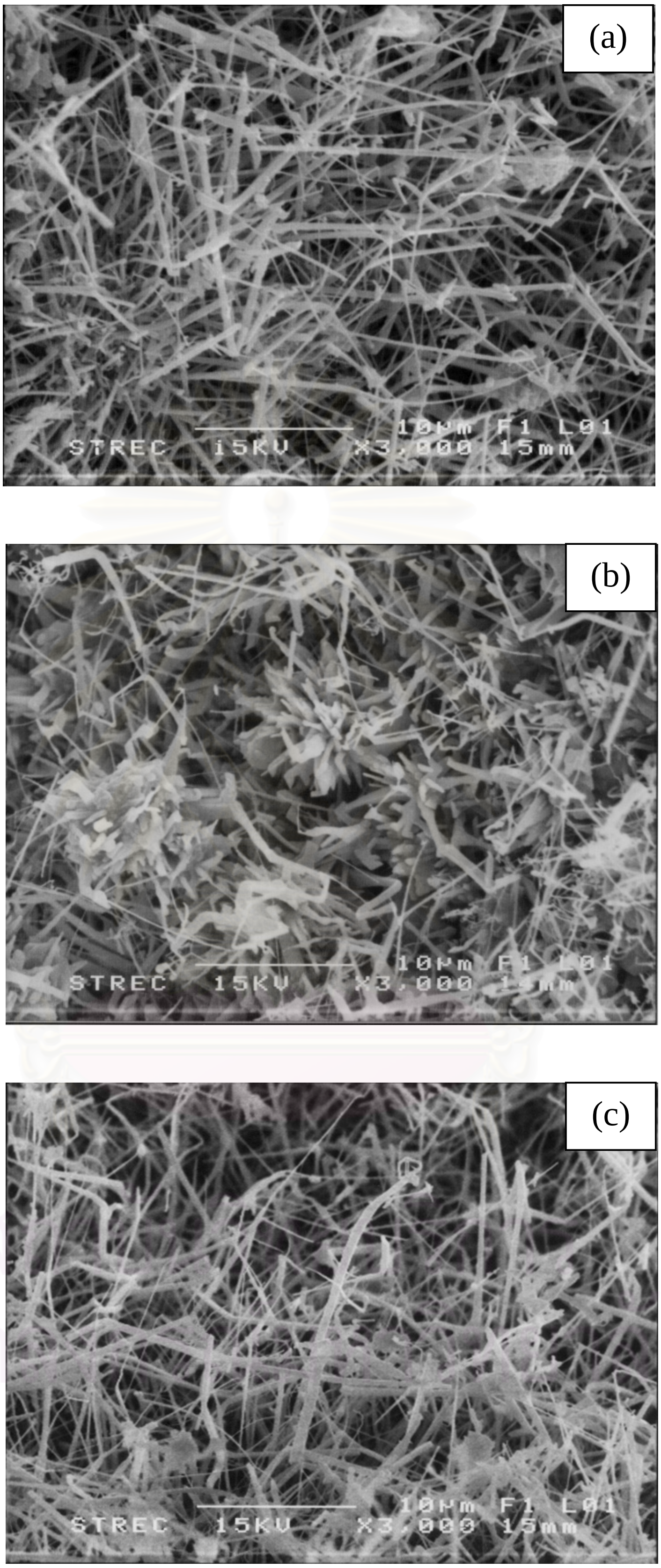

Figure 4.23 SEM micrograph of surface of 2% ytterbium-doped silicon nitride granules obtained from: (a) nitridation at 1300°C; (b) nitridation at 1390°C; (c) nitridation by using stepwised increase in temperature

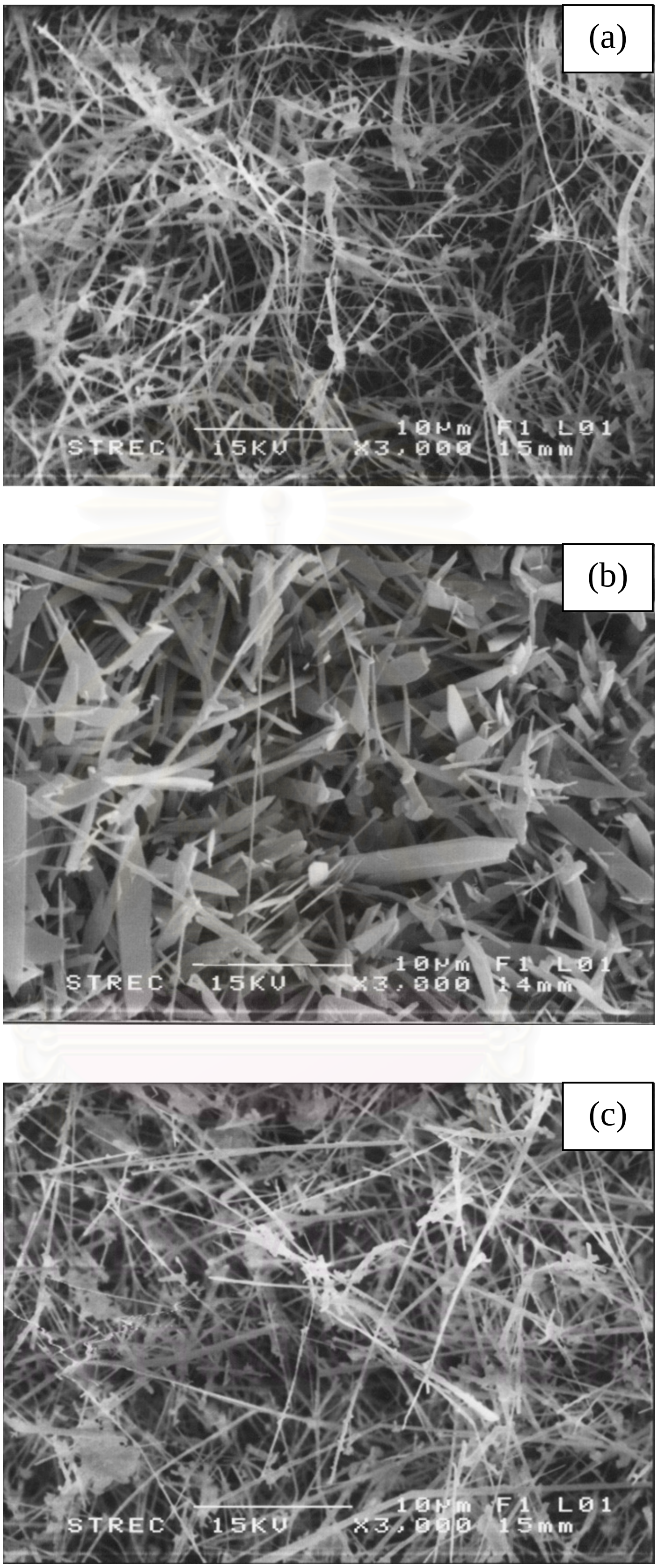

Figure 4.24 SEM micrograph of surface of 1% yttrium-doped silicon nitride granules obtained from: (a) nitridation at 1300°C; (b) nitridation at 1390°C; (c) nitridation by using stepwised increase in temperature

According to the different morphology on the surface of silicon nitride obtained from various reaction temperatures, it can be implied that the temperature does not only affect the reaction kinetics, but the mechanism of the nitridation as well.

Many researchers have discussed the effect of liquid phase on the nitridation of silicon [Boyer and Moulson, 1978; Pavarajarn and Kimura, 2001; Pigeon, *et al.*, 1993]. However, direct evidence for the presence of liquid in the system has never been presented because the reaction occurs at high temperature and many factors are involved in the reaction. In this work, although the presence of liquid phase can not be directly confirmed, the results suggest that the mechanism of the nitridation shifts from the reaction involving gas phase to another route when temperature is increased.

4.2.5 Effects of particle size on the synthesis of silicon nitride

In this section, the effects of particle size on the synthesis of silicon nitride via the direct nitridation of silicon were investigated. The nitridation of silicon granules (particle size of 300 μm) consisting of 2 μm grains were compared to the nitridation of silicon powder (average size 0.5 μm, from High Purity Chemicals, China) prepared by the same sample preparation procedures. Both forms of silicon were impregnated with calcium and ytterbium. The content of calcium and ytterbium was 0.125% and 1% by mass, respectively. The reaction was carried out by using stepwised increase in temperature for total reaction of 3 hours after 1-hour pretreatment. Results of the overall conversion as well as the fraction of α- and β-phase are shown in Figures 4.25 to 4.27, respectively.

According to Figures 4.25 and 4.26, it is shown that the obtained results are corresponding to another work which has reported that the overall conversion as well as α/β ratio from silicon with smaller grain-size is greater than those from bigger grain-size samples [Campos-Loriz and Riley, 1978]. Since the granule has more grain boundaries than powder, it would have less surface to react with nitrogen.

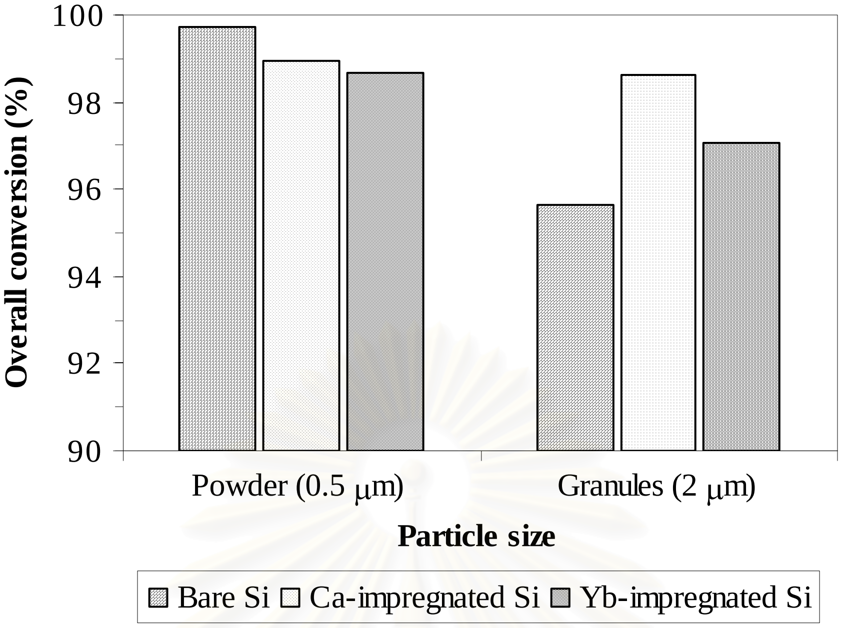

Figure 4.25 Comparison of the overall conversions of silicon powder and silicon granules in the nitridation by using stepwised increase in temperature

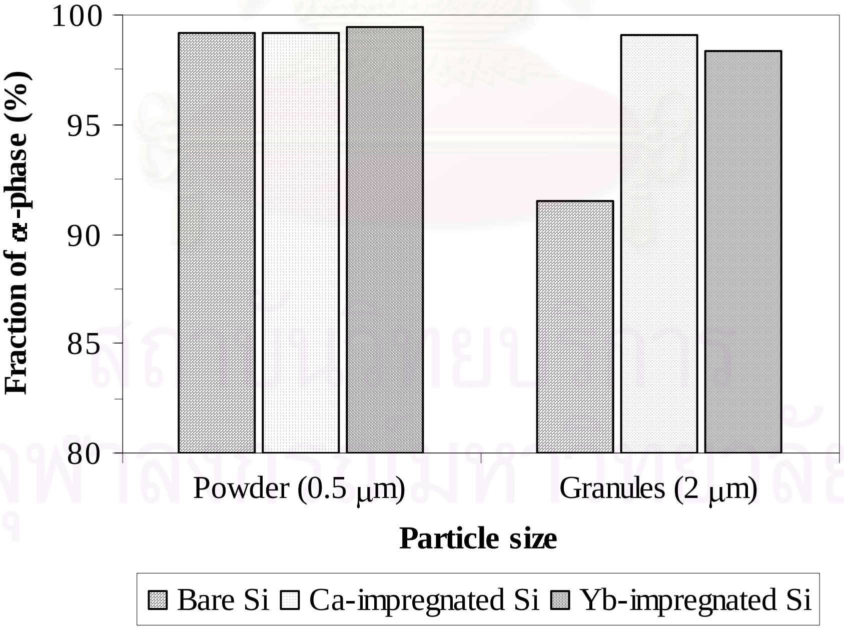

Figure 4.26 Comparison of the fraction of α-phase in silicon nitride product obtained from silicon powder and silicon granules in the nitridation by using stepwised increase in temperature

When metal is added to silicon, a deviation in the overall conversion from bare silicon is observed. This deviation in the overall conversion is characteristic of metal impregnated and is observed from both silicon powders and granules. However, smaller effects of metals are found on silicon with smaller grains. Therefore, it can be concluded that influence of metal on the overall conversion obtained from smaller size grains is less than those from bigger size. In this case, the effect of reaction surface is more dominant for smaller grain-size than the effect of metal. For the bigger grains, the reaction surface is more limited, thus the metal plays an important role to enhance the overall conversion, instead of the surface area.

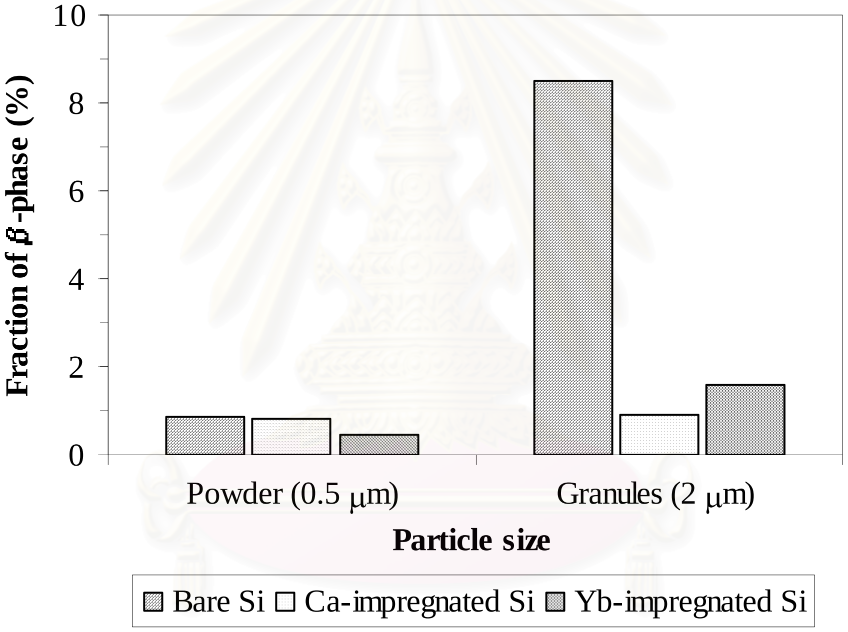

Figure 4.27 Comparison of the fraction of β-phase in silicon nitride product obtained from silicon powder and silicon granules in the nitridation by using stepwised increase in temperature

Similar to the overall conversion, the formation of α- and β-phase obtained from the nitridation of silicon powder does not significantly affected by metal added. The content of α-phase in silicon nitride obtained from metal impregnated silicon powder is roughly the same as those from bare silicon powder. On the other hand, the metal impregnation clearly influences the fraction of α-phase, in case of silicon granules.

Scanning electron microscope (SEM) was also used to observe the surface and morphology of silicon nitride product obtained from silicon powder. As presented in Figure 4.28, the overall observation is similar to those from silicon granules, as shown in figures in section 4.2.5.

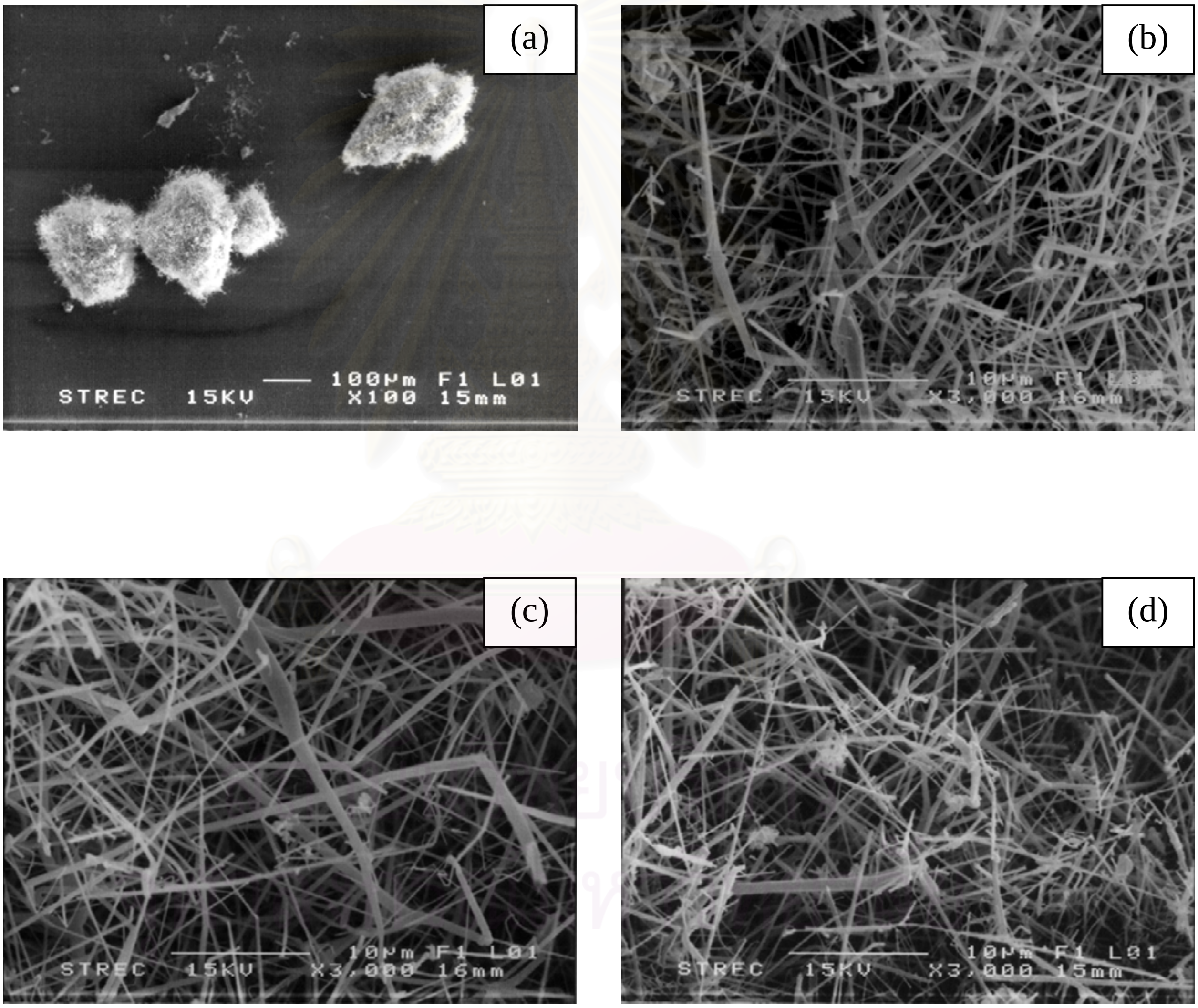

Figure 4.28 SEM micrograph of surface and morphology of silicon nitride from nitridation of silicon powder by using stepwised increase in temperature: (a) bare silicon in low magnification; (b) bare silicon in high magnification; (c) calcium 0.125% impregnated silicon; (d) ytterbium 1% impregnated silicon

4.3 Formation of Silicon Nitride Articles

As mentioned earlier, besides the investigation of catalytic effects of metals, the effects of their residual on the microstructure and the physical as well as the mechanical properties of silicon nitride articles were also investigated. The silicon nitride powders from the best condition of each metal were selected to fabricate into the specimen. The main consideration for the best condition was a high overall conversion of the nitridation as well as a high content of α-phase in the synthesized product.

4.3.1 Preliminary evaluation

4.3.1.1 Phase transformation observation

An example of X-ray diffraction pattern is shown in Figure 4.29. The pattern from silicon nitride powder is also shown for comparison. The sample was scanned in the range of 2θ = 26-38°, which covered main peaks of all phases. It can be observed from the figure that α-phase of silicon nitride was completely transformed into β-phase after sintering at 1750°C for 2 hours under N_2 pressure of 1 MPa. It should be noted that no silicon was found in the sintered product. It is indicated that, during the sintering process, remaining silicon in silicon nitride powder reacts with nitrogen to produce silicon nitride via the nitridation of silicon. Nevertheless, small amount of secondary crystalline phases, i.e. Y_2SiO_5 and $Y_2Si_2O_7$, were detected in sintered specimen, in addition to β-silicon nitride [Lu and Huang, 2001; McMurdie, *et al.*, 1986; Sainz, *et al.*, 2002].

Figure 4.30 shows the comparison between X-ray diffraction patterns of sintered specimen fabricated from bare silicon nitride and that from metal impregnated silicon nitride. It is shown that the pattern of the former is not different from the latter. No extra peak was observed in metal doped silicon nitride articles, even in the long scanning range of 2θ. This is probably due to too small the amount of metal added to be detected by X-ray diffraction. It should be noted that the peaks of Y_2SiO_5 and $Y_2Si_2O_7$ were found in sintered specimen fabricated from both bare and metal impregnated silicon nitride.

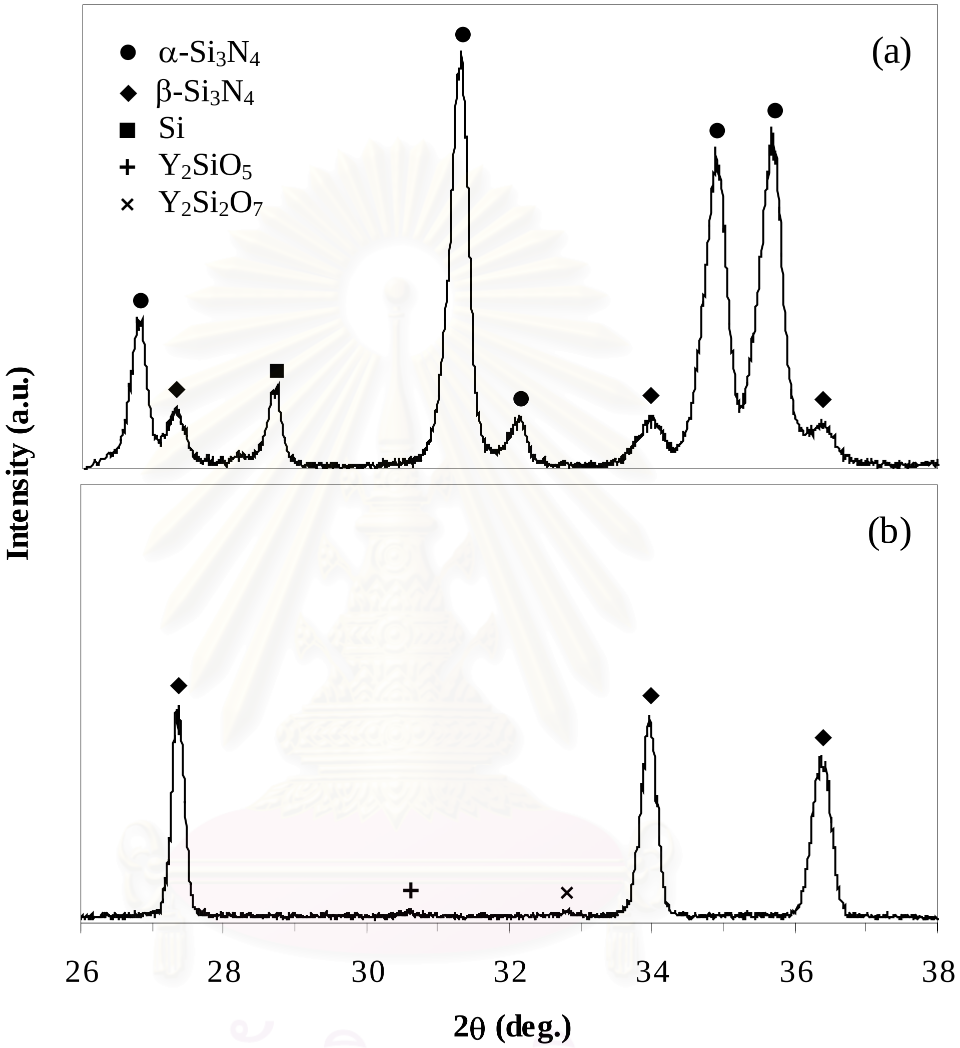

Figure 4.29 XRD patterns of selected silicon nitride specimen
(a) Silicon nitride powder before sintering
(b) Silicon nitride specimen after sintering

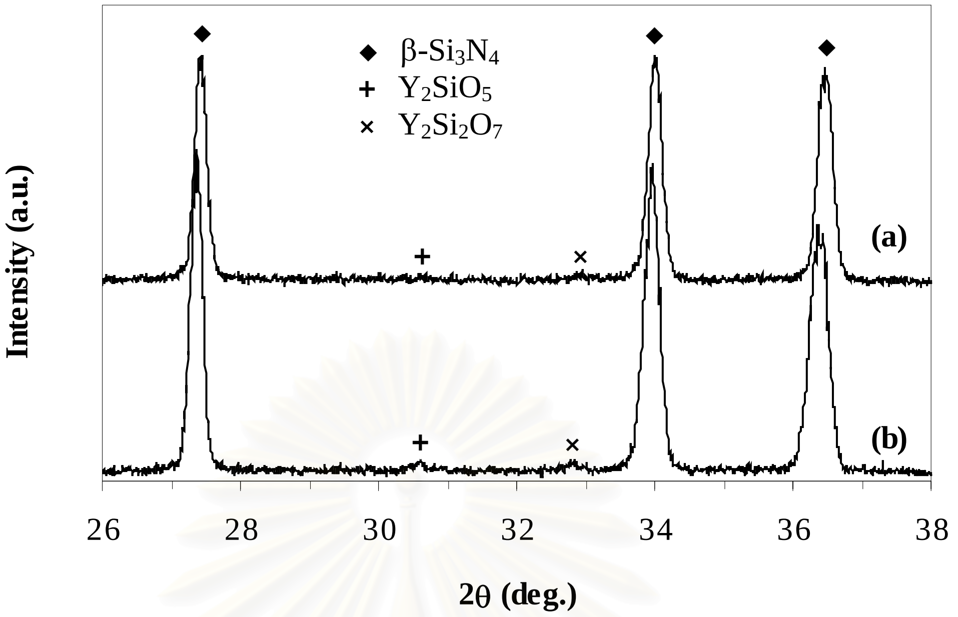

Figure 4.30 XRD patterns of selected sintered silicon nitride specimens
(a) Bare silicon nitride specimen.
(b) Metal-doped silicon nitride specimen (Yb-doped)

4.3.1.2 Effects of reaction temperature on the properties of articles

The effects of reaction temperature on the physical and mechanical properties of silicon nitride specimen were also studied by using bare silicon nitride powder obtained from various conditions of the nitridation. The results are shown in Table 4.4.

Table 4.4 Properties of specimens obtained from various nitridation temperatures

Nitridation conditions	R.D. (%)	H_v (GPa)	K_{1C} (MPa×m$^{1/2}$)
1300°C for 3 hours	95.90	15.0	4.74
1390°C for 3 hours	90.94	11.4	5.65
1300°C for 1 hour followed by 1390°C for 2 hours	95.68	14.7	5.28

According to the table, it indicates that the specimen obtained from the nitridation at 1300°C results in high relative density and hardness while the fracture toughness is relatively low. Conversely, the different behavior of these values was found in the specimen nitrided at 1390°C. The relative density and the hardness of specimen are significantly decreased while the fracture toughness is increased in case of the specimen obtained from the nitridation at 1390°C. At this point, it should be noted that the hardness shows a reverse behavior to the fracture toughness, which is in agreement with the results from literatures [Guo, *et al.*, 2003]. Moreover, all values investigated, i.e. relative density, hardness as well as fracture toughness, are relatively high when the specimen fabricated from silicon nitrided by using stepwised increase in temperature.

4.3.1.3 Effects of particle size of silicon raw material on the properties of silicon nitride articles

As discussed earlier, it was found that the particle size of silicon raw material affected the overall conversion and the formation of α-phase in silicon nitride product. Therefore, effects on the physical and mechanical properties of silicon nitride articles should be investigated as well. The specimens sintered by using silicon nitride which were synthesized from silicon powder and silicon granules were compared. Noted that the silicon granule are composed of 2 μm average grain size partially sintered into 300 μm average particle size while the silicon powder has an average particle size about 0.5 μm. Silicon in both sizes were impregnated with 0.125 and 1% by mass of calcium and ytterbium, respectively, and were nitrided for 3 hours by using stepwised increase in temperature. The formation and sintering of articles were done under the same condition. The results comparing relative density, hardness as well as fracture toughness are shown in Figures 4.31, 4.32 and 4.33, respectively.

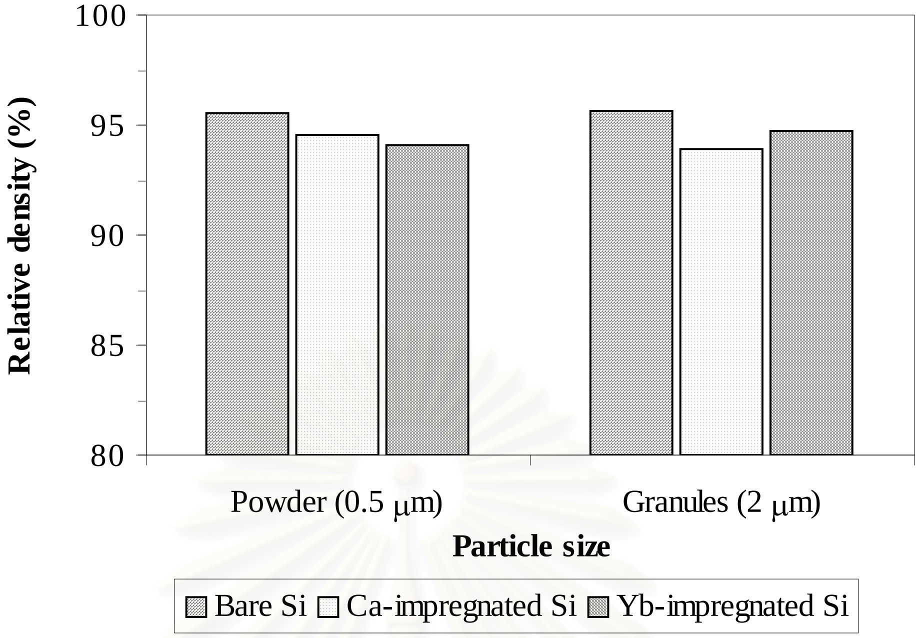

Figure 4.31 Relative density of specimens obtained from silicon nitride powder and silicon nitride granules

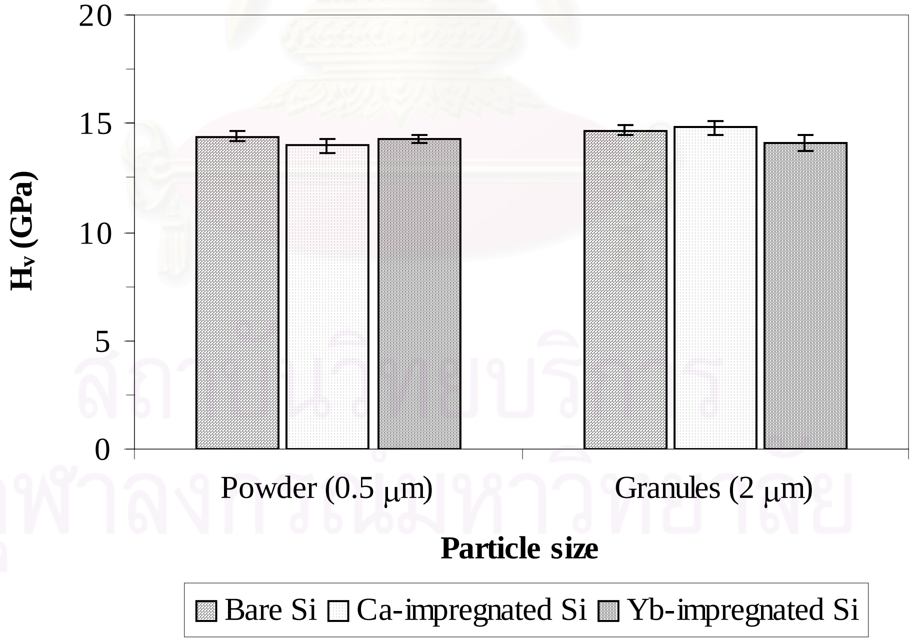

Figure 4.32 Hardness of specimens, H_v, obtained from silicon nitride powder and silicon nitride granules

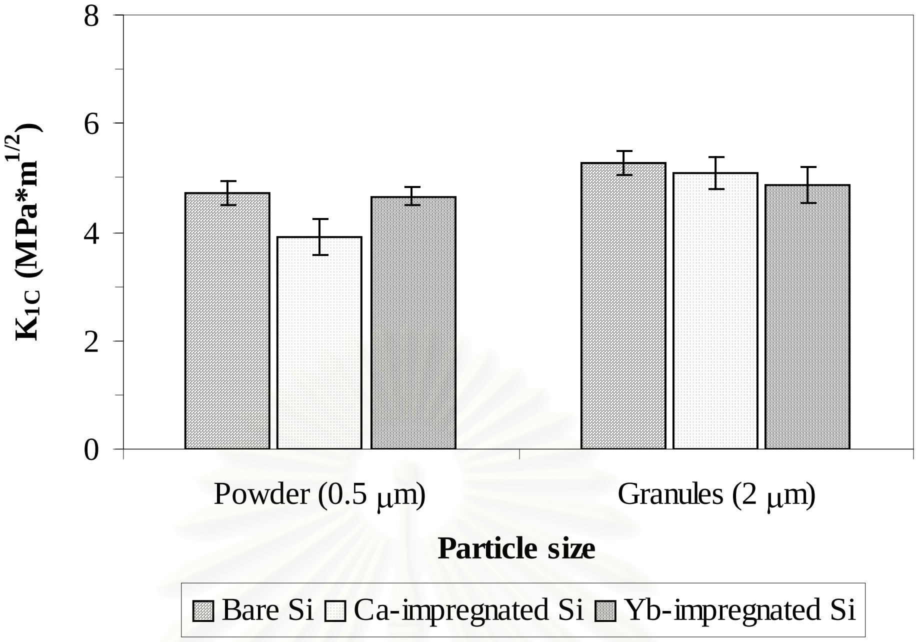

Figure 4.33 Fracture toughness of specimens, K_{1C}, obtained from silicon nitride powder and silicon nitride granules

The obtained results were in the same range reported by previous works [Chaiyapuck, 2003; Hirosaki, 2002; Lu and Huang, 2001; Song, *et al.*, 1996]. The results in Figure 4.31 indicate that the metal added in silicon raw material slightly influenced the relative density of sintered silicon nitride specimen. In case of metal impregnated silicon, small deviation from bare silicon nitride article was observed. When comparing with different particle size, it was shown that no difference in relative density was observed form both batches. It implies that particle size of silicon raw material does not affect the relative density of silicon nitride specimens. Similarly, according to Figure 4.32, it is shown that particle size does not significantly influence the hardness of specimens.

Figure 4.33 shows that, for bare silicon and calcium impregnated silicon, particle size of silicon raw material significantly affects the fracture toughness of sintered specimens. This result corresponds to previous work which was reported that the fracture toughness is increased with increasing particle size of silicon [Lee, *et al.*, 2003]. The specimens obtained from bare and 0.125% calcium added silicon nitride powder resulted in lower fracture toughness than those started from silicon granules.

It was found that fracture toughness of calcium added specimen was lower than those of bare silicon nitride for both particle sizes investigated. Moreover, the difference was more dominant in case of 0.5 μm particles. The specimen obtained from 0.5 μm silicon raw material impregnated with 0.125% calcium has the lowest value of fracture toughness among all specimens investigated. It has been found that an addition of CaO significantly increased the amount of non-elastic deformation occurring prior to fracture and decreased the flexural strength at elevated temperature of hot-pressed silicon nitride [Iskoe, *et al.*, 1976]. Moreover, it has also been reported that the subcritical crack-growth resistance as well as the creep resistance of silicon nitride doped with small amount of calcium (80-450 ppm) is significantly reduced [Tanaka, *et al.*, 1995]. So, in this work, it can be implied that calcium can disperse in silicon powder better than silicon granules. This make the fracture toughness of 0.125% calcium added specimen fabricated from silicon powder is significantly lower than that from silicon granules. On the other hand, fracture toughness of ytterbium added silicon nitride was less dependent of particle size. Moreover, the fracture toughness of 1% ytterbium specimens were roughly the same as bare silicon nitride articles, regardless of particle size. The cause of this particle size effect will be discussed in more detail in later section.

4.3.2 Effects of metals on the properties of silicon nitride

As mentioned earlier, the silicon nitride powder from the best condition of each metal was selected to be fabricated into the specimen in order to investigate the effects of metal residual on the microstructure and the physical as well as the mechanical properties of silicon nitride articles.

4.3.2.1 Relative density

The specimens obtained from calcium (0.125%), ytterbium (1%) and yttrium (2%) addition were compared with bare silicon nitride in their best conditions, i.e. nitridation by using stepwised increase in temperature from 1300 to 1390°C. While lutetium (0.125%), magnesium (2%) and their comparative bare silicon were nitrided at 1390°C for 3 hours.

As mentioned in chapter III, the sintering condition used in this work has been reported to result in sintered bodies with more than 98% of the theoretical density. But in this work, there was a problem about the small amount of silicon nitride obtained from each batch in the synthesis that made the processing of fabrication differ from the other works. However, the results in Figure 4.34 show that the density of articles fabricated from both bare and metal doped silicon nitride in this work are in the acceptable range for dense silicon nitride materials [Ziegler, *et al.*, 1987].

Addition of most metal affects the relative density in the same way, i.e. decreases the relative density. The value from calcium, lutetium and ytterbium added specimens are slightly lower than that from bare silicon nitride in their respective conditions. On the contrary, magnesium is the only metal investigated that results in an increases in relative density. For yttrium doped specimen, although the value of the relative density shows lower value than that from bare silicon nitride, it can be considered as roughly constant in relative density.

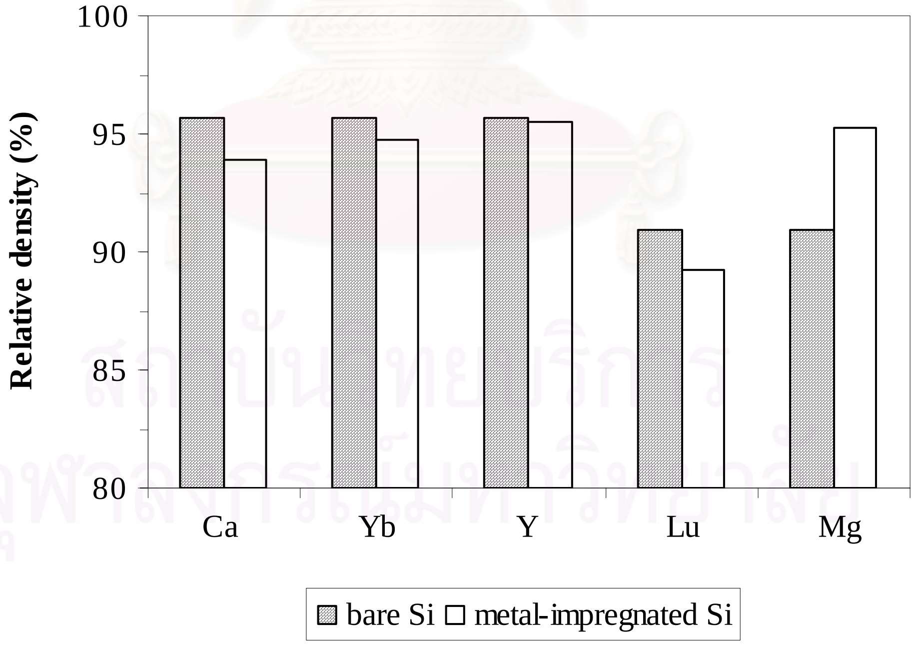

Figure 4.34 Comparison of the relative density of articles fabricated from bare silicon nitride and silicon nitride impregnated with various metals obtained from 3-hour nitridation at their best conditions

4.3.2.2 Hardness

In addition to the relative density, the effects of metal residual on the mechanical properties of silicon nitride were also studied. The preliminary observed shows that the values of hardness are nearly the same as those reported by previous works [Chaiyapuck, 2003; Hirosaki, 2002; Lu and Huang, 2001; Song, *et al.*, 1996; Ziegler, *et al.*, 1987].

The comparison of hardness of specimens obtained from bare silicon nitride and various metal-added silicon nitride are presented in Figure 4.35. The results indicate that residual of calcium or yttrium in silicon nitride specimen does not affect its Vickers hardness, while lutetium or ytterbium residual slightly influences the hardness of silicon nitride specimen. Ytterbium yields lower hardness while lutetium results in higher value than those of bare silicon nitride synthesized by the same nitridation conditions.

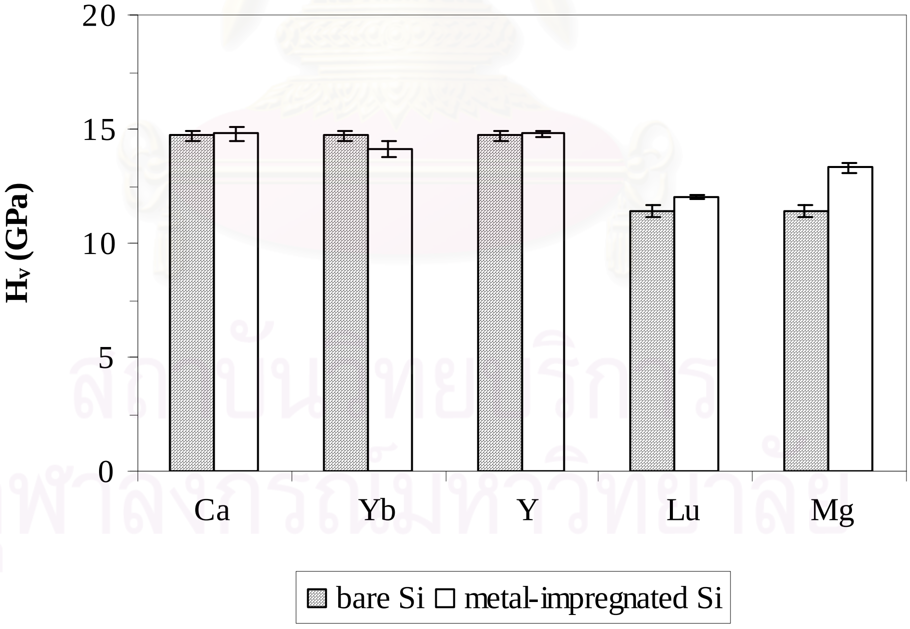

Figure 4.35 Comparison of the Vickers hardness of articles fabricated from bare silicon nitride and silicon nitride impregnated with various metals obtained from 3-hour nitridation at their best conditions

For magnesium, the significant effect on the hardness of the specimen was found. The hardness of magnesium added specimen is clearly increased from that of bare silicon nitride synthesized in the same condition.

4.3.2.3 Fracture toughness

Similarly to the Vickers hardness, the fracture toughness of the specimens in this work was also found to be in the same neighborhood of value reported in literatures [Chaiyapuck, 2003; Hirosaki, 2002; Lu and Huang, 2001; Song, *et al.*, 1996; Ziegler, *et al.*, 1987]. As shown in Figure 4.36, magnesium and ytterbium significantly influences the fracture toughness. It is found that the fracture toughness of specimens with magnesium or ytterbium addition is significantly decreased from bare silicon nitride at the same conditions. Calcium also affects the fracture toughness, but only slight decreases from bare specimen is observed. On the other hand, the effect of either lutetium or yttrium on the fracture toughness was not found.

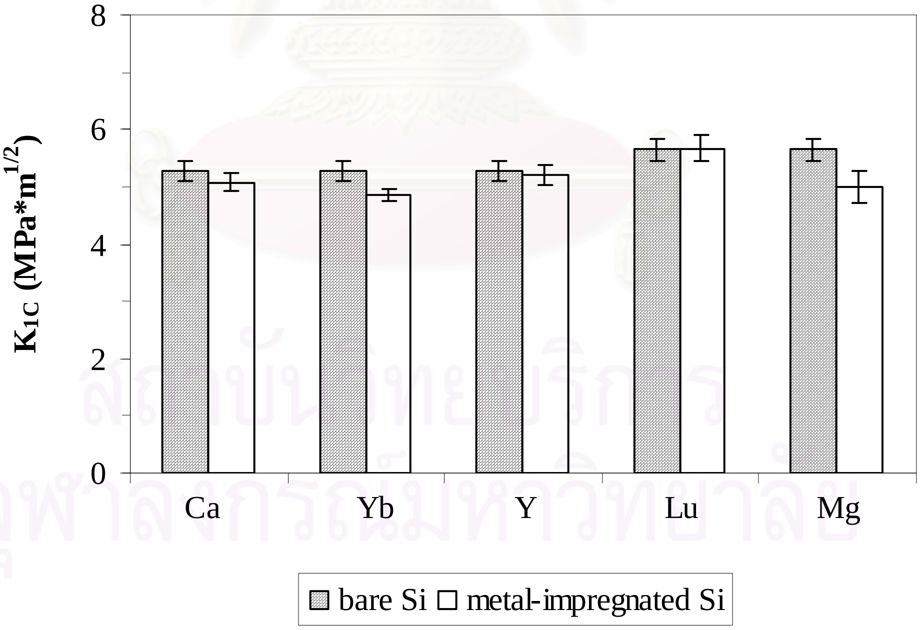

Figure 4.36 Comparison of the fracture toughness of articles fabricated from bare silicon nitride and silicon nitride impregnated with various metals obtained from 3-hour nitridation at their best conditions

According to the results discussed in this section, it can be observed that, among the metal investigated, yttrium is the only metal which does not affect both the physical and mechanical properties of silicon nitride specimens. Besides, it offers good effect on the direct nitridation of silicon, in terms of overall conversion and formation of high α-phase content. Therefore, it can be concluded that yttrium is the most appropriate metal to add in silicon raw materials to produce better quality of silicon nitride products. Conversely, magnesium strongly influences both physical and mechanical properties of silicon nitride articles. For relative density and hardness, magnesium results in higher values than those from bare silicon nitride, while the value of fracture toughness is significant lower than bare silicon nitride. At this point, it can be said that magnesium is suitable for improving quality of silicon nitride specimens for applications that demand hardness. It has been known that high-temperature and unlubricated roller as well as ball bearings required wear resistance, low friction and high stiffness of silicon nitride [Datton and Drobeck, 1986]. So, magnesium might be preferable for this application. In addition to yttrium and magnesium, calcium and ytterbium are two metals that also result in excellent enhancing effects on the direct nitridation of silicon without major effect on the properties of articles. For lutetium, since the relative density of the article is not high enough to be in the range of dense silicon nitride, but it offers appreciated values of hardness and fracture toughness. Therefore lutetium may suit for selected application, such as being parts of diesel engines because it has been reported that many parts of diesel engines, such as turbocharger rotors, required high strength and toughness to withstand impact damage [Tsuruto, *et al.*, 1990].

4.3.3 SEM pictures of fracture surfaces

The morphology of fracture surface of silicon nitride specimens was observed by using scanning electron microscope (SEM). The fracture surface of sintered specimens fabricated from bare and various metal-doped silicon nitride are shown in Figures 4.37 to 4.39. As shown, the overall feature of fracture surfaces consisted of mainly rod-like and elongated grains embedded in relatively small matrix grains. SEM results indicate that all of specimen investigated, i.e. bare and all metal-impregnated silicon nitride, have similar microstructure.

However, grains of fracture surface of bare, lutetium doped as well as magnesium doped silicon nitride articles seem to be larger than the others. It should be noted that all of these specimens are resulted from the same condition of nitridation, at 1390°C. This observation is corresponding to significantly decrease in the hardness and relatively high values in the fracture toughness, as discussed in the prior section. It has been known that the hardness of silicon nitride is affected by many factors such as grain size, grain morphology, β-silicon nitride content, intergranular phase and porosity of article [Riley, 2000]. The fracture toughness also depends on several factors, such as large elongated grains with a high aspect ratio, amount of glassy phase and porosity [Guo, *et al.*, 2003; Himsolt, *et al.*, 1979; Lee, *et al.*, 2003; Liu, 2003; Pyzik and Carroll, 1994]. Therefore, it is difficult to conclude the effects of metals form only fracture surface. Further study of microstructure with the aid of plasma or chemical etching is required.

SEM pictures of fracture surface of the specimens sintered by using silicon nitride which were synthesized from silicon powder and silicon granules were compared in Figures 4.40 to 4.42. It is shown that overall grains of fracture surface of specimens obtained from bare and 0.125% calcium impregnated silicon nitride powder are larger than those started from silicon granules. This is consistent with the results regarding relatively low fracture toughness of the specimens. It should be noted that this tendency is different from above discussion. On the contrary, grain size of fracture surface of 1% ytterbium added specimens obtained from both silicon powders and granules are roughly the same. The fracture toughness of both specimens are not different from each other as well. However, the actual conclusion of these results has not yet been reached due to the same complication mentioned above.

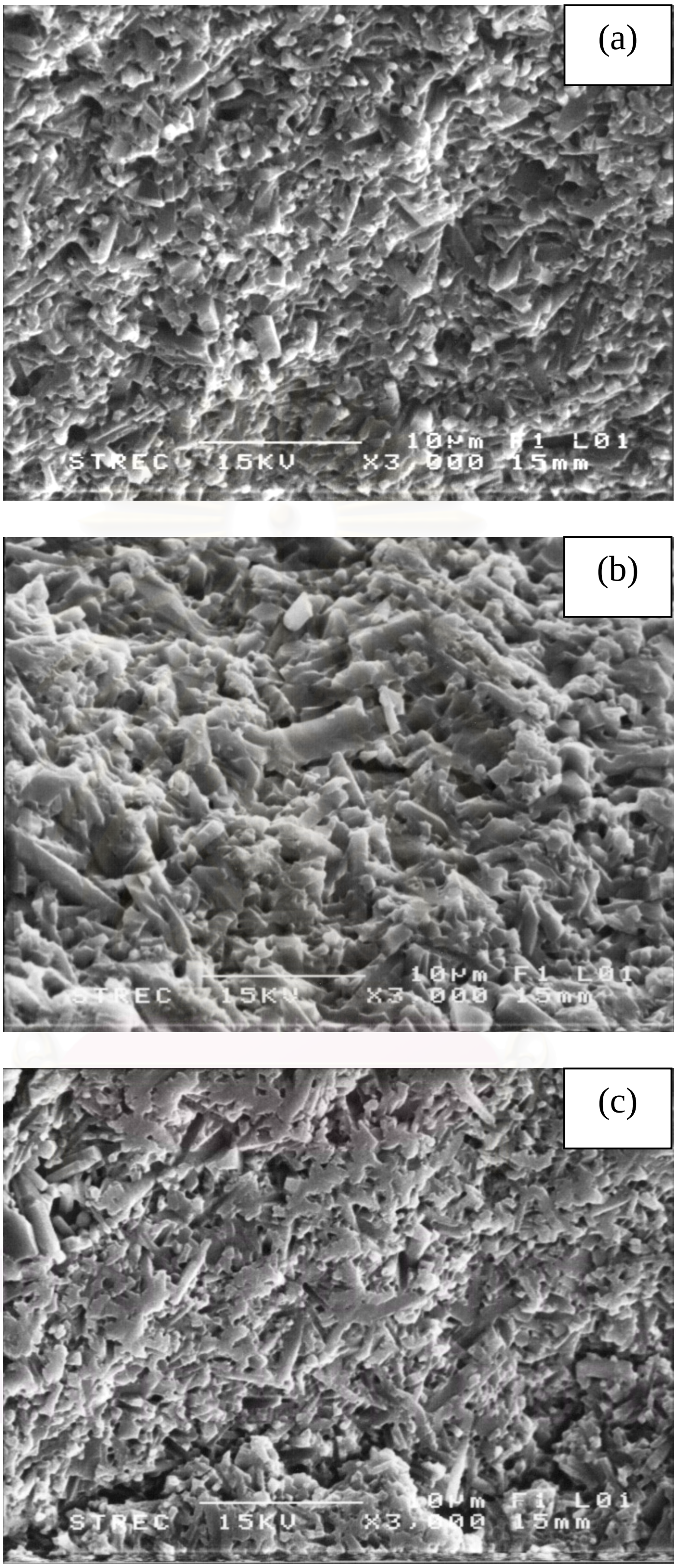

Figure 4.37 SEM micrograph of fracture surface of sintered specimens fabricated from the nitridation of bare Si: (a) at 1300°C; (b) at 1390°C; (c) using stepwised increase in temperature

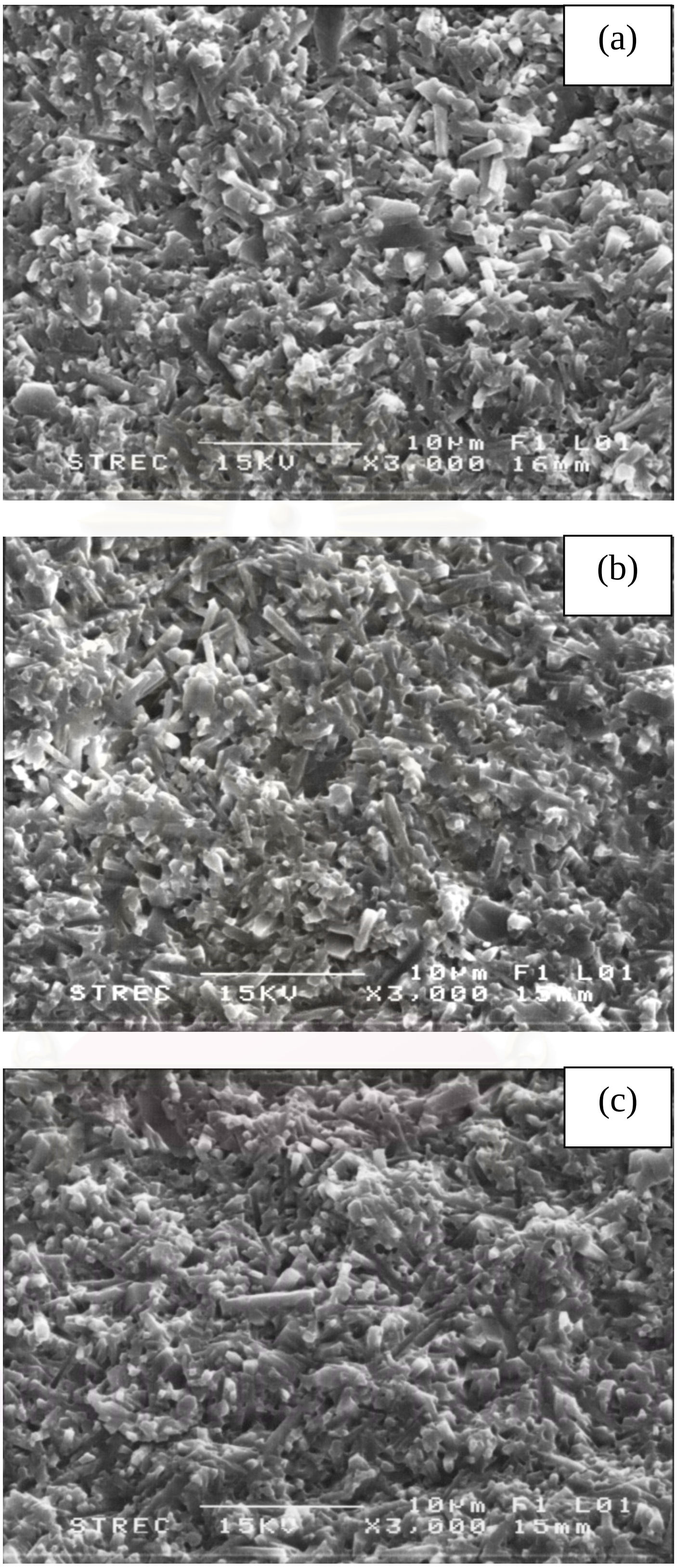

Figure 4.38 SEM micrograph of fracture surface of sintered specimens fabricated from the nitridation of: (a) 0.125% Ca-impregnated Si; (b) 1% Yb-impregnated Si; (c) 2% Y-impregnated Si. All specimens were nitrided by using stepwised increase in temperature.

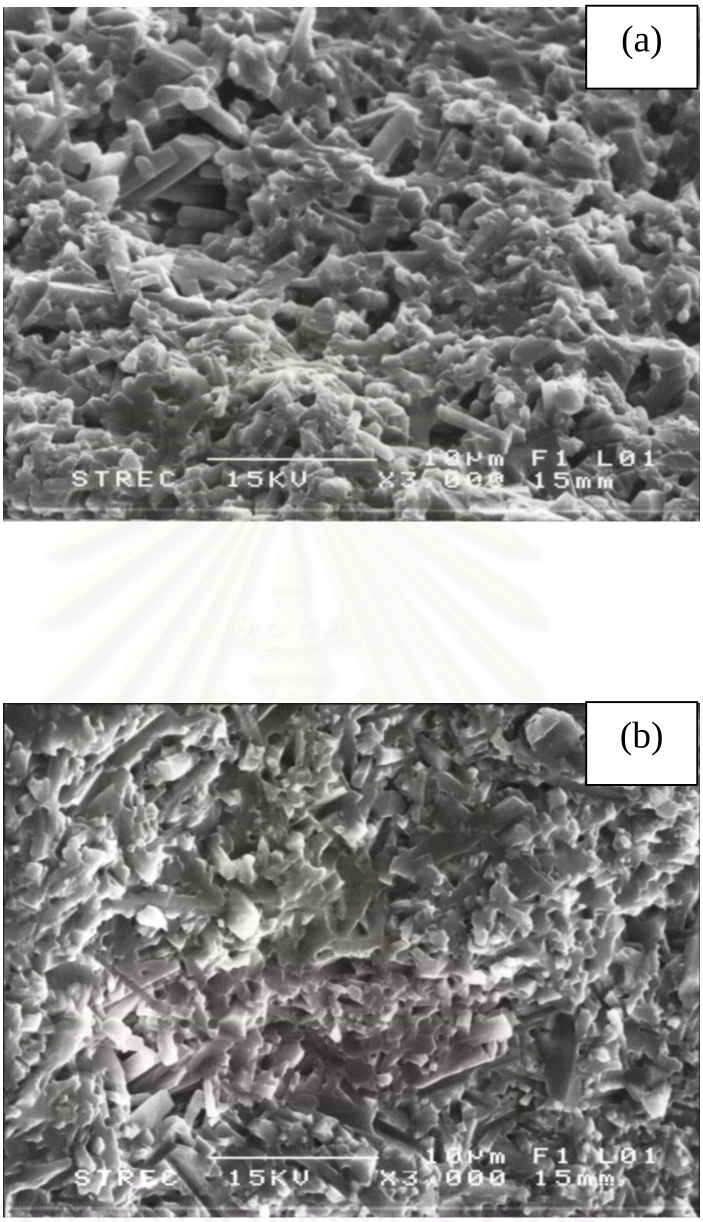

Figure 4.39 SEM micrograph of fracture surface of sintered specimens fabricated from the nitridation of: (a) 0.125% Lu-impregnated Si; (b) 2% Mg-impregnated Si. All specimens were nitrided at 1390°C.

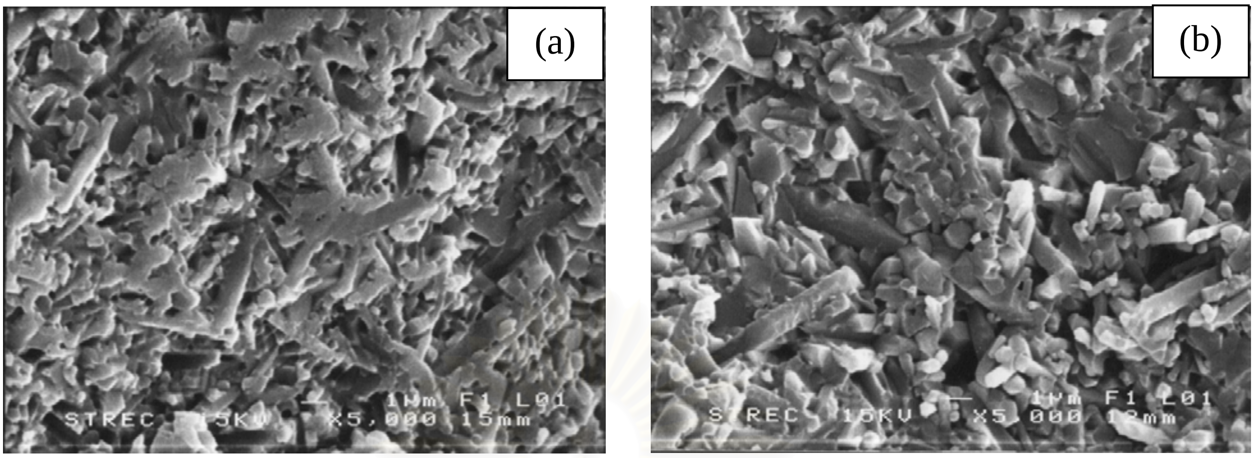

Figure 4.40 SEM micrograph of fracture surface of sintered specimens fabricated from bare silicon nitride obtained from: (a) the nitridation of silicon granules using stepwised increase in temperature; (b) the nitridation of silicon powder using stepwised increase in temperature

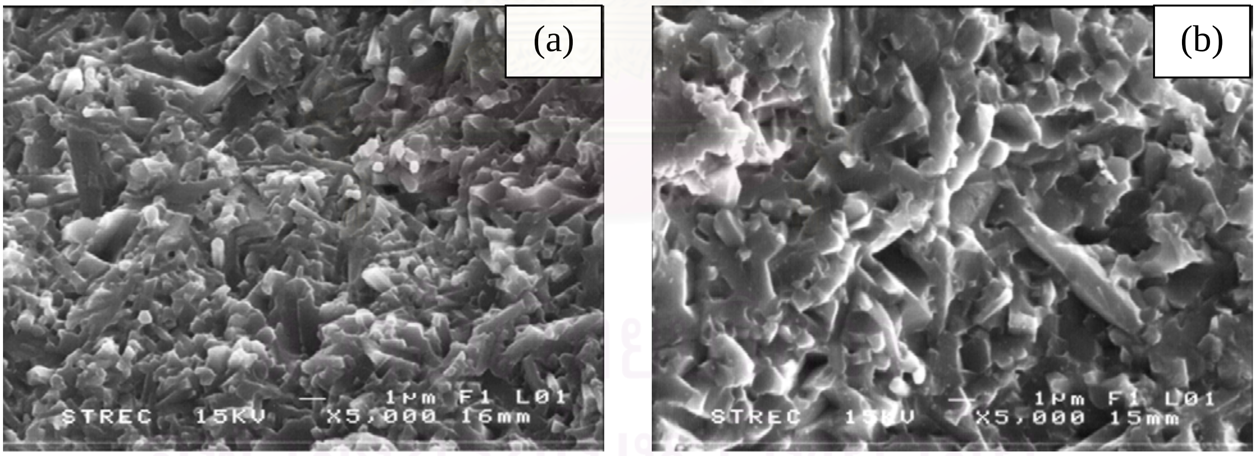

Figure 4.41 SEM micrograph of fracture surface of sintered specimens fabricated from 0.125% Ca-impregnated silicon nitride obtained from: (a) the nitridation of Ca-doped silicon granules using stepwised increase in temperature; (b) the nitridation of Ca-doped silicon powder using stepwised increase in temperature

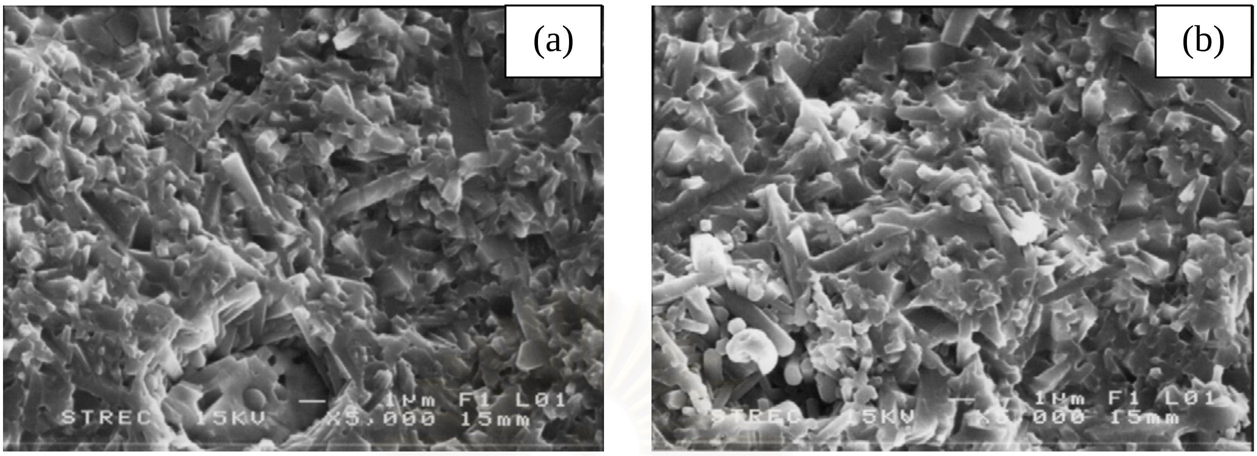

Figure 4.42 SEM micrograph of fracture surface of sintered specimens fabricated from 1% Yb-impregnated silicon nitride obtained from: (a) the nitridation of Yb-doped silicon granules using stepwised increase in temperature; (b) the nitridation of Yb-doped silicon powder using stepwised increase in temperature

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this work, the catalytic effects of metals, used as common sintering additives, on the nitridation of silicon and the effects of their residual in the silicon nitride product on its microstructure as well as mechanical properties were investigated. The results are summarized in the following sections.

5.1.1 Synthesis of Silicon Nitride Powder

(1) Significant enhanced selectivity of α-silicon nitride formation is achieved with an addition of calcium, ytterbium or yttrium into silicon raw material and nitrided by using a stepwised increase in the nitridation temperature from 1300°C to 1390°C. The nitridation of 0.125% calcium impregnated silicon yields both the overall conversion and the fraction of α-phase towards 100%, while 1% ytterbium or 2% yttrium addition results in the overall conversion as well as the α-phase content over 97%.

(2) Lutetium and magnesium have shown a significant enhancement in the nitridation at 1390°C. The nitridation of silicon with an addition of 0.125% lutetium at 1390°C yields high overall conversion with α-phase content higher than 98% while 2% magnesium results in over 94% overall conversion with an α-phase content about 97%.

(3) Among the metals investigated, only cerium enhances neither the overall conversion nor the fraction of α-silicon nitride in the product. It seems that cerium retards the nitridation of silicon, especially at 1390°C.

(4) Raising the reaction temperature stepwised from 1300°C to 1390°C can accelerate the overall conversion of the nitridation toward 100% while keeping high content of α-silicon nitride.

(5) Metal having the tendency to give up electron much easier than hydrogen tends to enhance the nitridation toward α-silicon nitride. This observation can be applied to all metals investigated, both in this work and in literature, except for cerium.

(6) Different morphology on the surface of silicon nitride obtained from various reaction temperatures suggest that the temperature does not only affect the reaction kinetics, but the mechanism of the nitridation as well. The results suggest that the mechanism of the nitridation shifts from the reaction involving gas phase to another route when temperature is increased.

(7) Particle size of silicon raw material affects the nitridation of silicon. The influence of metal on the overall conversion as well as the formation of α- and β-phase obtained from smaller size grains is less than those from bigger ones. The effect of reaction surface is dominant for smaller grain-size than the effect of metal. For the bigger grains, the reaction surface is more limited, thus the metal plays an important role to enhance the nitridation, instead of the surface area.

5.1.2 Formation of Silicon Nitride Articles

(1) Particle size of silicon raw material does not affect the relative density and the hardness of silicon nitride specimens but significantly affects the fracture toughness of sintered specimens.

(2) Residual metal contained in silicon nitride powder slightly affects the properties of silicon nitride articles. However, the physical and mechanical properties of silicon nitride article obtained still in the acceptable range for many applications.

5.2 Recommendations for Future Work

The direct nitridation of silicon is one of the most commonly used process for the mass production of silicon nitride. There are many critical factors involved in this process that have not been fully investigated. Detailed investigation of these factors can lead to more efficient process and improve the quality of the product. Some recommendations for future work are listed as follows:

(1) The mechanism for the nitridation of silicon impregnated with metals is not clear. The actual distribution of metals on the surface of silicon grains and the concentration of metals inside the grains should be investigated. Moreover, the oxidation number of metal should be also studied. Surface study using the X-ray photoelectron spectroscopy (XPS) is suggested.

(2) The influence of the nitridation temperature on the mechanism of the nitridation is not clear. Further study in details is needed to be done.

(3) The nitridation should be studied *in situ* by using high temperature X-ray diffraction.

(4) The kinetics of the nitridation of silicon impregnated with metals should be investigated.

(5) Plasma or chemical etching of the polished surface of specimens is suggested for the study involving sintered silicon nitride articles.

(6) The effects of metal residual on the flexural strength of specimens should be further studied.

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APPENDICES

APPENDIX A

CALCULATION OF MASS FRACTION OF EACH PHASE AND THE CONVERSION FROM SILICON TO α- AND β-SILICON NITRIDE

An example of X-ray diffraction pattern of synthesized silicon nitride product and the calculation are given below.

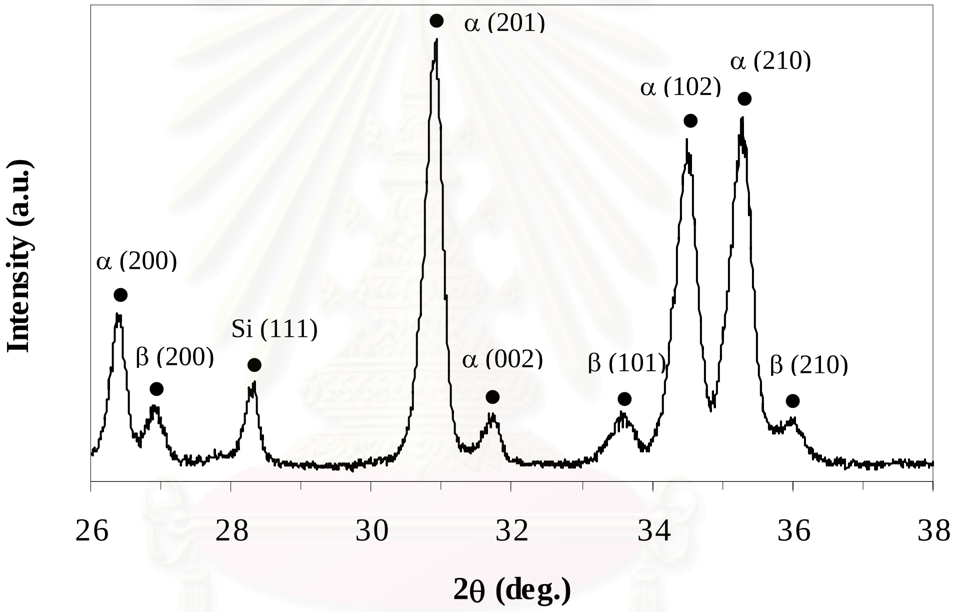

Figure A1 A sample of XRD pattern of product obtained from the nitridation of silicon granules by using stepwised increase in temperature for 3 hours.

As described in chapter III, the intensity of (111) peak of Si, the intensities of (102), (210) and (201) peaks of α-silicon nitride and those of (101) and (210) peaks of β-silicon nitride were integrated by using the Pseudo-Voight function in the Xfit-Koalariet software package from the Collaborative Computational Project number 14 (CCP14). The results of integrating are presented in Table A1.

Table A1 Integrated intensities of main peaks

Phase	Integrated intensity of peak
Si (111)	105.0158
α (201)	599.0194
β (101)	67.7267
α (102)	597.7218
α (210)	487.6996
β (210)	73.3734

Mass fraction of each phase as well as the conversion from silicon to α- and β-silicon nitride were calculated from the method proposed by Jovanovic and Kimura [1994] as follows:

$$\frac{I_{\alpha}(102)+I_{\alpha}(210)}{I_{\beta}(101)+I_{\beta}(210)}=K_{\alpha/\beta}\frac{W_{\alpha}}{W_{\beta}} \qquad \text{(A.1)}$$

$$\frac{I_{Si}(111)}{I_{\alpha}(201)}=K_{Si/\alpha}\frac{W_{Si}}{W_{\alpha}} \qquad \text{(A.2)}$$

and $$W_{\alpha}+W_{\beta}+W_{Si}=1 \qquad \text{(A.3)}$$

where $I_{\delta}(hkl)$ signifies the integrated intensity of the *hkl* reflection of phase δ, and W_{δ} is the mass fraction of corresponding phase δ in a mixture. The linear regression calibration constants, $K_{\alpha/\beta}$ and $K_{Si/\alpha}$ were evaluated to be 0.647 and 5.53 respectively [Jovanovic and Kimura, 1994].

Substitute the values in Table A1 to equation A.1-A.3:

$$\frac{597.7218+487.6996}{67.7267+73.3734}=0.647\frac{W_{\alpha}}{W_{\beta}} \qquad \text{(A.4)}$$

$$\frac{105.0158}{599.0194} = 5.53\frac{W_{Si}}{W_{\alpha}} \qquad \text{(A.5)}$$

and $$11.8896W_{\beta} + W_{\beta} + 0.3769W_{\beta} = 1 \qquad \text{(A.6)}$$

Thus, $W_{\alpha} = 0.8965$, $W_{\beta} = 0.0754$, and $W_{Si} = 0.0284$

The overall conversion of silicon, X, was calculated as:

$$X = \frac{1 - W_{Si}}{1 + \left(\frac{M_{SN}}{3M_{Si}} - 1\right)W_{Si}} \qquad \text{(A.7)}$$

where M_{SN} and M_{Si} are the molar masses of silicon nitride and silicon, and (M_{SN} / 3M_{Si})-1 = 0.665 is a converting factor.

Substitute W_{Si} to equation A.7:

$$X = \frac{1 - 0.0284}{1 + (0.665)0.0284} = 0.9536$$

The mass fractional yields of α-silicon nitride, X_{α}, and β-silicon nitride, X_{β}, were calculated as:

$$X_{\alpha} = \frac{1 - W_{Si}}{1 + 0.665W_{Si}}\left(\frac{W_{\alpha}}{W_{\alpha} + W_{\beta}}\right) \qquad \text{(A.8)}$$

and $$X_{\beta} = \frac{1 - W_{Si}}{1 + 0.665W_{Si}}\left(\frac{W_{\beta}}{W_{\alpha} + W_{\beta}}\right) \qquad \text{(A.9)}$$

Substitute W_{α}, and W_{β} to equation A.8 and A.9

Thus, $$X_\alpha = 0.9536\left(\frac{0.8965}{0.8965+0.0754}\right) = 0.8796$$

and $$X_\beta = 0.9536\left(\frac{0.0754}{0.8965+0.0754}\right) = 0.0740$$

The overall conversion of silicon, *X*, is therefore the sum of the mass fractional yields of α- and β-silicon nitride:

$$X = X_\alpha + X_\beta \tag{A.10}$$

Thus, $$X = 0.8796 + 0.0740 = 0.9536$$

The mass fraction of α-phase in silicon nitride product or selectivity of α-phase can be defined as:

$$\text{Selectivity of } \alpha\text{-phase} = \frac{X_\alpha}{X} = \frac{W_\alpha}{W_\alpha + W_\beta} \tag{A.11}$$

Thus, $$\text{Selectivity of } \alpha\text{-phase} = \frac{0.8796}{0.9536} = 0.9224$$

Therefore, the mass fraction of β-phase in silicon nitride product or selectivity of β-phase was calculated as:

$$\text{Selectivity of } \beta\text{-phase} = 1 - \frac{X_\alpha}{X} \tag{A.12}$$

Thus, $$\text{Selectivity of } \beta\text{-phase} = 0.0776$$

All calculations above can be concluded that the nitridation of silicon using stepwised increase in temperature yields 95.36% overall conversion of silicon to silicon nitride with 92.24% α-phase and 7.76% β-phase content in silicon nitride.

APPENDIX B

CALCULATION OF BULK DENSITY AND RELATIVE DENSITY

Bulk density of sintered specimens was measured by the Archimede’s method, according to ASTM-C830-93-1996 standard. As mentioned in chapter III, the bulk density can be calculated as follows:

$$B.D. = (\frac{D}{W - S}) \times \rho_w \qquad \text{(B.1)}$$

where $B.D.$ represents bulk density (g/cm^3), ρ_w is the density of water (g/cm^3), D is the dry weight of specimen (g), W is the saturated weight of specimen (g) and S is the suspended weight of specimen in water (g).

Relative density was also calculated based on theoretical density derived from each individual constituent and its content:

$$R.D. = (\frac{B.D.}{T.D.}) \times 100 \qquad \text{(B.2)}$$

where $R.D.$ and $T.D.$ represent relative density (%) and theoretical density (g/cm^3), respectively. The theoretical density was calculated as:

$T.D.$ = (weight fraction of Si_3N_4 × density of Si_3N_4) + (weight fraction of metal × density of metal) + (weight fraction of Al_2O_3 × density of Al_2O_3) + (weight fraction of Y_2O_3 × density of Y_2O_3) (B.3)

For example: Bulk density of silicon nitride specimen obtained from the nitridation of silicon impregnated with 2% magnesium at 1390°C for 3 hours was calculated as

$$B.D. = (\frac{0.6251}{0.6262 - 0.4289}) \times 0.99708 = 3.16 \quad \text{g/cm}^3$$

$$R.D. = (\frac{3.16}{3.287}) \times 100 = 96.14\,\%$$

where

$T.D.$ = $(0.8889 \times 3.17) + (0.0111 \times 1.74) + (0.05 \times 3.97) + (0.05 \times 5.03) = 3.287$ g/cm^3

Noted: the density of water at 25°C = 0.99708 g/cm^3

the density of silicon nitride = 3.17 g/cm^3

the density of magnesium = 1.74 g/cm^3

the density of alumina = 3.97 g/cm^3

the density of yttria = 5.03 g/cm^3 [Lide, 2000-2001]

APPENDIX C

CALCULATION OF VICKERS HARDNESS AND FRACTURE TOUGHNESS

As explained in chapter III, the fracture toughness was determined by measuring an indentation crack size from the load of 98 N of a Vickers indenter for 15 second in air at room temperature according to JIS-R1610-1991 standard. An example of Vickers indenter is shown in Figure C1.

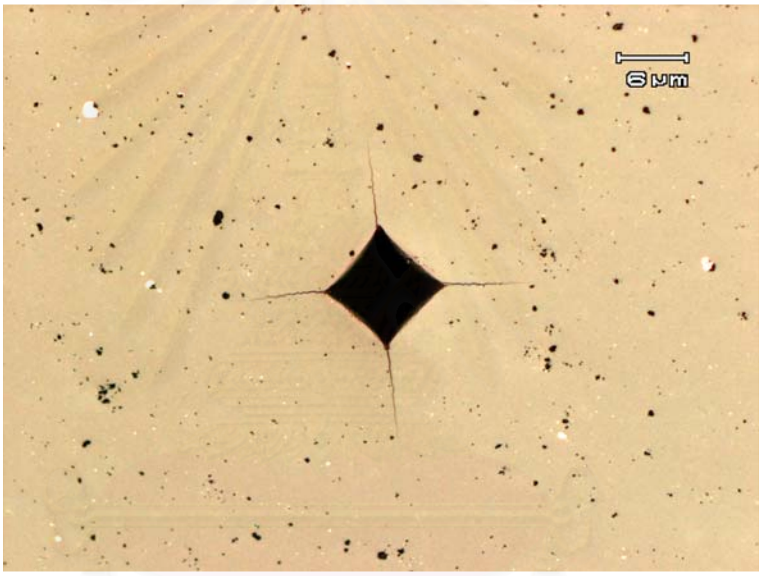

Figure C1 A sample of Vickers indenter of silicon nitride specimen obtained from the nitridation of bare silicon at 1300°C for 3 hours.

The Vickers hardness, H_v, was calculated by using the following equation:

$$H_v = 1.8544 \times \frac{P}{(2a)^2} \tag{C.1}$$

where P is the indentation load (kg), and $2a$ is the diagonal of indentation (mm).

The fracture toughness, K_{1C}, was calculated as:

$$K_{1C} = 0.018 \times (\frac{E}{H_v})^{1/2} (\frac{P}{c^{3/2}}) \qquad \text{(C.2)}$$

where E is the Young’s modulus (GPa), and c is crack length (mm).

For example: As shown in Figure C1, the values of diagonal length of the indentation and crack size measured by using an optical microscope are presented in Table C1.

Table C1 Diagonal length of the indentation and crack size

Length (μm)			
Diagonal X	Diagonal Y	Crack X	Crack Y
109.25	110.28	260.57	271.98

Substitute the values in Table C1 to equation C.1 and C.2:

$$H_v = 1.8544 \times \frac{98.07}{((\frac{109.25 + 110.28}{2}) \times 10^{-6})^2} = 1.51 \times 10^{10} \quad \text{Pa}$$

Thus, $H_v = 15.1 \quad \text{GPa}$

$$K_{1C} = 0.018 \times (\frac{270 \times 10^9}{1.51 \times 10^{10}})^{1/2} (\frac{98.07}{(\frac{260.57 + 271.98}{4} \times 10^{-6})^{3/2}})$$

Thus, $K_{1C} = 4.86 \quad \text{MPa} \times \text{m}^{1/2}$

Noted: the Young’s modulus of silicon nitride = 270 GPa [Chaiyapuck, 2003]

APPENDIX D

LIST OF PUBLICATIONS

1. Tananya Vongthavorn, Varong Pavarajarn and Piyasan Praserthdam, "Enchancement of Direct Nitridation of Silicon by Common Elements in Sintering Additives", Proceedings of the Regional Symposium on Chemical Engineering 2003, Metro Manila, Philippines, December 1-3, 2003: B8-1-B8-6.

Enhancement of Direct Nitridation of Silicon by Common Elements in Sintering Additives

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The direct nitridation of silicon has been recognized as one of the methods for mass-production of silicon nitride. Although this process is considered low-cost, the product obtained usually contains roughly 92% of desired phase of silicon nitride, α-phase. On the contrary, silicon nitride produced from more expensive method usually contains α-phase higher than 95%. In this study, catalytic effects of elements, often added during the process of sintering silicon nitride product, on the direct nitridation of silicon were investigated. Silicon granules impregnated with 0.125-2.0% by mass of yttrium, calcium, magnesium or cerium were nitrided in a tubular flow reactor operated at temperature in the range of 1300-1390°C. Enhanced selectivity of α-silicon nitride formation was observed when either calcium or yttrium was used. The products with α-phase content above 98% were obtained from 0.125% calcium addition or 1.0% yttrium addition to the silicon raw material. Magnesium also enhances the nitridation if the reaction temperature is 1390°C. It was also found that a stepwise increase in the nitridation temperature from 1300 to 1390°C enhanced the conversion of silicon while keeping high content of α-silicon nitride.

Key Words: Silicon nitride, Direct nitridation, Silicon, Sintering additives, Catalysts

INTRODUCTION

Silicon nitride (Si_3N_4) is one of the most promising structural materials for high-temperature and high mechanical-stress applications because of its excellent properties such as high strength retention at elevated temperature, good thermal shock resistance, high-temperature deformation resistance as well as high corrosion resistance. It can withstand erosion from many molten metals, including molten aluminum. Silicon nitride has much higher creep resistance than metals and its thermal shock resistance is much better than other ceramics.

Silicon nitride exists as amorphous and crystalline forms. Two well-known crystal structures of silicon nitride are designated as α-phase and β-phase, both appearing to be hexagonal (Wang, *et al.*, 1996). β-silicon nitride is more desirable structure for high-temperature engineering applications because of its high temperature strength and excellent thermal shock resistance (Lange, 1979). However, silicon nitride ceramics are commonly fabricated from α-silicon nitride powder rather than from β-silicon nitride powder because densification and sintering of α-silicon nitride powder is much easier than sintering of β-powder (Hirosaki, *et al.*, 1994). The fabrication of β-silicon nitride parts usually starts from α-silicon nitride powder mixed with sintering additives. The mixture is then shaped into a desired component. Finally, the component is sintered at high temperatures (1700-1800°C), during which the transformation of α-phase to β-phase occurs, providing desirable microstructure having high mechanical and thermal strength (Ault and Yeckley, 1994; Lange, 1979). Thus, α-silicon nitride powder is the important starting material for making silicon nitride components. A high content of α-form, usually higher than 95 %, is often desired.

The direct nitridation of silicon is one of the most commonly used process to produce silicon nitride powder, predominantly α-form. It is an inexpensive option for applications in which metal impurities contained in the silicon nitride product can be tolerated. However, the important disadvantage of this process is the quality of the product. Silicon nitride powder produced from the direct nitridation process usually contains about 92% of α-silicon nitride (Segal, 1985), which is considered as moderately low quality powder. On the contrary, very pure silicon nitride with a high content of α-form (> 95%) can be prepared from much more expensive method, the diimide process (Ault and Yeckley, 1994). Therefore, it is desired to increase the content of α-silicon nitride in the product from the direct nitridation of silicon.

It has been known that transition metals contained in silicon as impurities regulate kinetics of its nitridation as well as the phase formation (Boyer and Moulson, 1978; Jennings, 1983; Lin, 1977; Pavarajarn and Kimura, 2001; Pigeon*, et al.*, 1993). Many researchers have studied the effects of several transition metals on the nitridation of silicon by intentionally adding metals into silicon before the nitridation. However, metals investigated in the past are not elements commonly used in silicon nitride processing operation and the impact of metals residual on physical properties of the silicon nitride articles has not been reported. Since sintering additives are always used in the fabrication of articles from silicon nitride powder, yet no report on catalytic effects of the additives on the nitridation of silicon has been done, it is the objective of this work to investigate the enhancement of the direct nitridation of silicon from elements in the common sintering additives, e.g. yttrium, calcium, magnesium and cerium.

EXPERIMENTAL PROCEDURE

Raw material preparation

Raw material used in this study was 300 μm average-sized porous silicon granules composed of 2 μm average-sized grains. The impurities contained in the silicon granules are listed in Table 1. All other physical properties of the granules should be referred to elsewhere (Jovanovic*, et al.*, 1994).

Table 1. Specification of raw material silicon.

Trace impurities (% by mass)				
Fe	Al	Ca	C	O
0.08	0.10	0.02	0.02	0.51

Impregnation of metals onto the silicon raw materials was done by immersing about 10 g of silicon granules in 30 ml of methanol solutions of metal-nitrate compounds under continuous agitation by using ultrasonic bath. The amount of each metal-nitrate compound dissolved in methanol was adjusted so that a desired level of metal impregnation, e.g. 0.125, 0.45, 1.00 and 2.00 % by mass, was achieved after the decomposition and reduction of the nitrate compound at high temperature before the silicon-nitridation reaction. After all methanol was evaporated, the samples were put in an oven at 110°C for 24 hours to ensure the elimination of all possibly remaining methanol and moisture.

Silicon nitride synthesis

For the nitridation of silicon, about 0.5 g of impregnated silicon granules were put into an alumina tray (25 mm × 15 mm × 5 mm deep) and placed in the horizontal tubular flow reactor. The granules were then heated in continuous flow of argon to a predetermined temperature, in the range of 1300-1390°C, at the rate of 10°C/min. After the system had reached the prescribed temperature, the granules were pretreated by replacing the argon stream with a mixture of 90% argon and 10% hydrogen to remove any native oxide layer on silicon as well as to convert metal nitrates into reduced metals. The pretreatment was conducted for 1 hour. Then, the nitridation was initiated by substituting argon feed by nitrogen. The reactant gas mixture was supplied to the reactor at the constant rate of 4.28 l/min at room temperature. Hydrogen was always supplying into the reactor at the concentration of 10 vol. % to prevent the formation of the protective layer, which retarded the progress of the reaction (Pavarajarn and Kimura, 2003). The nitridation was done for 3 hours, since it was shown that the nitridation of silicon granules reached a stage of very slow progress in about 3 hours (Jovanovic*, et al.*, 1994).

Characterization

The obtained product was characterized by powder X-ray diffraction (XRD) using a SIEMENS D5000 diffractometer with CuKα radiation. The mass fractions of silicon as well as α- and β-silicon nitride in the product were calculated from the integrated intensity of various peaks of silicon, α- and β-silicon nitride (Jovanovic and Kimura, 1994).

RESULTS AND DISCUSSION

The direct nitridation at constant temperature

It has been known that the overall conversion of the direct nitridation at temperature lower than 1300°C is unacceptably low and the temperature near 1400°C would result in melting of the silicon raw materials (Jovanovic, 1998). Moreover, the extent of the nitridation at temperature in the range of 1300 to 1370°C are roughly constant (Pavarajarn and Kimura, 2001). Therefore, in this study, the nitridation was conducted only at 1300 and 1390°C. The results regarding the effects of each metal on the overall conversion and selectivity of α-phase are shown in Figure 1 and 2, respectively.

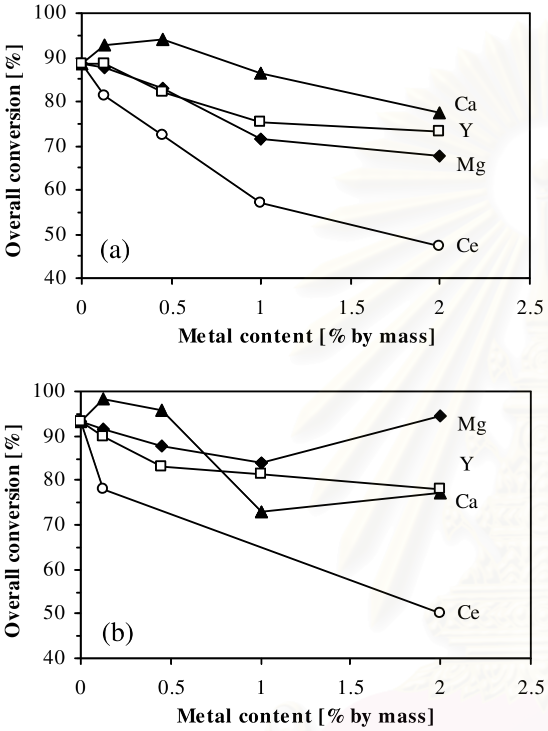

Figure 1. Effects of different metals on the overall conversion of the nitridation; (a) at 1300°C, and (b) at 1390°C: (□) – yttrium, (▲) – calcium, (◆) – magnesium, (○) – cerium.

Figure 1 shows that the overall conversions are generally decreased when metal is added to the silicon raw material. The higher the metal content, the lower the overall conversion, with exception of an addition of small amount of calcium which enhances the conversion of silicon to silicon nitride. When the reaction temperature of 1390°C is employed, the overall conversion is only slightly improved and the same trend is still observed, except for 2% magnesium impregnation.

Nevertheless, according to Figure 2, it is evident that an addition of these metals to the silicon before the nitridation can enhance the selectivity of α-silicon nitride formation. The products obtained from calcium or yttrium impregnated silicon always contain higher fraction of α-phase than the nitrided product from bare silicon, regardless of the reaction temperature or metal content. Silicon nitride with α-phase content over 98% can be produced by the direct nitridation of silicon granules impregnated with 1% yttrium or only 0.125% calcium. High fraction of α-phase can be achieved by magnesium addition as well, only when the reaction temperature is at 1390°C. It should be noted that, at this temperature, magnesium also enhances the overall conversion of the nitridation. When the reaction temperature is lowered to 1300°C, no enhancement from magnesium is found. Among the metals investigated, only cerium enhances neither the overall conversion nor the fraction of α-silicon nitride in the product. The nitridation of 2% cerium impregnated silicon resulted in only 49.9% conversion with 79.6% α-phase. It seems that cerium retards the nitridation of silicon, especially at 1390°C.

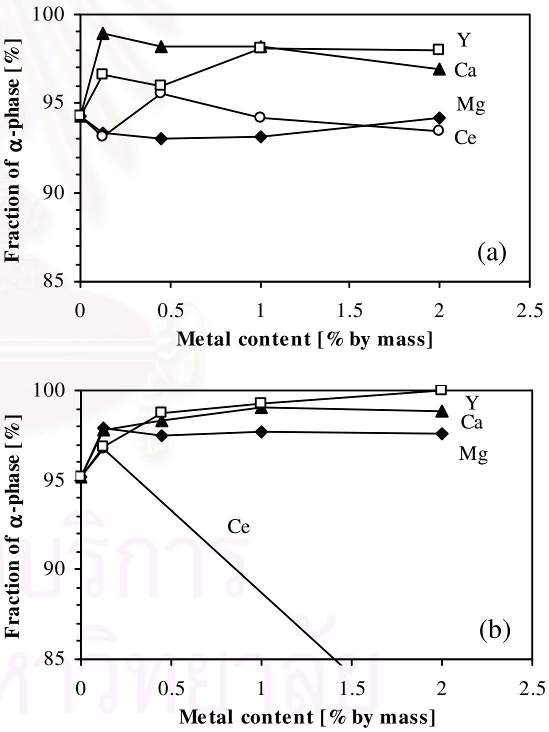

Figure 2. Effects of different metals on the formation of α-phase from the nitridation; (a) at 1300°C, and (b) at 1390°C: (□) – yttrium, (▲) – calcium, (◆) – magnesium, (○) – cerium.

Although the mechanisms of the enhancement observed in this work are not clear, the results agree with the report from literature that the characteristic of individual metals dominate the formation of α- or β-silicon nitride (Pavarajarn and Kimura, 2001). Detailed studies are needed to clarify actual roles of each metal on the direct nitridation of silicon. Furthermore, since the metal added to silicon raw materials remains in the final product, it is suggested that its effect on the physical and mechanical properties of the sintered silicon nitride articles should be investigated.

The direct nitridation using stepwise increase in temperature

The results in above section confirm the enhancement of the direct nitridation by the addition of some metals into silicon raw materials. However, the main problem lies on the fact that the achievable overall conversion of silicon is not high enough. The overall conversions achieved from metal-impregnated silicon granules are usually lower than that achieved by using bare silicon. This problem can be overcame by using a step-wise increase in the reaction temperature from 1300°C to 1390°C, as suggested elsewhere (Jovanovic*, et al.*, 1994). The reaction was carried out at 1300°C for one hour. Then, the temperature was raised at the rate of 10°C/min to 1390°C where the system was held at this temperature for two hours. The results of the operation with programmed temperature are shown in Figure 3 and 4, respectively.

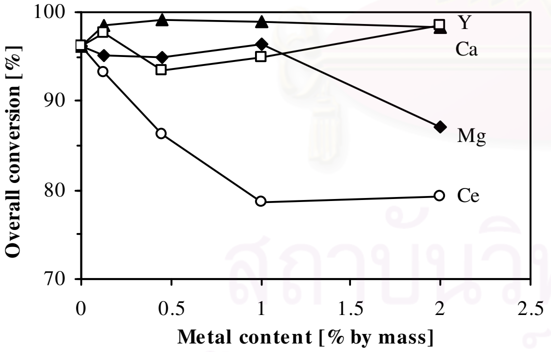

Figure 3. The overall conversion achieved from the nitridation under programmed temperature operations: (☐) – yttrium, (▲) – calcium, (◆) – magnesium, (○) – cerium.

Figure 3 clearly illustrates the significant improvement in the overall conversion achieved by using the programmed temperature operations, comparing to the nitridation at the constant temperature. Moreover, the fraction of α-form in the product remains at relatively high level, as shown in Figure 4, especially when calcium or yttrium is used. This operation is effective for achieving a high overall conversion within a short time

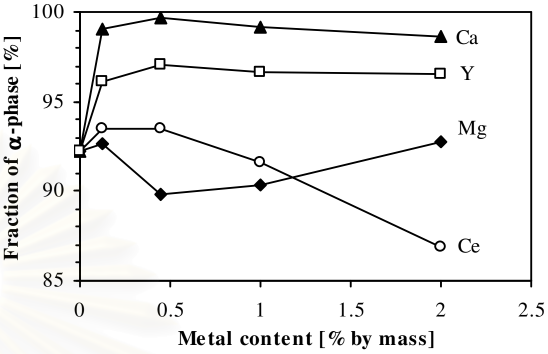

Figure 4. The fraction of α-phase in the products obtained from the nitridation under programmed temperature operations: (☐) – yttrium, (▲) – calcium, (◆) – magnesium, (○) – cerium.

CONCLUSION

This work has shown that the enhancement of the direct nitridation of silicon can be achieved by an addition of yttrium, calcium or magnesium into the silicon raw materials. The direct nitridation of silicon impregnated with calcium as small as 0.125% or yttrium 1% at 1300°C results in the product with α-phase content higher than 98%. The nitridation of 2% magnesium-impregnated silicon at 1390°C also results in high quality silicon nitride powder. High overall conversion can be achieved by raising the reaction temperature in step-wised fashion, from 1300°C to 1390°C.

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