Electronic Materials Letters, Vol. 5, No. 1 (2009), pp. 19-22
DOI: 10.3365/eml.2009.03.019

Pulsed Current Activated Combustion Synthesis and Consolidation of Nanostructured $ReSi_{1.75}$

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Dense nanostructured $ReSi_{1.75}$ was synthesized by the pulsed current activated combustion synthesis (PCACS) method within 2 min in one step from mechanically activated powders of Re and 1.75 Si. Simultaneous combustion synthesis and densification were accomplished under the combined effects of a pulsed current and mechanical pressure. Highly dense $ReSi_{1.75}$ was produced under simultaneous application of 80 MPa of pressure and a pulsed current. The average grain size and mechanical properties (hardness and fracture toughness) of the compound were investigated.

Keywords: pulsed current activated combustion, intermetallic, nanophase, $ReSi_{1.75}$

1. INTRODUCTION

Refractory metal disilicides have been used as Schottky barriers, ohmic contacts, gate materials, and interconnectors in intergrated circuits as a result of their low electrical resistivity, high stability, and good compatibility with silicon substrates.[1,2] Among the metal disilicides, rhenium silicides are candidates for promising thermoelectric applications.[3] The value of the dimensionless figure of merit (ZT) along [001] of rhenium silicides was 0.7 at 1073 K, which is comparable to the value of Si-Ge alloys currently used as a thermoelectric material for power generation.[4]

The crystal structure of the dicilicide formed with Re was first assigned to be a body-centered tetragonal $C11_b$ ($MoSi_2$-type, space group $I4/mmm$) structure.[5] However, recent investigations by Gottlib *et al*., Yamaguchi *et al*., and Takahashi *et al*.[6-8] revealed that the stoichiometry of the silicide was $ReSi_{1.75}$ instead of $ReSi_2$ and the unit cell was monoclinic (space group P1) with lattice parameters of a = 0.3138 nm, b = 0.3121 nm, and c = 0.7670 nm.

Nanostructured materials have been widely investigated because they display a wide functional diversity and exhibit enhanced or different properties compared with bulk materials.[9] Particularly in the case of nanostructured ceramics, the presence of a large fraction of grain boundaries can lead to unusual or better mechanical, electrical, optical, sensing, magnetic, and biomedical properties.[10-15] Recently, nanocrystalline powders have been developed by co-precipitation, the thermochemical and thermomechanical process known as the spray conversion process (SCP), and high energy milling.[18,19] However, the grain size in sintered materials becomes much larger than that in pre-sintered powders due to fast grain growth during the conventional sintering process. Therefore, even though the initial particle size is less than 100 nm, the grain size increases rapidly up to 500 nm or larger during conventional sintering.[20] Therefore, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. In this regard, the pulsed current activated sintering method, which can create dense materials within 2 min, has been shown to be effective in achieving this goal.[21-26]

The objective of this study is to investigate the preparation of dense nanophase $ReSi_{1.75}$ by the PCACS method, starting from a mixture of mechanically activated Re and 1.75 Si powders. Furthermore, the average grain size and mechanical properties (hardness and fracture toughness) of the compound were investigated.

2. EXPERIMENTAL PROCEDURE

Powders of 99.9% pure rhenium (5 um, rhenium Alloy Inc.) and 99% pure silicon (-325 mesh, Aldrich Products) were used as starting materials. Figure 1 shows SEM images of the raw materials used. Powder mixtures of Re and Si in the molar proportion of 1:1.75 were first milled in a high-energy ball mill (Pulverisette-5, planetary mill) at 250 rpm

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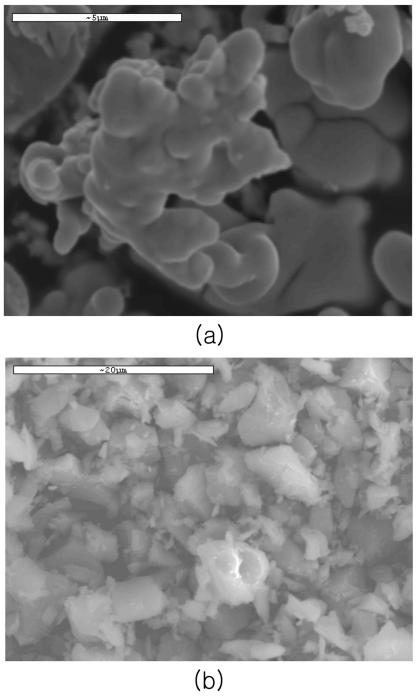

Fig. 1. Scanning electron microscope images of raw materials: (a) rhenium and (b) silicon powder.

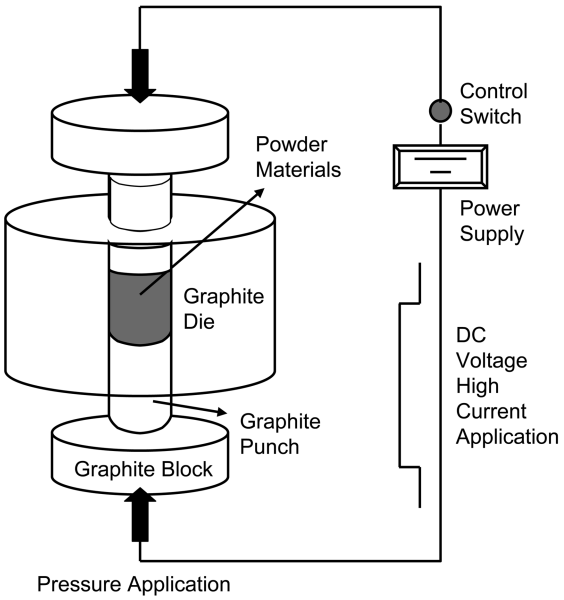

Fig. 2. Schematic diagram of the pulsed current activated combustion apparatus.

for 10 h. Tungsten carbide balls (8.5 mm in diameter) were used in a sealed cylindrical stainless steel vial under argon atmosphere. The weight ratio of the ball-to-powder was 30:1. Milling resulted in a significant reduction of grain size. The grain size and the internal strain were calculated by C. Suryanarayana and M. Grant Norton's formula,[27]

$$B_r\,(B_{crystalline} + B_{strain})\cos\theta = k\lambda/L + \eta\sin\theta, \quad (1)$$

where B_r is the full width at half-maximum (FWHM) of the diffraction peak after instrument correction; $B_{crystalline}$ and B_{strain} are the FWHM caused by small grain size and internal stress, respectively; k is constant (with a value of 0.9); λ is wavelength of the X-ray radiation; L and η are grain size and internal stress, respectively; and θ is the Bragg angle. The parameters B and B_r follow Cauchy's form with the relationship: $B = B_r + B_s$, where B and B_s are FWHM of the broadened Bragg peaks and the standard sample's Bragg peaks, respectively. The FWHM of the milled powder is greater than that of the raw powders due to internal strain and grain size reduction. The average grain sizes of the milled Re powders were determined to be 100 nm.

After milling, the mixed powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the pulsed current activated combustion synthesis system made by Eltek Co. in the Republic of Korea. Schematic diagrams of this method are shown in Fig. 2. The system was first evacuated, and a uniaxial pressure of 80 MPa was applied. The PCACS apparatus includes an 18 V, 2800 A DC power supply (which provides a pulsed current with 20 s on time and 10 s off time through the sample and die) and a 50 kN uniaxial press. A DC pulsed current (2000 A) was then activated and maintained until the densification rate was negligible, as indicated by the observed shrinkage of the sample. Sample shrinkage was measured in real time by a linear gauge measuring the vertical displacement. Temperatures were measured by a pyrometer focused on the surface of the graphite die. The heating rates were approximately 900 °C/min in the process. At the end of the process, the pulsed current was turned off and the sample was allowed to cool to room temperature. The entire process of densification using the PCACS technique consists of four major control stages. These are chamber evacuation, pressure application, power application, and cool down. The process was carried out under a vacuum of 40 mTorr.

The relative densities of the synthesized sample were measured by the Archimedes method. Microstructural characterization was made on product samples which had been polished and etched using a solution of HF (20 vol. %), HNO_3 (20 vol. %), and H_2O (60 vol. %) for 100 s at room temperature. Compositional and microstructural analyses of the products were made through X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX). Vickers hardness was measured by performing indentations at a load of 10 kg and a dwell time of 15 s.

3. RESULTS AND DISCUSSION

The variations in shrinkage displacement and temperature

with heating time during the processing of Re + 1.75 Si systems are shown Fig. 3. As the pulsed current was applied, thermal expansion occurred and then the shrinkage displacement abruptly increased at a temperature of 700°C. When the reactant mixture of Re + 1.75Si was heated under 80 MPa of pressure to point b, no reaction took place and there was no significant shrinkage displacement as judged by subsequent XRD analyses. Figures 4(a), (b), and (c) show the XRD results of (a) powder after milling, (b) a sample heated to point b, and (c) a sample heated to 1220°C, respectively.

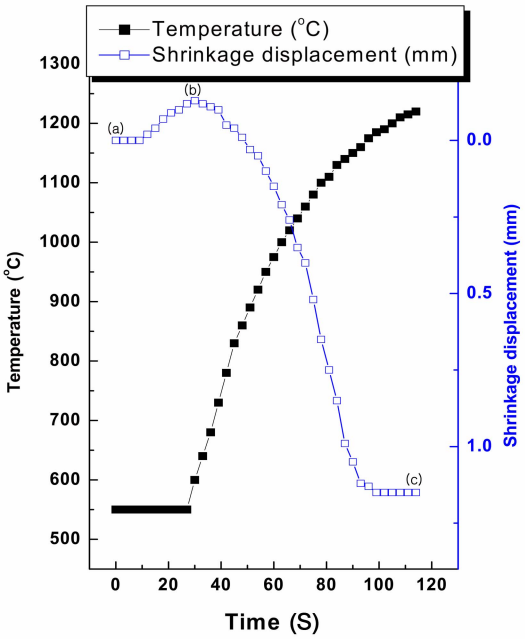

Fig. 3. Variations of temperature and shrinkage displacement with heating time during pulsed current activated combustion synthesis and densification of $ReSi_{1.75}$ (under 80 MPa and 2800 A).

Figures 4(a) and (b) exhibit peaks pertaining to the reactants (Re and Si) and mechanically alloyed $ReSi_{1.75}$. However, when the temperature was raised to 1220°C, the starting powders reacted, producing products. An SEM image of an etched surface of the samples heated to 1220°C under a pressure of 80 MPa is shown in Fig. 5(a). A complete reaction between Re and Si took place within 2 minutes under these conditions. X-ray diffraction analyses of this sample showed peaks of $ReSi_{1.75}$ and ReSi observed by X-ray diffraction analyses, as show in Fig. 4(c). The presence of ReSi in the sample suggests a deficiency of Si. This observation is thought to be related to entrapped oxygen in the pores of the interior portion of the sample during pressing or maybe due to the slight oxidation of Si during the heating. In the X-ray mapping in Fig. 5, Re and Si were uniformly distributed, but oxygen was only partially detected. This is thought to be due

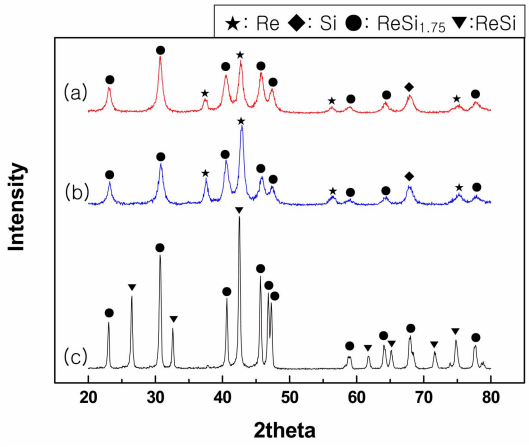

Fig. 4. XRD patterns of the Re+1.75Si system: (a) after milling, (b) before combustion synthesis (heated to 650°C), and (c) after combustion synthesis (heated to 1200°C).

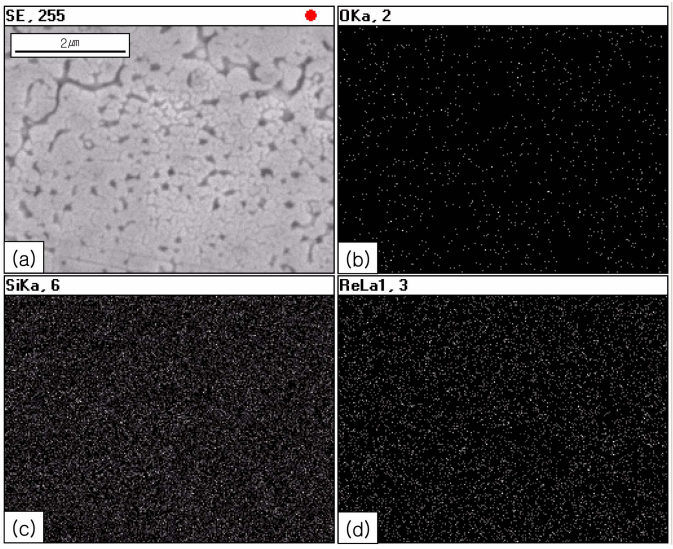

Fig. 5. SEM image and X-ray mapping of $ReSi_{1.75}$ (a) SEM image, (b) oxygen mapping (c) silicon mapping, and (d) rhenium mapping.

to the formation of SiO_2, which was observed by Takahashi.[8]

The abrupt increase in the shrinkage displacement at the ignition temperature is due to the increase in density as a result of molar volume change associated with the formation of $ReSi_{1.75}$ from the reactants (Re and 1.75Si) and the consolidation of the product. The average grain sizes of $ReSi_{1.75}$ calculated by the C. Suryanarayana and M. Grant Norton's formula[27] were about 78 nm.

Vickers hardness measurements were made on polished sections of the $ReSi_{1.75}$ using a 10 kg load and 15 s dwell time. The calculated hardness value, based on an average of five measurements, of the $ReSi_{1.75}$ is 1225 kg/mm^2. Indentations with sufficiently large loads produced median cracks around the indentation. The length of these cracks permited an estimation of the fracture toughness of the materials by Niihara *et al.*[28,29]

$$K_{IC} = 0.204(c/a)^{-3/2} \cdot H_v \cdot a^{1/2,} \quad (4)$$

where c is the trace length of the crack measured from the center of the indentation, a is half of average length of two indent diagonals, and H_v is the hardness. The calculated fracture toughness value of $ReSi_{1.75}$ is about 3.2 MPa $\cdot$ m$^{1/2}$. The absence of reported values for hardness and toughness on $ReSi_{1.75}$ precludes direct comparison to the results obtained in this work to show the influence of grain size.

4. SUMMARY

Using the pulsed current activated combustion method, the simultaneous synthesis and densification of nanostructured $ReSi_{1.75}$ were accomplished using powders of Re and 1.75 Si. Complete synthesis and densification can be achieved in one step within 2 min. The average grain sizes of $ReSi_{1.75}$ phases were about 78 nm, respectively. The average hardness and fracture toughness values obtained were 1225 kg/mm^2 and 3.2 MPa $\cdot$ m$^{1/2}$, respectively.

ACKNOWLEDGMENT

This work was supported by small and medium business administrations.

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