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High Frequency Induction Heated Synthesis and Consolidation of Nanostructured $TaSi_2$-WSi_2 Composite

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A dense nanostructured $TaSi_2$-WSi_2 composite was simultaneously synthesized and sintered by the high frequency induction heating method within 2 minutes from mechanically activated powder of Ta, W and Si. A highly-dense $TaSi_2$-WSi_2 composite was produced under simultaneous application of a 80 MPa pressure and the induced current. The mechanical properties and microstructure were investigated.

Keywords: Hard Materials, Nanostructured Materials, Sintering, Composite.

1. INTRODUCTION

An increase in operating temperature of a gas turbine engine will bring us reductions in both fuel consumption and CO_2 emissions. It requires ultra-high temperature structural materials which overwhelm the performance of nickel-based superalloys commercially used as turbine blade and rotors. In this regard, transition-metal silicides are very attractive for application temperature up to 1300 °C and higher because this class of materials has an attractive combination of properties, including high melting temperature, high modulus, high oxidation resistance in air, and a relatively low density. In addition, the thermal and electrical conductivities are relatively high and therefore they are also attractive for electronic interconnections and diffusion barriers. As in the case of many intermetallic compounds, the current concern about these materials focuses on their low fracture toughness below the ductile-brittle transition temperature. To improve on their mechanical properties, the approach commonly utilized has been the addition of a second phase to form composites and nanostructured materials.[1, 2]

The objective of this study is to make nanopowder by high energy ball milling and to investigate the preparation of dense nanostructured $TaSi_2$-WSi_2 composite by the HFIHS method starting from mechanically activated powders.

2. EXPERIMENTAL DETAILS

Powders of 99.97% pure Tantalum (−325 mesh, Alfa Aesar Products), 99.5% pure silicon (−325 mesh, Aldrich Products) and 99.5% pure tungsten (< 0.5 μm, Daegu Tec. Products) were used as starting materials. 0.5Ta, 0.5W and 2Si powder mixtures were first milled in a high-energy ball mill, Pulverisette-5 planetary mill, at 250 rpm and for 10 h. Tungsten carbide balls (8 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. A charge ratio (ratio of mass of balls to powder) of 30:1 was used. The grain size was calculated using Suryanarayana and Grant Norton's formula.[3] After milling, the powder was placed in a graphite die (outside diameter = 45 mm, inside diameter = 20 mm, and height = 40 mm) and then introduced into the high-frequency induction heated sintering system, shown schematically in shown in Refs. [4–6]. The four major stages in the sintering are as follows: The evacuation of the system to 40 mtorr (stage 1), the application of a uniaxial pressure of 80 MPa (stage 2), the activation of an induced current (frequency of about 50 kHz), which was maintained until densification was attained as indicated by a linear gauge measuring the shrinkage of the sample (stage 3). Temperatures were measured by a pyrometer focused on the surface of the graphite die. At the end of the process, the sample was cooled to room temperature (stage 4). The process was carried out under a vacuum of 40 mtorr (5.3 Pa).

The relative densities of the sintered sample were measured by the Archimedes method. Microstructural

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information was obtained from product samples which were polished and etched for 1 minute at room temperature using a solution composed of HF (10 vol%), HNO_3 (30 vol%), and H_2O (60 vol%). 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 on the synthesized samples.

3. RESULTS AND DISCUSSION

In XRD patterns of milled 0.5W-0.5Ta-2Si powders, only Mo, Nb, and Si peaks were observed. Therefore, it is obvious that no chemical reaction occurred between the component powders during milling.

The variations in shrinkage displacement and temperature of the surface of the graphite die with heating time during the synthesis and densification of $TaSi_2$-WSi_2 composite are shown Figure 1. As the induced current was applied the shrinkage displacement increased gradually with temperature up to about 550 °C, and then abruptly increased. Figure 2 displays the XRD pattern of a specimen sintered at 1200 °C from high-energy ball-milled 0.5Ta + 0.5W + 2Si powders. X-ray diffraction analyses of this sample showed peaks of $TaSi_2$ and WSi_2, as indicated in Figure 2. And minor phases (Ta_5Si_3 and W_5Si_3) observed by X-ray diffraction analyses, as show in Figure 2.

The presence of Ta_5Si_3 and W_5Si_3 of the sample suggests a deficiency of Si. It is considered that this observation is related to entrapped oxygen in the pores of the interior portion of the sample during pressing or maybe due to a little oxidation of Si during the heating. The interaction between these phases, i.e.,

$$0.5Ta + 0.5W + 2Si \rightarrow 0.5TaSi_2 + 0.5WSi_2 \quad (1)$$

is thermodynamically feasible, as shown in Figure 3.

The average crystalline sizes of the sintered $TaSi_2$ and WSi_2 measured by Suryanarayana and Grant Norton's formula[3] were 280 nm and 110 nm, respectively. A FE-SEM image and EDS of the etched surface of the sample heated to 1200 °C under a pressure of 80 MPa is shown in Figures 4(a) and (b), respectively.

The microstructure consists of nanophases in the FE-SEM image. The corresponding relative density is 99.4%. In Figure 4(a), gray phase and dark phase are WSi_2 and $TaSi_2$, respectively due to mass contrast. In EDS of Figure 4(b), only Ta, W, and Si peaks were detected. The milling process is known to introduce impurities from the ball and/or container. However, in this study, peaks of Fe and W were not identified.

The average grain sizes of the sintered $TaSi_2$ and WSi_2 are not significantly larger than that of the initial powders,

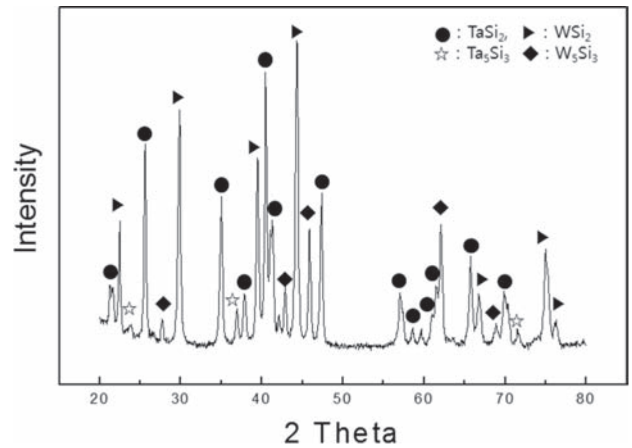

Figure 2. XRD patterns of the specimen sintered at 1200 °C from milled 0.5Ta-0.5W-2Si powders.

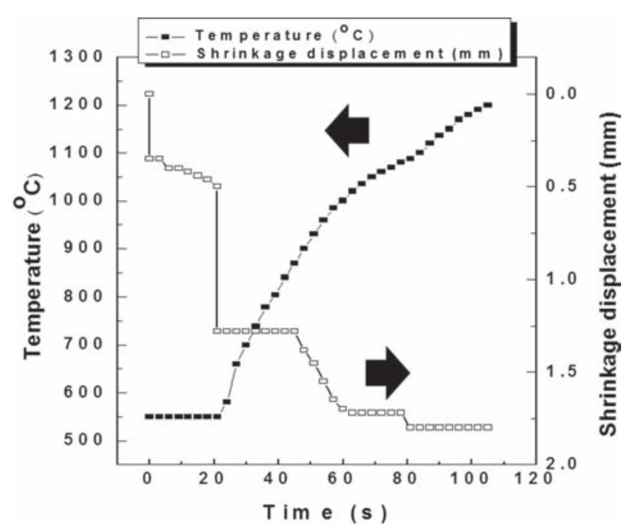

Figure 1. Variations of temperature and shrinkage displacement with heating time during synthesis and densification of $TaSi_2$-WSi_2.

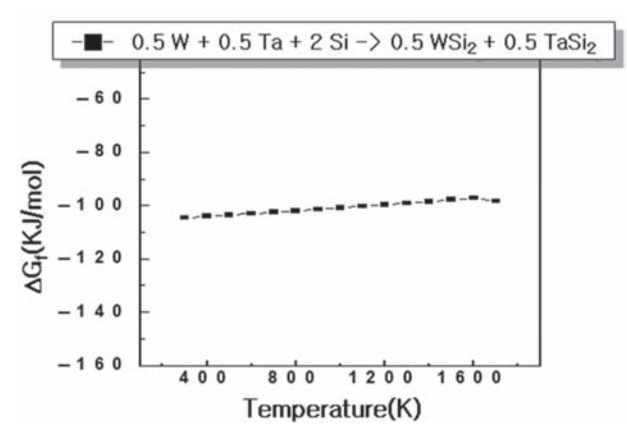

Figure 3. Temperature dependence of the Gibbs free energy for the formation of $TaSi_2$-WSi_2.

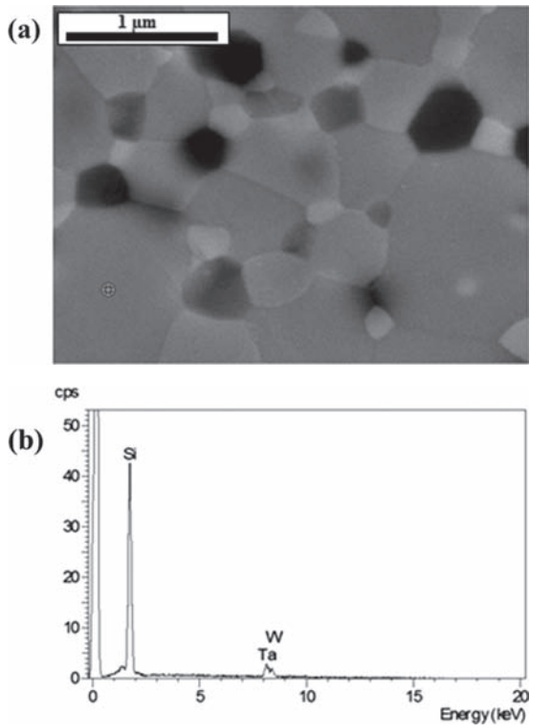

Figure 4. FE-SEM image and EDS of sintered $TaSi_2$-WSi_2 composites.

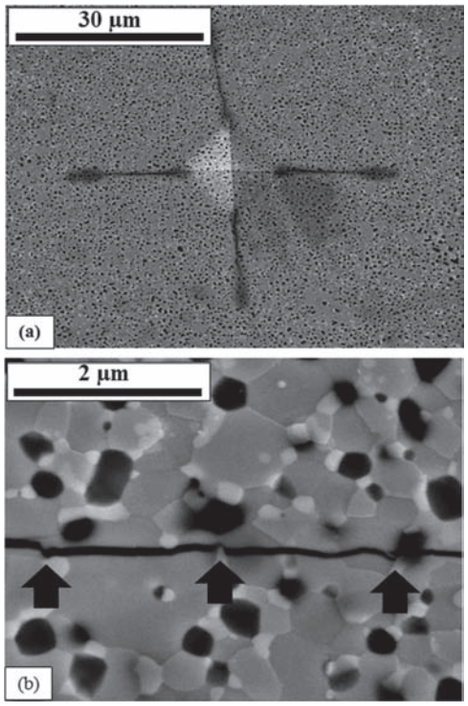

Figure 5. (a) Vickers hardness indentation and (b) median crack propagating in $TaSi_2$-WSi_2 composites.

indicating the absence of much grain growth during sintering. This retention of the grain size is attributed to the high heating rate, the relatively short-term exposure of the powders to the high temperature, the presence of plasma in pores separating powder particles, and the intrinsic contribution of the current to mass transport.[7, 8]

The abrupt increase in the shrinkage displacement at the ignition temperature is due to the increase in density resulting from the change in the molar volume associated with the formation of $TaSi_2$-WSi_2 composite from the reactants (Ta, W and Si) and the consolidation of the product.

Vickers hardness measurements were made on polished sections of the $TaSi_2$-WSi_2 using a 10 kg load and 15 s dwell time. The calculated hardness value of $TaSi_2$-WSi_2 was 1193 kg/mm^2. This value represents an average of five measurements. Indentations with large enough loads produced median cracks around the indent. From the length of these cracks, the fracture toughness can be determined using an expression, proposed by Niihara et al.[9]

$$K_{IC} = 0.023(c/a)^{-3/2} \cdot H_v \cdot a^{1/2} \quad (2)$$

where c is the trace length of the crack measured from the center of the indentation, a is half of the average length of two indent diagonals, and H_v is the hardness. The toughness values were derived from an average of five measurements. The toughness values obtained by this method of calculation is 4 MPa $\cdot$ m$^{1/2}$. These fracture toughness and hardness values of nanostuctured $TaSi_2$-WSi_2 composite are higher than those (fracture toughness; 3.5 MPa $\cdot$ m$^{1/2}$ hardness; 908 kg/mm^2) of micronstuctured $TaSi_2$.[10] A typical indentation pattern for the $TaSi_2$-WSi_2 composite is shown in Figure 5(a). Typically, one to three additional cracks were observed to propagate from the indentation corner. A higher magnification view of the indentation median crack in the composite is shown in Figure 5(b). This shows that the crack propagates in a deflective manner (↑). This is believed to suggest that $TaSi_2$ and WSi_2 in the composite may deter the propagation of cracks.

4. CONCLUSION

Nanopowders of Ta, W and Si were fabricated using high energy ball milling for 10 h. Using the high-frequency induction heated sintering method, $TaSi_2$-WSi_2 composite was simultaneously synthesized and consolidated using the mechanically activated powders of 0.5Ta, 0.5W and 2Si within 2 minutes. The relative density of the composite was 99% for the applied pressure of 80 MPa. The average crystalline size of $TaSi_2$ and WSi_2 prepared by this method were about 280 nm and 110 nm, respectively. The average hardness and fracture toughness values obtained were 1193 kg/mm^2 and 4 MPa $\cdot$ m$^{1/2}$, respectively. These fracture toughness and hardness values of nanostuctured $TaSi_2$-WSi_2 composite are higher than those of monolithic $TaSi_2$.

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