Study on Microstructure and room temperature fracture toughness of Nb/Nb₅Si₃ in-situ Composites Strengthened with CNTs

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ABSTRACT

CNTs were noncovalently modified with cetyltrimethyl ammonium bromide (CTAB). The Nb/Nb₅Si₃ In-Situ composite material strengthened with CNTs were prepared by Spark Plasma Sintering (SPS). The powders were mixed by mechanical milling in vacuum. The effects of CNTs content on microstructure and properties of Nb/Nb₅Si₃ in situ composites were investigated. The microstructures of the synthesised composites were analysed through scanning electron microscopy, X-ray diffraction, and electron probe microanalysis. The results show that the composite consists of Nb, α-Nb₅Si₃, and γ-Nb₅Si₃ phase. When adding over 2wt% CNTs, the new phase Nb₄C₃ was formed in the composites. The properties of the Nb/Nb₅Si₃ in situ composites were evidently affected by CNTs addition. The fracture toughness of composites increase obviously with increasing addition of CNTs. The fracture toughness of Nb/Nb₅Si₃ composites with 3wt% CNTs reached the maximum value and increased about ~35.6%. The micrographs observed by SEM of fractography show the fracture appearance of the composites belongs to brittle cleavage fracture and partial intercrystalline fracture. The toughening mechanisms of composites are mainly due to the CNTs pullout and bridging.

1. INTRODUCTION

Niobium silicide based composites have attracted considerable attention in recent years owing to their potential to replace Ni based superalloys in high temperature (>1100°C) structural applications in advanced gas turbine engines [1]. Intermetallic phases (Nb₅Si₃) impart high temperature strength and oxidation resistance, while (Nb) is thought to be necessary for enhanced ductility. According to Nb–Si binary phase diagram, Nb and Nb₅Si₃ coexist in wide range of temperature and silicon content. These features of the phase diagram allow us to fabricate Nb/Nb₅Si₃ in situ composites with desirable mechanical properties and excellent thermo-chemical stability. Alloying elements affect the volume fractions of Nbss and silicide/s and the type, chemistry, microstructures and properties of the latter. The Si concentration is important for the elevated temperature strength and creep properties by controlling the volume fraction of silicide.

Addition of Ti[2–5], Hf[6–9], Al, and Mg[10] in Nb–Si alloys reduces the density and stabilizes Nb₅Si₃ phase along with improvement inoxidation resistance [7,11]. Alloying with Ti [4,12] is typically performed to fabricate Nb-Si-Ti ternary alloys, which have higher fracture toughness than the binary Nb-Si alloys because the mobility of the dislocations in Nbss can be enhanced by the addition of Ti. Al addition has shown significant improvement in mechanical and oxidation properties of Nb–Si alloys [13].

Solid solution strengthening is affected by the addition of refractory elements. The Nbss provides the majority of the toughness, although microcracking and interface debonding are thought to make significant toughening contributions. Cr[5,6], Mo[10,11], Ta[14], V[15–17] and W[11,16] are solid solution strengtheners of Nb and improve its high temperature strength. These alloying additions also increase the density and reduce the oxidation resistance of the alloys[18]. The addition of 5 at.% Mo in Nb-16Si alloys increased the room temperature fracture toughness from 12 MPa.m¹/² to 15 MPa.m¹/², and the yield strength at 1500°C from ~250 MPa to 330 MPa[19, 20]. The addition of W in Nb-10Si alloy increased the yield strength to ~330 MPa at 1400°C and lowered the room temperature fracture toughness to ~8MPa.m¹/²[21]. The room temperature fracture toughness and high temperature oxidation resistance of Nbss/Nb-silicide material increased with the addition of V[15,16]. The strength of the materials will decreased by the increment of V content when the testing temperature is more than 1500°C [16]. It has been found that the Cr content significantly affected the fracture toughness at room temperature and the high temperature oxidation resistance [22, 23].
Carbon nanotubes (CNTs) are considered to be the most effective reinforcement in metal–matrix composites for structural applications [24–27] due to their extraordinary mechanical, thermal, and electrical properties and high aspect ratios. In the past, 1 vol% MWCNTs reinforced TiNi shape memory alloys matrix with enhanced compressive properties and wear resistance have been fabricated by hot-press sintering[28]. The elastic modulus, yield strength and ultimate tensile strength of these CNT/NiTi composites have also been reported. Relatively small additions of CNTs had little influence on the shape memory effects of the NiTi while improving the mechanical strength due to the presence of unreacted CNTs in the NiTi matrix [29]. Kondoh et al.[30] fabricated 0.35 wt% MWCNTs/Ti composites. After hot extrusion, the increase of tensile strength and yield stress was 157 MPa and 169 MPa.

Therefore, the effects of CNTs addition on the microstructure, and mechanical properties of Nb/Nb5Si3 in situ composites has been studied in the present investigation. The Nb/Nb5Si3 in situ composites were successfully fabricated via SPS.

2. EXPERIMENTAL PROCEDURE

These Nb/Nb5Si3 composites of Nb-20Si, Nb-20Si-1wt%CNTs, Nb-20Si-2wt%CNTs, and Nb-20Si-3wt%CNTs were prepared by SPS. The Nb (325 mesh, 99.9 wt % purity), and Si (200 mesh, 99.6 wt % purity) powders, and CNTs (Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences) with dimensions of 8–15 nm in diameter and 10–30 μm in length were chosen.

To remove the catalyst and impurities from the CNTs, the CNTs were first acid treated by a H2SO4/HNO3 mixture (3:1, v/v) in the ultrasonic bath for 1.5 h at 60°C. The colloid was scoured with deionized water until pH to be neutral before collecting on the filter paper. Then, the purified CNTs were dispersed in the cetyltrimethyl ammonium bromide (CTAB, at a fraction of 1.0g/L), mixed with ethyl alcohol and ultrasonicated at 30 °C. The CTAB-modified CNTs and Nb, Si powders were individually dispersed in methanol for 1 h with the ultrasonication and then the CNTs suspension was dropwise added into Nb, Si suspension. The volume fraction of CNTs was changed in the range from 0 to 3.0 wt. %. The mixed suspension was continuous ball milling for 20h, followed by drying in the oven at 353 K for 24 h.

The mixed powders were packed into a graphite die with an inside diameter of 28mm. The sintering was performed in a SPS facility (Sumitomo Coal Mining Co. Ltd. Japan) under a vacuum of 10 Pa at 1500°C. The heating rate up to the sintering temperature was 150°C/min. Dwell times at the sintering temperature were set to 10min under 40MPa. Finally, the sintered samples were cooled to the room temperature in the furnace.

The microstructures and resultant phases of the sintered samples were examined under a JSMT-200 scanning electron microscope (SEM) and a D/ MAX-IIIB X-ray diffractometer (XRD). The phase distribution and chemical species were determined using a JXA-800R electron microprobe analyser (EMPA). Three point bending tests were performed using single notched specimens with the dimensions 2 mm×4mm×22 mm. A single notch was introduced up to a/w = 0.5 (a: notch length and w: specimen wide) by an electro-discharge machining with 0.1 mm diameter wire, while not pre-cracked. The tests were executed with a span of 16 mm and at an initial crosshead speed of 0.05 mm/min in air. Fracture toughness values are calculated in accordance with the ASTM E399 standard testing method.

3. RESULTS AND DISCUSSION

3.1 Microstructures of the Nb/Nb5Si3 in situ composites

Fig. 1 shows the XRD patterns of the Nb-20Si, Nb-20Si-1wt%CNTs, Nb-20Si-2wt%CNTs, and Nb-20Si-3wt%CNTs composites. Note that the composites were composed of Nb, α-Nb5Si3, and γ-Nb5Si3. In addition, diffraction peaks corresponding to a Nb4C3 phase appeared in the XRD patterns of the Nb-20Si-2wt%CNTs and Nb-20Si-3wt%CNTs composites. The formation of Nb4C3 in the composites originated from the reaction CNTs with Nb. The Si and Nb5Si phase do not appear in all the composites.

During the SPS process, the pulse current was directly yielded by special power acting on the reactant powders, which induces to the rarefied gas ionization and discharge at the gaps of powders. The local high temperature created by plasma and Joule heating at the gaps of reactant powders, it leads to impurities gasification and surfaces activation take place on the reactant particle surfaces[18]. With increasing the sintering temperature, the diffusion rate of Nb and Si atoms rapidly increased, leading to a strong interfacial reaction. The pulse current uniformly passes through the reactant powder and the reaction of Nb and Si simultaneously takes place everywhere. As a result, the remaining Nb particles became finer and uniformly distributed in the synthesized Nb5Si3 matrix. Therefore, the dispersed microstructures of Nb/Nb5Si3
composites can be obtained.

Fig. 2 shows the SEM micrographs of the bulks specimens. The lightly and darkly contrasted regions in Fig. 2 correspond to Nbss and Nb5Si3, respectively.

Fig. 1 X-ray diffraction (XRD) patterns of Nb/Nb5Si3 composites

Fig. 2 scanning electron microscopy (SEM) image of Nb/Nb5Si3 composites with different CNTs contents

3.2 Densification

The relative density of composites was determined by the following equation:

$$\rho = \frac{\rho_0}{\rho_1} \times 100\%$$

Where $\rho$ is the relative density, $\rho_0$ is the theory density, $\rho_1$ is the actual density, which was measured by Archimedes method.

The relative density, actual density and theory density of the samples are shown in Table 1. The density of the as-sintered composites increases till the CNTs content amounts to 2 wt% and then decreases as the CNTs content continues to rise. When the content of CNTs is 2%, the relative density of the material reaches the maximum of 99.36%. It is probable that the addition of the CNTs can promote the fluidity of the powder particles and the densification of the composites during the SPS sintering.
Table 1 The result of the sample actual density test

<table>
<thead>
<tr>
<th>CNTS (wt.%)</th>
<th>Actual density (g.cm(^{-3}))</th>
<th>Teory density (g.cm(^{-3}))</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.70</td>
<td>7.86</td>
<td>97.96</td>
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<td>1</td>
<td>7.75</td>
<td>7.86</td>
<td>98.60</td>
</tr>
<tr>
<td>2</td>
<td>7.81</td>
<td>7.86</td>
<td>99.36</td>
</tr>
<tr>
<td>3</td>
<td>7.76</td>
<td>7.86</td>
<td>98.73</td>
</tr>
</tbody>
</table>

3.3 Room Temperature Fracture Toughness

Table 2 lists the room temperature fracture toughness values of these composites. Fig. 4 shows the variation of the fracture toughness of composites with different CNTs contents.

Table 2 Comparison of the fracture toughness of the composites

<table>
<thead>
<tr>
<th>CNTS (wt.%)</th>
<th>Test 1 (MPa.m(^{1/2}))</th>
<th>Test 2 (MPa.m(^{1/2}))</th>
<th>Average (MPa.m(^{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.46</td>
<td>2.76</td>
<td>2.61</td>
</tr>
<tr>
<td>1</td>
<td>2.76</td>
<td>3.10</td>
<td>2.93</td>
</tr>
<tr>
<td>2</td>
<td>2.96</td>
<td>3.28</td>
<td>3.12</td>
</tr>
<tr>
<td>3</td>
<td>3.27</td>
<td>3.81</td>
<td>3.54</td>
</tr>
</tbody>
</table>

Fig 3 The fracture toughness of composites with different CNTs contents

The results show that by adding low weight fraction of CNTs, the fracture toughness of the resulting composites had a large enhancement. With the increment of CNTs content, the room temperature fracture toughness of Nb/Nb\(_5\)Si\(_3\) composites increases (Fig. 3). The fracture toughness of the Nb-20Si is 2.61 MPa.m\(^{1/2}\) and increases to the highest with the increase of CNTs content up to 3wt.%, i.e., the average \(K_Q\) value was 3.54 MPa.m\(^{1/2}\), which is \(\sim 35.6\%\), 20.8%, and 13.5% higher than that of Nb-20Si, Nb-20Si-1wt.% CNTs, and Nb-20Si-2wt.% CNTs, respectively.

The fracture surface of the Nb-Si composite with different CNTs contents are shown in Fig. 4. It was worth noting that the predominant fracture mode of Nb-20Si alloys was transgranular fracture with river patterns in Nbss and relatively flat cleavage planes in silicides, shown in figure 4(a). As expected, the fracture surface was mostly covered by the smooth Nb\(_5\)Si\(_3\) phase (Fig. 4a), while in the region containing the Nb\(_{SS}\) phase, the fracture surface was bright and undulant (in Fig. 4a).

Embedded CNTs in Fig. 4(b), (c) and (d) strengthened the grain boundaries and caused transgranular fracture. Fracture surfaces of the Nb-20Si-1wt.%CNTs after bending tests are shown in Fig. 4(b), the main fracture mode is quasi-cleavage fracture in brittle matrix, whereas the niobium silicides fracture with no CNTs in a brittle cleavage model with river patterns. Some small holes and CNTs are distributed in the fracture surface of the composite material (arrows in Fig. 4b, c, d), suggesting that some carbon nanotubes are pulled out from the composite material, and others are fractured.
With the increase of CNTs addition, the composites rupture changes from cleavage fracture to quasi-cleavage fracture, and the brittle cleavage model with river patterns is not found (in Fig. 4c). When the CNTs content added over 2wt%, some dimples are found in the fracture morphology (see circles in Fig. 4c and Fig. 4d). The addition of CNTs results in an increase in the strength of Nb5Si3 phase. During crack propagation, crack arrest, renucleation, and reflection prevent the crack from continuing to propagate and would be contributed to the improvement of fracture toughness.

4. CONCLUSIONS

The effects of CNTs on the microstructure and properties of Nb/Nb5Si3 in situ composites prepared via SPS technology. The following conclusions were drawn from the results:

(1) The Nb/Nb5Si3 composites strengthened with CNTs were fabricated using Nb, Si and CNTs powders as raw materials. The composite consists of Nb, α- Nb5Si3, and γ- Nb5Si3 phase. When adding over 2wt% CNTs, the new phase Nb4C3 was formed in the composites.

(2) The fracture toughness of the Nb/Nb5Si3 composites increase obviously with increasing addition of CNTs. The fracture toughness of the Nb-20Si-3wt.% CNTs composite was highest, i.e., the average $K_{Q}$ value was 3.54 MPa.m$^{1/2}$, which is ~35.6%, 20.8%, and 13.5% higher than that of Nb-20Si, Nb-20Si-1wt.% CNTs, and Nb-20Si-2wt.% CNTs, respectively.

(3) The micrographs observed by SEM of fractography show the fracture appearance of the composites belongs to brittle cleavage fracture and partial intercrystalline fracture. The toughening mechanisms of composites are mainly due to the CNTs pullout and bridging.

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