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Microstructures of Nb/Nb_5Si_3 composites and it alloyed with W, Mo and W–Mo fabricated by spark plasma sintering

Bowen Xiong [a,b,*], Changchun Cai [a,b], Zhenjun Wang [a]

[a] National Defence Key Discipline Laboratory of Light Alloy Processing Science and Technology, Nanchang Hangkong University, Nanchang 330063, PR China
[b] School of Material Science and Engineering, Nanchang Hangkong University, Nanchang 330063, PR China

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ABSTRACT

Microstructures of Nb/Nb_5Si_3 composites and it alloyed with W, Mo and W–Mo fabricated by spark plasma sintering were investigated. The microstructures were examined using scanning electron microscope (SEM). X-ray diffraction (XRD) was performed on the bulk specimens for identification of phases. The chemical species were analyzed using electron-probe micro-analysis (EPMA). Results indicated that the microstructures Nb/Nb_5Si_3 composites include primary Nb and eutectic mixtures of Nb and Nb_5Si_3, and the coarse and fine eutectic mixtures are detected. The microstructure of Nb/Nb_5Si_3 composites alloyed with W or Mo is unaltered, and W and Mo elements solid solution in Nb and Nb_5Si_3 phase are detected, but that alloyed with W and Mo together, The microstructures are change obviously, including Nb phase, the solid solubility phases of W and Mo atoms in Nb, and the solid solubility phases of Nb atoms in W are also found, but the solid solubility phenomenon of Nb_5Si_3 phases is not detected. The microhardness of Nb and Nb_5Si_3 phases increases obviously because of solid solution strengthening.

1. Introduction

Niobium silicide based alloys have been extensively studied as high-temperature structural materials [1,2]. Nb_5Si_3 has high melting point (2515 °C), low density (7.16 g/cm^3) and excellent specific mechanical properties at high temperature [3–5], but Nb_5Si_3 has low fracture toughness at room temperature and poor deformability at high temperature, these drawbacks hinder the application of Nb_5Si_3. The Nb has high melting point (2472 °C), excellent fracture toughness and good deformability. According to Nb–Si binary phase diagram, Nb and Nb_5Si_3 coexist in wide range of temperature and silicon content. These features of the phase diagram allow us to fabricate Nb/Nb_5Si_3 in situ composites with desirable mechanical properties and excellent thermo-chemical stability [4,6].

Most studies succeeded in improving the fracture toughness at room temperature with the sacrifice of high temperature strength of Nb/Nb_5Si_3 in situ composites by increasing the volume fraction of the ductile Nb phase. Recent researches [7–11] have shown that the significant improvement in the strength of Nb/Nb_5Si_3 composites has been achieved by solid solution of Nb and Nb_5Si_3 on alloying with specific elements, such as Ti, Cr, Hf, W and Mo [6,12]. Currently, the Nb/Nb_5Si_3 composite was prepared mainly by arc melting [6,13], self-propagating high-temperature synthesis [3,14], directional solidification [1,13] and powder metallurgy [1,15]. Previous literatures have detected some difference in microstructures of Nb/Nb_5Si_3 composite fabricated by different preparation method [1], for example, at near eutectic composition, arc melting alloys exhibit a dispersed microstructures consisting of fine Nb phase in a Nb_5Si_3 matrix, while the microstructures of powder metallurgy alloys are characterized by aggregate structure and equiaxed structure [1]. Recently, the spark plasma sintering (hereafter abbreviated as SPS) has been drawing attention as a new process for fabricating advanced materials [16]. The most important feature of SPS is that the pressed powders are heated by the spark plasma, as a result, the samples can be sintered uniformly and rapidly and the dense materials with fine grains can be obtained in a very short holding time [4,16]. Therefore, SPS is considered to be a potential method for fabricating Nb/Nb_5Si_3 composites. However, from the available literatures, the investigations on microstructures of Nb/Nb_5Si_3 composite or it alloyed with specific elements fabricated by SPS are still rare. Therefore, in the present paper, using Nb–20Si, Nb–20Si–10 W, Nb–20Si–10Mo and Nb–20Si–10 W–10Mo as raw materials, Nb/Nb_5Si_3 in situ composites were fabricated by SPS. The objective of the present study was to experimentally investigate on microstructure of Nb/Nb_5Si_3 composites and it alloyed with W, Mo, and W–Mo. Moreover, the microhardness was measured to estimate the effect of solid solution of W, Mo, and W–Mo in Nb/Nb_5Si_3 composites. The significant information was expected to achieve for guiding the fabrication of Nb/Nb_5Si_3 composites by SPS.

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* Corresponding author at: National Defence Key Discipline Laboratory of Light Alloy Processing Science and Technology, Nanchang Hangkong University, Nanchang 330063, PR China. Tel.: +86 13576252965.

E-mail address: bowenxiongnc@sohu.com (B. Xiong).

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2. Experimental procedure

Nb–20Si, Nb–20Si–10 W, Nb–20Si–10Mo and Nb–20Si–10 W–10Mo elemental powder mixtures (at.%) were used to produce the Nb/Nb_5Si_3 composites by SPS respectively. The raw materials used in the present study were Nb (325 mesh), Si (200 mesh), W (300 mesh) and Mo (130 mesh) powders with purity of 99.9%, 99.6%, 99.5% and 99.5% (wt.%) respectively. These powders were dry mixed in a mechanical mixer for 24 h, and the mixed powders were packed into a graphite die with an inside diameter of 15 mm. The sintering was carried out on a SPS machine manufactured by Sumitomo Coal Mining Co. Ltd, Japan. A uniaxial load of 6 KN acted on the powders to realize sintering and densification simultaneously. The heating speed of 150 °C/min and the sintering temperature of 1500 °C were adopted under fixed sintering holding time 10 min in the present study.

The specimens were metallographically polished and etched using a reagent comprising 5 ml HNO_3, 10 ml HF, 15 ml H_2SO_4 and 50 ml distilled water. The microstructures have been examined using a MeF-3 optical microscope and a JSMT-200 scanning electron microscope. D/MAX-IIIB X-ray diffraction was performed on the bulk specimens for identification of phases. The distribution of phase and chemical species has been analyzed using JXA-800R electron-probe micro-analysis.

Microhardness of the primary phases and the eutectic colonies was measured with the help of a Leica microhardness tester operated using Vickers diamond indenter at loads of 10 gf. At least 10 measurements were taken for each alloy and condition.

3. Results and discussion

3.1. Microstructure

The microstructures of Nb–20Si, Nb–20Si–10 W, Nb–20Si–10Mo and Nb–20Si–10 W–10Mo samples by SPS are presented in Fig. 1. Compared with the conventional sintering process, the SPS technology has unique advantages. 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 [17]. At the beginning stage of SPS, the bed of reactant powders was very loose, which induces to the degree of rarefied gas ionization and discharge was low, and the force of powders rearrangement mainly supported by the uniaxial load of 6 KN. With the powders getting tight, the degree of rarefied gas ionization and discharge improves, simultaneously, a large amount of discharge heating as well as Joule heating yields. When the sintering temperature increase to the melting temperature of silicon (1414 °C), resulting in the increase of molten silicon, the liquid phase sintering takes place under a uniaxial load of 6 KN [18]. With increasing the sintering temperature, the density of samples improves and pores disappear, resulting in the function of rarefied gas ionization and discharge debases, even disappears finally. The samples with nearly full density are achieved by Joule heating and the uniaxial load. The pulse current uniformly pass through the reactant powder and the reaction of Nb and Si simultaneously takes place everywhere, otherwise, the reactant powders satisfactorily vibrated by the pulse current wallop and intermission discharge pressure leads the particle phase to take on uniform distribution [14]. Therefore, the dispersed microstructures of Nb/Nb_5Si_3 composites can be obtained.

The microstructures of Nb–20Si are indicated in Fig. 1(a). It is evident that the microstructures include primary Nb and eutectic mixtures of Nb and Nb_5Si_3. Furthermore, the eutectic mixtures observed in Fig. 1(a) may be categorized as course and fine, based on the size of lamellae of Nb present in eutectic mixtures. By comparing Fig. 1(b)and (c) with Fig. 1(a), it is evident that the effects of W and Mo on the microstructure of Nb/Nb_5Si_3 composites are unobvious and the microstructure is not changed, while by alloying with W and Mo together, the microstructure of Nb/Nb_5Si_3 composites changed significantly in Fig. 1(d). EPMA results of point 1 and point 2 in Nb–20Si–10 W sample were given in Table 1, which indicate that the particle phase in Fig. 1(b) (i.e. point 1) contains Nb and W and the matrix (point 2) contains both Nb and Si. The XRD pattern of Nb–20Si–10 W sample is shown in Fig. 2, individual phase was identified by matching the characteristic XRD peaks against JCPDS data. It is obvious from Fig. 2 that the peaks of Nb and Nb_5Si_3 are detected but no peaks of W, Si and Nb_3Si. Thus, combining the EPMA results with the analyzed results of XRD (Fig. 2), it is shown that the particle phases (point 1) are the solid solution of W in primary Nb and the matrix is the solid solution of W in Nb_5Si_3 phase. Mo and W are strong solid solution strengtheners of Nb and improve its high temperature strength. Atomic radii of Nb and W in pure substances are 0.143 nm and 0.136 nm, respectively. The atomic radii are very close, showing the Nb can be substituted by W. Many investigations have indicated W element as the solid solution strengthening can been dissolved completely into Nb/Nb_5Si_3 composites [19,20]. In this study, the W phase was not found, which indicates W element was dissolved completely, so the microstructure of Nb/Nb_5Si_3 composites alloyed with W is not changed.

The microstructures of Nb–20Si–10Mo sample are indicated in Fig. 1(c) and the XRD pattern of Nb–20Si–10Mo sample is shown in Fig. 3. Only the peaks of Nb and Nb_5Si_3 are detected in Fig. 3, combining the EPMA results of point 3 and point 4 (in Table 1), the particle phases (point 3) are the solid solution of Mo in primary Nb and the points 4 is the solid solution of Mo in Nb_5Si_3 phase. Atomic radius of Mo in pure substances is 0.140 nm. The atomic radius of Mo is closer to that of Nb than W, indicating Mo (10 at.%) is easier to dissolve completely into Nb/Nb_5Si_3 composites. Recently, Kim et al. have investigated in detail a partial isothermal section of Nb–Si–Mo system at 1973 K [1,13]. According to their result, Mo is preferentially dissolved in Nb solid solution than Nb_5Si_3 phase in the two-phase Nb/Nb_5Si_3 composites. Therefore, the concentration of Mo is higher in Nb solid solution than Nb_5Si_3 phase.

The microstructure of Nb–20Si–10 W–10Mo sample by SPS is given in Fig. 1(d). Because of the solid solution of W and Mo together, the microstructure of Nb–20Si–10 W–10Mo sample is different from other samples. In order to further analyze chemical species, the four points in Fig. 1(d) were analyzed using electron-probe micro-analysis (EPMA), as shown in Table.1. It is indicated that the phase (point 5) is single Nb phase, point 6 contains Nb (30.81 at.%) and W (69.19 at.%), point 7 comprises Nb (62.27 at.%) and Si (37.73 at.%), and point 8 includes Nb (68.74 at.%), Mo (24.97 at.%) and W (6.29 at.%). The XRD pattern of Nb–20Si–10 W–10Mo sample is presented in Fig. 4. It is evident from Fig. 4 that the peaks of Nb_5Si_3, Nb and W are found but no peaks of Mo and Si. Thus, combining the EPMA results with the analyzed results of XRD (Fig. 4), the microstructures of Nb–20Si–10 W–10Mo sample consist of the single Nb phase, Nb_5Si_3 phase, the solid solution of Nb atoms in W and the solid solution of Mo and W in Nb. It is obvious that no W or Mo element solid solution in Nb_5Si_3 phases (point 7) was detected in Nb–20Si–10 W–10Mo sample, although the solid solution of W and Mo in Nb_5Si_3 phases was detected in Nb–20Si–10 W and Nb–20Si–10Mo sample, respectively. By alloying with W and Mo together, why W and Mo cannot solid solution in Nb_5Si_3 phases will be considered detailedly in our future study.

3.2. Microhardness

Table 2 shows the variation of microhardness of Nb phase and Nb_5Si_3 phases. The microhardness of Nb and Nb_5Si_3 phases changes obviously by alloying. The microhardness of Nb phases solid solution of W, Mo and W–Mo increase obviously by about 39.35%, 36.66% and 53.17%, respectively which can be explained on the basis of solid solution strengthening. The atomic radii are very close, indicating the Nb can be substituted by Mo and W.