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Short communication

Effect of mechanical alloying on microstructure, mechanical properties and oxidation behavior of hot pressed nanocrystalline Cr–33 Nb alloys

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ABSTRACT

Cr–33 at.% Nb alloys were prepared by mechanical alloying and hot pressing (HP). The influences of mechanical alloying on microstructure, mechanical properties and oxidation behaviors of the hot pressed specimens were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron transmission microscopy. The results indicate that nanocrystallite $NbCr_2$ Laves phase is obtained. With increasing the milling time from 0 to 100 h, the relative density and microhardness of the hot pressed compacts increase and the grain size decreases gradually. The hot pressed alloy made with the as-MAed powders for 20 h has the best oxidation resistance. The fracture toughness values measured using the indentation method were observed to be 3.7–5.7 MPa$\sqrt{m}$, which are two to four times higher than that of cast materials (1.2 MPa$\sqrt{m}$).

1. Introduction

$NbCr_2$ Laves phase alloys are considered as attractive candidates for high-temperature structural materials due to their high melting point (1730 °C), relatively low density (7.7 g/cm^3), appreciable creep resistance and high strength at elevated temperatures [1–4]. The extremely brittleness at ambient temperature, however, greatly limits their potential applications [5,6]. During the past decades, considerable efforts have been devoted in improving their physical and mechanical properties, especially the ductility at ambient temperature, by adding the ductile-phase [7], or other elements such as Ti, Mo and V [8–11], etc.

It is known that many properties of materials are affected by the adopted fabrication and the resultant microstructure. Up to now nearly all of the reported chromium–niobium alloys were prepared by conventional methods such as ingot metallurgy and casting, powder metallurgy [1–13]. However, these methods will cause some metallurgical defects of alloys. For example, the relatively slow cooling rate and the rapid solidification of the casting resulted in coarse grains and high contiguity of $NbCr_2$ particles in the microstructure [13]. The powder metallurgy with no pressure induced low density and coarse grains.

In the last few years, the synthesis of nanocrystalline alloys and intermetallic compounds by mechanical alloying (MA) has been successfully achieved [14–16]. The corresponding bulk materials with nanocrystalline grain size are of great interest because of their improved hardness and better toughness. However, few studies have been carried out on preparing the Cr–Nb alloys by mechanical alloying and hot pressing (HP). The structure and properties of as-HPed materials are related to the state of powders such as size and shape. Lu et al. [17] have found that the MA technique not only provides an approach for obtaining milled powder with microcrystalline/nanocrystalline structure, but also lowers the Laves phase $NbCr_2$ solid phase reaction temperature from 1200 to 900 °C. However, reports on the effects of mechanical alloying on the structure and property of consolidated materials by hot pressing are rare.

In this research, Laves phase $NbCr_2$ was fabricated by MA process and subsequent HP treatment. The effects of mechanical alloying on the microstructure, mechanical properties and oxidation behaviors of hot pressed alloys have been investigated.

2. Experimental

Cr (100 mesh, 99.5%) and Nb (100 mesh, 99.5%) powders were mixed in the mole ratio of 2:1 and charged into a stainless steel vial with stainless steel balls under Ar atmosphere. The ball-to-material weight ratio was 13:1. The milling was performed in a Spex QM-ISP2-CL laboratory ball mill for periods varying from 0 to 100 h with the speed of 400 rpm.

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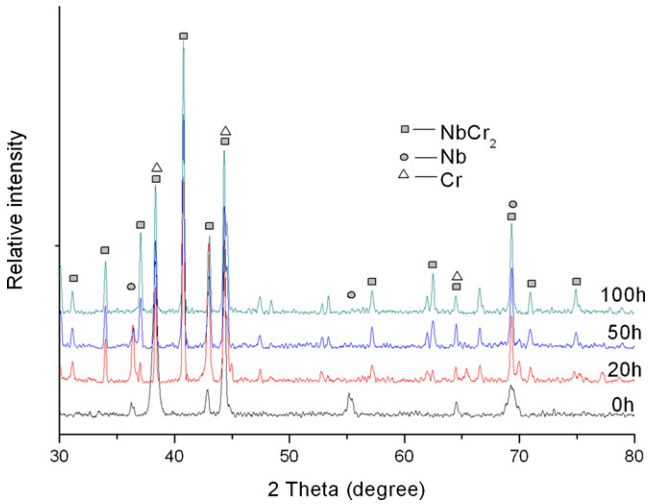

Fig. 1. XRD patterns of the hot pressed Cr–33Nb alloys milled for different time.

The mechanically alloyed powders were consolidated by hot pressing in a vacuum furnace as follows: (a) heated from room temperature to sintering temperature (1250 °C) with the heating rate of about 120 °C/min; (b) kept at the sintering temperature for 30 min [18]; (c) cooled down from the sintering temperature to 600 °C with the speed of about 150 °C/min, and then cooled to room temperature. The pressure in the die was kept at 45 MPa and the vacuum degree in the furnace was 80 Pa. The hot pressed compacts were 14 mm in diameter and about 7 mm in thickness. After hot pressing, the bulk specimens were grinded and polished.

The density of the hot pressed samples was determined by the immersion method in distilled water, based on Archimedes principle. The relative density has been calculated by relating these values to the theoretical density of Laves phase $NbCr_2$. The Vickers hardness was measured in a HV-1000 Vickers microhardness tester at loads of 1 kg with the dwell time of 15 s. Fracture toughness was evaluated by examining the crack lengths made during indentation (with a load of 10 kg). Scanning electron microscopy (SEM) was used to measure the crack lengths, and the toughness was determined by using the equation [19]:

$$K = 0.02\left(\frac{E}{H}\right)^{1/2}\left(\frac{P}{c^{3/2}}\right) \quad (1)$$

In the equation, E is the Young's modulus (218 GPa in $NbCr_2$ alloys [20]), H is the hardness, P is the applied load and c is the average crack length.

X-ray diffraction (XRD) was used to determine the crystallite size and the phase composition of the HP-ed bulk alloys. XRD analyses were performed on a D8 ADVANCE X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å), operating at 40 Kv and 20 mA. The scanning speed was 4° min^{-1}. Scanning electron microscopy was carried out to characterize the microstructure of specimens. To verify grain sizes determined by X-ray diffraction, selected samples were examined in transmission electron microscopy (TEM H800).

Oxidation tests were performed in air at 1473 K until 2530 min. The samples were placed in an alumina crucible (30 mm diameter), and the weight changes were monitored by a balance of Sartorius Type BT224S (sensitivity of 0.1 mg). Before oxidation of the specimens, their surfaces were abraded on sufficiently fine SiC paper, and were washed in running water and ultrasonically cleaned with alcohol.

Table 1
The volume fraction of phases in the hot pressed specimens as a function of milling time

Milling time (h)	0	20	50	100
Laves phase (Pct)	43.7	89.6	94.1	98.4
Cr solid solution (Pct)	25.9	5.0	1.8	0.4
Nb solid solution (Pct)	30.4	5.4	4.1	1.2

Table 2
Grain size of $NbCr_2$ in the hot pressed specimens as a function of milling time

Milling time (h)	0	10	20	50	70	100
Grain size (nm)	>100	>100	97	76	58	35

3. Results

3.1. Microstructure

X-ray diffraction patterns of the samples fabricated by mechanical alloying for different time duration and subsequent hot pressing at 1250 °C for 30 min are shown in Fig. 1. Based on the XRD analyses, the volume fraction of phases in the as-received specimens were determined by the Rietveld technique [21], as shown in Table 1. It can be seen that the milling duration affects the $NbCr_2$ Laves phase formation significantly in the hot pressed samples. For the compacts using unmilled powders, there is few Laves phase formation, the samples is mainly composed of chromium and niobium phases. In comparison, the $NbCr_2$ phase content in the nsintered samples using the milled powders increased with the increase of milling time. Chromium and niobium phases disappeared and formed $NbCr_2$ Laves phase completely in the sintered sample using 100 h ball milled powders.

According to the Scherrer formula, the average grain size of $NbCr_2$ in the hot pressed specimens was calculated from the integral width of peak broadening based on the X-ray diffraction analyses, and presented as a function of milling time in Table 2. It can be seen that the average grain size of $NbCr_2$ in the hot pressed compacts decreases from 97 to 35 nm with the milling time increasing from 20 to 100 h. The calculated grain size is consistent with the previous results [18]. The grain size of the samples hot pressed at 1250 °C for 30 min from 20 h ball milled powders was also studied using TEM (Fig. 2 [18]). The bright regions correspond to $NbCr_2$ particles with size ranging from 90 to 500 nm.

The effect of milling time on the consolidated compacts microstructure was shown in Fig. 3. In comparison with the unmilled sample (Fig. 3a), more homogeneous phase distributions

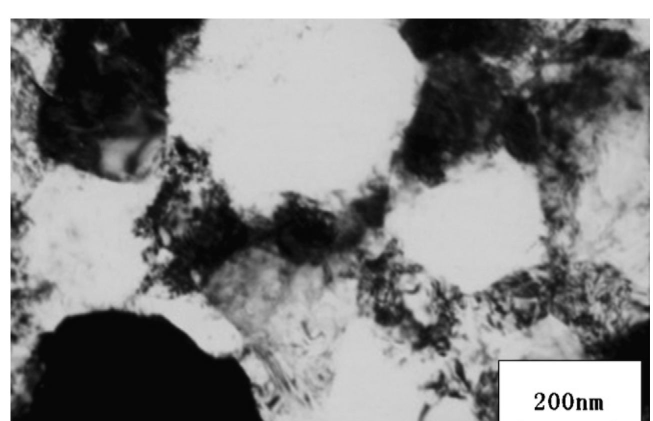

Fig. 2. TEM graph of the consolidated compacts hot pressed at 1250 °C for 30 min from mechanically alloyed powders for 20 h [18].