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Effect of Y_2O_3 doping on FCC to HCP phase transformation in cobalt produced by ball milling and spark plasma sintering

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ABSTRACT

In this paper, high purity cobalt (Co) powder and fine Y_2O_3 powder were used to fabricate Y_2O_3 doped Co bulks through ball milling and spark plasma sintering (SPS). The transformation from face-centered cubic (FCC) structure to hexagonal close-packed (HCP) structure during the cooling process after SPS was investigated. It has been shown that the addition of Y_2O_3 decreases significantly the grain size from 682 nm to 374 nm, since Y_2O_3 particles can effectively inhibit the grain growth by pinning the boundary migration. After doping the Y_2O_3, the FCC structured Co with a large volume fraction of over 70% can stably coexist with the HCP structured Co at room temperature, resulted from two possible reasons. First, Y_2O_3 particles hinder the dislocation movements. Second, Y_2O_3 particles occupy the deformation center of some defects in the FCC structure to reduce the number of potential nucleus of the HCP structure. In addition, due to the lower stacking fault energy of the FCC structured Co than that of the HCP structured Co, a lot of twins can be observed in the FCC grains in Y_2O_3 doped Co bulks after SPS.

1. Introduction

Cobalt (Co) has two different allotropic forms: hexagonal close-packed (HCP) structure and face-centered cubic (FCC) structure. HCP structure prefers to appear at low temperature, while FCC structure usually exists at high temperature. The phase transformation point from FCC structure to HCP structure is at 420 °C and the FCC to HCP transformation was usually thought as the HCP core nucleating from the stacking faults in the FCC structure and expending through the dislocation movements [1]. During the last twenty years, there are some investigations focusing on the structure transformation or magnetic properties during the HCP to FCC transformation in milled Co powder or nanocrystalline Co [2–5]. Although the FCC structured Co is unstable at room temperature and is easily being transferred to the HCP structured Co, Owen and Madoc Jones [6] found that pure FCC structured Co can be obtained at room temperature in ultrafine particles in 1954, and Granqvist and Buhrman [7] also observed this phenomenon in 1976.

Normally, the FCC structure shows better toughness than the HCP structure because FCC structure has more slip systems. In industrial manufacturing, cemented carbide is an important material to machining materials, and Co plays an important role in cemented carbide as a binder phase. The toughness of the cemented carbide is usually determined by Co. Under normal condition, Co exists as an HCP structure in the cemented carbides. However, one can imagine if more FCC structured Co binder exists in the cemented carbides at room temperature, the better toughness might be obtained for cemented carbides, and thus to extend the working life [8,9]. Jia et al. [10] found that a higher Co_{FCC}/Co_{HCP} ratio can be obtained in nanostructured cemented carbides than in conventional coarse grained cemented carbides, resulted from a higher tungsten and carbon dissolution in the binder phase of nanostructured materials. And the increased Co_{FCC}/Co_{HCP} ratio in the binder phase promotes the strength and ductility of the nanostructured cemented carbides.

In the last decade, some investigations showed that rare earth elements doping in Co binder phase of cemented carbides can increase the content of the FCC structured Co and thus improve the toughness of the cemented carbides. Sha [11] found that both rare-earth elements (including Y, Ce, La, Pr, Nd, Gd and Sm) doping and rare-earth oxides doping through milling method can achieve the above mentioned goal. Thus, in this work, yttria (Y_2O_3) was used to increase the fraction of the FCC structured Co at room temperature through ball milling method. The purposes of this work are to figure out what would happen in the Y_2O_3 doped Co after ball milling and sintering, and how Y_2O_3 addition affects the FCC to HCP phase transformation in Co. It is expected that using the FCC structured Co as the binder phase might significantly improve the toughness and working life of the cemented carbides as machining tools.

2. Experimental

High purity Co powder (99.98%, average particle size of 10 μm) and yttria powder (99.97%, average particle size of 5 μm) were mechanically milled in a planetary ball miller for 10 h with a speed of 300 rpm. A high ball-to-powder weight ratio of 10:1 was used to crush the powder

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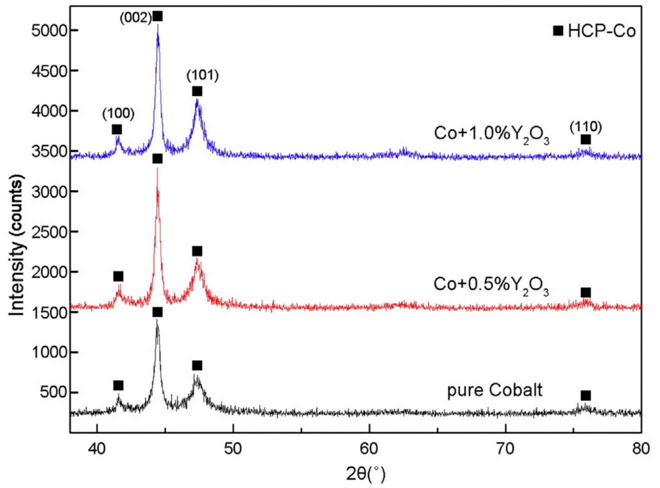

Fig. 1. XRD patterns of the pure Co powder, the 0.5 wt% Y_2O_3 doped Co powder and the 1.0 wt% Y_2O_3 doped Co powder after ball milling.

mixture as much as possible and to achieve a homogenous distribution of the powders. To avoid oxidation, stainless steel vials were inflated with Ar atmosphere before milling. Stearic acid (0.6 g) was added to avoid agglomeration of the composite powders, and the composite powders adhering to the balls and the vial's wall. After ball milling, the composite powders were compacted into a graphite die with a diameter of 20 mm, followed by spark plasma sintering (SPS) at 1000 °C for 10 min in a vacuum SPS furnace, with the heating rate being 50 °C per min and the cooling rate being 100 °C per min. Finally the samples were furnace cooled to the room temperature.

Both the powders and the sintered bulk materials were examined by an X-ray diffractometer with Cu Kα radiation (wave length of 0.1542 nm), with the step size of 0.02° and scanning rate of 2° per min. The XRD patterns were analyzed based on the Scherrer equation [12,13] to figure out the FCC and HCP crystalline size of the sintered Co and Y_2O_3 doped Co. MAUD software was used to calculate the phase constitution by Rietveld Method proposed by Young [14]. The Rietveld Method makes use of the computer software to compare the calculated value with the actual value of the diffraction intensity, and then uses least square method to adjust structure factor and peak shape factor. When the calculated peak shape is in accordance with the actual peak shape, the results of the phase, such as phase composition or crystalline size, are relatively accurate values. The microstructures of the bulks were examined by an FEI Tecnai G2-F20 transmission electron microscope (TEM). The TEM samples were firstly cut from the sintered bulks into thin foils with a thickness of 0.5 cm using a low speed diamond saw, followed by mechanical polishing to 50 μm thickness. Then the foils were prepared by twin jet electropolishing in a 90% ethylene glycol monobutyl ether and 10% perchloric acid solution at 5 °C.

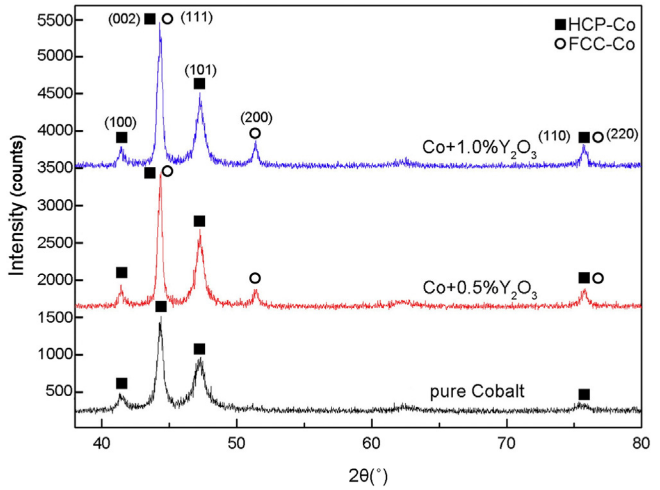

Fig. 2. XRD patterns of the pure Co bulk, the 0.5 wt% Y_2O_3 doped Co bulk and the 1.0 wt% Y_2O_3 doped Co bulk after SPS.

Table 1
The volume fraction of the HCP and FCC structures in the Y_2O_3 doped Co bulks.

Co bulks	Volume fraction	
	FCC	HCP
Co + 0.5%Y_2O_3	70.04%	29.96%
Co + 1.0%Y_2O_3	76.26%	23.74%

3. Results

3.1. XRD patterns of the as-milled powders

Fig. 1 shows the XRD patterns of the pure Co powder, 0.5 wt% Y_2O_3 doped Co powder, and 1.0 wt% Y_2O_3 doped Co powder after ball milling. A single HCP structure can be observed in the pure Co powder. The diffraction peaks are around 41.7°, 44.8°, 47.6° and 75.9°, corresponding to {100}, {002}, {101} and {110} planes of the HCP structured Co. Similar HCP diffraction peaks are also found in 0.5 wt% Y_2O_3 doped Co powder and 1.0 wt% Y_2O_3 doped Co powder.

3.2. XRD patterns of the sintered bulks

Fig. 2 shows the XRD patterns of the pure Co bulk, 0.5 wt% Y_2O_3 doped Co bulk and 1.0 wt% Y_2O_3 doped Co bulk after SPS. It can be seen from Fig. 2 that the sintered pure Co bulk has a single HCP structure, a typical structure for Co bulks at room temperature. It can also be seen that FCC diffraction peak of {200} planes around 51.5° can be observed for both the 0.5 wt% and 1.0 wt% Y_2O_3 doped Co bulks. This indicates that a phase transformation from HCP structure to FCC structure occurred during SPS process, and the FCC structured Co might exist stably at room temperature after doping Y_2O_3. It should be noted that the SPS temperature of 1000 °C is much higher than the phase transformation point of 420 °C, thus a complete transformation from FCC structure to HCP structure should be occurred during the cooling process theoretically. The absence of FCC peak in the pure Co bulk (see Fig. 2) indicates either no FCC phase in the pure Co bulk or the FCC phase fraction being too small to be detected by XRD. However, FCC structure can be detected in both the 0.5 wt% and 1.0 wt% Y_2O_3 doped Co bulks at room temperature, indicating that the FCC structured Co was not transformed to HCP structure completely during the cooling process and the fraction of the FCC phase is high enough to be detected by XRD. Thus, it can be concluded that the Y_2O_3 addition hindered the FCC to HCP transformation during the cooling process. Table 1 shows the volume fractions of the HCP and FCC phases. It can be seen that the content of the FCC structure increases with increasing the Y_2O_3 content.

Table 2 shows the average crystalline size of the pure Co, the 0.5 wt% and 1.0 wt% Y_2O_3 doped Co bulks. The pure Co bulk has an average

Table 2
The average crystalline grain size of the pure Co, and the 0.5 wt% and 1.0 wt% Y_2O_3 doped Co bulks.

Co bulks	Crystalline grain size	
	FCC grain	HCP grain
Pure Co		682 nm
Co + 0.5%Y_2O_3	396 nm	373 nm
Co + 1.0%Y_2O_3	368 nm	359 nm