Effect of thermal treatment on mechanically milled cobalt powder

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1. Introduction

Synthesis of metastable phases has been induced in the transition metals via several non-equilibrium processes such as mechanical milling (MM) [1–4], cold pressing (CP) [5], and water quenching (WQ) [6]. This area of study has attracted interest in engineering and materials science. For many years, these non-equilibrium techniques were employed on the metallic alloys, but for the past decade an effort to study pure metals has increased. In the current investigation, authors have decided to focus on the fine cobalt (Co) metal powder. Co is one of the vital transition metals used in electronics and magnetic recording [7]. It was found that in the face-centered-cubic (FCC), hexagonal-open-packed (HCP) and HCP/FCC, grains are small, large or mixed (small and large), respectively, depending on the processing technique [8,9]. When subjected to milling, HCP Co transform to FCC crystal structure [10–13]. Similar transformation occurs on heating Co around 330 to 417 °C [14]. Other than metastable FCC allotropic phase transformation, metastable BCC crystal structure has been reported on the Co films [15,16]. The stabilization of BCC Co seems to depend on the crystalline size range of 2 to 5 nm [17]. In cemented carbides powder processing, Co is a suitable binder for HCP WC particles. Recently nanocrystalline powders have been used with the aim of improving the strength of cemented carbides [18–20]. Therefore, nanocrystalline carbide powders have been synthesized successfully using MM technique [21,22]. In some instances, Co is milled together with carbide powder to promote reduced sintering temperatures [23,24]. There have been occasions whereby the XRD pattern of Co disappears in the early stages of milling [23,24]. In previous investigation, MM of Co, W, V and C powders has resulted in the formation of a new complex, Co-rich carbide structure after sintering [25]. Furthermore, it is known that excess Co, W and C facilitates eta phase formation. These complex structures are detrimental to the overall mechanical properties of the WC-Co cermet [26–30]. It is therefore necessary to study the metastable structures of Co. In the current paper, we report on the thermal stability of mechanically milled Co. Changes in the crystal structure of the unmilled and mechanically milled Co powder are monitored by the X-ray diffraction technique.

2. Experimental work

In this work, pure Co powder with 99.8% purity was used. This pure Co powder charge was milled under argon atmosphere at milling speed of 250 rpm for 10 h. Milling was performed in the stainless steel milling medium consisting of 5 mm diameter balls and vial at ball-to-powder ratio of 10:1. Milling vial was equipped with cooling system to avoid heating during milling. A small powder sample was used for crystal structure analysis and morphology. The unmilled and milled powders were cold pressed at a pressure of 20 MPa to form cylindrical compacts. These compacts were sintered in a Leycon Vacuum Furnace (manufactured by Xeron Germany) at 1400 °C for 1 h. The sintered Co compacts were cross-sectioned for microstructural analysis using Leica DMI 5000 M optical microscopy and LEO 1525 field-emission scanning electron microscope (FE-SEM) coupled with a Robinson Backscattered Electron Detector (RBSD) and an Oxford Link Pentafet energy dispersive X-ray spectroscopy (EDX).
detector operated at an accelerating voltage of 5 keV. Phase evolution was traced with a Philips PW 1830 X-ray diffractometer using Cu Kα radiation (0.154 nm) monochromated radiation source. XRD spectra were collected in 0–2θ scan (20–90°) with a measurement step of 0.02°. In order to determine the milled powder crystallite sizes, the Scherrer formula (Eq. (1)) was used:

\[ D = \frac{k\lambda}{\beta_hkl \cos(\theta_{hkl})} \]  

where \( \theta = \) diffraction angle, \( D = \) coherent diffraction length (closely related to the crystallite size), \( k = 0.9, \) \( \lambda = \) X-ray wavelength and \( \beta = \) the full width at half maximum.

The Microtac Bluewave particle analyser was utilized to determine the particle size of the unmilled and milled Co powders. Thermal analysis was carried out using DSC and TG incorporated in NETZSCH STA. Samples were heated up to 900 °C with Al₂O₃ as a baseline. A heating rate of 20 °C min⁻¹ under argon gas at 20 ml/L standard flow rate was used. The macro-hardness measurements were carried out using FV-700 Vickers hardness (HV) tester with 2 kg load.

3. Results and discussions

3.1. Powder characterization

Fig. 1(a) shows the SEM micrograph of the unmilled Co powder resembling an irregular spherical shape. In Fig. 1(b), it is evident that powder particles were flattened by the milling operation resulting in the thin flake-like particles. The \( D_{10}, D_{50} \) and \( D_{90} \) for the milled powder in Table 1 display a decrease in particle sizes.

<table>
<thead>
<tr>
<th>Powder</th>
<th>( D_{10} ) (µm)</th>
<th>( D_{50} ) (µm)</th>
<th>( D_{90} ) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmilled</td>
<td>19</td>
<td>32</td>
<td>52</td>
</tr>
<tr>
<td>10 h milled</td>
<td>11</td>
<td>29</td>
<td>39</td>
</tr>
</tbody>
</table>

Fig. 2(a) and (b) shows XRD patterns of the unmilled and milled Co powders. The XRD pattern of the unmilled Co resembles the behaviour of amorphous materials [31–33] or amorphous nanoparticles [34]. The background intensity for the 10 h milled Co is reduced probably due to a reduction of amorphous fraction in the material. The estimate crystalline size calculated using Scherrer equation is 25 nm after milling. In previous studies, amorphous to nanocrystalline behaviour can be achieved by milling [35,36]. It should also be highlighted that normally powders are purchased on the basis of their particle size and purity, but it is evident that processing methods can influence certain properties as well as their end application. Although the Co powder displays a micron-sized, it consists of nanocrystalline particles.

A broad exothermic peak on the DSC curve of the unmilled Co powder showing a peak finishing around 500 °C is shown in Fig. 3. This peak is attributed to the stress relief of a stressed material. This might confirm the amorphous behaviour of the unmilled Co powder. A small endothermic peak co-existing with this broad exothermic peak is visible at 249 °C. Similar endothermic peak was observed by Xie et al. [34] on amorphous Co material. To confirm the nature of such endothermic peak in Fig. 3, unmilled powder was annealed at 550 °C for 30 min. The XRD analysis in Fig. 5(a) identifies biphasic structure of the FCC and HCP on the annealed powder. It is assumed that the endothermic peak at 249 °C is due to the FCC phase transformation. The corresponding TG curved in Fig. 3 shows no indication of mass gain due to the contamination. The DSC curve of 10 h milled Co powder presented in Fig. 4 shows a broad endothermic peak starting from 314 to 404 °C. In addition, the observed exothermic peak at 597 °C is attributed to the crystallization of the remaining fraction.
of the amorphous powder. TG curve in Fig. 4 indicates a weight loss possibly due to the volume expansion during heating [37]. For any oxidation and compound formation, it should be shown with a weight gain [38]. In order to validate the structural development of the milled powder after thermal treatment, annealing was performed at 650 °C. The XRD pattern in Fig. 5(b) reveals the presence of a single FCC phase. It seems that the large surface area of thin flakes has paved way for FCC phase transformation to occur.

3.2. Sintering

The sintered unmilled Co retained its HCP crystal structure after sintering at 1400 °C, as listed in Table 2. In order to investigate the thermal stability and crystal structure of 10 h milled Co powders, compacts were sintered at 1000, 1200 and 1400 °C. Fig. 6(a)–(c) depicts the XRD patterns of sintered Co compacts. Fig. 6(a) shows a single FCC phase after the powder was sintered at 1000 °C. Owen et al. [8] and Kajiwara et al. [9] suggested that the stabilization of FCC phase to be attributed to the small grains which result after sintering. This means that the induced stresses by mechanical deformation of HCP Co structure facilitates FCC phase transformation. The XRD pattern of the Co compact sintered at 1200 °C has detected a biphasic FCC/rhombohedral (RHL) structure as shown in Fig. 6(b). A RHL diffraction peaks were detected with ICDD reference code (01-084-2139). Its space group number of $R-3m \# 166$ and lattice parameters $a = 3.82$; $c = 2.89$ Å as presented in Table 2. These lattice parameters are smaller than those obtained in Co$_7$W$_6$ phase [38]. This metastable structure may be the origin of RHL phase Co$_7$W$_6$ system. Sintering the milled powder at 1400 degrees celsius yielded single FCC phase. The corresponding XRD data for all considered samples are summarized in Table 2.

The optical micrographs of the sintered unmilled and mechanically milled Co for 10 h are shown in Fig. 7. Fig. 7(a) depicts the presence of fine and coarse grain structure, while Fig. 7(b) is composed of rings constructed by fine grain boundaries. The obtained Vickers hardness of 300 HV is attributed to these fine grains, which are not present in Fig. 7(a) with 50 HV. The high strength in the fine grained Co was also reported by Karimpoor et al. [39], hence our results validate those findings.

SEM micrographs of the unmilled and milled sintered Co powders at 1400 °C are displayed in Fig. 8(a) and (b). Fig. 8(a) demonstrates

![Fig. 4. DSC-TG curve of 10 h mechanically milled Co powder.](image)

![Fig. 5. XRD patterns of the annealed (a) unmilled and (b) mechanically milled Co powders.](image)

![Fig. 6. XRD patterns of the 10 h milled Co powder compacts sintered at (a) 1000, (b) 1200 and (c) 1400 degrees celsius.](image)

![Table 2](table)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Space group &amp; number</th>
<th>Phases</th>
<th>Lattice parameter (Å)</th>
<th>$a$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmilled powder</td>
<td>P63/mmc # 194</td>
<td>HCP</td>
<td>2.51</td>
<td>4.08</td>
<td></td>
</tr>
<tr>
<td>Milled powder</td>
<td>P63/mmc # 194</td>
<td>HCP</td>
<td>2.51</td>
<td>4.07</td>
<td></td>
</tr>
<tr>
<td>Annealed unmilled 550</td>
<td>P63/mmc # 194</td>
<td>HCP</td>
<td>2.51</td>
<td>4.08</td>
<td></td>
</tr>
<tr>
<td>Annealed MM 650</td>
<td>Fm-3 m #225</td>
<td>FCC</td>
<td>3.54</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Sint 1400 (unmilled)</td>
<td>P63/mmc # 194</td>
<td>HCP</td>
<td>2.51</td>
<td>4.09</td>
<td></td>
</tr>
<tr>
<td>Sint 1000 milled</td>
<td>Fm-3 m #225</td>
<td>FCC</td>
<td>3.54</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Sint 1200 milled</td>
<td>Fm-3 m #225</td>
<td>FCC</td>
<td>3.55</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Sint 1400 milled</td>
<td>R-3 m #166</td>
<td>RHL</td>
<td>3.82</td>
<td>2.89</td>
<td></td>
</tr>
</tbody>
</table>
a dark phase present on the grain boundaries of the material. This feature was not found in the microstructure of the milled sample (Fig. 8(b)). Compositional analysis performed using the EDS could not detect any form of contamination on all the sintered materials. Therefore, we propose both FCC and RHL to be metastable phases in Co. These findings may suggest that metastable phases of Co plays a role in the formation FCC Co-based [20,25–28], RHL [40], as well as amorphous structures [36,41–43].

4. Conclusions

In conclusion, we demonstrated that MM of Co powder for 10 h induced shape change from irregular-spherical shape to thin flakes. FCC phase was obtained after annealing and sintering of milled powder. Thermal analysis performed on the milled powder has revealed the broad FCC phase transformation around 314 °C. Crystallization exothermic peak of amorphous was observed at 597 °C. As a result of annealing the milled powder at 650 °C, FCC phase was formed and remained stable at 1400 °C. The microstructure of the sintered material demonstrated higher average hardness of 300 HV as compared to 50 HV obtained in the sintered unmilled Co. Due to the presence of amorphous particles in the unmilled Co, FCC co-existed with HCP structure.

Acknowledgements

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References


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