International Journal of Nonferrous Metallurgy, **2013, 2, 41-46**
http://dx.doi.org/10.4236/ijnm.2013.22006 Published Online April 2013 (http://www.scirp.org/journal/ijnm)

Ball Milling and Annealing of Co-50 at% W Powders

A. S. Bolokang[1,2*], M. J. Phasha[2*], D. E. Motaung[3]
[1]Department of Engineering Metallurgy, University of Johannesburg, Johannesburg, South Africa
[2]Transnet Rail Engineering, Pretoria, South Africa
[3]DST/CSIR Nanotechnology Innovation Centre, National Centre of Nano-Structured Materials, Council for Scientific and Industrial Research, Pretoria, South Africa
Email: *Amogelang.bolokang@transnet.net, *majay_phasha@yahoo.com

Received December 24, 2012; revised March 12, 2013; accepted March 20, 2013

ABSTRACT

Broadening and height reduction of X-ray diffraction peaks were observed after cold-pressing of unmilled Co-W powder mixture. It seems the effect of cold pressing has slightly reduced the lattice parameter of W from 3.165 to 3.143 Å. Consequent annealing of unmilled compacts yielded metastable phases. Upon 10 and 20 h ball milling of Co-W powder, no alloying was obtained. Although milling did not yield significant crystal changes in W and Co ground state structures, its effect is evident during subsequent annealing. An eta phase is obtained for the first time from unmilled-annealed Co-W powder mixture in the absence of interstitial elements like carbon, while the milled counterpart yielded the rhombohedral Co_7W_6-type phase with composition deviated from stoichiometric value.

Keywords: Ball Milling; Crystal Structure; XRD, Annealing; Co-W Powder

1. Introduction

Cobalt-tungsten (Co-W) alloy is a promising material that can be used for among others coatings and corrosion resistance applications. The alloy is often manufactured as thin films produced by deposition [1-4] or magnetron sputtering spanning [5]. Due to rapid cooling involved during deposition and sputtering, formation of novel metastable and amorphous phases is attained. Electrodeposited Co-W is a potential candidate to replace Co-Cr due to better mechanical properties such as high surface sliding hardness, wear resistance and good ductility [6]. In addition, the processing of Co-W system is environmentally friendly compared to Co-Cr. Some studies reveal that a deposited film of Co-W consists of a bi-phasic structure, mainly metastable hexagonal close-packed (HCP) and amorphous phases [6,7]. In some cases, only the existence of amorphous structure is observed [1,3,8]. To the best of our knowledge, the study on the influence of ball milling (BM) on Co-W powder mixture is still lacking. BM is a versatile solid-state powder synthesizing technique used to produce alloying of powders with reduced crystalline size [9,10]. The objective of the current study is to investigate the crystal structure of unmilled and milled Co 50 at% W powder mixtures after annealing.

*Corresponding authors.

2. Experimental Procedure

Commercial W and Co powders of 99.5% purity were used during ball milling and cold pressing experiments. The measured particle sizes has percentage particle distribution D_{50} = 32.40 and 5.42 μm for Co and W, respectively. Milling was conducted in a high-energy ball mill at 650 rpm and 20:1 ball to powder ratio for time intervals of 10 and 20 hours (h). In order to minimize contamination, milling was performed under inert atmosphere with no process control agent (PCA) added. The changes in powder particle morphology were analysed using the LEO 1525 field-emission scanning electron microscope (FE-SEM) coupled with a Robinson Backscatter Electron Detector (RBSD). Phase evolution was traced with a Panalytical X'pert PRO PW 3040/60 x-ray diffractometer (XRD) equipped with a Cu K_α monochromated radiation source, scanning from 20˚ to 90˚ (2θ) in 0.02˚ step size. The crystalline sizes (D) of unpressed and cold-pressed powders were estimated by Williamson-Hall (W-H) equation as follows:

$$\beta_{hkl}\cos\theta_{hkl} = \frac{k\lambda}{D} + 4\varepsilon\sin\theta_{hkl} \qquad (1)$$

where θ is the Bragg diffraction angle, D is the average crystalline size, ε is the average internal strain, k is a constant with a value of 0.9, λ = 0.154056 nm is the wavelength for Cu Kα radiation and β is the diffraction

peak width at half maximum intensity. The average internal strain (ε) is estimated from the slope of $\beta\cos\theta$ versus $4\sin\theta$ linear plot, while the average crystalline (D) is estimated from the y-intercept. Annealing of powder compacts was carried out in a Carbolite tube furnace under flowing argon gas at 800˚C and1200˚C.

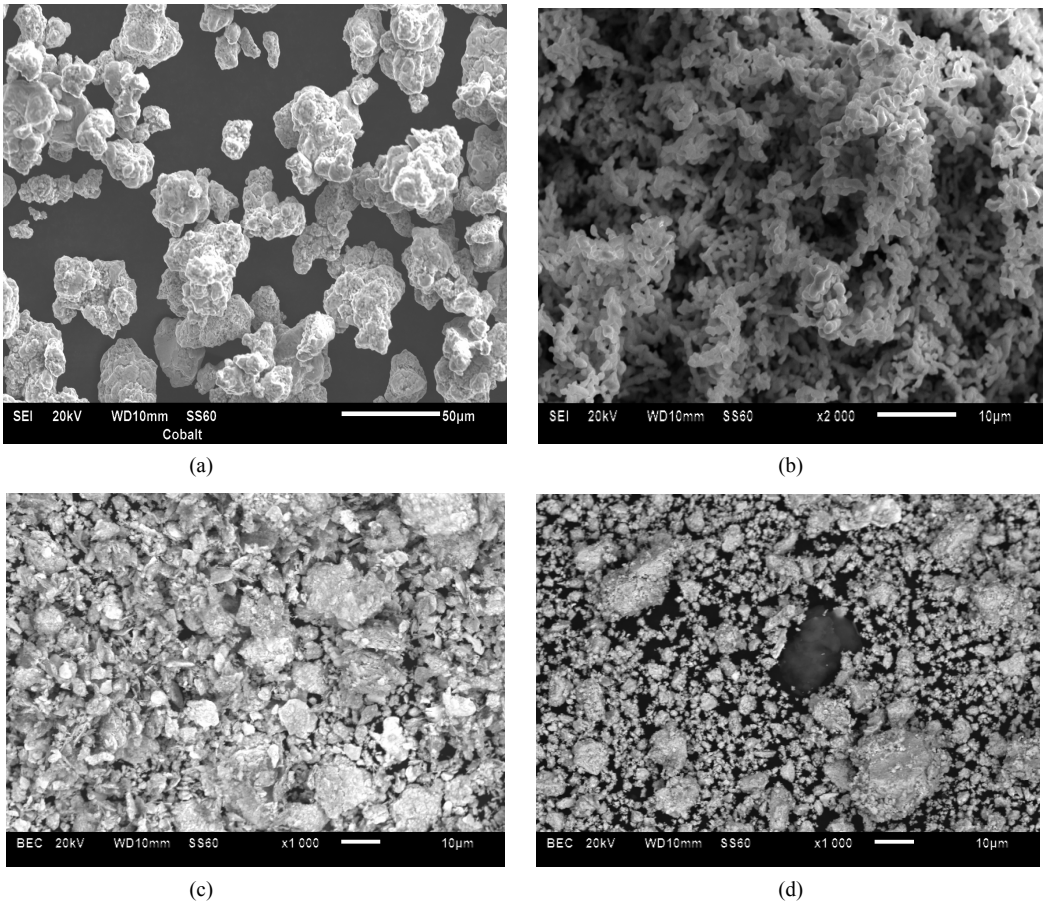
3. Results and Discussions

3.1. Unmilled Co-W Powders

Shown in **Figures 1(a)-(d)** is the SEM images of unmilled Co, W and milled Co-W powder mixture for 10 and 20 h, respectively. The Co particles appear coarse compared to those of W. The mixture of fine and large, flat-round particles is evident on both 10 and 20 h milled powders. This large particles could be due to agglomeration as a result of cold-welding during milling.

The XRD patterns of the Co-W compact after cold-pressing, 800˚C and 1200˚C annealing are presented in **Figures 2(a)-(c)**. It is evident from **Figures 2(a)** and **(b)** that the diffraction peaks belonging to body centered cubic (BCC) W are more intense compared to those representing HCP and FCC (face centered cubic) Co phases. In addition, these peaks indicate broadening.

XRD peak widening is well known to be caused by the refinement of particles and sometimes also associated with amorphous phases. However, the lattice parameter of the cold-pressed compact is 3.143 Å, smaller than that of pure W (3.165 Å). It is likely that thereduction of the lattice parameter is due to surface deformation during cold-pressing. Moreover, it has been reported that cold pressing can promote structural change on Co [11,12]. Although low melting temperature elements such as tin (Sn) and tellurium (Te) mixture were alloyed by repeated cold-pressing process [13], it is not logical to expect high melting temperature metals such as Co and W to be alloyed by cold-pressing, but their surfaces might be cold-welded. From the XRD analyses of Co-W compacts annealed at 800˚C and 1200˚C shown in **Figures 2(b)** and **(c)**, respectively, it is apparent that the peak broadening observed after cold-pressing was reversed by annealing as shown by sharp peaks. This behaviour is could be attributed to the beginning of sintering effect. In addition to the retained BCC phase with lattice parameter of 3.143 Å after annealing at 800˚C, FCC Co with lattice parameter of 3.554 Å was detected, as presented in **Table 1**.



(a) (b)

(c) (d)

Figure 1. SEM morphology of unmilled (a) Co and (b) W unmilled powders, and of powder mixture after 10 h BM (c) and 20 h BM (d).

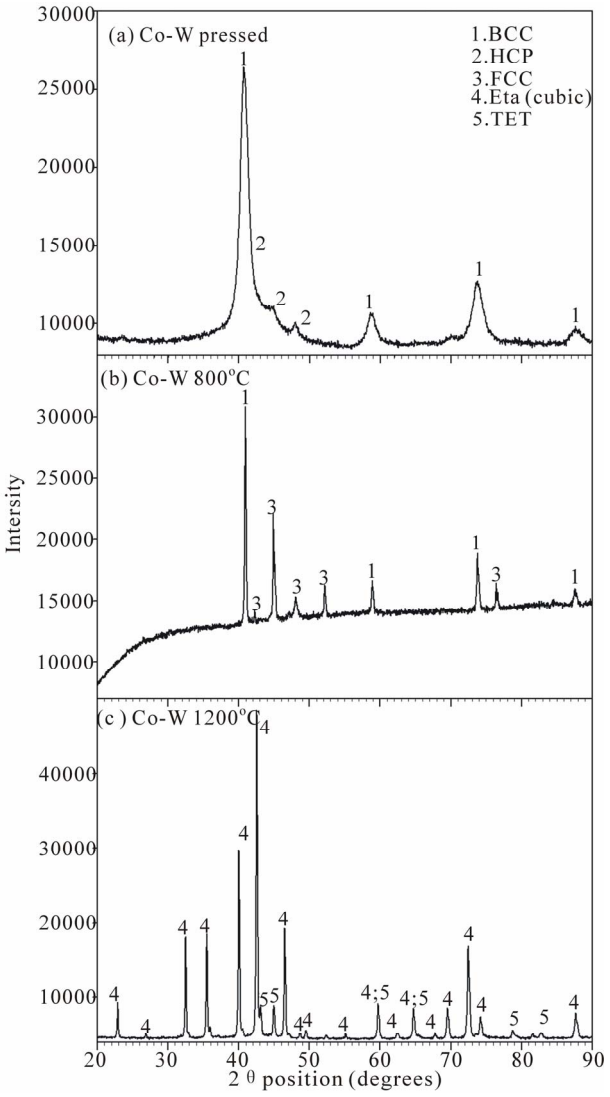


Figure 2. XRD patterns of (a) cold-pressed Co-W powder (b) sintered at 800˚C and (c) 1200˚C.

Table 1. Experimental XRD data of cold pressed, ball milled and annealed Co-W powders.

Sample condition	Crystal Structure	Lattice parameter (Å)	
		a	c
Co-W pressed	BCC W HCP Co	3.143 2.514	4.105
Co-W 800˚C	BCC W FCC Co	3.143 3.554	
Co-W 1200˚C	Eta TET	11.090 2.850	3.091
Co-W 10 h BM	BCC W HCP Co	3.147 2.514	4.105
Co-W 20 h BM	BCC W HCP Co	3.165 2.514	4.105
Co-W 10 h BM 1200˚C	RHL HCP	4.751 - 4.905 2.751 - 2.764	25.670 - 23.787 4.282 - 4.127
Co-W 20 h BM 1200˚C	RHL HCP	4.738 - 5.021 2.728	25.850 - 25.890 4.226

A similar FCC phase of about 3.506 Å was obtained in milled Co annealed at 800˚C in previous study [14]. Upon annealing Co-W compacts at 1200˚C, formation of tetragonal (TET) and FCC superstructure called eta (η) phase with space group Fd-3m # 227 were detected, as indicated in **Figure 2(c)**. Similar phases were obtained and reported as follows: 1) TET phase formed from ball milled W powder compacts annealed at 1200˚C [15], 2) eta phase obtained from milled and 800˚C annealed W [14], W milled and annealed at 730˚C [16], milled W-Ni powder mixture annealed at 730˚C and 1400˚C [16] as well as from mixture of separately milled elemental Co and W powders compacted and annealed at 800˚C [14]. The corresponding formation mechanisms were also provided. Although η-phase has been detected in pure W [14,16], pre-milled Co-W mixture [14], Ni-W [17] and Ni-Mo materials [18], it does not exist under equilibrium conditionsin any of the above systems including the Co-W, Ni-W and Ni-Mo systems in the absence of carbon. Furthermore, it is well known that this phase is unstable and dissociates at high temperatures [14,19]. The obtained lattice parameter (11.090 Å) of η-phase is larger than that found after reduction of cobalt-tungsten oxide (10.846 Å) [20]. The phases obtained in the current study are not found in Co-W equilibrium phase diagram shown in **Figure 1** in [14]. They are therefore regarded as metastable or rather intermediate.

3.2. Ball milled Co-W Powders

The XRD patterns of 0, 10 and 20 h ball milled Co-W powders are shown in **Figures 3(a)-(c)**. In comparison with the unmilled, the peaks of 10 h sample are slightly broader and their intensity significantly reduced. Almost similar to the compaction effect, the lattice parameter of BCC W was decreased from 3.165 to 3.147 Å with the estimated crystallite size of about 60 nm, while lattice parameters of HCP Co remained unchanged. Upon 20 h of BM, the peaks were further broadened and reduced in height. Surprisingly, the undeformed lattice of pure BCC W (3.165 Å) was recovered. This could imply that BM just reversed the deformation on the surface of W particles observed on the 10 h ball-milled powder. Similarly, crystallite size of ~60 nm was calculated. Since the crystal structure of Co did not change either, it thus follows that no alloying was induced by BM. For alloying to be achieved, high energy is required considering the melting temperatures of both Co and W. Physical properties such as thermal expansion coefficient, melting temperature, activation energy, elastic modulus and yield strength which are 13.4×10^{-6} C^{-1}, 1495˚C, Q_B = 117 KJ/mol, 211 GPa and 345 MPa for Co, and 4.5×10^{-6} C^{-1}, 3410˚C, Q_B = 385 KJ/mol, 411 GPa, and 550 MPa in the case of W, respectively [21], also play an important role in order for alloying to occur at approximately room temperature.

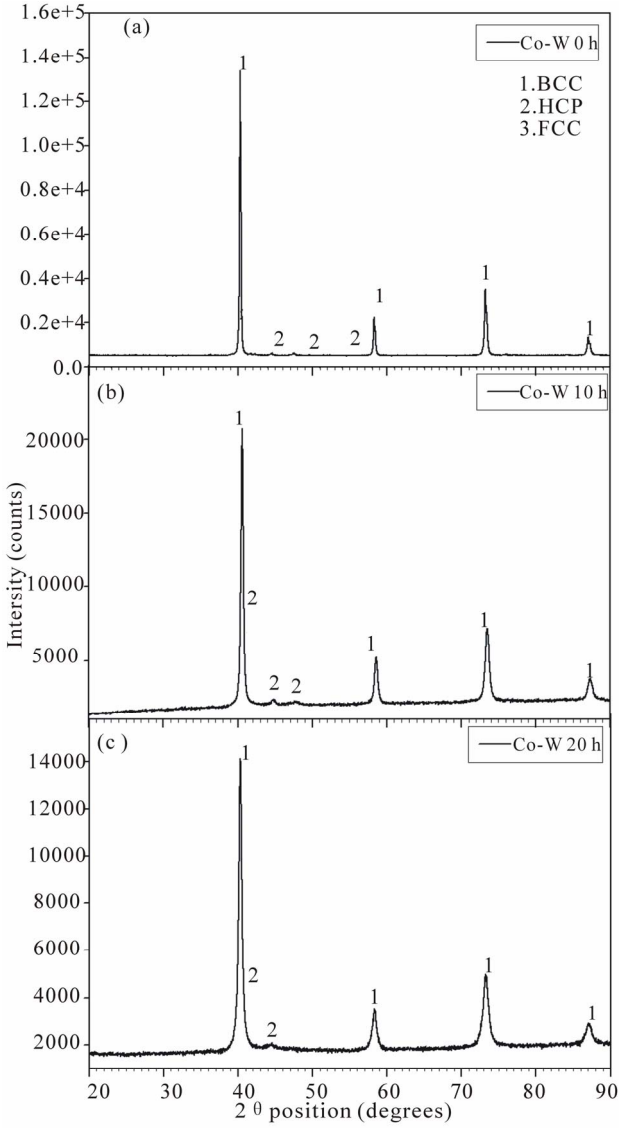


Figure 3. XRD patterns of (a) 0, (b) 10, and (c) 20 h ball milled Co-W powders.

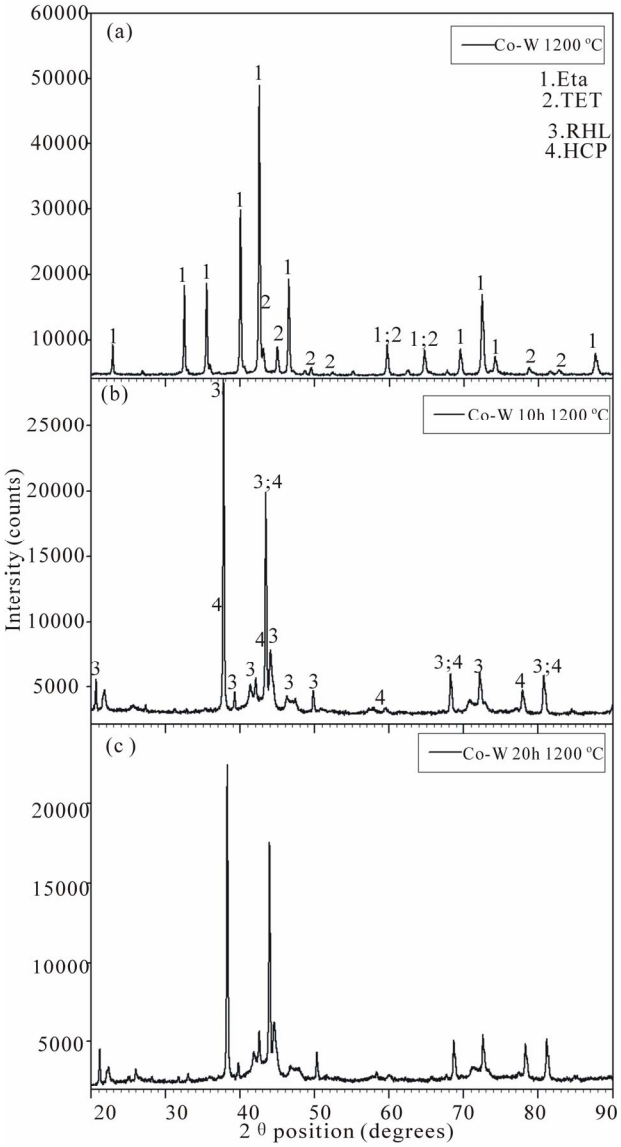


Figure 4. XRD patterns of 1200˚C annealed compacted powder unmilled (a), after 10 h (b) and 20 h (c) ball milling.

Other than quicker grain refinement, the above properties imply that W is expected to have higher resistance to deformation during BM compared to Co.

Figure 4 presents the XRD patterns of 1200˚C compacts, though the results for unmilled powder was only shown for comparison since it has been discussed in **Figure 2(c)**. The XRD patterns of annealed 10 and 20 h ball milled compacts show similar phases as shown in **Figures 4(b)** and **(c)**, though the peak intensities remains slightly higher for the 10 h milled compacts. Furthermore, the detected phases were alike in crystal structure, HCP and RHL (rhombohedral), though their corresponding lattice parameters varied as indicated in **Table 1**. This variation from the reported lattice parameters of equilibrium phases such as RHL Co_7W_6 (a = 4.751, c = 25.670 Å) is attributed to deviation from stoichiometric composition as a consequence of BM and subsequent annealing. A similar HCP phase was reported for milled W powder annealed at 730˚C [16], 1000˚C [14] and W-Ni compact milled-annealed at 1400˚C [16]. The agility of BM creates fresh surfaces of fine powder particles which promotes high diffusion rate during high temperature annealing. To date, solid state alloying of metal powders at lower temperatures (induced by BM process) is still a controversial topic, because powders produced by BM have to be shaped and sintered into products. As a result, thermal treatment dictates the final structure and properties of the product. However, mechanism of alloying elemental powders during BM is vastly different to those milled under the presence of interstitial elements such as C, N, O to form carbides, nitrides and oxides. In pure elementals,

welding of fresh surfaces is highly possible while diffusion may be the process for the formation of carbides, nitrides and oxides. Therefore, actual alloying of binary alloy occurs by annealing or sintering of powders, while BM influences the process by changing the surface properties of the particles.

4. Conclusion

Despite broadening and shortening of XRD peaks, no alloying was observed upon 10 and 20 h BM of Co-W powder mixtures. Even if BM did not yield significant crystal changes in W and Co ground state structures, its effect is evident during subsequent annealing. An eta phase is obtained for the first time from unmilled-annealed Co-W powder mixture in the absence of interstitial elements like carbon, while the milled counterpart yielded the rhombohedral Co_7W_6-type phase with composition deviated from stoichiometric value. Larger deviation corresponded with longer milled products. In addition, HCP Co-W solid solutions with slightly different lattice parameters were obtained from annealed powders milled for both periods.

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