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High energy milling on tungsten powders

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ABSTRACT

Nanocrystalline tungsten powders were produced by high energy mechanical milling, using both tungsten carbide (WC) and tungsten (W) balls as grinding media. X-ray diffraction study indicated that the lattice parameter of tungsten decreased (from 3.162 to 3.149 Å) with increasing milling time from 0 to 15 h. Considerable decrease in particle size was observed in both W and WC grinding media after 15 h of milling duration. Rietveld analysis of the X-ray data along the Williamson-Hall plots revealed that the crystallite size also decreased with increasing milling time. Chemical analyses showed that the total amount of cobalt and carbon in the milled samples were higher in WC grinding media, as compared to W grinding media. The sintered density increased from 80% to 98% from as received to milled tungsten powders, when sintered at 1790 °C. The mechanical properties of as sintered alloys were evaluated and were found to be strongly influenced by the milling time and grinding media.

Introduction

Tungsten (W) has the highest melting point (3450 °C) [1] among metals in the periodic table and therefore, it is used for high temperature applications (filaments in light bulbs, cathodes in high power lamps, rocket nozzles in space crafts) [2]. However, sintering of tungsten powders is usually very difficult because of its high melting point. Sintering experiments conducted on tungsten powders with particle size of 1.8 μm resulted in sintered density of 76% of its theoretical density at 1650 °C [3]. Often temperatures well over 2000 °C must be employed to manufacture bulk tungsten materials by sintering [3–8]. High energy milling of tungsten powders that yield nano-crystalline tungsten powders has a great potential in reducing the sintering temperature to attain the required density.

Mechanical/high energy milling is widely used for the preparation of nano-crystalline particles [4]. Some important variables in high energy milling process are milling time, milling speed, charge ratio, temperature, milling atmosphere, milling container, milling medium, etc. Among these, the milling container (or the vial/bowl) plays a significant role as regards the issue of contamination of the final product [9–11]. The materials from the grinding media (the bowl as well as the balls) may erode or react with the milled powders resulting in the introduction of contaminants or foreign materials in the final product. So far, there has been only one detailed work where nanocrystalline tungsten powders have been synthesized via high energy milling. Malewar et al. [12] employed planetary milling to produce fine tungsten powders and achieved 95% theoretical density after sintering at 1790 °C. Further, Oda et al. [13] showed that nanosized tungsten powder could be sintered at 1000 °C under pressure of 200 MPa using a Spark Plasma sintering (SPS) technique.

The current study deals with the effect of milling time on the particle size of the powder, impurity pickup during milling and the sintering response of milled tungsten powders. It also examines the effect of grinding media on the purity and properties of the as sintered product.

Experimental

The elemental powder of tungsten with approximately 11 μm average particle size was used as a starting material for the milling experiments. High energy milling was performed using a planetary ball mill (Insmart Systems, Model: BGD 2009, Hyderabad, India). The milling media consisted of tungsten carbide (WC) and tungsten (W) balls 8 mm in diameter and 500 ml tungsten carbide bowls. The ball to powder weight ratio was 5:1 and toluene was added by 1 wt.% as a process control agent to prevent agglomeration of powders during milling. In order to prevent contamination from the atmosphere, powder charging and withdrawal were performed in a glove box under argon atmosphere. Milling was done for different durations using WC as well as W grinding media. Particle sizes of the milled tungsten powders were measured using a laser diffractometer (Malvern, Model: DIF 2001, UK). The milled powders were subjected to X-ray diffraction (XRD) studies using a Philips PW 3020 diffractometer with Kα radiation equipped with a graphite monochrometer. Celn software was used in order to determine the lattice parameter. The crystallite size was determined by measuring the Bragg peak width at half the maximum intensity employing the Rietveld Profile fitting technique. The

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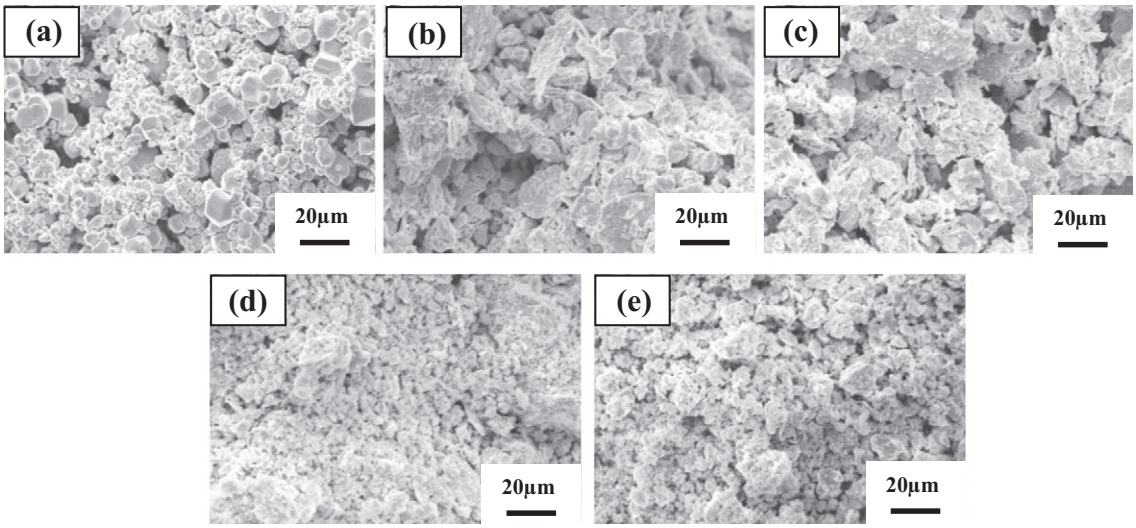

Fig. 1. Morphologies of (a) as received, (b) 1 h, (c) 5 h, (d) 10 h and (e) 15 h milled tungsten powders.

Williamson–Hall plot was then used for the determination of crystallite size and lattice parameters. The relevant equation is follows:

$$\beta\cos(\theta) = 0.9\lambda/D + \eta\sin(\theta) \quad (2)$$

where β = peak width at half maximum, θ the Bragg angle, λ the wavelength of the radiation, D the crystallite size and η is lattice strain. A plot of $\beta\cos(\theta)$ vs. $\sin(\theta)$ yields a straight line while the slope of this line and intercept gives the lattice strain (η) and crystallite size (D) respectively.

The milled powders were cold iso-statically pressed into cylindrical rods with a 20 mm diameter and 60 mm length. The compacts were then sintered in a furnace at 1790 °C for 5 h under hydrogen atmosphere (due point of −38 °C) and the sintered densities of the samples were determined by the Archimedes method. The SEM analyses were carried out in a scanning electron microscope (Model no: LEO 440i). The X-ray mappings of elements such as carbon, oxygen and cobalt were done using an electron probe micro analyzer (EPMA) (Make: Sx-100, Cameca, France). Chemical analysis for carbon and oxygen was carried out using a LECO chemical analyzer. Samples for optical micrography were prepared by mounting the sintered compacts into conductive bakelite and progressively grinding and polishing using 1/0, 2/0, 3/0, 4/0 SiC grinding papers followed by micron diamond polishing wheels. Murakami's reagent was used as an etchant. The morphologies of the as received and milled powders were observed under a scanning electron microscope (LEO Electron Microscopy Ltd, UK). Hardness of the sintered compacts was evaluated using the Vickers hardness tester (Vickers Instruments, Model: 1965, UK). All the tests were conducted at a load of 30 kg and an indentation time of 30 s was maintained. The Vickers hardness value for each sample was an average of six readings taken at random locations throughout the sample.

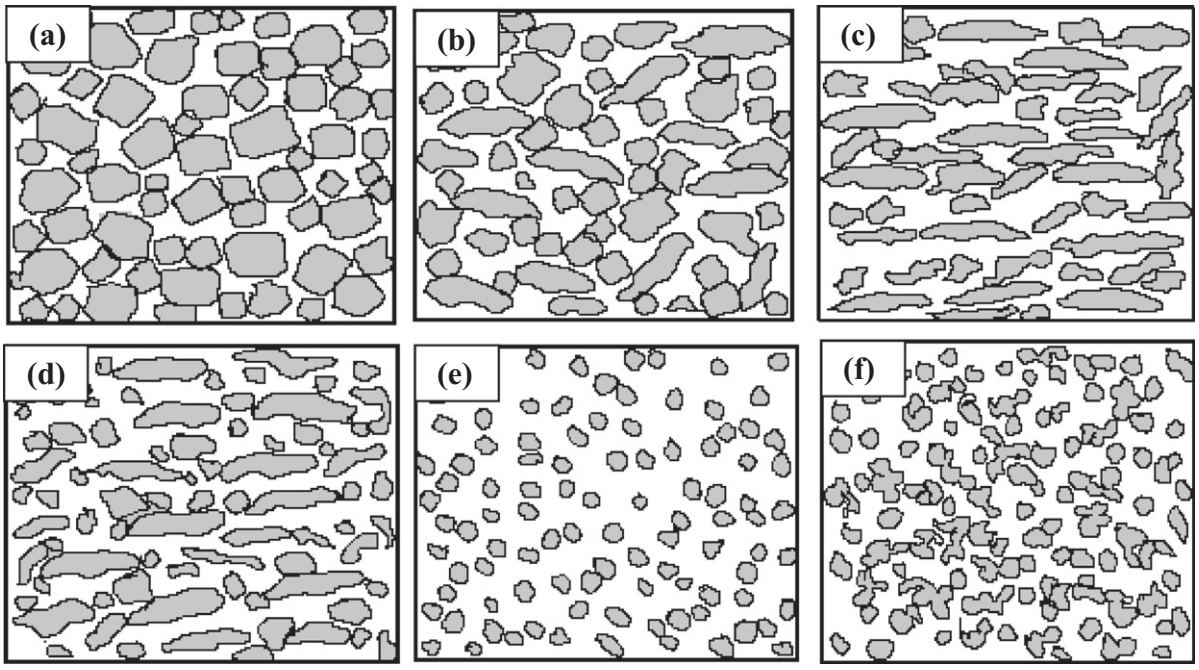

Fig. 2. Schematic diagram elucidating the forming mechanism of sub micron tungsten powders: (a) initial powder (cuboids), (b) elongated, (c) platelets, (d) fragmentation from corner (e) formation of sub micron or ultra fine particle formation and (f) sub micron particles with cold welding.