Direct laser sintered WC-10Co/Cu nanocomposites

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Abstract

In the present work, the direct metal laser sintering (DMLS) process was used to prepare the WC-Co/Cu nanocomposites in bulk form. The WC reinforcing nanoparticles were added in the form of WC-10 wt.% Co composite powder. The microstructural features and mechanical properties of the laser-sintered sample were characterized by X-ray diffraction (XRD), atomic force microscope (AFM), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), and nanoindentation tester. It showed that the original nanometric nature of the WC reinforcing particulates was well retained without appreciable grain growth after laser processing. A homogeneous distribution of the WC reinforcing nanoparticles with a coherent particulate/matrix interfacial bonding was obtained in the laser-sintered structure. The 94.3% dense nanocomposites have a dynamic nanohardness of 3.47 GPa and a reduced elastic modulus of 613.42 GPa.

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1. Introduction

Nanocomposites, which are characterized by dispersing second-phase nanometer-scaled particulates within the matrix grains and on the grain boundaries [1], are now increasingly becoming the object of growing interest, due to the enhanced mechanical, chemical, and physical properties [2]. However, consolidation of nanocomposite systems from loose powders to bulk formed components preserving nanostructures has always been a challenge. Conventional consolidation techniques, e.g., high-temperature sintering and hot pressing, have significant limitations of not being able to retain the nanometer-scaled grain size, due to the excessive grain growth during high-temperature processing [3,4]. On the other hand, a homogeneous dispersion of nanoparticles in the matrix cannot be easily obtained, since nanoparticles generally possess an extremely large specific surface area and the attendant enhanced kinetics of aggregation [2]. Therefore, in order to overcome the above-mentioned processing problems, novel methods for developing bulk nanocomposites should be innovatively designed.

Direct metal laser sintering (DMLS), as a typical solid freeform fabrication (SFF) process, enables the quick production of complex shaped three-dimensional (3D) parts directly from metal powder [5–8]. The DMLS process creates parts in a layer-by-layer fashion by selectively fusing and consolidation of thin layers of the loose powder with a scanning laser beam. Each scanned layer represents a two-dimensional (2D) cross-section of the object’s mathematically sliced CAD model [9,10]. After consolidation of one cross-section, a fresh layer of powder is deposited and the process is repeated until a 3D part is completed. The DMLS, due to its flexibility in feedstock and shapes, gives a great potential for producing complex shaped parts that cannot be developed by other conventional methods [11]. Furthermore, by using a mobile high-energy laser beam, the extremely rapid heating/cooling process during DMLS might lead to the formation of some particular structures and properties in the laser-processed materials.

In the present work, the DMLS process was used for the preparation of WC-Co/Cu bulk nanocomposites. The microstructural features and mechanical properties of the DMLS-processed nanocomposites were assessed and the role of laser
irradiation in the formation mechanism of these nanostructures was elucidated.

2. Experimental procedures

2.1. Powder materials

Electrolytic 99% purity Cu powder with a dendritic shape and a mean particle size of 15 μm, and irregularly shaped WC-10 wt.% Co nanocomposite powder were used in the current study. The Cu powder was provided by Haining Feida Metallurgy Powder Co., Ltd. The WC-10 wt.% Co nanocomposite powder was synthesized following the flowchart and the processing parameters shown in Fig. 1 [12]. The two components were mixed according to Cu:WC-Co weight ratio of 60:40 (the equivalent volume ratio of 71.5:28.5) in a Fritsch Pulverisette 6 planetary high-energy ball mill, using hard metal WC grinding balls. Powder milling was performed at a rotation speed of 350 rpm for 60 min, with ball-to-powder weight ratio of 5:1.

2.2. Laser processing

The used DMLS system mainly consisted of a continuous wave Gaussian CO₂ laser with a maximum power of 2000 W (type: Rofin-Sinar 2000SM, supplier: Rofin-Sinar Laser GmbH), an automatic powder delivery system, and a computer system for process control. Through a series of preliminary experiments, the following optimal processing parameters were chosen for DMLS: spot size 0.30 mm, laser power 700 W, scan speed 0.05 m/s, scan line spacing 0.15 mm, and powder layer thickness 0.20 mm. Rectangular specimens with dimensions of 50 mm × 10 mm × 9 mm were successfully prepared, showing very little dimensional deformation and balling phenomena (Fig. 2).

2.3. Microstructural characterization

Sintered densities were measured using Archimedes’ method. The internal sections for metallographic examinations were cut from as-sintered specimens and sequentially plane...
ground with SiC sandpaper to a 1000 grit finish. After plane grinding, the samples were further polished using Al₂O₃ suspensions on woven synthetic pads. The polished samples were washed by distilled water to remove any impurity left on the surfaces. No etching was performed.

A FEI Tecnai G2 20 S-TWIN transmission electron microscope (TEM) was used to examine the grain size of the starting WC-Co nanocomposite powder. Microstructures of as-prepared metallographic samples were characterized using a SPI 3800 atomic force microscope (AFM) in a contact mode and a Quanta 200 scanning electron microscope (SEM) operated at an accelerating voltage of 20 kV. Chemical compositions were examined by an EDAX Genesis 4000 energy dispersive X-ray spectroscopy (EDX) with a Sapphire Si(Li) liquid nitrogen (LN) cooled detector. Phase identification was performed using a Bruker D8 Advance X-ray diffraction (XRD) analyzer with Cu Kα radiation (λ = 0.15418 nm), operated at 40 kV and 40 mA. The crystallite size was determined based on XRD peak broadening using the Scherrer formula.

2.4. Nanoindentation test

Mechanical properties of the polished sample were examined using a Shimadzu DUH-W201S nanoindentation tester at room temperature. A loading–unloading test mode, a test force of 50 mN, a loading speed of 2.6478 mN/s, and a hold time of 10 s were used. In the measurements, the load (P) and indentation depth (h) were displayed. The raw data were then used to construct the loading–unloading plot. The hardness is generally defined as the ratio of the peak indentation load (P_max) to the projected area of the hardness impression (A_c). The dynamic nanohardness (H_d) is thus calculated by [13]:

\[
H_d = \frac{P_{\text{max}}}{A_c} \quad (A_c = 26.43 h_c^2)
\]  

Fig. 3. TEM image of as-prepared WC-Co nanocomposite powder (a); SEM image showing characteristic morphology of WC-Co/Cu powder mixture (b).

Fig. 4. XRD spectra of the starting WC-Co nanocomposite powder (a) and the laser-sintered sample (b).
where $h_c$ is the contact depth under the maximum indentation load. The reduced elastic modulus ($E_r$) can be calculated from the unloading curve using the following equation [14]:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_c}}$$

where $S$ is the slope of the unloading curve at the maximum displacement point.

3. Results and discussion

3.1. Powder characteristics

The characteristic morphology of as-prepared WC-Co nanocomposite powder is provided in Fig. 3a. It was clear that the Co was present as a binder in-between the WC particles. The average size of the WC grains was ranged from 20 to 50 nm. The typical morphology of the mixed powder, as shown in Fig. 3b, revealed that the fine WC-Co particles were dispersed around the comparatively coarse Cu particles in a homogeneous state.

3.2. Phase identification

Fig. 4a depicts the typical XRD spectrum of the starting WC-Co nanocomposite powder. According to the Scherrer formula, the size of WC crystallites could be calculated from the WC (1 0 0) peak to be 29 nm, which was in accordance with TEM characterization results. The typical XRD spectrum of the laser-sintered sample is shown in Fig. 4b. The strong diffraction peaks of Cu (fcc structure) and WC (hexagonal structure) were clearly observed. Despite the compressive stresses due to the Cu matrix, from the WC (1 0 0) peak, one could calculate the WC crystal size to be 36 nm. The Co peaks, however, were invisible, due to its comparatively small content in the starting powder system. Thus, it can be preliminarily considered that the laser-processed materials are mainly composed of the Cu and WC phases.

3.3. Sintering densification

The characteristic surface morphology of the laser-sintered sample is provided in Fig. 5a. It was observed that the solid particles were fused together to form a rather continuous and smooth sintered surface, exhibiting no apparent thermal cracks and balling phenomena. Fig. 5b shows the internal microstructure of the polished sample observed at a low magnification. It was clear that the internal sintered structure was pretty dense, showing no macroscopic pores. A careful measurement of the sintered density revealed that a high densification of 94.3% theoretical density was achieved.

On the other hand, the SEM characterization of the polished section at a high magnification exhibited the residue of a
certain amount of closed pores in the sintered structure (indicated by arrowheads in Fig. 6). The total influence of such microscopic pores throughout the sintered structure was well accounting for the residual porosity (5.7%) in the laser-sintered part. In DMLS process, the laser beam scans over the powder bed in a line-by-line fashion and the duration of the laser irradiation at any powder particles is extremely short (typically less than 4 ms) [15]. Moreover, the powder layer always contains a large amount of air inside it between particles. When this layer is melted during laser sintering, a certain portion of air is likely to be trapped as bubbles in the molten powder layer [16]. The rapid and localized nature of DMLS prevents the sufficient escape of air bubbles, especially those at the bottom of the powder layer, resulting in a certain amount of closed porosity.

In the present study, a close comparison of the sintering densification with the residual porosity (94.3% versus 5.7%) reveals that the DMLS process has a great promise to manufacture high-quality nanocomposites components with densification level equivalent to conventionally processed MMCs materials [17,18].

3.4. Particulate dispersion state

Fig. 6 shows the characteristic microstructure concerning the particulate dispersion in the polished section. It was clear that the ultrafine nanometer-scaled reinforcing particulates were homogeneously dispersed in the matrix. The EDX point analyses revealed that the white particulates were composed of the W and C elements with a near iso-atomic...
proportion, while the surrounding gray matrix was rich in the Cu and Co elements. Combined with the XRD results (Fig. 4b), it was confirmed that the WC particulate reinforced metal matrix nanocomposites were successfully prepared using DMLS.

In order to further characterize the distributions of various elements in the laser-sintered structure, an EDX elemental mapping was performed, as shown in Fig. 7. Interestingly, it was found that the Co element (Fig. 7d) showed a high concentration around the WC particulates (Fig. 7b and c). Fig. 8 illustrates the sintering mechanisms involved in laser sintering of such a WC-Co/Cu composite system. During DMLS, the laser energy is directly absorbed by the solid particles through both bulk coupling and powder coupling mechanisms [19], hence heating up the powder particles speedily. For the used ultrafine-grained WC-Co nanocomposite powder, the binder phase Co tends to spread on the WC grains after the sintering temperature reaches \( \sim 1000 \, ^\circ\text{C} \) [20], thereby wetting the WC particulates primarily (we termed it “first stage of wetting”, Fig. 8a and b). Here, it is noted that the initially formed Co-coated WC structure in the starting WC-Co composite powder (Fig. 3a) also favors the occurrence of the first stage of wetting. A further increase in the working temperature above the melting point of the matrix metal Cu \((\sim 1083 \, ^\circ\text{C})\) leads to a larger degree of melting, forming a so-called “sintering pool” containing both liquid (Cu) and solid (WC) phases in the laser irradiating region. The Co in a mushy state is expected to dissolve in the Cu liquid. Since a Gaussian laser beam is used in the sintering, a large temperature gradient tends to form between the center and edge of the sintering pool, giving rise to the surface tension gradient and the resultant Marangoni convection [21]. The formation of a significant Marangoni convection induces capillary forces for liquid flow, leading to a further wetting of the WC-Co system by the Cu liquid (we termed it “second stage of wetting”, Fig. 8c and d). With the action of such double stages of wetting, the WC reinforcing particulates experience a favorable wetting and, subsequently, a sufficient particle rearrangement, thereby limiting the neighboring WC grains from aggregating and coarsening. Under this condition, a homogenous dispersion of WC nanoparticles in the metal matrix can be easily obtained (Fig. 6).

For the two matrix metals (Cu and Co) in the solidifying system, the weight fraction of Co is 6.25 wt.%. According to the Co/Cu phase diagram (Fig. 9a), the high-temperature phase (\( \alpha \)-Co) precipitates primarily in some favorable sites around the WC particulate surface. Afterwards, the Cu phase presents and surrounds the primary phase (\( \alpha \)-Co) by means of the peritectic reaction. However, due to the laser-induced non-equilibrium rapid solidification process, the solute has insufficient time to transfer and penetrate the new-developed second-phase (Cu), handicapping a further proceeding of peritectic reaction and, accordingly, retaining the \( \alpha \)-Co phase between the WC and Cu phases (Fig. 9b) [23]. When the operating temperature decreases below the peritectic temperature, the residual liquid phase crystallizes to form Cu phase. Thus, it is reasonable to conclude that the constituent phases of matrix metals after laser sintering are \( \alpha \)-Co and Cu.

![Fig. 8. Schematic of double stages of wetting during direct laser sintering of WC-Co/Cu composite system.](image-url)
3.5. Particulate morphology

In order to further study the particulate morphology and particulate/matrix interfacial feature, a 3D AFM characterization of the polished internal section was performed, as shown in Fig. 10. It was clear that the reinforcing particulates generally had a smooth and round shape, with an average particle size less than 50 nm. Thus, it was reasonable to conclude that the original nanometric nature of the particulates, as shown in Fig. 3a, was well retained after laser sintering.

It is known that the high-energy laser beam tends to apply a significant action of the plasma backpressure on the present sintering pool, due to the well-known piston effect occurring in the laser irradiation [19]. On the other hand, as is evident in Tang et al.’s work [24], under a transient laser heating, the thermal deformation significantly lags behind the temperature rise. Consequently, a series of short pulses of non-equilibrium microscopic stress will generate in the sintering pool, due to the non-synchronous change of temperature rise and thermal deformation [25]. The action of such non-equilibrium stress tends to increase the anisotropic contraction of the particulates and, meanwhile, accelerate the migration of the particulates in a microscopic scale [26], thereby preventing the nanoparticles from growing coarsening. Furthermore, it is well known that the short-duration, high-density laser pulses give rise to superfast heating and melting, which is inevitably followed by a rapid solidification process. Based on Boccalini et al.’s results [27], the laser-induced cooling rate can reach a high value of $10^6$ K/s. Under this condition, a further grain refinement is expected, due to an insufficient time for grain growth, hence well retaining the initial nanometric nature of the reinforcing particulates (Fig. 10).

One the other hand, Fig. 10 revealed that the interfaces between the nanostructured reinforcing particulates and the metal matrix were continuous and compatible and free of any deleterious microcracks, showing a favorable metallurgical bonding feature.

In the present study, the WC reinforcing nanoparticles were added in the form of WC-10Co nanocomposite powder (Fig. 3a). As illustrated in Fig. 8, the binder phase Co is expected to homogeneously spread around the WC particulates during the first stage of wetting. Thus, during the second stage of wetting, the liquid Cu directly contacts the metallic Co, rather than the ceramic phase WC. For a metal/metal system, the wettability is generally better than a metal/ceramic system, due to a lower surface energy [28]. Therefore, in the sintering pool, the present Cu/Co (metal/metal) interfaces can efficiently improve liquid–solid wettability as relative to the Cu/WC (metal/ceramic) interfaces. In other words, the Cu/Co interface acts as a wetting intermedium, through which a sound metallurgical bonding between the WC nanoparticles and the...
Cu matrix can be obtained (Figs. 7 and 8). On the other hand, the presence of the WC reinforcing particulates with retained nanostructures (Fig. 10) leads to a significant reduction in the coefficient of thermal expansion (CTE) of the Cu matrix (CTE value: WC $6.0 \times 10^{-6}$ K$^{-1}$ versus Cu $17.0 \times 10^{-6}$ K$^{-1}$ [29]). In other words, the nanostructured reinforcement possesses a more effective ability to constrain the expansion of the matrix [30,31], thereby favoring the formation of coherent particulate/matrix interfaces (Fig. 10).

3.6. Nanoindentation characterization

Fig. 11 depicts the indentation load-depth curve measured on the polished section of the laser-sintered sample. According to Eqs. (1) and (2), the obtainable dynamic nanohardness ($H_d$) is 3.47 GPa and the reduced elastic modulus ($E_r$) is 613.42 GPa. Compared with the conventional casting or powder metallurgy copper materials ($H_d$ of 1.4–1.6 GPa [32] and $E_r$ of 130.5–201.5 GPa [14]), the mechanical properties of the DMLS-processed WC-10Co/Cu nanocomposites show a considerable improvement. This is mainly attributed to the significant reinforcing function of the uniformly dispersed WC nanoparticles in the Cu matrix (Figs. 6 and 10).

4. Conclusions

The direct metal laser sintering (DMLS) process was innovatively used to prepare the WC-Co/Cu nanocomposites. The highly non-equilibrium nature of laser irradiation well retained the original nanometric nature of the WC reinforcing particulates without appreciable grain growth. The addition of WC nanoparticles in the form of WC-Co composite powder favors the occurrence of double stages of wetting and, accordingly, the formation of Cu/Co (metal/metal) interfaces, so as to obtain a uniform distribution of the reinforcing nanoparticles with a coherent particulate/matrix interfacial bonding. The DMLS-processed WC-Co/Cu nanocomposites reached a density of 94.3%, resulting in a dynamic nanohardness of 3.47 GPa and a reduced elastic modulus of 613.42 GPa.

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