WC–Co particulate reinforcing Cu matrix composites produced by
direct laser sintering

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Abstract

Experimental investigations on the development of the WC–10%Co particulate reinforcing Cu matrix composite material have been conducted using direct laser sintering. The chemical compositions and microstructures of the laser-processed material have been characterized using X-ray diffraction (XRD), energy dispersive X-ray (EDX) spectroscopy, scanning electron microscopy (SEM), and atomic force microscope (AFM). An excellent interfacial bonding between the reinforcement and the matrix was obtained. The WC reinforcing particulates typically had two distinct morphologies, i.e., partially dissolved and smoothed or completely dissolved and refined. The effects of the WC–Co content on the microstructural characteristics and resultant properties of the laser-sintered parts have been studied. It was found that lowering the amount of WC–Co resulted in insufficient reinforcement, while at a higher amount of WC–Co the significant agglomeration of the WC reinforcing particulates occurred. A homogeneous sintered structure with a high average hardness of HV0,1384.6 was obtainable using 30 w% WC–Co.

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1. Introduction

Direct metal laser sintering (DMLS) is a newly developed material additive manufacturing process which enables the quick production of the complex shaped three-dimensional (3D) parts directly from metal powder [1,2]. The main advantages associated with this technique are high design flexibility, excellent process capabilities, and time- and cost-saving features [3,4]. Currently, the applications of metallic parts from the DMLS process include functional prototypes, moulds for injection and die casting, master patterns for casting, and small-lot manufacturing [5].

WC–Co hard metal combines favorable properties, such as high strength, high hardness, high toughness, and wear resistance [6]. Copper is characterized by its excellent electrical and thermal conductivities as well as outstanding resistance to fatigue and corrosion [7]. In order to combine their superior mechanical and thermal properties, the development of WC–Co reinforcing Cu matrix composite materials is significant. Generally, such materials are produced by the common casting or powder metallurgy methods, which need expensive and dedicated tools such as moulds or dies [5,8]. These techniques are very productive and can achieve rather dense structures, but they are not suitable for small volume production and complex shapes. Fortunately, recent research efforts have shown that the DMLS process might be highly feasible and effective in some special applications, due to its flexibility in materials and shapes [5]. In other words, the DMLS process might have the possibility for creating new materials that cannot be developed by other conventional means.

Furthermore, by using a scanning laser beam, the extremely rapid cooling during the sintering process might lead to the formation of some particular structures and properties [8]. This paper presents an investigation into the fabrication of WC–Co particulate reinforcing Cu matrix composites by the DMLS process. The microstructure, composition, and mechanical properties of the laser-processed materials were studied.

2. Experimental procedures

Electrolytic 99% purity Cu powder with round dendrite branches and mean particle size of 15 μm, and WC–10%Co
composite powder with irregular shape and mean equivalent spherical diameter of 0.6 μm were used in this study. The WC–Co composite powder was synthesized using a novel “spray drying and fixed bed” technique, which involved spray drying a precursor solution containing AMT-Co(NO₃)₂, followed by roasting, ball milling, reduction, and carbonization [9]. The two components were mixed according to Cu:WC–Co weight ratio of 80:20, 70:30, and 60:40, respectively. Powder dispersion was performed in a horizontal ball mill with a vacuum-pumping system at a rotation speed of 150 rpm for 60 min, with balls to powders weight ratio of 5:1. The characteristic morphology of a powder mixture with Cu:WC–Co weight ratio of 70:30 is shown in Fig. 1.

Laser sintering experiments were carried out on a DMLS system developed at the China Academy of Engineering Physics (CAEP). Fig. 2 depicts a schematic diagram of the apparatus. The system consists of a continuous wave CO₂ laser with a maximum output power of 2000 W, an automatic powder delivery system, and a computer system for process control. Rectangular test specimens with dimensions of 50×10×6 mm were prepared. When a part was to be built, a steel substrate was placed on the building platform and leveled. Then, a powder layer (0.3 mm in thickness) was spread on the substrate by the roller. Subsequently, a laser beam scanned the powder bed surface to form a layer-wise profile according to the CAD data. The similar process was repeated and the part was produced in a layer-by-layer fashion until completion. The entire sintering process was performed in air at room temperature. The laser processing parameters were optimized as follows: spot size of 0.30 mm, laser power of 700 W, scan speed of 0.06 m/s, and scan line spacing of 0.15 mm.

The density of the sintered specimens was calculated based on the Archimedes principle. Samples for metallographic examination were cut, ground, and polished according to the standard procedures. Microstructure was characterized using a SPI3800 atomic force microscope (AFM) and a QUANTA 200 scanning electron microscopy (SEM) in back-scattered electron (BSE) mode. Chemical composition was examined by an EDAX energy dispersive X-ray (EDX) spectroscopy. A BRUKER D8 ADVANCE X-ray diffraction (XRD) analyzer was employed in phase identification. An HXS-1000 micro-hardness tester was used to determine the Vickers hardness with a load of 0.1 kg and an indentation time of 20 s.

3. Results and discussion

3.1. Phase identification

Fig. 3 shows the typical XRD patterns of the starting powder mixture and the laser sintered sample of Cu to WC–Co ratio of 70:30. The powder blend mainly consisted of a matrix metal Cu and a hard
phase WC, while the Co peaks were weak due to its relatively small content (Fig. 3a). After laser sintering, the strong diffraction peaks of Cu and WC can be clearly observed (Fig. 3b). Thus, it is reasonable to consider that the laser processed material is mainly composed of Cu and WC phases. In addition, Fig. 3b reveals the presence of a metastable phase CoC0.25. This can be explained as follows. During laser sintering, the binder phase Co is expected to be molten at a relatively low temperature of 1000 °C for fine grained WC–Co powder [6], and, subsequently, the Cu powder tends to melt at 1083 °C. Since the preparation of the raw WC–Co composite powder involves a final step of carbonization, a small amount of dissociative carbon is expected to exist in the sintering system [9]. The C atoms diffuse preferentially towards the Co. However, due to the non-equilibrium effects induced by laser melting such as large degrees of undercooling and high solidification rate, C atoms have insufficient time to diffuse into the CoCx lattice to form stoichiometric CoC, leading to the formation of the metastable phase CoC0.25.

3.2. Microstructure

Fig. 4 shows the characteristic microstructures of the polished sample. It can be seen that the fine WC particulates dispersed uniformly in the Cu matrix (Fig. 4a). This is mainly attributed to the homogeneous distribution of WC–Co and Cu powder obtained by mechanical milling prior to laser sintering (Fig. 1) and the optimal laser processing parameters. Analyses have confirmed that there exists a critical laser scan speed, which determines the trapping or pushing of reinforcing particulates by the advancing solid/liquid interface. Trapping might bring about a uniform distribution of particulates, whereas pushing results in the segregation at regions finally solidified [10]. Local magnification of Fig. 4a shows the excellent interfacial integrity between the reinforcement and the matrix (Fig. 4b). During laser sintering, the presence of WC particles in the melt pool would influence the Marangoni effect, which is known as the movement of liquid due to surface tension action on free surfaces [11], and thus the material flow would be restricted, thereby limiting the neighboring WC grains from aggregating. The significant grain refinement would improve the wettability between the reinforcement and the matrix, so as to obtain a strong interfacial bonding [10].

Further enlargement of zones A and B in Fig. 4b reveals the diversity of the morphologies of reinforcing particulates (Fig. 4c,d). Fig. 4c shows the first kind of particulates, which had smooth and round shape with mean particle size of ~0.3 μm. Compared with the original particle characteristics, it is reasonable to conclude that the larger WC particles are dissolved partially with the wetting liquid. This might be followed by the rapid rearrangement of solid particles under the influence of capillary forces exerted on them by the liquid. Interestingly, the second kind of particulates, shown in Fig. 4d, had a completely different morphology from the above. Ultra-fine particulates with mean size of ~40 nm were dispersed uniformly in the matrix. In this instance, it is quite possible that the smaller WC particles are completely dissolved in the liquid. Due to the rapid cooling induced by
the laser beam, the molten WC might precipitate again in the form of refined and dispersed particles. Another possibility is that there already exist some ultra-fine nanometer-scaled WC particulates in the raw materials of WC–Co composite powder, and the highly non-equilibrium nature of laser sintering retains such nanophase in the laser processed materials.

3.3. Effect of WC–Co content on microstructure

Fig. 5 shows the typical microstructures of the polished samples using the same processing parameters but different contents of WC–Co. The EDX analysis reveals that all the white phase involved W and C elements, while the surrounding dark phase was rich in Cu and Co. Thus, it is reasonable to consider that WC particulate reinforcing Cu matrix composites can generally be fabricated. However, it is found that the densification level and the microstructural features of reinforcing particulates, e.g. dispersing homogeneity, particle size and shape are associated with the variation of the amount of WC–Co.

Fig. 6 shows the microhardness profiles measured on the corresponding cross-sections. The microhardness, which is generally

![Fig. 5. SEM images (BSE mode) of the polished samples using different amounts of WC–Co: (a) 20 wt.%; (b) 30 wt.%; and (c) 40 wt.%.](image)

![Fig. 6. Variations of microhardness on the cross-sections of the laser sintered samples at different WC–Co contents: (a) 20 wt.%; (b) 30 wt.%; (c) 40 wt.%.](image)
higher than common casting or powder metallurgy copper and copper alloys (HV$_{0.1}$120–180) [12], is also found to be depending on the WC–Co contents. At a low WC–Co level (20 wt.%), the WC reinforcing particulates exhibited ultra-fine morphology (Fig. 5a), indicating a sound liquid–solid wettability due to a larger amount of liquid formation. In consequence, a relatively high sintered density of 87.4% theoretical density was obtained. However, the microhardness was lowest in this case, with an average value of HV$_{0.1}$280.3 (Fig. 6a). This might be ascribed to the insufficient reinforcement of WC particulates because of the relatively small amount. Furthermore, the microhardness distribution was non-uniform (Fig. 6a). This would be caused by the local segregation of WC particulates since the excessive liquid presented tends to pull them together towards the center of a laser scan line. As the amount of WC–Co increased to 30 wt.%, a higher concentration of WC particulates was obtained, and, meanwhile, the particulates were uniformly dispersed in the matrix without any significant aggregation (Fig. 5b). This led to a higher sintered density of 90.7% theoretical density and a uniform microhardness distribution with a higher average value of HV$_{0.1}$384.6 (Fig. 6b). When 40 wt.% WC–Co was used, a poor sinterability with significant agglomeration of WC particles was obtained (Fig. 5c), resulting in a considerably low sintered density of 76.2% theoretical density. This is because the capillary force is too low to rearrange all WC particles, due to the reduced amount of liquid presented. In this instance, the hardness curve fluctuates considerably (Fig. 6c). This can be attributed to the significant pores distribution and WC agglomerates segregation throughout the sintered structure.

4. Conclusions

(1) The WC–10%Co particulate reinforcing Cu matrix composite material was successfully fabricated by direct laser sintering. An excellent interfacial bonding between the reinforcement and the matrix was obtained.

(2) The WC reinforcing particulates typically had two distinct morphologies, i.e., partially dissolved and smoothed or completely dissolved and refined.

(3) The microstructure and resultant microhardness changed with the variation of the amount of WC–Co. A homogeneous sintered structure with a high average hardness of HV$_{0.1}$384.6 was obtained using 30 wt.% WC–Co.

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