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Microstructure characteristics and formation mechanisms of in situ WC cemented carbide based hardmetals prepared by Selective Laser Melting

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ABSTRACT

Selective Laser Melting (SLM) of W–Ni–graphite powder mixture was performed to prepare in situ WC/Ni_2W_4C(M_6C) cemented carbide based hardmetals. The WC phase was developed via a multi-laminated growth mechanism and it experienced block-shaped–triangle–elliptical morphological change on decreasing the linear energy density. The amount of the formed M_6C increased and its structure changed from a granular form to a ring shape at a lower laser energy input. SLM-processed cemented carbide based hardmetals possessed a high densification level of 96.3% and a maximum microhardness of 1870.9 $HV_{0.1}$. The dominant metallurgical mechanisms behind the microstructural developments were also proposed.

1. Introduction

Cemented carbide based hardmetals hold a leading position in metal machining, moulds, and mineral applications due to their excellent properties in terms of high hardness, low coefficient of thermal expansion, and high wear/corrosion resistance [1]. In particular, tungsten carbide (WC) based hardmetals have been intensively studied, since WC possesses some unique properties such as a certain amount of plasticity and a sound wettability by molten metals [2]. Normally, cobalt (Co) acts as the traditional binder element for WC-based hardmetals and some other transition metals such as nickel (Ni) and iron (Fe) are used as alternatives [3,4]. The presence of a binder metal element in the boundaries of WC grains to form WC-based composites leads to the strain energy dissipation and accordingly increases toughness.

Recently, the development of novel in situ hardmetals, in which the constitutions are synthesized by chemical reactions between elements during processing, exhibits more significant advantages and thus attracts more interest. In situ hardmetals are thermodynamically stable, leading to less degradation in elevated-temperature applications. Furthermore, the present ceramic/metal interfaces within in situ hardmetals are generally cleaner and more compatible, yielding stronger interfacial bonding and elevated mechanical properties of the final products [5]. In situ hardmetals are usually produced following a powder metallurgy (PM) route, which involves mixing of elemental powder, pressing, and sintering [6,7]. Almost all the current production lines of hardmetals are based on high-temperature pressure sintering except a few which use spark plasma sintering. Therefore, high-temperature, high-pressure, and long reaction time are normally required. However, the conventional PM-processed hardmetals are usually of limited shape, high brittleness, and poor machinability, which inevitably restrict their practical applications.

Selective Laser Melting (SLM), as a newly developed Rapid Manufacturing (RM) technique, enables the quick production of three-dimensional parts with any complex configurations directly from metals, alloys, or ceramics powders [8]. SLM builds parts in a layer-by-layer fashion by selectively fusing and consolidation of thin layers of loose powder using a high-energy laser beam, without post-processing requirements such as furnace densification and secondary infiltration. So far, nearly all the researches on SLM have been focused on metallic and ceramic materials. Recent research efforts have demonstrated that SLM, due to its flexibility in feedstock and shapes, possesses a promising potential for the net-shape production of complex-shaped, high-performance composites parts. SLM of Al–Si–Mg/SiC [9], $Al_{50}Ti_{40}Si_{10}$ [10], WC/Co [11], TiN/Ti_5Si_3 [12], TiC/Ti–Al [13], and stainless steel/hydroxyapatite [14] composites have been reported. Nevertheless, due to the complex metallurgical nature of SLM, which involves multiple modes of heat, mass, and momentum transfer induced by localized laser scanning [15], processing problems such as gas entrapment, aggregation of constitution phases,

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and interfacial microcracks may be produced in SLM-processed composites. Furthermore, as to the composites synthesized in an in situ manner, the dynamic SLM process makes it rather difficult to control the morphology of the in situ formed phases. As the phase constitution and crystal structure may significantly influence the final properties of composites, it is highly necessary to be able to understand and control them during SLM. In this work, SLM of W–Ni–graphite elemental powder mixture was performed to prepare bulk-form in situ WC-based hardmetals. The microstructural characteristics and mechanical properties of SLM-processed composites were assessed and the formation mechanisms of in situ structures were elucidated.

2. Experimental

The starting powder materials were: 99.9% purity Ni powder with an irregular shape and a mean particle size of 45 μm (Haining Feida Metallurgy Powder Co., Ltd., China), 99.9% purity W powder with a polyangular structure and an average particle size of 2.5 μm (Zhuzhou Kete Industries Co., Ltd., China), and pure graphite powder with a mean particle size of 30 μm (Shanghai Shiyi Chemical Reagents Co., Ltd., China). The three components were uniformly mixed according to Ni:W:C weight ratio of 10:85:5 in a Pulverisette 6 planetary mono-mill (Fritsch GmbH, Germany) at a rotation velocity of 250 rpm for 30 min.

The applied SLM system consisted mainly of a 2000SM continuous wave Gaussian CO_2 laser (Rofin–Sinar Laser GmbH, Germany), an automatic powder delivery system with a stainless steel roller, and a computer system for process control. When a specimen was to be produced, a carbon steel substrate was placed on the building platform and leveled. A thin layer of the powder (thickness d = 0.1 mm) was then deposited on the substrate by the roller. Afterwards, the laser beam scanned the powder bed surface to form a layer-wise profile according to computer-aided design data of the specimen. The similar process was repeated and the specimen was produced in a layer-by-layer fashion until completion. The following suitable processing parameters were chosen for SLM: laser intensity (Φ) 2.55 kW mm^{-2}, scan speed (v) 0.8–1.2 m s^{-1}, and scan line spacing (l) 0.15 mm. Rectangular-shaped multi-layer specimens with dimensions of 20 mm × 5 mm × 3 mm were prepared.

The density of SLM-processed specimens was calculated based on the Archimedes principle. Phase identification of SLM-processed samples was performed by a D8 Advance X-ray diffractometer (XRD) (Bruker AXS GmbH, Germany) with Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA, using a continuous scan mode at 4°/min. Samples for metallographic examinations were cut, ground, and polished according to the standard procedures, and etched with a solution consisting of HF (10 mL), HNO_3 (30 mL), and distilled water (70 mL) for 15 s. Microstructures were characterized using a Quanta 200 (FEI Company, The Netherlands) scanning electron microscope (SEM) in a secondary electron mode at an accelerating voltage of 20 kV. An EDAX energy dispersive X-ray (EDX) spectroscope conforming to ISO 15632:2002 standard (EDAX Inc., USA) was used to determine chemical compositions, using a Genesis version of image analysis and a super-ultra thin window (SUTW) sapphire detector with a voltage of 20 kV and a beam current of 200 pA. X-ray photoelectron spectra were determined by an AXIS ULTRA X-ray photoelectron spectroscopy (XPS) system (Shimadzu Corporation, UK). The acquisition parameters were: source type AlK Alpha, spot size 500 μm, pass energy 20.0 eV, energy step size 0.100 eV, and number of energy steps 461. Peak identification was performed by reference to the standard XPS database [16]. Grain sizes within SLM-processed structures were measured using UTHSCSA ImageTool program and the standard deviation (SD) of the grain size measurement was calculated. The Vickers hardness was determined using a MicroMet 5101 microhardness tester (Buehler GmbH, Germany) at a load of 0.1 kg and an indentation time of 20 s.

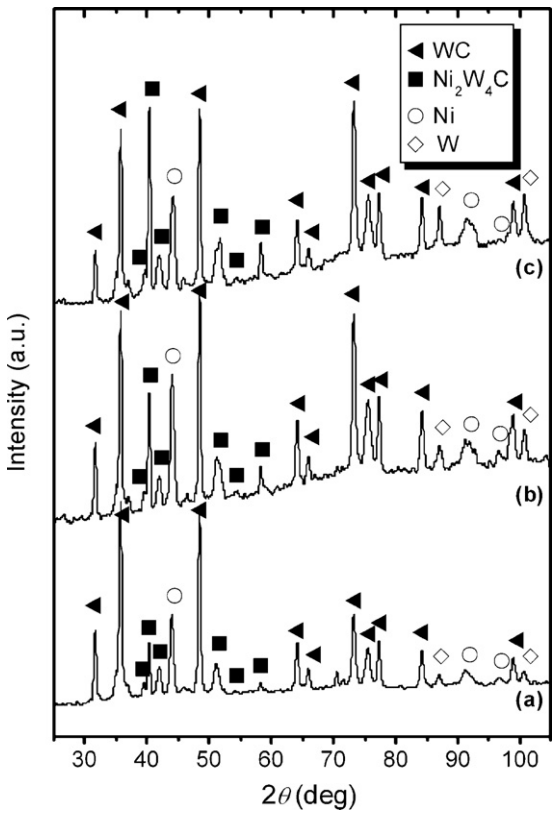

Fig. 1. XRD spectra of SLM-processed WC-based hardmetals using different scan speeds: (a) 0.8 m s^{-1}; (b) 1.0 m s^{-1}; (c) 1.2 m s^{-1}. Fixed processing parameters are laser intensity Φ = 2.55 kW mm^{-2}, scan line spacing l = 0.15 mm, and powder layer thickness d = 0.1 mm.

3. Results and discussion

3.1. Phase identification

Typical XRD patterns of SLM-processed parts at different scan speeds are depicted in Fig. 1. Generally, the strong diffraction peaks corresponding to WC with a hexagonal structure and Ni_2W_4C (Abbreviated as M_6C, where M were metal atoms) with a cubic structure were identified. According to Ref. [17], the Ni_2W_4C(M_6C) was identified as a η-carbide phase. The diffraction peaks for Ni, although the intensity was relatively lower, were also well detected (Fig. 1). Furthermore, the existence of the weak diffraction peaks for W suggested the residual of a small amount of W after SLM, especially for the sample processed at a higher scan speed (Fig. 1c). Thus, it was reasonable to conclude that SLM of the W–Ni–graphite powder mixture generally led to the formation of WC/M_6C (major phase) cemented carbide based hardmetals composed of Ni and W (minor phase) as the binder. Nevertheless, XRD results revealed that the intensity of WC and M_6C diffraction peaks and the resultant volumetric ratio of WC and M_6C phases were significantly influenced by the applied scan speeds. For the hardmetals processed at 0.8 m s^{-1}, 1.0 m s^{-1}, and 1.2 m s^{-1}, the ratio of the intensity of the strongest diffraction peaks of WC(1 0 0) (standard 2θ = 35.722°) and M_6C(5 1 1) (standard 2θ = 41.643°), I_{WC}/I_{M_6C}, was 2.7, 1.4, and 0.8, respectively. According to Ref. [18], the volumetric ratio of WC and