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Obtaining of reinforced Cu-Ti, Cu-Ti-TiB_2 foils through green compact laser sintering

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Homogenized Cu-4Ti (wt%) and Cu-4Ti-1.4B (wt%) powders were cold pressed and then sintered by pulsed, millisecond Nd:YAG laser system. Phases present in laser sintered samples were characterized by X-ray diffraction (XRD), while quantitative chemical analysis of the sintered samples was conducted using inductively coupled plasma-atomic emission spectrometry (ICP-AES). The microstructure of powders and laser sintered foils was examined with scanning electron microscope with an energy dispersive X-ray spectroscope (EDS). Optical microscopy was used also for microstructural characterization of the foils. The tensile test was carried out using a universal testing machine with a crosshead speed of 0.5 mm/min at room temperature. Foils with dimensions $20 \times 6 \times 0.4$ mm were used for tensile testing. In the obtained Cu-Ti foils, after aging at 550 °C for 4 h, rapidly solidified structure and metastable Cu_4Ti precipitates affected high degree of copper matrix strengthening (peak aged). In Cu-Ti-TiB_2 foils, after aging at 550 °C for 3 h, rapidly solidified structure, as well as the presence of TiB_2 particles and metastable Cu_4Ti precipitates, also affected high degree of copper matrix strengthening which, thanks to the ceramic particles, is retained at longer times (6 h). Fractured surfaces were observed with an optical microscope. It was determined that the best structural and mechanical properties of laser-sintered foils were reached using the following parameters: laser frequency 4 Hz, laser pulse duration 9 ms, pulse energy ~20 J, number of scans 2.

1. Introduction

Copper-based materials are of great interest due to high electrical and thermal conductivity, and their lack in mechanical strength can be overcome by various hardening mechanisms. Precipitation hardened copper alloys (e.g. Cu-Zr, Cu-Cr, Cu-Ti) have improved strength at room temperature, however dispersion hardening with thermally stable ceramic particles (such as TiB_2) provides maintaining of high strength up to very high temperatures [1]. Obtaining of Cu-TiB_2 directly from Cu and TiB_2 powder does not yield satisfactorial microstructure with uniformly distributed fine dispersions, so TiB_2 needs to be formed by *in situ* reaction. There are different methods for *in situ* creation of ceramic particles – by reactions of B_2O_3, carbon and titanium in copper–titanium melt [2], spray forming [3], mechanical alloying of Cu, Ti and B powders followed by hot pressing [4], gas atomization of Cu-Ti and Cu-B melt [5]. TiB_2 particles obtained by rapid solidification in gas atomization process are very fine and their presence along with their homogeneous distribution after HIP-ing process contributes to significant microhardness increase of the material [6].

The goal of this work was to achieve both dispersion and precipitation hardening of the selected Cu-material through a novel approach of selective laser sintering/melting (SLS/SLM). TiB_2 particles would be formed by *in situ* reaction due to rapid solidification, while hardening precipitates would be obtained in the subsequent aging following the SLS process. Physical processes during SLS are still a subject of research due to its nonequilibrium nature, and obtaining of *in situ* formed reinforcements is even more complex. Application of SLS for synthesis of copper-based materials is known in literature, with most of the studies employing several kW continuous lasers [7,8]. In this work, pulsed SLS process will be employed for obtaining *in situ* hardened copper-based alloys, Cu-Ti and Cu-Ti-TiB_2. Pulsed lasers are increasingly interesting for SLS applications due to better control of the heat delivered to the material. Alloys will be obtained in the form of foils through the so-called green compact laser sintering (GCLS). In our previous work GCLS method was successfully applied for obtaining of multiple

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hardened Cu-Zr-ZrB_2 composites [9]. Cu-based foils have a wide range of applications – copper foils are used in structural engineering, EMI/RFI shielding, circuit boards, heat exchangers [10], while in scientific investigations they are lately used for graphene growth [11,12]; Cu-Ti foils, characterized by extra-high strength, are used in connectors, springs for autofocus camera modules, etc. [13]. GCLS using pulsed laser will be applied on Cu-Ti and Cu-Ti-B cold-pressed samples with the aim of achieving precipitation hardening (in both alloys) as well as dispersion hardening (in ternary alloy).

2. Material and methods

The powders used as starting materials were copper (99.5% purity, particle size below 63 μm), titanium (99.5% purity, particle size below 63 μm) and amorphous boron (97% purity, particle size 0.08 μm). Mixtures of both Cu-4Ti (wt%) and Cu-4Ti-1.4B (wt%) powders were homogenized for 2 h in Turbula mixer. Homogenized mixtures were compacted into specimens at a pressure of 180 MPa, producing green compacts with 40-mm diameter and 0.5-mm height. The green compacts were subjected to Nd:YAG pulsed laser radiation in the argon atmosphere under different irradiation parameters. The laser sintered samples were characterized by X-ray diffraction (XRD) analysis which was performed using a Bruker system3 SAXS, Ultima IV type 2 with CuKα Ni filtered radiation. Quantitative chemical analysis of the samples was conducted using inductively coupled plasma-atomic emission spectrometry (ICP-AES). This method provided the weight ratio of the elements (Ti, B) contained in the master alloys, i.e. powders. Concentration of TiB_2 compound was determined from the internal standards formed for the referent samples of this compound. Density of the compacts was determined by Archimedes method in water (ASTM: B962-08). Laser sintered samples were aged at 550 °C for holding times 1–6 h in argon, and then cooled in water. The microstructure of powders and laser sintered foils was examined with a JEOL-JSM 5800LV scanning electron microscope at an accelerating voltage of 20 kV equipped with an energy dispersive X-ray spectroscope (EDS). Optical microscopy was used also for microstructural characterization of the foils. Specimens for optical microscopy were prepared by standard techniques and etched in KLEM III solution (40 g K_2S, 11 ml $N_2S_2O_3$ and 100 ml H_2O). The tensile test was carried out using a universal testing machine (Instron, England) with a cross-head speed of 0.5 mm/min at room temperature. Rectangular foils sized 20 × 6 × 0.4 mm were used for tensile test. The ultimate tensile strength and the elongation to fracture were determined. Fractured surfaces were observed with an optical microscope. The presented values for measured quantities, density and tensile characteristics, were obtained from an average of 3 and 2 indents, respectively. Uncertainty values were determined in accordance with the "Guide to expression of uncertainty in measurement" (GUM-ENV 13005).

3. Results

Fig. 1 shows the morphologies of the mixing powders. Particles of the Cu powder exhibited irregular as well as spherical morphology. Titanium particles were irregularly shaped with sharp edges, while the submicron boron particles had a spherical shape. Figure shows that the particles of alloying elements were dispersed uniformly around the particles of the base element after mixing. It is known that a homogeneous powder blend with less agglomeration of the binder is of critical importance to increase thermal absorption rate of the laser beam, so the number of present agglomerates made of small particles in the mixture was very important in the sintering process. In our case, certain number of agglomerates was registered, particularly in smaller, irregular particles of the base metal. This content of agglomerated particles can be reduced by ball mixing of the powders (electrostatic forces holding together the particles in the agglomerates are broken easier) which was not the case in this work.

Copper alloy foils (Fig. 2a) were obtained from the pressed powders using different input laser parameters, with two repeated scannings at scanning directions under 90° angle. Scanning pattern is schematically given in Fig. 2b. Laser pulse frequency applied in GCLS was 4 Hz, pulse energy 10–20 J and pulse length 7–10 ms.

Scanning of the green compact surface with lower laser pulse energy (under 15 J) resulted in poor densification of the material as the laser parameters were not sufficient to overpower high thermal conductivity of the copper. This resulted in a significant number of non-melted particles (titanium particles in Fig. 3a and b), and consequently larger or smaller regions of the remained green compact porosity. EDS analysis (Fig. 3b) has shown that in certain parts of the structure the formation of solid solutions of the alloying elements in copper did not take place. Particles of the base metal were detected, as well as free particles of boron and titanium. Densification was improved with increased pulse energy and optimum conditions of 4 Hz, 9 ms, 20 J caused full melting of Cu and Ti powder particles, i.e. formation of Cu-Ti solid solutions (Fig. 3c). In certain locations titanium-rich particles could be observed, as well as submicron particles of equilibrium β precipitate (Fig. 3d). On the other hand, excessive pulse energy (over 20 J) resulted in higher

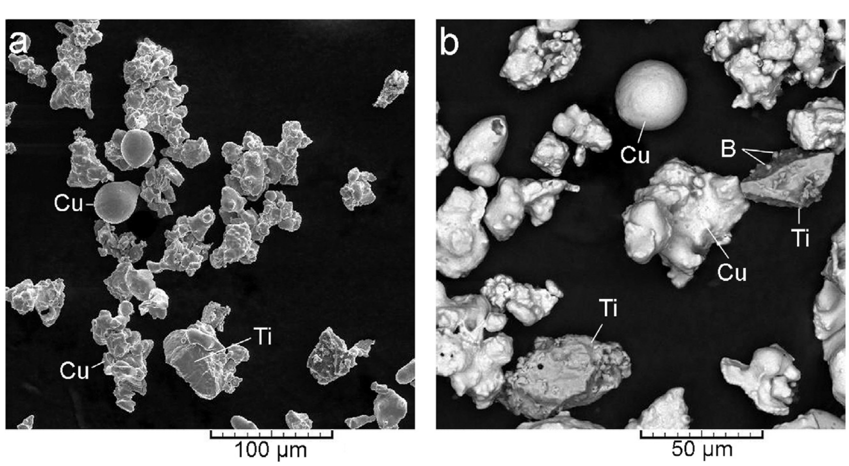

Fig. 1. SEM. Homogenized mixture of powders: a) Cu-4wt%Ti; b) Cu-4wt%Ti-1.4 wt%B.