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研究課題名（和文） レーザ積層造形により実現する耐酸化保護皮膜を有するMo基合金複合材料の開発

研究課題名（英文） In-situ formation of ceramic protective coating on Mo-based composites by laser powder bed fusion

研究代表者
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研究成果の概要（和文）：本研究では、カーボンナノチューブ（CNT）を使用して、ヘテロ凝集させナノセラミックス/金属粉末を製造する新しい手法を開発した。適切なレーザ３次元粉末積層造形法（L-PBF）パラメータを採用することにより、Mo基合金の表面は緻密なセラミックス層でコーティングされ、高温での耐酸化性を効果的に高めた。更に、TiCおよびAl203ナノ粒子は均一に分散され、マトリックスと緊密に接触しているため、ビッカース硬度が向上した。本研究は、超高温アプリケーションで高性能Moベースの材料を設計および製造するためのギルドを提供した。

研究成果の学術的意義や社会的意義
The applicant proposes a facile and effective coating approach via L-PBF. The protective layer works against the harsh oxidation environment, contributing to the applications of Mo-based alloys.

研究成果の概要（英文）：In this study, a novel strategy was developed to prepare nanoceramic/metal mixed powders by using acid-treated carbon nanotubes (CNTs) during hetero-agglomeration process. After L-PBF, a tight ceramic coating was formed on the surface of the Mo-based alloy, which effectively increased the resistance to oxidation at high temperatures. Meanwhile, the TiC and Al203 nanoparticles were homogenously dispersed and closely contacted with the matrix, giving rise to an enhanced Vickers hardness. This work shed light on designing and producing high-performance Mo-based materials in ultrahigh-temperature applications.

研究分野： 材料加工

キーワード： Laser powder bed fusion　Mo-based composites　Coatings　Oxidation resistance　Hetero-agglomeration　Microstructure

１．研究開始当初の背景

Owing to the high melting points, superior strength, and low thermal expansion coefficient, Mo-based alloys are promising candidates beyond the realm of Ni-based superalloys for energy efficiency improvements in heat engines, e.g., gas turbines and jet engines. However, poor oxidation resistance (molybdenum is easily oxidized to MoO3 and sublimates after exposure to oxygen above 923 K), and low processability for complex designs with traditional technologies, are their main concerns in practical applications. As we know, the surface coating is widely used to increase the integrity and corrosion resistance of metals. Nevertheless, a uniform, pore-free protective coating deposited with a physical/chemical vapor deposition (P/CVD) process is technically difficult and costly, particularly for complex targets.

Laser powder bed fusion (L-PBF), as a newly developed additive manufacturing technique, has attracted increasing attention for producing metallic products. For instance, thanks to its flexible, high-temperature metallurgical characteristic, L-PBF offers new technological opportunities for advanced metal matrix composites (MMCs) with tailed structures [Acta Mater 2014, 76 (13-21)]. More importantly, the movement and equilibrium of ceramic particles within molten pools is largely determined by relevant forces (e.g., buoyancy or Marangoni force) due to the density difference and high thermal gradient. Thus, it should be possible to introduce an in-situ ceramic layer on Mo-based composites by controlling the L-PBF parameters. Unfortunately, such a unique phenomenon has never been observed in L-PBF-processed MMCs so far.

２．研究の目的

It is known that fabricating suitable powders is a prerequisite, but the main challenge currently faced is to broaden L-PBF in MMCs. Generally, the composite powders should possess good flowability, suitable particle size and distribution. Obviously, such powders cannot be fabricated by widely used high-energy ball milling, which easily causes the powder deformation accompanied with poor flowability. Therefore, the purpose of this work was firstly to develop an approach of fabricating nanoceramic/Mo composite powders. Moreover, the feasibility of in-situ introducing ceramic layer during L-PBF, as well as the mechanical property and oxidation resistance of the Mo-based composite, were systematically investigated.

３．研究の方法

Hetero-agglomeration is an effective method for mixing two oppositely charged colloidal species by electrostatic attraction. Unfortunately, nanoceramic (e.g., Al_2O_3, ZrO_2) and metallic powders have the same positive surface-charge in ethanol. To address this issue, our idea was to introduce a negatively charged acid-treated CNT agent to bridge Al_2O_3 and metal powders for the powder fabrication, as shown in Fig. 1a. Firstly, appropriate amounts of acid-treated CNTs, Al_2O_3, and MoTiAl powders were separately suspended in ethanol under ultrasonication in a water bath equipped with a mechanical stirrer for 2 h. The CNT suspension was then added drop by drop into an Al_2O_3 colloid to form a 3% CNT/Al_2O_3 hybrid. Subsequently, this CNT/Al_2O_3 hybrid was slowly incorporated into desired amounts of MoTiAl colloid, followed by mechanical stirring for 0.5 h. Finally, the Al_2O_3-CNT/MoTiAl composite powders were obtained after completely drying in a vacuum at 353 K.

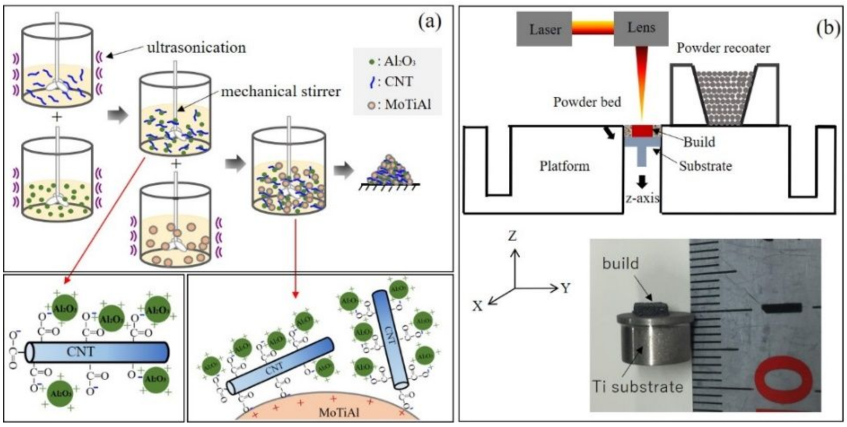

Fig. 1 Schematic illustration for (a) powder fabrication and (b) L-PBF process.

An in-house developed L-PBF machine, as shown in Fig. 1b, was utilized to process composite powders. This machine is equipped with a Yb: YAG fiber laser source, which produces a laser beam with a wavelength of 1070 nm and a maximum power of 22 W in continuous mode. A set of optimized L-PBF parameters, corresponding to the laser power of 20.6 W, scan speed of 10 mm s^{-1}, hatching distance of 100 µm, layer thickness of 25 µm, and “X–Y alternately scanning strategy”, was utilized for fabricating rectangular builds (~4 × 4 × 1.4 mm^3). The microstructure was evaluated via SEM, EBSD, EMPA, and TEM analysis. The mechanical performance was evaluated using a microhardness tester. Oxidation tests were conducted isothermally at 1173 K for 1 h in a thermogravimetric analyzer with an air flow of 100 ml/min.

４．研究成果

(1) Fabrication of uniform nanoceramic/metal composite powders for L-PBF

Fig. 2 shows the morphologies of 10%Al_2O_3-0.31%CNT/MoTiAl mixed powders via FESEM. The uniform dispersion of Al_2O_3 (see white granule phases in Fig. 2a-b) was observed. The Al_2O_3 nanoparticles are tightly and sparingly covering the surface of MoTiAl so that the MoTiAl powders remain in their original states, particle size and distribution. No obvious aggregation of Al_2O_3 was present. Few Al_2O_3 clusters were detected beyond 10%. That is mainly attributed to the limited contact surface of MoTiAl as compared to the total surface area of Al_2O_3 nanoparticles during powder mixing. Fig. 2c-d shows that the attached CNTs on the surface of CNTs (see black arrows). The critical role played by CNTs in bridging the Al_2O_3 and MoTiAl powders as predicted in Fig. 1a was exactly clarified. It is found that several Al_2O_3 nanoparticles coating the surface of a CNT, one tip of which is intimately bonded to a MoTiAl powder (Fig. 2c). Fig. 2d displays two CNTs partially wrapped with Al_2O_3 lying on the surface of the MoTiAl powder.

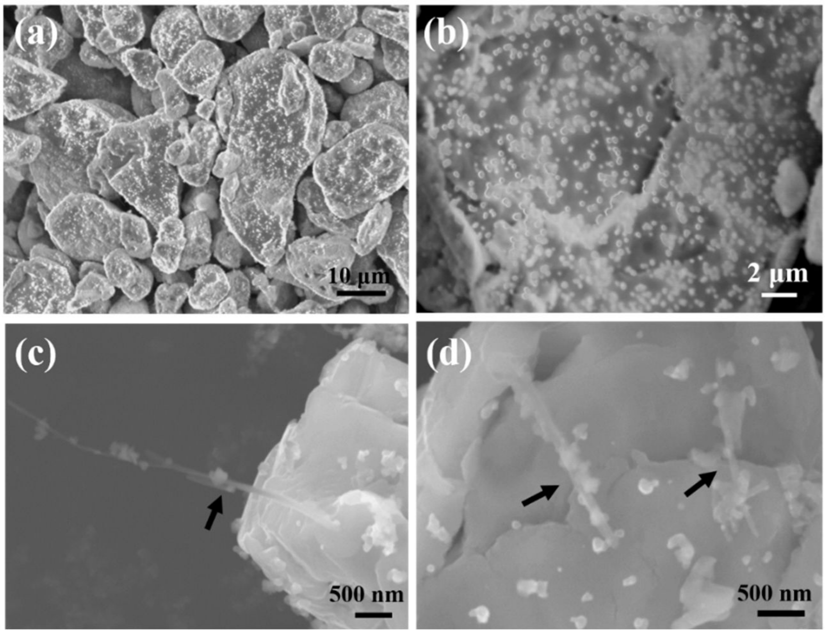

Fig. 2 SEM images of the 10%Al_2O_3-0.32%CNT/MoTiAl mixed powders.

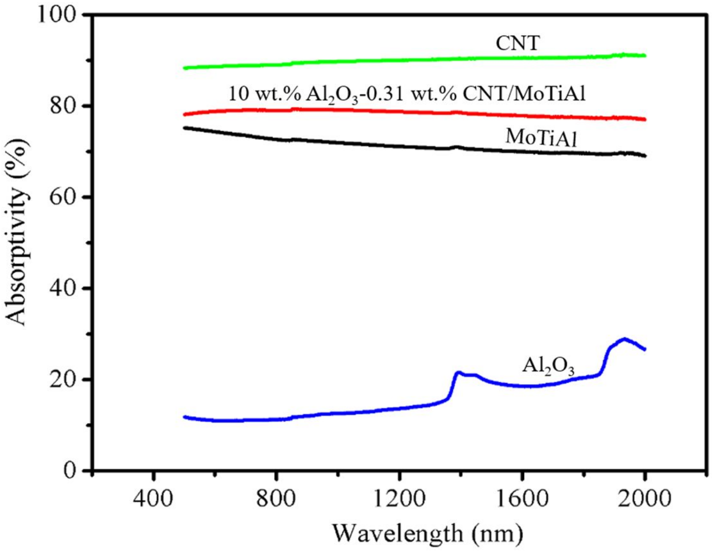

Fig. 3 Laser absorptivity of Al_2O_3, MoTiAl, 10%Al_2O_3-0.31%CNT/MoTiAl, and CNT powders as a function of laser wavelength in a range of 500–2000 nm.

It is known that laser absorptivity of powders is a key factor for influencing L-PBF processability. It directly determines how much power the powders absorb at a certain laser wavelength to form a melt. Fig. 3 shows the laser absorptivity of different powders as a function of wavelength. At the wavelength of 1070 nm used in this work, the laser absorptivity of CNT or MoTiAl was approximately 89.8% or 71.6%, respectively; in contrast, Al_2O_3 possesses a significantly lower value of 12.8%. It seems that Al_2O_3 is incorporated to reduce the absorptivity of MoTiAl powders. However, the absorptivity of 10%Al_2O_3-0.31%CNT/MoTiAl powders was determined to increase by 10.3%. This interesting result is due to an increased surface roughness of Al_2O_3-coated MoTiAl. In short, I have successfully fabricated the Al_2O_3-coated MoTiAl powders by using the CNT agent. The mixed powders remained similar in shape, particle size, and distribution to uncoated ones, simultaneously showing higher laser absorptivity, thus they are suitable for L-PBF.

(2) In-situ depositing tight ceramic layer on Mo-based composites with an enhanced oxidation resistance

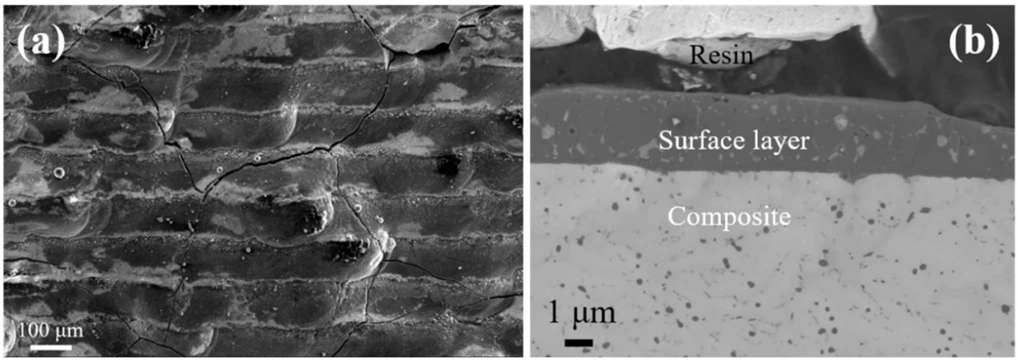

Fig. 4 (a) Surface morphology and (b) longitudinal cross section near the surface part of a L-PBF-processed Mo-based composite build.

After L-PBF processing of the 10 wt.%Al_2O_3-0.31wt.%CNT/MoTiAl mixed powders, the Mo-based composite build was fabricated. However, because of the intrinsic brittleness of Mo-based alloys and the possible high residual thermal stress arising from the rapid cooling, internal microcracks were formed in the composite builds (Fig. 4a). Moreover, a thin ceramic layer was in-situ formed on the composite during the L-PBF process (Fig. 4b). The surface layer consisted of an α-Al_2O_3 matrix with a dispersed TiC phase and had a controllable thickness. Meanwhile, the Al_2O_3 and TiC nanoparticles were homogenously dispersed and tightly contacted with the matrix, giving rise to an enhanced Vickers hardness. The TiC phase was formed via a reaction of CNTs and Ti atoms during L-PBF.

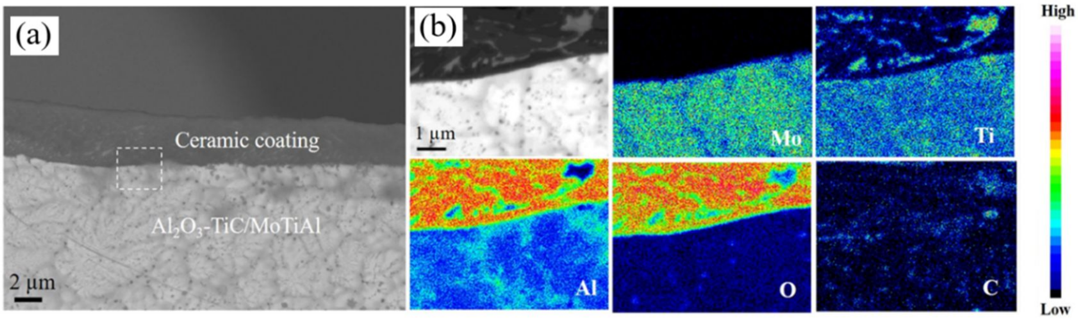

Fig. 5 (a) SEM image of an L-PBF-processed Al_2O_3-CNT/MoTiAl composite build in the longitudinal cross section near the surface part after oxidation test. (b) BSE image and EPMA elemental mappings taken from the white square in (a).

Fig. 5 displays the morphology of a 10 wt.%Al_2O_3-0.31wt.%CNT/MoTiAl composite build in the longitudinal cross section after oxidation at 1173 K for 1 h. Without the ceramic coating, an oxide layer consisting of Al and Ti oxides was introduced on the surface the MoTiAl alloy build. However, for the composite build, in contrast, no oxide layer formed between the ceramic coating and the composite (Fig. 5a-b). This result suggests that the ceramic coating could effectively increase the oxidation resistance by limiting the penetration and diffusion of oxygen atoms.

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３．雑誌名 Materials & Design	６．最初と最後の頁 109132～109132
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.matdes.2020.109132	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 Zhou Zhenxing、Guo Suxia、Zhou Weiwei、Nomura Naoyuki	４．巻 11
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3．雑誌名 Materials Science and Engineering: A	**6．最初と最後の頁** 142848～142848
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.msea.2022.142848	**査読の有無** 有
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〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関