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Original Article

# Combustion synthesis of $MoSi_2$ based composite and selective laser sintering thereof

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ABSTRACT

Additive manufacturing is gaining increasing attention as it provides cost-effective and waste-less production of materials with multi-axis geometries. Selective laser sintering of ceramics is very challenging in terms of poor sinterability caused by low thermal shock resistance and insufficient electron conductivity blocking absorption of laser beam energy.

Here, we present a novel strategy for manufacturing dense, hierarchically structured ceramics, particularly, $MoSi_2$-based composites by selective laser sintering. $MoSi_2$-Si composite powders were prepared by combustion synthesis technique, where the ceramic grains were covered with different amount of Si. $MoSi_2$-Si powder was consolidated by selective laser sintering reaching 92% of density. The hardness of the manufactured samples varied with the amount of Si and applied laser current from 7.7–11.4 GPa. The maximum value of the compressive strength was determined to be 636 MPa. The manufactured $MoSi_2$-Si was subjected to nitridation, which resulted in the growth of $Si_3N_4$ fibres on the surface and pores of the samples.

## 1. Introduction

The progress of the enabling technologies provides the best platform for cooperation across industry and science sectors and generates economic growth. Since approbation of the first commercial 3D printer in the 1980s, a manufacturing process shifts to a digital model in which the entire industrial sector evolves to become more local and entrepreneurial, changing towards creativity and design thinking.

The traditional means of fabrication for complex-shaped parts usually involve a series of steps resulting in huge material waste and a high labour cost along with limitations on design complexity. Despite the fact that the conventional net-shaping processes, such as ceramic injection moulding, slip casting, etc., enable large-scale production of complex-shaped components, they are not economically competitive in the case of small-scale production because of the need in costly tailor-made mould.

Being cost-effective and in some cases irreplaceable technique, 3D printing or additive manufacturing (AM) expanded the range of applications in modern industries, such as automotive, aerospace, defence, electronics and robotics sectors [1–3]. It allows minimization of manufacturing time, generated waste of materials, and energy consumed. Moreover, with the help of AM technique, the near-net shape structures can provide unprecedented control over an internal porosity of compounds, that is highly demanded by medicine, particularly for the preparation of body prostheses, dental and tissue engineering scaffolds [4,5].

Fabrication of ceramic parts by additive manufacturing is a challenging task, because of the high melting temperature, low thermal shock resistance, high thermal stability, high viscosity of the molten ceramic, etc. Several studies have reported fabrication of the fully dense ceramic parts with tailored mechanical properties; for example, the high density of structural ceramics ($Al_2O_3$, density > 97%; SiC, density > 95%, $Si_3N_4$ density > 99%) were achieved by robocasting [6]. However, the parts suffer from an anisotropic strength. Technology of fused deposition of ceramics (FDC) was successfully applied to processing WC/Co, $Al_2O_3$, and $Si_3N_4$ [7]. However, the huge amount of the required binder phase (50–60 vol.%) resulted in an anisotropic shrinkage and presence of defects deteriorating the mechanical properties. The obtained high density of $Si_3N_4$ part (96%) provides a comparable bending strength to those of extruded and iso-pressed samples

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[7]. Viscous suspensions of ceramic particles (60 vol.%) were also prepared to fabricate $Al_2O_3$ based materials by Ceramic On-Demand Extrusion (CODE) resulting in production of the high-density component after drying and high-temperature sintering [8]. It was suggested that the remained 1.5% porosity was caused by the bubbles in the paste, which can be eliminated via optimizing the drying process. One of the most commonly employed 3D printing techniques is stereolithography, which provides a good precision feature and a smooth surface of the products. Stereolithography enables production of the nearly full density and, therefore, mechanically reliable ceramic parts (e.g. zirconia [9], zirconia-toughened alumina [10], $Si_3N_4$ [11,12]) for industrial and biomedical applications. However, the stereolithography exhibits up to 60% shrinkage and geometric changes, which makes the technology uncertain.

Fabrication of ceramic parts by the selective laser sintering represents a fascinating challenge. Ceramics usually suffer from high level of porosity, poor interlayer adhesion, and low mechanical properties [13,14]. In [15], the potential of the selective laser sintering for consolidation of $Al_2O_3$-$ZrO_2$ based materials with almost 100% density and flexural strength above 500 MPa was highlighted exploiting the complete melting of the powder and no any post-treatment. Development of defects was overcame with the help of high temperature preheating up to1600 °C [15].

Several factors should be taken into account for successful launch of the SLS. Among them there are:

(i) *State of the powder during sintering.* By traditional techniques, densification of ceramics are usually relatively time-consuming process. In the case of SLS, the high-intensity laser heats the target over a microsize sport for a short period of time preventing diffusion. For a liquid phase sintering, a binder material (e.g. metal, polymer or glass) of comparatively low melting point is required to bind the ceramic particles.

(ii) *Powder flowability* is a key parameter greatly influencing powder bed density, which affects the sintered part quality including density, roughness, etc. Powder particle shape and size as well as particle size distribution play an important role in sintering kinetics and powder bed formation. For example, the spherical particles of the narrow size distribution have better flowability as compared to the angularly shaped powders. The density of the powders is another very important characteristic that deserves attention when choosing the powder for SLS.

(iii) *Laser beam-powder interaction.* The SLS laser should be carefully chosen taking into account the material to be sintered. For instance, the $CO_2$ laser with a wavelength of 10.6 μm is well absorbed by polymer powders and oxide ceramics; while Nd:YAG laser with wavelength of 1.06 μm is well absorbed by metals and carbides [16]. The materials absorbing at a short wavelength have a higher processing window when Nd:YAG is applied [16]. However, the $CO_2$ laser provides wider processing window, including energy density, particle size ranges for a large number of materials (e.g. HAPEX®) [17].

(iv) *Composition.* In general, laser sintering of a single-component powder is a complicated process due to the narrow processing window [18]. The single-component powder has to be densified at the well-established processing parameters (e.g. laser power, scanning speed, scan line spacing, temperature of the powder bed, etc.) usually exploiting complete melting of the powder. Full melting may cause a number of undesired effects, such as merging of droplets and minimising the surface energy. Formed liquid zone and temperature gradient can generate Marragoni convection, namely, mass flow from regions with a low surface tension to regions with a high surface tension. Marragoni flow may cause a tendency to balling of alloys containing a sufficiently high content of surface active elements during SLS [19].

(v) *Impurities.* Even the traces of oxygen influence dramatically the sintering of the powder. For instance, Fe containing 0.1 wt% oxygen has a much higher tendency to balling than Fe containing 0.02 wt% oxygen due to a higher surface tension gradient. Therefore, the addition of small amount of carbon as a deoxidizing agent to iron decreases the surface tension gradient and allows to obtain smoother layer [19]. The existence of impurities in the chamber (e.g. oxygen) usually changes the optical properties of the powder and hampers sintering [18].

(vi) *Scanning strategy.* Laser power, scanning speed, hatch spacing, and layer thickness have a high impact on the densification, microstructural features, and mechanical properties of the final part. The scanning parameters vary from powder to powder and should be optimized as a complex and evaluate their combined effect. For instance, the low scan speed of Fe powders prevents balling and leads to the formation of smooth layer [19]. A similar tendency is observed in the case of NiAl alloy [20]. However, the slow scan speeds result in pores development from gases trapped within the melt pool or evolved from the AlSi10Mg powder during consolidation [21]. In addition, evaporation of the molten material can harm a laser window and disrupt the delivery of the laser power. The evaporation of the material can be prevented by decreasing the laser power. To build a part with the full density and desired properties, complex optimization of all parameters (laser power, scanning speed, hatch spacing, and layer thickness) is necessary to successfully build the near full-density parts.

In this work, we report a novel strategy to fabricate ceramic parts, particularly $MoSi_2/Si_3N_4$ composite by the selective laser sintering. The strategy includes synthesis of ceramic/metalloid (particularly, $MoSi_2$/Si) composite powder enabling melting of the metalloid component and sintering by SLS technique. After consolidation the unique ceramic/metalloid composite is subjected to functionalizion (particularly, nitridation) converting the part into ceramic/ceramic composite (particularly, $MoSi_2/Si_3N_4$). Fig. 1 represents the scheme of the proposed approach. The effect of the amount of silicon and SLS conditions (laser current, point distance, exposure time) on the sinterability and density

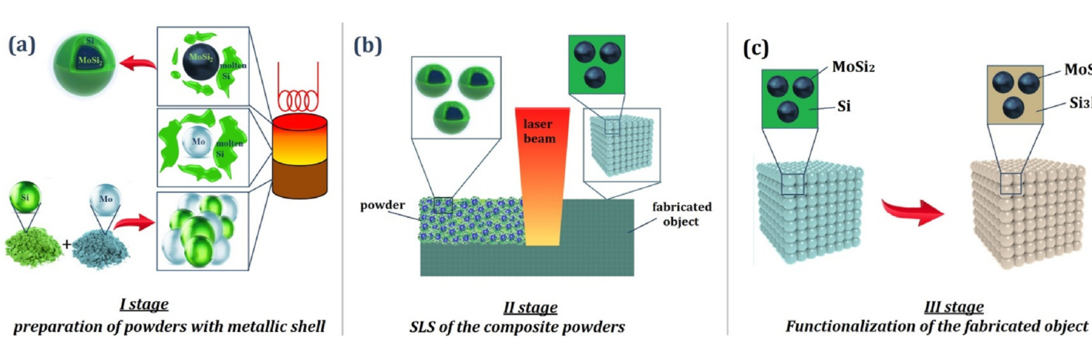


**Fig. 1.** The schematic representation of the novel strategy for fabrication of ceramic composites by selective laser sintering.