Potential of cold spray technology for 3D printing of dense TiO_2 green parts

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Abstract: Manufacturing ceramic parts, generally involves forming a green body and heating it to fuse the particles together, thereby densifying the part. Methods such as powder compaction in a die cavity using mechanical pressing, slip casting, and injection molding are widely employed in the industry for green body formation. However, these methods are costly, complex, and time-consuming. Recently, various 3D printing technologies have been adapted for manufacturing ceramic parts. These include slurry-based methods such as stereolithography and inkjet printing, powder-based systems like selective laser sintering/melting and binder jetting, and bulk solid-based methods such as laminated object manufacturing and fused deposition modeling. Regardless of the forming technology, the green density of the printed preform is a vital factor in achieving fully dense parts with high dimensional accuracy after firing. Among all these methods, injection molding achieves the highest green density, ranging from 75% to 85%, while 3D printing methods typically achieve green densities between 40% and 60%. Therefore, post-processing techniques such as cold isostatic pressing are often employed to enhance the density of parts up to 85%. In this research, we evaluate cold spray technology potential for 3D printing green TiO_2 parts with exceptionally high green density. By leveraging the supersonic impact of TiO_2 agglomerates, we demonstrate the ability to fabricate dense 3D structures with green densities ranging from 70% to 80%. Subsequent sintering further increases the density to well over 96.2%. This approach eliminates the need for powder modification, allowing as-received powders to be directly fed into the system for free-forming 3D printing, offering significant technical and cost advantages over conventional 3D printing techniques. These attributes can position cold spray as a promising manufacturing method in digital printing technologies.

Keywords: Cold spray additive manufacturing, TiO_2 nanoparticles, green density.

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1. Introduction

Ceramic manufacturing is one of the oldest technologies in human history. Thousands of years ago, early civilizations discovered that shaping clay and allowing it to dry could produce functional objects such as pots and plates. Over time, they learned that firing the dried clay significantly enhanced its strength and durability. This foundational practice laid the groundwork for a technological evolution that continues to influence modern materials science. Today, ceramics are essential not only in household items but also in advanced applications such as electronics, and sensors. Despite the progress in ceramic technology, the fundamental manufacturing process remains largely unchanged: forming the material into its final shape, followed by high temperature sintering to densify and strengthen the structure. The unique properties of ceramics, including ionic atomic bonding, high melting points, and brittleness pose significant challenges for manufacturing. Conventional metalworking methods like casting, forming, and machining are generally unsuitable for ceramics. Instead, ceramic forming typically begins with a paste, slurry, or powder that is shaped in a mold or die [1]. 3D printing technologies have also found their way into ceramic manufacturing. Methods such as powder bed laser sintering, binder jetting, stereolithography, inkjet printing, ceramic-loaded filament extrusion, and many other innovative techniques have been developed for printing 3D ceramic parts [2]. These traditional and modern processes often require specialized equipment, chemical additives, and controlled environments. Additives such as binders, lubricants, flocculants, and surfactants are commonly used to improve processability, but they can introduce contaminants [3- 5]. While trace levels of contamination may be acceptable in some applications, they can be detrimental in highly sensitive fields like electronics. Between the production methods, pressing powders in a die cavity requires minimal additives. However, this method can induce residual stress and spring back due to the brittle, non-deformable nature of ceramics, leading to cracking [6]. Lubricants can improve powder flow and reduce friction, but without them, the resulting parts are often porous and fragile. Aerosol deposition is currently the only widely established method for forming dense ceramic coatings at or near room temperature without binders or other chemical additives. Fine powder particles (<2 µm) are aerosolized in a gas stream, accelerated through a converging–diverging nozzle, and impacted onto a surface to create a green thick film (up to ~500 µm) with high green density. While effective for thick films, this approach is limited in scope, creating demand for faster, high-density, additive-free techniques for green ceramic components [7].

Cold spray (CS) is a solid-state deposition process in which a carrier gas is accelerated to supersonic speeds through a converging–diverging nozzle, propelling powder particles at high velocity toward a substrate, where they plastically deform upon impact to create both metallurgical bonds and mechanical interlocking. The process involves feeding powder into a heated processing gas, typically below the melting point of the material, and propelling it through a converging-diverging nozzle [8]. For bonding to occur, intimate atomic contact between the particle and substrate is required [9]. However, surface oxides on metallic powders can hinder this bonding by acting as barriers. In the case of ceramics, bonding is even more complex [10]. Most ceramic materials consist of at least two types of atoms (typically, metal and non-metal) held together by ionic bonds. Successful bonding requires not only close atomic proximity but also precise atomic alignment. However, electrostatic repulsion between similar-charged ions can prevent bonding, making cold spray deposition of ceramics particularly difficult. Moreover, the hard ceramic powder particles must undergo deformation to enable the mechanical interlocking feature for bonding during the cold spray process, an added challenge, since ceramics are inherently resistant to plastic deformation.

In this study, we investigate the feasibility of using cold spray technology to fabricate three-dimensional TiO_2 green ceramic parts. While ceramic particles are not expected to form direct bonds upon impact, we hypothesize that it may be possible to control the deposition process such that particles accumulate or condense and form a high-density green structure. We show that cold spray offers a promising a layer-by-layer accumulation of ceramic particles through successive impacts.

2. Materials and methods

The material used in this study was TiO_2 powder, supplied by Tayca Corporation (Japan). Figure 1 presents the morphology of the powder at two different magnifications. As shown, the powder consists of nanoscale primary particles, reported by the supplier to range between 10 and 50 nm, that are agglomerated into larger clusters measuring approximately 1 to 15 µm in size, with a D_{50} of 13 µm. This multiscale morphology renders the powder well-suited for cold spray applications.

A low-pressure SST™ Series P Cold Spray System (CenterLine, Windsor Limited) was employed for the fabrication of printed parts in this study. The system is equipped with a 6.5 mm exit diameter de Laval nozzle. During the experiments, the gas pressure (N_2) and temperature were examined within the ranges of 100–250 Psi and 200–350 °C, respectively. Characterization of the printed parts was performed using a field emission scanning electron microscope (Zeiss UltraPlus FESEM) equipped with an energy-dispersive X-ray spectrometer (EDX) detector. Sintering behavior was evaluated using the TOM-AC optical dilatometer (Fraunhofer ISC). Thermal analyses were conducted using the STA 449 Jupiter simultaneous thermal analyzer. The density of the sintered samples was measured by using Archimedes method. This involved measuring the weight of the samples in both air and deionized (DI) water with an analytical balance with 0.01 mg accuracy.

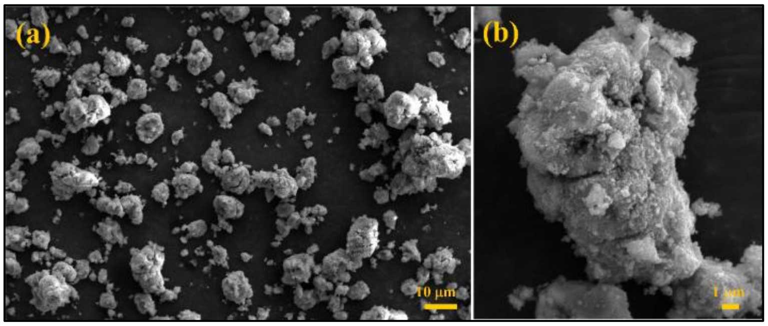

Figure 1. TiO_2 powder at two different magnifications, showing agglomerates of TiO_2 nanoparticles

3. Results and discussion

Figure 2 illustrates the macroscopic and microscopic features of the TiO_2 part fabricated using the cold spray technology. As shown in Figure 2a, the printed part demonstrates well-defined geometry with clean detachment from the build substrate and no visible surface cracking, indicating good mechanical integrity post-deposition. The low- and high-magnification SEM images (Figure 2b and 2c) reveal a textured surface morphology consistent with the porous nature expected from ceramic deposition. Despite the inherent porosity, the material appears to be compacted under the repeated impact of supersonic particles, suggesting particles deformation and the hammering effect contributes to enhanced green density. Notably, as shown in Figure 2d, localized regions of polymeric material are observed within the structure. This contamination, confirmed through SEM and EDX analyses, is likely derived from the feedstock powder and may have played a role in improving particle adhesion during the deposition process.

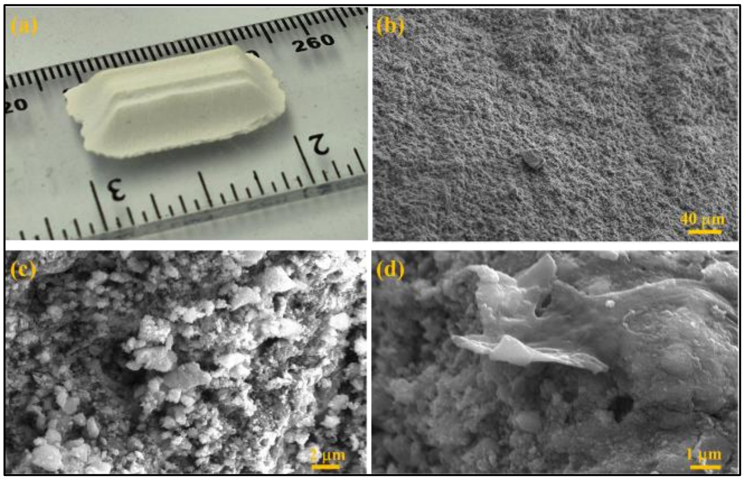

Figure 2. TiO_2 as-printed 3D part, a) with 20 mm length, 12mm width, and 5.5mm height; b) SEM image of the top surface; c) higher resolution SEM image of (b) showing the TiO_2 particles on the surface; d) polymer contamination observed on the surface

To assess the presence of carbon-containing, polymer-like residues in the TiO_2 powder, a thermogravimetric analysis (TGA) was conducted (Figure 3). The results show a total weight loss of approximately 10% as the sample was heated from room temperature to 700 °C. Of this, around 4% occurred below 100 °C, likely due to the evaporation of absorbed moisture. The remaining 6% weight loss, observed between 100 °C and 500 °C, likely indicates the presence of combustible organic material within the TiO_2 powder, confirming the existence of polymeric residues in the raw material.

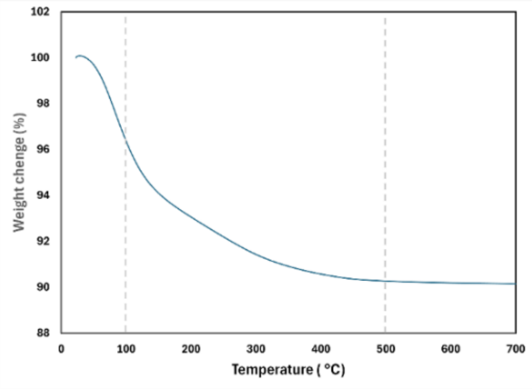

Figure 3. Thermogravimetry analysis of the printed parts

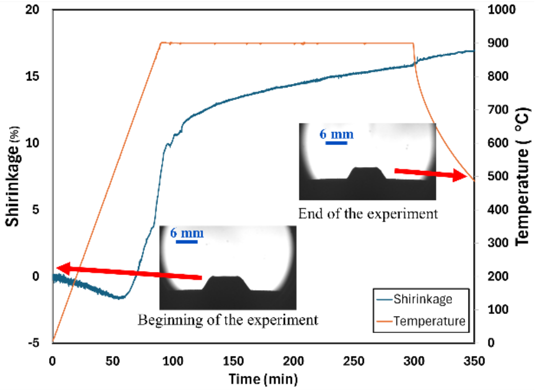

Figure 4. Dilatometry analysis of printed sample showing the dimensional change during heating the sample showing the shrinkage

To assess the sinterability of the printed TiO_2 parts by cold spray, a sample was subjected to thermal treatment using an optical dilatometer. The heating cycle reached a maximum temperature of 900 °C, maintained for 300 minutes, with a heating rate of 10 °C/min from room temperature. Figure 4 presents the shrinkage behavior of the sample as a function of time and temperature, as measured by the optical dilatometer. The curve shows an initial slight thermal expansion up to approximately 275 °C. Beyond this point, a steady shrinkage begins and continues throughout the isothermal hold, resulting in a total shrinkage of approximately 16% by the end of the cycle. Insets in the figure show optical images of the sample at the beginning and end of the experiment, clearly illustrating the dimensional change. Average density of the sintered samples was measured to be 96.2%. Considering the shrinkage observed during sintering, the green density of the printed part is estimated to be approximately 80%, which is relatively high compared to traditional ceramic manufacturing methods and other additive manufacturing techniques [1, 2]. Importantly, the sample remained structurally intact throughout the process, exhibiting no visible cracks or delamination.

Figure 5 shows high-magnification SEM images of the surface of the printed part (Figure 5a) and the sintered part (Figure 5b). Although full densification was not achieved -as indicated by the measured density and the porous microstructure observed in the SEM image of the sintered surface- the TiO_2 particles on the surface exhibit neck formation and growth (as seen in the areas marked by blue circles), suggesting effective sintering. Specifically, the areas marked by yellow circles in Figure 5b highlight micron-sized particles that formed after sintering. These features indicate that the nanoscale

TiO_2 particles, clearly visible in the green part (Figure 5a), fused together during thermal treatment to form larger, coalesced structures.

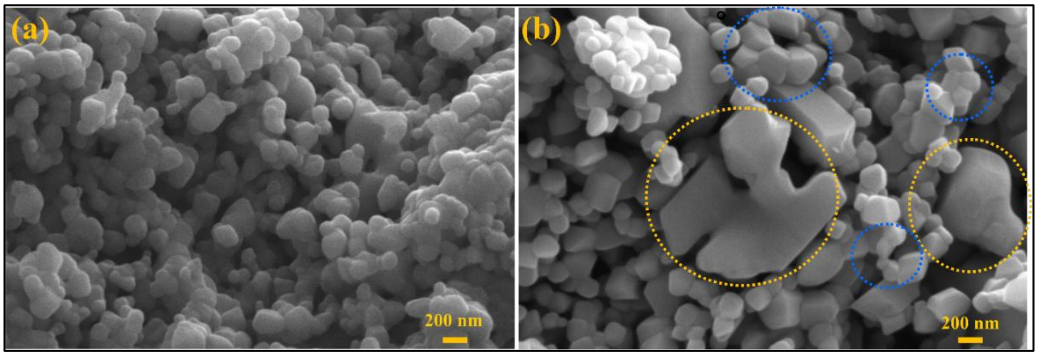

Figure 5. Top surface of the sample: a) before sintering; b) after sintering, showing that the TiO_2 particles sintered together and formed bigger particles

4. Conclusion

This research demonstrates the potential and feasibility of printing 3D ceramic structures - TiO_2 in this case- using cold spray technology. To the best of our knowledge, this study represents the first reported attempt to 3D print ceramic materials using this method. Given the inherent properties of ceramics, TiO_2 particles are not expected to undergo metallurgical bonding during deposition. However, our results show that the particles can be effectively compacted through mechanical impact, forming a relatively high-density green body. Subsequent sintering at 900 °C for 300 minutes resulted in a densified structure with approximately 16% shrinkage. The final density of the sintered parts was measured at 96.2%, indicating that the green body had an initial density of approximately 80%, which is relatively high compared to other ceramic manufacturing methods.

While this is an exciting first report of this printing technique, further research is needed to explore the bonding mechanisms between particles; examine the role of observed polymeric contamination in the TiO_2 powder on the strength of the green parts and their printability; optimize the sintering process; characterize the micro- and macro-scale properties of the printed parts; develop methods to maximize green body density; and evaluate the repeatability of this approach with other non-metallic materials.

5. Acknowledgments

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