Modification of Magnesium-Aluminate Spinel Powder for Thermal Spray Applications

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Abstract. Magnesium–aluminate spinel is a promising alternative to alumina for electrical insulation coatings in transport applications due to its high electrical resistivity and chemical stability. However, its low density, moderate hygroscopicity, and high melting point limit powder flowability, reduce molten particle formation in atmospheric plasma plume, and increase coating porosity. To address these issues, a novel transition-metal-doped magnesium–aluminate spinel powder was formulated and synthesized via an industrially scalable high-temperature solid-state route. Three different powder modification approaches were applied to improve flowability and tested in a standard thermal spray powder feeder to verify their transferability between thermal spray workshops. The first approach, based on chemical modification using binding or organic agents, had no effect on powder morphology and improved flowability only during the first spraying cycle. After interruption of the process, the powder accumulated in the feeding system, making this solution unsuitable for industrial scale-up. The second approach, spray drying, promoted partial spheroidization but exhibited similar flowability limitations. The third approach, thermal modification using two high-temperature prototype technologies, promoted initial powder spheroidization and the completion of residual phase reactions. Due to limited production capacity, only one variant was tested further. It demonstrated good powder flowability and high moisture resistance.

1. INTRODUCTION

Solid feedstock thermal spray powders can be classified as a specific group of functional application- driven materials, such as metals, composites, and ceramics, characterized by their guaranteed flow behaviour, a narrow particle size distribution from 25 to 150 µm, and highly scalable industrial production ranging from tens to hundreds of kilograms [1, 2]. However, even their number in terms of chemical compositions available on the market is quite limited, focusing mainly on major thermal spray application areas in the transport, energy, and general engineering industries. This demanding market is nowadays increasingly vulnerable and threatened by non-European countries in the delivery of raw materials, due to export license control [3].

Therefore, the development of new thermally sprayable solid feedstocks as alternatives to the existing ones becomes more important to ensure the sustainability of key industrial sectors in Europe. For the newly developed thermally sprayed powders, one key technological characteristic that must be achieved is flowability, which provides the consistent powder feeding into a torch and directly impacts coating quality.

This is especially challenging for ceramic powders when compared to metallic and composite ones because the contribution of density, particle morphology, triboelectric charge and hygroscopicity is much greater, and therefore various approaches must be used to improve their flowability.

Magnesium-aluminate spinel is considered as an alternative candidate to conventionally used alumina electrical insulation thermal-sprayed coatings in bearing transport applications [4] because of its low density (3.58 g/cm^3), wide band gap energy, low dielectric constant (ε=7.5), high electrical resistivity, and high resistance against chemical attack [5]. To overcome the limitation of its high melting point (2135 °C), reduce the porosity of the thermally sprayed coating, and increase its electrical resistivity, a new formulation of spinel doped with a transition metal element was developed. However, after solid-state synthesis, milling, and sieving, the powder was observed to be non-flowable. Therefore,

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several different strategies for its modification were designed and further tested directly in the thermal spray powder feeder. In the end, only one exceptional route was identified, providing both smooth spinel powder flow and resistance to ambient moisture.

2. SYNTHESIS OF SPINEL POWDER

The reactants were purchased commercially and used as received without further purification: aluminum(III) oxide (Al_2O_3, p.a., Lachner), magnesium(II) oxide (MgO, p.a., Penta), and a transition metal oxide MO_x (99.9%, Sigma Aldrich). The MO_x-Al_2MgO_4 powder samples were synthesized via a 2-step process composed of: (i) mechanochemical milling in a planetary ball mill (Pulverisette 6, Fritsch GmbH, Germany), and (iii) high-temperature solid-state reaction in a laboratory furnace (2017S, Clasic, Czech Republic) performed in platinum crucibles with volumes of 160 ml and 100 ml, as shown schematically in Figure 1. The reactants were weighed using a laboratory scale (Pioneer Plus PA, Ohaus Corporation, Switzerland) and subsequently milled in a planetary ball mill at 450 rpm for 10 minutes using a demineralized water as the milling medium. For milling, an agate milling jar with a volume of 0.5 dm^3 and 25 pieces of agate milling balls with a diameter of 20 mm were used. After milling, the milling balls were collected, and the suspension was poured into the stainless-steel bowl without additional rinsing. Before the next milling batch, the milling jar and balls were rinsed with demineralized water, and the process was repeated 7 times to obtain the required amount of ceramic suspension.

A mechanochemically prepared ceramic suspension was dried in a laboratory dryer (SLW 53-W STD, Pol-Eko Aparatura, Poland) at 105 °C for 6 h, producing both highly agglomerated and less agglomerated powders. Based on the dried powder's appearance, the dried material was divided into 2 fractions, namely: (i) spinel bulks (approximately 700 g), (ii) spinel powder (approximately 350 g). These fractions were heat-treated separately at 1500 °C with a 3-hour dwell time to promote the solid-state reaction between the oxides. Hypothetically, for solid-state reaction products, we presumed differences in phase composition between the sintered bulk and the sintered powder.

Sintered samples-spinel bulks and spinel powder were processed separately, firstly milled in a vibratory disc mill (RS200, Retsch GmbH, Germany) in a 200 ml stainless steel milling chamber for 13 seconds at 700 rpm. Then, the powders' rheological properties were enhanced in terms of flowability, necessary for the application in atmospheric plasma spray coating technology.

3. POWDER MODIFICATION

The synthesized powder was separated into two fractions, below 25 µm and 25–75 µm, using an automatic sieving machine AS200 Control (Retsch GmbH, Germany) before further flowability modification. Powder particles larger than 75 µm were repeatedly milled in the planetary ball mill Pulverisette 6 (Fritsch GmbH, Germany) to reduce the particle size to fit the indicated range. Three different powder modification strategies were than used: (i) Modification by organic agents, where binding dispersion for the powder size in a range 25–75 µm was used, in a laboratory dryer (SLW 53-W STD, Pol-Eko Aparatura, Poland), and crushed in a agate mortar, (ii) Modification by spray drying, where an initial stable suspension containing a powder particles below 25 µm with polymeric binder was produced and spray dried using a Mini Spray Dryer B-290 (BUCHI Labortechnik AG, Switzerland), and (iii) Thermal spray processing route, where two developed prototype units with different temperature regimes were applied, including a non-isothermal high-temperature plasma (CEITEC, Czech Republic) and a low-temperature flame plume (FunGlass, Slovak Republic).

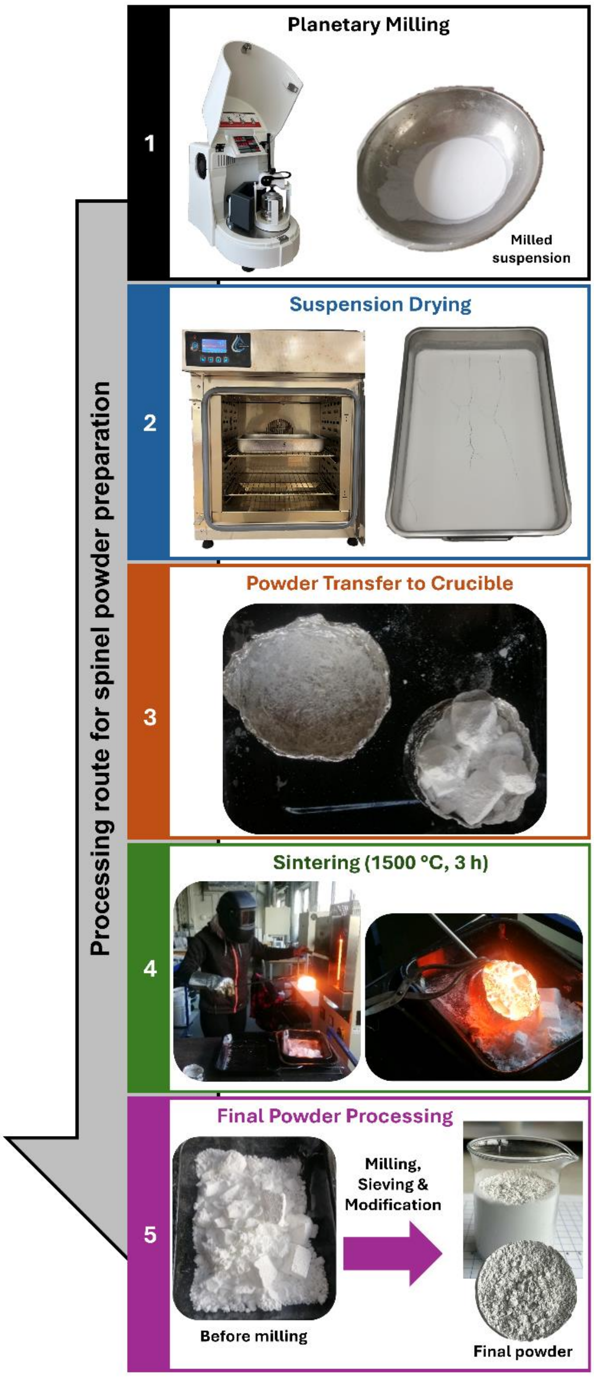

Figure 1. Processing route for spinel powder preparation.

4. POWDER CHARACTERIZATION AND TESTING

The powder morphology was examined and documented using scanning electron microscopy (SEM; Lyra3, Tescan, Czech Republic) in backscattered electron (BSE) mode.

Powder X-ray diffraction (PXRD) data at room temperature were collected in Bragg–Brentano geometry in reflection mode using monochromated Cu Kα radiation (λ = 1.54056 Å) on a Rigaku SmartLab 3 kW diffractometer (Rigaku, Japan), operated at 30 mA and 40 kV. Data were recorded over a 2θ range of 15–90°, with a step size of 0.02° and a scan rate of $3°\cdot min^{-1}$.

Thermogravimetric analysis (TGA) was performed using a TGA-Discovery thermogravimetric analyzer (TA Instruments, USA) under a pure nitrogen atmosphere ($25\ ml\cdot min^{-1}$). The sample was heated from 30 to 150 °C at a heating rate of $10\ K\cdot min^{-1}$ and held isothermally at 150 °C for 30 min to avoid any decomposition of organic agents (e.g. decarboxylation). The sample mass was approximately 25 mg.

A PF-50 powder feeder (FST, Netherlands), equipped with a heating jacket, was used for modified powder flowability testing.

The powder obtained after synthesis, crushing and sieving consisted of irregularly shaped agglomerated particles (Figure 2a). Its phase composition was a nearly single phase having a transition metal-doped magnesium-aluminate spinel as a major phase (98.5 wt.%), and a small amount of unreacted initial phase of MgO was still detected. The as-synthesized powder without any further modification did not exhibit flowability.

The powder modified with organic agents showed partial spheroidization of the particles (Figure 2b) while maintaining the same phase composition. Initial signs of improved flowability were observed. However, testing in a thermal spray feeder revealed that, although the powder flowed satisfactorily after aeration and filling, its flowability deteriorated whenever the spraying process was interrupted. In subsequent spraying cycles, the powder accumulated within the feeder transport system unless additional cleaning was performed.

Spray dried powder produced from a fine powder suspension exhibited a more regular spheroidal particle morphology (Figure 2c), which was expected to improve powder flow due to reduced mechanical friction. However, the experimental flowability behaviour was found to be similar to that of the powder modified with organic agents, producing a powder buildup in the feeder system in the next cycle after interruption of the process. Powder accumulation in the transport system was observed for both variants, regardless of whether powder preheating in the feeder was applied.

The prototypes developed for thermal powder modification at CEITEC and FunGlass research centres enabled remelting of the powder particles into a highly spheroidal morphology. As apparent from Figures 2d and 2e, the melting temperature had a pronounced effect on the internal structure of the spheroidized particles. Both approaches also resulted in a noticeable purification of the spinel phase (Figure 3), showing a pronounced decrease in MgO impurity content. Unfortunately, the powder modified at a lower temperature was produced in only a limited quantity, which was insufficient for further powder feeder testing. In contrast, the second approach promoted excellent flowability and, more importantly, high resistance to ambient moisture. This performance was maintained regardless of whether powder preheating was used and remained unchanged even after several months of storage.

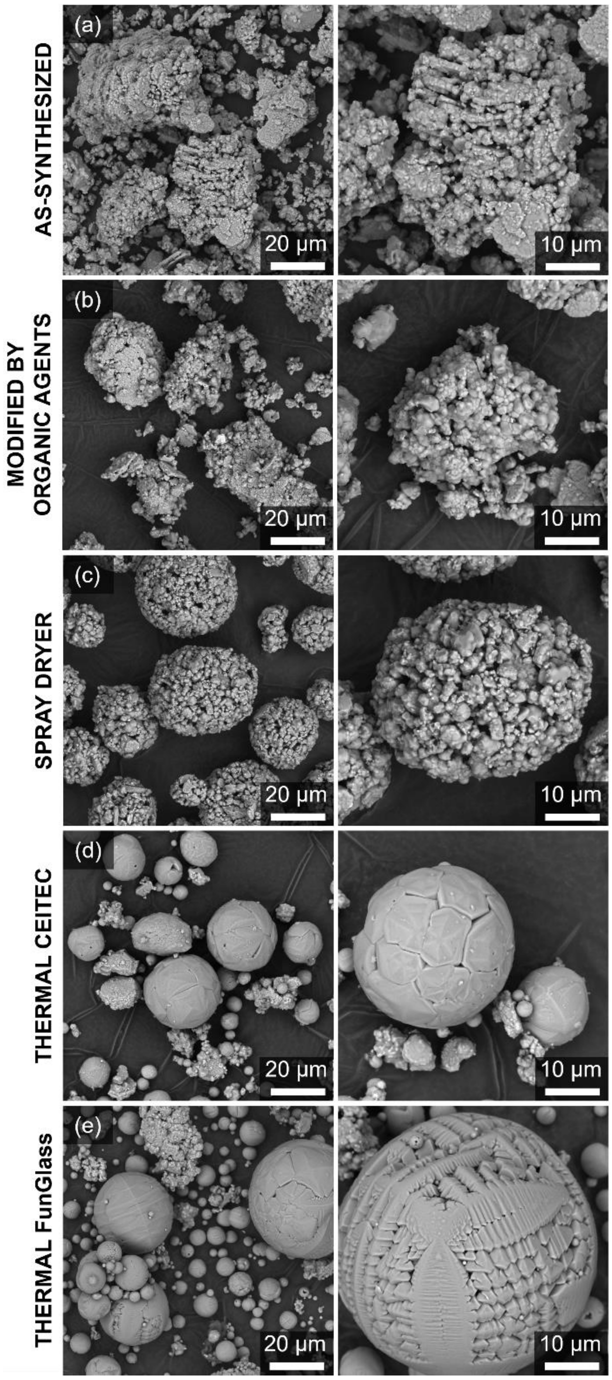

Figure 2. Surface morphology (SEM-BSE) micrographs of the transition-metal-doped magnesium–aluminate spinel powder in different states: (a) as-synthesized, (b) modified by organic agents, (c) processed by spray drying, (d) thermally treated using the CEITEC prototype, (e) thermally treated using the FunGlass prototype.

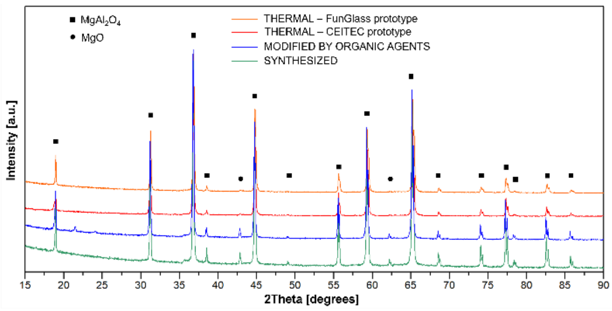

Figure 3. XRD diffractograms of transition-metal-doped magnesium–aluminate spinel powders in different states: as-synthesized (green), modified with organic agents (blue), thermally treated using the CEITEC prototype (red), and thermally treated using the FunGlass prototype.

The TGA measurements showed that the powder becomes more susceptible to moisture when an organic agent is used for its modification rather than the magnesium-aluminate spinel itself (Figure 4). Reducing the organic content to ensure the flowability of thermal spray powders is just as challenging as it is for pharmaceutical products [6]. It is clear that the lowest moisture absorption losses in the powder were measured for non-modified powders in their as-synthesized state and for thermally modified powders.

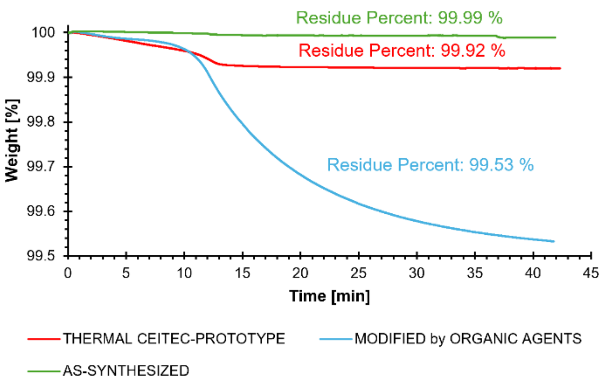

Figure 4. TGA curves of absorbed moisture loss in magnesium–aluminate spinel powders: as-synthesized (green), modified with organic agents (blue), thermally treated (red).

5. SUMMARY

A new formulation of a transition metal-doped magnesium-aluminate spinel powder was successfully synthesized. Three powder-to-powder modification approaches by (i) organic reagents, (ii) spray drying, and (iii) thermal technologies were designed to ensure the synthesized ceramic powder flowability. The first two approaches promoted temporary powder flow once the powder was filled into the feeder, but only until the thermal spray process was interrupted for the first time. The thermal approach enabled remelting of the synthesized spinel, resulting in particle spheroidization, enhanced purification through the completion of reactions with unreacted species, and revealed high resistance to ambient moisture, and ensured exceptional, reproducible flowability even after several months of powder storage. The flowability of the thermally modified powder was predominantly ensured by its change into a highly spherical morphology, which reduced friction between particles, and by an insignificant amount of organic reagents capable to absorb moisture. The resulting synthesized and thermally modified thermal spray powder, with a particle size in the range of 25–75 µm, fulfils the purity and flowability requirements and can be further scaled up for industrial production.

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