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Study on the plasma sprayed amorphous diopside and annealed fine-grained crystalline diopside

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Abstract

Natural diopside $CaMgSi_2O_6$ was processed by plasma spray technique into self-supporting plates. The experimental powder for spraying came from as-mined natural diopside and was crushed and sieved to the proper size for plasma spraying with a water-stabilized plasma torch (WSP). By removing the substrates after cooling, self-supporting plates (SSP) were obtained. These deposits were further studied with optical microscopy, SEM, X-ray diffraction, thermal analysis, mechanical tests and dielectric spectroscopy. Microhardness was measured on cross-sections prepared for microstructure observation. Wear resistance in wet conditions was tested as well. Dielectric properties of capacitor samples prepared from the self-supporting sprayed deposits were measured at low voltage. The results showed that diopside is an interesting candidate for various electrical applications as it has similar dielectric behavior as alumina or silicates. Thermal annealing of the SSP was done. Despite crystallization of the amorphous fraction (present after spraying) into a fine-grained structure, annealing worsened slightly dielectric responses of diopside. Differences between diopside and other silicates sprayed by the authors in the past are discussed.

Keywords: C. Dielectric properties; Plasma spraying; Diopside; Annealing

1. Introduction

Diopside is a calcium and magnesium silicate with the chemical formula $CaMgSi_2O_6$. It is a mineral from the diopside–hedenbergite series and forms solid solutions between $CaMgSi_2O_6$ and $CaFeSi_2O_6$. Diopside belongs to inosilicates, the calcic pyroxenes group, and its melting point is at 1390 °C. The origin of the mineral name is from two Greek words: "double" and "appearance" because the vertical zone of its crystal prism can be oriented in two ways. This mineral is monoclinic (2/m) and belongs to the C2/c space group. Diopside is common in metamorphic rocks. Transparent varieties of diopside are used as gems. The pyroxene structure consists of single chains of SiO_4 tetrahedra extending along the *c*-axis [1,2]. Diopside as a material is among others suitable also for ceramic glazes [3] or as an addition to porcelain improving its sintering [4] and mechanical strength [5].

Diopside is considered a prospective material for covering Mg-based bone implants [6] or dental implants [7] to improve their durability. It could also serve as a host material for persistent luminescence nanoparticles [8]. Plasma sprayed coatings of diopside on a Ti–6Al–4V alloy were made by a gas-stabilized plasma torch [7]. The XRD pattern belonging to diopside and several low-intensity peaks originating from cristobalite (SiO_2) were assigned to the feedstock powder (raw mineral) [7]. The XRD pattern of the coating indicated [7] that it is primarily composed of a diopside phase and an amorphous material.

Diopside is also suitable for the low-temperature co-fired ceramic (LTCC) technology applied in electrical industry as a substrate material [9,10] for its low relative permittivity minimizing signal propagation delay and for its low loss factor

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as well. As the microwave dielectric properties of diopside glass–ceramics depend on the degree of crystallization, enhancing these properties was reported to require an increase in crystallinity [11]. Relative permittivity of crystalline diopside was 9.7 and loss factor 0.0016, whereas for amorphous diopside it was 8.9 and 0.0021 respectively [12]. Lower permittivity together with a higher loss factor represents worse dielectric behavior in case of the amorphous material. The dielectric polarizability was reported as high as +15.9% for amorphous diopside whereas it was only +1.2% for crystalline diopside [12]. Such a finding indicates less proper response of the amorphous diopside especially at low frequencies. Materials for LTCC must have a low sintering temperature to co-fire with highly conductive electrodes such as silver, gold and copper (melting points 961 °C, 1064 °C and 1083 °C respectively) [13]. Plasma spraying offers preparation of silicate glasses on many kinds of substrates without thermal damage of the substrate [14–16]. Various silicates have dielectric properties suitable for LTCC application but these single-phase ceramics require sintering at a high temperature, which is sometimes a serious drawback. Since silicates are reliable, inexpensive and easy to process [13], the investigation on multi-phase silicates is also prospective, including natural geomaterials. Plasma spraying can offer selective evaporation of some unwanted admixtures (impurities) [17,18].

Reaching pore-free diopside is always difficult. Cold isostatic pressing of diopside was done at 1300 °C for 3 h and the final relative density was not higher than 97% [19]. The relative permittivity of this material was 7.6.

The goal of our current research is to spray and study thick self-supporting plates suitable for precise dielectric measurements. The need for self-supporting samples is mainly because such a low-permittivity and low-loss material should be tested without substrate for the acceptable precision of measurements. The same approach is also useful for a "Direct Write Thermal Spray" manufacturing, which is a technology enabling fabrication of multilayer thick-film electronic devices [20]. A water-stabilized plasma spray system (WSP) was used as an equipment able to process a large quantity of diopside with low costs. Selected mechanical, thermal, dielectric and optical characteristics are provided and discussed in connection with the structural observations of as-sprayed and also annealed deposits. The motivation was to obtain rigid and acceptably wear resistant materials with dielectric properties offering replacement high melting point synthetic silicates with this inexpensive geo-material with a low melting point. In the past significant microstructure changes in sprayed silicates after thermal posttreatment were observed, so the optimization process now included the annealing step.

2. Experimental

2.1. Plasma spray parameters adjusting

The samples were produced using a high-feedrate water-stabilized plasma spray system WSP® 500 (IPP, Prague, Czech Republic). This system operates at about 160 kW arc power and can process large amount of material per hour. Plasma spray parameters were adjusted using observation on single splats sprayed on non-treated surface of laboratory glass. The WSP system allows adjusting the feeding distance (FD), which is the axial position of the powder injector versus the plasma nozzle. Fig. 1 presents single splats sprayed from three different feeding distances at the fixed spray distance of 300 mm. For all FDs, variability in transparency of splats quite frequently represented by two major extremes – transparent splats and black splats – was observed. This can be attributed to a difference in chemical composition. However, such a difference is not manifested by different adherence to the glass – both splat types behave similarly.

For the shortest FD of 50 mm the splats were fragmented which signalizes impact in a too hot state and a too high

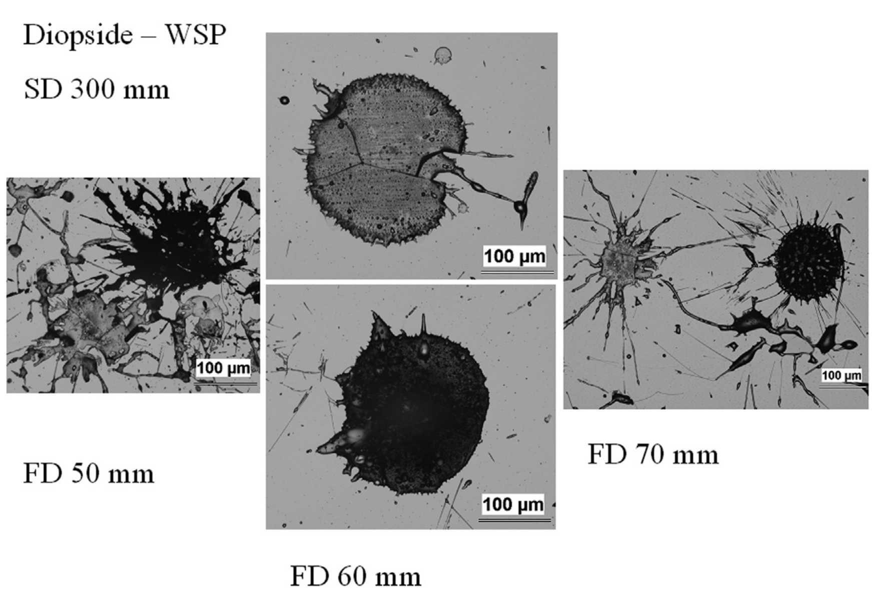

Fig. 1. Optical micrographs of splats on glass – FD 50 mm (top left) FD 70 mm (top right) and FD 60 mm (bottom).