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Carbon uptake and distribution in Spark Plasma Sintering (SPS) processed Sm(Co, Fe, Cu, Zr)$_z$

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ABSTRACT

Spark Plasma Sintering (SPS) rapidly consolidates high-melting point powders between carbon dies, but carbon can pose a risk for many materials. Carbon uptake in SPS and conventional, pressure-less sintered (CS) Sm(Co, Fe, Cu, Zr)$_z$ has been analysed using Electron Probe Micro-Analysis (EPMA) to produce high-detail elemental distribution maps. Field's metal was used as mounting material to avoid introducing carbon into the samples. The distribution maps show high surface carbon levels in the SPS-processed Sm (Co, Fe, Cu, Zr)z to a depth of 10 μm. Much less carbon was observed in CS Sm(Co, Fe, Cu, Zr)z. Furthermore, elemental carbon analysis (LECO-C) confirmed carbon was most abundant at the surface in SPS-processed Sm(Co, Fe, Cu, Zr)z but also at higher levels internally, when compared to the CS sample. It is inferred that the carbon contamination is due to the contact between the powder and the graphite die/paper at elevated temperatures during SPS process. The measured levels of carbon in the SPS-processed sample are not expected to significantly impact the magnetic properties of Sm(Co, Fe, Cu, Zr)z. These results may have implications for other powder materials processed by SPS with properties sensitive to carbon.

1. Introduction

The SPS technique is a method for processing powders into fully dense compacts much faster than standard conventional processes, such as pressure-less sintering [1,2]. SPS works by applying DC current and uniaxial force to the punch of a powder-containing die and direct heating of the powder allows heating rates of 100 °C and above, which relates to the rapid processing times achieved. This reduced time required for densification at high temperature allows SPS to retain fine microstructures, potentially to the nanoscale [3–5]. These features have garnered SPS a lot of attention as an interesting and attractive alternative to conventional powder processing routes for a number of materials and applications.

Due to the necessity for the die and punches to be electrically conductive and mechanically strong at high temperatures, the material most commonly used is graphite. This choice of material can raise concern, as the powder material is placed in direct contact with carbon at elevated temperatures.

Retained carbon, present after a variety of processing methods, can be detrimental for a number of material properties. For example, the permanent magnet material, Sm(Co, Fe, Cu, Zr)z (commonly used composition of SmCo based magnet) was produced by metal injection molding and shown to retain carbon due to the use of organic binders. In the work of Tian et al. [6], carbon was found to react with the Zr (forming ZrC) and was therefore unavailable to facilitate the formation of the necessary cellular Sm_2Co_{17} and boundary $SmCo_5$ phases in the microstructure during heat-treatment, which are essential for the strong magnetic performance of Sm(Co, Fe, Cu, Zr)z. Increasing the carbon content throughout their composition of Sm(Co, Fe, Cu, Zr)z gradually reduced the hard magnetic properties to zero once carbon within the bulk exceeded 0.49 wt%. Another example of carbon uptake is in SPS-processed spinels and glass-ceramics of a variety of materials, which have reduced transparency due to the carbon contamination. In these studies, the carbon contamination could not be specified to originate from the handling of the powder or due to contact with the high-carbon environment in the SPS process [7–11]. It is therefore crucial to investigate further the extent of carbon uptake during the SPS process to better evaluate the use of SPS as a processing method for high performance magnets and other material applications.

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Two samples of Sm(Co, Fe, Cu, Zr)z, processed via SPS and conventional, pressure-less sintering (CS), have been investigated using Electron Probe Micro-Analysis (EPMA) to acquire precise elemental maps. EPMA can infer the presence of elements as light as carbon [7] and here the distribution of carbon is used to make comparisons between the different processing methods. Samples were mounted in Field's metal (carbon free – polymeric mounting materials contain carbon) to reduce background noise near the sample boundary and remove a potential source of carbon contamination. Quantitative analysis of carbon at the surface, and internally, in both sets of samples was performed using thermal decomposition carbon analysis (LECO-C).

2. Methodology

Standard commercial grade Sm(Co, Fe, Cu, Zr)z-powder was provided by Arnold Magnetic Technologies (Sheffield, UK). For the SPS process, 13 g of Sm(Co, Fe, Cu, Zr)z-Powder was placed inside high-density graphite die (material grade 2333) and lined with 0.35 mm graphite paper, used to facilitate sample removal and protect the die from wear (both provided by Mersen UK). The powder is enclosed by 20 mm diameter graphite punches and subjected to 500 kg (15.6 MPa) cold-press in air (< 1 minute) before being transferred to the SPS vessel (FCT Systeme GmbH, Germany). The SPS process occurs in argon atmosphere under the following processing conditions optimized towards full sample density: 100 °C/min heating rate, 1100 °C sintering temperature, 5 min holding time and a maximum pressure of 51 MPa (16 kN). After consolidation, the disc-shaped samples were removed from the die and subjected to a surface polish using 120-grit silicon carbide paper to remove the compacted graphite paper until bare metal was observed, removing on average 0.25mm from each surface. For comparison, Sm(Co, Fe, Cu, Zr)z samples (18 × 12 × 5mm) produced by pressure-less sintering (powder press, sinter, anneal and finish with a surface polish [12]) were also provided by Arnold Magnetic Technologies.

For EPMA, the two samples were cross-sectioned and mounted within Field's metal (32.5 wt% Bi, 51 wt% In and 16.5 wt% Sn, Alfa Aesar, UK). After surface preparation (finished with 0.4 μm alumina) the samples underwent plasma cleaning to remove remaining polishing remnants. EPMA imaging and elemental mapping was performed using a Jeol JXA-8500 F.

Carbon analysis was performed using LECO CS-844 instrument (AMG-S, Rotherham, England). For this analysis, the SPS-processed and CS Sm(Co, Fe, Cu, Zr)z samples were sectioned and material taken from the middle and at the edges to provide examples of the internal and surface compositions. The internal segments underwent surface polishing to remove 1 mm of material from both the top and bottom faces, to ensure all surfaces were removed. LECO-C relates the amount of carbon present in a sample by thermal decomposition and measurement of the CO_2 levels by infrared absorption [13].

3. Results and discussion

Fig. 1a shows a backscattered SEM image, which contains the Field's metal material (light contrast) and the post surface polish SPS Sm(Co, Fe, Cu, Zr)z (dark contrast). The accompanying carbon map (Fig. 1b) shows a continuous region of carbon distributed along this boundary. Mostly uniform in thickness, the distribution of the carbon extends beyond the defined boundary in Fig. 1a and into the Sm(Co, Fe, Cu, Zr)z region at high levels to an inferred depth of around 10 μm. This observation is consistent in other regions imaged and mapped, although the surface carbon is sometimes less uniform, and can be discontinuous. These findings are consistent with work by Neamţu et al. who obtained EDX distribution maps of carbon in SPS-processed Fe-Si-B glassy powder (consolidated under different SPS processing parameters) and saw carbon detected at the surface of the compacts to a diffusion depth of 2–3 μm [14]. Examples of Inhomogeneity in the Sm (Co, Fe, Cu, Zr)z microstructure (examples highlighted as I, II and III in Fig. 1a), of which EPMA indicates are samarium-rich, correlate with slightly elevated levels of carbon (Fig. 1b) and could potentially be samarium carbide (Sm_3C). If confirmed, the action of carbon in these magnetic materials could be through removal of both samarium and zirconium from the main phase [6]. Also seen in Fig. 1b is a small carbon feature at the top of the Sm(Co, Fe, Cu, Zr)z carbon map, which does not correspond with the backscattered image. It is attributed to be a remnant of dirt/grease. Similar features were not observed in other regions imaged.

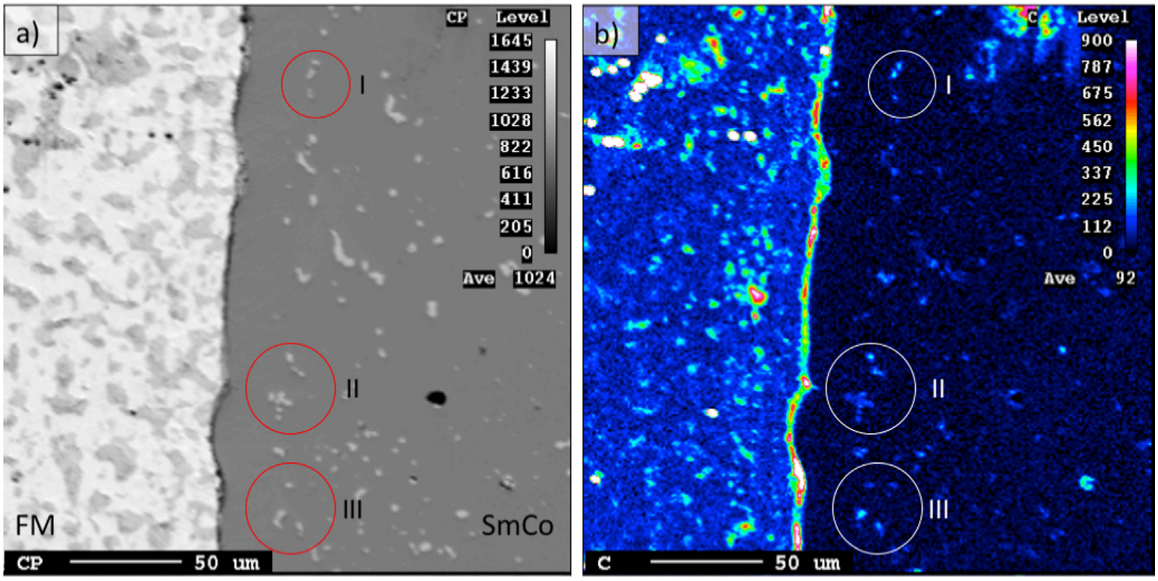

Fig. 1. SEM and EPMA carbon maps for the SPS-processed Sm(Co, Fe, Cu, Zr)z. (a) Backscattered electron mode. Annotations show Field's metal (FM) and Sm(Co, Fe, Cu, Zr)z (SmCo) regions. Imaging is performed after surface polishing. (b) EPMA carbon map of the same region. Carbon uniform and continuous and extends into SmCo region. Inserts (I, II and III) highlight areas rich in Sm (Fig. 1a) coinciding with areas of elevated carbon (Fig. 1b).