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Observation of Curie transition during spark plasma sintering of ferromagnetic materials

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ABSTRACT

The possibility of employing the ferromagnetic–paramagnetic phase transitions of magnetic materials to calibrate temperature during spark plasma sintering (SPS) was investigated using pure Fe and Fe–50Co alloy. A sharp and repeatable change was observed in the electrical current profile at the Curie temperature (T_c) during both sintering and reheating of the sintered samples. Under a pulsed DC current, an abrupt change in the electrical resistance was observed at T_c due to the sudden changes in the permeability and in turn, the skin depth during heating and cooling. These effects can be used to obtain a more accurate in-situ measurement of the sample temperature than the one provided by the pyrometers that are normally used for SPS processing. The temperature measured using a pyrometer was found to be significantly lower (up to 70 °C) than the actual temperature of the specimen.

1. Introduction

Spark plasma sintering (SPS) has been used to consolidate a wide variety of materials [1]. The sintering temperature is usually measured using pyrometers and thermocouples focussed on the punches and die close to the sample. The measured temperature is used to modulate the electric current in order to follow a set heating and cooling cycle. The accurate measurement of temperature during SPS processing remains a major challenge because of the occurrence of localised hot spots at the particle contact points [2]. The uncertainty in the temperature measurement can explain the discrepancies in processing conditions and non-reproducibility reported in the literature [3–5]. In order to obtain the actual sample temperature, the measurement should be made from the core of the sample. By employing materials that undergo distinctive phase transitions that can produce a noticeable and repeatable characteristic in the profile of any of the sintering parameters, it may be possible to obtain a more accurate measurement of temperature. Ferromagnetic materials exhibiting an abrupt change in the AC electrical resistance and magnetic permeability near the Curie transition could produce a detectable signal in the current profile recorded during SPS processing. This work investigated the possibility of using the Curie transition in electrically conductive ferromagnetic materials such as pure iron and Fe–50Co alloy to calibrate the temperature measurement during SPS processing.

2. Material and methods

Pure Fe (> 99%) and Fe–50Co–0.2Si powders with average particle sizes of 7 and 10 μm were obtained from Goodfellow Cambridge Ltd., UK and Sandvik Osprey Ltd.-Powder Group, respectively. The phase transitions in both the powders were studied using a differential scanning calorimeter (Perkin Elmer TGA/DTA/DSC 7) by heating and cooling 140 mg of each of the powders in the range of 30–1050 °C at a rate of 10 °C/min under flowing N_2 gas. For the sintering studies, about 20 g of the magnetic powders were packed in a 30 mm graphite die and were heated and cooled at the same rate of 10 °C/min in the SPS furnace (HPD 25/1, FCT Systems, Germany). A pulsed DC current with 15 ms on-time and 5 ms off-time, which corresponds to a frequency of 50 Hz, was applied. The pressure was linearly increased up to 80 MPa while heating up to 1100 °C and it was maintained constant at 80 MPa throughout the cooling cycle. A pressure of 80 MPa was preferred in order to minimise the thermo-electric contact resistances and in turn, the temperature difference inside the punch/die/sample assembly [6]. The SPS temperature was measured using a pyrometer pointed at the top graphite punch at a distance of 4 mm from the sample. The same heating, cooling and loading rates were repeated once for the sintered compacts.

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3. Results and discussion

The DSC curves recorded during heating and cooling of pure iron and Fe-Co are shown in Fig. 1. Pure iron displayed two distinct and reversible phase transitions: (a) magnetic or Curie transition (~760 °C); and (b) α–γ transformation (~900 °C). Smetana et al. [7], by performing DTA experiments on pure iron at 7 K min^{-1}, reported T_c as 763 and 761 °C during heating and cooling, respectively. The α–γ transition temperature obtained in the DSC experiment during heating and cooling are 921 and 871 °C, respectively. They are respectively 12 and 16 °C lower than that reported by [7]. The Curie transition involves no change of crystal structure, whereas the α–γ transformation is associated with a change of crystal structure between bcc and fcc (first order).

As shown in Fig. 1, two characteristic phase transformations were also observed for Fe–50Co alloy. The one at around 725 °C is related to an order–disorder transformation (T_{o-d}). The other phase transition at about 980 and 957 °C in the heating and cooling curves, respectively, corresponds to the α (bcc)–γ (fcc) reversible structural phase transformation [8]. Unlike in pure Fe, the T_c of Fe–50Co alloy coincides with that of the α–γ transition because its ferromagnetic behaviour is lost during heating and recovered during cooling due to the α–γ structural transition [9]. The phase transition temperatures identified in the heating curve of Fe–50Co are in good agreement with the values reported in the literature (T_{o-d}~730 °C; T_c=980 °C) [8]. However, no literature is available to compare with the cooling thermograms of Fe–50Co alloy. It is evident that all of the transformations in both systems are associated with thermal hysteresis as shown in Fig. 1.

The nominal temperature measured by SPS pyrometer and electric current profiles recorded in the SPS system during the heating and cooling cycles of: (a) pure Fe powder and sintered Fe compact; and (b) Fe–Co alloy powder and sintered Fe–Co alloy compact are plotted in Figs. 2 and 3, respectively. With a minimum mechanical pressure (7 MPa), the current profile was noisy due to poor electrical contacts inside the punch/die/sample assembly. Hence, it was difficult to detect any variation in the current associated with the phase transitions described in Fig. 1. A mechanical pressure of 80 MPa resulted in an improved electrical contact and hence, produced a more detectable change of the sintering data output in the vicinity of T_c. It has been reported that pure Fe exhibits a minor variation of the T_c under the application of mechanical pressure (0 ± 0.03 K under 100 MPa [10], 0.3 K under 100 MPa [11]). A similar behaviour is expected in Fe–50Co, in

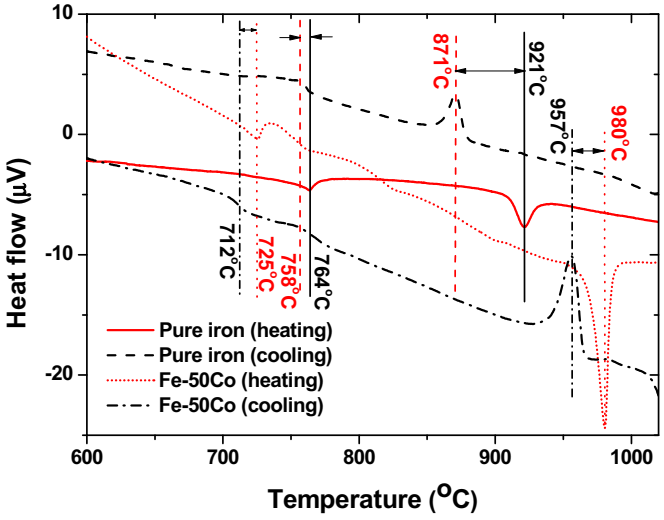

Fig. 1. DSC thermogram of pure Fe and Fe–Co powder heated and cooled at 10 °C/min.

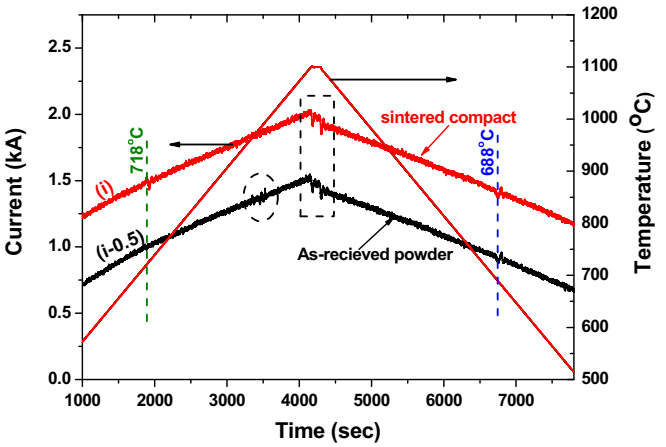

Fig. 2. SPS current and temperature profiles of pure Fe powder and sintered compacts heated and cooled at 10 °C/min; the soaking time was maintained as 2 min and the pressure was increased such that it was 80 MPa at 1100 °C. As shown, a constant (0.5) was subtracted from the SPS current values to stack the current profiles.

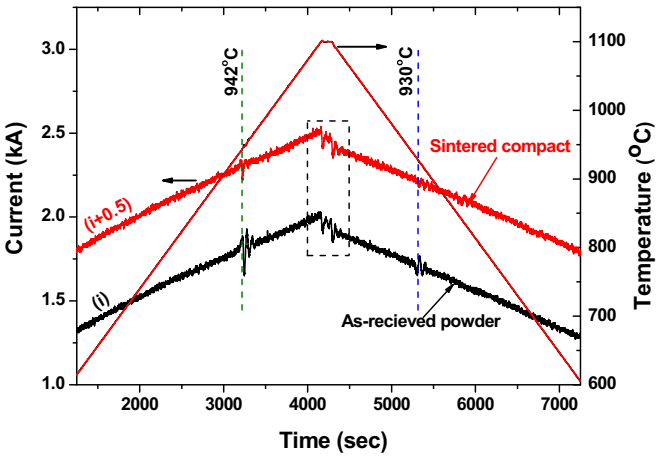

Fig. 3. SPS current and temperature profiles of Fe–50Co powder and sintered compacts heated and cooled at 10 °C/min; the soaking time was maintained as 2 min and the pressure was increased such that it was 80 MPa at 1100 °C. As shown, a constant (0.5) was added to the SPS current values to stack the current profiles.

which the bcc ferromagnetic phase changes to an hcp non-ferromagnetic structure under a mechanical pressure higher than 30 GPa [12]. Hence, the mechanical pressure of 80 MPa did not have a significant effect on the magnetic and structural phase transitions.

During the heating and cooling experiments of pure iron, the SPS current fluctuated at three characteristic points (Fig. 2). The SPS current instability during the first heating run highlighted by the oval shape (~1000 °C) could be associated with the sintering of the Fe powder, which would explain why it was not observed in the following cooling and heating runs. The current fluctuation marked by the rectangle in Fig. 2 was due to an instability in the power requirement during the dwell period. A similar phenomena is described in Ref. [13]. The electric current profile showed a characteristic fluctuation during the first cooling run at about 688 °C and in the successive heating run (about 718 °C) and cooling run (about 688 °C) for the densified compact. Due to the lower density and hence, the electrical conductivity and magnetic permeability of the compact, the transition was not visible during the first heating cycle. It is clear that the density of the magnetic material plays a significant role for the fluctuations to be apparent. The hysteresis in the heating/cooling transition temperatures measured from the SPS current profiles was 30 °C. This is greater