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Chapter 2

Spark Plasma Sintering of Negative Temperature Coefficient Thermistor Ceramics

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http://dx.doi.org/10.5772/58496

1. Introduction

Spark plasma sintering (SPS), also known as field assisted sintering technique (FAST), belongs to a class of sintering techniques in which densification is enhanced by the simultaneous application of axial pressure and elevated temperature generated by a high current flow [1, 2]. SPS has been successfully used in the preparation of functionally graded materials [3], ceramics [4-6], magnetic materials [7, 8], alloy [9], etc. It is believed that the SPS has a significant advantages in decreasing the sintering temperature and sintering periods, and also preparing high density ceramics [10]. Although SPS has been widely used to prepare dense transparent and structural ceramics, little reports focus on the application of this technique to prepare dense ceramics for negative temperature coefficient (NTC) thermistor applications [11,12]. So this chapter first provides a summary of fundamental theoretical aspects of spark plasma sintering, and then the application of spark plasma sintering in NTC thermistor ceramics are introduced emphatically. At the end, the future research and application of spark plasma sintering in the NTC thermistor ceramics are forecasted.

2. Theoretical aspects of spark plasma sintering

SPS is a novel effective sintering technique, which has been used in the research and development of various kinds of materials. However, there is no uniform understanding in the sintering mechanism of SPS. In general, SPS is a pressure sintering method based on the simultaneous application of axial pressure and high temperature plasma momentarily...
generated in the gaps between powder materials by electrical discharge at the beginning of ON-OFF DC pulse energizing [13]. In addition to have the Joule heating due to the electric current and plastic deformation produced by pressure, SPS also generates DC pulse voltage between the powder particles, and effectively makes use of the spontaneous heat generated by the discharge between powder particles, thus resulting in some special characteristics. Compared to the conventional sintering, SPS has two important characteristics [14, 15]: (1) SPS process can make high-energy pulse focus on the grain junction point, thus saving the energy; (2) A high energy, low voltage spark pulse current momentarily generates spark plasma and produces a high localized temperature from several to ten thousand °C between the particles and then resulting in optimum thermal diffusion and grain boundary migration, i.e. more material transfer can be intensified and thus high density ceramics can be obtained through spark plasma sintering with a low sintering temperature and a short sintering period. Fig. 1 shows the schematic of SPS furnace [16].

3. Application of spark plasma sintering in NTC thermistor ceramics

In the past decades, more advanced techniques such as microwave sintering [17, 18], and nitrogen atmosphere sintering [19] have been used for NTC ceramic powder consolidation. However, there are few reports focusing on the application of SPS technique to prepare dense
ceramics for NTC thermistor applications. The advantages of spark plasma sintering against conventional sintering for high temperature NTC thermistor ceramics are reviewed as follows.

3.1. Brief introduction of NTC thermistors

NTC thermistors are thermally sensitive resistors whose resistance decreases with increasing temperature. Their resistivity can be expressed by the following Arrhenius equation [20, 21]:

$$\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right),$$

where $\rho_0$ is the resistivity of the material at infinite temperature, $T$ is the absolute temperature, $E_a$ is the activation energy for electrical conduction, and $k$ is the Boltzmann constant. They are mainly used in industrial areas as elements for temperature measurements, control, etc [22].

In the past few years, development of novel high temperature NTC thermistor materials has been motivated by the requirements of particle filters and catalytic converters in exhaust pipe for automotive motors [23, 24]. NTC thermistor ceramics composed of spinel structure (MMn$_2$O$_4$, where M=Ni, Co, Fe, Cu, Zn) show aging of the electrical properties and their application is commonly limited to temperatures below 300°C [25, 26]. The literature suggests that rare earth (Sm, Tb, Y, etc) perovskite oxides (ABO$_3$) can be used for measurements from ambient to 1000°C [23]. In particular, YCrO$_3$ having an orthorhombic perovskite structure, has been considered as a candidate for high temperature NTC thermistor applications [19, 23, 27, 28]. However, the material shows poor sinterability and is difficult to densify under ambient atmospheric conditions or through pressureless sintering techniques [29, 30]. We have investigated the spark plasma sintering of YCr$_{1-x}$Mn$_x$O$_3$ ceramics and MgAl$_2$O$_4$-YCr$_{0.5}$Mn$_{0.5}$O$_3$ composite ceramics, and their NTC electrical properties.

3.2. Spark plasma sintering and electrical properties of YCr$_{1-x}$Mn$_x$O$_3$ NTC ceramics

In the conventional sintering processes, extremely high sintering temperatures (up to 1600°C) and long holding time (several hours) in air are applied in the fabrication of YCrO$_3$ ceramics to achieve the highest density and minimum porosity. The poor sinterability of YCrO$_3$ material is attributed to the loss of Cr$_2$O$_3$ through its volatility during sintering process [30, 31]. In our previous work [32, 33], YCr$_{1-x}$Mn$_x$O$_3$ (0≤x≤0.5) NTC ceramics with a high relative density have been obtained by combing the Pechini method synthesis and SPS. Fig.2 shows the flow chart for the fabrication of YCr$_{1-x}$Mn$_x$O$_3$ thermistor powders by a Pechini method. The molar ratio of citric acid, ethylene glycol and metal ions was 1.5:1.5:1. The spark plasma sintering was carried out in vacuum (6 Pa) with an apparatus (FCT Systeme GmbH, FCT, Rauenstein, Germany). The SPS equipment used in the experiments is shown in Fig. 3. Fig.4 shows the time dependence of the temperature and applied pressure during SPS process. The sintering temperature was 1300 °C, and the dwell time was 10 min. Fig.5 shows the XRD patterns of the SPS-sintered YCr$_{1-x}$Mn$_x$O$_3$ ceramics. All samples had a pure orthorhombic perovskite phase isomorphic to YCrO$_3$ (JCPDF 34-0365) described by the space group $Pnma$, and no secondary phase occurred with the increase of Mn concentration. Fig.6 shows the SEM images of surface section of SPS-sintered YCr$_{1-x}$Mn$_x$O$_3$ ceramics. It can be seen that as-sintered YCrO$_3$ ceramics were highly dense, and had a bulk density of 5.6112 g/cm$^3$, corresponding to 97.6% of the theoretical density (5.751 g/cm$^3$) [33]. One can observe that grain size decreased with the
increase of Mn content. This result may be due to the dragging effect between Mn ions and grain boundary, which increases the energy for the movement of grain boundary and retards the grain growth [34, 35]. The YCr$_{1-x}$Mn$_x$O$_3$ NTC thermistor over a wide temperature range of 25 to 300 °C showed a linear relationship between the logarithm of the resistivity and the reciprocal of the absolute temperature. And the resistivity increased at first and then decreased with increasing Mn contents, which had the same varying tendency with activation energy. This electrical conductivity anomaly has been revealed by using defect chemistry theory combination with X-ray photoelectron spectroscopy analysis [32]: The major carriers in YCrO$_3$ are holes. Mn ions are acting as an n-type dope, and partly compensate for the effect of metal vacancies, thus leading to an increase in the resistivity. Mn$^{4+}$ ions increase as Mn content increases from 0.2 to 0.5, which promote the rise in charge carriers and the electron hopping, thereby resulting in a decrease in the resistivity. Therefore, SPS has shown significant advantages against conventional sintering in the fabrication of high density YCr$_{1-x}$Mn$_x$O$_3$ ceramics, and provides efficient and viable means for the study of the conduction mechanism of NTC thermistors.

**Figure 2.** Flow chart for the fabrication of YCr$_{1-x}$Mn$_x$O$_3$ thermistor powders by a Pechini method.
Figure 3. Image of SPS equipment (From Alfred University).

Figure 4. Time dependence of the temperature and applied pressure during SPS process [33].
Figure 5. XRD patterns of the SPS-sintered YCr$_{1-x}$Mn$_x$O$_3$ ceramics [32].

Figure 6. SEM images of surface section of SPS-sintered YCr$_{1-x}$Mn$_x$O$_3$ ceramics: (a) $x=0$; (b) $x=0.2$; (c) $x=0.4$; (d) $x=0.5$. 
3.3. Spark plasma sintering and electrical properties of MgAl$_2$O$_4$-$\text{YCr}_{x}\text{Mn}_{1-x}$O$_3$ composite NTC ceramics

Recently, there is an increasing interest in exploring NTC behavior in composite materials because of their high temperature potential for combining properties that are difficult to attain separately with the individual component [24]. We have designed and prepared $x\text{MgAl}_2\text{O}_4-(1-x)\text{YCr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ high temperature composite thermistor ceramics by associating a less resistive phase YCr$_{0.5}$Mn$_{0.5}$O$_3$ with a high resistive MgAl$_2$O$_4$ combination with spark plasma sintering [12]. Fig. 7 shows the time dependence of the temperature and applied pressure during SPS process. The sintering temperature was 1200°C, and the dwell time was 20 min. The SPS-sintered composite ceramics consisted of a cubic spinel MgAl$_2$O$_4$ phase and an orthorhombic perovskite YCr$_{0.5}$Mn$_{0.5}$O$_3$ phase isomorphic to YCrO$_3$. Fig. 8 exhibits the microstructures of the SPS-sintered samples. The SPS-sintered ceramics were highly dense, and their grain sizes were ranging from 0.5 to 2 μm. The relative densities were 95.5%, 97.4% and 94.1% of the theoretical density for $x=0.1, 0.4, 0.6$, respectively. The resistivity of composite ceramics decreased with increasing temperature from 25 to 1000 °C, indicative of NTC characteristics. The obtained $\rho_{25}$, $B_{25-150}$, $B_{700-1000}$, $E_{25/150}$ and $E_{700/1000}$ of the SPS-sintered composite NTC thermistors were in the range of $1.53\times10^6$-$9.92\times10^9$ Ωcm, 3380-5172 K, 7239-9543 K, 0.291~0.446 eV, 0.624~0.823 eV, respectively. This result indicates that these values can be adjusted by changing MgAl$_2$O$_4$ content. Fig. 9 compares the temperature dependence of electrical resistivity $\rho$ of the samples $0.4\text{MgAl}_2\text{O}_4$-$0.6\text{YCr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ sintered by conventional sintering (CS) and SPS. It can be seen that the samples from SPS-sintered ceramics possessed a higher resistivity than that from conventional sintered ceramics. There are two possible reasons for the increase in the resistivity of SPS-sintered samples [12]: (1) During the SPS process, the short sintering period is advantageous in reducing chromium volatilization, thus leading to a decrease in Cr$^{4+}$ and Mn$^{4+}$ ion concentration, thereby increasing the resistivity as a result; (2) SPS-sintered
samples have a smaller grain size, resulting in a decrease in the time between electron scattering events of charge carriers and thus increasing the resistivity [36]. In conclusion to this, SPS has potential superiority on synthesis high temperature NTC ceramic materials.

Figure 8. SEM images of the SPS-sintered $\alpha\text{MgAl}_2\text{O}_4-(1-x)\text{YCr}_0.5\text{Mn}_0.5\text{O}_3$ composite ceramics: (a) $x=0.1$; (b) $x=0.4$; (c) $x=0.6$ [12].

Figure 9. Temperature dependence of electrical resistivity $\rho$ of the samples $0.4\text{MgAl}_2\text{O}_4-0.6\text{YCr}_0.5\text{Mn}_0.5\text{O}_3$ sintered by conventional sintering (CS) and SPS [12].
4. Summary

The fundamentals, applications of spark plasma sintering to thermistor ceramics are reviewed in this chapter. For thermistor ceramics, the advantages of spark plasma sintering against traditional sintering are as follows: (1) Faster heating rate decreases the sintering time by using spark plasma sintering, and thus saving energy than traditional sintering; (2) Spark plasma sintering can ensure ceramics with high density and small grain at a low sintering temperature and a short sintering period. What's more, spark plasma sintering has shown significant advantages in the fabrication of YCrO$_3$ perovskite-based thermistor ceramics and provides an efficient mean for the study of the conduction mechanism of NTC thermistors.

In the past years, there have had a significant developments and advances regarding to the spark plasma sintering of ceramics. However, the fundamental theory of spark plasma sintering is not fully understood, and also needs massive fundamental research and practical innovation to perfect. It can be forecasted that there is a great future for the successful commercialization of spark plasma sintering in ceramic preparation.

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