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Heating mechanism of spark plasma sintering

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Abstract

According to the plasma sintering process and our theoretical calculation, we analyzed the heating mechanism of spark plasma sintering (SPS). It is proposed that the sintering temperature of conductive materials rises faster mainly due to the contribution of the direct current (DC) component in pulse current, current skin effect and eddy current in the mould and blank, Joule's heat generated by eddy current in grains, small heat capacity of the heated system and direct-contact heating. For non-conductive materials, the similar reasons can be found except for the heat effect of eddy current. By analyzing the heating mechanism of SPS, it is concluded that the temperature on the surface of a conductive green body should be higher than that on the inner surface of the die, whereas the opposite case holds for a non-conductive blank, that has already been verified by Nagae et al. [Journal of the Japan Society of Powder and Powder Metallurgy 44 (1997) 945–950] and by Sumi et al. [Journal of the Japan Society of Powder and Powder Metallurgy 45 (1998) 153–157].
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1. Introduction

Spark plasma sintering is a novel sintering technique with characteristics of rapid temperature rise, short sintering time and uniform heating for sintered bodies, and has aroused great attention in material cycles and has been applied in the preparation of nanocomposites, functional materials, ceramics, cermets, intermetallic compounds, and so on. A broader scope of materials prepared by the SPS method is listed in Ref. [1]. Different from conversional sintering techniques that usually use an alternating current (AC) to heat, SPS utilizes an on–off pulse current to directly heat the graphite die to complete the sintering process. As to the sintering mechanism of SPS, it is mostly believed that an electric field among grains is created during sintering and high-temperature plasmas are excited under the action of pulse current so that it causes a cleansing effect on the surface of particles, leading to sintering enhancement [2], but there still exist many disputed interpretations [3,4]. High-temperature plasma is a kind of ironed gaseous mixture consisting of positive/negative electrons and irons from atoms losing electrons at high temperatures. However, the intermediate process and mechanism of creating plasma are complicated during SPS, and it is unknown whether plasma is produced or not, or how it is produced, especially for the sintering of non-conductive materials. After carefully analyzing the sintering process of SPS and calculating the heat produced by a pulse current, we propose the idea that it is not the high-temperature plasma but the comprehensive factors, such as DC component included in pulse current, direct-contact heating, the skin effect of alternating current on the surfaces of die and sintered body, and eddy current in grains, that lead to the rapid rise of temperatures. In the following, we will analyze the heat effects caused by the factors above.

2. Sintering of conductive materials

During sintering of conductive materials, current mainly flows through the die and the green body. For a conductor,

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current skin effect is produced when a high-frequency alternating current passes through it. More heat will be created in this case than in that if no skin effect is produced, which is common knowledge in the power industry. In the following we only discuss the heat generated by a hollow cylinder graphite die.

3. Heat produced by an alternating current when considering skin effect

Consider a hollow cylinder graphite die with length L, inner radius R_1 and outer radius R_2, shown in Fig. 1. It is well known that when an alternating current flows through a conductor the current distribution is uneven on its cross surface due to the electromagnetic induction. The current density becomes larger when close to the surface of the conductor and smaller when close to its center. This is called the skin effect of an alternating current. According to the knowledge of electrodynamics, for a hollow cylinder conductor the skin effect occurs on its inner surface. Usually, the extent that the current approaches to the surface is described by the skin depth d_s, which is the distance from the surface to where the current density reduces to 37% of its value on the surface. According to the electromagnetic theory, the current distribution on a conductor cross section can be expressed in the following equation [5]:

$$j = j_0 e^{-d/d_s} \tag{1}$$

where j_0 is the current density on the surface of conductor. The skin depth is determined by

$$d_s = \frac{503}{\sqrt{v\mu_r\sigma}} \tag{2}$$

where v is the frequency of current, σ and μ_r are the electrical conductivity and relative permeability of conductor, respectively. Obviously, the higher the frequency is, the smaller the skin depth will be, namely, the more significant the skin effect will be. For a graphite die we have $\rho \sim (8\text{–}13)\times 10^{-6}$ (Simens/m), $\mu_r \sim 1$, then the skin depth is 0.45–0.47 cm with 100 kHz alternating current based on Eq. (2). For ferromagnetic materials with $\mu_r \gg 1$, the skin effect will become more significant when the 100 kHz alternating current flows through them. In the following, we will calculate and compare the heat produced by an alternating current in two cases: considering and not considering current skin effects.

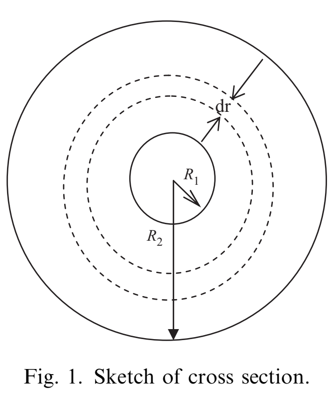

Fig. 1. Sketch of cross section.

Suppose the total current intensity through the die is I, and use Eq. (1), we have

$$I = \int_{R_1}^{R_2} 2\pi r j \mathrm{d}r = \int_{R_1}^{R_2} 2\pi r j_0 e^{-(R_2-r)/d_s}\mathrm{d}r = 2\pi j_0 d_s[(R_2-d_s)-(R_1-d_s)e^{(R_1-R_2)/d_s}] \tag{3}$$

thus

$$j_0 = \frac{I}{2\pi d_s[(R_2-d_s)-(R_1-d_s)e^{(R_1-R_2)/d_s}]} \tag{4}$$

So, the heat produced by the die is

$$Q_1 = \frac{1}{2}\frac{2\pi L j_0^2}{\sigma}\int_{R_1}^{R_2} e^{-2(R_2-r)/d_s} r\mathrm{d}r = \frac{I^2 L}{16\pi\sigma d_s}\frac{[(2R_2-d_s)-(2R_1-d_s)e^{2(R_1-R_2)/d_s}]}{[(R_2-d_s)-(R_1-d_s)e^{(R_1-R_2)/d_s}]^2} \tag{5}$$

Without considering the skin effect of current, the heat produced by the current with the same intensity is

$$Q_2 = \frac{1}{2}I^2 R = \frac{I^2 L}{2\pi\sigma(R_2^2-R_1^2)} \tag{6}$$

From Eqs. (5) and (6), we have

$$\frac{Q_1}{Q_2} = \frac{R_2^2-R_1^2}{8d_s}\frac{(2R_2-d_s)-(2R_1-d_s)e^{2(R_1-R_2)/d_s}}{[(R_2-d_s)-(R_1-d_s)e^{(R_1-R_2)/d_s}]^2} \tag{7}$$

Take a practical graphite die and 100 kHz alternating current as an example, approximately, we have $R_2 \sim 2R_1 \sim 10d_s$. Substituting it into Eq. (7), it is easy to obtain $Q_1/Q_2 \sim 2.2$. It is obvious that the heat produced by the die increases owing to the current skin effect, and the smaller the skin depth is, the larger the ratio Q_1/Q_2 will be.

4. Heat produced by pulse current

Suppose an on–off pulse current shown in Fig. 2 is used in SPS. From Fourier transformation we know that a periodic pulse current can be decomposed into AC components with different frequencies.

Consider the pulse current as follows:

$$I = \begin{cases} I_0, & 0 \le t \le T/2 \\ 0, & T/2 < t \le T \end{cases} \tag{8}$$

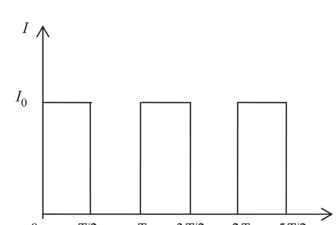

Fig. 2. Relation of pulse current with time.

where T is the period of the pulse current. Its Fourier decomposition is

$$I = a_0 + \sum_{k=1}^{\infty}\left(a_k \cos\frac{2\pi kt}{T} + b_k \sin\frac{2\pi kt}{T}\right) \tag{9}$$

in which

$$a_0 = \frac{1}{T}\int_{-T/2}^{T/2} I\,\mathrm{d}t = \frac{1}{T}\int_0^{T/2} I_0\,\mathrm{d}t = \frac{I_0}{2},$$

$$a_k = \frac{2}{T}\int_{-T/2}^{T/2} I\cos\frac{2k\pi t}{T}\mathrm{d}t = \frac{2}{T}\int_0^{T/2} I_0\cos\frac{2k\pi t}{T}\mathrm{d}t = 0$$

$$b_k = \frac{2}{T}\int_{-T/2}^{T/2} I\sin\frac{2k\pi t}{T}\mathrm{d}t = \frac{2}{T}\int_0^{T/2} I_0\sin\frac{2k\pi t}{T}\mathrm{d}t$$
$$= \frac{I_0}{k\pi}\left[(-1)^k - 1\right] = \begin{cases} 2I_0/k\pi & k \text{ is odd} \\ 0 & k \text{ is even} \end{cases}$$

Then Eq. (9) can be rewritten as

$$I = \frac{I_0}{2} + \sum_{k=1}^{\infty} b_k \sin\frac{2\pi kt}{T} = \frac{I_0}{2} + \sum_{n=0}^{\infty}\frac{2I_0}{(2n+1)\pi}\sin\frac{2(2n+1)\pi t}{T}, \quad n = 0, 1, 2, \ldots \tag{10}$$

It can be seen from Eq. (10) that a pulse current can be decomposed into the DC component with an intensity of $I_0/2$ and AC components with different frequencies and amplitudes.

From Eq. (10) we know that the amplitude and the frequency of AC component has the following relationship:

$$I_n = \frac{2I_0}{\pi T v_n} \tag{11}$$

It is clear that the higher the frequency is, the smaller the amplitude will be.

By using Eqs. (5) and (11), it is easy to obtain the heat ratio produced by AC components with different frequencies

$$\frac{Q_{1n}}{Q_{1m}} = \frac{I_n^2 d_{sm}}{I_m^2 d_{sn}}\frac{[(2R_2 - d_{sn}) - (2R_1 - d_{sn})\exp(2(R_1 - R_2)/d_{sn})]}{[(2R_2 - d_{sm}) - (2R_1 - d_{sm})\exp(2(R_1 - R_2)/d_{sm})]}$$
$$= \left(\frac{v_m}{v_n}\right)^{3/2}\frac{[(2R_2 - d_{sn}) - (2R_1 - d_{sn})\exp(2(R_1 - R_2)/d_{sn})]}{[(2R_2 - d_{sm}) - (2R_1 - d_{sm})\exp(2(R_1 - R_2)/d_{sm})]}$$
$$\times \frac{[(R_2 - d_{sm}) - (R_1 - d_{sm})\exp((R_1 - R_2)/d_{sm})]^2}{[(R_2 - d_{sn}) - (R_1 - d_{sn})\exp((R_1 - R_2)/d_{sn})]^2} \tag{12}$$

Obviously, the heat produced by AC components with different frequencies depends on the ratio of their frequencies. For example, for the two AC components of $v_n =$ 10 kHz and $v_m = 100$ kHz, we can obtain the ratio of their corresponding current amplitudes $I_n/I_m = 10$ and the ratio of their skin depths $d_{sn} : d_{sm} = \sqrt{10}$ from Eqs. (11) and (2), respectively. Suppose $R_2 \sim 2\ R_1 \sim 10 d_{sm} = \sqrt{10} d_{sn}$, we get $Q_{1n} \approx 36 Q_{1m}$ from Eq. (12). However, if we do not take the current skin effect into consideration, we have $Q_{1n} = 100 Q_{1m}$. In other words, the current skin effect makes high-frequency components contribute more to the sintering of materials.

5. Heat effect of eddy current and other factors

Due to the axially symmetric structure of the die, the pulse current passing through it distributes axially symmetric on its cross section thus no eddy current is produced in grains. However, due to the uneven microstructure of the green body, the current passing through it has an asymmetric distribution, and the magnetic flux through each grain will change with time so that an eddy current is induced in it. Each grain is being a small heat source and forms the in-situ sintering and speeds up the sintering of the green body. However, since the green body is of micro-unhomogeneity and there are too many kinds of grain shapes, it is impossible to quantitatively calculate the heat produced by the eddy current, only qualitative description is given here.

On the other hand, the small heat capacity of the heated system and the large heat conductivity of graphite die are the other two important factors for the rapid temperature rise. Compared with the conventional sintering methods, the heated system in SPS takes up smaller space and the die directly contacts with the green body so that it improves the heat transfer rate and thus makes a rapid rise in temperature.

6. Sintering of non-conductive materials

When sintering non-conductive materials, the pulse current mainly flows through the die so that almost all heat is produced by it. The rapid temperature rise is on account of the DC component in pulse current, the skin effect of AC components, contacting heating and small heat capacity of the heated system. The heat comes from the die and most heat is produced by its inner edge, so the temperature on its inner surface should be higher than that on the surface of the green body. This has already been verified by experiments [6].

7. Experiments and discussion

We succeeded in preparing 40% vol Ti/Al_2O_3 composite, metal Titanium and pure Alumina by using SPS technique under the same sintering conditions. A high-temperature thermocouple is used to measure the temperature on the surface of die and an automatic recording device to display it. The relationships between the heating time and the temperature are sketched in Fig. 3.

Fig. 3 shows a similar tendency of the temperature rise for the three different materials during sintering: the temperatures are around 420 °C during the first 200 s, then abruptly rise for about 200 s and finally reach up to

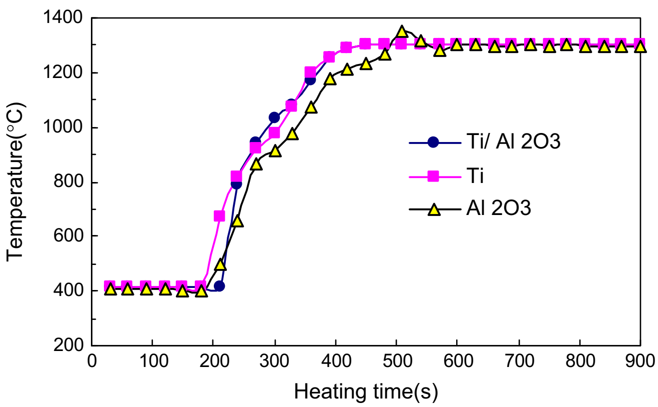

Fig. 3. The relation of temperature vs. heating time.

around 1300 °C after sintering for 400 s. Small deviation still exists in the three temperature-time curves. That is, the time the temperature spends when close to 1300 °C is different, say, more than 400 s for Alumina, 400 s for Ti/Al_2O_3 composite, and less than 400 s for Titanium, respectively. The causes of difference come from the following facts: the conductivities of the three materials are Ti > Ti/Al_2O_3 composite > pure Al_2O_3, while the values of their heat capacities have a reversed order. Titanium is a good conductor which can induces an obvious current skin effect on the surface of its green body and the heat effect of eddy current in its particles. However, Alumina is a poor conductor and the current mainly flows through the die and there is a little current going through its green body, which has been verified by Makino [6]. So among the three materials Titanium has the most rapid temperature rise, pure Alumina has the lowest, and Ti/Al_2O_3 composite has the middle.

It should be pointed out that the measuring point is on the surface of the die due to the limination of the SPS setup, the measuring results cannot adequately reflect the change of temperature on the surface of the blank, to say nothing of the temperature change inside the blank. If we can measure the temperature on the surface of blank, then the temperatures on the surfaces of blanks of different materials can be more acccurately determined and compared, and the above analysis can be directly verified.

8. Conclusions

From the analysis of the heating process of SPS, we conclude that the heating mechanism is of much difference between the sintering of conductive and non-conductive materials. For conductive materials, the Joule's heat comes from the graphite die, conductive blanks, and the reasons for rapid rise of temperature are due to the DC component in pulse current, the skin effect of AC components in pulse current, the small heat capacity of the heated system (including blank, graphite die and protecting gases), direct contact of die with blank, and the heat effect of eddy current in grains. For non-conductive materials, the reasons are the same as conductive materials except for the heat effect of eddy current. It is concluded that, generally speaking, without considering the difference between capacity of conductive and non-conductive blanks, the temperature rises more rapidly in conductive materials than in non-conductive materials, furthermore, the temperature on the inner surface of the graphite die is higher than the temperature on the surface of non-conductive blank and lower than that on the surface of conductive blank, which has already been confirmed through experiments [7,8].

In this paper we have analyzed the factors contributing to the temperaure rapid rise in SPS through the semi-quantitative calculation for the heat produced by pulse current. This does not completely uncover the mechanism of SPS, but it is a beneficial attempt to understand the essence of SPS. We think that the reasons for temperature rapid rise can be clearly understood if one can precisely measure the temperaure on the suface of blank and the current distribution on the cross sections of die and blank.

Acknowledgments

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