Study on the microwave sintering characteristics of spherical tin-silver alloy powder

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Abstract
In this study, the sintering behavior of a tin–silver alloy powder (Sn–3% Ag) is investigated during microwave melting, and a two-sphere model is used to study the main diffusion mechanism of sintering. The effect of microwave on the sintering process, microstructure and composition distribution of alloy was studied. The sintering neck growth of the tin-silver alloy powder suggests that the diffusion process of alloy components has been realized through the viscous flow mechanism during the sintering stage before melting under microwave irradiation. The rapidly heating and melting of tin-silver alloy powder can be realized by microwave heating, and the heating rate can reach to 153.4 °C·min⁻¹ at microwave power of 1.2 kW. In addition, microwave also showed a good heating effect on the metal melt. Microwave can promote the homogenization of alloy microstructural, and the precipitated phase of the alloy is refined and the element distribution is more uniform under microwave irradiation compared to the traditional process. These technology provides a new way for the preparation and performance improvement of alloy materials.

1. Introduction

The preparation methods and processes of materials play an important role in the study of materials, as they affect the ultimate comprehensive performance of materials [1]. At present, induction furnace, muffle furnace, and other methods are used in the alloy smelting process, but they have some shortcomings such as uneven heating, high energy consumption, and low efficiency [2, 3]. Therefore, the research of new material preparation methods is particularly important. Microwave technology is an effective approach of material processing. Moreover, microwave technology has been used in numerous fields for its various unique merits, such as high energy efficiency, clean utilization, and higher heating rate [4–9]. Further, the inverse heating of microwave heating compared to conventional techniques, where heat is transferred from the core to the surface, reveals that uniform heating of materials occurs when they interact with microwaves [10]. In material processing, microwave technology is a novel, energy-efficient, and unconventional rapid sintering technique [11, 12], whose advantages include improvement of mechanical properties, enhanced densification, fine microstructure, reducing defects, and environment friendliness [13–17].

Microwave technology encounters certain difficulties when heating metals and alloys, particularly bulk metals [18]. However, Roy et al [19] reported that the complete sintering of metal powders was achieved by microwave technology, and the mechanical properties of the products were better than those obtained by conventional heating in 1999. Their research also proved that a powdered metal could effectively absorb microwave energy to achieve sintering [20]. Rybakov and Buyanova [4] showed that it could realize a stable and efficient microwave sintering process by adaptively controlling the frequency and intensity of the microwave radiation.
In the past decade, microwave technology has been widely used in various types of powder sintering and alloy preparations. A functionally graded material, W/Cu, was successfully fabricated by microwaves, and it was an effective method to prepare composites with porosity and composition gradient [21]. Demirsky et al [13, 22] studied the microwave sintering of iron spheres and titanium diboride. Microwave sintering was beneficial for homogenization of microstructures under high-temperature conditions. It was confirmed that the activation energy for the neck growth in microwave sintering was lower than that of conventional sintering. Reddya et al [23–25] reported the synthesis of Al-based composites and Al alloys by the microwave sintering process, and they achieved excellent results. The heating and melting process of copper, aluminum, and lead were studied by Chandrasekaran et al under a microwave [18]. Their results suggested that the microwave melting process had a higher melting efficiency and higher energy utilization rate compared to conventional melting, and its process was clean and controllable. Ye et al [26] established that the preparation of metal-based diamond tool bits was accomplished by microwave hot-press sintering. This technology had the advantages of a short sintering time, low sintering temperature, uniform element diffusion, and good retention of diamond abrasives in an alloy matrix. Xu et al [27, 28] reported the application of microwave technology in the sintering of tin and copper powders. The heating rate for copper powder with particle size of 25 μm was 25.6 °C·min⁻¹, and the tin powder was 47.6 °C·min⁻¹. Shashank et al [29] used microwave hybrid heating (MHH) technology to melt bulk copper, the microwave frequency is 2450 MHz and power is 3.3 kW. The melted copper has a dense structure and the microhardness increased. Bansal et al [30] reported that the butt joining of Alloy-718 (980 °C solution treated condition) was achieved by microwave heating, the weldment revealed perfect diffusion bonding between the base materials by complete melting of the powder particles, and the flexural and tensile strength were found to be higher.

In the present work, the heating efficiency and energy utilization rate of alloy melting process have been improved by microwave heating. The temperature-increasing characteristics and transport mechanism of the material involved during microwave heating of a spherical tin alloy powder were investigated. The material transport mechanism between tin–silver alloy particles was studied during microwave sintering by Herring’s scaling. Moreover, the effects of microwave and conventional heating on the microstructure and element distribution of the Sn–3% Ag alloy have been studied.

2. Experimental procedure

At present experiments, the spherical tin–silver alloy powder (Sn–3% Ag) from Yunnan Tin Group (Holding) Company Limited, China as the raw material. The tin–silver alloy powder was prepared via rotating disk centrifugal atomization at a rotating speed of 24 000–30 000 r·min⁻¹, the particle size of tin–silver alloy powder is about 38 ± 5 μm. The sintering and melting experiments of the tin–silver alloy powder were performed in a 3.0 kW and 2.45 GHz multi-mode microwave cavity. The tin–silver alloy powder was heated by microwaves, without using any absorbing material as an auxiliary material.

A certain amount of the tin–silver alloy powder was weighted before the experiments, and a 200-ml alumina crucible was used as a container and placed in the microwave cavity. The thermal insulation material was composed of polycrystalline mullite fibers. A k-type thermocouple was used for measuring the temperature. The sample sintering and melting process was completed in a pure flowing argon atmosphere, and then slowly cooling to room temperature in a furnace. The heating of the tin–silver alloy powder was performed under different microwave power conditions (0.8 kW, 1 kW, and 1.2 kW). The material transport mechanism was studied under different times (20 s, 40 s, 60 s, and 100 s, respectively) in the sintering process of the tin–silver alloy powder. The microstructural changes of the tin–silver alloy powder by microwave irradiation were analyzed via scanning electron microscopy (SEM), and their element distribution of was analyzed via energy-dispersive x-ray spectroscopy (EDS) at different sintering condition.

3. Results and discussion

3.1. Behavior of melting and phase analysis

Figures 1(a) and (b) show the behavior of melting of 100 g of tin–silver alloy powder at different microwave power conditions. As shown in figure 1(a), the heating curves of the different power conditions tend to be consistent and can be divided into four step, i.e. fast heating process (I, III), slow heating process (II), and heating preservation process. In addition, the first stage of the rapid heating process was fitted linearly. As shown in figure 1(b), the slope of the heating curve (i.e., heating rate) continually increases with the increase in microwave power during the initial stage of microwave heating. The temperature rise curves at the different microwave powers (0.8 kW, 1 kW, 1.2 kW) are represented using the following equations:
where $T_1$, $T_2$, and $T_3$ are the temperatures of the tin–silver alloy powder under different microwave powers and $t$ is the duration of microwave heating. The temperature rise curves are almost linear. When the microwave power is 0.8 kW, 1 kW, and 1.2 kW, the heating rate is $111.7^\circ \text{C} \cdot \text{min}^{-1}$, $133.7^\circ \text{C} \cdot \text{min}^{-1}$, and up to $153.4^\circ \text{C} \cdot \text{min}^{-1}$, respectively. When the heating enters the second stage (II), the heating rate slows down compared to that in the first stage because a part of the tin–silver powder begins to sinter and absorb partial heat. When it reaches the third stage (III), the sintering temperature continues to rise rapidly and the heating rate appears to be the same at the different microwave powers. This indicates that the molten of tin silver alloy has good microwave absorbing properties. Then when the temperature rises to 240$^\circ$C, the temperature remains constant. From above, that microwaves have a good heating performance on the tin–silver alloy powder, and the heating rate is closely related with microwave power. Furthermore, the phase compositions of the tin–silver alloy after sintering were recorded via x-ray diffraction (XRD), as shown in figure 1(c). It shows the presence of tin, silver, and Ag$_3$Sn phases under microwave irradiation. There is no diffraction peak of Ag in figure 1(c), because of its relatively low content (it is only 3%), and it can form intermetallic compound with Sn element, which is in the form of Ag$_3$Sn phase, it has no obvious Ag diffraction peak.

### 3.2. Kinetics analysis of microwave sintering tin–silver alloy powder

The neck growth kinetics of the tin–silver alloy powder was studied during microwave sintering. A two-sphere model consists of two approximately sized spheres, and it is often used to analyze the growth kinetics of the sintering neck in the microwave sintering process. Figure 2 shows a typical sintering neck during microwave sintering (at a temperature of 180$^\circ$C for a heating of 20 s, 40 s, 60 s, and 100 s, respectively).

It can be seen from figure 2 that the size of the sintering neck increases with an increase of the sintering time, the contact area between the particles increases gradually, and the contact pores between the particles disappear for gradually. In figure 2(a), the sintering neck between two particles begins to form. The size of sintering neck increases with the sintering time as shown in figures 2(b) and (c). Eventually, it completes the diffusion joining.

Figure 1. The temperature change of tin–silver alloy powders with microwave heating time (a) and (b), XRD patterns of the tin–silver alloy after sintering (c).
process between two alloy particles, as shown in figure 2(d). And this is helpful to understand the influence of microwave on the diffusion behavior of the components in the low temperature sintering stage before melting. There are large differences between microwave heating metal materials and dielectric materials. In microwave field, the induced charge will collect on the surface because the metal with good conductivity. The effect of microwave on the metal surface has a certain skin depth, and the energy will decay rapidly when it propagates in the metal. The model of the microwave heating of the tin–silver alloy powder particles is shown in figure 3. The skin depth ($\delta$) is the depth of the microwave in the metal when its power is reduced to its surface power $1/e$ (36.8%), and its calculation formula is as follows [31]:

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} = 0.029 \sqrt{\rho \lambda_0}$$  \hspace{1cm} (4)

where $f$ is the microwave frequency (2450 MHz), $\rho$ is the resistivity of the material, $\mu$ is the magnetic permeability, and $\lambda_0$ is the corresponding wavelength (the wavelength is 0.12 m for the 2450 MHz microwave). The resistivity of the tin–silver powder is $12.9 \times 10^{-8} \Omega \cdot m$, and its skin depth is approximately 3.61 $\mu m$ by equation (4). Moreover, it is in agreement with the size of the neck ($x$) in the initial sintering stage, which is approximately 7 $\mu m$, as shown in figure 2(a). Based on figure 3, the volume fraction of the microwave action is 46.86% for a single tin–silver alloy powder, thus microwave has a large action volume on micron sized tin-silver alloy powder. In addition, the electrons within the skin depth of the metal surface will form Eddy currents under the action of electromagnetism in the microwave field; thus promoting alloy component migration, and effectively transfer the heat from the surface layer to the interior of the metal particles to realize the sintering and melting process of the metal.

The two-sphere model points out that the initial stage of sintering can be expressed by the following equation [32]:

**Figure 2.** SEM images of tin-silver alloy particles sintered at 180 °C for different sintering time: (a) 20 s, (b) 40 s, (c) 60 s, (d) 100 s.
where \( x/a \) is the neck size/particle size ratio, \( B \) is a constant (which includes particle size, temperature, and geometric and material terms), \( t \) is the sintering time, and \( n \) is an exponent of the characteristic that is dependent on the mechanism of the mass transfer process. The form of the neck growth, as given in equation (5), indicates that the plot of \( \ln(x/a) \) versus \( \ln(t) \) yields a straight line with a slope equal to \( 1/n \). Because \( n \) is an index dependent on the sintering mechanism, different values may be associated with different material transport mechanisms [33]. These were calculated as the sizes of the sintered neck and particles and as the sintering neck date, as listed in table 1. The size of the sintering neck \( (x) \) is consistent with the previous metallographic picture (figure 2(a)), and the size of the neck \( x \) gradually increases with the action time.

The data of the sintering neck listed in table 1 is plotted using Origin Pro2016 64 Bit (OriginLab, USA) as straight lines in figure 4 as an \( \ln(x/a) \) versus \( \ln(t) \) dependence. As it can be seen from figure 4, the relation between \( \ln(x/a) \) and \( \ln(t) \) is \( \ln(x/a) = 0.4485\ln t - 2.5525 \), where the slope \((1/n)\) is 0.4485. Further, the \( n \) value derived from figure 4 is 2.2296 at 180 °C, and the exponent of characteristic that is dependent on the mechanism of the mass transfer process is approximately 2. According to Herring’s scaling law [34], this might indicate that the viscous flow mechanism is the dominant diffusion mechanism in the initial stage of the sintering at 180 °C.

A viscous flow was proposed as a sintering model by Fraenkel in 1945 [35]; in this model, the trend of the temperature rise is divided into two stages. In the first stage, the contact surfaces between the tin–silver alloy particles increase until the pores are closed, and in the second stage, the remaining obturator pores gradually shrink. This is similar to the process of two droplets during from the starting point of contact to mutual combination in the initial stage of the sintering. The growth of the sintered neck can be regarded as a flow of viscous-liquid-like particles under the action of surface tension, thus reducing the total surface area of the system. The heating of the tin–silver alloy powder under microwave irradiation accords with the viscous flow mechanism, and the transport of matters is mainly based on the internal diffusion and flow of the particles until all the tin–silver alloy particles completely melt. Eddy current will be generated on the surface of alloy particles under the action of microwave electromagnetic field, which promotes the diffusion of alloy components on the surface [36]. The melting range of particle surface expands driven by the microwave electromagnetic field and eddy current effect, and the matter migration and transported is realized. In addition, the viscous flows are often

![Figure 3. The schematic illustration of the microwave penetration (a) and sintering neck (b).](image-url)

**Table 1. Data of the sintering neck.**

| Time s \(^{-1}\) | 20 | 40 | 60 | 100 |
|---|---|---|---|---|
| \( \ln(t) \) | 2.9957 | 3.6889 | 4.0943 | 4.6052 |
| \( x/a \) | 0.3124 | 0.3705 | 0.496 | 0.6337 |
| \( \ln(x/a) \) | −1.1635 | −0.9929 | −0.7012 | −0.4562 |

\[
\left( \frac{x}{a} \right)^n \sim Bt
\]  

(5)
associated with heat and mass transfer phenomena. This provides the possibility to realize the microwave high-efficiency sintering and smelting process of the alloy.

3.3. Microstructures of tin–silver alloy melted by microwave
Figure 4 shows the element distribution of the microstructure of the tin–silver alloy under conventional melting and microwave melting, respectively. According to the figure, all of the tin-silver alloy powders have been completely melted, and the compact structure of alloy has been formed. An Ag₃Sn phase is formed during the melting process, as shown in figure 1(c), and the precipitated phase is obvious notable under all conditions. The size of the precipitated phase under conventional sintering condition is larger than that under the microwave condition, and its distribution is comparatively more uniform under the microwave condition. In this study, the surface scanning analysis via EDS was used to investigate the element distribution. As shown in figure 5, the distributions of the Sn and Ag elements are more uniform under the microwave condition than those under the conventional sintering condition.

Figure 4. Fitting curve of $\ln(x/a)$ versus $\ln(t)$.

Figure 5. SEM images and EDS element mappings of tin–silver alloy under different heating method: (a) conventional sintering, (b) microwave sintering.
4. Conclusion

In summary, microwave heating can be used for heating of tin–silver alloy powders (Sn–3% Ag) without using any auxiliary microwave absorbing materials. Microwave sintering of the tin–silver alloy powder can be achieved if the particles to combine and the sintering neck to growth. And the studies of the tin–silver alloy powder (Sn–3% Ag) sintered at 180 °C clearly show that the viscous flow mechanism is the main transport mechanism. The skin depth of the microwaves is approximately 3.61 μm, and the volume fraction of the microwave action is 46.86% for a single tin–silver alloy powder particle. The heating rate increases with the increase of microwave power, and the heating process is divided into four parts corresponding to the phase transformation of the tin–silver alloy. Moreover, the microwave treatment process has an effect on the grain refinement and microstructural homogeneity.

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