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Effects of oxygen contents on sintering mechanism and sintering-neck growth behaviour of Fe—Cr powder

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ABSTRACT

The effects of oxygen contents and sintering time on the sintering-neck growth behaviour of Fe—15Cr powder were studied. The oxygen content was increased from 0.029 to 0.059 wt% by heat-treating the powder under air at different temperatures. SEM observations revealed that the length of the neck decreased as the oxygen content increased. The sintering-neck growth rate decreased most significantly when the oxygen content was increased from 0.029 to 0.034 wt%. The results of electron probe microanalysis suggested that the increase in oxygen content led to encapsulation of the powder particles by oxide films, but the oxygen content inside the sintering neck remained similar to that of the matrix. Theoretical analysis indicated that the growth of sintering necks was hindered by surface oxides and interstitial oxygen in the matrix. When the oxygen content was 0.029 wt%, the sintering necks grew via surface diffusion; when the oxygen content exceeded 0.034 wt%, the dominant sintering mechanism changed to grain-boundary diffusion. The diffusion coefficient of surface diffusion was 2.41×10^{-7} m^2/s, which far exceeded that of grain-boundary diffusion; when the oxygen content was 0.034 wt%, the diffusion coefficient of grain-boundary diffusion was only 5.79×10^{-9} m^2/s. It was also found that grain-boundary diffusion required the breaking of Fe—O bonds, so the diffusion coefficient gradually decreased to 1.12×10^{-9} m^2/s when the oxygen content was 0.059 wt%. The findings of this work will provide a theoretical basis for the optimisation of sintering processes of stainless steel with high oxygen level, such as the metal injection moulding process.

1. Introduction

Powder metallurgy of stainless steel, from powder preparation [1,2] to powder consolidation and product characterization [3,4], is widely under consideration for different applications from both theoretical and experimental points of view. Among various powder metallurgy methods, metal injection moulding (MIM) is an effective method for preparing structurally homogenous stainless steel components with complex shapes. At present, stainless steels are usually prepared by MIM from gas-atomised or water-atomised powders. Gas atomisation yields regular particles with low impurity content, but involves high costs. Water atomisation is relatively inexpensive, and has therefore become a focal point of research in this field [5–7]. However, water-atomised powders tend to have relatively high oxygen content, and it is difficult to obtain high-density sintered parts because oxide films are formed on the surface of the powder particles, which decreases the densification rate and extends the sintering holding time [8].

Compared to carbon, which may promote sintering of Cr- or Mn-alloyed steels, oxygen only hinders the sintering processes [9]. An et al. [10] found that the surface layer of atomised Fe—Mn powder mainly consists of γ-Fe_2O_3, FeO, Mn_2O_3, and MnO. Chasoglou et al. [11] found that Cu, Ni, and Mo in stainless steels can hardly form stable oxides, and their oxides have minimal effect on the hindering of densification; Cr and Mn, however, form extremely stable oxides that significantly decrease the densification rate. Lou et al. [12] indicated that water-atomised 316L powder has a stable SiO_2 layer which is detrimental to grain-boundary growth, density, and strength. Bergman [13] concluded that control of the oxygen partial pressure of the sintering atmosphere is extremely important for the sintering performance of pre-alloyed Cr—Mo steels.

At present, the effects of oxygen content on the sintered densities and sintering mechanisms are topics of keen interest in powder metallurgy [14,15]. Song [16] found that the early stage of sintering of MIM 316L stainless steel, in which sintering-neck formation and growth occur, takes place in the temperature range of 1050–1200 °C. Ortiz and Castro found that the Cr and Mn oxide film on Astaloy CrM powder can effectively obstruct the growth of sintering necks in the commonly applied sintering temperature range of 1120–1250 °C. Hence, reducing agents or reducing atmospheres need to be employed during the sintering of Astaloy CrM powders [17]. In addition, the decomposition and reduction of oxide components were found to be key factors of

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Table 1
Composition of Fe—15Cr powder.

Element	B	P	Si	Cr	Fe
Content (wt%)	0.01	0.04	0.01	15	Bal.

the sintered density of MIM stainless steel [18]. Chasoglou et al. [11] concluded that sintering necks form more easily on the reduced metallic surface of a powder particle than on the oxide layer. The study of Hrubovčáková et al. [19] on the fracture surfaces of sintering necks revealed that sintering-neck growth is mainly obstructed by the presence of stable spinel-type oxides. Although a number of studies have been performed on sintering-neck growth during the initial stage of sintering and the obstructive effects of oxides, reports on the mechanism with respect to sintering-neck growth remain scarce, and reports on diffusion coefficients during sintering-neck growth are similarly uncommon.

To address this gap in the literature, we performed research on sintering-neck growth behaviour during the initial stage of sintering of Fe—Cr powders with varying levels of oxygen content. Heat treatment was used to increase the oxygen content, and the effect of the sintering holding time on the sintering-neck growth was also studied. The sintering behaviour during the initial stage of sintering was determined by analysing the dominant sintering mechanism and diffusion coefficients of powders with different levels of oxygen content. The findings of this work will provide a theoretical basis for the optimisation of sintering processes.

2. Experiment

Gas-atomised Fe—15Cr spherical powder, supplied by Hunan Hengji Powder Technology Co., Ltd., China, was used in this work. Its composition is shown in Table 1, and it can be seen that the Cr content was very similar to that of the commonly used 17-4PH powder. The powder was screened by 160 and 180 mesh sieves to obtain a powder with similar particle size. The morphology and particle-size distribution of the Fe—15Cr powder are shown in Fig. 1, and the median particle diameter, D_{50}, was 104 μm. This powder was used to simplify the effects of alloying elements, powder shape, and particle-size distribution on the sintering behaviour.

The curves of differential thermal analysis (DTA) and thermogravimetric (TG) of the powder are shown in Fig. 2. Oxidation took place after 160 °C, but the oxidation rate was relatively slow up to 950 °C; the transition to austenite took place at 750 °C. The pre-oxidation heat-treatment temperatures used in this work were 160, 200, 250, 300, and 350 °C, and the holding time was 2 h; the oxygen contents of the resulting powders were 0.029, 0.034, 0.042, 0.052 and 0.059 wt%, respectively.

A scanning electron microscope (SEM; JSM-6360, JEOL, Japan) was used to observe the morphology of the powder and length of the sintering necks. Fifteen sintering-neck viewing fields were randomly selected for each type of powder, and the data of the sintering necks' length in each viewing field were recorded; the average sintering-neck lengths were then derived from the data. A TG analyser (EV018/24, Setaram, France) was used to perform DTA and TG analyses on the powder samples. A field-emission electron probe microanalyser (EPMA; JXA-8530F, JEOL, Japan) was used to analyse the surface oxide layer of the alloys, and a nitrogen/oxygen analyser (TC-436, Leco, USA) was used to analyse the oxygen content of the powder samples. A sintering furnace (VSF-112, China) was used at a vacuum level of 10^{-1} Pa. The sintering temperature was 1200 °C, at which relatively large sintering necks were formed without any liquid phase and were favourable for the observations.

3. Results

3.1. Sintering-neck growth behaviour

Low-magnification SEM images of the sintered powders with various levels of oxygen content are shown in Fig. 3. These images clearly demonstrate that powder particles containing 0.029 wt% oxygen formed the most distinct sintering necks, and the low-magnification images were sufficient to clearly illustrate the sintering necks among the particles. The sintering necks of powders with higher levels of oxygen content were more difficult to observe, however, especially powders with oxygen contents above 0.05 wt%. Therefore, it was determined that increasing oxygen contents significantly obstructed the formation and growth of sintering necks.

High-magnification SEM images of the sintered powders are shown in Fig. 4. The lengths of the sintering necks clearly decreased as the oxygen content was increased. The plots of the sintering-neck length as functions of the oxygen content and sintering holding time are shown in Fig. 4(f). It can be inferred from this figure that the sintering-neck sizes increased as the sintering holding time increased. When the holding time was the same, the sintering-neck size decreased as the oxygen content of the powder increased; the greatest decrease in neck length was observed when the oxygen content was increased from 0.029 to 0.034 wt%. In particular, 0.5 h of sintering of the 0.029 wt% powder resulted in a longer sintering-neck length than that of the 0.034 wt% powder which was sintered for 2.5 h.

3.2. Distribution of oxygen in sintered powders

The distribution of oxygen in the as-sintered powders obtained by EPMA is shown in Fig. 5. The images indicate that oxidation primarily occurred on the particle surfaces of the metallic powder, and these surfaces were enveloped by an oxidised layer. A small amount of oxides was formed on the particle surface of the powder with 0.029 wt% oxygen. When the oxygen content exceeded 0.034 wt%, the solubilised oxygen content of the matrix increased, and the oxidised layer on the particle surface gradually enveloped the entire particle, thus increasing

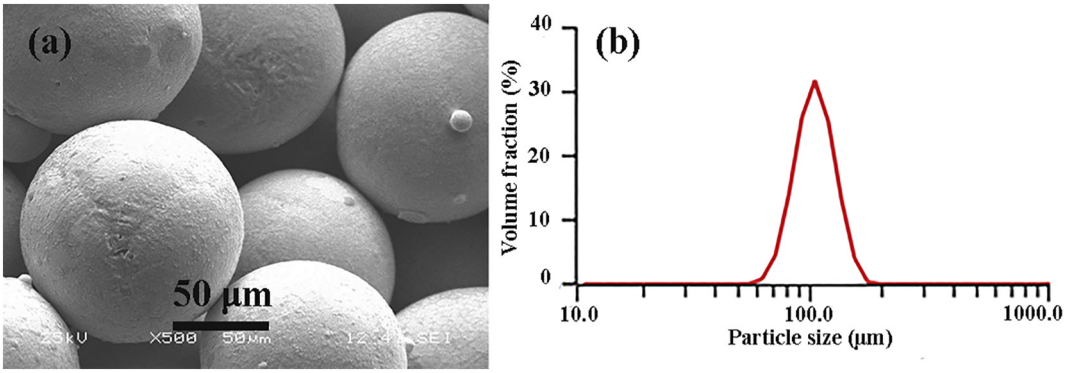

Fig. 1. (a) Morphology and (b) particle-size distribution of Fe—15Cr powder.