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Chapter

Prologue: The New Era of Sintering

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1. Introduction

Nowadays, the new era of development of the sintering process has begun. The sintering of metal and ceramic powders plays an important role in our industry.

Sintering is a one-way processing technique which allows the production of density-controlled materials and components from metal or/and ceramic powders through particle bonding. This process of powder consolidation is quite famous and has been applied in different fields for more than 5000 years [1–4].

In general, sintering processes can be classified according to the material state during the sintering process as solid-state sintering and liquid phase sintering. The ability to achieve consolidation without melting is made possible by the thermal activation of mass transport processes driven by reduction of surface and grain boundary energies. To optimize thermal activation and attain high density with concomitant strength, sintering is carried out at high temperatures, relative to the melting point of the material. Optimal parameters for sintering result from a combination of material variables and process parameters [5], as shown in **Table 1**.

The sintering process generates an increase in the compact strength and rigidity, together with a dimensional change of the powder particles, with the formation of necks between contacting spheres. Typically, longer sintering times produce larger necks and, therefore, samples with higher strength.

Money-saving reasons moved the scientific research toward a variety of means of thermal activation and, in particular, electric current, in order to produce high-density objects in a faster way and using lower temperatures. Spark plasma sintering (SPS) and pulsed electric current sintering (PECS) techniques are only a few examples of how far the research is pushing the performance of sintering, at both fundamental and applied levels [7–9].

In terms of heating methods, the most common can be synthesized as follows: (i) contact methods, such as thermal conduction, radiation, or convection and (ii) noncontact heating methods, such as induction, radio frequency (RF), or microwave heating.

This book consists of six sections; the new era of sintering is presented at the beginning of the book. This first section opens with the introduction on sintering followed by an overview on the different sintering techniques and thermodynamics and kinetics of sintering. The second section focuses on the influence of sintering on microstructure and mechanical properties. The third section provides a comprehensive summary on the solid-state sintering of materials (intermetallics, ceramics, metals, and composites). The fourth section is dedicated to sintering-based 3D printing as a new technology. The fifth section addresses on the composite sintering and applications. The mathematical models and numerical methods for continuous sintering approaches are fully discussed in the last section.

Material (powder) parameters		Process parameters
Physics	**Chemistry**	
Shape	Composition	Temperature
Size	Impurity	Time
Size distribution	Stoichiometry	Pressure
Agglomeration	Homogeneity	Atmosphere
Mixedness		Heating/cooling rate

Table 1.
Summary of the major sintering parameters (adapted from [6]).

The book aims to provide informative chapters to the readers, researchers, and material engineering and industrial material scientists. The chapters in this book are from specialists in their respective disciplines. In addition, this book is very important for the diffusion of the scientific knowledge.

2. Sintering techniques

Sintering is the process of consolidating powder compact by a thermal treatment to obtain materials with special properties. It is one of the widely used techniques in the powder metallurgy and ceramic processing. These techniques enable heating through interaction between electromagnetic field and materials.

2.1 Conventional sintering

Powder forming and, in particular, pressing are among the best ways to build flat objects. At first, the metal powder is pressed into a die, having a geometry close to the one of the final part, together with binders (to increase compact ability) at room temperature to form the so-called green part, which is typically strong enough to be handled gently. The sintering of the green part can be divided into three stages: (i) preheating; (ii) sintering, at a temperature maintained for a time depending on the strength of the bond which needs to be obtained; and (iii) cooling. Usually all the three stages are performed in a controlled atmosphere furnace, in order to prevent phenomena such as oxidation or unwanted chemical reactions. Sintering of stainless steel and refractories is usually performed under vacuum conditions.

As the name might suggest, in liquid sintering a portion of the material is in the liquid phase. This procedure is typically used for cermet, metal, and ceramic sintering. During liquid phase sintering, a liquid phase coexists with a particulate solid at sintering temperature. The goodness of sintering in this case depends strongly on the wetting properties of the liquid part [10].

2.2 Electric current-aided sintering

Heating induced by electric current has some interesting advantages with respect to conventional heating sources such as the lower sintering temperature, which allows to process nanometric powders, shorter time duration, and better material properties [11–13].

Pulsed electric current sintering (PECS) is characterized by the simultaneous action of a current-induced heating and a uniaxial pressure. PECS allows to reach high heating rates and influences mass transport. Typically, a pulsed DC current

is applied with a relatively low voltage (below 10 V), and the current is applied by pulsing patterns. The pulsing pattern is made up of a sequence of pulses (3.3 ms each) followed by an interruption of current, i.e., a pulse pattern of 12-2 means that 12 pulses are applied, followed by a duration of 2 pulses where the current is not applied [9].

The same simultaneous application of heating and uniaxial pressure is performed during spark plasma sintering (SPS) high densification at temperatures which are typically around 200°C lower than in conventional sintering. Thus, SPS is a new powder consolidation technique used to fabricate bulk shapes and nanostructured materials. This method uses uniaxial pressure and pulsed direct electric current to consolidate the powders at short sintering time and a relatively low sintering temperature compared to conventional hot pressing sintering techniques. The short sintering time is suitable for preserving the amorphous structure without undesirable phase transformations. During SPS heating is due to a pulsed DC current passing through the die which contains the powder, while pressure is applied on it. The characteristics, therefore, include the high heating rate, the application of a pressure, and the effect of the current. While similar for some features to conventional sintering, the SPS process is typically characterized by a higher heating rate such as 300°C/min compared to a maximum of 10°C/min reachable during conventional sintering. Therefore, high relative densities can be obtained in a very short time, allowing to sinter nanometric powders, nanostructured ceramics, or nanocomposites, avoiding considerable grain growth [8].

2.3 Microwave sintering

Microwave sintering, which includes heating and sintering, is a powerful process for sintering ceramic, ceramic composites, cermets, and metals. In microwave sintering the heating is obtained through a noncontact method which results in enhancement of the process in terms of reaction and diffusion kinetics, shorter cycle time, finer microstructures, and other unique features leading to considerable improvement in the mechanical properties and further energy savings [14–16]. While developed for ceramic, inorganic, and polymeric materials, microwave sintering is now employed also for all metal powders [17–21].

During microwave sintering, heating takes place via absorption/coupling.

of the microwave field followed by the so-called volumetric heating (viz., heating of the material as a whole) due to the conversion of the electromagnetic energy into.

thermal energy. In this particular case, heating is generated within the material in an instantaneous way, which depends strongly on the material properties. Therefore, with respect to conventional sintering, the heating profile is inside-out instead of outside-in [22].

2.4 Hot isostatic pressing

Hot isostatic pressing (HIP) is a manufacturing technique based on the simultaneous application of temperature and pressure to materials (usually powders) for a definite time to increase the density of materials. This process was invented in 1955 to improve aircraft systems and nuclear industry. Today it became an emerging technology in the processing of high-density powders that is used in aerospace, automotive, medical defense, etc. [23]. This technique has several advantages and involves highly complex shapes of finished parts, the powders are consolidated at lower temperatures achieving higher densities, the finished parts have homogenous density, the high gas density results in rapid heating and shorter time, and the

brittle materials can be processed because of the more uniform heating [24]. Thus, HIP involves the simultaneous application of high temperature and pressure cycles [25]. In the first cycle (cold loading cycle), the temperature is increased some time after the pressure reaching their peak at the same time to give good geometric control in sheet metal encapsulation. In the second cycle (hot loading cycle), the pressure is applied after the temperature has reached its desired value. In the third cycle, the temperature is raised only after pressure reaches its desired value. In the final cycle, the pressure and the temperature are increased simultaneously to reduce the processing time.

The advantage of HIP is the reduction of production times and the variation of properties in the solid, obtaining almost finished parts and parts with complex shapes or small sizes due to its isostatic processing. It is noteworthy in this instance that the model used will be validated over similar powder forming processes where the application of temperature and pressure is performed simultaneously [26–28].

2.5 Sintering-based 3D printing

3D printing is a new technology, which appeared since the 1980s, used to produce bulk materials (metals, ceramics, composites, etc.) with complex geometry. This technique is based on extrusion followed by sintering. Thus, the advantages of this method are the low cost and the versatile printing strategy. 3D printing allows to fabricate parts in a discrete layer by layer or line by line or point by point from 3D computer-aided design (CAD) models. It is the unique technique that enables to fabricate precise and highly complex parts that are difficult to obtain using traditional techniques [29]. Three-dimensional printing technology is expected to solve the limitations that are inevitably encountered when using traditional methods. 3D printing, also known as additive manufacturing, is based on the principle of layered manufacturing, in which materials are overlapped layer by layer [30]. This technology can be used to quickly fabricate components with any complex shape by accurately accumulating material using solid modeling according to a CAD model or computed tomography (CT) scan under computer control [31]. The 3D printing industry has recently exploded due to the reduced manufacturing costs of 3D printers and to their improved printing precision and speed, allowing for huge advances in medical equipment, implant material, and cell printing.

3. Thermodynamics and kinetics of sintering

The basic of sintering is the formation of necks between powder particles. While neck formation depends on system thermodynamics, the rate of sintering is mostly due to the temperature of the process. At room temperature, the atoms in a material are not noticeably mobile, so the particles do not sinter. When a material is heated at a temperature close to its melting point, the atoms increase their mobility and produce bonding formation, which lowers the overall system energy. The energy changes in sintering are small so that the rate of change during sintering is slow [22].

At the beginning of sintering, the interparticle neck grows to the point where its size is less than one-third of the particle size, often associated with a little dimensional change. Sintering proceeds with necks growing to a dimension which is larger than one-third of the particle size but still lower than half of the particle dimension, corresponding to a density between 70 and 92% for spheres. The pores are tubular

and connected to the external surface, and the green sintering body is compact but not fully dense so that gas can still pass through it. In the end, the final stage of sintering corresponds to the elimination of surface pores, while internal isolated pores are filled with process atmosphere.

Sintering is mainly driven by the reduction of surface energy associated with the decrease in the pore-solid surface area. Locally, there is a chemical potential shift on each component of surface on the interface, from the value for a flat interface in the same system, which is proportional to the local mean curvature H at the surface element, as shown by thermodynamics.

Assuming that local equilibrium exists at each interfacial element, the chemical potential of vacancies in a volume close to a curved surface element is given by Eq. (1):

$$\mu_v(H) = \mu_v^0 + 2\gamma VH \tag{1}$$

where V is the molar volume of the solid phase, γ is the specific interfacial free energy, and $\mu_v{}^0$ is the chemical potential of vacancies adjacent to a flat surface at a given temperature and external pressure of the system. The chemical potential shift reflects in a change in the molar concentration of vacancies ($c_v(H)$), which form a dilute solution. Given that a system with a flat surface has a local mean curvature equal to zero, the shift in vacancy molar concentration can be written as Eq. (2):

$$c_v(H) = c_v^0 - \frac{2\gamma V c_v^0}{kT}H \tag{2}$$

where T is the absolute temperature and k is Boltzmann's constant. This theoretical treatment shows that the local mean curvature on the surface determines the distribution of vacancy concentrations in volume elements close to the pore-solid interface. Therefore, for convex surface elements, the local stress state is compressive, and $c_v(H) < c_v{}^0$, while for concave surface elements, the local stress state is the opposite, and $c_v(H) > c_v{}^0$. The vacancy molar concentration distribution modifies their flow distribution, and grain boundaries act like sinks, while surface elements defined by $H = 0$ are source of vacancies. The densification in conventional sintering is, therefore, due to the vacancy annihilation at the grain boundaries.

In terms of kinetics, there is a variety of mechanisms which control the sintering process at different levels, such as volume, grain boundary and surface diffusions, plastic deformation, and vapor transport. Densification is mainly influenced only by the first two mechanisms, being defined as a decrease in volume of the pore-solid structure. Plastic deformation generates only a limited amount of surface tensions and gives, namely, a negligible contribution to sintering densification control. Vapor transport is the dominant mechanism when the solid phase has a high vapor pressure, although it is not able to produce densification since both vacancy sources and sinks are on the surface. This limitation is verified also for the surface diffusion mechanism [22].

4. Conclusions

Conventional and new sintering systems, based on various mechanisms of heat generation, are changing the world of powder metallurgy. The combination of different parameters, which can be related to the materials used or to the particular process, allows the production of objects having properties which can make them suitable for different applications. This book inspires materials scientists to carry on efforts concerning sintering.

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Conflict of interest

All authors have seen and approved the manuscript being submitted. We warrant that the chapter is the authors' original work. We warrant that the chapter has not received prior publication and is not under consideration for publication elsewhere. On behalf of all the co-authors, the corresponding author shall bear full responsibility for the submission.

This work has not been submitted for publication, nor has it been published in whole or in part elsewhere. We attest to the fact that all authors have contributed significantly to the work, have read the manuscript, attest to the validity and legitimacy of the data and its interpretation, and agree to its submission to the IntechOpen.

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