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Thermodynamic aspects during the processing of sintered materials

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ABSTRACT

This study highlights the thermodynamic aspects that should be considered in the development and processing of powder materials. Several reactions that can occur during sintering of powder mixtures in which particles of different compositions and phases are present, as well as reactions with the furnace atmosphere were discussed. A theoretical basis is presented to predict, evaluate and, in some cases, avoid these reactions. Experiments involving sintering of ferrous materials were performed in order to exemplify the theories addressed in the work. In these experiments were studied the solubility of elementary Mo in Fe–Mo powder compacts, solid lubricant obtaining in situ during sintering by dissociation of silicon carbide, reactions between MoS_2 and iron-based matrix, oxidation of a Si-containing alloy, and copper sublimation from 17-4 PH stainless steel parts. The microstructure analysis and properties evaluation of sintered materials indicated to be possible to predict metallurgical aspects using thermodynamic knowledge.

1. Introduction

The current advanced stage of technological development requires advanced materials and components with increasingly high performance. Thus, materials with particular properties designed especially for each specific application are required. In this scenario, sintered materials are becoming increasingly important because their microstructure can easily be controlled and tailored.

Sintered materials (or powder materials) are a large group that includes metallic, ceramic and composite materials, ranging from porous to nearly full dense parts. These materials are used today in several distinct engineering applications, such as mechanical parts for the automobile industry, household appliances, the electronic industry, metallic and ceramic filters, porous materials for catalytic substrates used in the chemical industry, hard metals, ceramic cutting tools and structural ceramic components.

Many techniques can be used in the formulation of the chemical and phase composition of sintered materials, with the mixture of powders being the most traditional method. Using this method, powders with distinct phases or compositions can be mixed such that the desired final phase composition of the material is obtained through reactions "in situ" during the sintering of the green parts. The final microstructure obtained in the sintered material and its properties depend largely upon the particular set of phases of the powders mixed with each other. That is, the powder feedstock prepared by mixing a set of selected phases or compounds that react together during the sintering process is responsible for forming the desired final material. Reactions between the particles of the different raw materials present in the feedstock occur in the direction towards thermodynamic equilibrium. Often this process involves both the formation of new phases or compounds and the elimination of others. Accordingly, the evolution of microstructure passes through several transient states, with each one having a particular set of properties that could be useful for any specific application. Thus, sintering could be interrupted at the right time to freeze the transient microstructure and/or phase composition desired for the tailor-made sintered material.

Knowledge about phase diagrams, thermodynamic driving forces and final thermodynamic equilibrium is essential to predict the reactions that may occur during the sintering. This knowledge is the background for the selection of the correct powder components for the formulation of the powder feedstock. Special attention is needed to avoid undesired reactions between the sintering atmosphere and the phases present in the compact. When any undesired chemical potential gradients exist between these phases and the sintering atmosphere, undesirable reactions occur with a normally negative effect on the quality of the sintered material.

Therefore, the main goal of this work is to review some aspects of the thermodynamic equilibrium that may occur during the sintering

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of distinct powder mixtures, in particular by presenting the theoretical background on this topic and some practical examples observed during the development of sintered materials.

2. Background

Considering the Gibbs free energy of formation of a solid solution, the chemical elements present in the green body are more easily protected against oxidation or any other reaction with species present in sintering atmosphere than when these elements are mixed in elemental powder form; the same behaviour is also observed for compounds present in the powder mixture. For example, it is difficult to avoid oxidation of some metallic elements, such as silicon, manganese, chromium, titanium and magnesium, when used in powder metallurgy under industrial production conditions because of the high stability of their oxides. Consequently, these elements require a high purity of the sintering atmospheres in terms of the chemical potential of oxygen to avoid oxides in the sintered material.

In this case, the use of pre-alloyed powders, powders of compounds or even any specially designed master alloy in the powder-feedstock induces increased protection against reactions with non-metallic elements present in the sintering atmosphere. Furthermore, special attention is needed to avoid contamination of the compacts during sintering by atoms sublimated or evaporated from the hot zone of the furnace or from the heaters or other materials that are inside the processing environment. Likewise, atoms sublimated or evaporated from the samples can cause damage of the structural components of the sintering furnace.

During the thermal treatment of sintering, a green body produced from a powder mixture formed by particles of distinct phases undergoes several reactions while the system tries to reach its final state of thermodynamic equilibrium. The reactions that occur in reality depend on the particular alloy system under sintering as well as on the applied sintering conditions. Among the possible reactions, the most common are the following:

- Dissolution of alloying elements in the matrix, forming solid solutions;
- Dissociation of compounds and dissolution of the chemical elements released by the dissociation;
- Formation of new phases or compounds due to reactions between the powder particles of distinct components;
- Reactions between compact and chemical species present in the sintering atmosphere, modifying the chemical composition and leading to the formation of new undesirable phases;
- Sublimation and evaporation/condensation, resulting in contamination of samples as well as the furnace hot-zone.

Using thermodynamic data and the phase diagrams of the specific metallurgical system as well as controlling the chemical potentials of all chemical species present in the sintering atmosphere, the reactions can be predicted and controlled. Some knowledge that is useful in examining the system and predicting possible reactions are summarised below.

2.1. Interactions between powders from different materials

2.1.1. Dissolution of chemical elements into a matrix forming a solid solution

Let us suppose that a powder feedstock is produced by mixing an elemental powder of the alloying elements A and B with elemental powder M (matrix of the alloy). As established thermodynamically, the driving force for dissolution of the alloying elements A and B in the matrix M (the main constituent of the material) is the variation of the Gibbs free energy due to the chemical potential variation of each chemical element in the solid solution.

The variation of Gibbs free energy, $\Delta g(T)_{sol}$, of the formed solid solution can be calculated using Eq. (1):

$$\Delta g(T)_{sol} = n_A RT \ln a_A + n_B RT \ln a_B + n_M RT \ln a_M. \tag{1}$$

In these equations, n_A, n_B, and n_M represent the mol numbers of each chemical element in the solid solution, R is the gas constant (1.986 cal/mol-K), T is the absolute temperature (measured in K) and a_A, a_B, a_M are, respectively, the activities of the elements A, B, and M in the solution at the reaction temperature T. The activity values vary with the concentration of each element in the solution and with temperature.

The activity a_A of a generic chemical element A can be expressed as $a_A = x_A y_A$. In this equation, x_A is the molar fraction of the chemical element A in solution, and y_A is the activity coefficient, which expresses the atomic interaction of A with its neighbouring atoms in the solid solution. A strong interaction between a solute atom and its solvent atoms leads to a higher binding energy and hence a lower coefficient of activity, leading to greater stability of the solute in the solution. Accordingly, in this case, the activity of the solute in the solution is said to be low. As the activities are quantities that are smaller than the unity, Eq. (1) always leads to negative values for $\Delta g(T)_{sol}$. Lower activity coefficients of the soluble alloying element in solution lead to higher magnitudes of the Gibbs free energy variation associated with the solid solution formation and higher stability of the solute in the solid solution. This result means that a higher stability of the solute in the solid solution results in a lower reactivity with chemical species present in the sintering atmosphere, i.e., the chemical species of the sintering atmosphere need higher chemical potentials to react with the solute.

The molar quantities of Gibbs free energy variation for the individual chemical components of the solution are given by the following equations:

$$\Delta G(T)_A = RT \ln a_A \tag{2}$$

$$\Delta G(T)_B = RT \ln a_B \tag{3}$$

$$\Delta G(T)_M = RT \ln a_M. \tag{4}$$

These quantities represent how much of each element (A, B or M) contributes to the free energy variation of the solution when a mol of the element is present in the solution. The value precisely represents the variation of the chemical potential of the element due to its dissolution in the considered solution.

2.1.2. Dissociation of compounds and dissolution of the generated elements in the matrix

The dissociation of a compound mixed in a matrix followed by dissolution of its chemical elements during sintering can also be examined using thermodynamic data. For simplification, let us suppose that 1 mol of element A reacts with 1 mol of element B to form 1 mol of compound AB. The driving force for the compound formation is the decrease in the Gibbs free energy. The variation of the Gibbs free energy for the formation of 1 mol of compound AB is given by Eq. (5) as a function of temperature T:

$$\Delta G^0(T)_{AB} = C_1 + C_2 T \log T + C_3 T. \tag{5}$$

In this relation, C_1, C_2 and C_3 are constants that can be found in thermodynamic data books [1], allowing us to calculate $\Delta G^0(T)_{AB}$ as a function of temperature T. Dissociation is the reaction in the opposite direction, which means that the dissociation of 1 mol of the compound AB requires the same amount $\Delta G^0(T)_{AB}$ of energy as positive energy in the energy balance. According to the second law of thermodynamics, dissociation only occurs if further reactions provide a greater amount of energy decrease in the same system, as, for example, dissolution of