PHASE EQUILIBRIA AND MICROSTRUCTURE

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Summary

The understanding and modern development of materials is based on a knowledge of the phase equilibria and the microstructure. Since the properties of a material are determined by the composition and microstructure, application of a material requires a knowledge of both. The Gibbs phase rule provides us with a guiding principal for understanding phase equilibria for a given composition. Using this rule and experimental observation, sometimes coupled with thermodynamic modelling, we can produce phase diagrams which provide us with a map of the phase equilibria in temperature-composition space. However, a knowledge of phase diagrams is not sufficient, since materials may be processed to produce non-equilibrium states and a variety of microstructures. Microstructural characterization of materials correlated to the measured properties has been used to develop an understanding of the effects of various microstructural details on different properties. This understanding is still being developed. Nevertheless, many principals of microstucture-property relationships are

understood and can be applied to the development of new materials.

1. Phase Equilibria

1.1. Introduction

The history of the development of materials for use by society dates back to the beginning of civilization. For millennia this development was mostly in the hands of skilled artisans who made improvements through trial and error methods. From the beginning of the 19th century the scientific basis for the understanding of materials began to be laid through the development of thermodynamics. Only in the last 100 years has the fundamental understanding of materials developed to the level of a scientific and engineering discipline. This understanding has been brought about through the theoretical development of thermodynamics, studies on phase equilibria, phase transformations and phase diagrams, and the correlation of material microstructure with properties. At the beginning of the 21st century we are beginning to develop sophisticated modelling and simulation techniques that will eventually lead to more rapid and application specific materials development.

A fundamental principle of materials engineering is that the microstructure of a material controls the properties. By microstructure we mean the type and composition of phases present in a material, their morphology and distribution, and their internal structure. For a given alloy composition the phases present at equilibrium are determined by the thermodynamics of the alloy system. Theoretical equilibrium is achieved when the system has minimized its Gibbs free energy, although in practice equilibrium is often considered to be when the state of the system does not change over some appreciable length of time. One of the fundamental methods of describing the equilibrium relationships in an alloy is through the use of a phase diagram. This kind of diagram "maps" the phase equilibria in a composition, temperature and pressure space. The phase diagram is a manifestation of the thermodynamics of the system. An important relationship relating the number of phases in equilibrium to the number of components in a system and their composition, pressure and temperature was derived by Gibbs. This relationship, known as the Gibbs phase rule, is the guiding principle for the construction of phase diagrams.

1.2. Gibbs Phase Rule

The phase rule derived by Gibbs is simply a statement of the number of independent thermodynamic variables available given a specific number of relationships between all of the variables. The derivation can be demonstrated by defining the factors involved and determining the number of relationships between them.

1.2.1. Phase

A material system may consist of one or more phases. A phase may be defined as all those portions of a system, each of which is separated from its surroundings by a definite interface, possessing the same intensive and molar properties when the system is in thermodynamic equilibrium or exhibiting a continuous variation in intensive and

molar properties when the system is in a nonequilibrium condition.

1.2.2. Components

The number of components in a system in which the chemical species do not react with one another is given by the number of individual chemical species. If the individual species can react to form other chemical entities (compounds) then the number of components, C, is given by the total number of chemical species less the number of independent relationships between them, R

$$C = N - R$$

1.2.3. System

In order to specify the state of a system we must specify the composition, temperature and pressure variables of each phase. Specifying the composition in terms of mole fractions of the components we need only give C-1 compositions to completely specify the composition of the phase. If there are P phases then the total number of variables, is:

$$Variables = P(C + 1)$$

1.2.4. Equilibrium Relationships

For thermal equilibrium the temperature of each phase should be the same in each phase:

$$T_1 = T_2 = T_3 = \dots$$

For mechanical equilibrium the pressure of each phase should be the same:

$$P_1 = P_2 = P_3 = \dots$$

For chemical equilibrium the chemical potential, μ_i of each component should be the same in every phase:

$$\mu_i^1 = \mu_i^2 = \mu_i^3 = \dots$$

There is a similar set of relationships for the chemical potential of each component of the system.

The chemical potential of a component may be defined as the increase in Gibbs free energy of a system on addition of an infinitesimal amount of that component with all other factors held constant. Each of the equilibrium relationships results in P-1 independent relationships giving a total number of relationships, of:

$$Relationships = (C + 2)(P - 1)$$

1.2.5. Gibbs Phase Rule

The degrees of freedom, F, available in the system are given by the difference between the number of variables and the number of relationships:

$$F = Variables - Relationships$$
$$F = P(C+1) - (P-1)(C+2)$$
$$P + F = C + 2$$

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Biographical Sketch

Professor Philip Nash received his B.Sc. in Metallurgy in 1973 from City of London Polytechnic and his PhD in Materials Science in 1978 from Queen Mary College, University of London, U.K. After graduation he worked as a postdoctoral research associate at Imperial College, University of London, with Professor David West, on the experimental determination of ternary nickel-base alloy phase diagrams. In 1981 he was appointed as an Assistant Professor at Illinois Institute of Technology (IIT) in Chicago, Illinois, USA. Since 1991 he has been a Professor of Metallurgical Engineering and also serves as the Director of the Thermal Processing Technology Center at IIT.