

GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES

SPINODAL DECOMPOSITION IN THE BINARY SYSTEM

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ABSTRACT

Spinodal decomposition is a phase separation mechanism within the miscibility gap. Its importance in case of binary system, this work is aimed at a better understanding of the phase separation process in the binary system. Fully ferritic microstructured alloys was observed that hardness of homogenized samples increased monotonically with increasing one of metal content up to 55 wt.% which can be attributed to solution hardening [1]. However, it means that alloys are suffering phase separation. For compositions inside the miscibility gap, hardening effect is a result of phase separation either by nucleation and growth or spinodal decomposition [3]. According to the previous studies, the Spinodal boundary is most probably located in this composition range. However, no change in hardness was observed even up to 24h. Further investigations are needed to confirm and explain this result.

Keywords- *binary system, phase diagram, miscibility gap, spinodal decomposition, nucleation and growth, hardness.*

I. INTRODUCTION

Miscibility gap is a range of temperature and composition on the phase diagram where a phase that is stable at higher temperatures decomposes into two or more phases. There are two modes of phase separation inside the miscibility gap, nucleation and growth and Spinodal decomposition, distinction between which has both theoretical and practical importance [20].

The binary system is susceptible to phase separation at intermediate and low temperatures. The Importance of the miscibility gap in this case is due to the fact that this system forms the basis. Spinodal decomposition introduces embrittlement in some binary alloy when service temperature lies between 200 and 550°C. In fact ferrite or martensite of based alloys suffers a microstructural evolution which results in embrittlement.

This process leads to the ruin of mechanical properties by decreasing the impact toughness and ductility. Accordingly one finds that understanding the phase separation mechanism is of great importance to solve the embrittlement problem [25].

Although the general belief that Transmission Electron Microscopy (TEM) is not effective in spinodal studies, because of low mass-thickness and diffraction contrast, it has been recently employed by a number of researchers and proved effective in characterizing spinodal mechanism from nucleation and growth.

II. SPINODAL DECOMPOSITION

In phase separation by nucleation and growth, first embryos of the stable phase with a composition completely different from the matrix nucleate and then grow by diffusion of solute atoms until equilibrium is reached. In this process difference in the Gibbs energy of new and parent phases is the driving force and the interfacial energy acts as a barrier against nucleation, thus a retarding force. Because of the latter, embryos of the new phase nucleate on preferred sites such as grain boundaries or inclusions which give rise to a reduction in the retarding force. In addition, embryos of the second phase need to be larger than a critical size to be thermodynamically stable [16].

Unlike nucleation and growth, phase separation by spinodal decomposition is uniform all over the microstructure since inside the spinodal there is no thermodynamic barrier, except a diffusional one, opposing the formation of second phase embryos.

Spinodal decomposition can change the properties of a material to a great extent and possesses both positive and negative consequences. Microstructure can become brittle and the hardness and strength could increase remarkably. Electrical resistivity and corrosion resistance decrease while Curie temperature is enhanced; also a significant amount of heat is released.

Spinodal decomposition can be employed to improve the mechanical or magnetic properties, for example in cemented carbide coatings such phase separation is favorable because it results in an increased resistance to abrasive wear [8]. Vycor glass is another example [9] where fine-scale phase separated microstructure due to spinodal decomposition is exploited to produce catalyst substrates and molecular sieves.

Nucleation versus spinodal

Nucleation/growth and spinodal decomposition occur within a meta-stable supersaturated solid solution. In the case of Nucleation and growth process a nucleus form and grows subsequently as illustrated in Figure 1

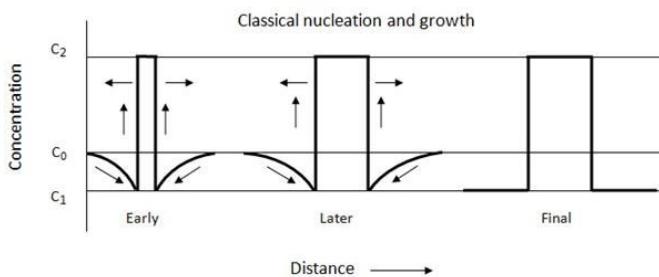


Figure 1 Nucleation

This process is accomplished by the diffusion of solute atom from the matrix towards the nucleus, a phenomenon called down-hill diffusion. The new phase formed by the process may have a different structure from the parent matrix and a sharp interface exists between the parent matrix and the precipitates (Figure 1). Normally, there is an incubation period for this process.

In the case of spinodal hardening, a small fluctuation in the solute concentration takes place and the fluctuation enlarges subsequently as illustrated in Figure 2. No new phase forms in this case but only a composition gradient exists, depicting solute-rich and solute-lean regions, with no sharp boundary between these two. This process is accomplished by the diffusion of solute atom from one region to another as shown in Figure 2, a phenomenon called up-hill diffusion. The solute-rich and solute-lean regions have the same crystal structure. There is no incubation period in this process.

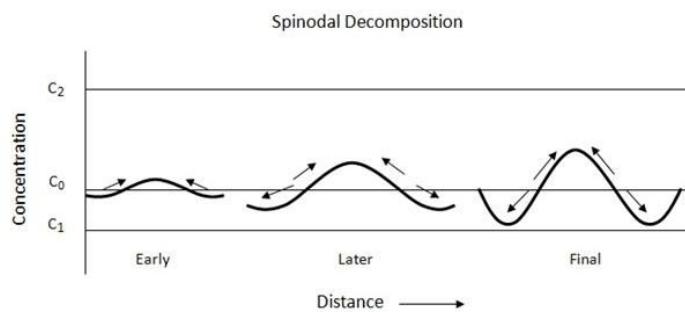


Figure 2 Spinodal decomposition process

III. NUMERICAL METHOD

A) Cahn-Hilliard equations

The linear Cahn-Hilliard equation is the basis for the theory of the spinodal decomposition in alloys, developed by Cahn and Hilliard. This theory has been used to analyze the phase decomposition in numerous alloys. The most common mathematical expression is the following:

$$\frac{\partial c}{\partial t} = M \left(\frac{\partial^2 f}{\partial c^2} \Big|_{c_0} \nabla^2 c - 2K \nabla^4 c \right) \quad (1)$$

where c is the concentration of either A or B elements as a function of a position vector and time t , M is the atomic mobility, f the local free energy, and K the gradient energy coefficient.

In contrast, the nonlinear Cahn-Hilliard equation has been the base for numerical simulation of different metallurgical phenomena⁵ such as, solidification, recrystallization, phase decomposition, etc. This equation is expressed as follows:

$$\frac{\partial c}{\partial t} = M \nabla^2 \left(\frac{\partial f(c)}{\partial c} - K \nabla^2 c \right) \quad (2)$$

The same type of parameters of the linear equation is also involved in the nonlinear one. The linearization of equation, Equation 1, can be obtained from Equation 2, if c is assumed to be only slightly different from its average value.

Both equations are partial differential equations and therefore, they can be solved using the finite difference method [4].

B) Thermodynamical parameters

As stated above, one of the important parameters of the nonlinear Cahn-Hilliard equation corresponds to the local free energy f which can be defined in a simple way using the strict regular solution model [13] for a binary alloy system as follows:

$$f = X_A f_A + X_B f_B + \Omega_{A-B} X_A X_B + RT (X_A \ln X_A + X_B \ln X_B) \quad (3)$$

where R is the gas constant, T is the absolute temperature. X_A and X_B are the mole fractions of A and B, respectively. f_A and f_B are the molar free energy of pure element A and B, respectively, and Ω_{A-B} is the interaction parameter between the A and B atoms. $\Omega_{A-B} > 0$ when A and B atoms are repulsive. On the contrary, $\Omega_{A-B} < 0$ when A and B atoms are attractive. Figure 3 shows the plots of free energy f versus composition c for the A-B binary system at different temperatures considering the value of Ω_{A-B} as a multiple value of gas constant R, 1000R, 1500R and 2000R. The values of f_A and f_B were assumed to be equal to R (T-T_A) and R (T-T_B), respectively. T_A and T_B correspond to the melting point of A and B, respectively.

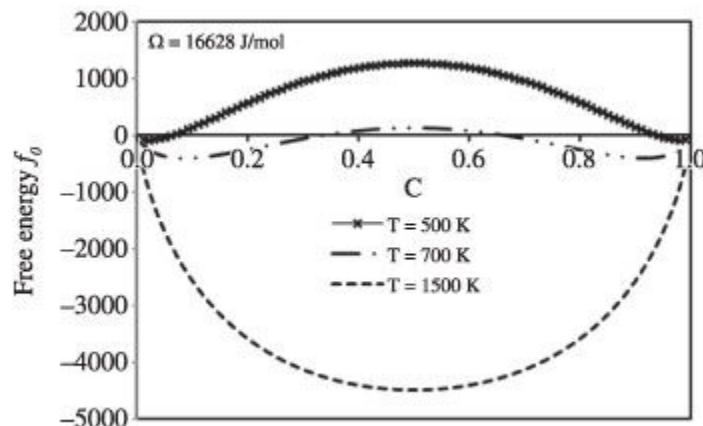


Figure 3. Plot of free energy f , vs. composition c .

IV. CONCLUSION

In a binary solid solution, the hardness of the alloy increases with increasing metal A content up to 55 wt.%. Hardness method is able to show the phase separation effects for compositions well inside the miscibility gap. For those close to the immiscibility boundary. The increase in the thermodynamic interaction parameter Ω_{A-B} caused a shorter start time for the phase decomposition. The higher aging temperature promoted the faster phase decomposition due to the higher atomic diffusion. The microstructure evolution and kinetics of phase decomposition of Cu-Ni and Fe-Cr alloys showed a good agreement with the present work results.

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