International Journal of Advanced Technology in Engineering and Science www.ijates.com
Volume No.03, Special Issue No. 02, February 2015 ISSN (online): 2348 – 7550

# "SPINODAL DECOMPOSITION"- AN EFFECTIVE METHOD OF STRENGTHENING

**Jirapure S.C[1], Borade A.B[2], Kongre U.V[3]**

*[1]Scholar, [2]Professor & Head, [3]Associate Professor,*

*Mechanical Engg. Dept., JD Institute of Engg. & Tech., Yavatmal M.S, (India)*

## ABSTRACT

*Alloys that harden during low-to-intermediate temperature treatments following solution quenching include spinodal-hardening. Spinodal decomposition is regarded as small composition fluctuations over a large space, while a classical nucleation process is categorized by large composition fluctuations over a small space. The consequential microstructure contains a homogeneous distribution of diminutive, coherent interconnected particles. In this study, after detection the theories of spinodal reactions and hardening mechanisms experimental research and numerical studies on spinodal decomposition are reviewed. Also, future developments in spinodal decomposition are predicted and criticized in an outlook.*

***Keywords: Diffusion, Metastable, Microstructure, Miscibility, Spinodal Decomposition***

## 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.

The Fe-Cr 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 for the whole stainless steel family which is amongst the most important engineering materials. Spinodal decomposition introduces embrittlement in some stainless steels when service temperature lies between 200 and 550oC. In fact ferrite or martensite of Fe-Cr 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.

Despite the general belief that Transmission Electron Microscopy (TEM) is not effective in spinodal studies, because of low mass-thickness and diffraction contrast [1], it has been recently employed by a number of researchers [4] and proved effective in characterizing spinodal mechanism from nucleation and growth.

### 1.1 What is 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.

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 [7].

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.

### 1.2 History

Back in 1941, in an effort to construct a phase diagram for Cu-Ni-Fe ternary system by means of powder X-ray diffractometry, Bradley [10] observed sidebands around the X-ray peaks of samples that had been quenched and annealed within the miscibility gap. Two years later Daniel and Lipson [11] repeated Bradley’s experiments and described these sidebands as a result of periodic variations of chemical composition and measured the wavelength to be 90Å.

Development of concentration gradients in an originally homogeneous system translates to uphill diffusion, i.e. a negative diffusion coefficient. In fact, when the diffusion coefficient is negative the ordinary diffusion equation becomes ill-posed. The first successful explanation for the periodicity of fluctuations was given by Hillert [12] in 1956. He assumed the solution to be regular and derived a flux equation for one dimensional diffusion in a discrete lattice. His equation included a term allowing for the effect of interfacial energy between neighboring planes of different composition, on the driving force. Numerical solution of the flux equation led to a periodic concentration profile within the spinodal region, also wavelength of composition variation was of the same order of what had been observed in the case of Cu-Ni-Fe. Subsequently Cahn [13] proposed a continuum model, including the effects from coherency strains as well as gradient energy, which led to a modified diffusion equation that has so far been the most referred tool for quantitative analysis of spinodal decomposition.

A pair of partially miscible solids, i.e. solids that do not mix in all proportions at all temperatures, show a miscibility gap in the temperature-composition diagram. Figure 1.1 (Favvas et al., 2008) shows a phase diagram with a miscibility gap (lower frame) and a diagram of the free energy change (upper frame). Line (1) is the phase boundary. Above this line the two solids are miscible and the system is stable (region-s). Below this line there is a meta-stable region (m). Within that region (point a to b) the system is stable. Line (2) is the spinodal. Below this line, the system is unstable (region-u) . With the spinodal region (u), the unstable phase will decompose into solute rich and solute lean regions.

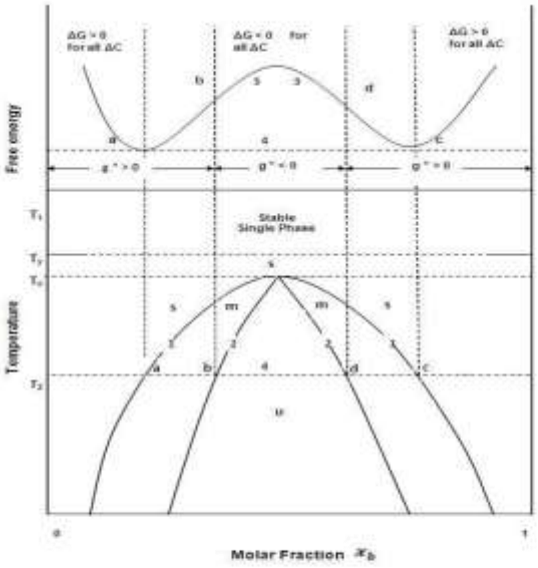

**Fig1.1 Phase diagram with a miscibility gap (Favvas et al., 2008)**

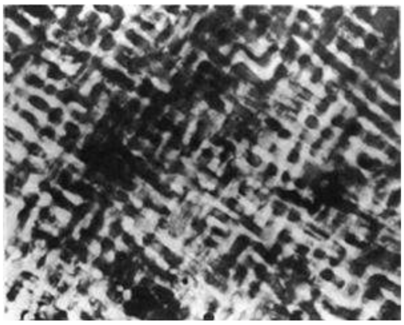

**Fig1.2 Modulated spinodal microstructure**

This process is called spinodal decomposition. The modulated structure as shown in Figure 1.2 produced by the spinodal decomposition causes the hardening of the alloys. The spinodal decomposition depends on the temperature. For example above Tc (Figure 1.1) the spinodal decomposition will not takes place

### 1.3 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 1.3.

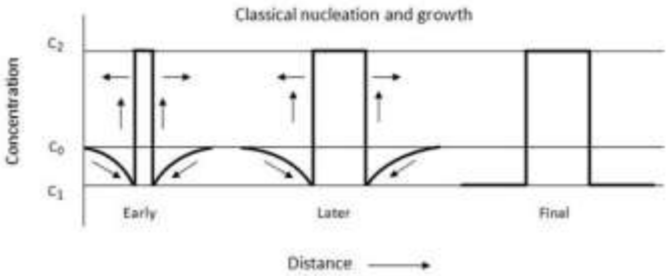

**Figure 1.3 Nucleation**

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 1.3). 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 1.4. 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 1.4, a phenomenon called up-hill diffusion. The soluterich and solute-lean regions have the same crystal structure. There is no incubation period in this process.

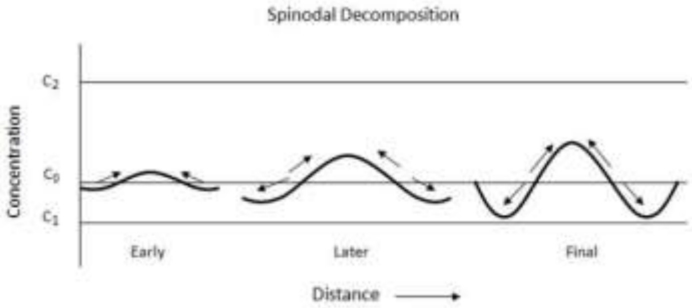

**Figure 1.4 Spinodal Decomposition Process**

## II THERMODYNAMICS OF SPINODAL DECOMPOSITION

In this section we are going to discuss conditions under which creation of composition fluctuations is spontaneous. It has been shown that change in the total Gibbs energy of the system due to concentration variations consists of chemical, interfacial and mechanical components.

Consider an initially homogeneous alloy of composition o X. Creation of a sinusoidal composition fluctuation of amplitude ΔX and wavelength λ, results in the following change in the total Gibbs energy of the system:

$$\Delta G = \frac{1}{2}\frac{d^2G}{dX^2}(\Delta X)^2 + K\left(\frac{\Delta X}{\lambda}\right)^2 + \eta^2(\Delta X)^2 E' V_m$$

The first term corresponds to the contribution from chemical energy. Since inside the spinodal d2G/dX2 is negative, one finds that the chemical energy is in favor of decomposition.

Second term takes care of interfacial energy. In fact, creation of a chemical composition gradient is equivalent to neighboring crystallographic planes of different compositions. This indeed translates to an interfacial energy or surface tension, ΔGγ, whose contribution to the total Gibbs energy must be considered. The extent of ΔGγ depends on the chemical composition gradient across the interface; hence it is called “gradient energy”. In eq., K is a proportionality constant that depends on the bonding energy difference between similar and dissimilar atom pairs.

Since there is generally a lattice parameter difference between product phases, coherency strains at the interface will contribute to the total energy of the system. This effect is included by the last term in eq. In this equation parameter η is defined as η = (da/dX)/a, Vm stands for the molar volume, (a) is the lattice parameter and E′= E/(1− ν) in which ν is the Poisson’s ratio.

Two important conclusions can be drawn from eq. First is that in order for the formation of composition modulations to lead to a decrease in the total Gibbs energy, their wavelength must be larger than a critical value, c λ , defined as follows:

$$\Delta G < 0 \Leftrightarrow \lambda > \lambda_c = \left[-2K \Big/ \left(\frac{d^2G}{dX^2} + 2\eta^2 E' V_m\right)\right]^{1/2}$$

The second conclusion is that the chemical spinodal, which is defined as d2G/dX2 = 0, is equivalent to neglecting the coherency strain effects. Therefore this concept is not factual and should only be used on equilibrium phase diagrams.

On the other hand by considering the contribution from elastic energy, a realistic temperature and composition range for spinodal region can be calculated. Assuming λ=∞ to achieve the spinodal limit we have:

$$\frac{d^2G}{dX^2} = -2\eta^2 E' V_m$$

The boundary defined by eq. is called coherent spinodal and lies inside the chemical spinodal on the phase diagram. The same account holds true for the miscibility gap concept. In other words coherent and incoherent miscibility gaps must be distinguished from each other since the latter does not consider coherency strain effects, see figure 2.1. In the Fe-Cr binary system due to the similarity in atom size as well as lattice parameter and type, contribution from elastic energy is small therefore coherent and incoherent lines are expected to be close to each other.

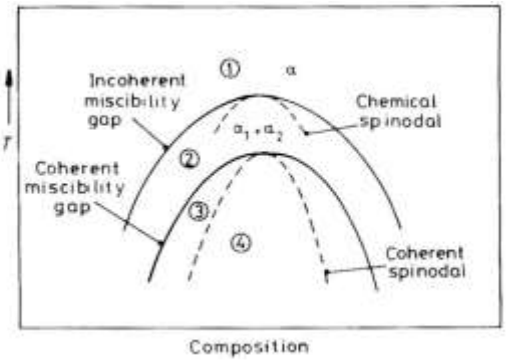

**Figure 2.1 Coherent spinodal lies inside the chemical spinodal. [14]**

In an equilibrium phase diagram the apex of incoherent miscibility gap, the temperature above which system shows complete miscibility, is called the critical temperature and is denoted by c T [15]. Therefore assuming a regular solution, a simple relation can be derived for the chemical spinodal line:

$$T = 4TC\ XB(\ 1-XB)$$

In other words spinodal boundary is defined by a parabola. Therefore deviation from parabolic behavior denotes deviation from regular solution model.

## III SPINODAL BRONZE

The addition of Ni between 4 and 15% and Sn between 4 and 8% to the Cu matrix constitutes spinodally decomposable Cu-Ni-Sn alloy system. The spinodally decomposable Cu-Ni-Sn Bronze alloys produce a modulated microstructure during the heat treatment process and its mechanical properties comparable to those of Cu-Be alloys, while being relatively inexpensive and hazard free. The modulated microstructure significantly increases the strength of the Cu-Ni-Sn alloys, and the increase is attributed to (a) alloy composition (b) condition of the alloy (cast or wrought) (c) amount of cold work prior to aging (d) aging temperature and (e) aging time. The Cu-Ni-Sn Bronze alloys can be used as the friction-reducing and anti-wear materials to make high performance bearings for aerospace, roller cone rock bit and heavy duty mobile industrial equipment etc.

It has been generally observed that five different transformation products exist in the Cu-Ni-Sn system as shown in Figure 3.1. They are: (a) modulated structure resulting from spinodal decomposition (b) DO22 ordered structure (c) L12 ordered structure (d) grain boundary and intra-granular γ (DO3) precipitates and (e) discontinuous γ precipitates. The above transformation is dependent on temperature and time (Refer to Figure 3.1). At high temperature the grain boundary and intergranular γ (DO3) precipitates form, whereas, in the middle range of temperature a discontinuous γ precipitates forms. Below the critical temperature (TR ~457°C), the spinodal decomposition takes place. When the aging time is increased, an ordering reaction takes place forming DO22 and L12 ordered structure (Refer to Figure 3.1).

The spinodal decomposition and ordering reaction increases the hardness and the YS of the alloys.

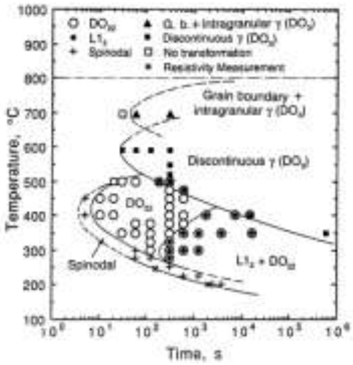

**Figure 3.1 A typical phase transformation diagram for the Cu-Ni-Sn Bronze alloy (Zhao and Notis, 1998)**

If a homogeneous high-temperature mixture of two metallic components is rapidly cooled to a lower temperature, then a sudden phase separation can set in. That is, the mixture becomes inhomogeneous and forms a fine-grained structure, more or less alternating between the two metal components. This numerical numerical simulation shows the phase separation occuring, as modeled by the Cahn-Hilliard equation. The color represents the concentration of the two metals. Green corresponds to an even mixture of metal A and metal B. Red corresponds to all metal A, blue to all metal B. Notice that the mixture starts out as an even mixture, and after some time, becomes an inhomogeneous mixture. Although the patterns formed are not completely symmetric, they are also not random. Understanding these patterns has been the subject of much research, going back to the original works of Cahn and Hilliard. Numerical simulations and subsequent analytical results have been carried out jointly with Thomas Wanner to understand these patterns. Our work has lead to a new approach to understanding the underlying mechanism for this pattern formation.

## IV SPINODAL HARDENING ALLOYS

Alloys that harden by spinodal decomposition are hardened by a treatment similar to that used for precipitation hardening alloys. The soft and ductile spinodal structure is generated by a high-temperature solution treatment followed by quenching. The material can be cold worked or formed in this condition. A lower-temperature spinodal-decomposition treatment, commonly referred to as ageing, is then used to increase the hardness and strength of the alloy.

Spinodal-hardening alloys are basically copper-nickel alloys with chromium or tin additions. The hardening mechanism is related to a miscibility gap in the solid solution and does not result in precipitation. The spinodal-hardening mechanism results in chemical segregation of the alpha crystal matrix on a very fine scale, and requires the electron microscope to discern the metallographic effects. Since no crystallographic changes take place, spinodal-hardening alloys retain excellent dimensional stability during hardening.

### 4.1 Advantages of spinodal decomposition

a) The decomposition-product phases have the identical structure but are dissimilar in composition, while in the case of precipitation the precipitate phase has a unlike structure and composition from that of the matrix. The principal advantage of the products having the identical structure is that microstructure is consistent. Consequently there are no local anodes and cathodes (eg grain boundary precipitates) to deteriorate corrosion resistance.

b) In spinodal decomposition, there is no nucleation barrier and thus there is no need to offer activation energy. Therefore, hardening by spinodal decomposition is not predisposed by section thickness or quenching rate. Though, in the case of precipitation hardening, there is a nucleation barrier. Hence, if the radius of the precipitate nuclei is less than a critical value, the precipitate phases cannot be nucleated. As a result, the quenching rate and section size considerably influences enlarge of hardening in precipitation strengthening.

c) The most significant advantage of spinodal hardening is that it is homogeneous throughout the section.

d) Easy melting and casting are used to build the modulated (spinodal) alloy as against the P/M method or internal oxidation to be used for dispersion strengthening.

e) At usual temperatures of application modulated (spinodal) alloys are not probable to over-age or recrystallize, while precipitation hardening alloys show a slow however exact over-ageing tendency.

### 4.2 Limitations of spinodal decomposition

1. Limited alloying compositions are suitable for spinodal hardening.
2. It requires homogenization, solution treatment and aging treatment i.e. it is time consuming.
3. In ternary alloys metastable phase is of very short moment, so special care should be taken to achieve this region.
4. Micro examinations are needed in every stage of experiment.
5. Behavior of Spinodal decomposition may sometimes unpredictable.

### 4.3 Applications

1. Marine Environment
2. Automotive
3. Offshore oil and gas
4. Aerospace

## V CONCLUSIONS

Precipitation hardening, dispersion strengthening and spinodal decomposition methods provide almost the identical strength values. Conversely there are definite advantageous [21] of using spinodal decomposition process as against the precipitation hardening method. . Since no crystallographic changes take place, spinodal-hardening alloys retain excellent dimensional stability during hardening.

## REFERENCES

1. Binder,K C. Billotet and P. Mirold (1978), “On the theory of spinodal decomposition in solid and liquid binary mixtures”, Zeitschrift fur Physik -Condensed Matter, Vol. 30, Issue 2, pp. 183-195.
2. Carpenter, M.A (1981), “A "conditional spinodal" within the peristerite miscibility gap of plagioclase feldspars”, American Mineralogist, Vol. 66, pages 553-560.
3. Jantzen,C. (1984), “On spinodal decompositioni n Fe-free pyroxene”, American Mineralogist, Vol. 69, pp. 277-282.
4. Burgio, G.F, et.al. (1993), “Non-linear mean field dynamics in the nuclear spinodal zone”, Catania University preprint no.93/20, pp.01-11.
5. Erukhimovich and Prostomolotova (1997), “New approach to the theory of spinodal decomposition”,

Journal of Experimental and Theoretical Physics, Vol. 66, Issue 6, pp. 463-469.

6. Antonov and Popov (1999), “Model of spinodal decomposition of phases under hyperbolic diffusion”, Physics of the Solid State, Vol. 41, Issue 5, pp 824-826.
7. Kirkaldy, J. S. (2000), “A Ginzburg-Landau treatment of ternary spinodal decomposition”, Journal of Materials Science, Vol. 35, No. 5, pp. 1177-1180.
8. Cribb, W.R and John raka (2002), “Copper Spinodal alloys”,Advanced materials and processes/AP0056 pp.01-04.
9. Ramnarayan and Abhinandan (2003), “Spinodal decomposition in fine grained materials”, Bulletin of Materials Science, Vol. 26, Issue 1, pp. 189-192.
10. Dobretsov, V.Yu, et.al.(2004), “Stochastic description of phase separation near the spinodal curve in alloys”,Journal of Experimental and Theoretical Physics, Vol. 80, Issue 9, pp. 602-607.
11. Cribb, W.R. (2006), “Spinodal alloys for aerospace”, Advanced materials and process magazine, AR0022.
12. Kuksin, A.Yu. (2007), “The Phase Diagram and Spinodal Decomposition of Metastable States of Lennard-Jones System”, High Temperature-Pleiades Publishing, Ltd ,Vol. 45, No. 1, pp. 37–48.
13. Harald, P.C. (2008), “ Theory and Examples of Spinodal Decomposition in a Variety of Materials”, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, pp.1-17.
14. Kim, M.U. et al. (2009), “Application of spinodal decomposition to produce metallic glass matrix composite with simultaneous improvement of strength and plasticity”, Springer- Metals and materials international, Vol. 15, Issue No.2, pp.193-196.
15. Gedeon, M. (2010), “Thermal Strengthening Mechanisms”, ©2010 Brush Wellman Inc., Issue No. 18,
16. Ullbrand, J. (2012), “Phase field modeling of Spinodal decomposition”, Linkoping Studies in Science and Technology Licentiate thesis No. 1545, LIU-TEK-LIC-2012:30Nanostructured Materials Department of Physics, Chemistry and Biology (IFM) Linkoping University SE-581 83 Linkoping, Sweden.
17. Petrishcheva, E. and Abart, R. (2012), “Ex-solution by spinodal decomposition in Multi-component mineral solutions”, Acta Materialia, 60, pp. 5481–5493.
18. Fehim Findik (2013), “Modulated (Spinodal) Alloys”, Periodicals Of Engineering And Natural

Sciences Vol. 1 No. 1, ISSN 2303-4521, pp.47-55.

19. Rundman, K.B., “Spinodal structures”, Metals handbook 8th Ed., Vol.8, pp. 184-185.
20. Kodgire, V.D. and Kodgire, S.V. (2011), “Material Science and Metallurgy for Engineers”, 30th Edition, A Text book published by Everest Publishing house with ISBN 8186314008.
21. Rajput, R.K. (2009), “Material Science and Engineering”, 3rd Edition, A Text book published by KATSON Books with ISBN 8185749922.