NPTEL
NATIONAL PROGRAMME ON
TECHNOLOGY ENHANCED LEARNING

IIT BOMBAY

CDEEP
IIT BOMBAY

Phase field modeling: the materials science, mathematics and computational aspects

Prof. M P Gururajan
Department of Metallurgical Engineering
And materials Science, IIT Bombay

Module No.3
Lecture No.11
Spinodal decomposition:
Some history

Welcome in this module we are going to discuss about what is known as spinodal decomposition so i am going to follow Hilliard's article and i am going to tell you about some historical information as to how this understanding of spinodal came about or what are the important steps towards the development of an understanding of spinodal decomposition. Reportedly the first observation of this are reported observation of spinodal was by Bradley he was looking at the copper nickel iron alloys these were quenched and annealed inside the visibility gap.

When he did that he is reportedly had seen in x-ray diffraction pattern side bands or satellite spots around the brackets so he took copper nickel iron alloy he quenched and annealed it inside the visibility gap and when he did x-ray diffraction he saw extra spots are streaking of the existing spots. In addition to the regular brat Peaks that you would see so this is reported because this is not Bradley's paper but in a paper which was written so this happened in early 1940s in 1943-44 Daniel and Lipson we're the ones who took this copper nickel iron alloy and did the lot more of studies and they report that Bradley had actually reported this.

And what they did is that they tried to explain these side bands they showed that the side bands correspond to periodic composition modulations, if there are periodic composition modulations then such sidebands or satellite spots are expected so that is the first and the second thing is that they showed that this happens composition modulation for they from the experiments that this composition modulations are along the 100 directions of crystallographic directions of the sample and in addition they also calculated the wavelength and they showed that it is of the order of 100a angstroms okay.

So Bradley has reported satellite spots or streaking of black sports and Daniel and Lipson explained that such spots can arise because of compositional modulations and specifically in copper nickel iron they said that these composition modulations are or along the100 direction and the wavelength of the composition modulation that they calculated from their experiments was about 100 angstroms.

Now growth of a composition modulation in an initially homogeneous alloy implies uphill diffusion this we have seen the classical diffusion equation fick's law in addition to if you combine it with the law of conservation of mass the so called Fick's second law is a statement of the fact that if there are compositional heterogeneities they will be evened out. So if you are starting with in a lie which does not have composition heterogeneity and if it develops compositional heterogeneities that means the diffusion is taking place from regions which are poor in some composition two regions which are richer in some composition.

Now that means uphill diffusion and by fick's first law uphill diffusion means negative diffusion coefficient, so basically Lipson and Daniel and Lipson and experiment showed that they there are regions which behave as if the diffusion is the diffusion coefficient is negative, so the appeal diffusion is what they have reported independently much earlier in some time in 1937 Becker and the Dillinger both of them but independently have shown that anytime you have this kind of firm spinodal region or phase separating region we will exactly define what the spinodal is.

For now it is a region in which some regions which are rich in a become richer in a and some regions which are for will be become poorer will be so whenever there are such a spinodal

regions, it is expected that the diffusivity will be negative so this was independently sort of postulated by Becker and Dillinger some time in1937. So the experiments of Daniel and Lipson or in 1943-44 and they sort of agreed with Becker and Dellinger prediction that the inside the spheroid region you will find the diffusivities to be negative.

But what are the Becker and the Dillinger kind of theories cannot explain in fact any theory which is based on fixed loss like the classical fick's laws cannot explain is the fact that there is an wavelength of the order of 100 angstroms, okay so we will show as part of this course at some point that if you use classical fick's laws then it leads to contradictions in terms of its predictions. So that was a problem so it was known that you will have this negative diffusion coefficient regions or up till diffusion in some systems which undergo this kind of a separation and but what was more that was given by Daniel and Lipson is the wavelength of a modulation which was not predicted which was it was it was very difficult to understand why such wavelengths exist.

So in fact we can show that any model which is based on fick's law will give you wrong results contradictory device then Hillert, max Hillert in his PhD thesis written some time in 1956 and a paper which followed sometime in 1961 had done atomistic model ok so he took a regular solution model and his model was based on the regular solution model and he took discrete lattice and on that he tried to solve the one be diffusion equation.

So he setup a flux equation for 1d diffusion on the discrete lattice and he solved this problem numerically and using a regular solution model using the discrete lattice setting up 1d diffusion equation for the flux of atoms and taking such equations and solving them numerically Hillert obtained the solution namely that the periodic variation of composition with the position is expected in such systems, so it is a regular solution model it's on discrete lattice and it's a flux law that was proposed but that is slightly different from fick's law in which may we will see later.

And using that he showed that it is possible to get solutions of this type where the composition modulates with position and he also did some calculations to show that these compositional fluctuations are expected to be of the order of hundred angstroms which was seen by in copper

nickel iron by Daniel and Lipson. So this was one of the important improvements in the understanding off then nodal decomposition.

So this is one of the important studies that happen and Carl in 1961-62 came up with a more flexible continuum version which basically incorporated the same physics as was suggested by the model of life okay, so we are going to look in greater detail as to what this modification that was suggested by Hillert is and how it was incorporated in the continuum models by Carl which led to eventually be so-called Carl Hillert equation for studying spinodal decomposition.

So this is the sort of historical timeline so 37or so we people knew that diffusivities can become negative inside the spinodal regime but experimentally that there is something strange going on was first reported by Bradley then Daniel and Lipson did in copper nickel iron alloys lots of detailed studies which showed that there are composition modulations specifically along the 100 directions in these alloys and the composition modulations have a wavelength of about100 angstroms.

But the Becker and the Dellinger kind of theories will not explain such composition modulation even though they do explain after diffusion and negative diffusion coefficient or are they at least postulate that there will be negative diffusion coefficient regions, so it is seen that there are such regions so experimental evidence is available but what is not clear is why a particular wavelength is chosen.

And later the Hillert with his regular solution model and discrete lattice based theories he postulated the problem of flux of atoms in 1d on such discrete lattice or in systems which obey regular solution model he did some modifications which we will discuss in greater detail later. So he showed that it is possible to get the solution of composition modulations the compositions which change with position as a solution for such problems and he sort of indicated that the 100angstrom wavelength that has been seen in experiments he is he's expected under certain circumstances.

So it is a very simple model it is a discrete lattice model and later it was developed into a continuum model by Khan in 1961-62 resulting in the so-called convenient model which is the modified diffusion equation or non classical diffusion equation. So we are going to look at these things in greater detail so what Khan did along with his co-workers and how it explains what is happening in phase separating systems is something that we are going to do in greater detail.

So in the next couple of modules, so we will discuss about spinodal in greater detail what is spinodal and why does it happen what is its physical significance and things like that is what we will discuss in the next couple of modules. Thank you.

NPTEL
Principal Investigator
IIT Bombay

Prof. R.K Shevgaonkar

Head CDEEP

Prof. V.M Gadre

Producer

Arun Kalwankar

Digital Video Cameraman

&Graphics Designer

Amin B Shaikh

Online Editor

&Digital Video Editor

Tushar Deshpande

Jr. Technical Assistant

Vijay Kedare

Teaching Assistants

Arijit Roy

G Kamalakshi

Sr. Web Designer

Bharati Sakpal

Research Assistant

Riya Surange

Sr. Web Designer

Bharati M. Sarang

Web Designer

Nisha Thakur

Project Attendant

Ravi Paswan

Vinayak Raut

NATIONAL PROGRAMME ON TECHNOLOGY

ENHANCED LEARNING

(NPTEL)

Copyright NPTEL CDEEP IIT Bombay