Phase Separation in Stainless Steels Studied by Small-angle Neutron Scattering

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路漫漫其修远兮，吾将上下而求索。

--屈原《离骚》

The road ahead will be long and the climb will be steep, but I shall keep seeking high and low for the truth.

--QU Yuan, “Li Sao”
To my beloved parents

游子吟
—孟郊·唐

慈母手中线，游子身上衣。
临行密密缝，意恐迟迟归。
谁言寸草心，报得三春晖？

The Song of a Wandering Son

by MENG Jiao, Tang Dynasty (translated by John C. H. Wu)

Thread in the hands of a doting mother:

Clothes on the body of a far-journeying son.

Upon his leaving, she adds one stitch after another,

Lest haply he may not return so soon.

Ah! How could the heart of an inch-long grass

Requite a whole spring’s infinite love and grace?
Abstract

Fe-Cr based steels, i.e. stainless steels, possessing a combination of excellent corrosion resistance and good mechanical properties, have indispensable applications ranging from low-end cooking utensils, to sophisticated components for nuclear power plants. However, the bcc/bct phase containing stainless steels which have a miscibility gap (MG) suffer from the so-called “475 °C embrittlement” leading to hardness increase and toughness deterioration. It occurs due to demixing of Fe and Cr leading to the formation of Fe-rich (α) and Cr-rich (α’) regions in bcc/bct phases. The demixing is referred to as phase separation (PS).

The goal of this work was to study PS in ferrite containing stainless steels mainly by small-angle neutron scattering (SANS). Firstly, the application of different experimental techniques for the study of phase separation in Fe-Cr based steels was reviewed and supplemented by new measurements. SANS was shown to be very sensitive to the nanostructure change caused by PS and capable of characterizing the early stages of PS in Fe-Cr alloys. However, atom probe tomography and transmission electron microscopy are complementary to SANS. Therefore, in order to have a more complete view of the microstructure, the combination of these techniques should be pursued. Secondly, the factors affecting the initial microstructure prior to aging treatment and the effect of the resulted initial microstructure on PS were systematically investigated using binary Fe-Cr model alloys. The critical temperature of the MG was determined to be located between 560 and 580 °C in binary Fe-Cr. The results indicate that the solution treatment temperature above the MG and the cooling rate after solution treatment have significant effects on the initial microstructure and thus on PS during subsequent aging. The mechanisms responsible for the changed aging behavior are Cr clustering, quenched-in vacancy and decomposition during cooling. Therefore, computational simulations should take into account these factors and the initial microstructure to make predictions that are more accurate. Thirdly, the study was extended to PS in commercial duplex stainless steels (DSSs) which are of practical importance in various industries, e.g., nuclear power. It is found that alloying elements have an important effect on PS in DSSs. The grade 2507 (25 %Cr, 7 %Ni) experiences stronger PS than grade 2205 (22 %Cr, 5 % Ni) for the same heat treatment. Moreover, the fracture mechanisms as well as the mechanical properties depend on the extent of PS. Finally, the
fundamental aspects regarding the neutron scattering behavior for Fe-Cr alloys were examined. The results show that the nuclear and magnetic scattering of neutrons depend on the evolution of the nanoscale compositional fluctuation in Fe-Cr alloys. The ratio of the magnitude of nuclear scattering versus magnetic scattering varies with the extent of PS.

**Keywords:**
Fe-Cr alloys, stainless steels, spinodal decomposition, phase separation, small-angle neutron scattering, mechanical properties.
Sammanfattning

Stål baserade på Fe-Cr systemet, det vill säga rostfria stål, som har en kombination av utmärkta korrosionsegenskaper och bra mekaniska egenskaper, har många tillämpningar; allt från köksredskap, till sofistikerade komponenter för kärnkraftverk. Rostfria stål som innehåller Bcc / bctfasen och som således har en blandningslucka, är känsliga för den så kallade "475 °C försprödningen" som leder till en hårdhetsökning men kraftigt försämrad slagseighet. Detta uppstår på grund av en uppdelning av Fe och Cr som leder till bildandet av Fe-rika (α) och Cr-rika (α’) regioner i bcc / bct-fasen. Denna uppdelning brukar kallas fasseparation.

Målet med detta arbete var att studera fasseparationen i ferrit-innehållande rostfria stål främst genom lågvinkel-spridning av neutroner (SANS). Till att börja med studerades och jämfördes olika experimentella tekniker för undersökning av fasseparation i Fe-Cr-baserade stål med nya SANS-mätningar. SANS visade sig vara mycket känslig för förändringar på nano-skala orsakad av fasseparation och tekniken visade sig även kapabel att karakterisera de tidiga stadierna av fasseparation i Fe-Cr-legeringar. För att få en mer fullständig bild av mikrostrukturen efter fasseparation, bör emellertid en kombination av SANS och komplementära tekniker, såsom atomsond och transmissions-elektronmikroskopi, användas. Vidare undersöktes de faktorer som påverkar den ursprungliga mikrostrukturen före åldringsbehandling, och effekten av den initiala mikrostrukturen på fasseparation studerades systematiskt med användning av binära modell-legeringar av Fe-Cr. Den kritiska temperaturen för blandningsluckan i Fe-Cr bestämdes vara belägen mellan 560 och 580 °C. Resultaten indikerar att temperaturen för upplösningsbehandling ovanför blandningsluckan och kylhastigheten har en signifikant inverkan på den initiala mikrostrukturen och därmed på fasseparationen under efterföljande åldring. Mekanismerna som är ansvariga för det förändrade åldringsbeteendet är: Cr-klustering, släckt vakanser och fasseparation under kylning. Simuleringsar av fasseparationen bör därför ta hänsyn till dessa faktorer och den ursprungliga mikrostrukturen för att göra mer exakta förutsägelser av hur mikrostrukturen utvecklar sig med åldringstiden.
Fasseparationen i kommersiella duplexa rostfria stål (DSS), som är av stor praktisk betydelse i olika branscher, t ex kärnkraft, studerades också med SANS. Det visade sig att mängden av olika legeringselement har en viktig effekt på graden av fasseparation i DSS. Legeringen 2507 uppvisade en tydligare fasseparation jämfört med legering 2205 för samma värmehandling. Brottmekanismerna såväl som de mekaniska egenskaperna visade sig bero på omfattningen av fasseparationen.

Slutligen undersöktes de grundläggande aspekterna hos neutronspridnings-beteendet för binära Fe-Cr-legeringar. Resultaten visade att kärn- och magnetisk spridning av neutroner beror på utvecklingen av sammansättningsfluktuationerna på en nanoskala i Fe-Cr-legeringar. Förhållandet mellan magnetisk- och kärnspridning varierar med omfattningen av fasseparationen.
Appended papers and the author’s contribution


Contribution: literature survey, major part of experiments, data analysis, writing the manuscript.


Contribution: taking part in planning the work, literature survey, major part of experiments, data analysis, discussion on simulations, writing the manuscript.


Contribution: planning of the work, literature survey, major part of experiments, data analysis, discussion on TEM experiments, writing the manuscript.

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Contribution: planning of the work, literature survey, major part of experiments, data analysis, writing the manuscript.

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Chapter 1

Introduction

1.1 Stainless steels

Stainless steels, containing at least about 11 wt.% Cr, were discovered approximately between 1905 and 1912, which have been serving us for more than a century and become one of the most successful materials families with a myriad of applications in our daily life and different industries [1,2]. Due to the high Cr content, they can form a thin and Cr-rich oxide layer on their surface, which prevents them from further staining and rusting, hence the name “stainless steel” [1]. In order to improve the corrosion resistance to more aggressive environments and also the mechanical properties, more Cr and other alloying elements, such as Ni, Mo, Mn, Cu, Nb, Al, Si, C, N etc., are often added to stainless steels [1]. Possessing the remarkable combination of the excellent stainlessness and good mechanical properties, stainless steels are omnipresent in our society, with indispensable applications ranging from low-end cooking utensils and cutlery to sophisticated components for aircrafts and nuclear power plants [1–4].

Since the first stainless steel had been discovered, new grades have been continually introduced into the family during the past century. Therefore, the classification of stainless steels is also evolving. Traditionally, stainless steels were classified into four categories according to their crystalline structures [1]: (1) ferritic (bcc phase), (2) austenitic (fcc phase), (3) martensitic (bct phase) and (4) duplex (bcc plus fcc phases) stainless steels. Later, a fifth category was introduced, namely the precipitation-hardening (PH) stainless steels based on the strengthening mechanism in austenite and martensite [1]. Moreover, a category called Mn-N substituted austenitic stainless steels has been proposed by some researchers [5,6]. However, this category plausibly belongs to austenitic stainless steels according to their crystalline structure. Different types of stainless steels have their own characteristic properties determined by
their microstructures which are basically decided by the chemical composition and processing.

Although a plentitude of stainless steels have been discovered and successfully applied in different areas, there is still a need for stainless steels with better mechanical and corrosion performance in harsh conditions. Thus, many challenges have been put forward in the stainless steel development community. One of the challenges associated with the bcc/bct phase (ferrite and martensite) containing stainless steels is the so called “475 °C embrittlement” which deteriorate the toughness of these alloys. It occurs at intermediate temperature or below due to the demixing of Fe and Cr and formation of bcc Fe-rich (α) and bcc Cr-rich (α’) regions in bcc/bct phases. The underlying phase transformation is known as phase separation (PS).

1.2 Scope of this work

It is still a challenge to quantitatively study phase separation in ferrite/martensite containing stainless steels. The experimental investigation of phase separation in ferrite containing stainless steels is the focus of this work.

Different experimental techniques, e.g., small-angle neutron scattering (SANS), atom probe tomography (APT), transmission electron microscopy (TEM) and Mössbauer spectroscopy, for the study of phase separation in Fe-Cr based steels was briefly reviewed and discussed in order to investigate the complementarity of them and choose suitable techniques for further studies. Due to its unique advantages, SANS has been adopted as the main technique in this work.

The early stage of phase separation is not fully understood. Hence, a large part of this work concerns the early stages of phase separation. Moreover, the factors affecting the initial microstructure prior to aging treatment and the effect of the resulted initial microstructure on PS were systematically investigated using binary Fe-Cr model alloys since different factors can be isolated easier in model alloys than in commercial alloys. The critical temperature of the miscibility gap was determined for binary Fe-Cr system using in-situ neutron scattering measurements.
Commercial duplex stainless steels (DSSs) are of practical significance in various industries, e.g., nuclear power. Hence, the study was extended from the binary alloys to DSSs and the effect of phase separation on mechanical properties and fracture mechanisms for DSSs has been studied. As the understanding of neutron scattering deepened, I found that there is a lack of discussions on the magnetic neutron scattering behavior for decomposed Fe-Cr alloys in the literature. Therefore, the final part of this work was on the nuclear and magnetic neutron scattering dependence on the evolution of nanoscale compositional fluctuation in Fe-Cr alloys.
Chapter 2

Fundamental aspects of phase separation in Fe-Cr alloys

2.1 Phase separation in Fe-Cr alloys

Phase separation in Fe-Cr alloys has been studied for decades. Early reports by Becket [7] and Reidrich and Loib [8] on embrittlement phenomenon in Fe-Cr alloys showed the increase of hardness accompanied by the ductility deterioration for ferritic stainless steels after aging at around 475 °C. These observations motivated Fisher et al. [9] to pursue studies to reveal the underlying mechanism for this phenomenon. They systematically studied the age hardening behavior and characteristics of precipitates in Fe-Cr alloys which had 14-28 wt.% Cr contents and were aged at 475 °C for up to four years. They found that spherical particles of about 20 nm diameter with the bcc structure precipitated in the ferrite matrix. The lattice parameter of the precipitate was between that of pure Fe and pure Cr. Moreover, they showed that the Cr content of the precipitate could reach 82 wt.% and the mass proportion of the precipitate could be 10 % for a Fe-27 wt.%Cr alloy aged for four years. The precipitate was also reported showing no or weak magnetism and highly coherent with the ferrite matrix [9]. They claimed that the “475 °C embrittlement” is due to the internal strain resulted from the coherency between the Cr-rich precipitate and the matrix [9]. It is the first time that decomposition of ferrite into Cr-rich (α’) and Fe-rich (α) phases was proposed to be responsible for the “475 °C embrittlement”. Later, further exploration of the decomposition mechanism and the determination of the phase diagram of binary Fe-Cr system were performed. Williams and Paxton [10,11] reported firstly that there is a miscibility gap in the phase diagram of the Fe-Cr system below 600 °C (Fig. 2.1(a)) and it leads to the separation of Fe and Cr. Furthermore, they suggested that chemical or/and magnetic energies should be account for the presence of the miscibility gap [10]. The hardening of Fe-Cr alloys has been shown to depend on the
amount of $\alpha'$ precipitates and may be a consequence of the interaction between $\alpha'$ and dislocations [10]. Then Hillert [12,13], Cahn and Hilliard [14–16] developed the theory of spinodal decomposition, which was treated as a new type of phase transformation within the miscibility gap and was blamed as one of the mechanisms in addition to nucleation and growth, responsible for the embrittlement for Fe-Cr alloys. Imai et al. [17] performed thermodynamic calculations for the Fe-Cr system and added the spinodal line to the Fe-Cr phase diagram, as shown in Fig. 2.1(b). Afterward, numerous experimental and computational works have contributed to determining the miscibility gap and the mechanisms of phase separation for the Fe-Cr system and different versions of the Fe-Cr phase diagram have been reported [18–24]. However, there are contradictions between thermodynamically calculated phase diagrams as well as between experimental data and calculated diagrams. One of the main controversies is the position of the spinodal regime and miscibility gap, where phase separation takes place. Fig. 2.2 compares two thermodynamically assessed Fe-Cr phase diagrams which show different shapes of the miscibility gap and spinodal line in equilibrium and metastable phase diagrams, respectively [21–23]. Meanwhile, the effect of various parameters on the kinetics of phase separation are not fully understood.

The difficulties in the investigation of the miscibility gap and phase separation mechanisms for the Fe-Cr system come from two aspects. Theoretically, models for phase separation are still under development. Present models cannot describe phase separation in Fe-Cr alloys in a completely quantitative way. Experimentally, the characterization of the microstructure formed by phase separation in Fe-Cr alloys is a challenge since it is at nanoscale and the difference between Fe and Cr atoms is minute.
Fig. 2.1 (a) Partial phase diagram of Fe-Cr system proposed by Williams and Paxton [10] and (b) phase diagram of Fe-Cr system proposed by Imai et al. [17].

Fig. 2.2 (a) Equilibrium and (b) metastable phase diagrams of binary Fe-Cr assessed by Andersson and Sundman [21] and Xiong et al. [23].

2.2 Theory of phase separation

The most widely spread theoretical model of phase separation was developed by Cahn and Hilliard (CH model) [14–16] from Hillert’s theory [12,13], which is a continuum model.
For solid solutions, phase separation takes place within the miscibility gap where, for example, a solution $\alpha$ of solvent A and solute B, is metastable or unstable and decomposes into two phases, one of which is solvent A-rich phase ($\alpha_1$) and the other of which is solute B-rich phase ($\alpha_2$). $\alpha_1$ and $\alpha_2$ have the same crystal structure. If the lattice parameters of pure A and pure B are similar, in order to lower the interfacial energy, the two phases are coherent. The coherency between the two phases results in coherency strains which move the miscibility gap to lower temperatures.

Thermodynamically, phase separation can only occur when the phase transformation lowers the total Gibbs energy ($G$) of the system, i.e. $\Delta G<0$. Based on the sign of the second derivative of the molar Gibbs energy $G_m$, the miscibility gap can be divided into two regimes which correspond to two mechanisms of phase separation, as shown in Fig. 2.4 and below [25]:

Metastable regime; nucleation and growth, $\frac{d^2G_m}{dX^2} > 0$ (2.1)

Unstable regime: spinodal decomposition, $\frac{d^2G_m}{dX^2} < 0$ (2.2)

where, $X$ is the content of solute B in molar fraction. When the sign of the second derivative of $G_m$ is positive, the solution is metastable and decomposes via nucleation and growth (NG). Thermal compositional fluctuations initiates the formation of nuclei with a composition close to the equilibrium one, which is different from the matrix. In the formation of a nucleus a nucleation barrier needs to be overcome. The nucleus then grows through a down-hill diffusion process, see Fig. 2.4. When the sign of the second derivative of $G_m$ is negative, there is no barrier to the compositional fluctuation. Therefore, the solid solution is unstable and decomposes via spinodal decomposition (SD) where compositional fluctuations develop spontaneously at an extensive scale but with small compositional amplitudes in the solution. Subsequently, the compositional fluctuation grows with time through an up-hill diffusion process as illustrated in Fig. 2.4. The inflection points where $d^2G_m/dX^2=0$ are defined as the chemical spinodal line (Fig. 2.4). As described above,
NG is governed by both nucleation and subsequent diffusional growth followed by coarsening, but for SD the nucleation step is missing.

Fig. 2.4 Schematic diagrams of miscibility gap, chemical spinodal line and the two mechanisms of phase separation, nucleation and growth and spinodal decomposition in a binary system [25].

In the CH model [14–16,26–28], the Gibbs energy \( G_0 \) of a homogeneous system with composition \( x_0 \) is expressed as:

\[
G_0 = \frac{1}{V_m} \int_V G_m(x_0) dV \quad (2.3)
\]

where \( V_m \) is the molar volume, \( V \) is the volume of the system. When compositional fluctuations occur, the local composition changes to \( x \) and a gradient energy \( \kappa(\nabla x)^2 \) (\( \kappa \) is the gradient energy coefficient) exists due to the composition gradient \( \nabla x \) between regions with different composition. Hence, the total Gibbs energy \( G \) of an inhomogeneous system can be associated with the gradient energy as:

\[
G = \frac{1}{V_m} \int_V \left[ G_m(x) + \kappa(\nabla x)^2 \right] dV \quad (2.4)
\]

Therefore, the Gibbs energy change is:
\[ \Delta G = G - G_0 = \frac{1}{V_m} \int_V \left[ G_m(x) - G_m(x_0) + \kappa (\nabla x)^2 \right] dV \quad (2.5) \]

Since the two phases are coherent after the decomposition, which results in coherency strains between them, an elastic energy should be taken into consideration in \( \Delta G \). The elastic energy can be expressed as:

\[ G_m^{el}(x) = \eta^2 YV_m(x - x_0)^2 \quad (2.6) \]

where \( \eta \) is the change in lattice parameter with composition and \( Y = E/(1-\nu) \) (\( E \) is the Young’s modulus and \( \nu \) is the Poisson’s ratio) denotes a combination of elastic constants when the elastic strain is isotropic. Combining Eqs. (2.5) and (2.6) yields:

\[ \Delta G = G - G_0 = \frac{1}{V_m} \int_V \left[ G_m(x) - G_m(x_0) + \kappa (\nabla x)^2 + \eta^2 YV_m(x - x_0)^2 \right] dV \quad (2.7) \]

Based on Eq. (2.7), Eq. (2.8) were derived by Cahn and Hilliard [15,26], to describe the diffusion process during phase separation:

\[ \frac{\partial x(r,t)}{\partial t} = M \left( \frac{\partial^2 G_m}{\partial x^2} + 2\eta^2 YV_m \right) \nabla^2 x - 2M \kappa \nabla^4 x \quad (2.8) \]

where \( M \) is a combination of atomic mobilities. Eq. (2.8) is the master equation of CH model. The linearized CH model considers \( M, \frac{\partial^2 G_m}{\partial x^2} \) and \( \kappa \) as constants, i.e. independent of composition, which restricts it to the very early stage of phase separation. Furthermore, the CH model omits the random statistical fluctuations when phase separation takes place at a certain temperature. Therefore, Cook [29] extended Eq. (2.8) with a random force term \( \zeta_T(x,t) \) which describes the random statistical fluctuations at a certain temperature:

\[ \frac{\partial x(r,t)}{\partial t} = M \left( \frac{\partial^2 G_m}{\partial x^2} + 2\eta^2 YV_m \right) \nabla^2 x - 2M \kappa \nabla^4 x + \zeta_T(x,t) \quad (2.9) \]

\[ \left\langle \zeta_T^2 \right\rangle = 2k_B TM \quad (2.10) \]

where \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature. Eq. 2.9 together with Eq. 2.10 is the so-called Cahn-Hilliard-Cook (CHC) model.
Although the CH and CHC models are frequently used to study phase separation, a discontinuity of the decomposition mechanism exists at the spinodal line where the mechanism of decomposition would change abruptly from NG to SD when crossing the border between metastable and unstable regimes.

In the CH model, the compositional fluctuation in a solid solution can be described by a sinusoidal function characterized by the fluctuation wavelength \( d \) and compositional amplitude which could be \( (x-x_0) \) or the difference between the peak composition and trough composition of Cr or Fe. Under the linearized approximation of the CH model, i.e. \( M, \frac{\partial^2 G_m}{\partial x^2} \) and \( \kappa \) are independent of \( x, x \) in Eq. (2.8) can be expanded in the Fourier space (reciprocal space) in the following way [14,16,30,31]:

\[
\begin{align*}
x(\vec{r}, t) - x_0 &= \int A(\tilde{\beta}, t) \exp(i \tilde{\beta} x) d \tilde{\beta} \quad (2.11)
\end{align*}
\]

where \( \beta = 2\pi/d \) is the wavenumber or the magnitude of wave vector of the compositional fluctuation, \( A(\beta, t) \) is the amplitude of the Fourier component at time \( t \).

\[
A(\tilde{\beta}, t) = A(\tilde{\beta}, 0) \exp \left[ R(\tilde{\beta}) t \right] \quad (2.12)
\]

where \( A(\beta, 0) \) is the initial value of \( A(\beta, t) \). \( R(\beta) \) is the amplification factor:

\[
R(\beta) = -M \left( \frac{\partial^2 G_m}{\partial x^2} + 2\eta^2 Y V_m + 2\kappa \beta^2 \right) \beta^2 \quad (2.13)
\]

Defining the two-point correlation function at \( t \) as \( \langle [x(\vec{r}, t) - x_0][x(\vec{r}_0, t) - x_0] \rangle \), one can get the Fourier transform of the correlation function from Eqs. (2.11)–(2.13) [14,16,30,31], i.e. the structure factor:

\[
S(\tilde{\beta}, t) = S(\tilde{\beta}, 0) \exp \left[ 2R(\tilde{\beta}) t \right] \quad (2.14)
\]

\( S(\beta, 0) \) is the initial state of the structure factor. For CHC model, \( S(\beta, t) \) is:
\[ S(\vec{\beta}, t) = \left[ S(\vec{\beta}, 0) - \frac{RT}{\partial^2 G_m / \partial x^2 + 2\kappa \vec{\beta}^2} \right] \exp \left[ 2R(\vec{\beta})t \right] \frac{RT}{\partial^2 G_m / \partial x^2 + 2\kappa \vec{\beta}^2} \]

(2.15)

where $R$ is the gas constant. $S(\vec{\beta}, t)$ is associated with the scattering intensity of small-angle scattering (SAS), therefore, the simulated $S(\vec{\beta}, t)$ has been frequently compared with the experimental results of SAS for validating the CH model. This aspect will be discussed more in the following text. It should be pointed out that the CH model also have non-linearized form. Another non-linearized model which is usually referred to as LBM model has also been used to study SD [32]. There are also other simulation methods for phase separation, such as the Monte Carlo technique [33,34]. Readers are referred to the references for details.
Chapter 3
Experimental study of phase separation in stainless steels

3.1 Nanostructure of phase separation

Depending on the mechanism of phase separation, the microstructure after the decomposition of the bcc phase has different features. A microstructure consisting of Cr-rich ($\alpha'$) particles embedded in Fe-rich ($\alpha$) matrix is formed via nucleation and growth (NG), see Fig. 3.1(a) [23]. Whereas, an interconnected microstructure is developed via spinodal decomposition (SD), as shown in Fig. 3.1(c) [23]. As mentioned before, there is a discontinuity at the boundary between NG and SD regimes according to the CH theory. However, a transition region has been found between NG and SD regimes and the microstructure formed in this region has features resembling both particles and interconnected microstructures, see Fig.2.1(b) [23]. The microstructure is usually at nanoscale with fluctuations extending only a few nanometers. Furthermore, both $\alpha$ and $\alpha'$ have the same lattice structure, i.e. bcc lattice, and the atomic number of Fe and Cr is very close, meaning that the lattice misfit between the two phases is very small. Therefore, characterization of the decomposed nanostructure in stainless steels is still a challenge, particularly at the early stages where the composition fluctuates only a few atomic percent.

3.2 Characterization of the nanostructure of phase separation

It is not easy to characterize the nanostructure formed by phase separation quantitatively. In the following text, a few experimental techniques will be briefly introduced.
Fig. 3.1 Cr atom maps measured by atom probe tomography for Fe-Cr alloys: (a) 26.65, (b) 31.95 and (c) 37.76 at.%Cr. The size of the analyzed volume is $30 \times 15 \times 8 \text{nm}^3$ [23].

3.2.1 Characterization techniques for nanostructure of phase separation

The experimental techniques utilized to study the nanostructure of phase separation in stainless steels can be categorized into two groups: (1) morphologic imaging techniques which can map the morphology of the decomposed nanostructure in the real space, namely transmission electron microscopy (TEM) and atom probe tomography (APT) which is developed from atom probe field ion microscopy (APFIM), and (2) non-morphologic characterization techniques, such as Mössbauer spectroscopy (MS), small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), which use physical parameters deduced from measured data to describe decomposed nanostructures instead of providing direct images of the morphology. In this chapter, applications of TEM, APT, MS and SAXS for the study of phase separation in stainless steels are briefly reviewed. SANS will be introduced in Chapter 4.
3.2.2 Morphologic imaging techniques: TEM and APT

Due to the high coherency between $\alpha$ and $\alpha'$ and similar number of electrons for the Fe and Cr atoms, the phase contrast in TEM is weak. Worse still, the wavelength and amplitude of phase separation are minute at early stages. Hence, conventional TEM is usually considered to be not suitable for characterizing the early stages of phase separation in Fe-Cr alloys. Even for the later stages and commercial stainless steels when the phase contrast is large enough for observation (Fig. 3.2(a)), the mottled orange-peel-look morphology can be hardly mapped clearly by conventional TEM [35]. High resolution TEM (HRTEM) has better resolution which can resolve sub-nanometer microstructures. However, it is still just able to image the later stages of phase separation in Fe-Cr alloys and is generally used as a qualitative method, see Fig. 3.2(b) [36].

The development of aberration-corrected TEM (STEM) has brought the resolution of TEM to the sub-Ångström level such that it can now resolve individual atoms and is more sensitive to compositional variations [37–39]. Therefore, it is promising in the characterization of early stages of phase separation in Fe-Cr alloys. A recent study on the early stages of SD in a Fe-36 wt.%Cr alloy using a double Cs (spherical aberration) corrected analytical scanning TEM (STEM) has shown the capability of STEM in the study of phase separation in Fe-Cr alloys, see Fig. 3.3 [40]. It can be seen that STEM can map the nanostructure formed after 1 h aging at 500 °C for Fe-36 wt.%Cr alloy. Furthermore, the wavelength of SD can be estimated disregarding that the thickness of the specimen is several times larger. The reason is unclear yet. Nonetheless, the concentration amplitude is severely affected by the thickness [40]. The thickness of the specimen should be similar to the domain size of $\alpha$ and $\alpha'$ in order to determine the amplitude accurately, which is extremely difficult for the sample preparation. Another drawback of TEM is that the measured sample volume is very small. However, it has a unique advantage over other techniques that it can provide the crystal orientations which is important in studying the anisotropic decomposition [16,41,42].
So far, APT is considered as the only technique that can be used to simultaneously obtain the 3D morphology maps and quantitative parameters, i.e. the wavelength \((d)\) and amplitude \((A)\), of phase separation in stainless steels. It can reconstruct 3D distribution of atoms in a wide range of materials, thus is extensively used to study phase transformations in alloys [43]. APT is capable of studying the early stages of decomposition in stainless steels and \(d\) and \(A\) can be estimated by statistical methods [33,44–47]. It has been used to determine the decomposition mechanisms for Fe-Cr alloys [23,33,48], see Fig. 3.1 [23], and investigate the kinetics of phase separation [33,46,49–53], see Fig. 3.4. Decomposed nanostructures simulated by phase-field and Monte Carlo simulations are also frequently compared with APT atom maps to develop theoretical models and explore the mechanisms of phase separation [50,54–56]. Furthermore, atomic level chemical mapping makes APT a good probe to shed light on the effect of alloying elements on phase separation [51,57–59]. Despite the advantages of APT, there are drawbacks. The typical probe volume for APT is 50 nm×50 nm×250 nm,
which is really small. Since the detection efficiency is generally below 65%, the analysis omits nearly half of the atoms. Although the most advanced APT can reach a detection efficiency of about 80%, some complicated physics regarding the field evaporation, for example the local magnification effect, is present when alloys contain more than one element, which leads to some uncertainties in 3D reconstructions and quantitative results [43,60].

![Fig. 3.4 Sections of atom maps of Cr, Mn, and Si for a decomposed duplex stainless steel 2101 aged at 427 °C for different times. Sections are in 40 nm×15 nm [53].](image)

### 3.2.3 Non-morphologic characterization techniques: MS and SAXS

MS is generally treated as a qualitative technique in characterization of the nanostructure of phase separation. It takes advantage of the change of the magnetic neighborhood of the $^{57}$Fe to probe the variation of the hyperfine field which is characterized by changes of the paramagnetic and ferromagnetic peaks. The changes of ferromagnetic peaks indicates the evolution of the decomposed microstructure [61–64]. However, $d$ of phase separation is hard to be quantified.

SAXS and SANS are non-destructive techniques which provide information of nanostructures in the reciprocal space using instruments most often based at large facilities, i.e. synchrotrons and neutron sources, respectively. Both of them can characterize phase separation in bulk
stainless steels and evaluate parameters, e.g., \( d \). Furthermore, they are very efficient that many samples can be measured in a short period of time and they are capable of in-situ measurements meaning phase transformations can be traced when they are taking place. These features are some of their advantages over TEM and APT.

However, the X-rays interact with electron cloud of atoms through electromagnetic effects. Therefore, the scattering length of X-rays increases gradually with atomic numbers, meaning that elements with close atomic numbers have similar “apparent size” to X-rays. Consequently, X-ray scattering generally has little contrast between Fe and Cr. As a result, there is few reports on phase separation in Fe-Cr alloys studied by SAXS. Fortunately, the contrast can be strengthened by the anomalous effect, which enables SAXS to characterize the nanostructure of phase separation in Fe-Cr based alloys [65,66], see Fig. 3.5. The peak in the data indicates that a periodic microstructure has been formed in the materials. The peak position and the peak intensity are indicators of the progress of phase separation that smaller peak position and larger peak intensity mean more significant decomposition. The SAXS data have been also compared to the APT data of the same materials via correlation function [66], which can benefit the interpretation of data obtained by both techniques.

Fig. 3.5 Anomalous SAXS measurements of phase separation in a 15-5PH alloy [66].
3.3 Effect of phase separation on mechanical properties of stainless steels

It is well known that phase separation increases the hardness but deteriorates the ductility and toughness of ferrite-containing stainless steels, see Fig. 3.6 [67,68]. Moreover, it also significantly influences the fracture behavior of these alloys. Hardness and impact toughness tests are frequently used to indicate the effect of phase separation on the mechanical performance of the alloys. From Fig. 3.6 [67,68], it can be seen that the toughness decreases sharply after short-period aging at 475 °C when there is a pronounced hardening effect.

![Fig. 3.6](image)

Fig. 3.6 (a) Charpy-V impact toughness at 80 °C vs. aging time at 475 °C and (b) Vickers hardness vs. aging time at 475 °C for a Fe-38.8 wt.%Cr alloy [67]; (c) 50% reduction of impact toughness at different temperatures for duplex stainless steels [68].

The hardening mechanisms have been investigated too. Since α and α′ are coherent, internal stresses due to the coherency strain exist in the materials [9]. Cahn [69] theoretically studied the effect of internal stresses and composition gradients on dislocations and suggested that internal stresses could restrict the slip motion of dislocations. The resistance effect of internal stresses to dislocation migration was confirmed by further work [35,70]. Moreover, Cortie and Pollak [67] suggested that the effect has a
proportional relation with the $A$ of phase separation. Later APT studies revealed the correlation between the hardness and the progress of phase separation which is indicated by $V$ values, see Fig. 3.7 [49]. Furthermore, Capdevila et al. [71] found that the hardness increases linearly with compositional variations for a Fe-based PM 2000TM oxide dispersion strengthened (ODS) steel.

![Micro-hardness vs. V values obtained by APT for CF8M alloy [49].](image)

The hardening of ferrite also have important impact on the deformation and fracture behavior of ferritic and duplex stainless steels. Since the dislocation slip is hindered, the deformation is inclined to occur via twinning in phase separation hardened ferrite [35,67,72]. Accompanying the advance of phase separation, the fracture mechanism is also found to change from ductile mode to cleavage mode and the so-called delamination in duplex stainless steels is more severe [72,73].
Chapter 4

Small-angle neutron scattering

SANS is powerful in the study of nanostructures at the length scale of ~1‒100 nm. It has succeeded in many fields and provided the insight into the microstructure of an extensive range of materials, such as alloys, polymers, biomaterials etc. In this chapter, a brief review on the neutron source, SANS theory and technique, and the application of SANS for the study of phase separation in Fe-Cr based alloys is presented.

4.1 Neutron scattering

Neutrons with a magnetic moment are electrically neutral. They interact with nuclei via the short-range interaction (nuclear scattering) (Fig. 4.1(a)) [74,75]. Therefore, the distribution of nuclei can be probed by neutrons. Moreover, neutrons have deep penetrations for most elements endowing neutron scattering to probe even larger bulk samples than high-energy X-rays. Neutrons also interact with magnetic moments of unpaired electrons (magnetic scattering) surrounding nuclei. This is often utilized to study magnetic structures of materials. Furthermore, the variation of the neutron scattering length with atomic numbers is irregular (Fig. 4.1(b)) [75,76], meaning that neutron scattering can have good contrast between elements that are close in the periodic table, for example Fe and Cr. Neutrons can also easily distinguish light elements, e.g., H, from heavy ones in materials. These are the advantages of neutrons over X-rays. Hence, SANS has been successfully applied for the investigation of phase separation and other phase transformations in stainless steels.
Commonly, neutrons can be produced by two methods, i.e. fission chain and spallation nuclear reactions. The continuous reactor generates neutrons in a continuous mode via the former reaction, while spallation source uses the spallation reaction to generate neutrons in a pulsed mode, see Fig. 4.2 [75]. The operating mode determines the configuration of the neutron scattering instruments. The incident neutrons used by a continuous reactor instrument are selected by a monochromator and become monochromatic, therefore, the detector needs to move to collect scattered neutrons so that data with a wide range of scattering vector \((Q=4\pi\sin\theta/\lambda, \text{where } 2\theta \text{ is the scattering angle and } \lambda \text{ is the neutron wavelength})\) can be obtained. Whereas, a spallation source instrument uses a chopper to produce neutron beam pulses with neutrons of a wide range of \(\lambda\) and generally utilizes the time-of-flight technique, thus, the detector is fixed and can simultaneously accumulate data with a wide \(Q\)-range. The neutron flux produced by continuous reactors has reached their limit, while spallation sources still have the potential to generate higher fluxes. Hence, spallation sources represent the future trend of new neutron facilities, e.g., European Spallation Source (ESS), see Fig. 4.3 [77]. However, it should be pointed out that neutron sources have lower fluxes compared to synchrotrons, making them less attractive in studies requiring high time resolution.
4.2 Small-angle neutron scattering technique

As mentioned before, neutrons interact with both nuclei (nuclear scattering) and unpaired electrons (magnetic scattering). Therefore,
SANS can detect the density fluctuation and composition fluctuation as well as the spatial variation of magnetism at the nanoscale in materials. It characterizes the structures in the reciprocal (Fourier) space. Thus, theoretical models and information from other methods are often used to interpret the data.

Fig. 4.4 (a) LOQ diffractometer at ISIS Pulsed Neutron and Muon Facility, UK and (b) schematic diagrams of the SANS technique. $\vec{k}_i = \frac{2\pi}{\lambda}$ is the incident wave vector, $\vec{k}_s$ is the scattered wave vector and $\vec{Q} = \vec{k}_s - \vec{k}_i$ is the scattering vector. For the elastic scattering, $Q = 4\pi\sin\theta/\lambda$, where $2\theta$ is the scattering angle and $\lambda$ is the neutron wavelength.
Fig. 4.4 shows a SANS instrument, the LOQ diffractometer at ISIS Pulsed Neutron and Muon Facility, UK, which uses the time-of-flight technique, and a schematic representation of the SANS technique. The experimental procedure is that the monochromatic or pulsed neutron beam is collimated and illuminates the sample with an incident wave vector $\vec{k}_i = 2\pi / \lambda$. Some of the incident neutrons are transmitted and absorbed by the sample. The other neutrons are scattered by the sample and have a wave vector $\vec{k}_s$. The scattered neutrons are then collected by detectors for data processing. SANS makes use of the elastically scattered neutrons, which means the scattered neutron has the same energy with the incident neutron (no energy loss), i.e. $k_s = k_i$. The scattering vector ( $\vec{Q} = \vec{k}_s - \vec{k}_i$ ) is $Q = 4\pi \sin \theta / \lambda$. Combining with the Bragg’s law, $\lambda = 2d \sin \theta$, one gets the expression of the characteristic distance by SANS:

$$d = \frac{2\pi}{Q} \quad (4.1)$$

The reciprocal space and real space are correlated by Eq. 4.1 and the detected length scale in real space can be calculated according to Eq. 4.1 for a SANS instrument.

The recorded scattered neutron flux can be described as [75,78]:

$$I_s(Q) = I_i(\lambda)\Delta\Omega \eta(\lambda)T(\lambda)V \frac{\partial\Sigma}{\partial\Omega}(Q) \quad (4.2)$$

where $I_i(\lambda)$ is the incident flux, $\Delta\Omega$ is the solid angle corresponding to a detector cell, $\eta(\lambda)$ is the detector efficiency, $T(\lambda)$ is the sample transmission, $V = At_s$ is the illuminated sample volume ($A$ is the illuminated sample area, i.e. the beam cross-section area, $t_s$ is the sample thickness) and $\partial\Sigma(Q) / \partial\Omega$ is the coherent macroscopic differential cross-section which is often simplified to $I(Q)$. It is $\partial\Sigma(Q) / \partial\Omega$ that contains all the information of the microstructure of materials. Therefore, the SANS experiment is designed to obtain $\partial\Sigma(Q) / \partial\Omega$. Before calculating $\partial\Sigma(Q) / \partial\Omega$, all other parameters should be determined [79,80]. $I_i(\lambda)$ is measured by an empty beam measurement run, $T(\lambda)$ is measured by a sample transmission run. $\eta(\lambda)$ can be calculated from the flux monitor counts and the counts on the detector for an empty beam. The collected
raw data is then corrected for the above parameters and the instrumental background to get \( \partial \Sigma(Q) / \partial \Omega \). In order to make the corrected \( \partial \Sigma(Q) / \partial \Omega \) independent of the used instrument, a measurement on a standard sample of known cross sections is performed with the same instrumental configuration. The corrected \( \partial \Sigma(Q) / \partial \Omega \) is subsequently put onto an absolute scale in the unit of cm\(^{-1}\). Fig. 4.5 (a) and (b) show the raw data and corrected 2D \( \partial \Sigma(Q) / \partial \Omega \). If the system is isotropic, namely the scattering is isotropic in the reciprocal space (the example used in Fig. 4.5), the 2D data is finally azimuthally averaged and merged into 1D data, as shown in Fig. 4.5(c).

On the other hand, the incident neutrons can be described as plane waves and the scattered neutrons are described as spherical waves. The theory for SANS analysis is based on the first Born approximation, namely the single scattering approximation of the Schrödinger equation. Theoretically, \( \partial \Sigma(Q) / \partial \Omega \) of a two phase system can expressed as [75,78,81,82]:

\[
\frac{\partial \Sigma}{\partial \Omega}(Q) = N_P V_P^2 (\Delta \delta)^2 P(Q) S(Q) + B_{inc} \quad (4.3)
\]

where \( B_{inc} \) is the \( Q \)-independent incoherent scattering, which is treated as the background. The first term describes the coherent scattering, namely the structure information. \( N_P \) is the number density of the second phase (the precipitate), \( V_P \) is the volume of a single precipitate. \((\Delta \delta)^2\) is the scattering contrast which determines whether neutron scattering has contrast between the two phases and \( \Delta \delta = \rho_P - \rho_M \) (\( \rho_P \) and \( \rho_M \) are the
nuclear scattering length density of the precipitate and the matrix, respectively, which are related to their compositions). $P(Q)$ is the form factor for a single precipitate and is decided by the shape and size of it. $P(Q)$ has analytical forms for simple shapes such as sphere, disc and rod etc [75,78,81,82]. For complex shapes, $P(Q)$ can be fitted by theoretical models using software packages, e.g., SasView [83], to get the structure information. $S(Q)$ is the structure factor and indicates the inter-precipitate correlation, which can be obtained by the Fourier transform of the static pair correlation function. When the number density of precipitates is very low, i.e. for a dilute system, the correlation between precipitates is negligible, thus $S(Q)\rightarrow 1$ and \( \frac{\partial \Sigma(Q)}{\partial \Omega} \) is dominated by the contribution of $P(Q)$. When the precipitates are dense enough to have obvious correlations, the profile of \( \frac{\partial \Sigma(Q)}{\partial \Omega} \) will show a correlation peak (Fig. 4.5(c)), which is very common for phase separation in Fe-Cr alloys. The interpretation of $S(Q)$ can also be performed by theoretical model fits using software packages, for instance, SasView [83]. As mentioned in Chapter 2, CH and CHC models [14,16,30,31] also contain the structure factor (Eqs. (2.14) and (2.15)). Therefore, SANS results are frequently compared to simulation results by CH and CHC models.

The above description does not take the magnetic scattering into account. For a magnetic system, both nuclear and magnetic scattering will be present. In order to disentangle the two contributions, an external saturation magnetic field is usually applied to the sample during SANS measurements and \( \frac{\partial \Sigma}{\partial \Omega} \) depends on both $Q$ and the angle ($\Psi$) between the saturation magnetic field and $\vec{Q}$. \( \frac{\partial \Sigma(Q,\Psi)}{\partial \Omega} \) can be separated into two parts [84]:

\[
\frac{\partial \Sigma}{\partial \Omega} (Q, \Psi) = \left( \frac{\partial \Sigma}{\partial \Omega} \right)_N (Q) + \left( \frac{\partial \Sigma}{\partial \Omega} \right)_M (Q) \sin^2 \Psi \quad (4.4)
\]

The \( \left( \frac{\partial \Sigma}{\partial \Omega} \right)_N \) corresponds to the nuclear scattering, while \( \left( \frac{\partial \Sigma}{\partial \Omega} \right)_M \) corresponds to the magnetic scattering. From Eq. (4.4), it can be seen that the scattering is anisotropic in this case, as shown in Fig. 4.6. The scattering along the external magnetic field is just the nuclear scattering, \( \left( \frac{\partial \Sigma}{\partial \Omega} \right)_N \), and the scattering perpendicular to the external magnetic field is the sum of \( \left( \frac{\partial \Sigma}{\partial \Omega} \right)_N + \left( \frac{\partial \Sigma}{\partial \Omega} \right)_M \). Hence, the two parts can be separated.
Fig. 4.6 Corrected 2D SANS data of a Fe-40 wt.%Cr alloy aged for 100 h at 475 °C measured under an external saturation magnetic field.

4.3 Small-angle neutron scattering data interpretation

4.3.1 Guinier approximation

For a dilute system consisting of particles and matrix, the Guinier plot is used to obtain the approximate particle sizes [85]. The scattering function $I(Q)$ (for convenience, $\frac{\partial \Sigma(Q)}{\partial \Omega}$ is represented by $I(Q)$ hereafter) can be written as:

$$I(Q) = I(0) \exp \left( -\frac{Q^2 R_G^2}{3} \right) \quad (4.5)$$

where $I(0)$ is the value of scattering function when $Q=0$, $R_G$ is called the Guinier radius (radius of gyration). $R_G$ can be converted to the particle radius ($R_P$) via $R_P = \sqrt{5/3} R_G$ if the particle is assumed to be spherical and monodispersed. Therefore, $R_G$ can be assessed from the plot of $\ln(I(Q))$ vs. $Q^2$, thus $R_P$ can be also obtained. The data used for this approximation should satisfy $Q R_G \leq 1.2$. It should be noted that the polydispersity and correlation between particles could tarnish the accuracy of the estimated $R_P$ by the Guinier plot [75,85].

4.3.2 Porod law

Another model which is commonly used to interpret $I(Q)$ of a dilute system is the Porod law [84,86]. For a single particle with a well-defined
surface area $A_P$ and volume $V_P$, at the high-$Q$ range, the form factor $P(Q)$ is:

$$P(Q) = 2\pi \left( \frac{A_p}{V_p^2} \right) \frac{1}{Q^3} \quad (4.6)$$

Hence, $I(Q) \sim 1/Q^4$ at high-$Q$ range. $(A_P/V_P)$ is the ratio of the surface area to precipitate volume. Since $Q$ is large for the Porod region, the detected length scale is smaller than the particle size. The data in this region reflects the information of the local structure, for example, the feature of the interface between the particle and the matrix, through e.g., the fractal dimension. If one expresses the Porod approximation as

$$I(Q) = \frac{A}{Q^n} + B \quad (4.7)$$

where $A$ and $B$ are constants, $n=4$ represents a smooth interface and $n<4$ represents a rough surface.

### 4.3.3 Kratky plot

In the quantitative analysis of SANS data for a two phase system, the Kratky plot $I(Q)Q^2$ vs. $Q$ is also a good tool [87]. The integration ($K_0$) of the scattering function using the Kratky plot is related to the volume fraction ($f_v$) of precipitates:

$$K_0 = \int_0^\infty I(Q)Q^2dQ = 2\pi^2(\Delta\delta)^2f_v(1-f_v) \quad (4.8)$$

$K_0$ is often called invariant as the invariance can be seen from Eq. (4.8). For a system with a precipitate number density of $N_P$ and single precipitate volume of $V_P$, one gets $f_v=N_PV_P/NV_P/V$ ($N$ is the number of precipitates in the system, $V$ is the volume of the system).

Combining Eqs. (4.5)–(4.8), one can evaluate the evolution of $R_P$, $V_P$, $f_v$, $N_P$ and $(A_P/V_P)$ of precipitates [88–90]. Moreover, if size distribution functions are included in the scattering function, the distribution of the size and volume of the precipitate can be obtained as well [88–90], see Fig. 4.7 [89].
4.3.4 Broad peak model

If precipitates are concentrated in the system, there is a correlation between them, which results in a correlation peak in SANS data and the correlation is described by $S(Q)$. Important structure information can be deduced from the peak. The average distance ($d$) between precipitates is calculated from the peak position, $Q_P$, via $d=2\pi/Q_P$. An empirical model is also used to analyze the correlation peak, called the broad peak model [75]:

$$I(Q) = \frac{C}{1+\left(\frac{Q-Q_P}{\xi}\right)^m} + D \quad (4.9)$$

where $C$ is the scale factor for the correlation peak, $D$ is the background. $\xi$ is the correlation length and it could be interpreted as the distance between regions with the similar atomic number density within the precipitate. $m$ is the exponent of the peak function.

4.4 Small-angle neutron scattering studies of phase separation in Fe-Cr alloys

As depicted above, SANS is a good probe for phase separation in Fe-Cr based alloys and has been applied in this field since the 1960s [91–93]. Since the volume fraction of $\alpha'$ is large, the correlation between $\alpha'$ is pronounced. Therefore, the SANS data of decomposed Fe-Cr alloys often possess a correlation peak. The variation of the peak is frequently treated as the characteristics of the evolution of phase separation.

Vintaykin et al. [91–93] studied the effect of Cr contents, aging temperature, heat treatment history, and aging time on phase separation.
of binary Fe-Cr alloys by SANS. They clearly showed that higher Cr contents lead to faster kinetics of phase separation. When the aging temperature is below 500 °C, higher aging temperatures leads to more pronounced decomposition. Additionally, more severe decomposition was found for lower solution treatment temperatures during subsequent aging. Later work also showed similar results [54,94]. These studies indicate that heat treatment history have significant influences on phase separation. Katano and Iizumi [95–97] reported that the peak intensity ($I(Q_P)$) and peak position ($Q_P$) obey power laws with aging time when the aging temperature was below 525 °C for phase separated Fe-24, 34, 40 at.%Cr alloys (Fig. 4.8), which has been predicted by Binder and Stauffer [98] and Marro et al. [99], namely $I(Q_P) \propto t^a$ and $Q_P \propto t^{-b}$ ($t$ is aging time). This feature has been frequently observed by other SANS studies as well [42,100–102]. Furthermore, the investigated alloys and aging temperatures were around the spinodal line, however, the SANS data of these alloys were similar. Thus, Katano and Iizumi [96] claimed that the phase separation mechanism changes smoothly between NG and SD. On the other hand, the decomposition isotropy for Fe-30%Cr alloys has been checked by SANS in single crystals [103]. No orientation dependence was found, therefore, it was concluded that the decomposition in Fe-Cr alloys is isotropic due to the small difference in crystal structures of α and α'. Since the linearized CH and CHC models could be valid at the early stage of phase separation and the early stages have a significant impact on mechanical properties but the definition of the early stage is vague, some researchers have tried to use the feature at the high-$Q$ side of the correlation peak shown by SANS data to distinguish the early and late stages [101,104,105]. They claimed that if $I(Q) \propto Q^{-2}$ at the high-$Q$ side of the peak, the decomposition was treated as the early stage, while $I(Q) \propto Q^{-4}$ describes the late stage of the decomposition. However, the exponent of the $Q$-dependence at this $Q$-range is not always $-2$ or $-4$. Instead, it increases gradually as phase separation progresses [42,102]. Furthermore, in-situ SANS measurements have been used to gain an insight into the kinetics of the early stages of phase separation in Fe-Cr based alloys [102,106,107].
Fig. 4.8 Power laws for the peak intensity and peak position which are expressed as $I(Q_m)$ and $Q_m$, respectively, by Katano and Iizumi [96]. The alloy was Fe-34 at.%Cr.

An advantage of SANS in study phase separation is that the result can be directly compared with simulations using theoretical models expressed in reciprocal space. CH, CHC and LBM models have been used to reproduce the experimental results. The scattering function is often approximated by the models through [94,108]:

$$I_T(Q) = N_v X_{Cr} (1 - X_{Cr}) (b_{Cr} - b_{Fe})^2 S_T(Q, t) \quad (4.10)$$

where $I_T(Q)$ is the theoretical approximation of $I(Q)$, $S_T(Q, t)$ is the structure factor depicted by CH, CHC and LBM models, $N_v$ is the atomic number density, $X_{Cr}$ is the Cr content, $b_{Cr}$ and $b_{Fe}$ are the scattering length of Cr and Fe, respectively.

Vintaykin et al. [93] compared their SANS results with the linearized CH model and indicated the validity of the model for short aging times. Furusaka et al. [109] made comparisons between SANS results and the LBM model and found that the early stages of SD can be qualitatively described by the LBM model but not the later stages. Reports have also shown that CHC and LBM models cannot repeat the SANS results if the initial microstructure prior to the aging treatment is not homogeneous [94,110]. Some studies made attempts to estimate the thermodynamic parameters involved in the CH, CHC and LBM models by just fitting the models to SANS data [101,108]. However, the obtained thermodynamic
parameters should be treated with caution since there are more than one parameters involved in the fit meaning that they could be correlated during the fit, thus large uncertainty could exist for the fitted values. Besides, the experimental data are hardly fitted thoroughly, see Fig. 4.9 [108]. Furthermore, the models are only possibly valid at the early stages. The comparison between the in-situ SANS results and the linearized CHC model indicates that a small change of the atomic mobility leads to large deviations for the model from experimental results even at the early stages of phase separation, implying the importance of accurate thermodynamic parameters to the validity of theoretical models [102].

![Fig. 4.9 SANS data fitted by CHC model [108].](image)
Chapter 5

Methodologies

5.1 Instruments and sample preparation

The SANS measurement in this work has been performed using the LOQ diffractometer and Near and InterMediate Range Order Diffractometer (NIMROD) at the ISIS Pulsed Neutron and Muon Source, Oxfordshire, UK, see Fig. 4.4(a) and Fig. 5.1 [111]. Both of them make use of the time-of-flight technique. LOQ is around 15.1 m long. Neutrons with wavelengths of $2.2 \leq \lambda \leq 10$ Å are utilized to simultaneously reach $Q$ of $0.008 \sim 1.4$ Å$^{-1}$, meaning probed length scales of $\sim 1$–100 nm. The beam diameter for LOQ is 2-20 mm. The total length of NIMROD is 30 m. It can collect data at the $Q$-range of $0.02 \leq Q \leq 50$ Å$^{-1}$ corresponding to the length scales from the interatomic ($< 1$ Å) to the nanoscopic ($> 300$ Å) using neutrons with wavelengths of $0.05 \leq \lambda \leq 14$ Å. The beam size for NIMROD can reach 30 mm×30 mm. Various sample environments can be used at both instruments for in-situ measurements, e.g., different temperatures, pressure, gases, magnetic fields, see Fig. 5.2.

![Near and InterMediate Range Order Diffractometer (NIMROD)](image)

Fig. 5.1 Near and InterMediate Range Order Diffractometer (NIMROD) at the ISIS Pulsed Neutron and Muon Source, UK [111].

The sample preparation is relatively simple. To avoid multiple scattering and get enough signals, the sample thickness was 1.5 mm and 2 mm for LOQ and NIMROD, respectively, in this work. Grinding and polishing using sand papers (up to P1200 grit) were employed to remove the oxide layers after heat treatment. The final dimension of samples was either
5×5×1.5 mm³ or 10×10×1.5 mm³ for LOQ, and 20×20×2 mm³ for NIMROD.

Fig. 5.2 Sample environment equipments: (a) electromagnet and (b) heat treatment furnace and (c) sample hold.

5.2 Small-angle neutron scattering data analysis

The LOQ and NIMROD data were corrected using MantidPlot framework [112,113] and GudrunN package [114], respectively, to give $I(Q)$ on the absolute scale, see Fig. 5.3 [42]. The correlation peak of phase separation on the data was then isolated through the following procedure as shown in Fig. 5.4 [42,102,110]. The data for the undecomposed (e.g., solution treated) sample represent the background and showed a power law function behavior, therefore, the background was fitted by a power law function $I_b=x+yQ^z$ for decomposed samples. Then normalization was applied to $I(Q)$ by $I_b$, $I_n=I(Q)/I_b$. Subsequently, a Gaussian function ($I_G$) was fitted to $I_n$. Finally, the scattering function of phase separation ($I_{PS}$) was deduced as $I_{PS}=I_b(I_G-1)$. This procedure ensures positive values for $I_{PS}$ since $I_G \geq 1$. The peak position $Q_m$ and peak intensity $I_{PS}(Q_m)$ were obtained from the profile of $I_{PS}$. Then the characteristic distance (wavelength) $d=2\pi/Q_m$ was calculated. Meanwhile, the slope $n$ at the high-$Q$ side of the correlation peak was also determined as shown in Fig. 5.3 [42]. $d$, $I_{PS}(Q_m)$ and $n$ were used to quantify the evolution of phase separation. Generally, they increases with the development of phase separation.
For alloy conditions which could decompose via nucleation and growth (NG) or were at the transition region between NG and spinodal decomposition (SD), the Guinier plot, ln$I(Q)$ vs. $Q^2$, was adopted to get the average radius ($R$) of the Cr-rich ($\alpha'$) particle, see Fig. 5.4 [42]. The fitted slope equals to $-R_G^2/3$ ($R_G$ is the Guinier radius). Under the assumption that the particles are monodispersed spheres, $R = \sqrt{5/3}R_G$. 

Fig. 5.3 Corrected SANS data [42].

Fig. 5.4 Illustration of the background subtraction and extraction of peak position $Q_m$ and peak intensity $I_{PS}(Q_m)$ [42].
The evolution of $d$ or $Q_m$, $I_{PS}(Q_m)$ and $R$ were fitted by power laws [98,99,115]:

\[ d \propto t^a \text{ or } Q_m \propto t^{-a} \quad (5.1) \]

\[ I_{PS}(Q_m) \propto t^b \quad (5.2) \]

\[ R \propto t^c \quad (5.3) \]

where $t$ is aging time, $a$, $b$ and $c$ are the kinetic coefficients. $a=1/3$ implies a coarsening stage according to the Lifshitz-Slyozov-Wagner theory [116,117]. $a<1/3$ may indicate an early stage of decomposition.

### 5.3 Mechanical property tests

#### 5.3.1 Hardness tests

Both macro-hardness and micro-hardness of Fe-Cr based alloys have been measured. Vickers macro-hardness were measured using a KB 250-3000 BVRZ Standalone universal hardness testing machine with a load of 30 kg (HV30). The sample for macro-hardness tests were ground and polished using sand papers (up to P1200 grit). Vickers micro-hardness were performed with two loads on fine-polished samples. For ferritic stainless steels, the load was 50 g (HV0.05). For duplex stainless steels, micro-hardness of both ferrite and austenite have been measured and the applied load was 2 g (HV0.002) in order to ensure that the indentation was within the phase area. Fig. 5.6 is the micro-hardness of ferrite (bcc) and austenite (fcc) in duplex stainless steel 2507 aged at 325 °C for different times.
5.3.2 Impact toughness tests

The toughness degradation after aging within the miscibility gap was indicated by the impact toughness. The measurement was conducted at room temperature and employed sub-size Charpy–V samples of a dimension 55 mm × 10 mm × 5 mm. Some results of toughness tests are shown in Fig. 5.7.
Chapter 6

Summary of appended papers

Paper I. Structural characterization of phase separation in Fe-Cr: a current comparison of experimental methods

Phase separation (PS) in Fe-Cr model alloys was studied using small-angle neutron scattering (SANS). The Cr contents were 25‒36 wt.% representing different decomposition mechanisms. A method was proposed to subtract the background of SANS data and extract the scattering function of PS. Quantitative parameters, i.e. the wavelength ($d$) of PS, the peak intensity ($I(Q_m)$), the size of Cr-rich domains ($\alpha'$) and the slope ($n$) at the high-$Q$ side of the correlation SANS peak were evaluated from SANS data. Moreover, the advantages and drawbacks of techniques which have been applied in the study of PS in Fe-Cr alloys were reviewed. The SANS results were compared to the results obtained by atom probe tomography (APT) and transmission electron microscopy (TEM) from the same alloys. It is shown that SANS is sensitive to the microstructure change caused by PS and capable to characterize the very early stages of PS in Fe-Cr alloys. The discussion of the complementarity of SANS, APT and TEM indicates that the combination of them can lead to a more complete view of the microstructure of PS in Fe-Cr alloys.

Paper II. Effect of cooling rate after solution treatment on subsequent phase separation during aging of Fe-Cr alloys: A small-angle neutron scattering study

The initial microstructure of binary Fe-Cr alloys was tuned through different cooling rates (fast brine quenching and slow furnace cooling) after solution treatment. Then the same aging treatment was imposed on all samples to investigate the effect of the initial microstructure on phase separation (PS). The studied alloys decompose via either nucleation and growth (NG) or spinodal decomposition (SD) depending on the Cr content. Both small-angle neutron scattering (SANS) and the Cahn-Hilliard-Cook (CHC) model were used to study the nanoscale compositional fluctuations and the results from SANS and CHC model were compared. It is shown that the cooling process after solution treatment influences the initial
microstructure significantly, and thus the decomposition during subsequent aging. PS has already occurred during slow cooling and the initial decomposition leads to slower kinetics for SD in high Cr content alloys, however, it accelerates the kinetics for NG in lower Cr content alloys. For all alloys, the more non-random initial microstructure results in more significant decomposition, even after 300 h aging at 475°C. The CHC model can qualitatively agree the SANS results of SD for short aging periods (shorter than 10 h). For longer aging time, the CHC model predicts much faster kinetics than experimental results, meaning that the heat treatment history should be considered to improve the accuracy of simulations.

**Paper III. Effect of heat treatment above the miscibility gap on nanostructure formation due to spinodal decomposition in Fe-52.85 at.% Cr**

In-situ total neutron scattering were used to trace the microstructure variation during the stepwise cooling process from 1000 to 475 °C, i.e. from the temperature above the miscibility gap (MG) to the inside of MG, for Fe–52.85 at.%Cr. The critical temperature was found between 560 and 580 °C which is lower than the recent assessment by the CALPHAD (Calculation of PHAse Diagrams) approach, indicating that further investigation of the Fe-Cr phase diagram is needed. The nanostructure formed at different solution temperatures above the miscibility gap were quenched-in by rapid quenching. The effect of the nanostructure on spinodal decomposition (SD) was studied using small-angle neutron scattering (SANS). Micro-hardness was measured and used as the indicator of the mechanical property evolution. The results show that Cr clustering occurs above MG and it becomes more significant at lower solution temperatures. Solution treatment has important impacts on SD during aging for the alloy. At the temperature range 600–800 °C, SD is more enhanced for lower solution temperatures during aging, indicating that the enhancement of SD is dominated by Cr clustering. Nevertheless, 1000 °C solution treated sample possesses stronger SD than 800 °C solution treated sample during aging. The possibilities for this phenomenon are quenched-in vacancies, and/or the driving force to form σ phase since 800 °C is within the σ phase region while 1000 °C is outside the σ phase region, both of which may change the local atomic configuration. It is suggested that the initial microstructure formed prior
to aging treatment should be taken into account for the practical processing and computational simulations.

**Paper IV. Nanostructural evolution and mechanical properties during low-temperature aging of duplex stainless steels**

Duplex stainless steels (DSSs) have almost equal volume fraction of ferrite (bcc) and austenite (fcc) in the microstructure. When DSSs are exposed to temperatures within the miscibility gap, phase separation (PS) will take place in ferrite and form nanoscale compositional fluctuations leading to embrittlement for DSSs. The aim of this work was to study the effect of the compositional fluctuations on the mechanical properties and fracture mechanisms of DSSs. Standard grade 2205 and super grade 2507 aged at 325 °C up to 6000 h were employed. Small-angle neutron scattering (SANS) was used to characterize the nanostructure formed by PS. Macro- and micro-hardness and impact toughness were measured. Scanning electron microscope and electron backscatter diffraction were used to perform fractography. It is found that SANS is capable to characterize PS in DSSs although other phases exist. Due to different compositions, PS in alloy 2507 is more severe than in alloy 2205 when they experience the same heat treatment. Therefore, alloy 2507 is more hardened and less ductile than alloy 2205 after aging. The deformation mode for ferrite shifts from ductile to quasi-cleavage type due to the decomposition in ferrite. Deformation twins were observed in ferrite after aging, which could assist fracture as the crack initiation site. Large cracks were found on the fracture surface of Charpy V specimens, which was formed by the so-called delamination. Deformed ferrite and austenite and small grains were observed, which may consume a part of the energy during the fracture. However, more investigations are needed to shed light on fracture mechanisms.

**Paper V. Nuclear and magnetic small-angle neutron scattering in self-organizing nanostructured Fe$_x$Cr$_{1-x}$ alloys**

In this study, the nuclear and magnetic scattering were separated using a saturation magnetic field in small-angle neutron scattering (SANS) measurements to study their relations with phase separation (PS) in binary Fe-Cr alloys with different Cr contents representing different PS mechanisms, i.e. nucleation and growth (NG) and spinodal decomposition (SD). The ratio of the magnitude of magnetic scattering to that of nuclear
scattering depends on the extent of PS. When PS is still minute, the magnitude of magnetic scattering is very small. However, when PS is pronounced, e.g., for longer aging time, the scattering function of nuclear and magnetic scattering is identical under a saturation magnetic field, but it takes longer time for alloys with lower Cr contents to reach this stage.
Chapter 7
Concluding remarks and outlook on future work

7.1 Concluding remarks

The main objective of this work was to improve the understanding of phase separation in stainless steels which have a miscibility gap. Firstly, the application of different experimental techniques in the study of phase separation was reviewed and discussed. Small-angle neutron scattering (SANS) was chosen as the main technique, though it was also combined with other techniques, for the characterization of the decomposed nanostructure. Methods of analyzing the SANS data were implemented and applied for quantitative study. Secondly, the factors affecting the initial microstructure prior to aging treatment and the effect of the resulted initial microstructure on phase separation were systematically investigated using binary Fe-Cr model alloys. Thirdly, the study was extended to phase separation in commercial duplex stainless steels which are of practical importance in various industries, e.g., nuclear power. Finally, the fundamental aspect regarding the neutron scattering behavior for Fe-Cr alloys was examined.

From the work, the following conclusions are drawn:

(1) SANS is very sensitive to the nanostructure change caused by phase separation in stainless steels and capable to characterize the early stages of phase separation in Fe-Cr alloys. A method for extracting quantitative nanostructure parameters (wavelength and peak intensity) of phase separation in Fe-Cr alloys from SANS data has been developed. However, in order to have a more complete view of the microstructure, the combination of SANS with complementary techniques, e.g., atom probe tomography (APT) and transmission electron microscopy (TEM), should be pursued.

(2) The critical temperature of the miscibility gap of binary Fe-Cr was determined to be between 560 and 580 °C. In this work, it has been clearly shown that initial microstructures formed at different solution
treatment temperatures and by different cooling rates after solution treatment above the miscibility gap have significant effects on phase separation during subsequent aging. Lower solution temperature above the miscibility gap leads to less homogeneous initial microstructure. However, lower solution temperature do not necessarily results in more severe decomposition during aging. In addition, more significant phase separation occurs during slow cooling after solution treatment. This leads to more enhanced decomposition during aging in Fe-Cr alloys. The mechanisms affect the initial microstructure in these processes are indicated to be Cr clustering, quenched-in vacancy and decomposition during cooling as well as the atomic configuration changes due to the driving force of other phase transformations. Therefore, computational simulations should take into account these factors and the initial microstructure to make more accurate predictions.

(3) Alloying elements have an important influence on phase separation in duplex stainless steels. Grade 2507 has more significant decomposition than grade 2205 after experiencing same heat treatment. The fracture mechanisms, and the mechanical properties, depend on the extent of phase separation.

(4) The neutron nuclear and magnetic scattering depend on the evolution of nanoscale compositional fluctuations in Fe-Cr alloys. The ratio of the magnitude of nuclear scattering to that of magnetic scattering varies with the extent of phase separation, which has been ignored in many studies on phase separation in stainless steels.

7.2 Outlook on future work

Regardless the efforts in this work and the achievement in the literature on phase separation in stainless steels, some challenges still remains:

(1) The effect of factors, e.g., Cr clustering and quenched-in vacancy, on phase separation is still not fully understood. Different techniques, such as SANS, APT, TEM etc. and computational simulations should be combined to isolate each factor and shed light on the mechanisms.

(2) The effect of alloying elements, e.g., Mn, Mo, C, N, on phase separation in stainless steels should be studied more.
(3) The connection of phase separation in ferrite with mechanical properties and fracture mechanisms for duplex stainless steels needs more investigation.

(4) The amplitude of phase separation is still hard to deduce from SANS data. Studies making comparisons between SANS results and simulations using non-linear models are few. More efforts should be put into this aspect to take advantage of the theoretical similarity between SANS and the models, e.g., Cahn-Hilliard and Langer-Baron-Miller models, in order to develop more robust theories which can describe the whole process of phase separation.

(5) Magnetic neutron scattering may be a good probe to gain insight into the variation of magnetism due to phase separation in Fe-Cr based alloys. More work is needed to shed light on this issue.
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