

**THE STUDY OF THE DETERIORATION OF Fe-Cr-Ni
ALLOYS BY MÖSSBAUER SPECTROSCOPY**

BY

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ABSTRACT

Duplex stainless steels (alloys) with chromium content in the ferritic phase greater than 13% are subject to embrittlement due to hardening of the ferrite phase. Some components of the primary loops of Pressurised Water reactors (PWRs) are made of cast duplex stainless steels (austenite and ferrite). This kind of steel may age even at relatively low temperatures (under 400°C i.e. in the temperature range of PWR service conditions) due to a micro structural evolution of the ferritic phase to a hard and brittle chromium-rich α' -phase, and the ageing results in degradation of mechanical properties. In spite of this, the cast stainless steels are frequently used in primary coolant piping because of their high resistance to corrosion. To prevent hot cracking in the cast materials, the presence of some delta (δ) ferrite is required. An important consequence of this ageing process is the hardening or the embrittlement of the ferritic phase, caused by a chromium rich α' -prime phase, possibly produced by either nucleation-and-growth or spinodal decomposition.

In the present research, the samples from the Hot leg and Crossover Leg elbows in the primary loop of the PWRs from the Koeberg Nuclear Power Plant were investigated for mechanical degradation. The impact energy measurements were performed on these samples at the ESKOM TRI Centre by means of the Charpy V-notch measurements at room temperature. From these measurements, it was found that the samples that were not aged have high impact energy strength and this strength decreases with increasing ageing time.

The δ -ferrite and the γ -phase (austenite) content have been determined by means of Mössbauer spectroscopy and electron microscopy. The Mössbauer spectra obtained for these samples consisted of a paramagnetic singlet arising from the austenite and the magnetically split sextet resulting from δ -ferrite phase in the sample. From both the Mössbauer and the electron microscopy, the amount of δ -ferrite was found to be about 10 to 20%.

The amount of the ferrite and the γ -phase present in the samples is thought to be in direct relation to the impact energy. The amount of δ -ferrite obtained from Mössbauer spectroscopy was compared with Charpy impact energy values. No clear correlation existed between the δ -ferrite content and the Charpy impact energy values.

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CHAPTER 1

AN OVERVIEW

1.1 INTRODUCTION

Duplex stainless steels are usually manufactured by a continuous casting technique and consist of a paramagnetic austenitic phase or gamma (γ) phase, and a ferromagnetic ferrite phase or delta (δ) ferrite [1-3]. A ^{57}Fe Mössbauer spectroscopy measurement used for duplex stainless steel will result in a spectrum that consists of the single resonance line arising from the austenite. The other component is a magnetically split sextet arising from the ferrite [4].

The samples investigated in this project were Fe-Cr-Ni alloys supplied by ESKOM. These samples were cross-sections of Charpy Impact strength specimens, cut from the Hot leg and Crossover leg elbows in the primary loops of the Ringhals 2 Steam Generators which has been operating for 15 years [5]. These alloys, having different aging times, were analysed using Mössbauer Spectroscopy as the primary tool. This technique was chosen since it can detect small Fe-rich concentration changes resulting in different phases developing during the decomposition of the Fe-Cr system. The changes in the Fe-rich phase can be monitored by the measurement of the change in the material's magnetic field which is proportional to the Cr content of the Fe-rich phase [6]. The average magnetic field strength increases slowly with aging time, while the intensity of the paramagnetic singlet formed due to the α' -Cr rich phase, increases faster, as shown in

Figure 1.1. This singlet is the best parameter for the determination of the amount of decomposition that has taken place in such an alloy.

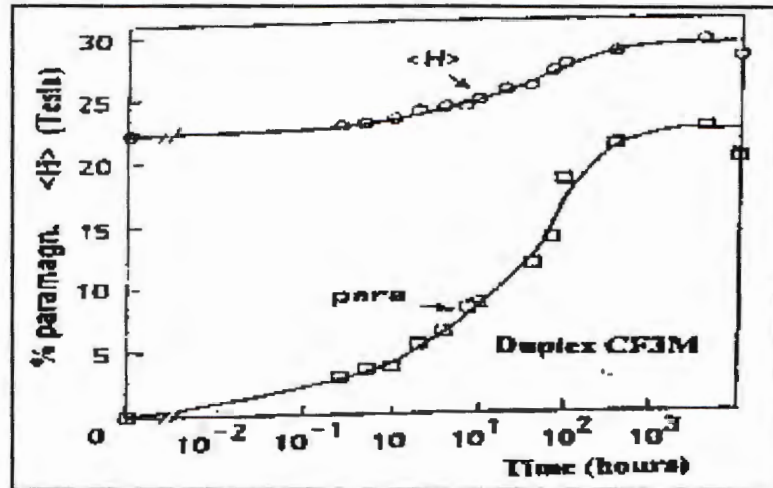


Figure 1.1 Time dependence of the paramagnetic fraction and of the average magnetic hyperfine field for a duplex CF3M steel as a function of aging time [6].

According to Pollak, Waanders and Karfunkel [6], the standard method to follow the embrittlement of duplex and high Cr stainless steels is the use of Charpy impact test, which is a macroscopic approach. The embrittlement as a function of time, increases with the decomposition of the steel, but not in a linear way. **Figure 1.2** presents data on the evolution of the intensity of the paramagnetic fraction for various Fe-Cr alloys, and shows that there is a plateau where the embrittlement of the steel does not change any more with time. This means that the rate of transformation or decomposition is either slowing down, or is almost complete. For the alloys presented in **Figure 1.1**, a stable alloy is reached after about 5×10^2 hours, while for alloys used in **Figure 1.2**, the final stage seems to be reached after a shorter time of approximately 2×10^2 hours. The growth is the fastest in

the alloy with 2.3 wt.% Ni, suggesting the importance of Ni, for forming the singlet of the α' -Cr rich phase [6].

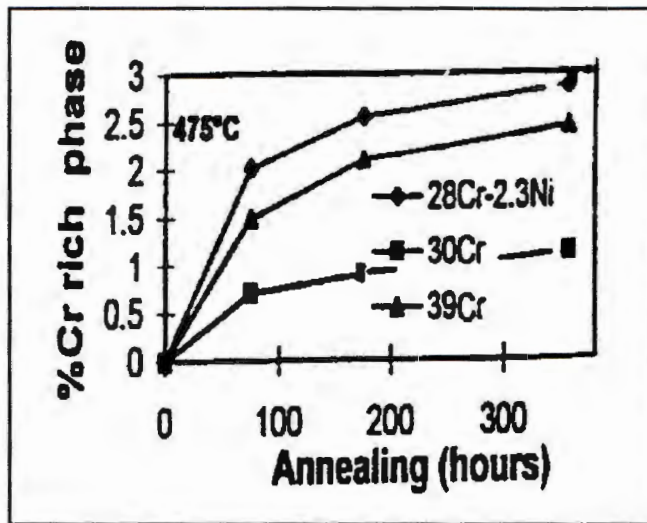


Figure 1.2 Intensity of the paramagnetic phase as function of aging at 475°C [6].

From the Mössbauer spectra, the amount of ferrite and the austenite in the sample can be determined. The results obtained can then be compared with the impact strength test results determined by Charpy V-notch measurements at room temperature. The Charpy V-notch measurements were performed at the ESKOM Technological Research Institute (TRI).

Another technique employed in the present study was to utilize the Scanning Electron Microscopy (SEM) facility, and the microphotographs obtained were used to determine the amounts of each phase present in each sample. The SEM, fitted with an energy dispersive X-ray (EDAX) detector was used to determine the δ -ferrite and the γ -austenite amounts present in the samples.

1.2 Statement of the Problem

Duplex stainless steel alloys are used in the primary cooling circuits of the Pressurised Water Reactors (PWRs) e.g. primary loops of PWRs in the Koeberg Nuclear Power plant. They are subject to embrittlement when aged at temperatures between 200°C and 400°C, which involves hardening due to the precipitation of a α' -Cr-rich phase, possibly produced by spinodal decomposition or a nucleation and growth mechanism [1,2,3].

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The aging and embrittlement of these steels reduces the lifespan of the pressure vessels and reactors. Because of the embrittlement of these steels, there is an increased demand in recent years for alloys that can be used at elevated temperatures and corrosive environments [6]. **Figure 1.3** shows the schematic reactor loop in a PWR.

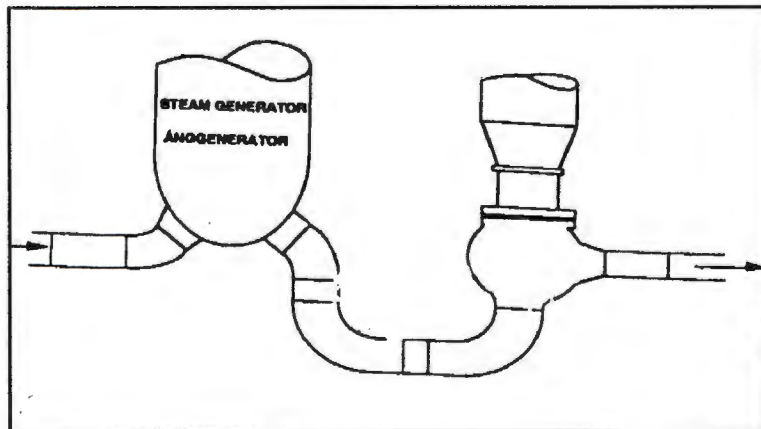


Figure 1.3 Schematic diagram of the elbows of primary cooling circuits of PWRs [5].

1.3 Objective of the Investigation

The objective of this investigation was to study the elbows of the primary loops of the PWRs from Koeberg Nuclear Power Plant for mechanical degradation. The amount of δ -ferrite present in the sample, after different aging times, was determined and the results compared with the impact energy measurements determined by means of Charpy V-notch measurements which were done at room temperature. The amounts of each phase present in the sample, as determined by electron microscopy were compared with the Mössbauer measurements.

CHAPTER 2

MÖSSBAUER SPECTROSCOPY

2.1 INTRODUCTION

Mössbauer Spectroscopy is the name given to a technique of studying the absorption and re-emission of gamma (γ) rays by the nuclei of atoms. The nuclear processes producing this effect were first observed and reported by Rudolph L Mössbauer in 1958 [7, 8]. The method makes use of nuclear properties to obtain information regarding the environment surrounding the nucleus. This technique has found applications in diverse fields such as solid state physics, metallurgy, chemistry and biochemistry [8].

Mössbauer Spectroscopy is described as nuclear gamma ray resonance spectroscopy (NGR), and, as the name implies, the nucleus is probed using γ -rays as the exciting radiation [9]

2.2 NUCLEAR GAMMA RAY RESONANCE SPECTROSCOPY

The processes occurring in nuclear γ - ray resonance spectroscopy can be described as follows: Nuclei are the heavy cores of atoms and are generally considered to be composed of protons and neutrons. The number of protons in the nucleus is the atomic number of the atom, and it determines the chemical properties of the atom [7]. For each element (atomic number), a number of different isotopes, corresponding to different numbers of neutrons in the nucleus may be stable. These are the naturally occurring

isotopes of that element, identified by the mass number (sum of protons and neutrons). Unstable (radioactive) nuclei undergo decay, or transformation, with the emission of various kinds of radiation such as γ -radiation [7].

Stable nuclei have excited states, configurations in which the nucleus has some discrete, well-defined quantity of added energy over that present in the stable, or ground state configuration. These excited states often decay to the ground state, with the extra energy being emitted in the form of a γ -ray. When γ - rays pass through matter, they are absorbed or scattered primarily by occasional energetic collisions with electrons [8]. In NGR, the γ - rays are absorbed and then re-emitted in a recoilless fashion and this results in a typical Mössbauer spectrum. Those γ - rays that are not absorbed or scattered, continue to propagate with their original velocity [9].

2.3 MÖSSBAUER EFFECT

The Mössbauer effect is based on what is known as a recoil-free γ -ray resonance absorption phenomena. Its unique feature is the production of highly monochromatic electromagnetic radiation so that it can be used to resolve minute energy perturbations [8]. The application of the Mössbauer effect arises from its ability to detect the small variations in the energy of interaction between the nucleus and the extra-nuclear electrons [10].

2.3.1 Absorption and Recoil-free Emission

Resonance absorption involves the excitation of a quantized system (*absorber*)

from its ground state (E_g) to an excited state (E_e) by absorption of a photon emitted from an identical system (*source*) decaying from state (E_e) to state (E_g) [8].

When a nucleus undergoes a transition from state E_e to state E_g by the emission of a photon, the conservation of momentum requires that the momentum of the atom, (p_M), recoiling in one direction, must be equal and opposite to the momentum of the photon (p_γ) emitted in the opposite direction[10,11]. The kinetic energy of the recoiling atom is E_R , so that for an atom of mass M and velocity v

$$E_R = \frac{1}{2} Mv^2 = \frac{p_M^2}{2M} \quad (2.1)$$

Moreover, the momentum of a photon of zero rest mass is related to the energy by

$$E = p_\gamma c \quad (2.2)$$

thus

$$p_\gamma^2 = \frac{E_\gamma^2}{c^2} \quad (2.3)$$

Since the two momentums must be equal, it follows that

$$E_R = \frac{E_\gamma^2}{2 Mc^2} \quad (2.4)$$

where E_γ is the photon energy, M is the mass of the recoiling system, c is the speed of light and E_R is the recoil energy [11]. The recoil energy makes the energy of the emitted γ -ray E_γ , smaller than the energy E_0 which would have been obtained in the absence of recoil [10, 11]. If a photon is produced as a result of the transition from an excited state to the ground state of the nucleus, it follows that

$$E_e - E_g = E_0 = \frac{p^2}{2M} + E_\gamma = E_R + E_\gamma \quad (2.5)$$

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In absorption, the energy required by the nucleus for the same transition is given by $E_0 + E_R$, due to the fact that the absorbing atom also recoils. It thus follows that the emission and the absorption lines are separated by $2E_R$, as shown in **Figure 2.1**:

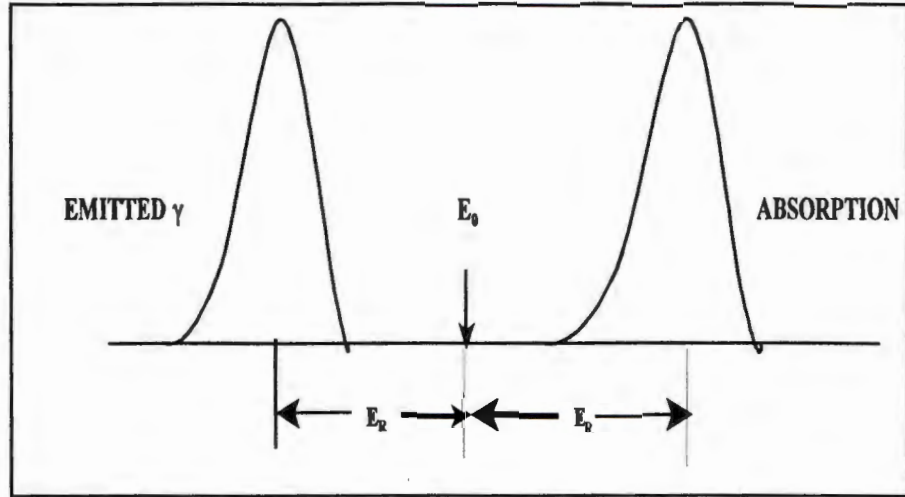


Figure 2.1 In a γ -ray resonance fluorescence experiment, it follows that if recoil energy E_R is large compared to the natural line width Γ , resonance fluorescence cannot take place [12].

If these lines have a small natural line width Γ_g compared with E_R , resonant fluorescence in which one nucleus emits and another absorbs the photon will not occur. The natural line width Γ of the 14.4 keV transition of ^{57}Fe from the excited state to the ground state is of the order of 10^{-9} eV. The recoil energy E_R for this nucleus is of the order of 10^{-3} eV. Thus at low temperature, where the lines are not broadened due to thermal motion of the emitting and absorbing nuclei (Doppler broadening), the overlap between the two lines vanishes and the resonance absorption does not take place [10, 12]. As the temperature T is increased, the Doppler line width, given by

$$E_0 \frac{v}{c} = E_0 (3k_B T / Mc^2)^{1/2} \quad (2.6)$$

increases, where v is the thermal velocity of the atom and $(3/2) k_B T$ is the average kinetic energy of the atom in a solid at temperature T . For the 14.4 keV transition the Doppler

line width at room temperature is $\sim 10^{-3}$ eV. It is evident that with an increase in temperature, the possibility for the nuclear resonance fluorescence should increase [10].

Contrary to this expectation, the resonance fluorescence in ^{57}Fe increases as T decreases and reaches a maximum as T tends to 0 K. Similar observations were made by Mössbauer in 1957 on ^{191}Ir nuclei and he proposed that some of the ^{191}Ir nuclei are not free in the solid but are firmly embedded in the crystal lattice so that when they decay the recoil momentum is effectively taken up by the whole solid. If this occurs, the mass M in Equation (2.5) has to be replaced by NM where N is the total number of atoms in the solid, which is in the order of 10^{23} [11]. Consequently, the energy of the emitted photon to a sufficiently good approximation is

$$E_0 = E_\gamma \quad (2.7)$$

and hence the emission is recoilless. A nucleus embedded in the absorber in a similar manner will absorb this recoil energy [10, 11].

The process of absorption and recoilless emission of γ -rays from nuclei bound in solids is known as the *Mössbauer effect*. Mössbauer discovered that atoms in a solid can emit and/or absorb γ -rays without recoiling. The effect is caused by the quantum nature of the lattice vibrations which would take up the recoil energy. If the smallest energy quantum for the excitation of a lattice vibration is $\hbar\omega_0$, any recoil energy which is smaller than $\hbar\omega_0$, is unable to excite a lattice vibration i.e. the emitting atoms remains at rest [13]. When many emission processes are considered not all atoms remain at rest, some of them suffer a recoil with an energy of $\hbar\omega_0$. The average recoil energy per emitting atom is equal

to the free-atom recoil energy, given by

$$E_R = (1 - f) h\omega_0 \quad (2.8)$$

provided $E_R \ll h\omega_0$ and the temperature is very low. Hence the Mössbauer coefficient f is given by

$$f = 1 - \frac{E_R}{h\omega_0} \quad (2.9)$$

or

$$f = \exp \left(\frac{-4\pi^2 X^2}{\lambda^2} \right) \quad (2.10)$$

which is the more general expression incorporating the thermal mean-square displacement X^2 of the emitting atoms in the direction of the emitted γ -quantum. It can be seen from Equation (2.10) that X^2 should be as small as possible i.e the temperature as low as possible if a large Mössbauer effect is desired [10, 12, 13].

2.3.2 The Mössbauer Spectrum

To demonstrate the Mössbauer effect, a solid matrix containing the excited nuclei of a given isotope (the source) is placed in front of a second matrix containing the same

isotope in the ground state (the absorber). The intensity of the beam emitted from the source, and then transmitted through the absorber, can be measured as a function of the temperature of the matrix. In the absence of resonant absorption, the transmission rate will be independent of temperature, but a decrease in the counting rate (i.e an increase in the resonant absorption) would be expected as the temperature is lowered and the recoilless fraction increases [13].

The of resonant absorption is determined by the overlap of the energy profiles of the source and the absorber as shown in **Figure 2.2 (a)**. Because of this, the Mössbauer resonance effect is specific to atoms of a particular isotope of an element, and is therefore a highly selective form of spectroscopy. The effective energy value, or E_γ , can be altered by moving the source and the absorber relative to each other with a velocity v , i.e by using a Doppler shift energy of $\epsilon = (v/c) E_\gamma$ [13]. If the effective energy values, E_γ , for the source and absorber are exactly matched, at a certain Doppler velocity, resonance absorption will be at a maximum and the count rate a minimum. At any higher or lower applied velocity, the resonance effect will decrease. In the extreme of large velocities, such that there is no overlap of the two energy distributions, there will be no resonant absorption. Thus the basic principle of obtaining a Mössbauer spectrum is to record the transmission of γ -rays from a source through an absorber as a function of the Doppler velocity v [13]. This principle is illustrated schematically in **Figure 2.2(b)**.

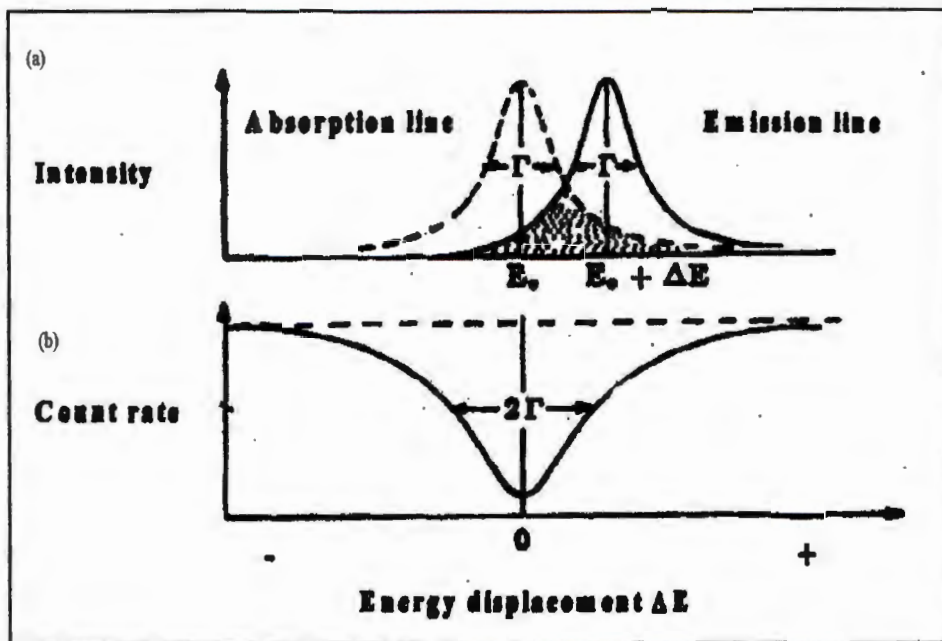


Figure 2.2(a) and (b) A Mössbauer absorption spectrum recorded by means of a Doppler scanning Technique ($\Gamma = \hbar/\tau$ and τ is the half-life of the excited nucleus) [14].

The line-shape of the absorption spectrum is derived from the mathematics of the source and the absorber energy distributions. The source has a recoilless fraction f_s and a Heisenberg width Γ_s . The number of transitions $N(E)$ between $(E_\gamma - E)$ and $(E_\gamma - E + dE)$ is given by the Lorentzian distribution:

$$N(E) dE = \frac{f_s \Gamma_s}{2\pi} \frac{dE}{(E - E_\gamma)^2 + (\Gamma_s/2)^2} \quad (2.11)$$

which has a maximum at $E = E_\gamma$. The cross-section for resonant absorption $\sigma(E)$ is similarly expressed as:

$$\sigma(E) = \sigma_0 \frac{(\Gamma_a/2)^2}{(E - E_\gamma)^2 + (\Gamma_a/2)^2} \quad (2.12)$$

where Γ_a is the Heisenberg width of the absorber energy distribution. The cross-section σ_0 is constant for a particular transition [13, 14].

The resonant line-shape, as measured experimentally can be related to $N(E)$ and $\sigma(E)$ and the thickness of the absorber, but is most usefully considered in the limit of a very thin source and absorber for which the line-shape is Lorentzian in shape but with a width of $\Gamma_r = 2\Gamma_s$ [13, 14]. An increase in absorber thickness causes a gradual increase in the magnitude of Γ_r but with minimal distortion from the Lorentzian shape. The intensity of the absorption maximum can be related to $\sigma(E)$, the absorber thickness, and the recoilless fraction in the absorber f_a [13].

The value of the Mössbauer effect lies in the extremely small line width of the emitted γ -ray. When lattice vibrations are excited during the emission process, the line width of the γ -ray is of the order of the energies of the lattice vibrations, which is about 0.01 eV [6] When the lattice is not excited, the line width is of the order of the width of the nuclear levels, about 10^{-8} eV. Thus the Mössbauer line width is smaller than the energy level changes caused by the magnetic dipole and electric quadrupole interactions of nuclei with their surrounding electrons. The Mössbauer effect is therefore ideally suited for the study of these interactions which are usually called *hyperfine interactions* [15].

2.4 HYPERFINE INTERACTIONS

The Mössbauer effect produces monochromatic γ -radiation with a definition of the order of 1 part in 10^{12} and this high precision can be used to obtain chemical information about the material being studied [12]. The total Hamiltonian for the atom, which contains the terms relating to interactions between the nucleus and the electrons (and hence the chemical environment), can be written as

$$H = H_0 + E_0 + M_1 + E_2 + \dots \quad (2.13)$$

where H_0 represents all terms in the Hamiltonian for the atom except the hyperfine interactions being considered; E_0 refers to electric monopole (i.e Coulombic) interactions between the nucleus and the electrons; M_1 refers to magnetic dipole hyperfine interaction; and E_2 refers to electric quadrupole interactions. Higher terms are usually negligible [12].

The Coulombic interaction (E_0) alters the energy separation between the ground state and the excited state of the nucleus, thereby causing a slight shift in the position of the observed resonance line. The shift will be different in various chemical compounds and it is frequently referred to as the isomer shift (or chemical shift) [12,15].

The electric quadrupole (E_2) and the magnetic dipole interactions (M_1) both generate multiple line spectra, and consequently can give a great deal of information. All the three interactions (E_0 , M_1 and E_2) can be expressed as the product of a nuclear term

which is a constant for given Mössbauer γ -transition and the electronic term which can be varied and related to the chemistry of the resonant absorber being studied[12], and are discussed in more detail in the following section.

2.4.1 The Isomer Shift (IS)

The isomer shift arises from the interaction energy of the part of the electronic cloud inside the volume of the nucleus with the nuclear charge. The isomer shift provides information about the electron density at the nucleus. The effect arises because the nucleus is not a point charge but occupies a finite volume [7].

For a spherical nucleus, this volume is $V = 4/3 \pi R^3$, where $R \sim 1.20 \times 10^{-13} A^{1/3}$. If a uniform nuclear charge distribution is assumed inside the nucleus, the potential due to this charge at a radial distance r from the origin is

$$V(r) = \frac{Ze^2}{R} \left[-\frac{3}{2} + \frac{1}{2} \left(\frac{r}{R} \right)^2 \right] \quad (2.14)$$

for $r < R$ and is $V(r) = -Ze^2/r$ for $r > R$. In a non-relativistic approximation, the electron density at the nucleus is appreciably large only for s electrons and can be approximated by $\psi_a^2(0)$ [7, 16].

Since nuclear excited and ground states do not have the same radius of equivalent charge distribution (in the case of the ^{57}Fe the ground state radius is larger than the radius of the $3/2$ state), the s electrons will interact to a different extent with the nuclear charge

[7]. Specifically, the perturbation energy due to this interaction is given by

$$\Delta E = \frac{2}{5} \pi Z e^2 R^2 \psi_s^2(0) \quad (2.15)$$

and the perturbation difference between the excited state and the ground state is

$$\delta(\Delta E) = \frac{2}{5} \pi Z e^2 \psi_s^2(0) R^2 \frac{\delta R}{R} \quad (2.16)$$

where $\delta R = R_{\text{excited}} - r_{\text{ground}}$.

In practice, $\delta(\Delta E)$ is not measurable by itself, but can be evaluated only with respect to a given source-absorber pair. For such a pair of resonant atoms, the isomer-shift energy is

$$E_{IS} = \frac{2}{5} \pi Z e^2 R^2 \frac{\delta R}{R} [|\psi_s^2(0)|_a - |\psi_s^2(0)|_s] \quad (2.17)$$

in which the two s electron wave functions refer to the absorber and source respectively [16]. The isomer shift is observed in a resonant experiment as a Doppler shift, which occurs at a velocity

$$v = \frac{4\pi}{5} Z e^2 r^2 \frac{\delta r}{r} [|\psi(0)|_a^2 - |\psi(0)|_s^2] = IS \quad (2.18)$$

where $|\psi(0)|^2$ is the total electron density at the nucleus. This can be simplified to

$$IS = \text{const.} \cdot \frac{\delta R}{R} \cdot \delta |\psi(0)|^2 \quad (2.19)$$

where $\delta|\psi(0)|^2$ is the change in s electron density at the nucleus in going from the source to the absorber. The isomer shift therefore depends on a nuclear factor, $\delta R/R$, and an extra nuclear factor [16]. For isotopes for which $\delta R/R$ is positive, any factor which increases the s -orbital population increases the isomer shift. Thus an increase in the covalency of the bonds, or donation by the ligands, increases the total electron density and, therefore, the s -electron density [7]. The isomer shift is also increased, but to a smaller extent by the factors which decrease the p - or d - populations, owing to the decrease in shielding of the nucleus from the s - electron density. The most obvious such factor is an increase in the oxidation state of the Mössbauer atom. A decrease in coordination number also increases the contribution of the s -orbital and decreases the p - and d -populations, resulting in the isomer shift. When $\delta R/R$ is negative (e.g -1.8×10^{-3} for ^{57}Fe), these effects are reversed [7].

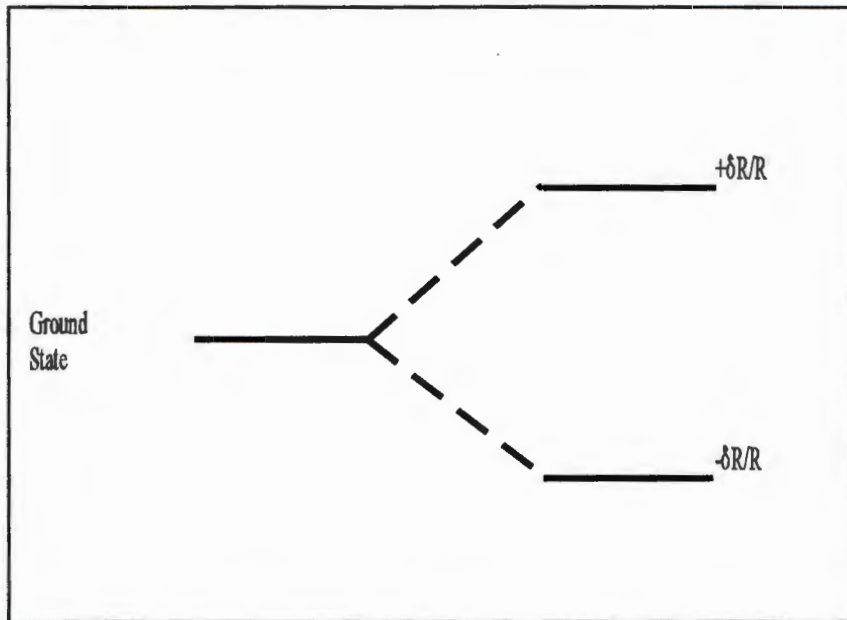


Figure 2.3 Nuclear energy level diagram showing the effect of isomer shift.

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2.4.2 Quadrupole Splitting

In addition to the changes in the nuclear energy levels produced by the isomer shift, the levels may be split by the electric quadrupole interaction. This splitting leads to a number of possible absorption energies, and thus a number of lines in the absorption (or emission) spectrum. In **Figure 2.4** the splitting is shown for the $I = 3/2$ state in ^{57}Fe isotope. The nuclear excited state ($I = 3/2$) and ground state ($I = 1/2$) produce two absorption lines due to the quadrupole interaction [7,12,16].

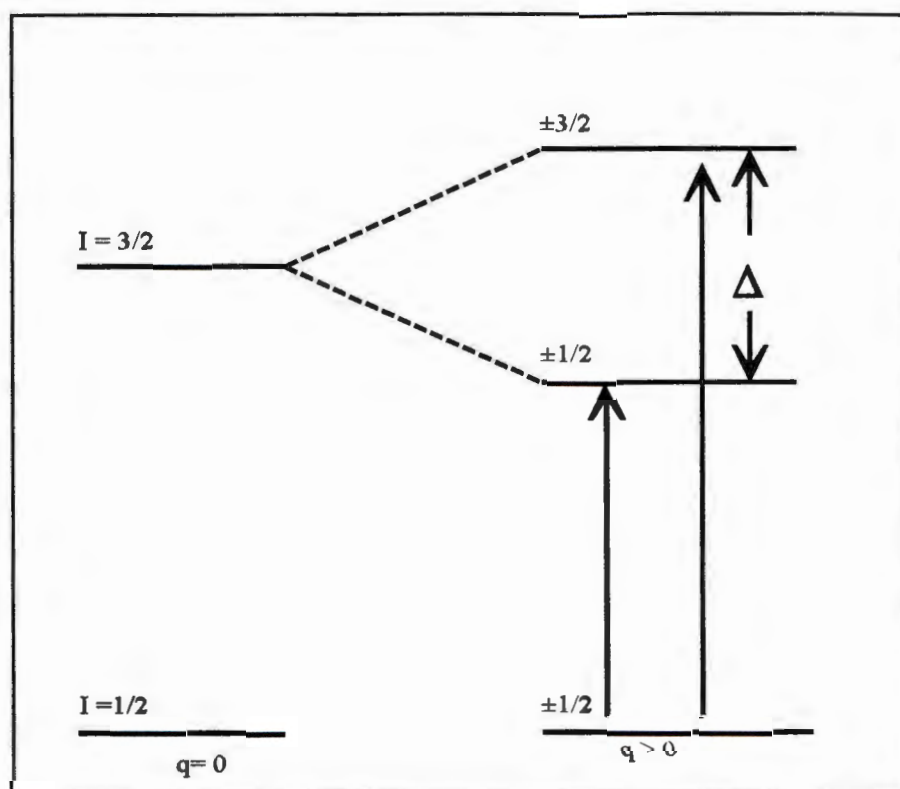


Figure 2.4 Nuclear energy level diagram showing the effect of quadrupole interactions $I = 3/2$ [16].

The quadrupole splitting arises from the fact that the nucleus is not perfectly spherical, but may be ellipsoidal, either elongated (prolate) or flattened (oblate). As can be seen in **Figure 2.5**, the electrostatic forces between the surrounding ligands (assumed to be negatively charged) and the non-spherical part of the nuclear charge tend to make the nuclear axis point towards the ligands. This state is then the lower energy state of the quadrupole interaction, and the state with the nuclear axis perpendicular to the ligand axis is the higher energy state [7].

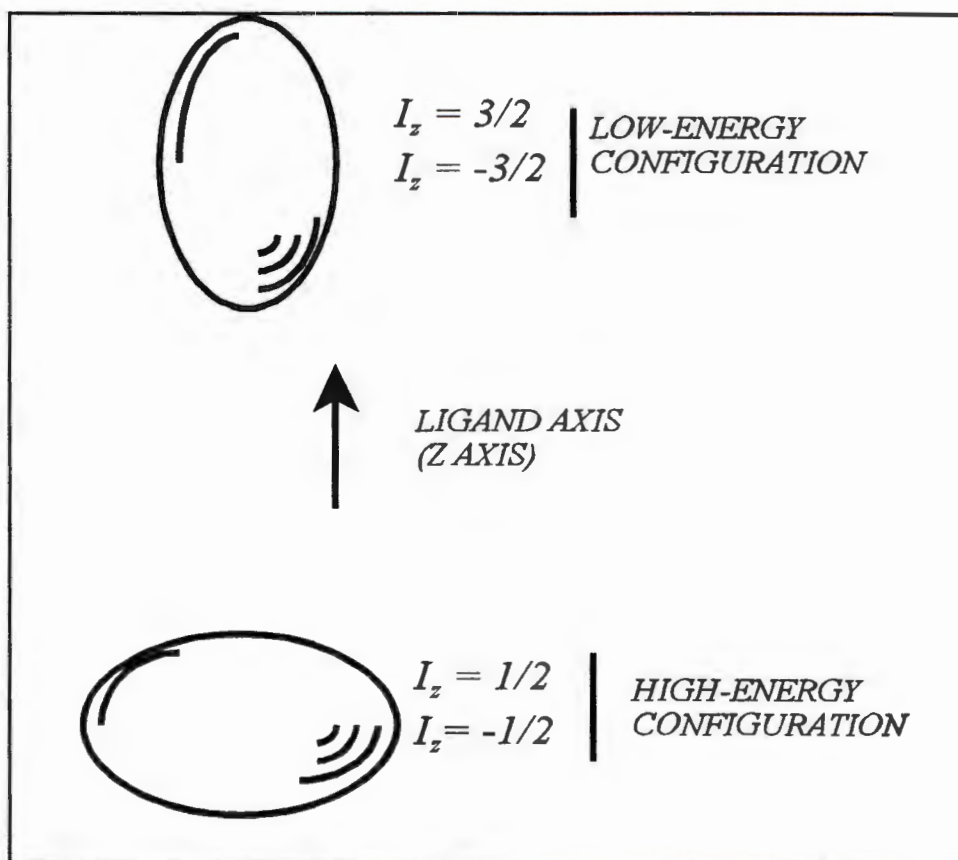


Figure 2.5 Coupling of the nuclear quadrupole moment with nearby charges to illustrate the two possibilities that can occur [7].

In the case with the excited state $I = 3/2$, it simplifies to a doublet of separation Δ where

$$\Delta = \text{const.} \cdot Q \cdot q \quad (2.20)$$

As with the isomer shift, the quadrupole splitting, Δ , is the product of the nuclear factor Q , and a term due to the ion and its surroundings given by the field gradient V_{zz} . The field gradient arises from the non-symmetric disposition of the electronic charge in the ion

under study and its surroundings [7].

The Mössbauer nucleus can therefore be used as a probe to get information about site symmetries and field gradients within a crystal and to give details of imbalance of p and d electrons [7].

2.4.3 Magnetic Hyperfine Interactions

The last of the major types of interaction that can be investigated by Mössbauer spectroscopy is the hyperfine Zeeman splitting of the nuclear energy levels in a magnetic field. The magnetic field can originate either within the atom itself, within the crystal via exchange interactions, or as a result of placing the compound in an externally applied magnetic field [12,15].

The Hamiltonian describing the magnetic dipole hyperfine interaction is given by

$$\mathcal{H} = - \boldsymbol{\mu} \cdot \mathbf{H} = - g\mu_N \mathbf{I} \cdot \mathbf{H} \quad (2.21)$$

where μ_N is the nuclear Bohr magneton ($e\hbar/2Mc$), μ is the nuclear magnetic moment, I is the nuclear spin, and g is the nuclear g -factor [$g = \mu/(\mathbf{I} \mu_N)$]. The Bohr magneton μ_N has the value of $5.04929 \times 10^{-27} \text{ JT}^{-1}$. Each level of spin quantum number I will split into $(2I + 1)$ equally spaced non-degenerate sub-levels. The energy of these levels is given by

$$E = - \frac{\mu}{I} H m_I = - g\mu_N H m_I \quad (2.22)$$

where m_I is the magnetic quantum number representing the z -component of I (i.e. $m_I = I, I-1, \dots, -I$). Mössbauer transitions can take place between different nuclear levels if $\Delta m_I = 0, \pm 1$,

or additionally in some cases as ± 2 [12]. The allowed possibilities for a $3/2 \rightarrow 1/2$ Mössbauer γ -ray transitions are illustrated in the Figure 2.6.

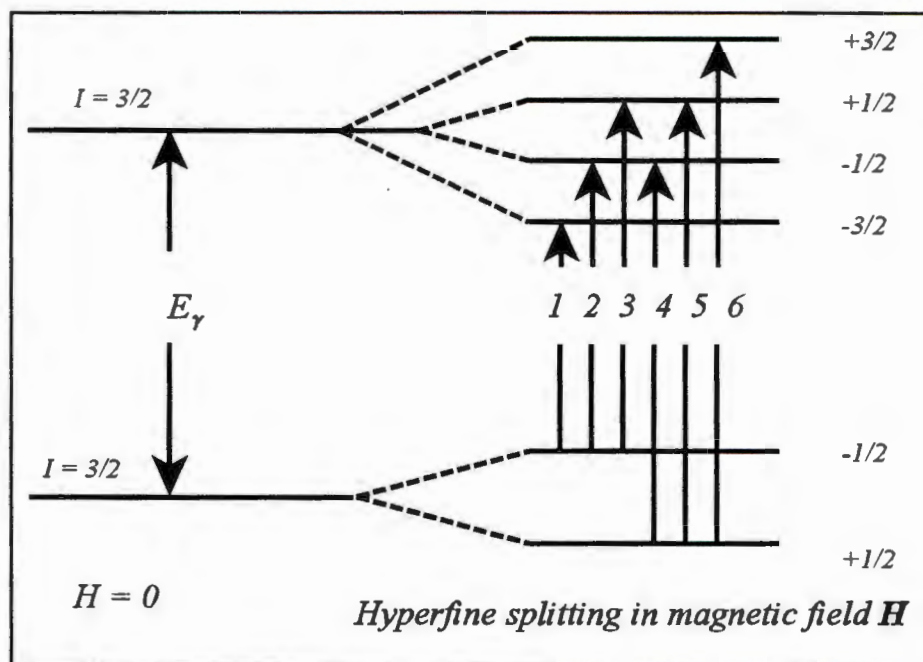


Figure 2.6 Hyperfine splitting of nuclear energy levels in a magnetic field, H [16].

As in the case of isomer shifts and quadrupole splitting, the magnetic hyperfine effect is the product of a nuclear term, which is a constant for a given Mössbauer transition, and the magnetic field H [16].

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It is worth noting that in conventional nuclear magnetic resonance (NMR), transitions are observed between the adjacent sub-levels of the ground state, whereas in Mössbauer spectroscopy transitions between one of the sub-levels of the excited state and one of the sub-levels of the ground state are observed [7]. The energy of the γ -ray transition is some 10^{-12} times that of the NMR transition and it is only the tremendous precision of the Mössbauer effect which enables the hyperfine interactions to be resolved.

2.5 Conversion Electron Mössbauer Scattering (CEMS)

CEMS is used for structural analysis of thin films and subsurfaces in solids. This technique has established itself as a sensitive depth-selective method for materials characterisation in different areas of high technology and related basic research because of :

- (i) the attractive probing depth, with depth ranging from first atomic layers on surface to about $1\mu\text{m}$ below the surface
- (ii) the high sensitivity, which in most favourable cases enables studies of films as thin as 1 to $100\mu\text{g}/\text{cm}^2$ i.e 10^{13} to $10^{15}\text{at}/\text{cm}^2$ [10]

Various problems currently investigated with the help of CEMS, include surface physics and chemistry, studies of thin films and interfaces, magnetism, materials fatigue, corrosion, ion implantation, radiation damage and plasma wall interaction, as well as fields like metallurgy and catalysis [10].

2.5.1 The CEMS Principle

The nucleus, resonantly excited by the recoil-free absorption of a gamma ray, can discharge its surplus energy in various ways, involving either the re-emission of gamma rays or internal conversion electrons. Since the low energy isomeric states in nuclei are usually characterized by large electron conversion coefficients (1 - 100), the resonant Mössbauer scattering of gamma rays is dominated by electron conversion processes [10].

A total intensity of conversion is determined by the internal conversion coefficient for the given gamma ray transition, defined as the ratio between the probability of electron conversion and gamma ray emission, such that

$$\alpha = N_e / N_\gamma = \alpha_k + \alpha_l + \alpha_m + \dots \quad (2.22)$$

Internal electron conversion is accompanied by Auger electrons, X-rays as well as by numerous secondary electrons and low energy photons [10].

Figure 2.7 represents the scheme of the de-excitation processes after the resonant absorption of the 14.4 keV γ -rays in ^{57}Fe nuclei has taken place. The energies and relative intensities of the main electron transitions in this case are: conversion electrons - K (7.3 keV, 79%), L (13.6 keV, 8%) and M (14.3 keV, 1%); Auger electrons - KLL (5.4 keV, 60%), LMM (0.5 keV, 60%). The relative intensities of the conversion and Auger lines are given in percent per one resonant absorption [10].

All radiation emitted after the resonant absorption can be employed in recording the Mössbauer spectrum. The technique which is based on detection of electrons is commonly denoted as Conversion Electron Mössbauer Spectroscopy (CEMS.)

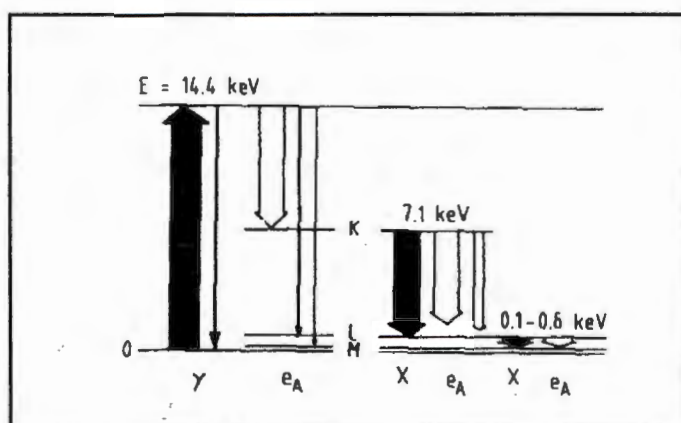


Fig. 2.7 The resonant absorption of 14.4 keV by ^{57}Fe nucleus is followed either by the emission of 14.4 keV γ -rays or internal conversion electrons, e_c , which is accompanied by X-rays or Auger electrons, e_A . The relative intensities are represented in the scheme by the widths of the corresponding arrows [10].

2.5.2 Probing Depth of CEMS

The probing depth of CEMS is determined by the escape range of the conversion, Auger and secondary electrons in the absorber. This depth is usually by two to three orders of magnitude smaller than the depth probed by Mössbauer transmission spectroscopy or by γ -ray and x-ray scattering techniques. An estimate of the electron penetration range can be given on the basis of the formula derived from the analysis of electron transmission measurements [10]. For electrons with kinetic energies, E , between 5 and 50 keV, the flux of electrons after transversing a distance x in a material with density, d , given in g / cm³, is attenuated exponentially,

$$I = I_0 e^{-x/T} \quad (2.23)$$

with the mean penetration depth τ in nm⁻¹ given by

$$\tau = A \frac{E^n}{d} \quad (2.24)$$

where A and n are material dependent parameters [10].

CHAPTER 3

IRON-CHROMIUM-NICKEL (FE-CR-NI) SYSTEM

3.1 Introduction

In recent years, there has been an increased demand for alloys that can be used at elevated temperatures and in corrosive environments. Austenitic stainless steels have been widely used by petrochemical and power plant utilities where their good mechanical and high temperature properties have been exploited [17].

Austenitic stainless steels normally have better corrosion resistance than ferritic and martensitic ones because the carbides can be retained in solid solution by rapid cooling from high temperatures. However, if these alloys are to be welded or slowly cooled from high temperatures through the 870 to 600°C range, they can become susceptible to intergranular corrosion, because Cr- containing carbides precipitate at the grain boundaries [17].

3.2 The Fe-Cr Phase Diagrams

The simplest stainless steel consists of an iron-chromium alloy but in fact the binary Fe-Cr system can give rise to a wide variety of microstructures with markedly different mechanical properties [12]. The general Fe-Cr equilibrium diagram is shown in **Figure 3.1**. One of the characteristics of this phase diagram is the restricted austenite phase field called the γ -loop [17].

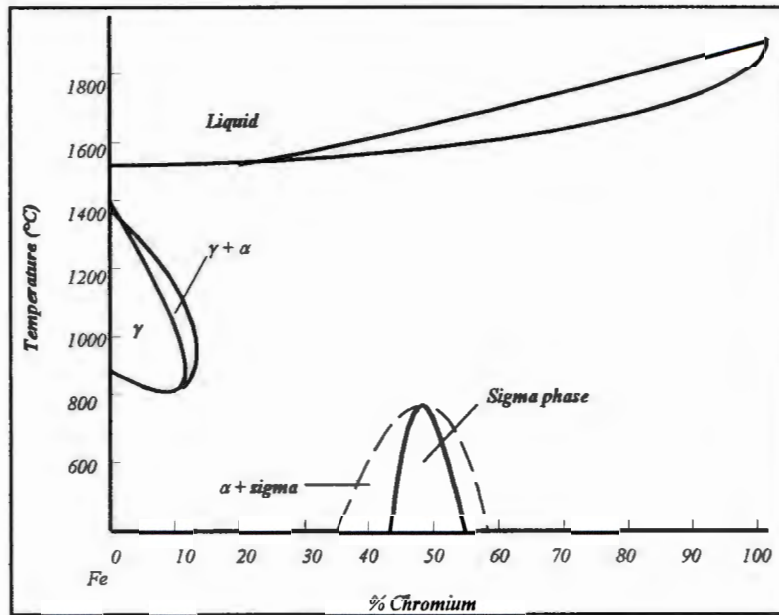


Figure 3.1 A schematic representation of the Fe-Cr equilibrium diagram [17].

A simplified illustration of the region of the Fe-Cr phase diagram containing up to about 25% Cr is shown in **Figure 3.2**.

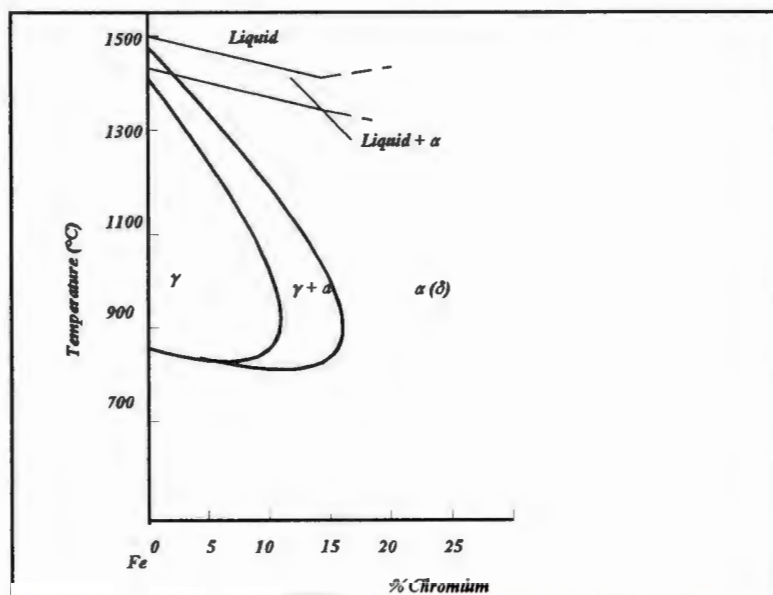


Figure 3.2. The phase diagram to illustrate the Fe-Cr alloys containing 0.1% C and less than 25% Cr [17].

As shown in **Figure 3.2** steels can accommodate up to 13% Cr at a temperature of 1050°C and still remain austenitic with a face-centred-cubic (FCC) structure. As the Cr content is increased above 13%, the single phase austenite region gives way to the duplex (austenite plus ferrite) field. The ferrite formed at high temperature undergoes no phase transformation. This high temperature ferrite is body-centred-cubic (bcc) in structure and is generally called delta ferrite(δ) [17, 18]. As illustrated in **Figure 3.3**, it is shown how the δ -ferrite content increases progressively with further addition of Cr and, in a 0.1% C steel. The material becomes completely ferritic with the addition of just over 18% Cr. Between about 13% and 18% Cr, the hardness of these steels is reduced as the micro-structure changes progressively from 100% martensite to 100% ferritic [17].

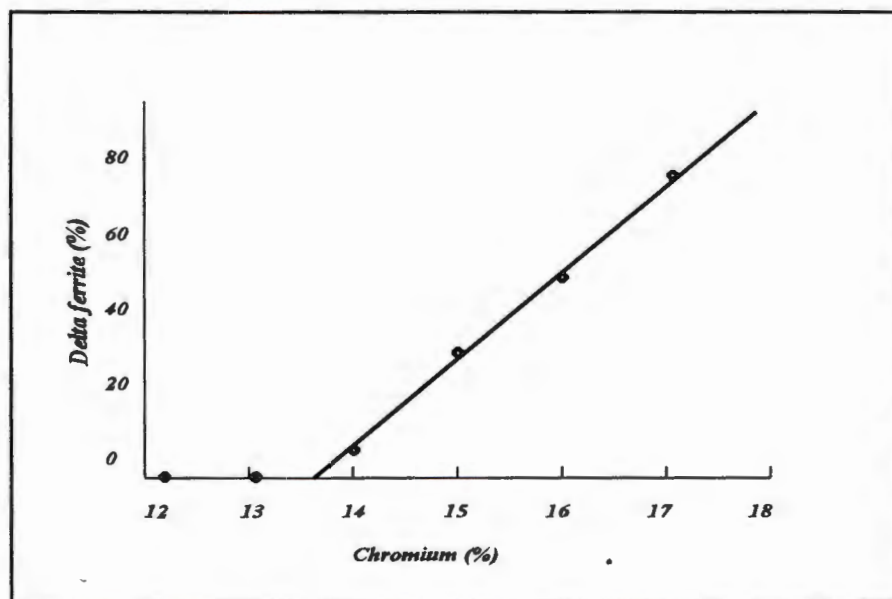


Figure 3.3 Effect of Cr content on a 0.1% C steels solution treated at 1050°C [17].

Larger additions of Cr have no effect on the micro-structure, although such materials become increasingly more susceptible to the formation of sigma phase (σ). Sigma phase is a hard and brittle inter-metallic compound and can be produced in alloys containing between a few percent Cr to almost 100 % Cr, with a maximum at about 50 %Cr [17]. It also has an adverse effect on the corrosion resistance of stainless steels and therefore care should be taken to avoid extended exposure in the temperature range of 550 - 820°C which favours its formation [6,17,18].

The changes from $\gamma \rightarrow \gamma + \delta$ and $\gamma + \delta \rightarrow \delta$ occur at chromium levels of about 13% to 18% respectively, in an alloy containing a maximum of about 0.1% C at a reference temperature of around 1050 °C [17]. Higher amounts of carbon, or the addition of other alloying elements, will have a major effect on the micro-structure associated with specific Cr levels. Additionally, for a given composition, an increase in the solution treatment temperature above 1050°C will also increase the amount of delta ferrite at the expense of austenite [17,18].

3.2.1 The Fe-Cr-Ni Alloys

Whereas Cr restricts the formation of austenite, Ni has the opposite effect and, as shown in **Figure 3.4**, the Fe-Ni equilibrium diagram displays an expanded austenite phase field [17]. In the context of stainless steels, Cr is termed a *ferrite former* and Ni an *austenite former*. Thus, having created a substantially ferritic micro-structure with a large addition of Cr, the process can be reversed and an austenitic structure can be re-established by adding a large amount of Ni to a high chromium steel [17,18].

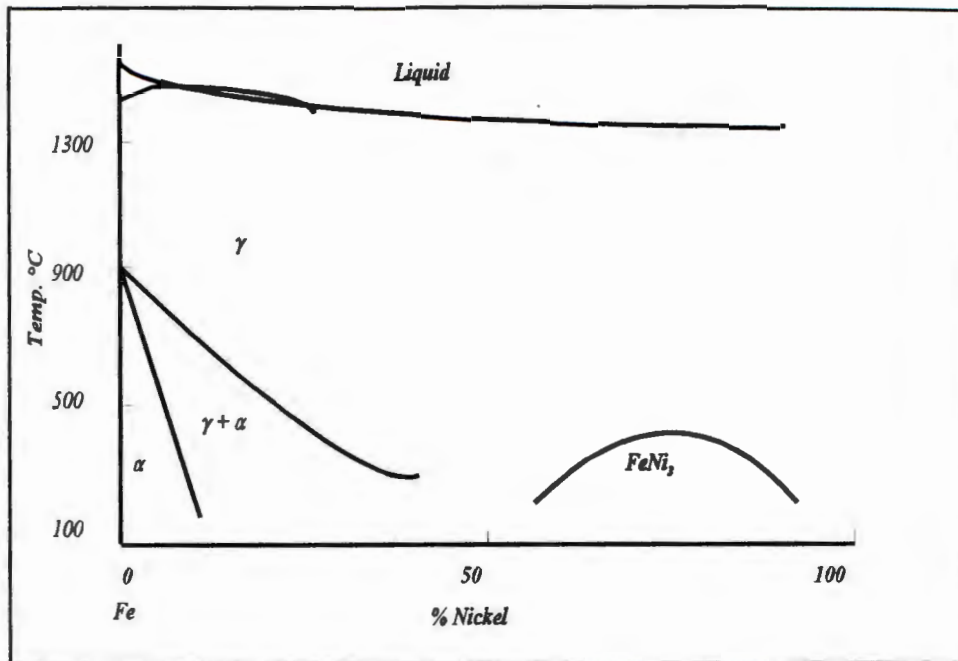


Figure 3.4 Schematic representation of the Fe-Ni equilibrium diagram[19].

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3.2.2 Effect of Other Alloying Elements

Whereas Cr and Ni are the principal alloying elements in stainless steels, other elements may be added for specific purposes and therefore consideration must be given to the effect of these elements on the micro structure of the steel [17, 18]. Like Cr and Ni, these alloying elements can be classed as ferrite or austenite formers and their behaviour is illustrated in **Figure 3.5**.

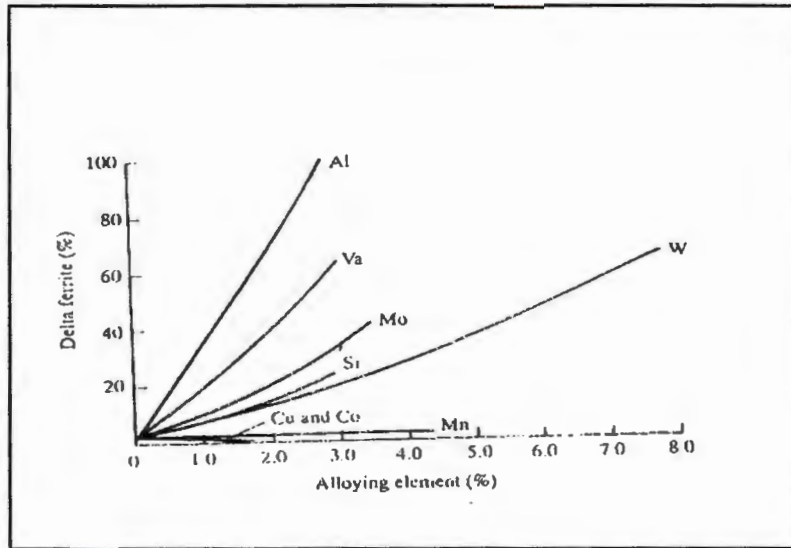


Figure 3.5 Effect of various alloying elements on the structure of 17% Cr 4% Ni alloys [17].

Elements such as Al, Va, Mo, Si and W behave like Cr and promote the formation of δ -ferrite. These elements stabilise the ferrite and reinforce the effect of Cr, and the ferrite stabilisers shift the ($\gamma / \gamma + \alpha$) phase boundary upwards. On the other hand, Cu, Mn, Co, C and N like Ni and promote the formation of austenite. These elements stabilise the austenite and tend to reinforce the effect of Ni. For a given Cr content they decrease the amount of Ni required to retain the fully austenitic structure. These austenite stabilisers shift the ($\gamma / \gamma + \alpha$) phase boundary downwards [17, 18].

3.3 Degradation of the Mechanical Properties of Fe-Cr Alloys

3.3.1 The Mechanism of phase changes

3.3.1.1 Nucleation and Growth

Nucleation is the formation of stable nuclei in the melt [18]. If during a phase change, an atom is moved from an α - phase lattice site to a more favourable β - phase lattice site, the energy of the atom should vary with position, as shown in **Figure 3. 6**, where the potential barrier which has to be overcome arises from the interatomic forces between the moving atom and the group of atoms which adjoin it and the new site [19].

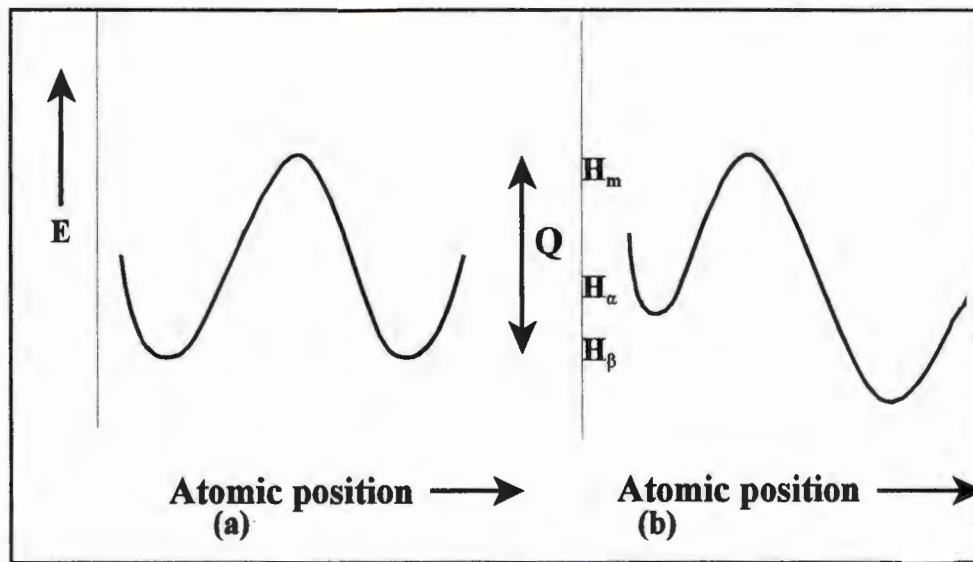


Figure 3.6 Internal energy of an atom as a function of its position [19].

Only those atoms with an energy greater than Q are able to make the jump where

$$Q_{\alpha-\beta} = H_m - H_\alpha \quad (3.1)$$

and

$$Q_{\beta \rightarrow \alpha} = H_m - H_\beta \quad (3.2)$$

are the activation energies for heating and cooling respectively. The reaction rate is given by inserting the appropriate activation energy (enthalpy) in the rate equation and the net energy release,

$$H = H_\alpha - H_\beta \quad (3.3)$$

is the heat of reaction [19].

It is not necessary for the entire system to go from α to β in one jump during the transformation, otherwise phase changes would practically never occur [19].

Most phase changes occur by a process of nucleation and growth. Random thermal fluctuations provide a small number of atoms with sufficient activation energy to breakaway from the matrix (old structure) and form a small nucleus of the new phase, which then grows at the expense of the matrix until the whole structure is transformed. By this mechanism, the amount of material in the intermediate configuration of higher free energy is kept to a minimum, as it is localized into atomically thin layers at the interface between the phases [19]. Because of this mechanism of transformation the factors which determine the rate of phase change are:

- i) the rate of nucleation, N (i.e the number of nuclei formed in unit volume in unit time) and
- ii) the rate of growth, G (i.e the rate of increase in radius with time).

Both processes require activation energies, which in general are not equal, but the values are much smaller than that needed to change the whole lattice from α to β in one operation [19].

Even with a process such as nucleation and growth, transformation difficulties occur and it is common to find that the temperature, even under the best experimental conditions, is slightly higher on heating than on cooling. This sluggishness of the transformation is known as hysteresis, and is attributed to the difficulties of nucleation, since diffusion, which controls the growth process, is usually high at temperatures near transformation temperature and is, therefore not rate controlling [18, 19].

The two main mechanisms by which nucleation of solid particles in liquid metals occurs are homogeneous nucleation and heterogeneous nucleation.

3.3.1.2 Homogeneous Nucleation

This is the simplest case of nucleation. It occurs when the metal itself provides the atoms to form nuclei. Consider the case of a metal solidifying. When a pure liquid metal is cooled below its equilibrium freezing temperature to a sufficient degree, numerous homogeneous nuclei are created by slow-moving atoms bonding together [18, 19]. Homogeneous nucleation usually requires a considerable amount of undercooling which may be as much as several hundreds degrees Celsius for some metals. For a nucleus to be stable so that it can grow into a crystal, it must reach a *critical size*. A cluster of atoms bonded together which is less than the critical size is called an *embryo*, and a cluster which is larger than the critical size is called a *nucleus*. Because of their instability, embryos are

continuously being formed and re-dissolved in the molten metal due to the agitation of the atoms [18].

In the homogeneous nucleation of a solidifying pure metal, two kinds of energy changes must be considered:

- i) the volume (or bulk) free energy released by the liquid to solid transformation and
- ii) the surface energy required to form the new solid surfaces of the solidifies particles [19].

Since ΔG_v depends on the volume of the nucleus and ΔG_s is proportional to its surface area, we can write for a spherical nucleus of radius γ ,

$$\Delta G = (-4\pi r^3 \Delta G_v) + 4\pi r^2 \gamma \quad (3.4)$$

where

ΔG_v = bulk free energy of unit area

γ = surface free energy of unit area

$4\pi r^2$ = surface area of sphere

r = radius of nucleus

When the nuclei are small, the positive surface energy term predominates, while the negative volume term predominates when the nuclei are large [19], so that the change in free energy, as function of nucleus size can be represented by the curve shown in **Figure 3.7**.

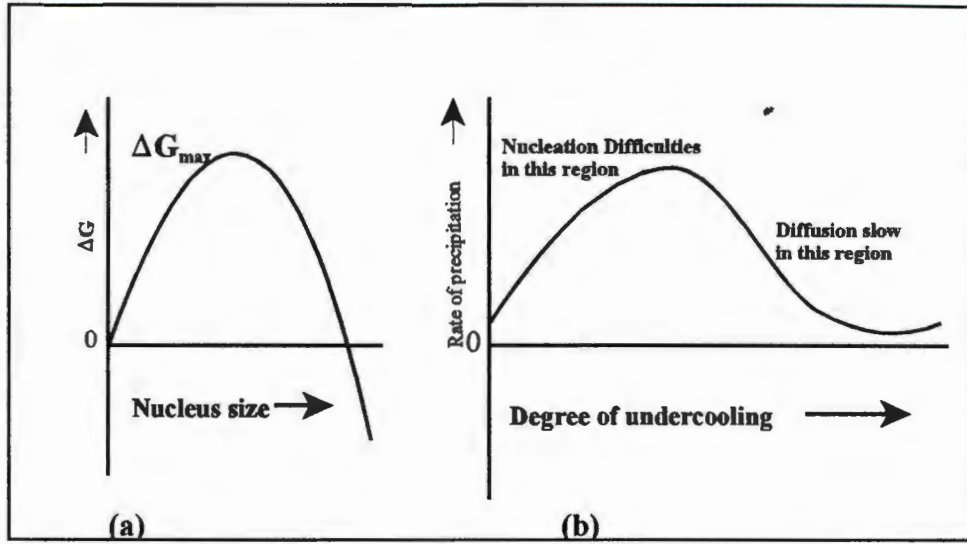


Figure 3.7 Graphical representation of (a) Effect of nucleus size on the free energy of nucleus formation (b) Effect of undercooling on the rate of precipitation [19].

Thus a critical nucleus size exists, below which the free energy increases as the nucleus grows, and above which further growth can proceed with a lowering of free energy. The surface energy γ is not strongly dependent on temperature but on the chemical free energy and, therefore the greater the degree of undercooling or super-saturation, the greater is the release of chemical free energy and the smaller the critical nucleus size and the energy of nucleation [18].

Since nuclei are formed by thermal fluctuations, the probability of forming a smaller nucleus is greatly improved, and the rate of nucleation increases according to

$$Rate = A \exp \left[- \frac{(Q + \Delta G_{max})}{kt} \right] \quad (3.5)$$

with very extensive degrees of undercooling. When $\Delta G_{max} \ll Q$, the rate of nucleation approaches $\exp[(-Q/kT)]$ and, because of slowness of atomic mobility, this becomes small at

low temperatures. Nucleation of liquid metal normally occurs at temperatures before this condition is reached. Practically homogeneous nucleation rarely takes place [19].

3.3.1.3 Heterogeneous Nucleation

Heterogeneous nucleation occurs either on the mould walls, insoluble particles or other structural materials which lower the critical free energy required to form a stable nucleus. Since large amounts of undercooling do not occur during industrial casting operations and usually range between 0.1 to 10°C, the nucleation must be heterogeneous and not homogeneous [18, 19].

The conditions for heterogeneous nucleation to take place are that the solid nucleating agent must be wetted by the liquid metal and the liquid should solidify easily on the nucleating agent. Heterogeneous nucleation takes place on the nucleating agent because the surface energy needed to form a stable nucleus is lower on this material than if a nucleus is formed in the pure liquid itself. Since the surface energy is lower for heterogeneous nucleation, the total free energy change for the formation of a stable nucleus will be lower and the critical size of the nucleus will be smaller. Thus a much smaller amount of undercooling is required to form a stable nucleus produced by heterogeneous nucleation [18, 19].



Nucleation in solids is almost always heterogeneous and occurs most rapidly on non-equilibrium sites such as free surfaces, grain and interface boundaries, where the activation energy, is smallest. The optimum initial shape for nucleation should be that which minimises the interfacial free energy, and the initial stages of the transformation will

be dominated by those nucleation sites which first produce a measurable nucleation rate [18, 19].

3.3.1.4 Growth of Nuclei

After stable nuclei have been formed in a solidifying metal, these nuclei grow into crystals. In each crystal, the atoms are arranged in an essentially regular pattern, with varying orientation for each crystal [18].

When solidification of the metal is finally completed, the crystals join together in different orientations and form crystal boundaries at which changes in orientation take place over a distance of a few atoms. Solidified metal containing many crystals is said to be polycrystalline. The crystals in a solidified metal are called grains, and the surfaces between them are called grain boundaries [18].

The successful nuclei are those with the smallest nucleation energy, i.e. the smallest critical energy. In the absence of elastic strain energy effects, the precipitate shape satisfying this criterion is that which minimizes the total interfacial free energy. Thus, nuclei will usually be bound by a combination of coherent or semi-coherent facets and smoothly curved incoherent interfaces. For the precipitation to grow, these interfaces must migrate and the shape that develops during growth will be determined by the relative migration rates [18, 19].

The grain boundaries are the likely place for nucleation-and-growth to start as the nucleation energy is the smallest. Since this interface is incoherent, diffusion-controlled growth and local equilibrium can be assumed at the interface (**Figure 3.8(a)**). The

concentration of the solute in the matrix adjacent to the nucleus β will thus be the equilibrium value C_e in **Figure 3.8(b)**.

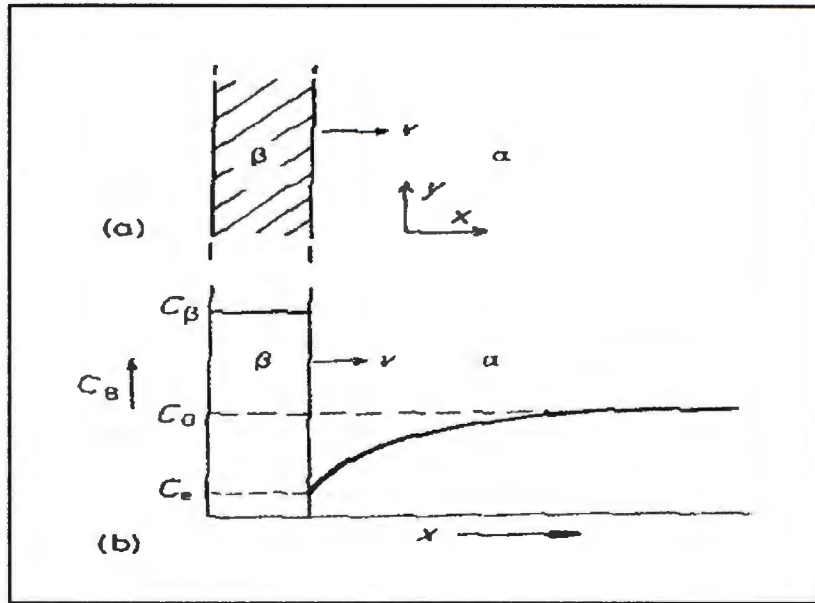


Figure 3.8 Schematic representation of (a) & (b) on the diffusion-controlled thickening of a precipitate plate [20].

3.3.1.5 Spinodal Decomposition

For an alloy composition (pure component A and B) where the free energy curve has a negative curvature i.e. $(d^2G/dC^2) < 0$, small fluctuations in compositions that produce A-rich and B-rich regions will bring about a lowering of the total free energy. At a given temperature the alloy must lie between two points of inflection (where $d^2G / dC^2 = 0$) and the locus of these points at different temperature is depicted on the phase diagram by the **chemical spinodal line** [19, 20].

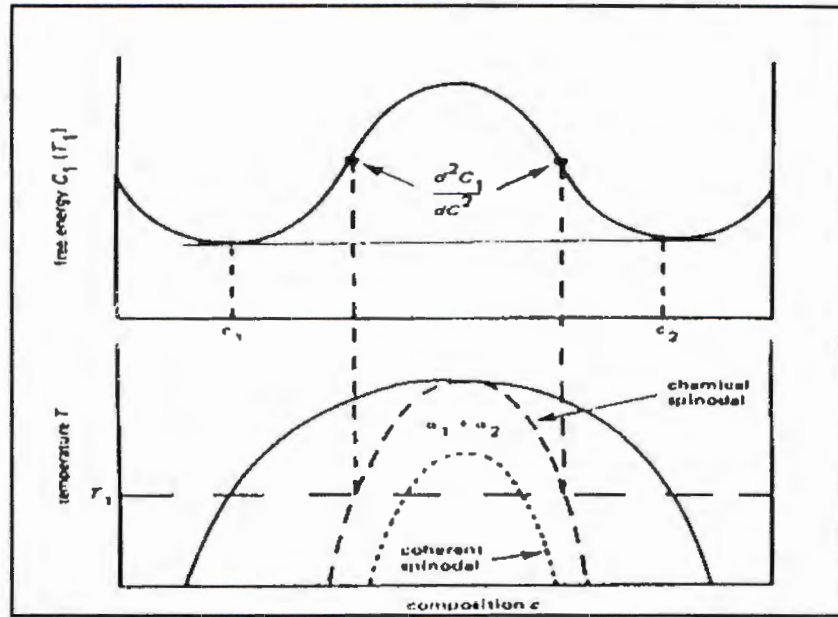


Figure 3.9 Graphical representation of the variation of chemical and coherent spinodal with composition [19].

For an alloy C_0 quenched inside this spinodal, composition fluctuations increase very rapidly with time and have a time constant $\tau = -\lambda / 4\pi^2 D$, where λ is the wavelength of composition modulations in one-dimension and D is the inter-diffusion coefficient [19].

For such a kinetic process, uphill diffusion takes place, i.e. regions richer in solute than the average become poorer until the equilibrium compositions C_1 and C_2 of the A-rich and B-rich regions are formed. If the alloy lies outside the spinodal region, small variations in composition lead to an increase in free energy and the alloy is **meta-stable**. The free energy of the system can only decrease if the nuclei are formed with a composition very different from the matrix [19, 20]. Thus outside the spinodal, the transformation proceeds by a process of nucleation-and-growth and normal down-hill diffusion occurs, as shown in **Figure 3.10**. The rate of spinodal transformation is controlled by the inter-diffusion

coefficient, D . Within the spinodal, $D < 0$ and the fluctuations in composition will therefore increase exponentially with time [19, 20].

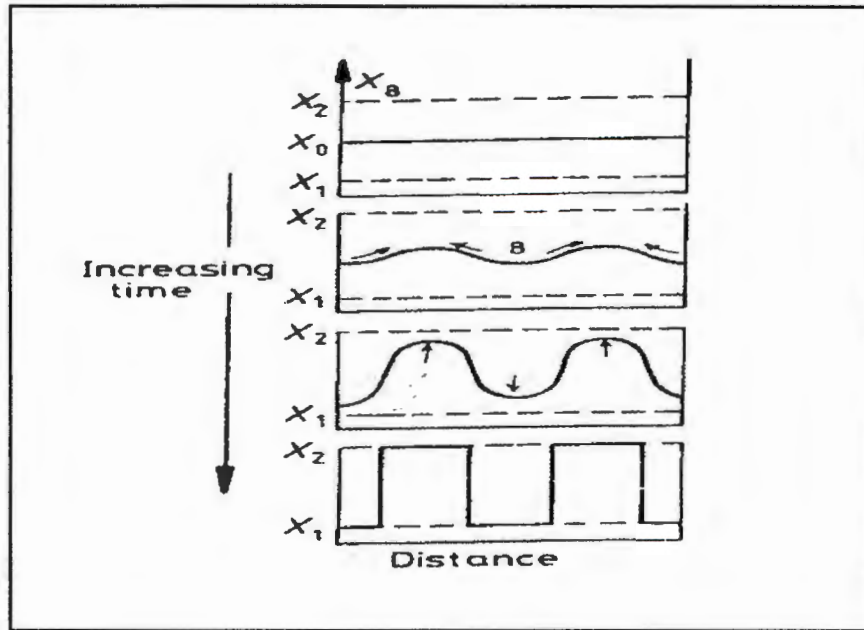


Figure 3.10 Schematic composition profiles with increasing time for an alloy quenched (a) inside the spinodal region and (b) outside the spinodal region

3.4 Comparison between Spinodal Decomposition and Nucleation-and-Growth

Spinodal decomposition can occur where there is no energy barrier for the separation. However, this energy barrier does exist in the case of nucleation-and-growth. In the aging of Fe-Cr alloys, it is important to determine whether the embrittlement is due to spinodal decomposition or nucleation-and-growth [20].

3.5 Mössbauer Studies on Embrittlement in Fe-Cr Alloys

Various authors have studied the embrittlement of Fe-Cr alloys. De Nys and Gielen did the first study of embrittlement in these alloys [21]. These authors observed that any Cr-rich α' -phase (above 68 at.% Cr) will give a singlet in a room temperature Mössbauer spectrum, and if the phase has Cr content below 68 at.%, the spectrum will display a distribution of magnetic sextets. They observed that a 20 wt.% Cr coupon aged at 470 °C induced a singlet near zero velocity, while no singlet was observed after 410h of aging at 540°C. It was concluded that the aging product at 470°C was due to nucleation-and-growth. However, for samples with more than 30 wt.% Cr, an opposite behaviour was observed since these samples showed no singlet at 470°C, even after an aging period of 1050h. Therefore the aging process in these samples was ascribed to spinodal decomposition [20, 21]. In all the cases, there was an increase in the average magnetic field with aging time, demonstrating that further decomposition occurred during the aging by one of these processes. **Figure 3.11** shows the spectra for the 20 and 50 wt.% Cr for two aging temperatures [6, 21].

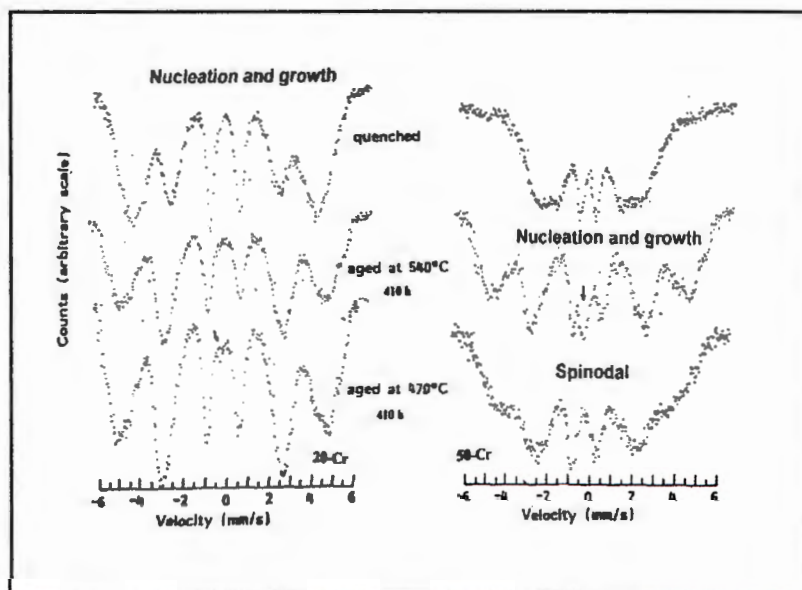


Figure 3.11 Decomposition of 20 and 50 wt.% Cr samples at 470°C and 540°C [6, 21].

The two types of decomposition presented in **Figure 3.11** can be differentiated using the fact that, at 540°C the sample with 20 wt.% Cr lies outside the spinodal region, while at 470°C, the samples with 30, 40 and 50 wt% Cr lie within the spinodal region. Therefore the 30, 40 and 50 wt.% Cr samples decompose via spinodal transition when aged at 470°C, while at 540°C the decomposition is through nucleation and growth [6, 21]. The different behaviour of the 20 wt.% Cr sample may have to do with the exact limits of the solubility limit, and the impurities in the sample. However, the observation of a paramagnetic singlet, or its absence in the Mössbauer spectra of an Fe-Cr alloy, is to some extent an ambiguous rule as whether the embrittlement occurs via the nucleation-and-growth or the spinodal transition. This is the case because a singlet could indicate an advanced stage of the spinodal decomposition, when the α' -phase starts separating from

the Cr-rich regions formed during the early stage of the spinodal transition [20].

Chandra and Schwartz [22] performed the same type of experiment at the same time but independently, by aging samples only at 475°C. The time range for aging was extended from short to very long periods. The Mössbauer spectra for samples aged for 1300h and 276h presented a very strong paramagnetic singlet, due to the α' -Cr rich phase, as well as very well developed sextets [23]. The singlet indicates the presence of Fe atoms that are almost completely surrounded by Cr atoms. This is agreement with **Figure 3.10** which indicates that after a long time of aging, both the spinodal decomposition and nucleation-and-growth must arrive to the same type of final state. Changes start immediately during the aging treatment, as revealed by Mössbauer spectra which show sharper lines, especially lines 1 and 6. The paramagnetic peak is originally very broad due to the α' -Cr rich phase, and becomes more narrow with aging, ending with a normal width [20].

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CHAPTER 4

EXPERIMENTAL TECHNIQUES

4.1 INTRODUCTION

The test specimens from the Hot leg and Crossover leg elbows of the primary loop of the PWRs from the Koeberg Nuclear Power plant used in this investigation had the composition shown in Table 4.1. The PWRs had been in service for about 15 years [5]. The optical measurements to determine the δ -ferrite were also performed on these samples. These measurements were performed at the ESKOM centre (TRI).

Table 4.1 Chemical Composition of Samples Investigated														
	C	Si	Mn	P	S	Cr	Ni	Mo	Ti	Mb	Cu	Co	N	Ferrite
H	0.037	1.03	0.77	0.022	0.008	20.0	10.6	2.09	0.004	0.003	0.17	0.04	0.044	20.10
C	0.039	1.11	0.82	0.020	0.012	19.6	10.5	2.08	0.004	0.002	0.08	0.035	0.037	19.08
H = Hot leg; C = Cross leg														

The test samples were cut from the impact test specimens of about 100 mm² surface, and these were ready to be analyzed using Mössbauer Spectroscopy.

Natural iron was used as an absorber for the calibration of the spectrometer. The calibration was performed for the velocities of 6, 8 and 10 mm/s. Samples with a high and low Cr-contents were also used as absorbers for reference purposes.

The Fe-Cr-Ni-samples with low and high δ -ferrite content were etched by immersing them in 10 % Nital solution for about 60 seconds. This is the most common

etchant for alloy steels and was prepared by mixing 10ml nitric acid (HNO_3) with 90ml ethanol. This etching technique was done in order to reveal the general structure to ensure preferential dissolution to reveal the discriminating phases [23]. The samples were then analyzed to determine the content of δ -ferrite by an electron microscope. The percentages of the δ -ferrite and the γ -phase (austenite) were also determined making use of the scanning electron microscope (SEM) fitted with an EDAX.

4.2 Charpy Impact Strength Measurements

Impact strength tests on various aged and unaged samples from the Crossover and Hot Leg elbows of the primary loop of the PWRs from Koeberg Nuclear Power plant were done on the samples.

The test employs a pendulum apparatus of the type shown schematically in **Figure 4.1**. In this test, the specimen is loaded as a simple beam with the anvil of the pendulum hammer striking on the side opposite the notch. The kinetic energy of the pendulum at the point of impact is known because the starting point and the mass of the pendulum are known. The energy lost by the pendulum is absorbed by the specimen and the follow through swing is reduced in proportion to the amount of energy absorbed. The energy absorbed by the specimen is the impact energy (in Joules/ cm^2), and this indicates the amount of energy the specimen can absorb before fracture [24].

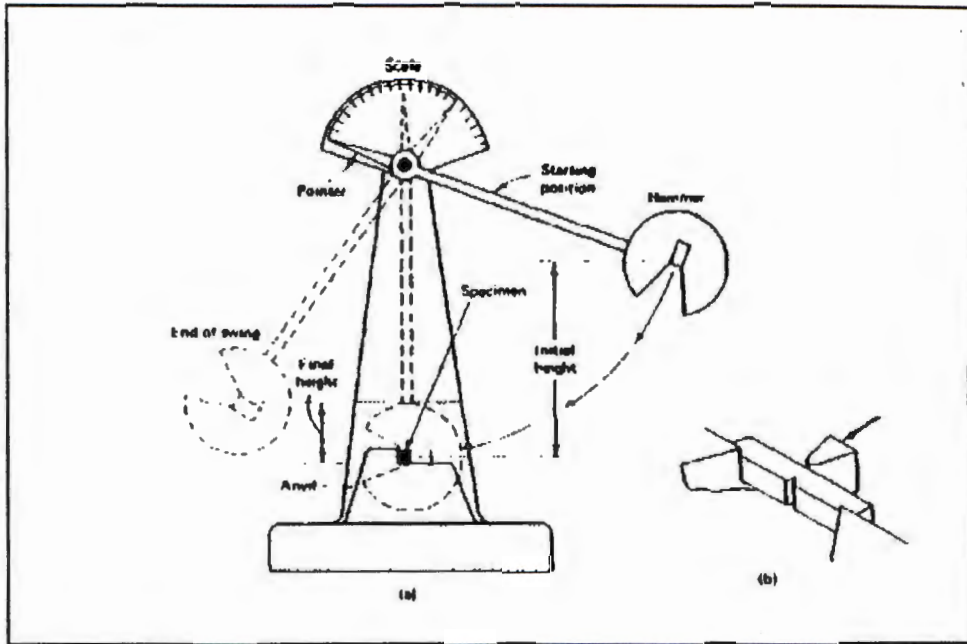


Figure 4.1 Schematic representation of the Charpy V-notch and sample configuration [24].

4.3 Conversion Electron Mössbauer Spectroscopy (CEMS)

A conversion electron Mössbauer spectrum is a technique based on the detection of electrons emitted after the resonant absorption of gamma-rays. These electrons are referred to as conversion electrons.

A velocity range of 10mm/s was chosen to ensure that all possible transitions would be included. The baseline level is one of the parameters needed for fitting and sufficient statistics ensured a proper fit of the data to the theoretical parameters [13].

4.3.1 The Spectrometer

The spectrometer allows variation of the range of velocities that can be covered and offers a choice of the number of channels in which the Mössbauer spectrum can be accumulated, usually in multiples of 256.

In this investigation, the samples were studied by means of CEMS at 295 K with the aid of a Halder Mössbauer spectrometer capable of operating in conventional constant acceleration mode, using a backscatter-type gas flow detector. In the detection of back-scattered radiation, the detector is positioned on the same side as the incoming γ -radiation. The detected radiation may be γ -photons emitted during the decay of the probe nuclei in the absorber or the electrons emitted in the nuclear process called internal conversion [25]. A 50 mCi $^{57}\text{Co}(\text{Rh})$ was used as a γ -ray source and the samples used as γ -ray absorbers at room temperature. The velocity was calibrated against the α -Fe spectrum for velocities of 6, 8 and 10 mm/s. The spectra were stored in a multi-channel analyser and analysed by a least squares computer program by superimposing Lorentzian line shapes. The CEMS determination is based on the detection of the 6.3 KeV X-rays emitted from the metal surface after absorption of the 14.4 KeV γ -rays.



Figure 4.3 shows the schematic representation of the experimental set-up for CEMS measurements.

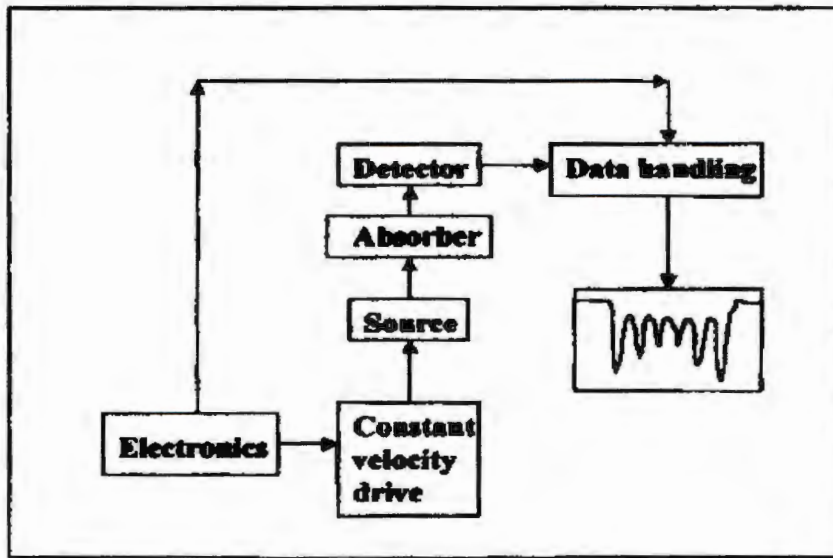


Figure 4.3 Schematic representation of the experimental set-up for CEMS .

4.3.2 The Multi-channel Analyzer (MCA)

The spectrometer incorporates a multi-channel analyser (MCA), which can store an accumulated total of γ -counts in any one of the channel addresses in a similar way to a small computer. Each channel is held open in turn for a short fixed time interval, and any count registered during that time interval are added to the accumulated total counts stored in the channel [13]. This timing pulse signal is used as a reference signal to control an electro-mechanical servo-drive system. The multi-channel analyser and the drive are coupled so that the velocity changes linearly from $-v$ to $+v$ with increasing channel address, and then the scan is repeated. Alternatively, the velocity changes from $-v$ to $+v$ in the first half of the scan, and then reverts to $-v$ during the second half, thereby accumulating a mirror-image spectrum that may be folded on to the first half [13].

4.3.3 The Source

The source used in this investigation had a nominal strength of 50mCi ^{57}Co . The source was embedded in a rhodium matrix. The rhodium matrix is of advantageous use since it provides γ -rays with narrow line width, and also, there are no X-rays emitted with energies close to that of 14.4 KeV ensuring that the proportional counter can resolve them. **Figure 4.4** shows the energy levels representing the decay scheme of ^{57}Co to ^{57}Fe due to electron capture by the ^{57}Co -nucleus.

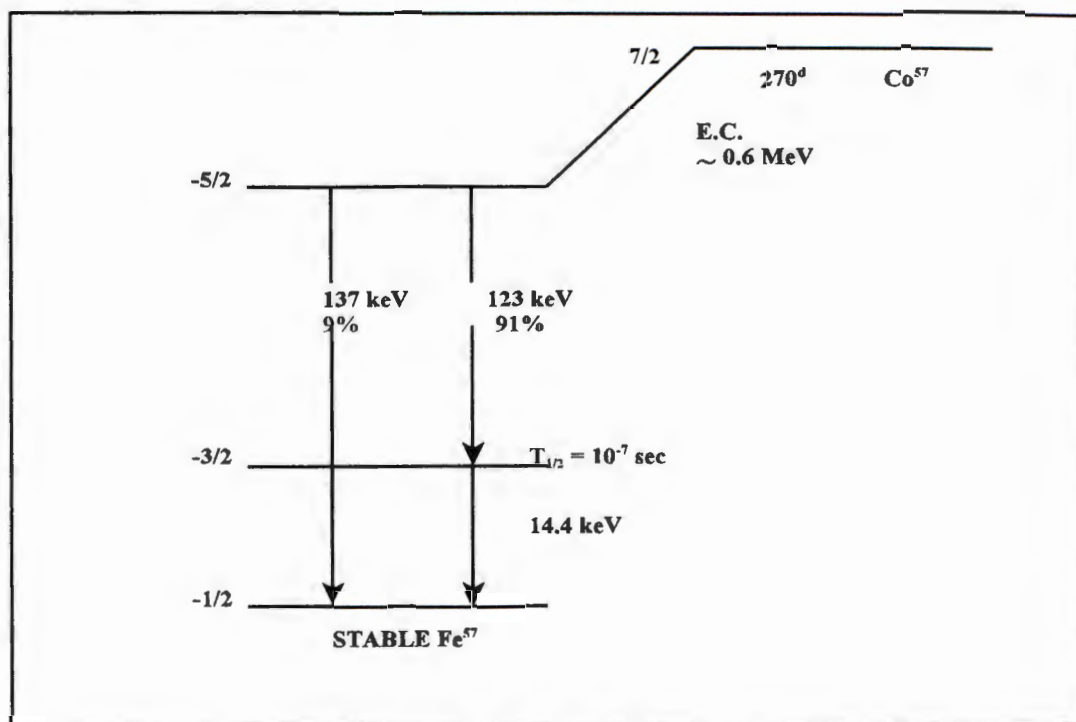


Figure 4.4 Decay scheme of ^{57}Co [12].

The ^{57}Fe -nucleus formed is in the excited state and emits γ -rays of energies 14.4 keV, 123 keV and 137 keV on decaying to the stable ^{57}Fe ground state. This decay scheme is the source of the 14.4 keV γ -radiation used in Mössbauer spectroscopy [12].

4.3.3 The Absorber (Sample)

Flat samples, cut from the impact test specimens of about 100mm² surface, which were aged for various times, were used as absorbers. For Mössbauer spectroscopy, the absorber must be a solid containing iron, so that the nuclei under investigation must be prevented from recoiling when absorbing γ -radiation. This means the atoms containing the nuclei must be securely fixed in solid lattice [9].

4.4 Scanning Electron Microscopy (SEM) Analysis

The scanning electron microscope (SEM) is an instrument that impinges a beam of electrons in a pinpointed spot on the surface of a target specimen and collects and displays the X-rays given off by the target material. Basically, an electron gun produces the electron beam in an evacuated column that is focused and directed so that it impinges on a small spot of about 5nm on the target. Figure 4.5 schematically illustrates the principle of operation of the SEM.

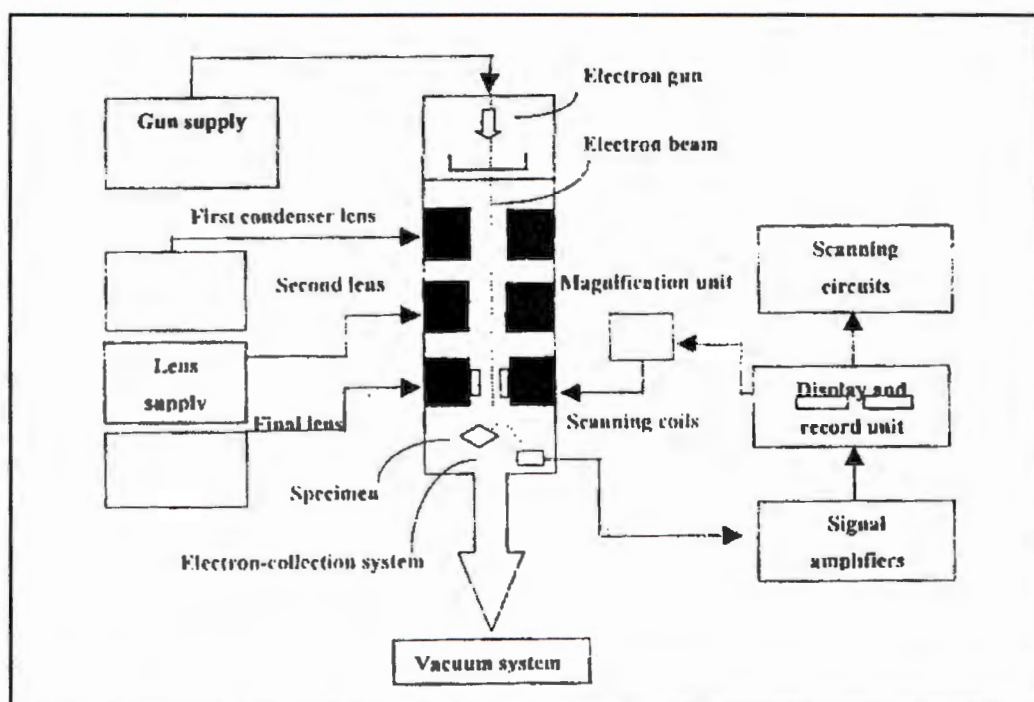


Figure 4.5 Schematic diagram of the basic design of a SEM [26].

Scanning coils allow the beam to scan a small area of surface of the sample. Low-angle back-scattered electrons interact with the protuberances of the surface and generate secondary back-scattered electrons (electrons that are ejected from the target metal atoms after being struck by primary electrons from the electron beam) to produce an electronic signal. The electronic signal in turn produces an image having a depth of field of up to about 300 times that of the optical microscope (about 10 μm at 10 000 diameters magnification). The resolution of many SEM instruments is about 5 nm, with a wide range of magnification possibilities varying from about 15 to 100 000 enlargement).

According to Brown et al [27], the chemical composition of the ferrite in each sample can be determined by electron probe analysis. The austenite compositions can also be measured by extending the traverses either side of the ferrite islands. The ferrite phase of these duplex steels contains more or less 6 % more Cr than the austenitic phase, but it also contains half as much Ni as there is in the austenitic phase.

4.5 Microscopic Image Analysis

The microphotographs obtained from electron microscopy were used to determine the amount of δ -ferrite present by means of image analysis. The grains of δ -ferrite were traced from the photographs onto the transparency. These grains appeared as black spots on the photographs, and the ratio of the dark spots to the light phase was determined. These were then counted using the image analyzer at random areas and the mean values for each sample was determined.



CHAPTER 5

RESULTS

5.1 CHARPY IMPACT STRENGTH

The Charpy impact energy test results, as measured at the ESKOM, TRI centre, are shown in **Table 5.1**.

Table 5.1 Charpy Impact Strength Measurements Results [5]

Sample No	Equivalent Ageing Time	Impact Energy J/cm ²
CB	75khrs @ 291°C	169.7
CI	"	156.5
CN	156khrs @ 291°C	144.7
CM	"	122.3
CF	Start of Life (No Spinodal)	181.5
CD	"	176.2
HC	80khrs @ 325°C	82.9
HB	"	77.6
HS	15khrs @ 325°C	130.2
HT	"	110.5
HE	Start of life (No Spinodal)	210.4
HD	"	97.3
HM	120khrs @ 325°C	87.5
HK	"	57.5

From **Table 5.1**, it is clear that the samples that have not been aged have comparatively very high impact energies and that the impact energy decreases with increasing ageing time.

Figure 5.1 shows the graphs of the impact energy plotted against ageing time for the (a) Crossover and (b) Hot leg elbows respectively. The graphs show that there is a decrease in Charpy impact energy with increasing ageing time (See **Page 59**).

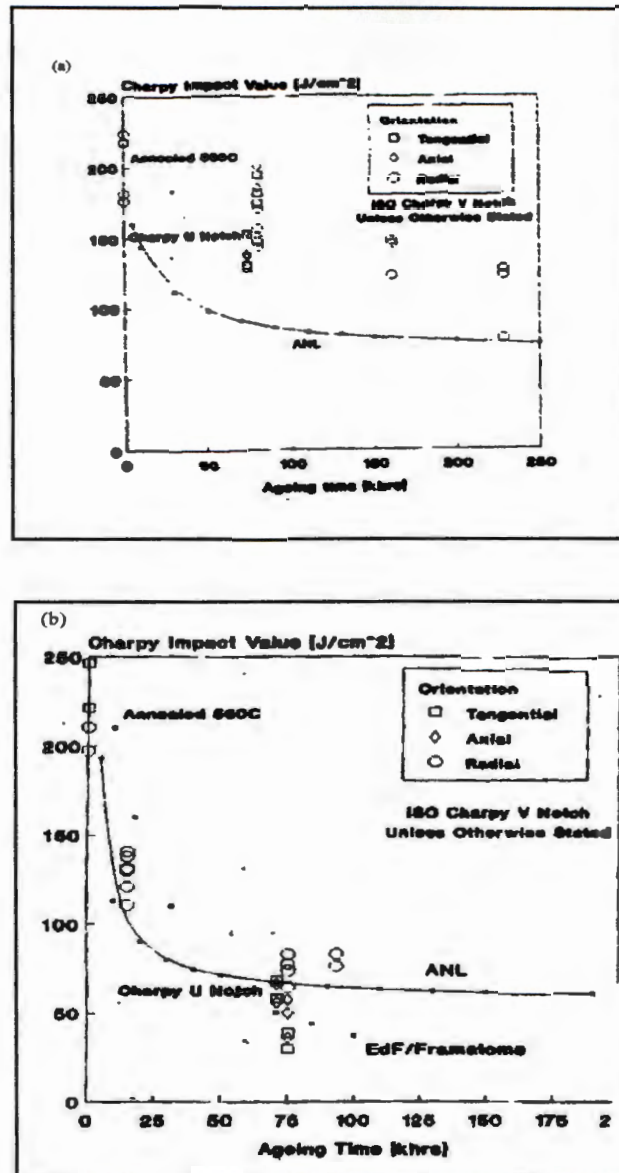


Figure 5.1 The graphs of Charpy Impact Energy vs Ageing time for (a)Crossover and (b)Hot leg elbows respectively[6]

The graphs shown in Figure 5.1 indicate that the strength of the material under investigation deteriorates with increasing ageing time. Since the high impact energy implies that the material that has not been aged has the highest impact energy value, it can be concluded that ageing deteriorates the material strength and this could be detrimental and possibly cause failure.

5.2 CEMS MEASUREMENTS

In Figure 5.2 a typical Mössbauer spectrum obtained for natural iron (α -Fe) that was used for the calibration of the spectrometer is shown.

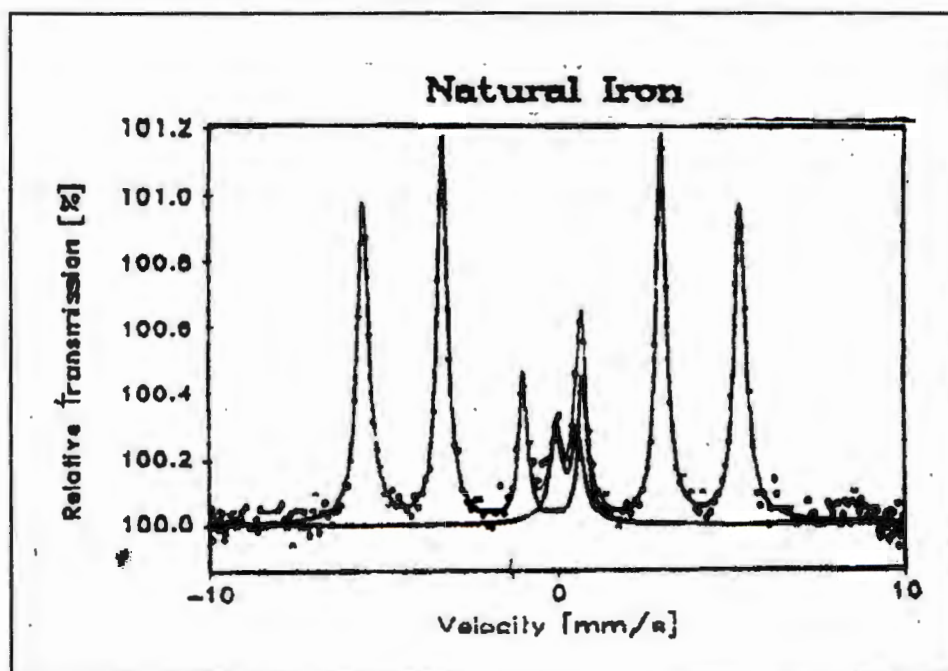


Figure 5.2 Typical Mössbauer spectra for natural iron used for the calibration (maximum velocity 10 mm/s).

Pure α -Fe, which is of bcc symmetry and magnetic, gives a pattern consisting of six peaks. The splitting between the first and the sixth peak is a measure of the magnetic internal field. This magnetic field was found to be 33.77 Tesla for a ^{57}Fe nucleus in pure iron used as reference, and this is in accordance with the theory which gives the magnetic field for pure iron as approximately 33 Tesla [13]. The relative intensities of the six peaks in a magnetically split Mössbauer spectrum depend on the angle between the direction of the magnetic field and the direction of the gamma rays. Since α -Fe can be easily

magnetised, and because of the saturation effects, the observed relative intensities from the spectrum in **Figure 5.2** are 3:4: 1:1:4: 3. For an absorption spectrum, the ratio 3:2:1:1:2:3 holds if the gamma rays are perpendicular to the direction of the field. The doublet appearing near zero velocity is the iron oxide (α -FeOOH) due to oxidation of the top layer of the iron.

The α -Fe spectrum was used as reference standard for calibration purposes. The spectrum for α -Fe has six hyperfine components giving a linearity check. The energy of the source transition was used as the arbitrary reference point when defining the isomer shift, since the isomer shift observed depends on the type of the source matrix [12]. For this investigation, the ^{57}Co source, embedded in rhodium foil, was used. For the rhodium foil, the isomer shift is +0.113 mm/s. Adding this to the isomer shift for pure iron which is -0.113 mm/s gives a value of 0.00mm/s. This is in agreement with the theoretical value for the isomer shift of the commonly used ^{57}Co source with respect to the iron metal at room temperature, which is observed as 0.00 mm/s [12].

The calibration of the spectrometer was performed for velocities of 6, 8 and 10mm/s respectively and the calibration curves are shown in **Figure 5.3**. From the calibration curves it is clear that the spectrometer performed according to specifications and that the data obtained for the samples investigated would be acceptable.

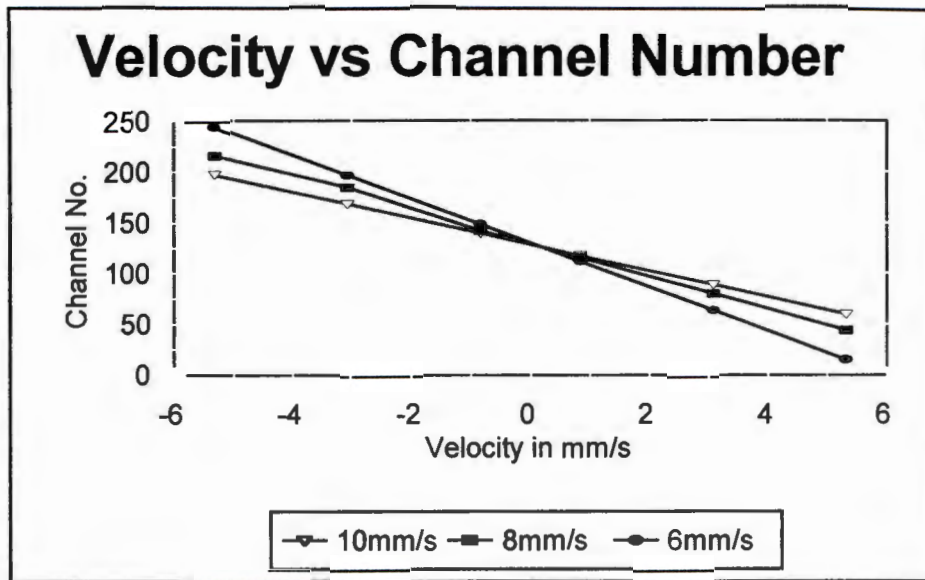


Figure 5.3 Calibration curve for velocities of 6, 8 and 10 mm/s.

Figures 5.4(a) & (b) show typical Mössbauer spectra obtained for the duplex stainless steel under investigation. All the spectra obtained for the different samples consisted of a paramagnetic peak (singlet) and a magnetically split sextet. This singlet arises from the austenite, which is a Cr-rich α -phase. A single line corresponds to an iron impurity within a Cr-matrix and indicates a non-magnetic compound. The magnetically split sextet resulted from the δ -ferrite phase, which is a Fe-rich phase. The sextet corresponds to iron with Cr as an impurity, which indicates that the iron atoms are in an environment with at least one non-iron atom in the next nearest shell [6]. The separation between the lines is proportional to the magnetic field at the nucleus.

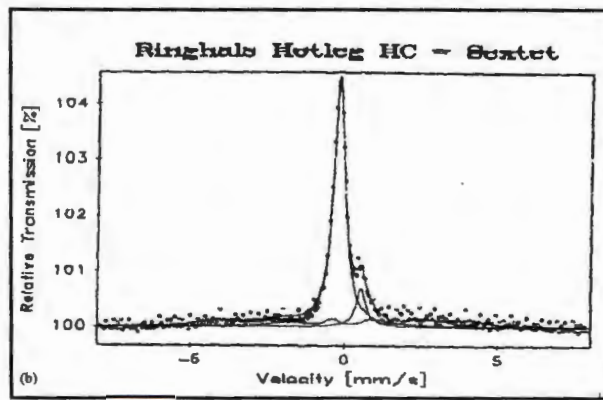
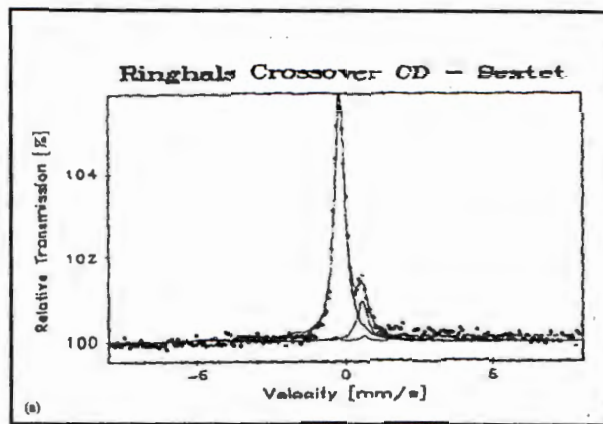


Figure 5.4 Typical CEMS spectra for (a) Crossover (b) Hot leg Elbows (Note: the small singlet is due to an overflow of electrons and is part of the paramagnetic γ -component).

The total contribution of the paramagnetic austenitic component was determined to be in the range of 80 to 90%, represented by the singlet and the δ -ferrite content was found to lie between 10 to 20% which is represented by the sextet in the spectrum. The error on the area computed for the δ -ferrite component is relatively large due to the fact that the sextet is obscured below the much bigger singlet of the austenite, which makes the accurate determination of the area difficult.

Figures 5.5 (a), (b) and (c) show the typical Mössbauer spectra for stainless steel

alloy samples containing 64%Cr, 52%Cr and 30% Cr respectively. These samples were used for reference purposes in order to prove that the magnetic field strength of the samples investigated were correctly determined.

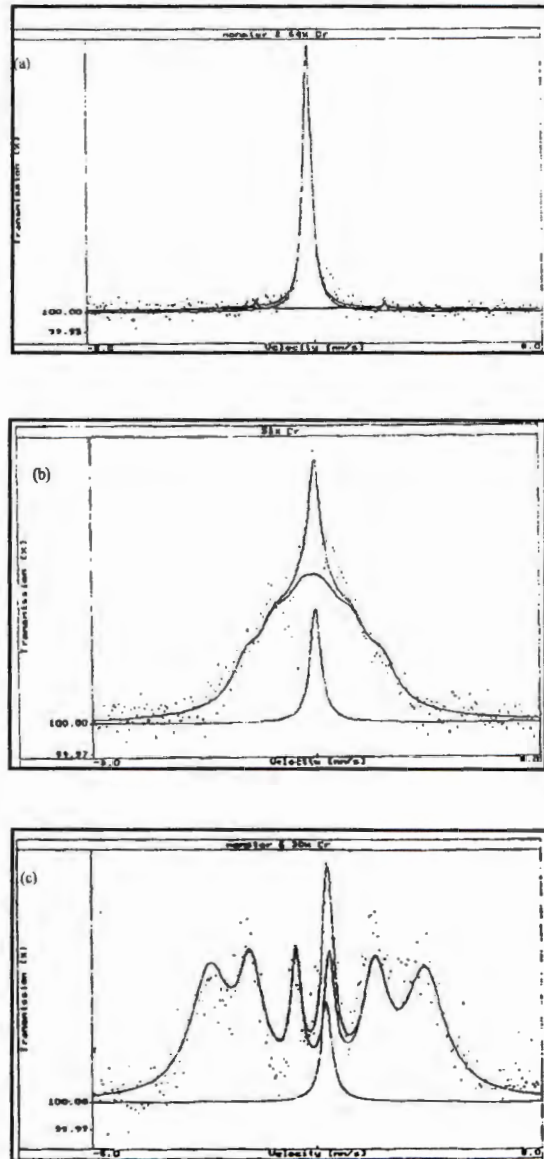


Figure 5.5 Typical CEMS spectra for stainless steel alloys with 64%Cr, 52% Cr and 30% Cr used for reference respectively

The above spectra show that there is a shrinking of magnetic field strength towards a single line with increasing Cr-content. The single peak is due to the fact that if Cr is added to iron in diluted concentrations, a new structure appears in a Mössbauer spectrum due to a reduction of the hyperfine field of the iron nuclei. Therefore the splitting of the absorption lines will be slightly less, since the average hyperfine field of the whole pattern decreases. Depending on the various possible iron-chromium configurations, a Cr-steel will provide a pattern that is the superposition of all possible fields. With increasing amount of Cr, the magnetic field shrinks as more Cr atoms surround the iron atoms [6].

Table 5.2 shows the hyperfine interaction parameters obtained for the natural stainless steel samples that were used for reference purposes.



Table 5.2 Mössbauer spectral analysis for Natural stainless steel

Sample No	Isomer Shift (IS) mm/s	Quadrupole Split (QS) mm/s	Magnetic Field (H)		
			Minimum	Maximum	Average
30% Cr	0.152	0.041	23.836	23.961	23.9
52%Cr	-0.09	0.022	15.361	18.961	17.2
64%Cr	-0.09	0.57	13.961	13.961	14.0

From the spectra, the total contribution of the austenite was determined to be 94%, 10% and 6% for the above alloys respectively. These values show that the stainless steel with 64% Cr has iron atoms completely surrounded by Cr atoms, and this makes it to be Cr-rich, and the magnetic field for this steel was found to be 14.0T.

A 30% Cr stainless steel is more Fe-rich, and this is indicated by the magnetic field of 23.9 T which is higher than that of the 64% Cr. For the 52% Cr stainless steel, the magnetic field was obtained as 17.2 T, which is an average of the high and low Cr stainless steels.

According to Waanders et al [28], there exists a linear relationship between the magnetic field H and Cr-concentration for various Fe-Cr-alloys and this was found to be

$$H = 33.01T - 29.61c$$

where c depicts the Cr-concentration [28], with errors of ± 0.02 on both coefficients.

From the above equation, the magnetic field for the 30% Cr, 52% Cr and 64% Cr used for reference purposes were found to be 23.13 T, 17.61 T and 14.06 T respectively. These theoretical values fit in well with experimental values, which makes the calibration to be satisfactory.

The nominal composition for the samples from ESKOM investigated is shown in **Table 5.3:**

Table 5.3 Nominal composition of the duplex stainless steel under investigation

Element	% Composition
Fe	67.4
Cr	20.0
Ni	10.5
Mo	2.1

From the above alloy composition, and if Cr, Ni and Mo are added as approximation to give the concentration c , the value of the magnetic field strength H should be about 27 T, for the type of steel under investigation. From the above formula,

the magnetic field for the samples was found to be about $(23.35 \pm 0.02)\text{T}$. This value is similar to the magnetic field value obtained for the 30% Cr, which is about 23.9 T. The ferrite under investigation contains about 10% Ni and 20% Cr as alloying elements which cause the decrease in magnetic hyperfine field at the ^{57}Fe nucleus.

In **Table 5.4**, the Mössbauer parameters for the sextet (δ -ferrite), as obtained from Mössbauer spectral analysis are shown.

Table 5.4 Mössbauer Parameters Spectral Analysis (where no magnetic field is indicated, the singlet component suppressed the sextet completely)

Sample Name	Isomer Shift (IS) mm/s	Quadrupole Split (QS) mm/s	Magnetic Field (H)	
			Minimum	Maximum
CB	0.0077	-0.330	27.45	27.85
CD	0.1124	-0.048	24.00	24.00
CF	-0.3969	0.155	24.91	25.91
CI	0.1433	-0.207	23.83	24.21
CM	0.2204	-0.119	22.81	25.01
CN	0.2652	-0.817		
HB	0.0604	-0.332	29.13	33.13
HC	0.0518	-0.345	24.43	24.63
HD	0.2773	0.336		
HE	0.0576	-0.375		
HK	0.4630	-0.295		
HM	-0.2452	-0.851		
HS	-0.1038	0.073		

The results in **Table 5.4** show that values for the magnetic field strength determined in the present investigation compare well with values found in literature. (IS: -0.02, QS: varies, H: 27 T) [28].

5.3 SEM ANALYSIS

The microphotographs shown in **Figure 5.6** were obtained from the SEM measurements. **Figure 5.6 (a)** shows the microphotograph for the sample with the low δ -ferrite content and **Figure 5.6 (b)** shows the microphotograph of the sample with a high δ -ferrite content.

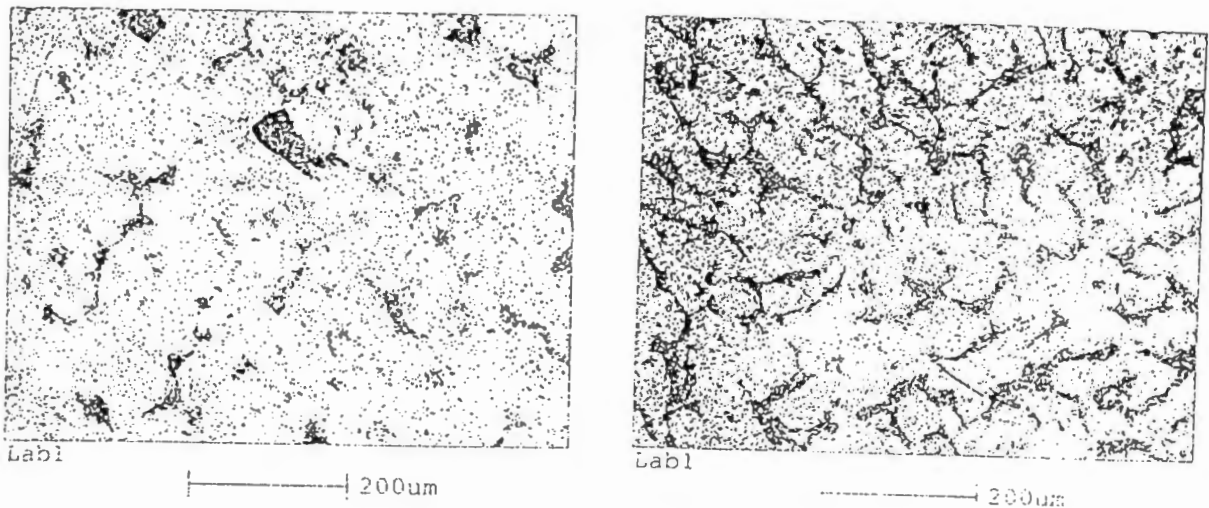


Figure 5.6 Typical SEM microphotographs for samples with (a) low and (b) high δ -ferrite content respectively

On the photographs, the dark phase represents the δ -ferrite and the austenite is represented by the light phase. The amounts of the ferrite were found to be 10.08% and 22.24% for both **Figures 5.6 (a) and (b)** respectively.

The compositional variation of the samples, determined by means of the SEM fitted with an EDAX are shown in Figure 5.7 (a) and (b) for the same samples which had a low and high δ -ferrite contents respectively.

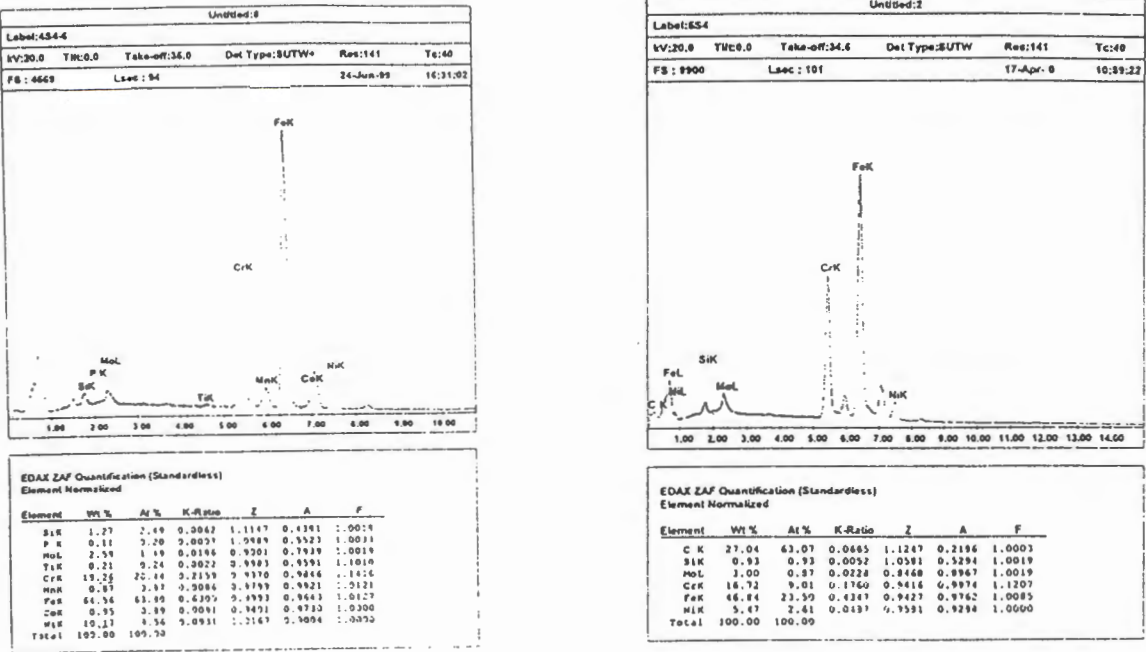


Figure 5.7 Typical compositions for samples with (a) low and (b) high δ -ferrite respectively.

From the analysis of these samples, the amount of the different elements present in the samples is in agreement with the chemical composition shown in Table 4.1.

The dark and the light phases in the samples were analyzed for Cr- and Ni-contents in order to confirm whether they are the ferrite and the austenite phases respectively, and the results are shown in **Table 5.5**.

Table 5.5 Cr- and Ni-contents of the dark and light phases.

PHASE	ELEMENT	WEIGHT PERCENTAGE (%)	
		Low δ -content	High δ -content
Dark	Cr	24.21	23.63
	Ni	7.97	8.16
Light	Cr	19.4	17.8
	Ni	12.3	12.33

Table 5.5 shows the difference between the Cr- and Ni-contents between the two phases present in the samples. In the dark phase, the Cr content is larger than in the light phase, while the Ni content in the dark phase is smaller than in the light phase for both low and high δ -ferrite samples. According to Brown et al [27], the δ -ferrite phase of the duplex stainless steel contains more Cr than the austenite phase, while the content of Ni in the δ -ferrite phase is smaller than that in the austenite phase [28]. From the results, the dark phase is the δ -ferrite and the austenite is represented by the light phase.

5.4 MICROSCOPIC IMAGE ANALYSIS

Figure 5.8 shows the microphotographs of Figure 5.6 (a) and (b) that were traced onto the transparencies so that only the grains of the δ -ferrite could appear and be counted by the image analyzer.

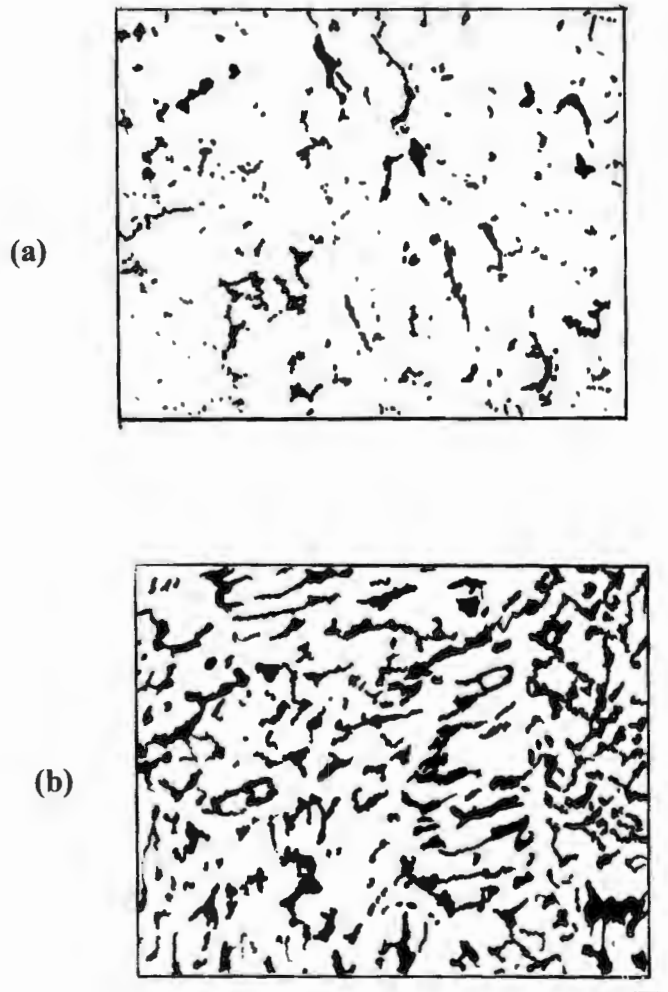


Figure 5.8 Samples with (a) low and (b) high δ -ferrite content traced on transparencies.

Table 5.6 shows the results of the amount of δ -ferrite as obtained from these transparencies.

Table 5.6 δ -ferrite content from photos traced onto transparencies

TYPE OF STEEL	MEAN δ-FERRITE (%)
Low ferrite content	10.1
High ferrite content	20.0

The amounts of the δ -ferrite for both the samples are the same as those obtained by Mössbauer spectroscopy and SEM analyses.

5.5 DISCUSSION

Charpy impact tests were used to follow the embrittlement of the steel. From Table 5.1, unaged samples have high impact energies and this energy decreases with increasing ageing time. This implies that ageing deteriorates the material strength and this causes the decomposition of the steel. The decomposition of the Cr-steel is mainly due to the diffusion of iron and Cr atoms within the material [6].



According to Massoud [29], the embrittlement of duplex stainless steels during ageing, at temperatures below 475°C, is basically due to micro structural evolution of the ferritic phase. The main micro structural evolutions in the ferrite are the spinodal decomposition of the ferritic Fe-Cr solid solution and sometimes the precipitation of the inter-metallic compound. The spinodal decomposition leads to a fluctuation of the Cr concentration corresponding to the formation of α' Cr-rich domains [29].

De Nys and Gielen [21] studied a 20 and 50 wt % Cr samples for two temperatures of ageing, as shown in the spectra of Figure 3.11. From these authors, it was observed that the sample with 20 wt % Cr induced a singlet near zero velocity at an ageing temperature of 470°C, while no singlet was observed at ageing temperature of 540°C. For a 50 wt % Cr sample, no singlet was observed at 470°C. At 540°C, the 20 wt % Cr sample lies outside the spinodal region, while the 50 wt % Cr sample lie within the spinodal region at temperature of 470°C, and this implies that at this temperature, this sample decomposes via spinodal transition. The actual behavior of the 20 wt % Cr sample may have to do with exact limits of solubility and impurities [30].

Many authors proposed that it is possible to differentiate between spinodal decomposition and nucleation-and-growth by using Mössbauer spectroscopy. However, according to Waanders et al [30], the observation of a paramagnetic singlet or its absence in the Mössbauer spectra of an Fe-Cr alloy, is an ambiguous rule as to whether the embrittlement will occur via the spinodal decomposition or nucleation-and-growth mechanism, as a singlet could indicate an advanced stage of spinodal decomposition when the α' -phase starts separating from the Cr-rich region formed during the early stage of spinodal transition [30].

Table 5.7 shows the results of the mean δ -ferrite content measured optically at the ESKOM TRI center and by Mössbauer spectroscopy, done in the present research.

Table 5.7 Mean δ -ferrite Values

SAMPLE NAME	EQUIVALENT AGEING TIME	IMPACT ENERGY J/cm ²	Δ FERRITE (OPTICAL)	Δ FERRITE (MÖSSBAUER)
CB	75khr @ 2911 °C	169.7	7.2	11
CI	"	156.5	7.7	10
CN	156khr @ 2911 °C	144.7	5.8	8
CM	"	122.3	6.6	19
CF	Start of Life No Spinodal	181.5	6.0	10
CD	"	176.2	7.6	11
HC	80khr@325 °C	82.9	8.6	21
HB	"	77.6	9.6	21
HS	15khr@325 °C	130.2	7.8	21
HT	"	110.5	9.7	21
HE	Start of life No Spinodal	210.4	9.4	13
HD	"	97.3	10.1	12
HM	120khr@325 °C	87.5	9.4	17
HK	"	57.5	16.3	13

From the optical measurements, the δ -ferrite content was found to be about 10% for both Crossover and Hot Leg samples. However, from Mössbauer measurements, the δ -ferrite content was found to lie between 10 to 20%, represented by the sextet on the Mössbauer spectrum.

The comparison of the mean δ -ferrite content, as determined by optical and

Mössbauer measurements is in about half the cases not conclusive. This is so especially in the case of Hot leg, due to the fact that the peaks of the sextet are obscured below the much bigger singlet, which makes it difficult to determine the area covered by the sextet. Therefore, the error on the δ -ferrite component is relatively large. The results of both optical and CEMS measurements show that there is no correlation in the amount of δ -ferrite found in the samples.

The sample under investigation had about 20 wt % Cr and 10 wt % Ni as alloying elements. This is a typical composition for duplex stainless steel containing both ferritic (bcc α phase) and austenitic (FCC γ phase) Fe compound. The Mössbauer spectra of all the samples showed the appearance of the α' -Cr rich singlet near zero velocity, after different ageing times and temperatures below 400°C. Mössbauer spectroscopy can detect small Fe-rich concentration changes resulting in different phases developing during the decomposition of the steel. According to Waanders et al [6], these changes can be monitored by the measurement of the change in internal magnetic field that is proportional to the Cr content of the Fe-rich phase. The average magnetic field for these samples was found to be about 23 T. According to these authors, the average magnetic field increases slowly with increasing ageing time, while the intensity of the paramagnetic singlet which is formed due to the α' -Cr rich phase, increases faster. However, for the samples under investigation, this increase in the magnetic field with increasing ageing time is not evident. This might be brought about by the fact that Ni, which is one of the alloying elements, is an austenizing agent [17, 18]. Addition of this element creates an austenitic micro structure, and this reverses the effect produced by the addition of Cr in larger amounts, which creates

a ferritic micro structure.

The microphotographs from SEM analysis also indicate that the sample with low and high δ -ferrite content had about 10% and 20% δ -ferrite content respectively. The δ -ferrite phase is represented by the dark phase on the microphotographs whereas the austenite is represented by the light phase.

The results of SEM fitted with an EDAX reveal the compositional variations for both samples with high and low δ -ferrite content. The δ -ferrite phase of both samples contains about 24 wt % Cr and 8 wt % Ni, while the austenite phase of both the samples contains about 19 wt % Cr and 12 wt % Ni. According to Brown et al [27], the δ -ferrite phase of the duplex stainless steel contains more Cr than the austenite phase, while the content of Ni in the δ -ferrite phase is smaller than that in the austenite phase.

5.6 CONCLUSION

There is no clear correlation between the δ -ferrite content and Charpy impact strength values. From the impact strength measurements, the impact energy decreased with increasing ageing time. If the impact energy decreases, the hardness of the stainless steel will be reduced and this would lead to the degradation of the stainless steel. The reduction in the hardness of the steel is brought about by the fact that during ageing of the stainless steel, there is a micro structural evolution of the ferrite phase to a hard and brittle Cr-rich phase. However, the increase in δ -ferrite with increasing ageing time is not evident. Thus, some other mechanisms might be responsible for the decrease in impact energy.

From Mössbauer measurements, the average magnetic field for the samples

investigated was found to be about 23 T. The δ -ferrite component for both the Hot leg and the Crossover leg samples were found to be about 10% to 20%, whereas the austenite component was found to be about 80% to 90%. However, no correlation was found between the amount of the δ -ferrite in the samples and their ageing times, as determined by CEMS measurements.

The SEM results reveal the two phases present in the samples under investigation. One of these phases is the ferrite phase represented by the dark area on the microphotographs of **Figure 5.8**, and the content was found to be 10% and 20% for the samples investigated. The other phase that was observed is the austenite represented by the light area on the microphotographs. This phase was found to be about 80% and 90% for the samples investigated. For all the samples investigated, the δ -ferrite contains about 24 wt % Cr and 8 wt % Ni, while the austenite phase for the samples contained about 19 wt % Cr and 12 wt % Ni. This is in agreement with the results by Brown et al [27], that the δ -ferrite phase of the duplex stainless steel contains more Cr than the austenitic phase, while the Ni content in the δ -ferrite phase is smaller than that in the austenite phase.

The samples used in this investigation had about 20%wt Cr and these samples were aged below 400°C. At this ageing temperature, the samples showed a large singlet near zero velocity. These samples are thought to decompose via spinodal decomposition.

5.7 RECOMMENDATIONS

The current research shows that the impact energy decreased with increasing ageing time. This decrease in impact energy indicates the degradation of the stainless steel.

However, the increase in δ -ferrite with increasing ageing time is not evident. Thus, some other mechanisms might be responsible for the decrease in impact energy. Therefore, the measurement of other mechanical properties is suggested.

The Mössbauer spectra of all the samples investigated showed the appearance of the Cr rich singlet near zero velocity. Mössbauer spectroscopy can detect small Fe-rich concentration changes resulting in different phases developing during the decomposition of the steel. These changes can be monitored by the measurement of the change in internal magnetic field that is proportional to the Cr content of the Fe-rich phase. The average magnetic field for these samples was found to be about 23 T. However, there is currently no sufficient information on the mechanisms of the embrittlement by either spinodal decomposition or by nucleation-and-growth. The author therefore suggest the use of Mössbauer Spectroscopy for samples aged at various temperatures in order to follow the steps in the spinodal transformation. This can be done by choosing a temperature at which the Cr rich region will appear paramagnetic [30]. Since Mössbauer spectroscopy can assess how far the transformation has advanced, this technique can also be employed to determine the activation energy of embrittlement in the case of nucleation-and-growth. The simulation of the plot of spinodal decomposition for an alloy with 20 wt % Cr and 10 wt % Ni is also suggested, and the results can then be compared with the experimental results found by Mössbauer spectroscopy.



In order to describe what happens at the atomic level when the Cr steel is aged, the micro structural changes in the stainless steel alloy can be investigated by using atomic probe techniques such as ion field microscopy(IFM).

The samples under investigation had about 10 % Ni as the main alloying element. However, there are some other impurities like Si, Mn, Mo and Cu. It is also recommended that the effect of these impurities on the type and degree of transformation be investigated. The effect of Ni as a function of these impurities needs also to be investigated.

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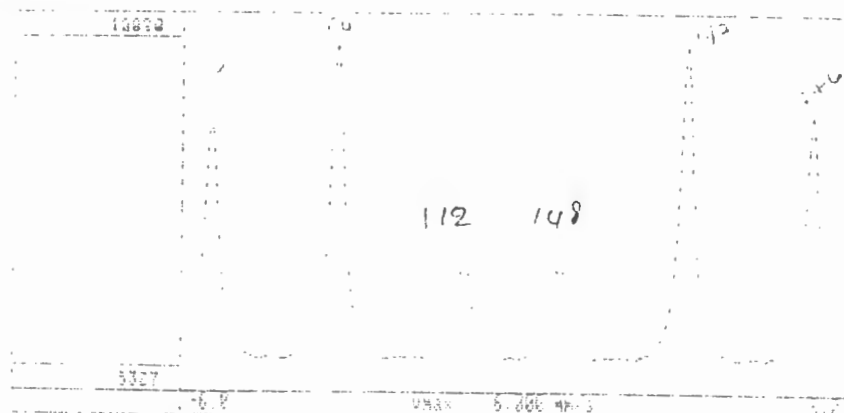
APPENDIX A - CEMS SPECTRA

In this Appendix, Mössbauer spectra for natural iron used for the calibration of the spectrometer at velocities of 6, 8 and 10mm/s are presented. The spectra for the stainless steel samples used for reference purposes as well as for all the samples under investigation are also presented.

APPENDIX A1

Spectra obtained for natural iron used for calibration purposes.

A1.1 Natural iron: 6mm/s velocity



ykling op 6 mm/s 18/6/98

Channelnumber : 512
Foldingpoint : 256.5
Geom. Effect : 15

Results of Fit

Jun 18 1998 12:57:41

SP800 - Calibration - 6u Fe-foil **

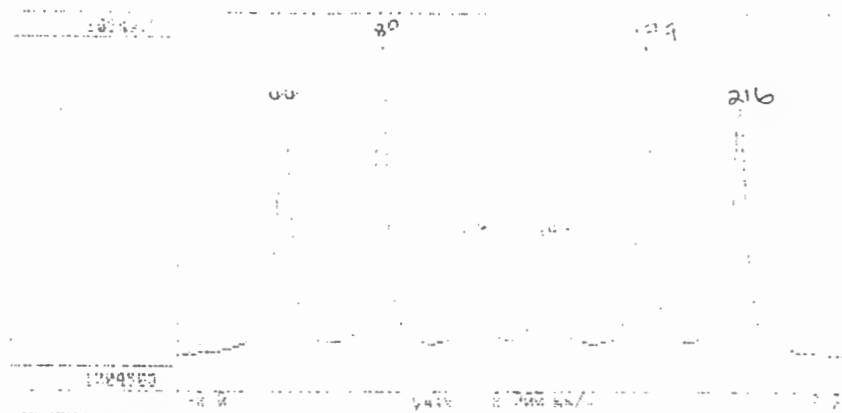
Theory : 3

Number of Parameters : 10 Number of Iterations : 7

Chi² : 2.6286

Name	Initial	Final	Error	Check	
baseline	7348	6307	7.4631	1.000	1.000
Total Area	-0.7500	-1.2584	0.0109	1.997	1.998
Mag Field	33.0000	33.4804	0.0101	0.988	0.958
Quad Mag	0.0030	0.0212	0.0024	0.976	0.980
Shift Mag	-0.1100	-0.1039	0.0013	1.051	1.058
Width Out	0.3400	0.2827	0.0048	1.342	1.282
Width Mid	0.3000	0.2787	0.0046	1.847	1.751
Width In	0.2500	0.3298	0.0101	1.162	0.992
Area Out	0.5000	0.3607	0.0036	1.923	1.918
Area Mid	0.3500	0.4583	0.0044	2.810	2.812

A1.2 Natural iron: 8mm/s velocity



Kalibrasie CFMS opstelling 15/10/98

Channelnumber : 512
 Foldingpoint : 256.5
 Geom. Effect : 3437

Results of Fit

Oct 15 1998 13:09:02

SP800 - Calibration - 6u Fe-foil **

Theory : 3

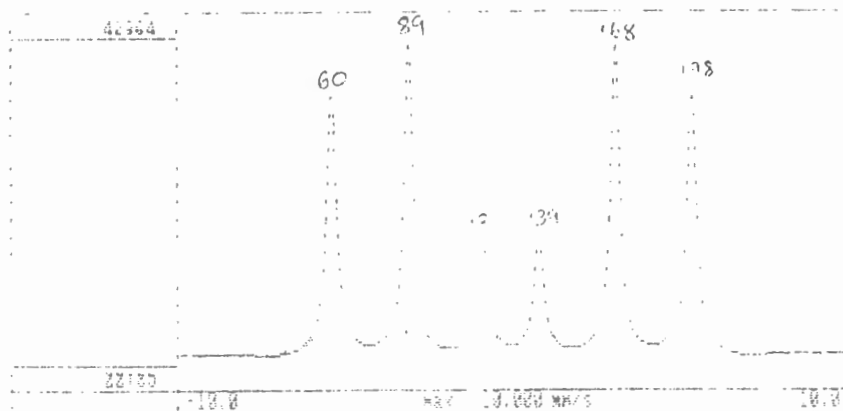
Number of Parameters : 10 Number of Iterations : 6

Chi² : 1.1663

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Name	Initial	Final	Error	Check	
baseline	1006149	1005835	67.4130	1.000	1.000
Total Area	-0.0500	-0.0430	0.0005	1.526	1.529
Mag Field	33.0000	33.5518	0.0194	0.995	0.961
Quad Mag	0.0030	-0.0030	0.0046	0.955	0.998
Shift Mag	-0.1100	-0.1120	0.0025	1.152	1.087
Width Out	0.3400	0.3690	0.0094	1.410	1.323
Width Mid	0.3000	0.2992	0.0079	2.012	1.872
Width Inn	0.2500	0.4538	0.0229	1.173	0.875
Area Out	0.5000	0.3941	0.0065	2.091	2.085
Area Mid	0.3500	0.4052	0.0076	3.142	3.125

A1.3 Natural iron: 10mm/s velocity



ykling op 10mm/s 18/6/98

Channelnumber : 512
Foldingpoint : 256.5
Geom. Effect : -63

Results of Fit

Jun 18 1998 12:42:16

SP800 - Calibration - 6u Fe-foil **

Theory : 3

Number of Parameters : 10 Number of Iterations : 6

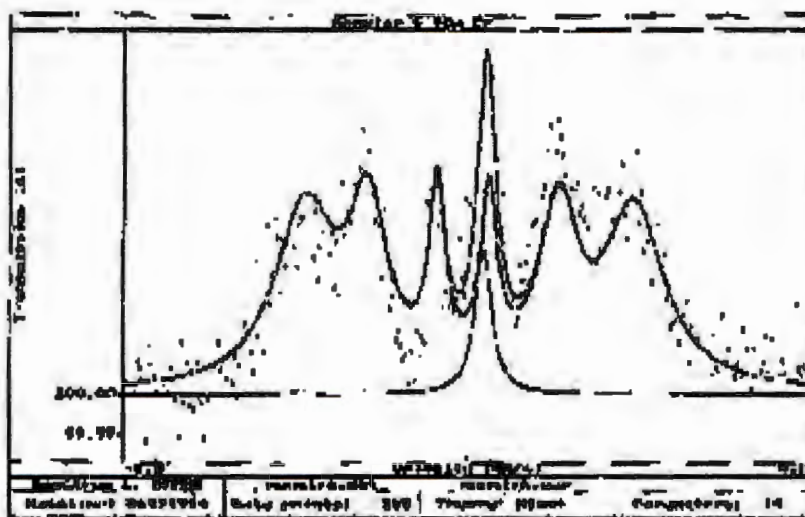
Chi² : 7.6952

Name	Initial	Final	Error	Check	
baseline	22598	22598	24.8583	1.000	1.000
Total Area	-1.2204	-1.2204	0.0113	1.528	1.531
Mag Field	33.2403	33.2403	0.0133	0.994	0.930
Quad Mag	0.0019	0.0019	0.0032	0.955	0.981
Shift Mag	-0.1094	-0.1094	0.0017	1.049	1.042
Width Out	0.3222	0.3222	0.0063	1.297	1.363
Width Mid	0.2850	0.2850	0.0055	1.639	1.386
Width Inn	0.3292	0.3292	0.0121	1.132	0.964
Area Out	0.3990	0.3990	0.0042	1.827	1.743
Area Mid	0.4238	0.4238	0.0052	2.665	2.731

APPENDIX A 2

Spectra for stainless steel used for reference purposes.

A2.1 Stainless steel: 30% Cr



```

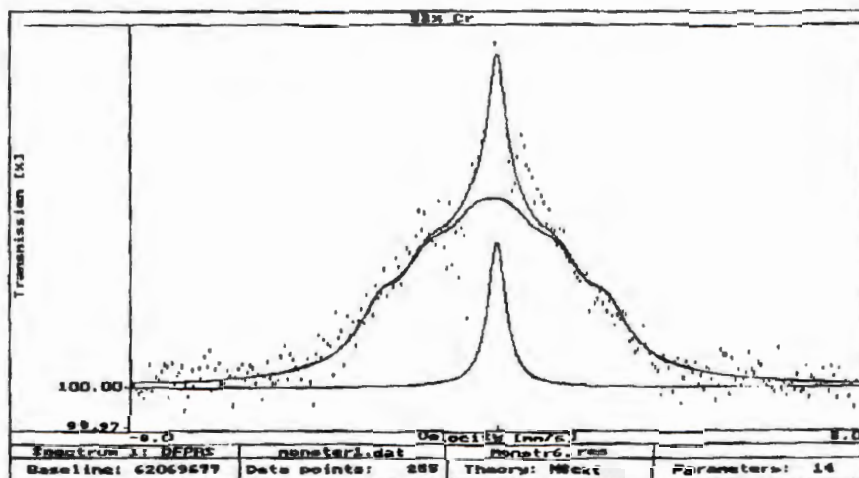
=====
title: results of data 1
author: L. J. 1991
file: results
summary: results
library: results
date: Sun Jan 26 22:34:19 2001
=====

```

1. Logo	
2. Parameters	1
3. Call	1, 1, 1, 1, 1, 1
4. Child-Tree	0.0000
5. Core-Leaf	0.0000
6. Flycatcher	7
7. Similar	5%
8. Parameter	1
9. Child-Tree	1
10. Parameters	1
11. Name: No	26882020
12. Total Area	-0.0000
13. Wxless	1.0000
14. Total Area	1.0000
15. Map Field 1	0.1, 0.1, 0.1
16. Quad Tree 1	0.1, 0.1, 0.1
17. Child Map 1	-0.0000
18. Child Map 2	0.0000
19. Child Map 3	0.0000
20. Child Map 4	0.0000
21. Child Map 5	0.0000
22. Child Map 6	0.0000
23. Child Map 7	0.0000
24. Child Map 8	0.0000
25. Child Map 9	0.0000
26. Child Map 10	0.0000
27. Child Map 11	0.0000
28. Child Map 12	0.0000
29. Child Map 13	0.0000
30. Child Map 14	0.0000
31. Child Map 15	0.0000
32. Child Map 16	0.0000
33. Child Map 17	0.0000
34. Child Map 18	0.0000
35. Child Map 19	0.0000
36. Child Map 20	0.0000
37. Child Map 21	0.0000
38. Child Map 22	0.0000
39. Child Map 23	0.0000
40. Child Map 24	0.0000
41. Child Map 25	0.0000
42. Child Map 26	0.0000
43. Child Map 27	0.0000
44. Child Map 28	0.0000
45. Child Map 29	0.0000
46. Child Map 30	0.0000
47. Child Map 31	0.0000
48. Child Map 32	0.0000
49. Child Map 33	0.0000
50. Child Map 34	0.0000
51. Child Map 35	0.0000
52. Child Map 36	0.0000
53. Child Map 37	0.0000
54. Child Map 38	0.0000
55. Child Map 39	0.0000
56. Child Map 40	0.0000
57. Child Map 41	0.0000
58. Child Map 42	0.0000
59. Child Map 43	0.0000
60. Child Map 44	0.0000
61. Child Map 45	0.0000
62. Child Map 46	0.0000
63. Child Map 47	0.0000
64. Child Map 48	0.0000
65. Child Map 49	0.0000
66. Child Map 50	0.0000
67. Child Map 51	0.0000
68. Child Map 52	0.0000
69. Child Map 53	0.0000
70. Child Map 54	0.0000
71. Child Map 55	0.0000
72. Child Map 56	0.0000
73. Child Map 57	0.0000
74. Child Map 58	0.0000
75. Child Map 59	0.0000
76. Child Map 60	0.0000
77. Child Map 61	0.0000
78. Child Map 62	0.0000
79. Child Map 63	0.0000
80. Child Map 64	0.0000
81. Child Map 65	0.0000
82. Child Map 66	0.0000
83. Child Map 67	0.0000
84. Child Map 68	0.0000
85. Child Map 69	0.0000
86. Child Map 70	0.0000
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89. Child Map 73	0.0000
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91. Child Map 75	0.0000
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93. Child Map 77	0.0000
94. Child Map 78	0.0000
95. Child Map 79	0.0000
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98. Child Map 82	0.0000
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100. Child Map 84	0.0000
101. Child Map 85	0.0000
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104. Child Map 88	0.0000
105. Child Map 89	0.0000
106. Child Map 90	0.0000
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113. Child Map 97	0.0000
114. Child Map 98	0.0000
115. Child Map 99	0.0000
116. Child Map 100	0.0000
117. Child Map 101	0.0000
118. Child Map 102	0.0000
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121. Child Map 105	0.0000
122. Child Map 106	0.0000
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124. Child Map 108	0.0000
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[illegible]

A2.2 Stainless steel: 52% Cr

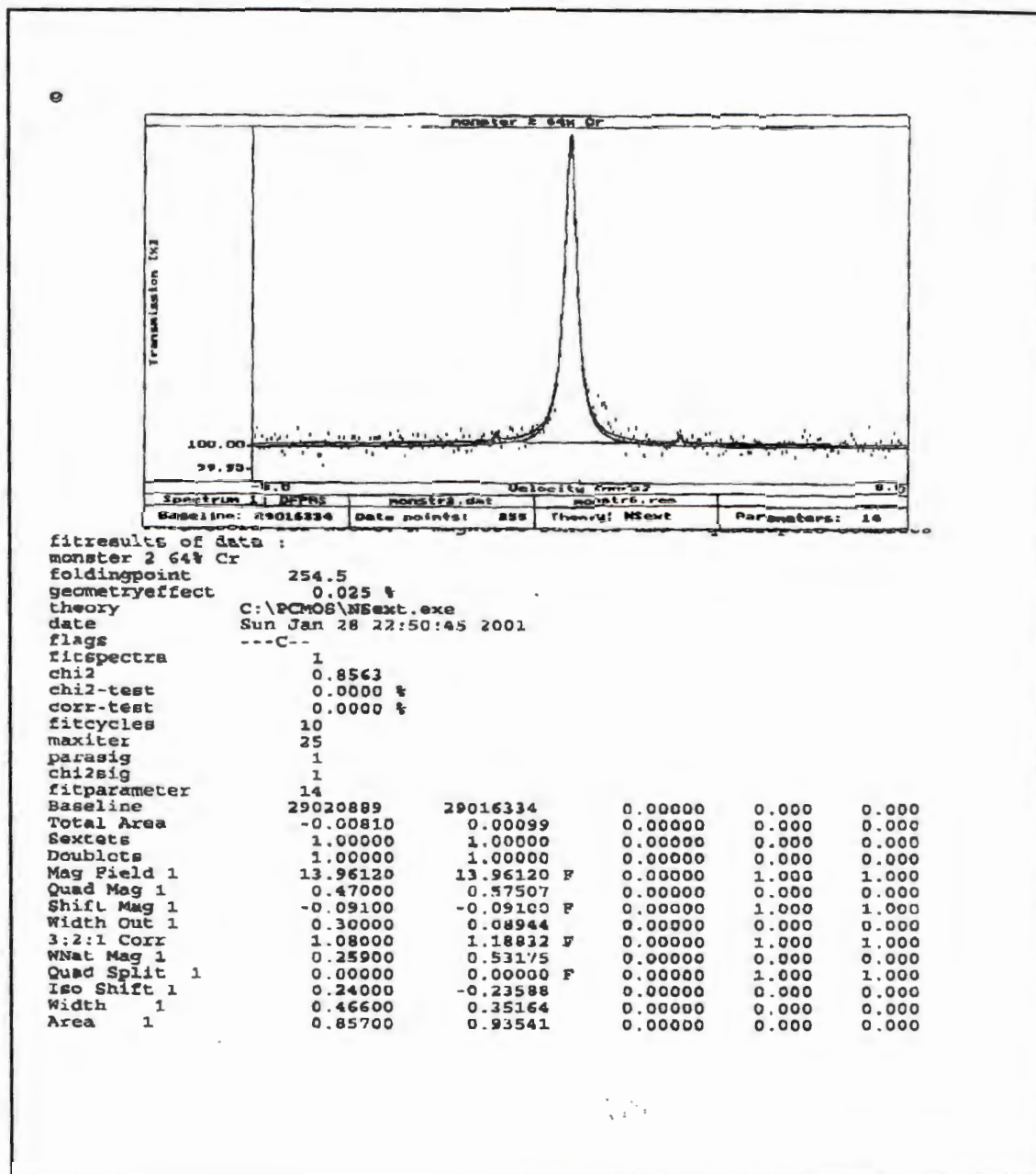


fitresults of data :

```

52% Cr
foldingpoint      254.5
geometryeffect    0.032 %
theory            C:\PCMODS\NSext.exe
date             Sun Jan 28 22:41:26 2001
flags            ---C---
fitspectra       1
chi2             1.3293
chi2-test        0.0000 %
corr-test        0.0000 %
fitcycles        13
maxiter          25
parasisg         1
chi2sig          1
fitparameter     14
Baseline         62071831      62069677      0.00000      0.000      0.000
Total Area      -0.00810      -0.00565      0.00000      0.000      0.000
Sextets         1.00000      1.00000      0.00000      0.000      0.000
Doublets        1.00000      1.00000      0.00000      0.000      0.000
Mag Field 1     18.96120      15.36144      0.00000      0.000      0.000
Quad Mag 1      0.47000      0.02158      0.00000      0.000      0.000
Shift Mag 1     -0.09100      -0.09100 F      0.00000      0.000      0.000
Width Out 1     0.30000      1.18226      0.00000      0.000      0.000
3:2:1 Corr      1.08000      3.10238      0.00000      0.000      0.000
WNat Mag 1      0.25900      1.93491      0.00000      0.000      0.000
Quad Split 1    0.00000      0.00000 F      0.00000      0.000      0.000
Iso Shift 1     0.24000      -0.01154      0.00000      0.000      0.000
Width 1         0.46600      0.46600 F      0.00000      0.000      0.000
Area 1          0.15700      0.09434      0.00000      0.000      0.000
  
```

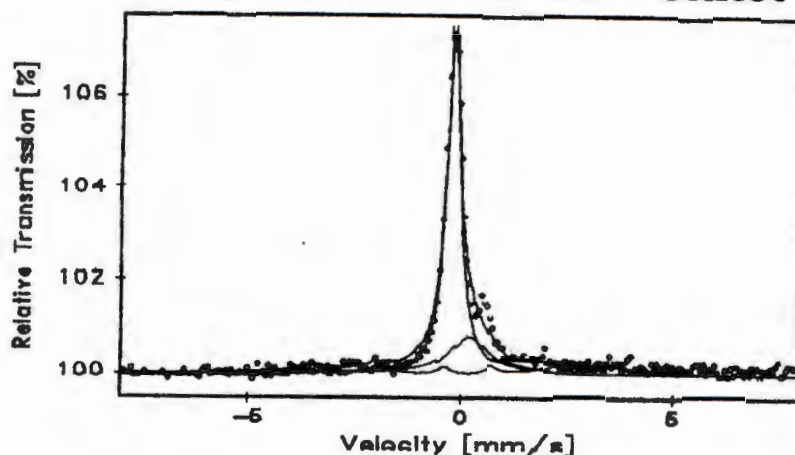
A2.3 Stainless steel: 64% Cr



APPENDIX A3

Spectra for crossover samples under investigation

Ringhals Crossover CB - Sextet



Parameters for NSext: N magnetic sextets and M quadrupole doublets
fitresults of data :

sample crossover leg cb

foldingpoint 255.0

geometryeffect 0.202 %

theory C:\PCMO5\NSext.exe

date Fri Oct 23 14:54:58 1998

flags ---CE-

fitspectra

chi2 7.2260

chi2-test 0.0000 %

corr-test 0.0000 %

fitcycles 8

maxiter 25

parasig 1

chi2sig 1

fitparameter 18

Baseline

Total Area

Sextets

Doublets

Mag Field 1

Quad Mag 1

Shift Mag 1

Width Out 1

3:2:1 Corr

WNat Mag 1

Quad split 1

Iso shift 1

Width 1

Area 1

Quad split 2

Iso shift 2

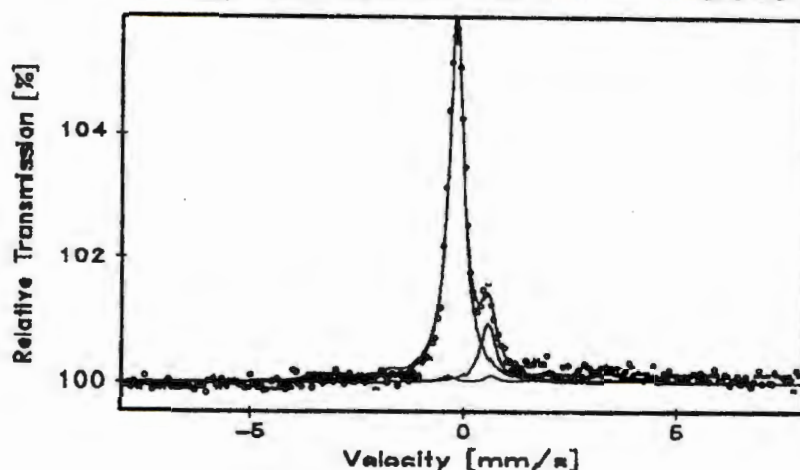
Width 2

Area 2

3157981	3165043	191.07811	-0.882	3.180
-0.03750	-0.04080	0.00053	-1.121	3.599
1.00000	1.00000 F	0.00000	1.000	1.000
2.00000	2.00000 F	0.00000	1.000	1.000
24.21330	21.94105	0.27342	0.810	0.542
-0.03530	-0.11534	0.05922	4.812	-1.870
-0.11590	0.10207	0.03122	-1.657	4.964
0.11400	0.82860	0.13458	4.536	-0.637
1.00000	1.00000 F	0.00000	1.000	1.000
0.25000	0.25000 F	0.00000	1.000	1.000
0.00000	0.00000 F	0.00000	1.000	1.000
-0.20930	-0.21339	0.00114	1.444	0.625
0.36100	0.37673	0.00385	1.659	1.332
0.58740	0.67761	0.01103	0.117	2.332
0.00000	0.00000 F	0.00000	1.000	1.000
0.18730	0.18730 F	0.00000	1.000	1.000
1.39640	2.91459	0.16544	1.289	3.478
0.18720	0.20694	0.01184	-0.560	4.222

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Ringhals Crossover CD - Sextet



Parameters for NSext: N magnetic sextets and M quadrupole doublets
fitresults of data :

sample CD Crossover

foldingpoint 254.5

geometryeffect 0.203 %

theory C:\PCMO5\NSext.exe

date Mon Oct 26 10:33:13 1998

flags ---CE-

fitspectra

chi2 5.8779

chi2-test 0.0000 %

corr-test 0.0000 %

fitcycles 22

maxiter 25

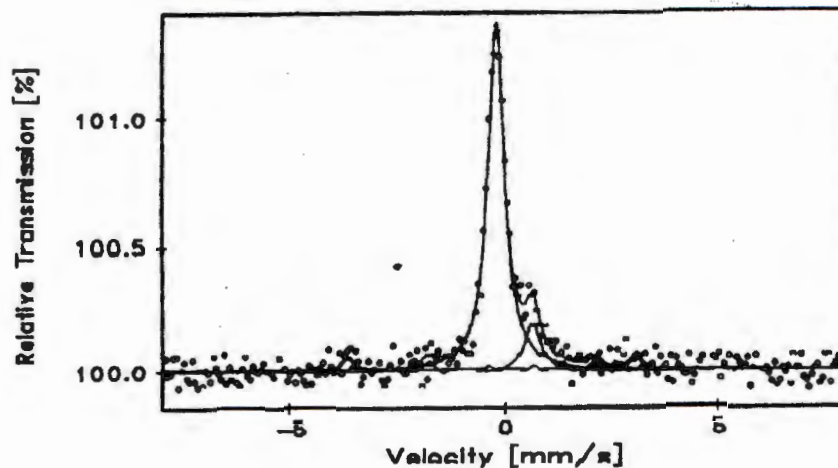
parasig 1

chi2sig 1

fitparameter 18

Baseline	3432453	3426630	186.57775	3.545	-1.265
Total Area	-0.03160	-0.03228	0.00046	4.187	-1.695
Sextets	1.00000	1.00000 F	0.00000	1.000	1.000
Doublets	2.00000	2.00000 F	0.00000	1.000	1.000
Mag Field 1	24.21330	19.95558	0.29769	0.731	0.332
Quad Mag 1	-0.03530	-0.04899	0.06869	3.834	0.272
Shift Mag 1	-0.11590	0.11238	0.03644	0.258	4.352
Width Out 1	1.11400	0.74575	0.13613	0.754	2.704
3:2:1 Corr	1.00000	1.00000 F	0.00000	1.000	1.000
WNat Mag 1	0.25000	0.25000 F	0.00000	1.000	1.000
Quad split 1	0.00000	0.00000 F	0.00000	1.000	1.000
Iso shift 1	-0.21610	-0.19728	0.00131	1.823	-0.010
Width 1	0.37530	0.42039	0.00449	3.310	0.328
Area 1	0.60160	0.75848	0.01239	5.208	-2.449
Quad split 2	0.00000	0.00000 F	0.00000	1.000	1.000
Iso shift 2	0.22030	0.56873	0.00863	3.144	0.079
Width 2	1.17550	1.05669	0.07135	-1.496	3.939
Area 2	0.20920	0.13084	0.00666	-0.893	2.990

Ringhals Crossover CE1 - Sextet



Parameters for NSext: N magnetic sextets and M quadrupole doublets
fitresults of data :

Ringhals Crossover Sample CE1

foldingpoint 267.0

geometryeffect 0.187 %

theory C:\PCMO5\NSext.exe

date Mon Oct 26 10:01:54 1998

flags ---CE-

fitspectra

chi2 1

chi2-test 1.0054

corr-test 46.4252 %

fitcycles 20.8672 %

maxiter 9

parasig 25

chi2sig 1

fitparameter 1

Baseline 6175905 6174665 222.60380 1.013 0.917

Total Area -0.03750 -0.00794 0.00027 0.957 0.911

Sextets 1.00000 1.00000 F 0.00000 1.000 1.000

Doublets 2.00000 2.00000 F 0.00000 1.000 1.000

Mag Field 1 21.85120 20.77906 0.39824 0.635 1.304

Quad Mag 1 -0.33530 -0.47674 0.10489 1.361 1.670

Shift Mag 1 -0.11690 -0.09505 0.05336 2.140 0.821

Width Out 1 1.21400 0.37768 0.18634 1.309 0.644

3:2:1 Corr 1.00000 1.00000 F 0.00000 1.000 1.000

WNat Mag 1 0.25000 0.25000 F 0.00000 1.000 1.000

Quad Split 1 0.00000 0.00000 F 0.00000 1.000 1.000

Iso Shift 1 -0.22696 -0.21286 0.00435 0.869 0.994

Width 1 0.36600 0.47137 0.01422 1.329 0.992

Area 1 0.12452 0.79990 0.03039 0.995 0.830

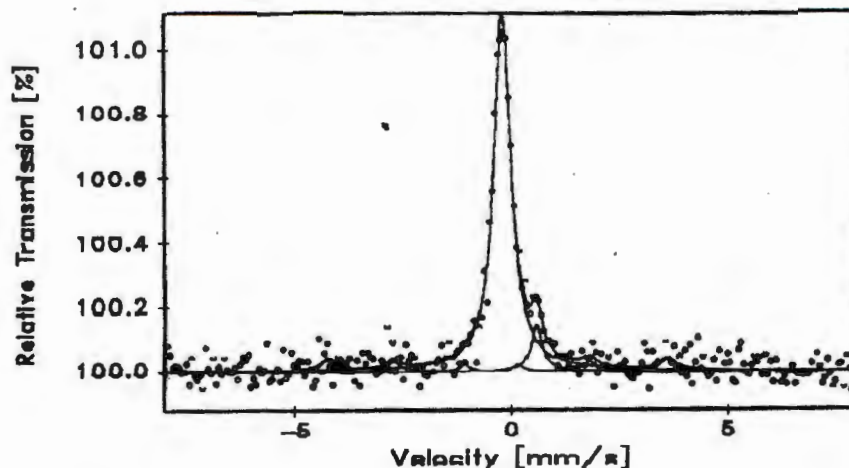
Quad Split 2 0.00000 0.00000 F 0.00000 1.000 1.000

Iso Shift 2 0.53400 0.63830 0.03173 0.997 1.340

Width 2 1.02100 0.95097 0.22008 0.978 0.815

Area 2 0.19400 0.10657 0.01817 0.982 0.887

Ringhals Crossover CF - Sextet



Parameters for NSext: N magnetic sextets and M quadrupole doublets
fitresults of data :

Ringhals Crossover Sample cf

foldingpoint 255.0

geometryeffect 0.185 %

theory C:\PCMO5\NSext.exe

date Mon Oct 26 10:55:54 1998

flags ---CE-

fitspectra 1

chi2 0.8984

chi2-test 87.1250 %

corr-test 66.1670 %

fitcycles 12

maxiter 25

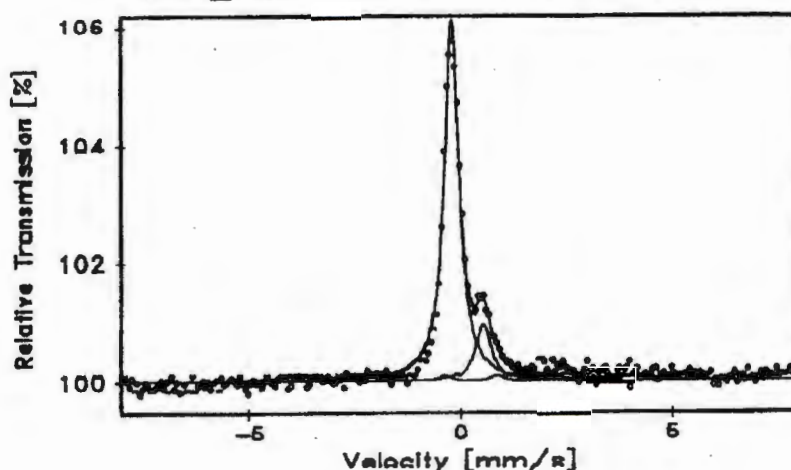
parasig 1

chi2sig 1

fitparameter 18

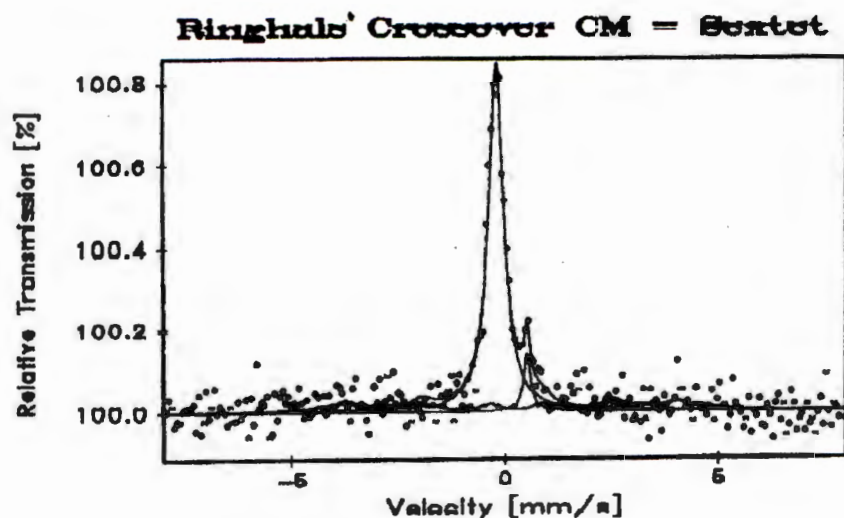
Baseline	6504502	6504519	247.95207	0.763	1.278
Total Area	-0.03750	-0.00616	0.00031	0.633	1.478
Sextets	1.00000	1.00000 F	0.00000	1.000	1.000
Doublets	2.00000	2.00000 F	0.00000	1.000	1.000
Mag Field 1	24.21330	24.21330 F	0.00000	1.000	1.000
Quad Mag 1	-0.03530	0.15558	0.15734	0.421	0.918
Shift Mag 1	-0.11580	-0.39697	0.07928	0.386	0.942
Width Out 1	0.11400	0.44050	0.31348	3.401	0.420
3:2:1 Corr	1.00000	1.00000 F	0.00000	1.000	1.000
WNat Mag 1	0.25000	0.25000 F	0.00000	1.000	1.000
Quad split 1	0.00000	0.00000 F	0.00000	1.000	1.000
Iso shift 1	-0.30030	-0.21555	0.00508	0.897	0.933
Width 1	0.36100	0.46756	0.01593	1.108	1.143
Area 1	0.58740	0.84500	0.04424	0.695	1.416
Quad split 2	0.00000	0.00000 F	0.00000	1.000	1.000
Iso shift 2	0.18730	0.57126	0.03169	1.004	1.026
Width 2	1.37220	0.62411	0.21917	1.427	0.676
Area 2	0.20970	0.06457	0.01678	1.122	0.852

Ringhals Crossover CI - Sextet



```

fitresults of data :
sample ci crossover lag
foldingpoint      255.0
geometryeffect     0.191 %
theory             C:\PCMO5\NSext.exe
date              Mon Oct 26 11:18:32 1998
flags             ---CE-
fitspectra        1
chi2               2.9469
chi2-test          0.0000 %
corr-test          0.0000 %
fitcycles          9
maxiter            25
parasig            1
chi2sig            1
fitparameter       18
Baseline           1903544      1900805      153.99841      -1.445      3.505
Total Area         -0.03360      -0.03182      0.00072      -1.934      4.027
Sextets            1.00000      1.00000 F      0.00000      1.000      1.000
Doublets           2.00000      2.00000 F      0.00000      1.000      1.000
Mag Field 1        24.21330      24.21330 F      0.00000      1.000      1.000
Quad Mag 1         -0.03530      -0.20712      0.10842      2.161      2.569
Shift Mag 1        -0.11590      0.14331      0.05617      2.587      2.497
Width Out 1         1.11400      0.76490      0.23285      3.001      -0.846
3:2:1 Corr         1.00000      1.00000 F      0.00000      1.000      1.000
WNat Mag 1         0.25000      0.25000 F      0.00000      1.000      1.000
Quad split 1       0.00000      0.00000 F      0.00000      1.000      1.000
Iso Shift 1        -0.20470      -0.20395      0.00169      1.338      0.517
Width 1            0.37380      0.41029      0.00572      2.074      1.717
Area 1             0.62010      0.77317      0.01898      -1.539      3.911
Quad split 2       0.00000      0.00000 F      0.00000      1.000      1.000
Iso Shift 2        0.27310      0.54573      0.01078      0.768      1.922
Width 2            0.86890      1.04959      0.09044      0.936      1.396
Area 2             0.20800      0.13085      0.00882      -0.311      2.241
    
```



fitresults of data :
 Ringhals Crossover Sample CM1
 foldingpoint 256.0
 geometryeffect 0.183 %
 theory C:\PCMO5\NSext.exe
 date Wed Oct 28 12:17:17 1998
 flags ---CE-

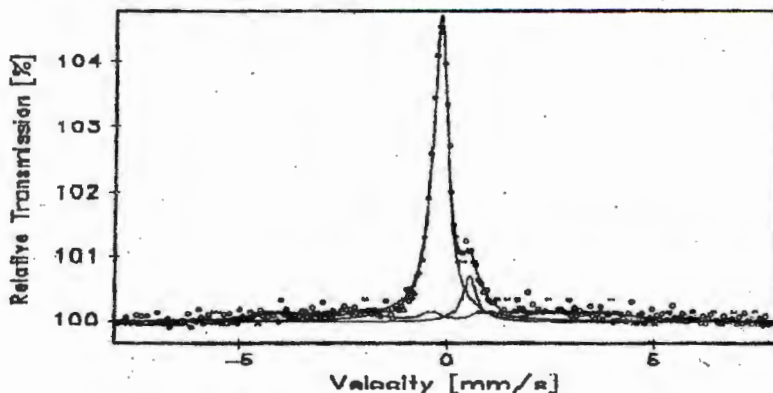
fitspectra	1				
chi2	0.8318				
chi2-test	97.3952 %				
corr-test	98.9610 %				
fitcycles	5				
maxiter	25				
parasig	1				
chi2sig	1				
fitparameter	18				
Baseline	6221510	6221886	293.88868	1.153	0.616
Total Area	-0.05360	-0.00484	0.00043	1.121	0.586
Sextets	1.00000	1.00000 F	0.00000	1.000	1.000
Doublets	2.00000	2.00000 F	0.00000	1.000	1.000
Mag Field 1	24.21330	24.21330 F	0.00000	1.000	1.000
Quad Mag 1	-0.07506	-0.11945	0.25967	2.495	1.497
Shift Mag 1	0.21669	0.22037	0.13717	1.723	2.599
Width Out 1	1.22400	0.94266	0.66535	0.220	0.693
3:2:1 Corr	1.00000	1.00000 F	0.00000	1.000	1.000
WNat Mag 1	0.25000	0.25000 F	0.00000	1.000	1.000
Quad split 1	0.00000	0.00000 F	0.00000	1.000	1.000
Iso Shift 1	-0.20116	-0.20811	0.00692	1.282	0.883
Width 1	0.45524	0.43843	0.02186	1.222	1.560
Area 1	0.72043	0.74888	0.07153	1.218	0.404
Quad split 2	0.00000	0.00000 F	0.00000	1.000	1.000
Iso Shift 2	0.51695	0.52743	0.02578	0.928	1.263
Width 2	0.71267	0.46622	0.18608	1.213	0.629
Area 2	0.06262	0.06019	0.01846	1.010	0.725

#

APPENDIX A4

Spectra for hot-leg samples under investigation.

Ringhals Hotleg HB - Sextet

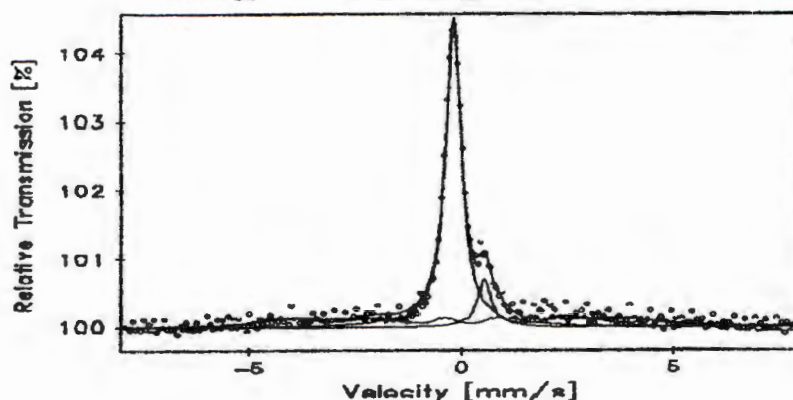


Parameters for NSext: N magnetic sextets and M quadrupole doublets
 fitresults of data ;
 ringhals hot leg hb

```

foldingpoint      254.5
geometryeffect    0.197 %
theory            C:\PCMO5\NSext.exe
date              Mon Oct 26 16:46:52 1998
flags             ---CE-
fitspectra        1
chi2              3.2867
chi2-test         0.0000 %
corr-test         6.8874 %
fitcycles         10
maxiter           25
parasig           1
chi2sig           1
fitparameter      18
Baseline          4371757      4370791      292.28419      0.651      1.664
Total Area        -0.03250      -0.02923      0.00069      0.671      1.787
Sextets           1.00000      1.00000 F      0.00000      1.000      1.000
Doublets          2.00000      2.00000 F      0.00000      1.000      1.000
Mag Field 1       24.21330      24.21330 F      0.00000      1.000      1.000
Quad Mag 1        -0.03630      -0.33295      0.09910      0.678      1.225
Shift Mag 1       -0.11580      0.06036      0.05482      1.844      0.874
Width Out 1       1.11400      1.70741      0.24873      1.845      1.048
3:2:1 Corr        1.00000      1.00000 F      0.00000      1.000      1.000
WNat Mag 1        0.19000      0.19000 F      0.00000      1.000      1.000
Quad Split 1      0.00000      0.00000 F      0.00000      1.000      1.000
Iso Shift 1       -0.21680      -0.19971      0.00154      1.205      0.708
Width 1           0.42320      0.44217      0.00559      2.446      1.071
Area 1            0.82100      0.88783      0.04846      1.074      1.598
Quad Split 2      0.00000      0.00000 F      0.00000      1.000      1.000
Iso Shift 2       0.27660      0.54810      0.00981      1.428      1.002
Width 2           1.10071      0.89711      0.07739      0.517      2.048
Area 2            0.37299      0.09226      0.00667      0.235      1.898
    
```

Ringhals Hotleg HC = Sextet



Parameters for NSext: N magnetic sextets and M quadrupole doublets
fitresults of data :

ringhals hot leg hb

foldingpoint

254.5

geometryeffect

0.197 %

effect

0.078 %

theory

C:\PCNOS\NSext.exe

date

Tue Oct 27 10:11:51 1998

flags

---CE-

fitspectra

1

chi2

6.2338

chi2-test

0.0000 %

corr-test

39.3411 %

fitcycles

14

maxiter

25

parasig

1

chi2sig

1

fitparameter

18

Baseline

9035668

9037351

426.34437

-1.938

4.330

Total Area

-0.03220

-0.02877

0.00049

-2.169

4.743

Sextets

1.00000

1.00000 F

0.00000

1.000

1.000

Doublets

2.00000

2.00000 F

0.00000

1.000

1.000

Mag Field 1

24.42550

24.42550 F

0.00000

1.000

1.000

Quad Mag 1

-0.03450

0.32209

0.06969

0.801

0.930

Shift Mag 1

-0.11590

0.06576

0.03855

2.043

0.307

Width Out 1

0.98480

1.74467

0.17440

3.994

-0.815

3:2:1 Corr

1.00000

1.00000 F

0.00000

1.000

1.000

WNet Mag 1

0.19000

0.19000 F

0.00000

1.000

1.000

Quad split 1

0.00000

0.00000 F

0.00000

1.000

1.000

Iso shift 1

0.22100

-0.19930

0.00112

1.047

0.861

Width 1

0.42430

0.44784

0.00405

1.424

1.914

Area 1

0.82080

0.68121

0.01320

-1.986

4.744

Quad split 2

0.00000

0.00000 F

0.00000

1.000

1.000

Iso shift 2

0.27560

0.54737

0.00683

0.732

1.611

Width 2

0.98700

0.86965

0.05275

1.168

1.334

Area 2

0.37173

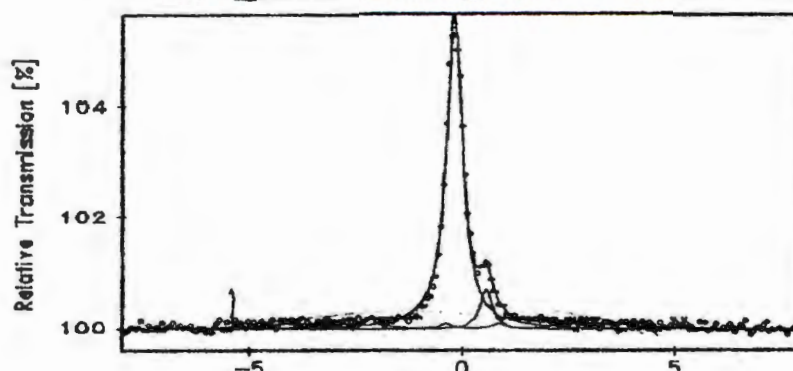
0.09110

0.00467

-0.133

2.357

Ringhals Hotleg HE - Sextet



Parameters for NSext: N magnetic sextets and M quadrupole doublets

fitresults of data :

Ringhals Hot Leg Sample HE

foldingpoint 255.0

geometryeffect 0.199 %

effect 0.078 %

theory C:\PCMO5\NSext.exe

date Tue Oct 27 10:20:24 1998

flags ---CE-

fitspectra 1
chi2 2.5389
chi2-test 0.0000 %
corr-test 0.0000 %

fitcycles 11

maxiter 25

parasig 1

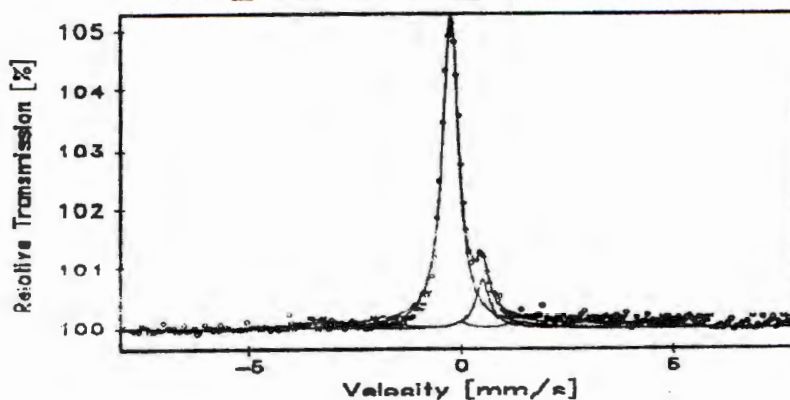
chi2sig 1

fitparameter 10

Baseline	3654606	3656404	243.10587	1.313	1.148
Total Area	-0.05200	-0.03131	0.00065	1.407	1.268
Sextets	1.00000	1.00000 F	0.00000	1.000	1.000
Doublets	2.00000	2.00000 F	0.00000	1.000	1.000
Mag Field 1	24.31120	24.31120 F	0.00000	1.000	1.000
Quad Mag 1	-0.35100	-0.37475	0.12024	0.881	2.057
Shift Mag 1	-0.11950	0.05760	0.06593	2.629	1.332
Width Out 1	0.30000	1.24230	0.28057	1.806	1.649
3:2:1 Corr	1.00000	1.00000 F	0.00000	1.000	1.000
Wnat Mag 1	0.24900	0.24900 F	0.00000	1.000	1.000
Quad Split 1	0.00000	0.00000 F	0.00000	1.000	1.000
Iso Shift 1	-0.22240	-0.20032	0.00137	0.777	1.325
Width 1	0.35670	0.45076	0.00466	2.674	1.242
Area 1	0.59470	0.80471	0.01797	1.679	1.223
Quad Split 2	0.00000	0.00000 F	0.00000	1.000	1.000
Iso Shift 2	0.22480	0.56736	0.00895	1.631	0.895
Width 2	1.18340	0.72779	0.06464	0.882	1.289
Area 2	0.21500	0.07478	0.00537	1.164	0.968

NWU
LIBRARY

Ringhals Hotleg HK - Sextet

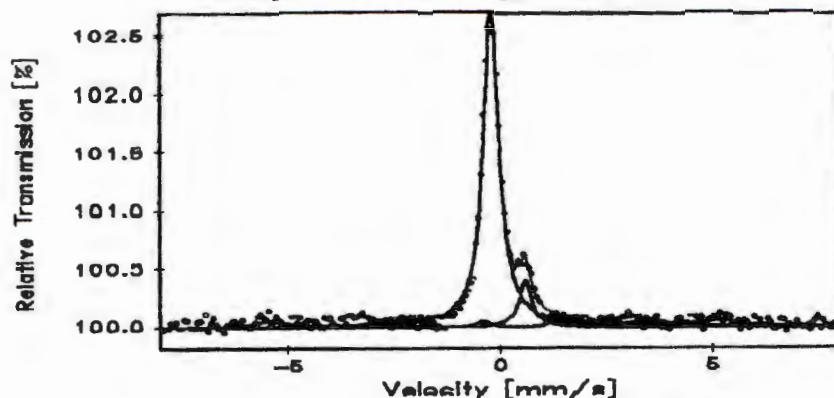


Parameters for NSext: N magnetic sextets and M quadrupole doublets
fitresults of data :

```

hk hotleg
foldingpoint      255.0
geometryeffect    0.195 %
effect            0.078 %
theory            C:\PCMO5\NSext.exe
date              Tue Oct 27 11:03:19 1998
flags             ---CE-
fitspectra        1
chi2               7.6550
chi2-test          0.0000 %
corr-test          0.0000 %
fitcycles          9
maxiter           25
parasis           1
chi2sig            1
fitparameter       18
Baseline           8144771      8141569      384.18175      2.236      -0.014
Total Area         -0.05332      -0.03015      0.00047      2.471      -0.159
Sextets            1.00000      1.00000 F      0.00000      1.000      1.000
Doublets           2.00000      2.00000 F      0.00000      1.000      1.000
Mag Field 1        24.31120      24.31120 F      0.00000      1.000      1.000
Quad Mag 1         -0.53500      -0.29449      0.10824      2.388      -0.375
Shift Mag 1        -0.17159      0.46303      0.05883      1.240      1.303
Width Out 1         0.96700      1.55387      0.26779      -0.153      2.499
3:2:1 Corr         1.00000      1.00000 F      0.00000      1.000      1.000
WNat Mag 1         0.19000      0.19000 F      0.00000      1.000      1.000
Quad Split 1       0.00000      0.00000 F      0.00000      1.000      1.000
Iso Shift 1        -0.20330      -0.26083      0.00098      0.413      1.414
Width 1            0.43897      0.44592      0.00317      0.897      1.651
Area 1             0.82520      0.77280      0.01324      2.172      0.184
Quad Split 2       0.00000      0.00000 F      0.00000      1.000      1.000
Iso Shift 2        0.59432      0.49896      0.00595      0.655      1.684
Width 2            0.74300      0.88528      0.04502      2.604      -0.631
Area 2             0.06321      0.10460      0.00461      3.051      -1.010
    
```

Ringhals Hotleg HL - Sextet



Parameters for NSext: N magnetic sextets and M quadrupole doublets
fitresults of data :

Ringhals Crossover Sample HL

foldingpoint 255.0

geometryeffect 0.192 %

theory C:\PCMO5\NSext.exe

date Fri Oct 23 10:41:43 1998

flags ---CE-

fitspectra 1

chi2 1.6332

chi2-test 0.0000 %

corr-test 0.0059 %

fitcycles 16

maxiter 25

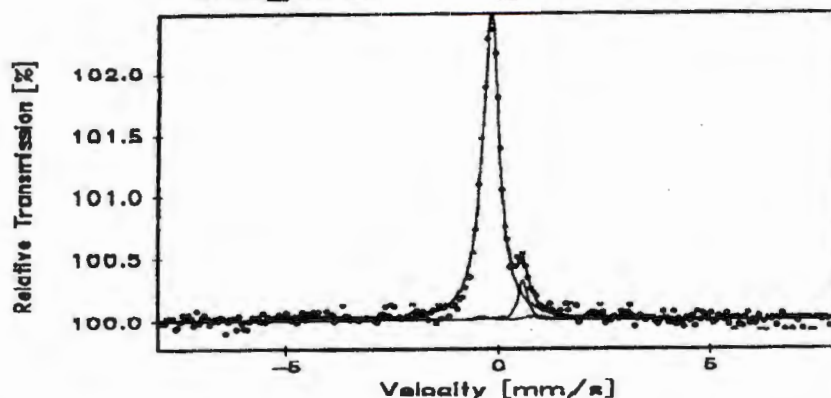
parasig 1

chi2sig 1

fitparameter 18

Baseline	7174840	7176546	407.29925	1.817	0.162
Total Area	-0.00520	-0.01263	0.00058	1.980	0.100
Sextets	1.00000	1.00000	F 0.00000	1.000	1.000
Doublets	2.00000	2.00000	F 0.00000	1.000	1.000
Mag Field 1	24.31120	32.77477	0.57227	1.079	1.351
Quad Mag 1	0.03500	-0.53671	0.12679	1.072	2.908
Shift Mag 1	-0.11590	0.17208	0.06526	2.471	1.647
Width Out 1	1.30000	0.96753	0.32582	-0.159	1.810
3:2:1 Corr	1.00000	1.00000	F 0.00000	1.000	1.000
WNat Mag 1	0.25000	0.25000	F 0.00000	1.000	1.000
Quad Split 1	0.00000	0.00000	F 0.00000	1.000	1.000
Iso Shift 1	-0.20070	-0.20443	0.00197	0.573	1.353
Width 1	0.39660	0.44890	0.00649	1.716	1.146
Area 1	0.82520	0.96182	0.04294	2.073	-0.039
Quad Split 2	0.00000	0.00000	F 0.00000	1.000	1.000
Iso Shift 2	0.58600	0.59351	0.01149	1.015	0.748
Width 2	0.43000	-0.76166	0.08416	1.064	1.681
Area 2	0.03586	-0.10582	0.01094	0.489	1.898

Ringhals Hotleg HM - Sextet



Parameters for NSext: N magnetic sextets and M quadrupole doublets
fitresults of data :

ringhals hotleg sample hm

foldingpoint 255.5

geometryeffect 0.187 %

effect 0.078 %

theory C:\PCMO5\NSext.exe

date Tue Oct 27 11:30:59 1998

flag ---CE-

fitspectra

chi2 1.1108

chi2-test 11.2911 %

corr-test 1.4089 %

fitcycles 22

maxiter 25

parasig 1

chi2sig 1

fitparameter 18

Baseline 5213276 5214167 194.84938 1.067 0.926

Total Area -0.03200 -0.01314 0.00027 1.033 0.971

Sextets 1.00000 1.00000 F 0.00000 1.000 1.000

Doublets 2.00000 2.00000 F 0.00000 1.000 1.000

Mag Field 1 24.31120 22.93489 0.29214 1.011 1.092

Quad Mag 1 -0.05350 -0.85083 0.07886 1.786 1.824

Shift Mag 1 -0.11590 -0.24524 0.04035 1.748 1.941

Width Out 1 0.97800 0.31079 0.13432 1.618 0.729

3:2:1 Corr 1.00000 1.00000 F 0.00000 1.000 1.000

WNat Mag 1 0.25000 0.25000 F 0.00000 1.000 1.000

Quad Split 1 0.00000 0.00000 F 0.00000 1.000 1.000

Iso Shift 1 -0.20460 -0.20570 0.00250 0.904 0.972

Width 1 0.40120 0.46105 0.00797 1.195 1.230

Area 1 0.81980 0.87098 0.01766 1.031 1.006

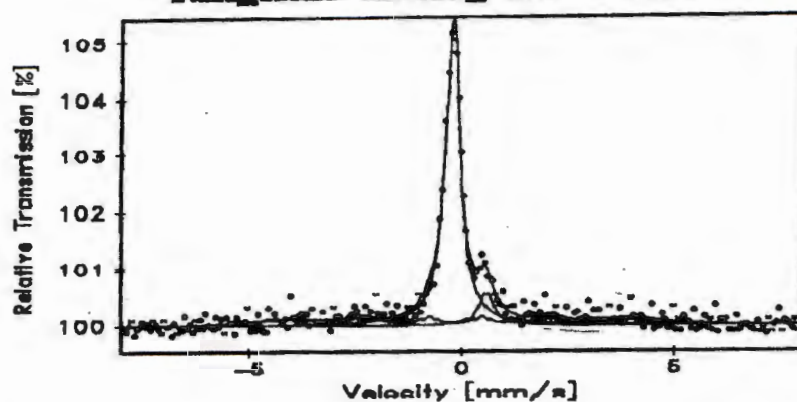
Quad Split 2 0.00000 0.00000 F 0.00000 1.000 1.000

Iso Shift 2 0.57800 0.57641 0.01482 1.002 0.985

Width 2 0.42300 0.58901 0.10330 1.375 0.924

Area 2 0.03686 0.06516 0.00842 1.203 0.917

Ringhals Hotleg HS - Sextet



Parameters for NSext: N magnetic sextets and M quadrupole doublets

fitresults of data :

Ringhals Hot Leg Sample HS

foldingpoint 255.0

geometryeffect 0.197 %

effect 0.078 %

theory C:\PCMO5\NSext.exe

data Tue Oct 27 12:00:10 1998

flags

---CE-

fitspectra

1

chi2

3.3879

chi2-test

0.0000 %

corr-test

14.8195 %

fitcycles

9

maxiter

25

parasig

1

chi2sig

1

fitparameter

18

Baseline

1864813

1867125

175.17629

0.839

1.102

Total Area

-0.03384

-0.03096

0.00091

0.780

1.141

Sextets

1.00000

1.00000 F

0.00000

1.000

1.000

Doublets

2.00000

2.00000 F

0.00000

1.000

1.000

Mag Field 1

24.36630

24.36630 F

0.00000

1.000

1.000

Quad Mag 1

-0.03540

0.07250

0.10063

1.221

0.972

Shift Mag 1

-0.11590

-0.10375

0.05505

0.870

1.444

Width Out 1

1.11400

1.30747

0.23738

1.349

0.559

3:2:1 Corr

1.00000

1.00000 F

0.00000

1.000

1.000

WNat Mag 1

0.19000

0.19000 F

0.00000

1.000

1.000

Quad split 1

0.00000

0.00000 F

0.00000

1.000

1.000

Iso shift 1

-0.23680

-0.21647

0.00185

0.960

0.895

Width 1

0.37840

0.40692

0.00602

1.458

1.073

Area 1

0.82110

0.70671

0.02301

0.932

0.998

Quad split 2

0.00000

0.00000 F

0.00000

1.000

1.000

Iso shift 2

0.25380

0.59187

0.01940

1.506

1.037

Width 2

0.72890

1.05865

0.15964

1.416

1.886

Area 2

0.37145

0.08054

0.00904

1.053

1.688

APPENDIX B - SEM SPECTRA

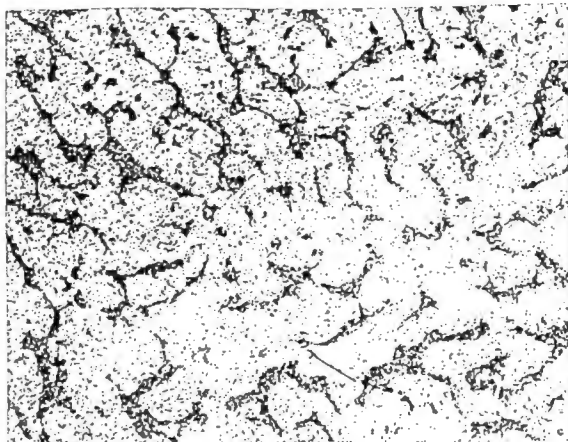
In this Appendix, microphotographs obtained from SEM analysis are presented. The spectra for compositional variations of the samples, determined by SEM fitted with an EDAX are also shown.

APPENDIX B1

SEM MICRO-PHOTOGRAPHS

APPENDIX B1

SEM MICROPHOTOGRAPHS



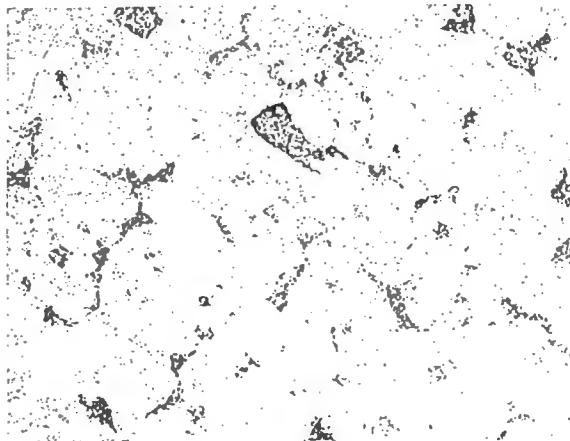
Lab1

4.20 um

Matrix: 512x400
Data Type: Lab1 (ADC)
Magnification: 345x
Image Size: 0.7130x0.5362mm
kV: 10
Tilt: 0
Range: 0 - 2103
Area Fraction: 22.24%

c:\dx4\img\scratch.spc

kV:20.0	Tilt:0.00	Tkoff:34.62	Det:SUTW	Res:140.55	TC:40
FS : 200	LSec : 0	Prst:None	4-Apr- 0	12:24:50	



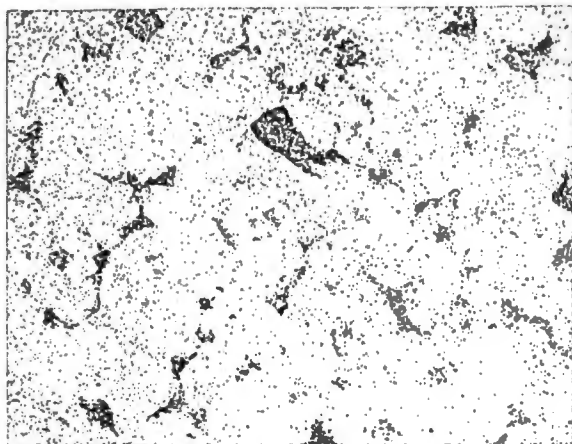
Lab1

4.20 um

Matrix: 512x400
Data Type: Lab1 (ADC)
Magnification: 345x
Image Size: 0.7130x0.5362mm
kV: 10
Tilt: 0
Range: 16 - 2906
Area Fraction: 10.08%

c:\dx4\img\scratch.spc

kV:20.0	Tilt:0.00	Tkoff:34.62	Det:SUTW	Res:140.55	TC:40
FS : 200	LSec : 0	Prst:None	4-Apr- 0	12:24:50	



Matrix: 512x400
Data Type: Lab1 (ADC)
Magnification: 345x
Image Size: 0.7130x0.5362mm
kV: 10
Tilt: 0
Range: 16 - 2906
Area Fraction: 10.08%

Lab1

200um

c:\dx4\img\scratch.spc

kV:20.0

Tilt:0.00

Tkoff:34.62

Det:SUTW

Res:140.55

TC:40

FS : 200

LSec : 0

Prst:None

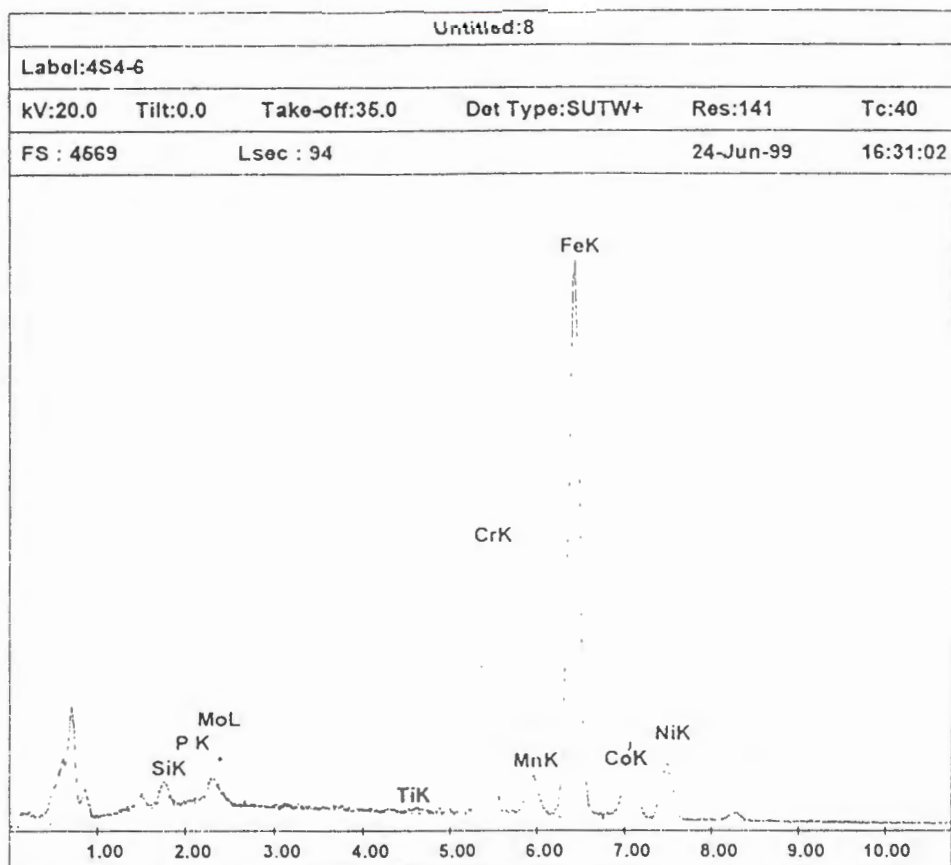
4-Apr-0

12:24:50

APPENDIX B2

Spectra for compositional variations of samples
determined by SEM fitted with an EDAX.

**NWU
LIBRARY**

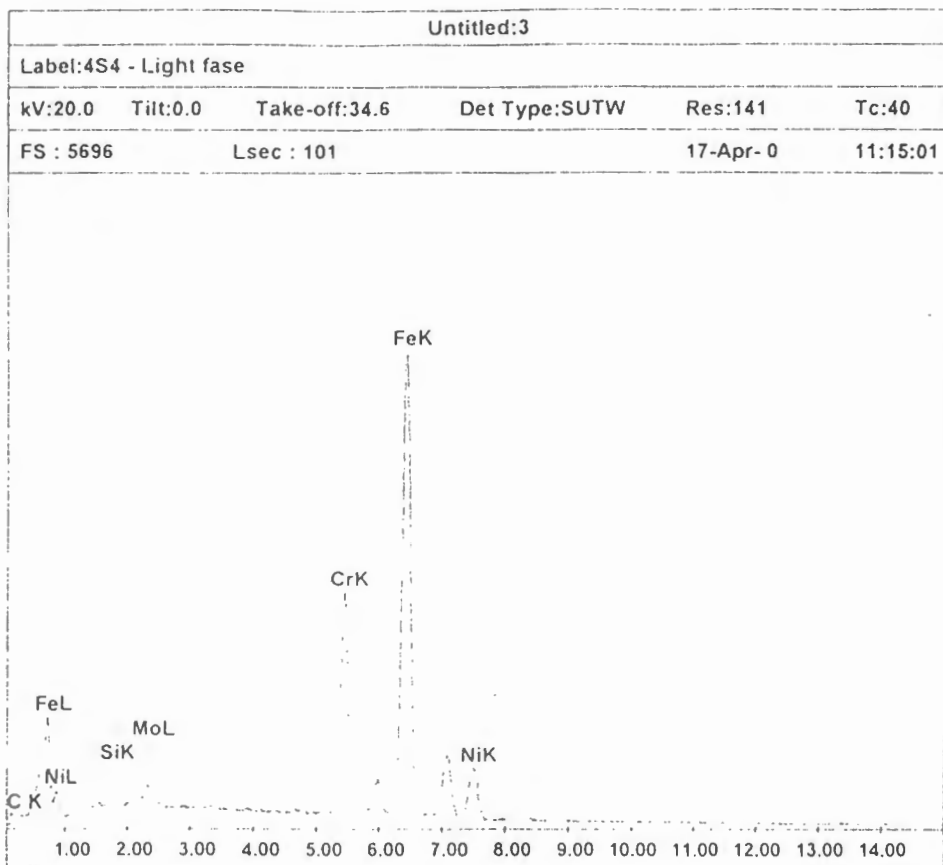


EDAX ZAF Quantification (Standardless)						
Element Normalized						
Element	Wt %	At %	K-Ratio	Z	A	F
SiK	1.27	2.49	0.0062	1.1147	0.4381	1.0018
P K	0.11	0.20	0.0007	1.0897	0.5523	1.0033
MoL	2.59	1.49	0.0186	0.9001	0.7939	1.0019
TiK	0.21	0.24	0.0022	0.9983	0.9591	1.1010
CrK	19.26	20.44	0.2159	0.9970	0.9846	1.1116
MnK	0.87	0.87	0.0086	0.9799	0.9921	1.0121
FeK	64.56	63.80	0.6300	0.9993	0.9643	1.0127
CoK	0.95	0.89	0.0091	0.9801	0.9730	1.0000
NiK	10.17	9.56	0.0931	1.0167	0.9004	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
SiK	16.97	16.99	3.54	1.00
P K	1.70	18.66	27.37	0.03
MoL	19.33	18.02	3.26	1.07
TiK	3.02	14.37	14.21	0.21
CrK	227.62	11.66	0.70	19.51
MnK	7.80	11.17	5.75	0.70
FeK	493.26	9.96	0.47	49.54
CoK	6.03	9.40	6.70	0.64
NiK	51.86	8.28	1.54	6.26
MoK	0.57	0.73	20.54	0.78

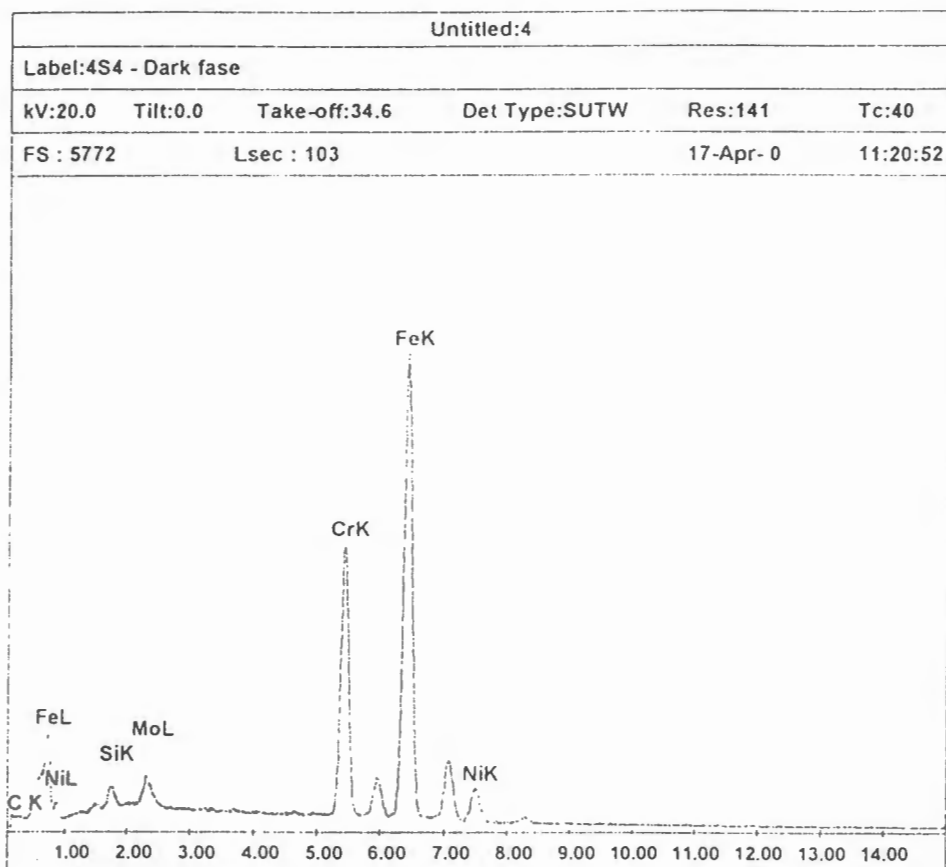
APPENDIX B3

Composition of the Light and Dark phases of the samples
under investigation.



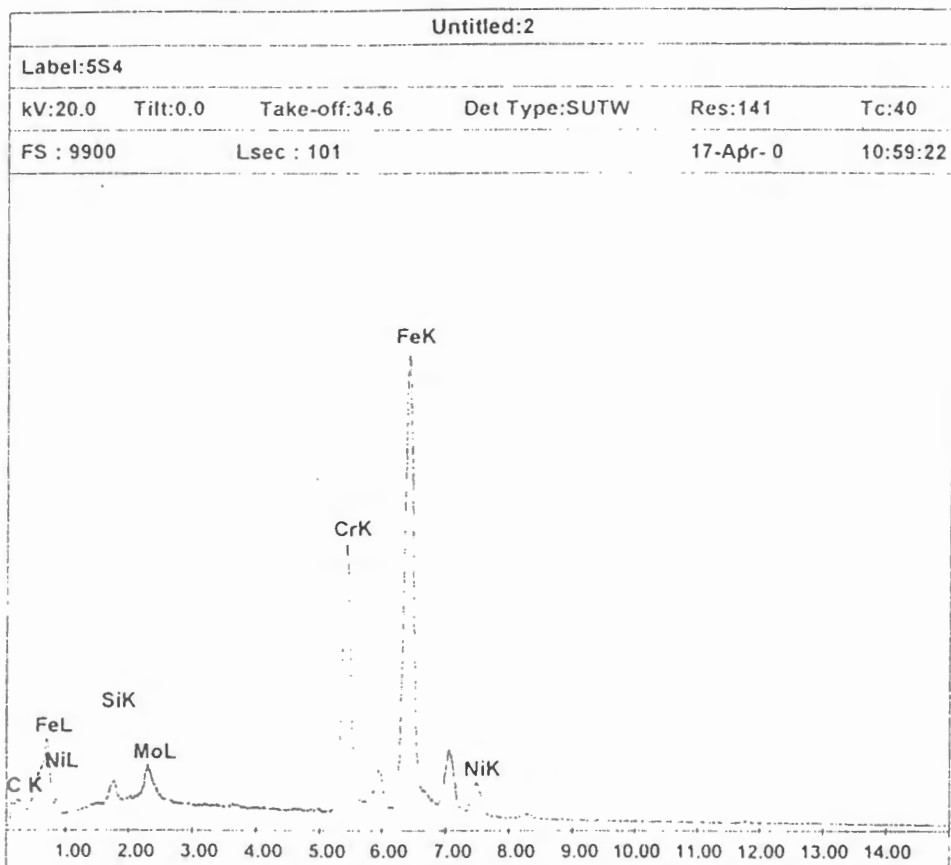
EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
C K	15.08	45.02	0.0335	1.1495	0.1329	1.0003
Si K	1.00	1.28	0.0052	1.0809	0.4792	1.0016
Mo L	2.19	0.82	0.0161	0.8683	0.8438	1.0017
Cr K	16.16	11.13	0.1761	0.9640	0.9924	1.1389
Fe K	55.69	35.73	0.5312	0.9655	0.9742	1.0141
Ni K	9.86	6.02	0.0888	0.9818	0.9177	1.0000
Total	100.00	100.00				



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
C K	8.95	30.84	0.0190	1.1650	0.1829	1.0004
SiK	1.15	1.72	0.0059	1.0956	0.4676	1.0019
MoL	3.05	1.33	0.0224	0.8820	0.8302	1.0021
CrK	21.36	17.20	0.2331	0.9783	0.8891	1.1275
FeK	58.75	44.04	0.5596	0.9801	0.9633	1.0089
NiK	6.83	4.87	0.0617	0.9905	1.9073	1.0000
Total	100.00	100.00				



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
C K	27.04	63.07	0.0665	1.1247	0.2186	1.0023
Si K	0.93	0.93	0.0052	1.0581	0.5294	1.0014
Mo L	3.00	0.87	0.0228	0.8468	0.3567	1.0019
Cr K	16.72	9.01	0.1760	0.9416	0.9974	1.1207
Fe K	46.84	23.50	0.4347	0.9427	0.9762	1.0035
Ni K	5.47	2.61	0.0487	0.9581	0.9298	1.0000
Total	100.00	100.00				