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School of Chemical
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**NUCLEATION OF ACICULAR FERRITE ON NANOPARTICLES ADDED
TO STEEL**

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Abstract

This thesis is mainly a literature research on how to obtain a microstructure of acicular ferrite by nucleation on added nanosized particles to improve the mechanical properties of steels. Also equilibrium calculations with the software FactSage were made on ten selected particle types.

Acicular ferrite is a structure composed of thin laths oriented quite randomly, which makes it hard for irregularities and cracks to spread and thus the mechanical properties of the steel are very good. It is formed using mainly four mechanisms: the reduction of interfacial energy, lattice matching with ferrite, thermal strains and the depletion of elements. These act usually together to enable the nucleation.

The nucleation sites need to be numerous enough for the acicular ferrite to form throughout the steel matrix, but too many particles could cause defects to the structure. The ideal size of the nucleation sites is approximately 400 nm in diameter.

The particles can be added in the form of pellets, wire or powder. Out of these pellet or wire additions are preferred because a powder of nanosized particles is very difficult to handle. The additions can be made during the continuous casting process either in the ladle, the tundish or the mold. The tundish is preferred because the mixing of the particles is assured. But if too much clogging occurs, the mold needs to be considered as a good option because any clogging can then be avoided.

Based on the thermodynamic equilibrium calculations that were made on ten selected particle types, the particles best suited for the addition into the steel melt seemed to be TiN, ZrN and ZrO₂. Although they are not stable in the base steel, CeO₂, CeS and TiO₂ should transform into compounds that could also nucleate acicular ferrite, so they can also be considered to be good options. If all relevant properties of the particles are taken into account, the best options seem to be CeO₂, CeS, TiN and TiO₂.

Keywords Nanoparticles, acicular ferrite, inclusions, steel

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Tämä diplomityö on kirjallisuustutkimus siitä miten saadaan teräkseen lisättyjen nanopartikkeleiden avulla muodostumaan asikulaarisferriittinen mikrorakenne ja sitä kautta paremmat mekaaniset ominaisuudet materiaalille. Lisäksi työssä on laskettu termodynaamisia tasapainolaskelmia FactSage-ohjelmalla kymmenelle valitulle partikkelikoostumukselle.

Asikulaarisen ferriitin rakeet ovat ohuita säleitä, jotka ovat sijoittuneet toisiinsa nähdessä melko satunnaisesti. Tällainen epäsäännöllinen rakenne vaikeuttaa rakennevirheiden ja halkeamien etenemistä ja takaa siten hyvät mekaaniset ominaisuudet. Asikulaarisen ferriitin muodostumisessa vaikuttavat neljä pääasiallista mekanismia: rajapintaenergian pienentäminen, hilan yhteensopivuus ferriitin kanssa, lämpöjännitykset sekä joidenkin alkuaineiden kato. Nämä mekanismit toimivat yleensä yhdessä mahdollistaakseen asikulaarisen ferriitin ydintymisen.

Ydintymispaikkoja, eli partikkeleita, on oltava riittävä määrä, jotta asikulaarista ferriittiä muodostuisi teräksen koko tilavuuteen. Liian suuri partikkelien määrä voi kuitenkin aiheuttaa vikoja rakenteeseen. Partikkelien kokoluokan tulisi olla noin 400 nm.

Partikkelit voidaan lisätä pellettien, langan tai jauheen muodossa. Näistä pelletti- ja lankalisäykset ovat suotavampia sillä nanokokoisista partikkeleista koostuvan jauheen käsittely on haasteellista. Lisäykset voidaan jatkuvavalussa tehdä joko senkkaan, välialtaaseen tai kokilliin. Väliallas on näistä luultavasti paras vaihtoehto, sillä siten saadaan varmistettua riittävä sekoittuminen. Jos kuitenkin aiheutuu liikaa kuromista, täytyy harkita kokillia myös hyvänä vaihtoehtona, sillä silloin vältetään kuromiselta.

Termodynaamisten tasapainolaskelmien perusteella kymmenestä tarkastellusta partikkelikoostumuksesta parhaiten sopivilta lisäyksiltä terässulaan vaikuttavat TiN, ZrN ja ZrO₂. Myös CeO₂, CeS ja TiO₂ voivat olla hyviä vaihtoehtoja, sillä vaikka ne eivät itse ole stabiileja terässulassa, ne muodostavat sellaisia yhdisteitä, jotka ovat myös hyviä asikulaarisen ferriitin ydintäjiä. Jos otetaan huomioon kaikki asikulaarisen ferriitin muodostumiseen vaikuttavat ominaisuudet, parhaiten sopivilta partikkeleilta vaikuttavat CeO₂, CeS, TiN ja TiO₂.

Avainsanat Nanopartikkeli, asikulaarinen ferriitti, sulkeuma, teräs

PREFACE

This thesis was done between October 2012 and February 2013 in the research group of metallurgy at the department of Materials Science and Engineering of the School of Chemical Technology at Aalto University. The thesis is a part of the project Nanoparticle Addition into Molten Steel - NAMOS of the European Union's Research Fund for Coal and Steel (RFCS) programme and has received funding under the grant agreement no. RFSR-CT-2012-00016.

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TABLE OF CONTENTS

1. Introduction	7
2. Nanoparticles in Steel	9
3. Acicular Ferrite	11
3.1. Properties of Acicular Ferrite	14
3.2. Acicular Ferrite vs. Bainite	15
3.3. Benefits of Acicular Ferrite	17
4. Formation of Acicular Ferrite	20
4.1. Formation Mechanisms	20
4.1.1. Interfacial Energy	21
4.1.2. Lattice Match	22
4.1.3. Thermal strains	23
4.1.4. Depletion Zones	24
4.2. Properties of the Suitable Inclusions	26
4.2.1. Size of the Inclusions	26
4.2.2. Amount of Inclusions	28
4.2.3. Composition of the Inclusions	29
4.2.4. Properties of the Added Particles	32
4.3. Properties of the Suitable Steel	34
4.3.1. Austenite Grain Size	34
4.3.2. Alloying Elements of the Steel	36
4.4. Conditions of Formation	37
5. Addition of Nanoparticles into Liquid Steel	38
5.1. Addition Locations	39
5.2. Addition Methods	41

6. Selection of Suitable Nanoparticles	43
7. Equilibrium Calculations.....	45
8. Results and Discussion	46
8.1. CeO ₂	47
8.2. CeS	47
8.3. CuS.....	48
8.4. SiO ₂	48
8.5. TiN.....	49
8.6. TiO ₂	49
8.7. VC.....	49
8.8. VN	50
8.9. ZrN	50
8.10. ZrO ₂	50
9. Conclusions	51
10. References.....	53
Appendix A: Particle properties table	57
Appendix B: FactSage Equilibrium Calculation Results.....	58

1. INTRODUCTION

Steel can be strengthened in several different ways, and often the strengthening needs to be done without compromising ductility or other mechanical properties. The microstructure of the steel has an important role in defining its strength, and in this thesis the focus is on obtaining a strong acicular ferritic structure. The strength of steels can also be enhanced by using several different strengthening methods. The most common methods for strengthening steel can be organized under four categories:

- Work hardening
- Solid solution strengthening by interstitial or substitutional atoms
- Refinement of grain size
- Dispersion strengthening

These methods can also be combined to obtain different types of steel properties. If a combination of several methods is used, it can however be difficult to estimate the total effect on the overall strength. The acicular ferritic structure that is the focus of this thesis can be classified into the grain size refinement category. The small needle-like plates obtained can be considered to be separate grains, and their form and positioning are the reasons why the structure is so strong.¹

There has been an increasing amount of researches in the recent years on the grain refinement of steels by formation of acicular ferrite on non-metallic inclusions². Yield strength levels of for example 550-560 MPa can be reached with an acicular ferritic microstructure³. New steels with better mechanical properties are needed in many applications, like for example the automobile industry where the material should be lighter but better than before for environmental and economical reasons.

The nano scale cannot be defined unambiguously. The definition of a nanosize particle could be for example 1 to 100 nm in diameter⁴. Another definition could be the submicron scale, meaning approximately 1 to 999 nanometers. In this thesis the

later of these two is used to define the nano size. The acicular ferrite forms on small inclusion particles added to the steel. A typical size for these inclusions is about 400 nm in diameter¹.

This thesis is a part of the NAMOS project of the European Union's Research Fund for Coal and Steel programme. The objective of the project is to create a new type of steel with exceptional mechanical properties by adding nanosized particles into molten steel and having acicular ferrite nucleate on them. The particles are added into the melt as such and not formed by precipitation in it so that they could possibly also strengthen the steel by other mechanisms.

The objective of this thesis is to gather all the available information on the conditions, mechanisms and particle properties needed for the formation of acicular ferrite. Thermodynamic equilibrium calculations will then be made to selected potential nanoparticles to obtain more useful information on them.

2. NANOPARTICLES IN STEEL

Generally non-metallic inclusions in steel are seen as harmful to the mechanical properties, and the removal from the steel of such inclusions is quite a big area of research. The addition of certain nano or micro sized particles can however in some cases result in the improvement of the mechanical properties of the steel and the refinement of the grain size.⁵

One possibility is the nucleation of acicular ferrite on the added inclusions, which is the focus of this thesis. Another example are nanoparticles of metal combined with carbon or nitrogen that can be used to improve the mechanical properties like the creep resistance by acting as links between vulnerable regions such as grain boundaries. Especially the addition of very small such particles of approximately 5 to 10 nm is effective to increase the creep resistance of low carbon steels.⁶

One widely used method of strengthening steels by adding nanoparticles is the oxide dispersion strengthening of steels (ODS). It improves the steel's strength at very high temperatures. A special case of oxide dispersion strengthened steels are the thermo mechanically treated ferritic martensitic steels.^{7,8}

The oxide dispersion strengthened steels are strengthened by adding about 0,3 to 0,5 wt-% small oxide particles, very commonly for example yttria particles (Y_2O_3). Figure 1 represents TEM micrographs of ferrite grain boundaries of ODSs decorated by carbides as a result of adding yttria. The carbides formed are responsible for the strengthening of the steel. In the case of a smaller addition of 0,3 wt-% of yttria the formed carbides are smaller and thus better for the mechanical properties, but even the bigger carbides obtained with a 0,5 wt-% addition of yttria result in a better strength than with no additions at all.⁷⁻⁹

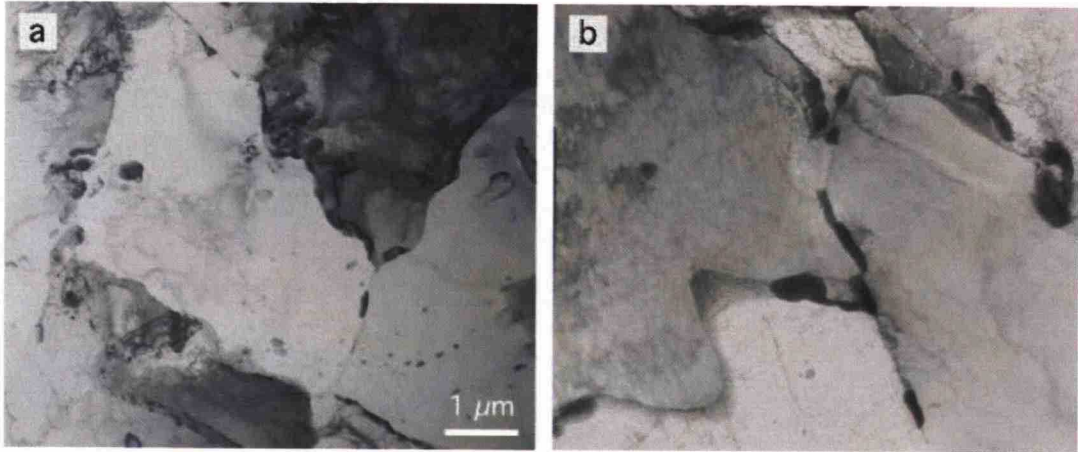


Figure 1: TEM micrographs of ferrite grain boundaries decorated by Cr_{23}C_6 carbides. In (a) the added amount of yttria is 0,3 wt-% and in (b) 0,5 wt-%.⁹

ODSs are however traditionally produced by very complicated and expensive methods of mechanical alloying and powder metallurgy, which is why the dispersion of nanoparticles in thermo mechanically treated ferritic martensitic steels has been developed. The thermo mechanical treatment without particle additions can lead to good mechanical properties up to a temperature range of about 500°C to 600°C, but the addition of particles can elevate the temperature where the steel can be used up to 700°C or even 900°C. The dispersed particles provide obstacles for dislocations so that they will not move and thus strengthen the microstructure. These steels are promising materials for future nuclear fission and fusion reactors, and a good alternative to austenitic steels.⁷⁻⁹

3. ACICULAR FERRITE

The different forms of ferrite can be classified under the following six categories:

- Grain boundary allotriomorphic ferrite (GBA or GBF)
- Polygonal ferrite (PF or IPF)
- Widmanstätten ferrite (WF or FSP)
- Intragranular acicular ferrite (AF or IAF)
- Bainite (B)
- Martensite (M)

The formation of the ferrite microstructures and the choice of which of them is obtained is controlled by different factors including the cooling rate and the metal's chemical composition. In Figure 2 are illustrated the transformation temperatures and carbon content ranges for the formation of some ferrite morphologies.^{5,10}

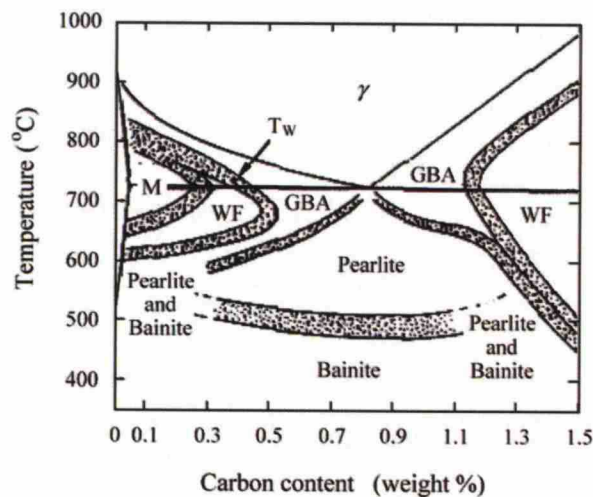


Figure 2: Diagram of transformation temperatures and carbon content ranges for the formation of some ferrite morphologies. The temperatures and carbon contents are the same for acicular ferrite as for bainite.⁵

Grain boundary allotriomorphic ferrite

The term allotriomorphic means in this case that the ferrite structure grows along the grain boundaries without the outer shape being influenced by the inner

crystalline form. The surface form of an allotriomorphic ferrite crystal is not symmetrical to its internal structure.¹¹

Polygonal Ferrite

Polygonal ferrite, also known as blocky ferrite, can nucleate both intragranularly and on grain boundaries. It forms at high transformation temperatures and is not as strong as other ferrite structures, especially ferrite forming on grain boundaries.¹²⁻

¹⁴

Widmanstätten ferrite

Widmanstätten ferrite forms at quite high temperatures and grows in the form of parallel side plates. It can either form primarily on austenite grain boundaries or on allotriomorphic ferrite at the boundaries, or it can form secondarily on already formed plates.¹⁵

Martensite

Martensite is a carbon saturated form of ferrite. The cooling needs to be fast to prevent the diffusion of the iron and carbon atoms resulting in the formation of pearlite. The martensitic microstructure can be either in the form of slats or lenticular plates, the size of which depend on the size of the austenite grains.¹⁶

Bainite

Bainite forms at temperatures between the ones pearlite and martensite form at. It grows in packets of parallel plates but is otherwise very similar to acicular ferrite and also forms in very similar temperatures and other conditions. Bainite is formed at the grain boundaries and acicular ferrite intragranularly.^{5,10}

Acicular ferrite

Acicular ferrite is a structure that was first found in the heat affected zones of low carbon low alloy steel welds, and has also been studied mostly in researches related to welds. The mechanical properties of acicular ferrite are very good compared to most other microstructures, which makes it a favorable structure for other applications than welds as well.¹⁰

The microstructure of acicular ferrite can be described as chaotic. It consists of ferrite plates nucleated intragranularly on small non-metallic inclusions. The plates can virtually radiate in all different directions, resulting in a very unorganized but hard structure (Figure 3).^{1,5,17,18}

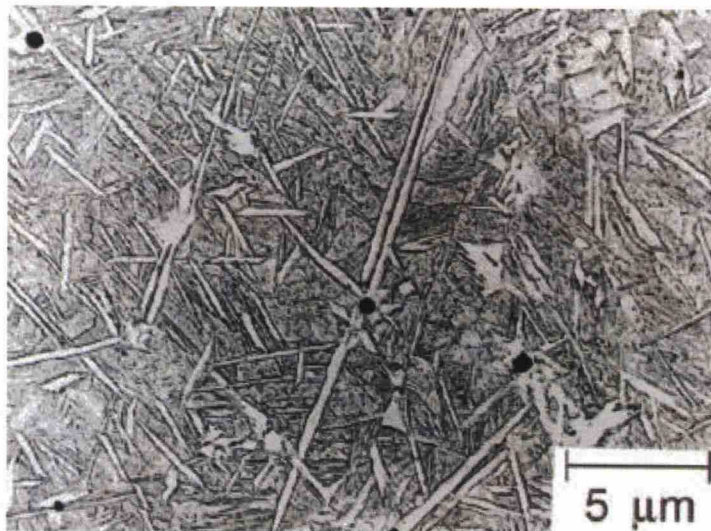


Figure 3: The chaotic microstructure of acicular ferrite in a steel weld deposit by Barritte, 1982.¹⁷

Acicular ferrite gives the steel very good mechanical properties like strength, ductility and toughness. In many cases the strength and toughness of a metal can be determined by the ratio of acicular ferrite in the microstructure.⁵

The other types of ferrite usually grow in the form of packets consisting of parallel plates of the same crystallographic orientation. This organized structure allows cleavage cracks and deformation processes to easily extend across the crystals, which is not favorable for the mechanical properties of the steel. In a microstructure consisting of acicular ferrite the propagating cracks must extend

using tortuous paths, which results in a better toughness. This is the main reason why acicular ferrite can be favored in many cases (Figure 4).^{1,5,14,17,18}

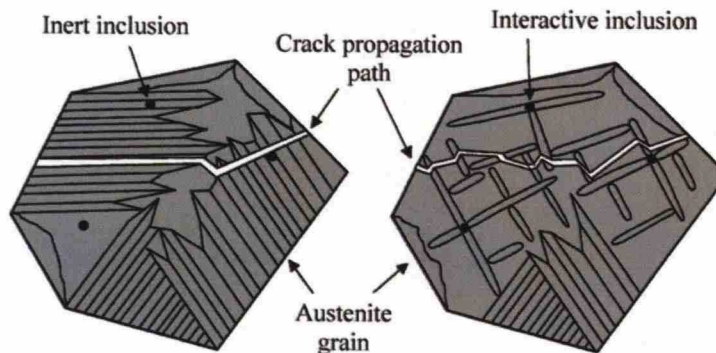


Figure 4: The cleavage crack propagation path for ferrite side plates on the left and acicular ferrite on the right. The crack advances much easier in the plate microstructure.⁵

3.1. Properties of Acicular Ferrite

Acicular ferrite is a hypoeutectoid steel microstructure. According to its name, it is supposedly shaped like needles, and this can be true from a two dimensional perspective. When viewed three dimensionally the structure can however be better described as thin lenticular plates or laths, depending on for example the steel's chemical composition and thermal treatment. The length, width and thickness of the acicular ferrite plates are usually less than about 36, 6 and 3 μm respectively.^{1,10,17,18}

Although the microstructure of acicular ferrite does not make it easy for cleavage cracks and other irregularities to extend further, it is not entirely good for the mechanical properties of the steel. That is because the inclusions can be responsible for nucleating voids and cleavage cracks in the first place. For this reason the number of inclusions must be kept at a minimum and the possible effects of the inclusions' microstructures must be taken into account as well.^{17,18} Acicular ferrite also has a much higher dislocation density than for example Widmanstätten ferrite, $10^6\text{-}10^8 \text{ mm}^{-2}$ compared to $\sim 10^{10} \text{ mm}^{-2}$.⁵ Like bainite, acicular ferrite can also be

divided into upper and lower types, depending on the transformation temperature.¹⁰

3.2. Acicular Ferrite vs. Bainite

Bainite and acicular ferrite are similar in many ways. Their formation mechanisms are essentially the same, their transformation temperatures and cooling rates generally overlap, and the differences between them are mostly a result of their different nucleation sites. While acicular ferrite nucleates at point nucleation sites, the non-metallic inclusions, bainite nucleates at grain surfaces. This results in the bainitic microstructure consisting of sheaves of parallel platelets like the Widmanstätten ferrite.^{1,10,17-19}

The choice of getting either bainite or acicular ferrite can be controlled by changing the ratio between austenite grain surface nucleation sites and intragranular point nucleation sites. If the austenite grain size is bigger and the inclusions within the grains are numerous, acicular ferrite will be obtained. Respectively bainite will be obtained in cases where the austenite grain size is smaller and the ratio of inclusions compared to the number of grains is smaller. This is illustrated in Figure 5.^{1,10,17,19}

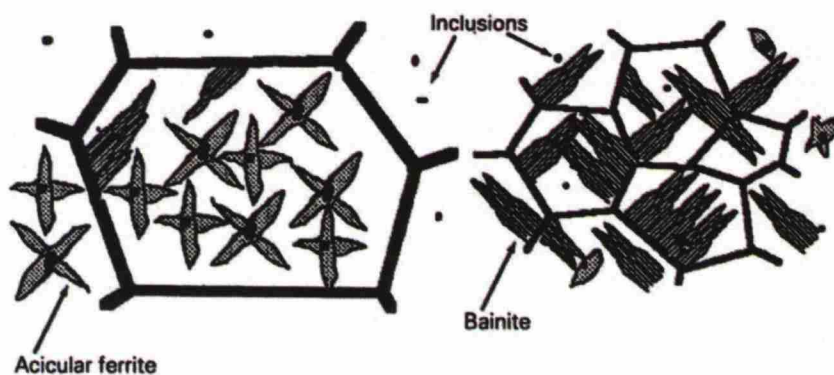


Figure 5: On the left a structure with acicular ferrite formed when the austenite grain size is bigger and there are more inclusions, and on the right a bainitic structure formed when the austenite grain size is refined and there are fewer inclusions.¹

If the conditions in the steel are favorable for acicular ferrite, and bainite is the desired microstructure, they can be changed by for example by using in the manufacturing the special process vacuum arc melting. With the vacuum arc melting a very clean steel is obtained since the inclusions are removed. Another possibility is to leave the inclusions, but to refine the austenite grains.^{1,17,19}

Respectively it is also possible to transform an otherwise bainitic structure into acicular ferrite by making the grain surfaces ineffective as nucleation sites. This can be done by decorating the boundaries with a thin layer of inert allotriomorphic ferrite (Figure 6) or by adding a small amount of boron (30 ppm)^{1,17,19}. The added boron accumulates at the grain boundaries. There it reduces the boundary energy, increases the energy barrier of ferrite nucleation at the grain boundaries and makes the boundaries less favorable for nucleation.¹⁹

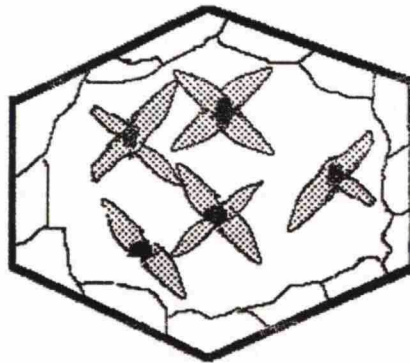


Figure 6: A layer of inert allotriomorphic ferrite at the austenite grain surface makes the conditions more favorable for the formation of acicular ferrite than bainite.¹⁹

The cooling rate also has an impact on the choice between obtaining a microstructure with either acicular ferrite or bainite and martensite. A cooling rate of about 3°C/s is the limit for a microstructure that is mainly acicular ferrite. Faster cooling causes the formation of bainite and martensite.²⁰

The ferrite layer at the austenite grain surfaces should be inert, meaning that it won't develop into Widmanstätten ferrite or bainite at lower transformation temperatures. The layer should of course form before the bainite transformation temperature is reached. The formation of the allotriomorphic ferrite can be

accelerated by adding titanium or slowed down by adding vanadium into the steel.¹⁰ The reason why the allotriomorphic ferrite at the austenite grain boundaries can affect the choice of nucleation sites is that it by nature forms earlier and faster than bainite and especially acicular ferrite, which is one of the last transformation products²⁰.

It has been experimentally confirmed that the heat treatment for obtaining an inert layer of ferrite and thus intragranular acicular ferrite must be done as illustrated in Figure 7. The bainite or acicular ferrite transformation temperature T_b is approximately 500°C. Inert ferrite resulting in a transformation to acicular ferrite was obtained with a holding at $T_\alpha \approx 660^\circ\text{C}$ and active ferrite resulting in a transformation to bainite was obtained with a holding at $T_\alpha \approx 740^\circ\text{C}$ (Figure 7).¹⁹

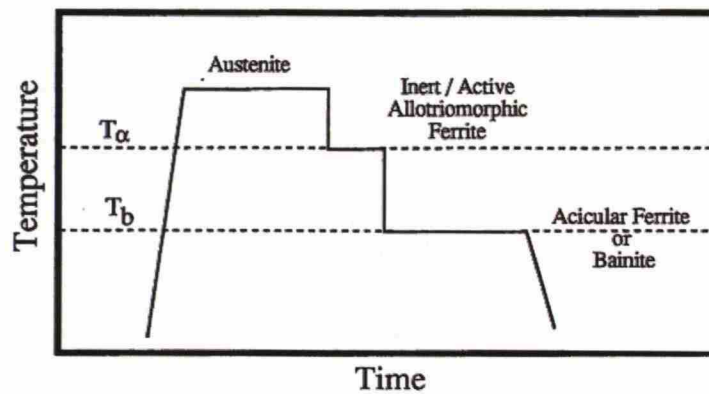


Figure 7: The heat treatment needed for obtaining an inert layer of ferrite at the austenite grain surfaces, so that acicular ferrite will form. $T_b \approx 500^\circ\text{C}$; Holding temperature $T_\alpha \approx 660^\circ\text{C}$ for inert ferrite and $T_\alpha \approx 740^\circ\text{C}$ for active ferrite.¹⁹

3.3. Benefits of Acicular Ferrite

If we want to obtain a microstructure with a good strength and a fine grain size, and want to do it in a traditional way by having ferrite nucleate at the austenite grain boundaries, we need to have a fine austenite grain size. This can be difficult to achieve, since the austenite grain size is in many cases very coarse by nature. In these situations the formation of acicular ferrite is very beneficial, since it on the contrary needs big austenite grains to form so that the intragranular nucleation

sites are numerous compared to the grain boundary nucleation sites, and the result is actually even better for the mechanical properties of the steel than with the traditional method.^{14,21}

A tensile strength that can be obtained in the case of ultra fine grain sized (2-3 μm) acicular ferrite is approximately 750 N/mm^2 with 80 Joules of impact energy at -100°C . The tensile strength of steels is normally approximately 500 N/mm^2 .²¹

An acicular ferritic structure ensures a very good strength and toughness to fire resistant steels at high temperatures. Another good quality of the structure is the superior stress-corrosion-cracking resistance in line-pipe steel grades. Steels used in the construction of ships and pressure vessels are also expected to benefit from this structure. With an increased proportion of acicular ferrite in the microstructure, the strength and toughness of the steel are increased and the fracture-appearance transition-temperature is lowered. This can be seen for the yield strength and the fracture-appearance transition-temperature in Figure 8.^{5,14}

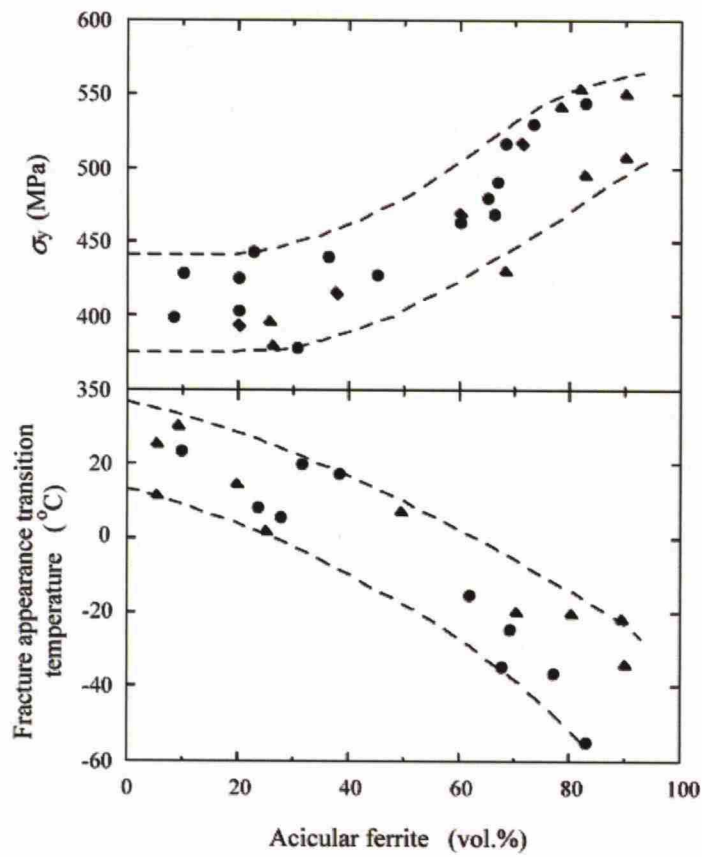


Figure 8: The effect of the proportion of acicular ferrite in C-Mn-Nb weld metals on the yield strength and the fracture-appearance transition temperature of the steel.⁵

4. FORMATION OF ACICULAR FERRITE

The formation of acicular ferrite has been studied by many in the last few decades, but it is still quite uncertain what the mechanisms in more details are and what are the detailed properties of the inclusions responsible for the nucleation. It has been however deduced that for example the chemical composition of the suitable inclusions is often a combination of an individual impurity element, most often S, O or N, and of an alloying element such as Mn, Al, Si, Ti or Ce.^{1,5}

Acicular ferrite's nucleation mechanism is similar to bainite's, making it intragranularly nucleated bainite, but in some cases a very similar structure can actually be Widmanstätten ferrite or a mix of it and bainite. The formation mechanism of Widmanstätten ferrite is however different from bainite's, which is why the term acicular ferrite is usually reserved to the fine structure resembling bainite to avoid confusions.^{10,17}

Although acicular ferrite plates nucleate on small non-metallic inclusions, such an inclusion can be observed in only approximately 7 to 13 % of the plates. This is probably due to the autocatalysis effect, which means that the plates can not only nucleate from the inclusions but also from other already nucleated plates.^{1,10,17}

4.1. Formation Mechanisms

It is rather difficult to study the nucleation mechanism because of the complex multiphase microstructures of the inclusions, which is why no entirely confirmed or lone theories about it are available to date.^{1,5,17}

The following four mechanisms and phenomena are considered to have an effect on the acicular ferrite formation:

- The reduction in the interfacial energy at the surface of the inclusions
- Lattice mismatch strains between the inclusions and ferrite
- Thermal strains at the inclusions

- The depletion of elements such as Mn near the inclusions

These mechanisms are often found to work together to promote the nucleation of acicular ferrite plates on the non-metallic inclusions, but their individual importance for the nucleation in each different situation has not been determined.⁵

4.1.1. Interfacial Energy

The nucleation of ferrite at inclusions needs more energy than the nucleation at austenite grain boundaries. But the heterogeneous nucleation at inclusion does need less energy than the homogeneous nucleation.⁵

The inclusions are in general less favorable for nucleation because of their curved shape. It can be seen in Figure 9 that the austenite grain boundary is energetically a more favorable nucleation site regardless of the inclusion size, but also that the amount of energy needed for nucleation at inclusions starts to significantly grow when the inclusion size is less than about 0,5 μm in radius. This is explained by the more sharply curved shape of the smaller inclusion particles compared to the steel's microstructure.⁵

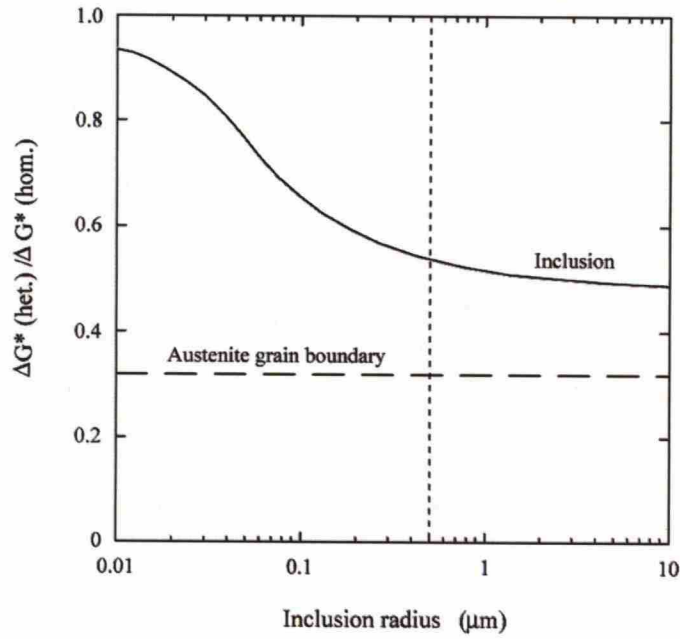


Figure 9: Effect of the particle radius on the energy barrier for nucleation of acicular ferrite at inclusions. ⁵

A low interfacial energy is also favorable for keeping the inclusions in the steel, since a high interfacial energy is beneficial for them to be removed from the melt at the surface. ²²

4.1.2. Lattice Match

The popular theory about lattice matching has been extrapolated from similar phenomena in aluminum to the formation of acicular ferrite in steels. The inclusions with the best "lattice match" with ferrite are considered to be the best for the nucleation of ferrite. Low mismatch strains between the inclusions and ferrite imply a simple crystallographic orientation relationship between them. ^{1,5,17}

To compare the different inclusions with each other, a mean percentage planar misfit value K is used. It is calculated with Bramfitt's equation, eq. 1. The inclusions are assumed to be faceted on a plane $(h\ k\ l)_i$ and the ferrite to deposit epitaxially with $(h\ k\ l)_\alpha \parallel (h\ k\ l)_i$, with corresponding rational directions $[u\ v\ w]_i$ and $[u\ v\ w]_\alpha$ inclined at an angle ϕ to each other. In the equation d_x are the interatomic spacings along three directions $j = 1, 2, 3$. ^{1,5,17}

$$K = \frac{100}{3} \sum_{j=1}^3 \frac{|d_j^I \cos \Phi - d_j^\alpha|}{d_j^\alpha} \quad (1)$$

In Figure 10 are illustrated the lattice matches of δ -iron and TiC or WC. TiC has a lower misfit with ferrite and has therefore more potential for nucleating ferrite. ⁵

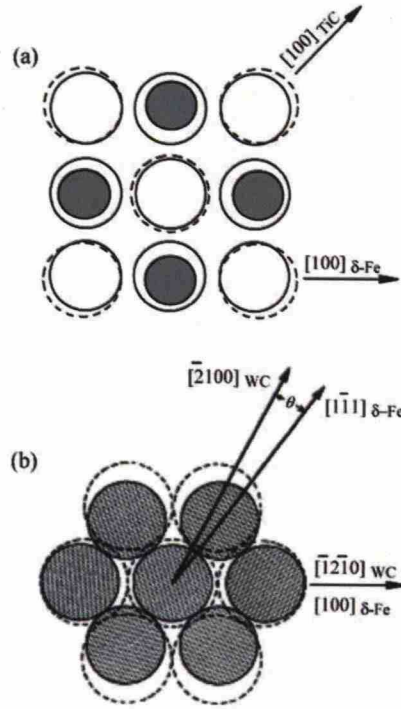


Figure 10: Lattice match between δ -iron and TiC (a) & WC (b). ⁵

4.1.3. Thermal strains

The thermal expansion coefficients of the non-metallic inclusions and of the steel are usually different. This causes stresses when the temperature is cooled down. The bigger the difference in the values of the thermal expansion coefficients, the higher will the stresses and thus the strains in the steel matrix be and the easier will it be for the acicular ferrite to nucleate. In Figure 11 are shown the thermal expansion coefficients for different chemical compositions of inclusions and they can be compared to the coefficient of austenite. The probability for acicular ferrite nucleation increases from the left to the right. ⁵

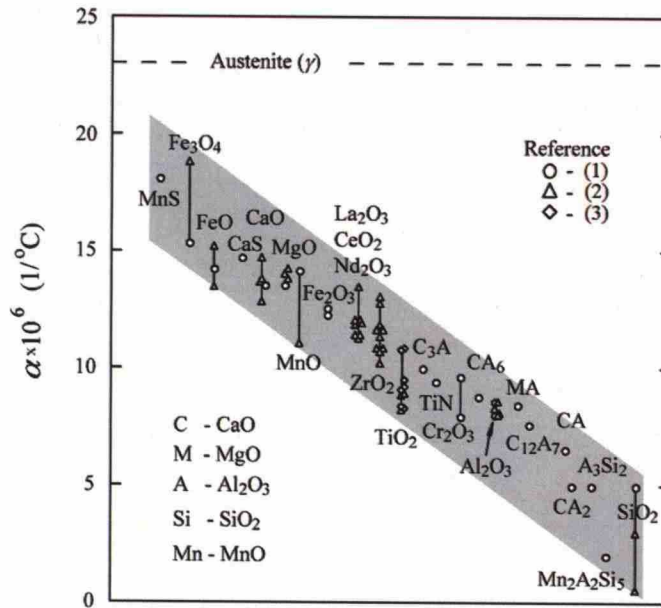


Figure 11: Thermal expansion coefficients for different inclusion compositions. Original references: (1) Brooksbank & Andrews, J. Iron Steel Inst., 1972 ; (2) The Physical-chemical properties of Oxides, 1978; (3) Touloukian, The Thermo-Physical Properties of High Temperatures of Solid Materials, 1967. ⁵

Differences in the values of the thermal expansion coefficients are not expected to have such an important influence on the nucleation of acicular ferrite in cases where the inclusions are added and stay in solid state compared to cases where the inclusions precipitate from a liquid state. This is because contraction stresses are not expected to form in equivalent magnitudes. ¹⁸

4.1.4. Depletion Zones

The depletion of some elements, such as boron, carbon ¹⁸ or manganese in the surroundings of the nucleation inclusions can also promote the formation of acicular ferrite. Mn is the most common depleted element related to this phenomenon.

The Mn-depleted zones, or MDZs, are areas near precipitated MnS inclusions where the Mn concentration has decreased because of the formation of the inclusions. An increased Mn concentration in the steel is known to promote the enlargement of austenite zones and respectively a decrease of the concentration reduces them.

Therefore the probability for an acicular ferrite nucleation in a MDZ near a MnS inclusion increases. This effect can be observed in Figure 12, where the activation energy of the nucleation is shown at different inclusion radii and Mn contents of the MDZs. With 0 wt-% of Mn the activation energy of the heterogeneous ferrite nucleation at inclusions of a radius bigger than approximately 0,3 μm is even lower than for the nucleation at austenite grain boundaries. The MnS inclusion is often located near another more effective inclusion (Figure 13), and several other formation mechanisms will then also affect the acicular ferrite formation. MnS inclusions alone are usually not sufficient for activating the nucleation.⁵

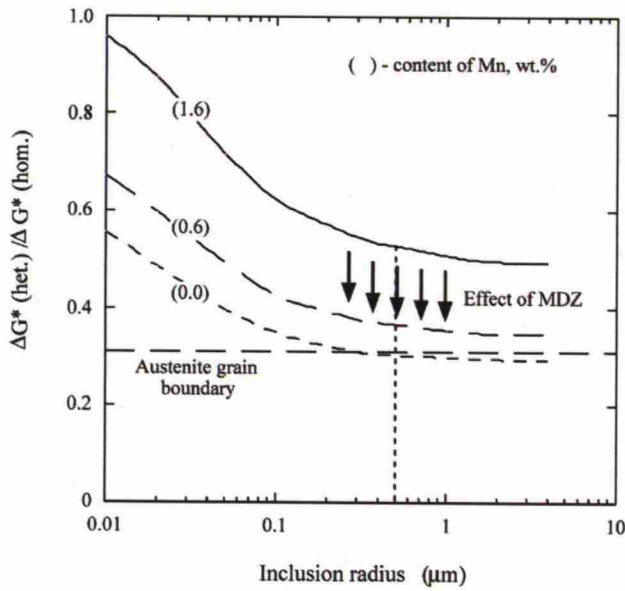


Figure 12: The effect of the Mn-content in MDZs on the activation energy of a heterogeneous ferrite nucleation.⁵

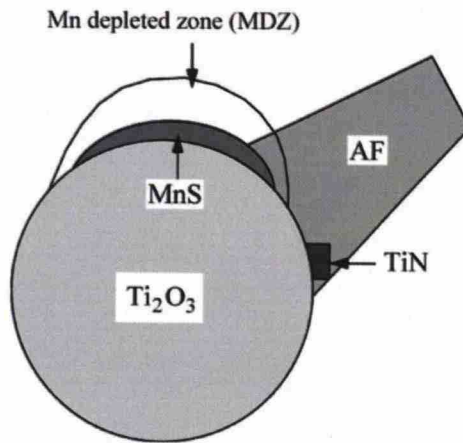


Figure 13: Nucleation of acicular ferrite on a Ti_2O_3 inclusion near a MDZ next to a MnS inclusion.⁵

4.2. Properties of the Suitable Inclusions

The inclusions acting as nucleation sites in the formation of acicular ferrite need to be carefully selected in order to obtain the best possible properties and the biggest fraction of acicular ferrite. The size, amount and chemical composition have a major influence on the final result. In many cases the inclusions are not added directly with their final chemical composition, but they are precipitated partially or even entirely from alloying elements of the steel⁵. However in the case of this thesis the objective is to have the acicular ferrite form directly on particles added to the molten steel without having them melt or react significantly with the steel matrix. Special attention needs therefore to be paid to the chemical composition of the particles.

4.2.1. Size of the Inclusions

As can be seen in Figure 9 the energy barrier for ferrite nucleation decreases significantly when the particle size grows in the range from about 0 to 1 μm in radius. After that the energy barrier doesn't decrease so much anymore, so no major advantage can be gained from that point of view if the particles are bigger. The smaller the particles are, the better is it in general for the steel's mechanical

properties, because smaller particles deform the steel matrix less than bigger particles.⁵ In Figure 14 is illustrated the effect of the particle size distribution on the nucleation potency. The peak is reached at roughly $1\text{ }\mu\text{m}$.²³

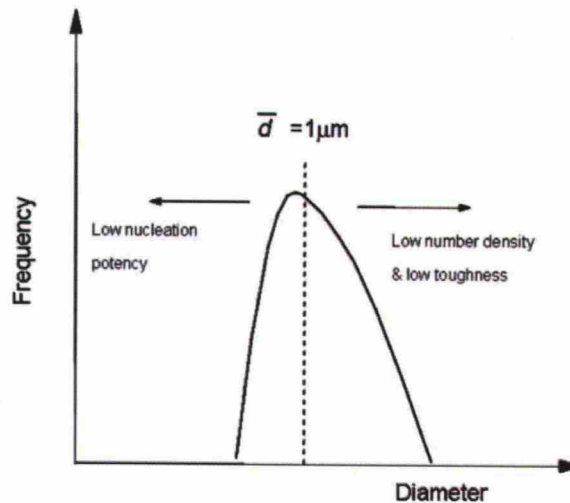


Figure 14: Effect of the size distribution of the particles on the nucleation potency²³

Many have also tried to determine experimentally the best size of inclusions for the acicular ferrite nucleation. Depending on the case, the obtained size ranges have been for example $0,4 - 0,8\text{ }\mu\text{m}$, $0,25 - 0,8\text{ }\mu\text{m}$ or $\sim 0,4\text{ }\mu\text{m}$. The results of one experimental research as can be seen in Figure 15 also indicate that the probability for acicular ferrite nucleation increases quickly between about $0,4\text{ }\mu\text{m}$ and $0,8\text{ }\mu\text{m}$. With such small inclusions one major benefit is that because of their size they don't have a negative effect on the mechanical properties of the steel.⁵

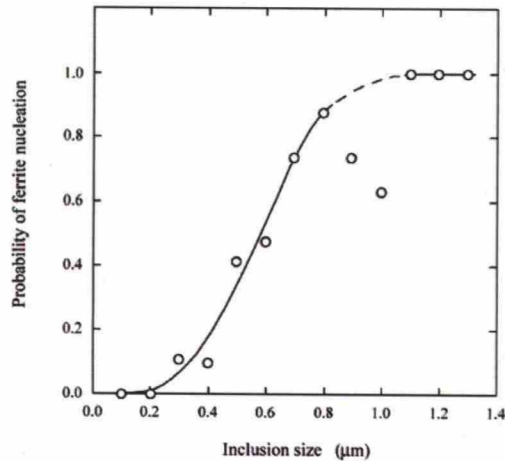


Figure 15: Effect of the inclusion size on the probability of ferrite nucleation. ⁵

To obtain an optimal inclusion size the added particles need to be either directly of the wanted size or should reach it by forming agglomerates. In the case of particles directly big enough there is however a risk of some agglomeration happening as well, and the formed inclusion would then possibly be so big that they could have an unwanted impact on the steel's mechanical properties. From this point of view the choice of smaller additions that will agglomerate into bigger inclusions is safer.

4.2.2. Amount of Inclusions

The amount of inclusions is also a very important factor in the formation of acicular ferrite. There should be enough inclusions to enable the nucleation of acicular ferrite and not obtain for example bainite. On the other hand, although single inclusions are so small that they are not harmful to the mechanical properties of the steel, a large number of inclusions can have a combined negative effect and cause irregularities in the microstructure. It is possible that the volume fraction of the inclusions is even more important in the formation of acicular ferrite than their type or size distribution. ^{5,18} An important fraction of inclusions in the steel can also cause nozzle clogging making it difficult or impossible to use the continuous casting method. The clogging is however not a problem if the particles are not added before the mold. ²²

Depending on the size of the inclusions, a different fraction of them are active as nucleants for acicular ferrite (Figure 16). The fraction of active nucleants for each size range was calculated as the product of the inclusion number and the probability of acicular ferrite nucleation, from Figure 15.⁵

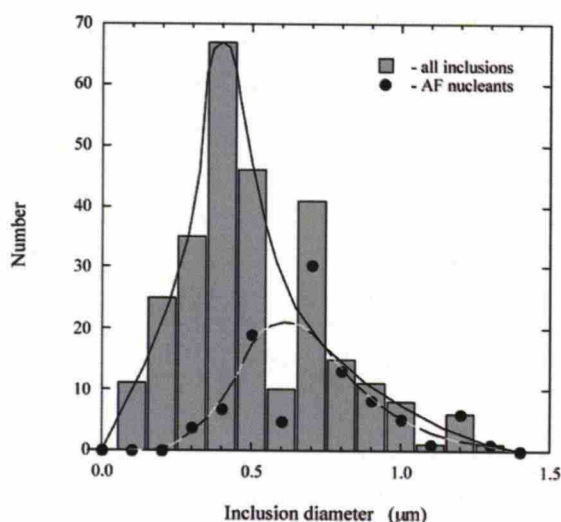


Figure 16: The influence of the size and number of the inclusions on the fraction of those that are active nucleants for acicular ferrite formation.⁵

It can be deduced that the inclusions with sizes from about 0,5 to 0,8 μm have the biggest impact on the acicular ferrite nucleation, since their total number is large and the fraction of active nucleants is quite big too. However, the fraction of active nucleants in different size and number categories of inclusions does not have a direct impact on the ratio of acicular ferrite in the formed structure. Other factors, such as the precipitation ratio of MnS inclusions, also affect the formation of the acicular ferrite structure. The autocatalysis effect also ensures that microstructures with over 80 % of acicular ferrite can be obtained with various inclusion sizes and numbers.⁵

4.2.3. Composition of the Inclusions

The chemical composition of the inclusions is a key factor in the nucleation process. To understand the role of the inclusions in stimulating the nucleation of the ferrite

it is important to also observe the microstructure of inclusions that have nucleated this structure. Many different chemical compositions and combinations of them have been found to enable the nucleation.^{1,17,18}

The inclusions on which acicular ferrite can nucleate can be classified into oxides, nitrides and sulfides according to their chemical composition. Certain complex and multiphase inclusions, which are a mix of the three categories, can naturally also act as nucleation sites.^{5,18} Also some carbides are considered to be able to nucleate acicular ferrite²⁴.

In the oxides category, especially Ti-oxides have been found to be very effective. These include TiO, that has a low misfit with ferrite and a simple orientation relationship, Ti₂O₃ and (Ti,Mn)₂O₃ in some Mn-bearing steels as well as MnTiO₂ formed in a C-Mn steel killed with only titanium and when the Ti content is more than 50 ppm. Active Ti₂O₃ inclusions can also be obtained by adding Ti to wrought C-Mn steels. Other examples of acicular ferrite nucleating inclusions are some specific Si-Mn oxide inclusions and galaxite inclusions, such as galaxite spinel MnO*Al₂O₃ with a high thermal expansion difference from iron. These galaxite inclusions, which are actually aluminium-manganese silicates, can form in steels that have been deoxidized by Al and that contain Mn.^{5,18} Also zirconium oxides, like ZrO₂, have been studied as inclusion sites².

In the nitrides category, TiN has been studied the most. The results on its effectiveness for nucleating acicular ferrite are however contradictory in different studies done by different researchers. The reason why it might be effective is its good coherency with ferrite. Also the results on the effectiveness of VN inclusions are contradictory.^{5,18}

The most important sulfide related to the nucleation of acicular ferrite is MnS. It is not an active nucleant itself but next to other inclusions the Mn-depleted zone created around it can help the nucleation significantly (Figure 13).^{5,18} Especially together with titanium oxides the manganese depleted zones caused by MnS are effective nucleants of acicular ferrite. It is strongly suspected that neither titanium

oxides nor manganese sulfides would be able to act as nucleation sites on their own.
25

Also cerium sulfide particle dispersions are very promising for nucleating acicular ferrite. The inclusions are formed by the addition of cerium and sulfur into the steel and consist of CeS , Ce_3S_4 and $\text{Ce}_2\text{O}_2\text{S}$ compounds. Their benefits are that they have a good lattice match with ferrite and they are stable at liquid metal temperatures. In Figure 17 are illustrated the acicular ferrite percentages that can be obtained by varying the cooling rate for three different base steels containing cerium sulfides.²¹ When adding cerium, the dissolved oxygen content needs to be minimal for cerium sulfides to form instead of oxides²².

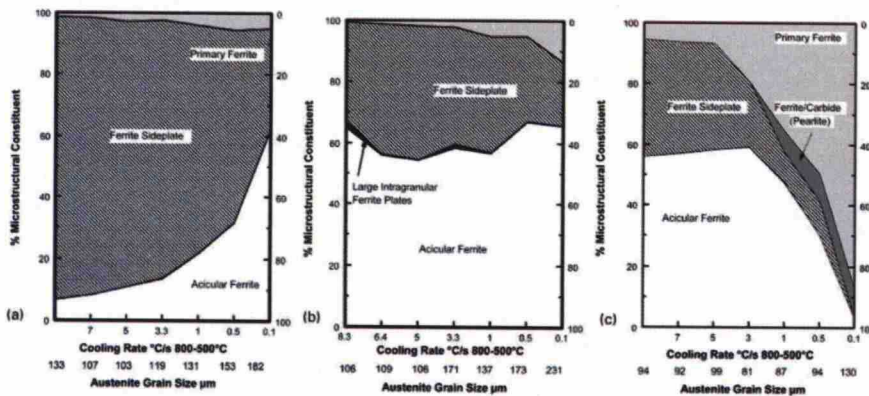


Figure 17: The obtained microstructure constituents at different cooling rates, austenite grain sizes and base hardenability for the different base steels containing cerium sulfides. (a) Fe-0,06Ce-0,014S-0,0016O ; (b) Fe-0,02Ce-0,018S-0,0017O ; (c) Fe-0,02Ce-0,019S-0,0013O²¹

Compared to simple oxides, sulfides and nitrides complex oxy-sulfides and multi-phase inclusions are in general much more effective in nucleating acicular ferrite. This is because they can take advantage of several formation mechanisms at once.⁵

In studies of submerged arc weld deposits the inclusions that nucleated acicular ferrite have been found to be inhomogeneous, containing several different oxides and sulfides^{1,17}. (Mn, Ti)-silicates and (Mn, Cu)S are good examples of complex inclusions capable of nucleating acicular ferrite. The composition of the complex inclusions often varies from the center to the surface.⁵

Ti and Ti-Ca oxy-sulfides as well as TiN-MnS complex precipitates have been found to be very effective nucleants for acicular ferrite. For example Ti_2O_3 inclusions need MnS or TiN precipitations on their surface to become effective nucleants. They also seem to be inert in Mn-free steels but active in Mn-containing steels.⁵

4.2.4. Properties of the Added Particles

Certain specific properties are needed from the added nanoparticles to have them spread evenly to the steel matrix, not disappear or deform and not float into the slag.

Pushing or engulfment by the solidification front

During the solidification of the steel the inclusions interact with the advancing solidification front. The inclusions are either engulfed or pushed by the solidification front. In the case of engulfment an even distribution of particles in the solid steel is obtained, but since the solidification advances from the sides of the slab, the scenario of the front pushing the inclusions results in a higher concentration of particles in the central part of the slab. An illustration of the solidification front can be seen in Figure 18. Particles smaller than the primary dendrite arm spacings should be engulfed when they enter the boundary layer region and touch the solidifying steel shell²⁶. To control the behavior of pushing or engulfment of particles at the solidification front, the main factor that can be influenced is the solidification front's velocity. It needs to be slow enough to allow the engulfment of the added particles. The smaller the particles are, the slower should be the solidification front's velocity.²⁷

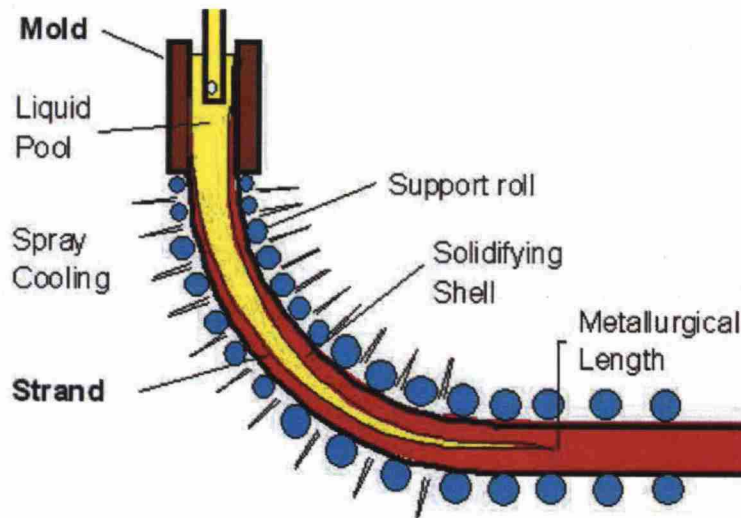


Figure 18: The solidification front in continuous casting²⁶

Agglomeration

Since a specific size of inclusions is needed, depending on the size of the added particles either no agglomeration at all or just some of it will be needed to obtain the best possible inclusion size for the nucleation of acicular ferrite. The wetting of the particles as well as the mixing and stirring of the steel must be optimized to result in the wanted amount of agglomeration.

Wetting

A good wetting of the particles by the steel is required to lower the interfacial energy. Also, it is considered to be much easier for the particles to float into the slag out of the steel matrix or to agglomerate with other particles if the wetting is bad. A good wetting means that the contact angle between the particle and the steel should be as small as possible.²⁸

Density

To prevent the particles from floating out of the steel matrix or sinking downwards in the melt, their density should be as close as possible to the density of the surrounding steel. If the particles are less dense than the steel they will easily float

into the slag and respectively very dense particles could easily sink in the melt causing an uneven distribution.

4.3. Properties of the Suitable Steel

The chemical composition and other qualities of the steel itself have a major effect on the final microstructure and mechanical properties. The formation of acicular ferrite has been studied mostly in low to medium carbon steels, with fairly low amounts of alloying elements. Steels with these qualities can in general be considered to have properties allowing the nucleation of acicular ferrite. The alloying elements and their amounts have an important effect on the amount of acicular ferrite that is obtained, but the result can vary a lot depending on for example the carbon content and the other alloying elements. Therefore not all the details about the effects of alloying elements that are mentioned below can be applied to all types of steel.^{5,10}

The steel compositions in studies involving acicular ferrite nucleation on particles vary a lot. Therefore it can be concluded that the variation of the nucleation inclusions and other parameters can make it possible to have acicular ferrite nucleate with many different types of base steels.^{2,3,14,18}

4.3.1. Austenite Grain Size

The austenite grain size also affects the nucleation, but the optimal size varies depending on the steel and its alloying elements. In one study it was found to be approximately 80 μm (Barbaro et al., 1989), but in another one about 180-185 μm (Lee et al., 1995).⁵ In either case a smaller grain size would result in the formation of bainite and as usually it is preferred in this case as well to have the smallest possible grain size to get the best possible mechanical properties.¹⁰ Also the further increase of the austenite grain size would need a decrease of the amount of inclusions, which would result in the fraction of acicular ferrite decreasing as well.

The effect of the austenite grain size on the fraction of acicular ferrite can be seen in Figure 19. It can also be seen that at a slower cooling rate the austenite grain size has a bigger effect but at a faster cooling rate more acicular ferrite is obtained at all grain sizes making the austenite grain size a less important factor than the cooling rate.⁵

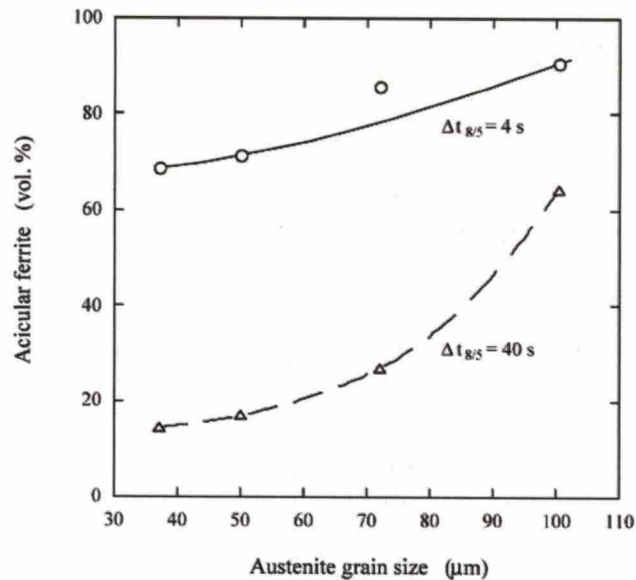


Figure 19: The influence of the austenite grain size on the amount of nucleated acicular ferrite at two different cooling rates. $\Delta t_{8/5}$ is the cooling time from 800 to 500°C.⁵

The austenite grain size also has an impact on the amount of inert allotriomorphic ferrite formed at the grain boundaries. A smaller grain size increases the fraction of the inert ferrite and decreases the areas of austenite where the acicular ferrite plates form. The plates are therefore smaller, and this improves the strength and toughness of the steel since the number of barriers in the micro crack propagation path is increased (Figure 20).²⁰

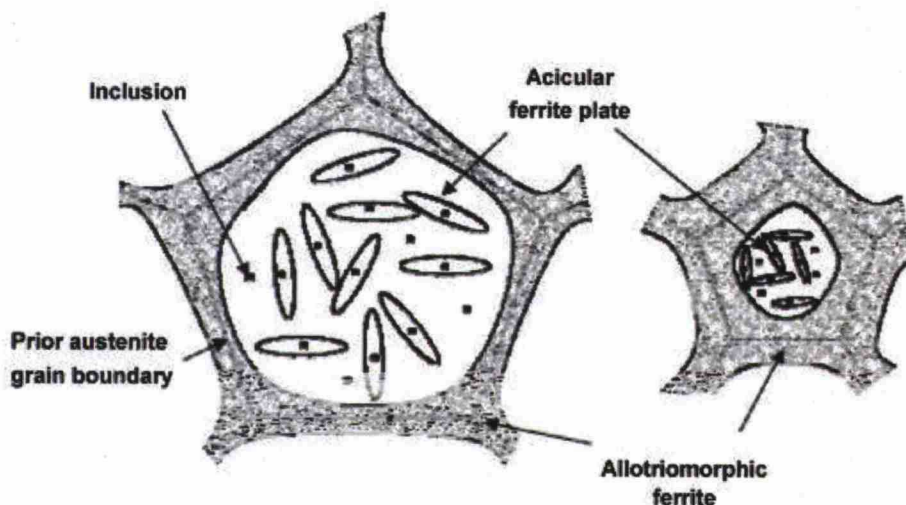


Figure 20: The effect of the grain size and volume fraction of allotriomorphic ferrite on the amount and size of the acicular ferrite plates.²⁰

4.3.2. Alloying Elements of the Steel

Many alloying elements affect the austenite – ferrite transformation temperature and therefore also the size of the austenite zone. Mn, Ni, C and some other elements increase the austenite zone while Al, Si, V, Cr, Mo, Ti and other elements decrease it. Especially the optimal amount of Mn, which is about 1,5 %, decreasing the transformation temperature increases the fraction of acicular ferrite. This happens especially at high cooling rates. The optimal amount of Ni is about 3 %, but already 1 % decreases the transformation temperature enough to have a positive effect on the amount of acicular ferrite. As mentioned earlier, the addition of small amounts of boron also favors the nucleation of acicular ferrite since the boron reduces the grain boundary energy and increases the energy barrier of ferrite nucleation at the grain boundaries.⁵

An increase in the amount of vanadium has been found to increase the fraction of acicular ferrite. At a cooling rate of 2,0°C/s and an increase in the percentage of vanadium from 0,10 wt-% to wt-0,18 % the fraction of acicular ferrite increased in the experiment from 0,33 to 0,80. However after a certain percentage of vanadium, there wasn't any additional effect on the amount of acicular ferrite.¹⁰ It was also

observed in another study that an addition of about 0,3 wt-% V and 0,01 wt-% N to a low-carbon steel increased the formation of acicular ferrite.⁵

In several studies of medium-carbon steels the addition of silicon increased the amount of acicular ferrite. In one study with a low-carbon steel the addition of silicon was on the other hand found to decrease the fraction of acicular ferrite. Depending on the carbon level of the steel, special attention to the amount of silicon should therefore be paid.¹⁰

4.4. Conditions of Formation

To enable the formation of acicular ferrite, not only the steel and the inclusions need to have specific favorable properties, but the formation conditions also need to be considered. The most important factors are the austenitisation temperature and time together with the cooling rate especially in the temperature range from 800°C to 500°C.⁵ However in the case of the NAMOS project these factors cannot be changed since the objective is to obtain an as-cast acicular ferrite microstructure with continuous casting.

An austenitisation time of 10 minutes at 1200°C has been found to be effective to reach an austenite grain size of approximately 80 µm in certain medium-carbon steels. In the same study, a cooling rate of approximately 2,0°C/s was found to be the most effective for reaching a large fraction of acicular ferrite. At cooling rates higher than 3,0°C/s the fraction of acicular ferrite diminishes significantly while the fraction of martensite increases. A layer of allotriomorphic ferrite was present in all cases where the cooling rate was less or equal to 10,0°C/s.¹⁰

In another study, the cooling rates of 3°C/s, 7°C/s and 15°C/s were tested. A similar conclusion of the effect of the cooling rate was reached in this case as well. With a cooling rate of 3°C/s acicular ferrite was obtained, and with the faster cooling rates the microstructure was mainly bainite and martensite.²⁰

5. ADDITION OF NANOPARTICLES INTO LIQUID STEEL

Many different things must be considered when nanoparticles are added to the steel. The steel must of course be as clean as possible of impurity inclusions, because they have a very negative effect on the mechanical properties. There is also a risk that the just added nanoparticles could be removed by accident in the inclusion removal process, so the steel should be as clean as possible before the addition of the particles. The particles must also be added so that they can spread evenly to the steel matrix and so that they don't have any unwanted chemical reactions with the steel or the slag.⁵ A uniform particle distribution throughout the cast strand is essential to obtain a continuous acicular ferrite structure and good mechanical properties. Also factors such as superheat, cooling rate and prevention of reoxidation need to be considered.²¹

The location of the particle addition is a key factor in obtaining the wanted even distribution and it influences also the choice of the addition method. The continuous casting process consists of three locations where the addition could be made. The steel arrives to the caster in a ladle, which is the first possible addition location. From there it runs through a nozzle into the tundish, the second possible addition location. One main function of the tundish is to provide a continuous flow of liquid steel further to the mold during the ladle exchange, but it also enhances the oxide inclusion separation. The third possible addition location is the mold, where the steel starts to solidify. (Figure 21)^{29,30}

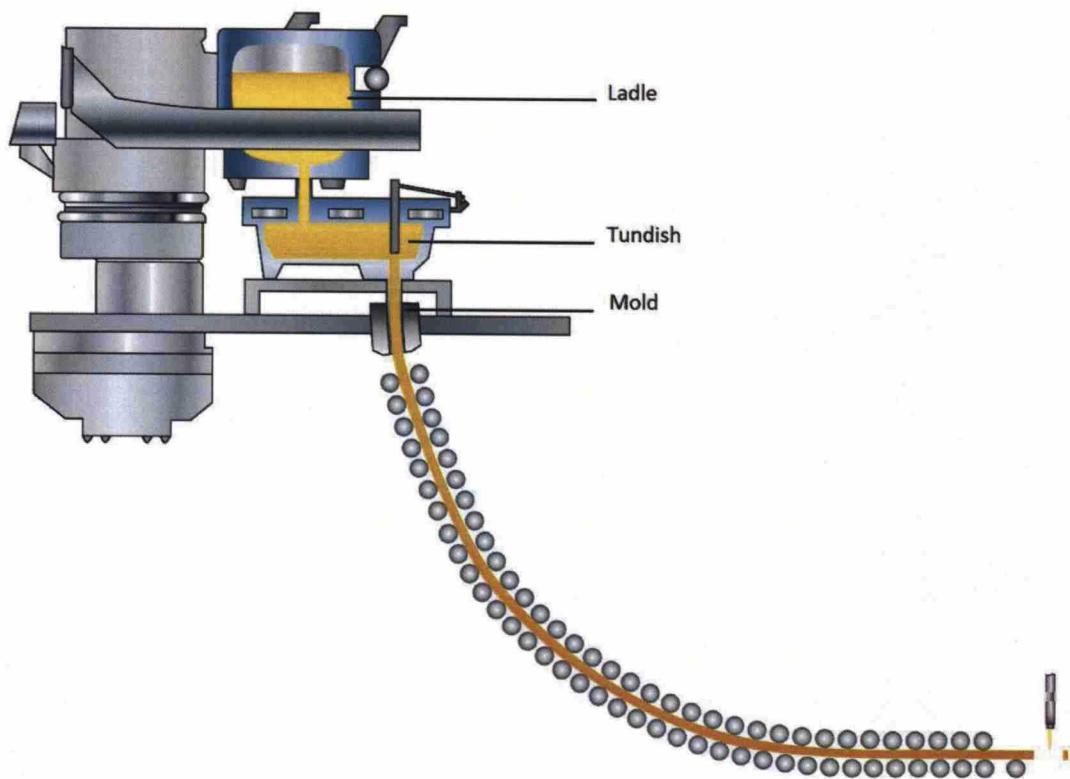


Figure 21: A continuous caster³⁰

5.1. Addition Locations

The particles could be added either into the ladle, the tundish or the mold during the continuous casting process. All three possibilities have of course their pros and cons, and no self-evidently best method and place of particle addition can be found. The behavior of the added particles can of course be determined experimentally, but the prediction by models such as CFD models is also very helpful to better understand what happens.³¹

If the particles are added already into the ladle, the steel is stirred a lot afterwards and the particles can spread evenly, but they also have a risk of clustering and agglomerating during the stirring, the transfer into the tundish or the further transfer into the mold. This is however also the only addition location at which steel samples are still taken and where the success of the addition can thus be verified.³¹

The particles also spend a lot of time in the molten steel before the solidification and they could very probably also have the time to dissolve or react.

The addition of the particles into the tundish could also prevent big concentrations but there is still a risk of clogging at the transfer into the mold. The stirring is not very thorough at the tundish stage anymore, so there is also a risk that the particles are not mixed into the steel well enough. This can be influenced by choosing the right location for the addition into the tundish, so that the fluid flow will be utilized for distributing the particles. Since these small added particles follow the fluid flow, they need to be added in a place where the fluid flow will mix them well into the liquid steel.³¹ If added early in the tundish, the time that the particles spend at a high temperature is however still quite long and the risk of unwanted chemical reactions is still present.

If the addition of the particles is not done before the mold, all clogging can be avoided and there is not such a big risk of clustering either. However, there is not that much mixing in the mold before the solidification of the steel, so there is also a big risk to have areas with big concentrations of particles as well as others with very few particles.³¹ There are also often multiple molds in one continuous caster^{29,30}, which would make it necessary to build multiple addition instruments and thus make it a more expensive choice than with only one set of addition equipment for each caster. With this choice of addition location the particles will have the least time to react with the molten steel.

The choice of the addition location is not easy. Possibly the tundish could be considered to be the best place, since there still is some stirring of the molten steel but not that much³¹. The research on the subject is however very limited and therefore this is not an entirely reliable conclusion. For example the addition into the ladle could be better because it can be done very easily simultaneously with the addition of all the other alloying elements. The addition into to mold would on the other hand ensure a minimal risk of unwanted chemical reactions and clogging.

In an experiment at a pilot plant with a continuous billet cast of cerium sulfide particle dispersed steel the cerium was added by feeding a mischmetal wire into the steel stream as it entered the tundish. The results of this experiment were promising. The obtained inclusion volume fraction and size distribution were comparable with vacuum melts but not as good as with submerged arc welds.²¹ This is not an entirely comparable situation to the addition of nanoparticles, since the added cerium of this case was supposed to react with the sulfur of the melt to form cerium sulfides, but it is still an example that confirms the potency of additions into the tundish.

5.2. Addition Methods

There are several methods that can be considered for the addition of the nanoparticles or the compounds forming them into the base steel. The most obvious possibilities would be wire, pellet or powder additions.

As mentioned earlier, the addition of cerium by feeding mischmetal wire was successful in one pilot plant experiment²¹. The feeding of a wire with nanoparticle powder should therefore be considered a very promising addition method. One of this method's possible downsides is that all the particles might not have the time to spread evenly into the steel. It might also not be applicable to all types of particles or chemical compounds.

Pellets of nanoparticles can also be quite easily added to the melt. Compared to wires, the nanoparticles are more densely together in pellets and they therefore need a longer time for unclustering and spreading to the matrix.

The pellets can be formed from a mix of the wanted particle and Fe. In one study where TiO₂-pellets were used, they had a diameter of 10 mm and contained 10 wt-% TiO₂, 5 wt-% Al₂O₃ and the rest was metallic Fe. Also cylinders prepared from 10 wt-% chemically pure TiO₂ and 90 wt-% pure carbonyl iron powders were used in the same study. Their diameter was 10 mm and the height varied between 10 mm and

20 mm. The TiO_2 particles were in the size range from 0,2 to 3 μm . Cylinders of compressed powders can also be considered a good possibility for the addition of particles into the steel melt.²⁵

Direct powder addition would be difficult in the case of nanoparticles because of their small size. There would be a big risk of the particles spreading into the air, so the powder is therefore more easily added when integrated into a wire for example.

6. SELECTION OF SUITABLE NANOPARTICLES

When selecting suitable nanoparticles all the properties mentioned in the earlier paragraphs must be taken into account. The available information on the properties of possibly interesting particles was gathered in Table A 1 of the appendix A. Since no exact information was available on the following complex particles, they were not included in the table: $(\text{Ti}, \text{Mn})_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{MnS}$, $\text{CaO-Al}_2\text{O}_3$, FeS-(Mn, Cu)S , MnS-V(C, N) , MnS-VC , Ti- and Ti-ca-oxy-sulfides, $\text{Ti}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-MnS}$, $\text{Ti}_2\text{O}_3\text{-TiN-MnS}$, $\text{TiO}_2\text{-(MnO-Al}_2\text{O}_3)$, $\text{TiO}_x\text{-TiN-MnS}$.

In addition to the properties mentioned earlier, also the melting temperatures as well as some information about commercially available nanopowders and their prices were added. The melting temperatures are listed to verify that they are above the temperature of the liquid steel in the steel making process. All listed temperatures are high enough but it should be noted that there could be small risks involved in the cases where the temperature is close to 1700°C.

The prices of the nanopowders are from several different companies in Europe, USA and China: Cymit-Quimica (EU), Sigma-Aldrich (EU), Tec-Star (EU), Skyspring nanomaterials (USA), US Research Inc. (USA), Nanoamor (USA), PlasmaChem (USA) and DK Nanomaterials (China)³². The prices vary a lot depending on the company, the particle size and the amount of powder. The lowest prices are in most cases from DK Nanomaterials for packages of 1 kg, and the highest prices from the European companies for small packages of 10 to 100 g.

Since the prices are not very precise and they don't appear to differ drastically from one particle type to another, they will not at this stage be taken into account when selecting the most suitable particles. Also the prices mentioned in the table are for low scale demand, and they could be very different for bigger amounts for industrial scale. Therefore the prices of different nanoparticles should be examined in detail only after more experimental results on the effectiveness of the particles are available.

By observing the Table A 1 ten promising particles were selected for thermodynamic calculations. The selected particles are CeS, ZrO₂, CeO₂, TiO₂, VN, VC, CuS, TiN, ZrN and SiO₂. Some of the particles were selected based on their very good values for some of the observed properties and others based more on previously reported experience of effectiveness.

MnS was not selected because it is considered to be already present in the steel and therefore it can contribute to the nucleation of acicular ferrite by the mechanism of Mn depleted zones, but only when the actual added particles are of another chemical composition.

7. EQUILIBRIUM CALCULATIONS

Thermodynamic equilibrium calculations were done for the selected ten nanoparticle types CeS, ZrO₂, CeO₂, TiO₂, VN, VC, CuS, TiN, ZrN and SiO₂. These were done by using the software FactSage version 6.3.

The basic steel composition used in the calculations is the one selected in the NAMOS project as being the most suitable for the nucleation of acicular ferrite when nanoparticles are added to it. The composition of this steel is listed in Table 1.

Table 1 : The chemical composition of the steel used in the calculations (wt-%)

C	Mn	Si	P	S	Cr	Ni	Mo	V	Al	Ti	Ca
0,28	1,43	0,65	0,012	0,042	0,18	0,13	0,037	0,084	0,013	0,022	0,004

In the calculations the N amount used was 0,012 wt-% and the O amount 0,002 wt-%. The thermodynamic equilibrium was calculated in the temperature range from 1100°C to 1600°C. The liquidus temperature of this steel is 1498°C and the solidus temperature 1418°C. The amount of basic steel used was 100g, and to this additions of 0,5 wt-% and 0,8 wt-% of each of the ten selected particle compositions were made. These two amounts were selected based on the knowledge that the additions should not be more than a few percents. The addition amount of 0,5 wt-% was selected because it is big enough to see an impact on the equilibrium of the system. The amount 0,8 wt-% was found to represent well the direction in which the equilibrium evolved from the smaller addition amount, but it is also close enough to 0,5 % so that the figures can be presented with the same scale.

8. RESULTS AND DISCUSSION

The equilibrium of the solid phases of the base steel without any additions is plotted in Figure 22. It should be noted that this figure has a different scale in the weight axis than the figures of the equilibriums with additions.

It can be observed that MnS is quite stable in lower temperatures than approximately 1300°C, but its amount is not very large. Even though the MnS is only stable at temperatures below the solidus temperature, it can still be formed since the reactions don't stop entirely at the solid state. The MnS could help with the nucleation of acicular ferrite, but since the amount of it is quite small it will probably not have a very significant role in the nucleation process. The only solid phases at the liquid steel temperatures are Ca-aluminates, and they are not considered to be effective nucleation sites for acicular ferrite.

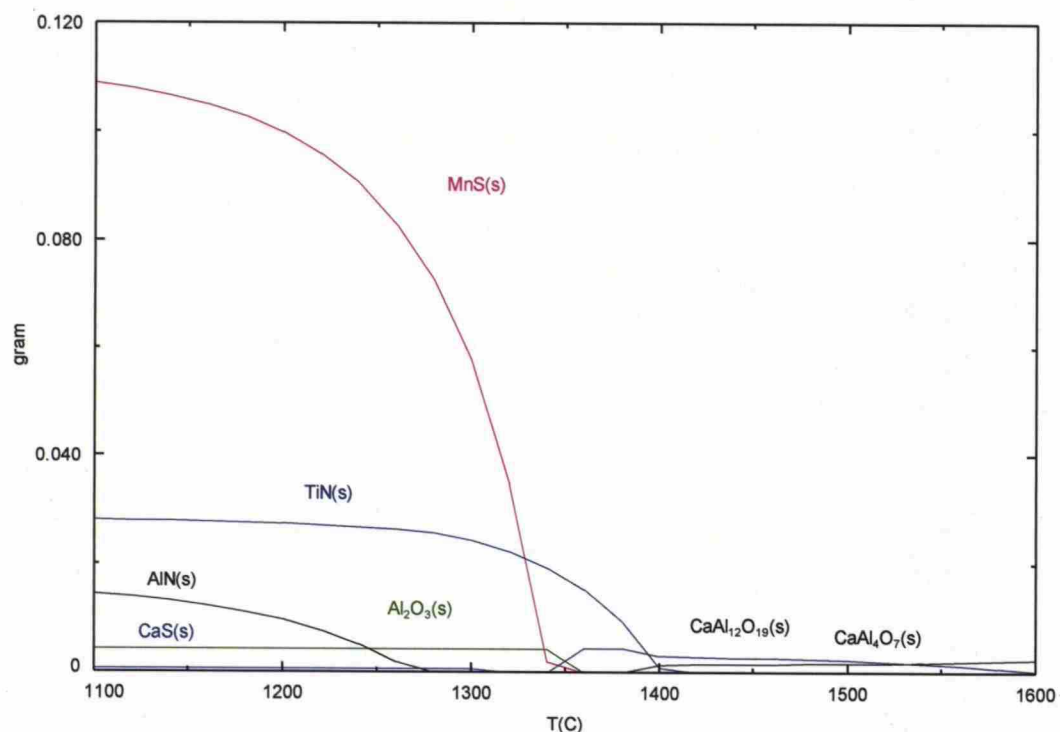


Figure 22 : The equilibrium of the base steel without any additions

The FactSage equilibrium calculation results for the steel with additions of the ten selected chemical compositions of particles separately can be seen in the appendix

B. For each case the first figure is with an addition of 0,5 wt-% and the second figure with an addition of 0,8 wt-%. The resulting phases were in most cases similar for both amounts of addition, at the exemption of course of the main phase which amount varied depending on the amount of addition. Since the particles should be solid in the liquid steel temperatures to ensure the nucleation of acicular ferrite, only the solid phases are plotted in the the figures and not the liquid or gas phases.

8.1. CeO_2

The equilibriums of CeO_2 additions are plotted in Figure B 1 and Figure B 2. CeO_2 is not stable in the steel at the observed temperature range, and mostly transforms into Ce_2O_3 . This form of cerium oxide is also regarded as being good for the nucleation of acicular ferrite, so from the thermodynamic stability point of view the addition of CeO_2 nano particles can be considered to be a good option. The original goal of having the acicular ferrite nucleate directly on the added nano particles would however not be achieved by using CeO_2 .

The aluminum doesn't in this case form any chemical compounds with Ca, O and N like in the base steel without additions. Instead AlCeO_3 is formed. Also some SiO_2 is present in the figures. The obtained results are very similar for the addition amounts of both 0,5 wt-% and 0,8 wt-%. The main difference is the amount of Ce_2O_3 . To avoid an excess formation of AlCeO_3 the aluminum content needs to be minimized. AlCeO_3 is not considered a good compound for enabling the nucleation of acicular ferrite.

8.2. CeS

The equilibriums of CeS additions are plotted in Figure B 3 and Figure B 4. CeS as such is not very stable at these temperatures. In the case of an addition of 0,8 wt-% a small amount of CeS is present in the figure in temperatures lower than approximately 1440°C, but it seems to mostly transform into Ce_2S_3 above about

1550°C and into Ce_3S_4 below this temperature. In the case of the smaller amount of 0,5 wt-% of added CeS the transformation product is mostly Ce_2S_3 .

Both Ce_2S_3 and Ce_3S_4 are considered to be good for the nucleation of acicular ferrite, but it would not happen on the added inclusions but only after chemical reactions, which would be different from the original objective. Therefore CeS is not a very good choice from the thermodynamic stability point of view.

In the case of CeS additions no MnS inclusions are formed because cerium has a higher affinity to sulfur than manganese. The lack of MnS inclusions results in a decrease in the machineability of the steel.

8.3. CuS

The results of the CuS additions are plotted in Figure B 5 and Figure B 6. It can be observed from these figures that CuS is not stable at all at these temperatures. Instead a large amount of MnS is formed. But since the ability of MnS to nucleate acicular ferrite on its own is questionable, CuS should not be considered a good choice of nano particle type.

8.4. SiO_2

The results for the addition of SiO_2 are plotted in Figure B 7 and Figure B 8. It can be observed that approximately half of the added SiO_2 is stable in both cases at the solidus temperature. The amount increases at lower temperatures, which is a good sign if also the kinetics is taken into consideration, and it is assumed that not all the SiO_2 will have the time to chemically react before sufficiently low temperatures are reached. The change in the curve that occurs around approximately 1470°C represents a change in the crystal system of SiO_2 , but since no chemical reactions with other compounds are involved this shouldn't affect the potential for acicular ferrite nucleation.

From the point of view of thermodynamics SiO_2 seems to be a good option, but not one of the best since only approximately half of the SiO_2 is stable. The amount of SiO_2 particles that don't react with the steel melt and stay potential nucleation sites for acicular ferrite formation as such can be influenced by varying the amount of added particles.

8.5. TiN

As can be observed in Figure B 9 and Figure B 10 TiN is quite stable at all temperatures of the observed range. In the case of 0,8 wt-% of added TiN there is even more of it at temperatures below 1400°C than the amount added. TiN seems to be a good choice of particles for the addition into the steel melt.

8.6. TiO_2

From Figure B 11 and Figure B 12 it can be observed that solid TiO_2 is not stable at this temperature range. The stable phase of titanium oxide is Ti_3O_5 , which could also nucleate acicular ferrite. But like in the case of CeO_2 and CeS , the nucleation of acicular ferrite on particles that have reacted with the melt is not the objective. Therefore TiO_2 is maybe not a very good choice for this purpose.

8.7. VC

The equilibriums for VC additions are plotted in Figure B 13 and Figure B 14. It can be observed that VC is not stable at these temperatures. Below about 1200°C in the case of the 0,8 wt-% addition and below about 1160°C in the case of the 0,5 wt-% addition V_{10}C_8 is stable. Since this form is not considered especially good for nucleating acicular ferrite, the addition of VC particles into the steel does not seem a very good choice.

8.8. VN

In Figure B 15 and Figure B 16 are plotted the results for VN additions. VN seems to be stable only at temperatures below approximately 1300°C in the case of a 0,5 wt-% addition and 1340°C in the case of a 0,8 wt-% addition. Since the added VN particles would react at higher temperatures, they are probably not a very good choice.

8.9. ZrN

The results for ZrN additions can be observed in Figure B 17 and Figure B 18. At all temperatures ZrN appears to be stable, although a fraction of the added ZrN seems to form compounds with Ca, Al and O. But since most of the ZrN is stable, the addition of ZrN particles for the nucleation of acicular ferrite seems to be a good choice.

8.10. ZrO₂

The equilibriums for ZrO₂ additions are plotted in Figure B 19 and Figure B 20. ZrO₂ appears to be very stable throughout the entire observed temperature range. A change in the crystal system occurs at about 1210°C, but no reactions with other compound take place then. Since over 90 % of the added ZrO₂ stays stable in the steel, ZrO₂ particles should be considered a very good choice for the formation of acicular ferrite.

9. CONCLUSIONS

The objective of the NAMOS project is to create a new type of steel with good mechanical properties. This is done by having acicular ferrite form on nanoparticles that are added into the steel melt.

This thesis started with a literature research on the formation of acicular ferrite. The objective was to determine the required conditions for the nucleation to happen and the properties needed from the added particles to enable the nucleation.

The formation of acicular ferrite is a result of several different mechanisms that work together. Depending on the conditions and type of nucleation particles each mechanism can have a more or less important role. Also depending on the mechanism and the conditions very different types of oxide, nitride, sulfide or carbide particles can be the most effective for acting as nucleation sites.

Thermodynamic equilibrium calculations were done to ten types of particles in a selected steel. The particles that were the most stable in the steel melt in the temperature range from 1100°C to 1600°C were TiN, ZrN and ZrO₂. They can thus be considered good choices from the thermodynamic point of view. If a transformation into another chemical compound that is also able to nucleate acicular ferrite is accepted, also CeO₂, CeS and TiO₂ could also be good choices. Out of the particles for which the equilibriums were calculated CuS, VC and VN seem to have the less potential for acting as nucleation sites for the formation of acicular ferrite from the thermodynamic point of view.

If all relevant properties of the particles listed in Table A 1 of the appendix A in addition to the equilibrium calculations are taken into account, the best options seem to be CeO₂, CeS, TiN and TiO₂. CeO₂ has a small density difference with steel, a good wetting in it and a quite big thermal expansion coefficient difference with austenite. CeS and TiN have good lattice matches with ferrite, small density differences with steel and TiN also has a beneficial thermal expansion coefficient

difference with austenite. TiO_2 's advantage is the depletion of Mn and C near the inclusions and its thermal expansion coefficient. All four of these particles have also successfully nucleated acicular ferrite in some earlier studies, and that is a major reason for favoring them.

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APPENDIX A: PARTICLE PROPERTIES TABLE

Particle	Misfit % with ferrite at 1500°C	ref	Crystal system	Melting point (°C)	Density (g/cm ³)	Density difference with steel (7,0 g/cm ³)	Contact angle	Thermal expansion coeff. difference from austenite (approx.) [1/K]	Depletion of elements	Commercially available powder + amount used in a previous case	Powder particle size	Nanopowder approx. price (€/kg)
CeS	1,2	24	Cubic F	2440	5,9	1,1				Ce and S; S-aim 0,025%; mischmetal wire -> 0,1-0,2% added Ce ²¹		
ZrO ₂			Monoclinic -> 1100°C -> Tetragonal -> 2370°C -> Cubic	2700	5,89	1,11	115-125			Sigma Aldrich nano ZrO ₂	< 100 nm	100-2300
CeO ₂	5,84	24	Cubic F	2400	7,65	0,65	0	11		TECNAN nano CeO ₂	5-10 nm	300-1700
TiO ₂	8,8	24	Tetrag.	1835	4,26	2,74	0-92	14	C, Mn ²⁵	TiO2 Degussa P25 0,5 w-% ²⁵	r=12,5nm ²⁵	100-4800
VN	0,7	24	Cubic	2050	6,13	0,87						49300
VC	1,3	24	Cubic	2648								1300
CuS	2,8											900
TiN	3,9	24	Cubic	2949	5,44	1,56	40-132	14				600-2800
ZrN	11,2			2950	7,09	0,09	120					1500-4000
SiO ₂		24	Hex.	1720	2,32	4,68	115	20				100-1600
Ce ₃ S ₄	0,4									Ce and S; S-aim 0,025%; mischmetal wire -> 0,1-0,2% added Ce ²¹		
Ce ₂ O ₃ S	1,83	24	Hexagonal							Ce and S; S-aim 0,025%; mischmetal wire -> 0,1-0,2% added Ce ²¹		
TiC	5,3	24	Cubic	3067	4,93	2,07	28-125			Sigma Aldrich nano TiC; 1600°C -> TiC + O ₂ = TiO ₂		600-4500
Y ₂ O ₃			Monoclinic -> 1600°C -> Cubic	2410	5,01	1,99				Sigma Aldrich nano Y ₂ O ₃	< 50 nm	
Y ₃ Al ₅ O ₁₂			Cubic	1940	4,56	2,44	138-147			Sigma Aldrich nano YAG	< 150 nm	5400
ZrO ₂ -Y ₂ O ₃			Tetragonal	2600	5	2				Sigma Aldrich nano ZrO ₂ -Y ₂ O ₃	< 100 nm	
Ce ₂ O ₃	4,26	24	Hex.	2230	6,2	0,8	105			TECNAN nano CeO ₂		
TiO	3	24	Cubic	1750	4,95	2,05			C, Mn ²⁵	TiO2 Degussa P25 0,5 w-% ²⁵		2100-2800
Ti ₂ O ₃	3,9	24	Hex.	1842	4,49	2,51			C, Mn ²⁵	TiO2 Degussa P25 0,5 w-% ²⁵		2900
TiMnO ₃	0,4		Trigonal	1360	4,55	2,45						
Ce ₂ S ₃	0,46	24	Cubic I	2450	5	2						12500
MgO-Al ₂ O ₃	1,4			2135	3,6	3,4		14				
Al ₂ O ₃ -MnO galaxite spinel	1,8											
NbN	1,8	24	Hex.									3100
Ti ₂ O ₅	2,2		Monoclinic									
γ-Al ₂ O ₃	3,2	24	Cubic	2040	3,97	3,03	93-148					
MgO	3,45		Cubic F	2832	3,58	3,42	123	9				150-2600
CeN	3,46	24	Cubic F									
MgS	4,8		Cubic F	2227	2,68	4,32						
AlCeO ₃	5,4		tetragon.									
SiC	6			2830	3,16	3,84	30-90					250-6300
Ti(C,N)	6	24	Cubic									1600-7600
CeAlO ₃	6,41	24	Cubic F, Hex[30]	2300								
BN	6,7		Cubic F	2967	2,18	4,82	112					
La ₂ O ₃	7,9	24	Hex.	2305	6,5	0,5	110					350-1200
(La,Ce) ₂ (O,S) ₃	7,9	24	Hex.	2305	6,5	0,5						
MnS	8,8		Cubic					5	Mn			
NbC	9,35		Cubic F	3608	7,82	0,82						
ZrC	14,4			3532	6,73	0,27						
Al ₂ O ₃	16	24	Hex.	2040	3,97	3,03	119	15				250-600
CaO	16		Cubic	2899	3,34	3,66		9				
AlN	26,8			3000	3,26	3,745	130					
WC	29,4			2785	15,6	8,63	0					
MnO				1842	5,37	1,63	113	10				
(MnO) ₂ (Al ₂ O ₃) ₂ (SiO ₂) ₅								21				
(Al ₂ O ₃) ₃ (SiO ₂) ₂								18				
CaO(Al ₂ O ₃) ₂								18				
BC							36					
C							37					
TiN-AlN							53-79					

Table A 1 : Nanoparticles and their properties. The first ten particles listed were selected for thermodynamic equilibrium calculations. Where no reference is mentioned, the reference is ³².

APPENDIX B: FACTSAGE EQUILIBRIUM CALCULATION RESULTS

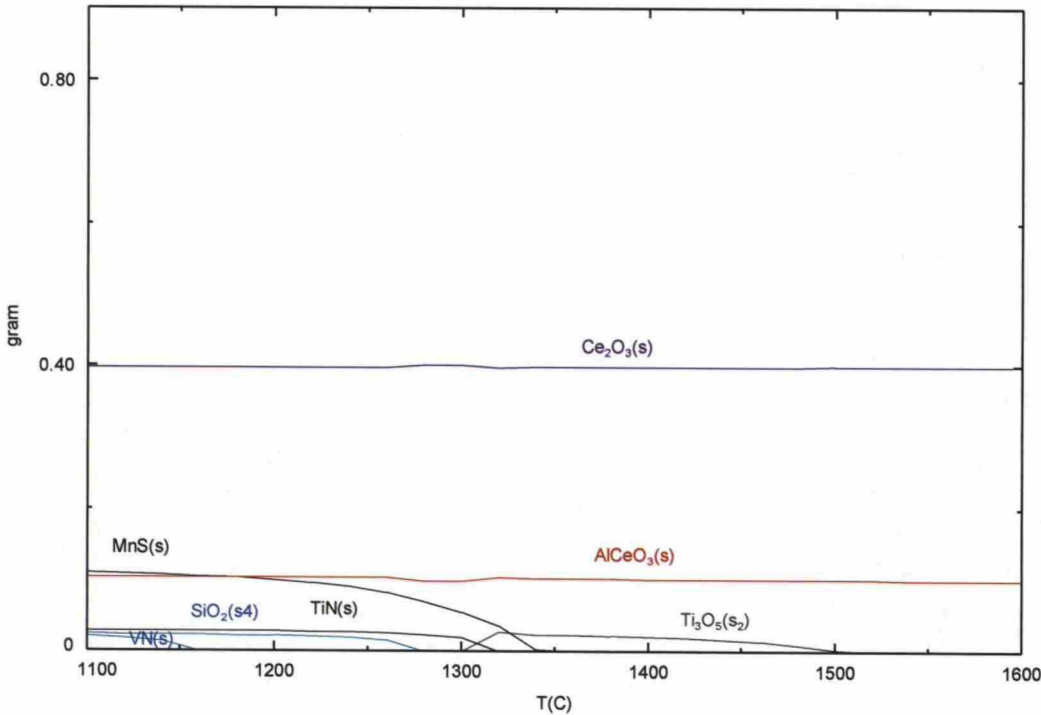


Figure B 1: 0,5 wt-% addition of CeO_2

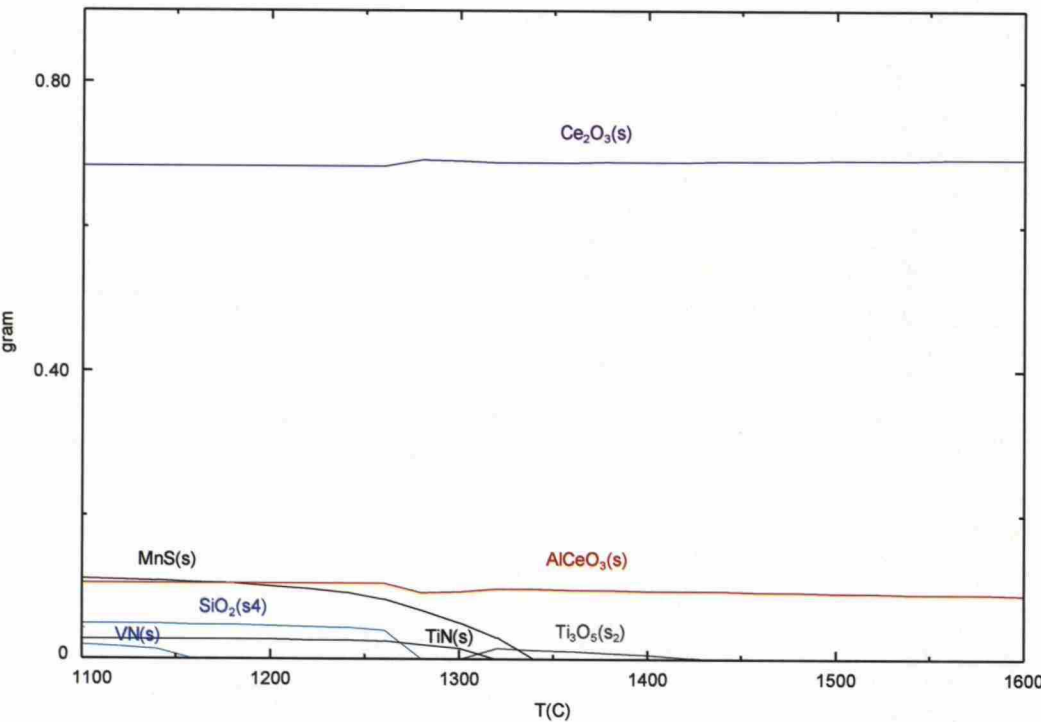


Figure B 2: 0,8 wt-% addition of CeO_2

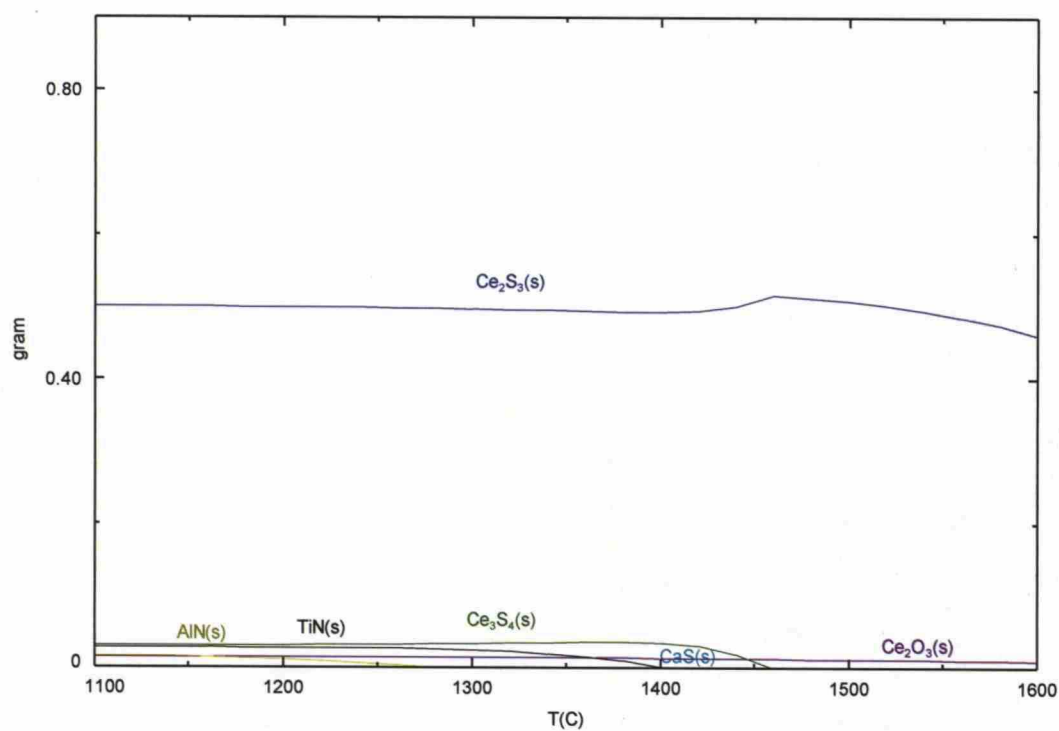


Figure B 3: 0,5 wt-% addition of CeS

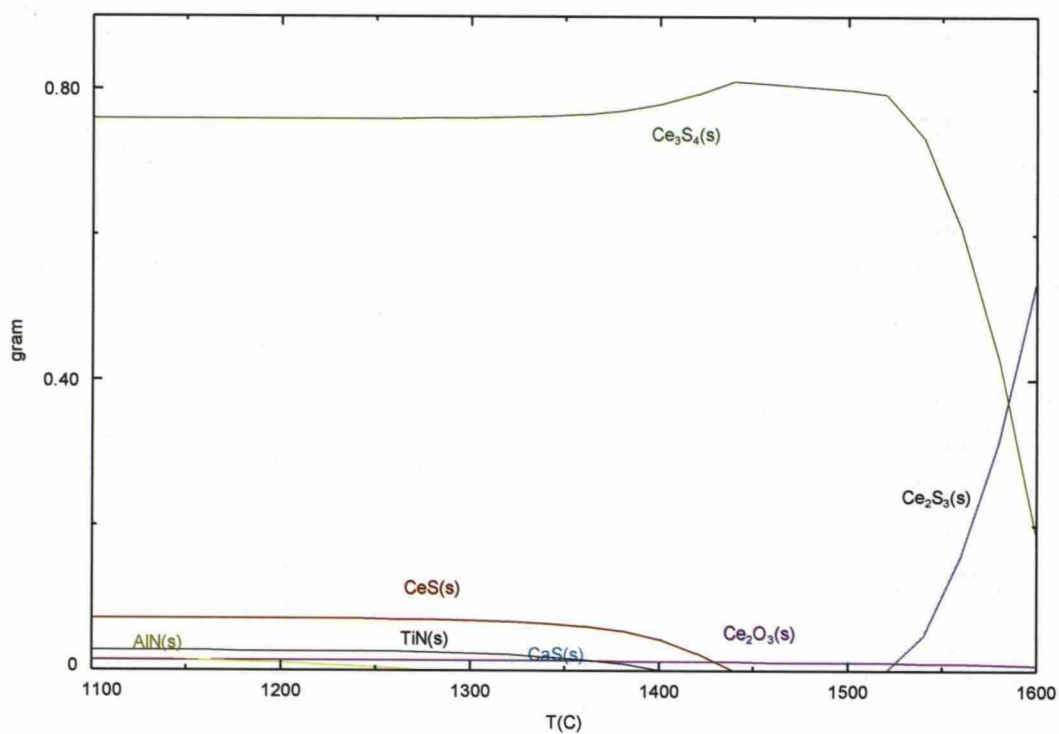


Figure B 4: 0,8 wt-% addition of CeS

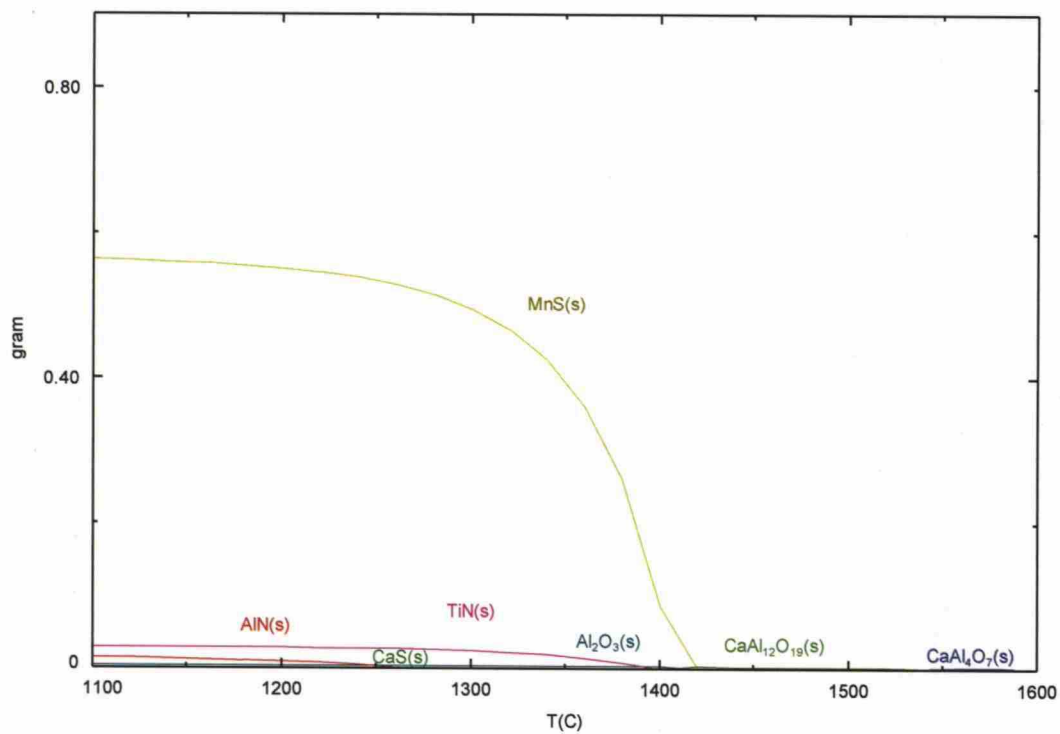


Figure B 5: 0,5 wt-% addition of CuS

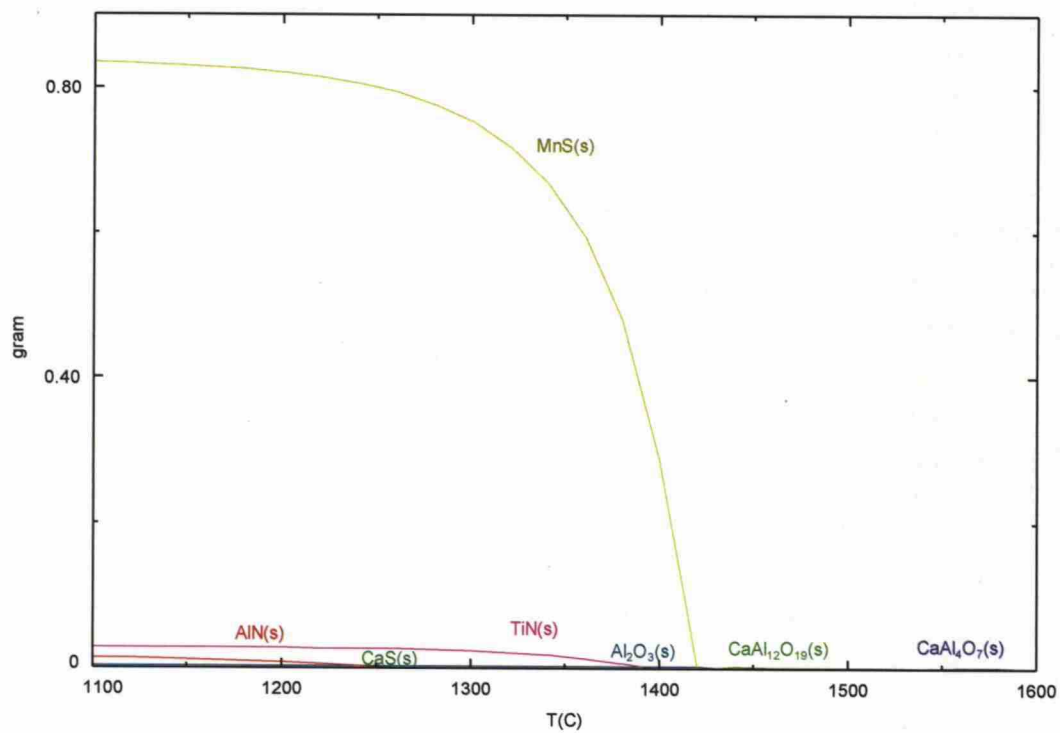


Figure B 6: 0,8 wt-% addition of CuS

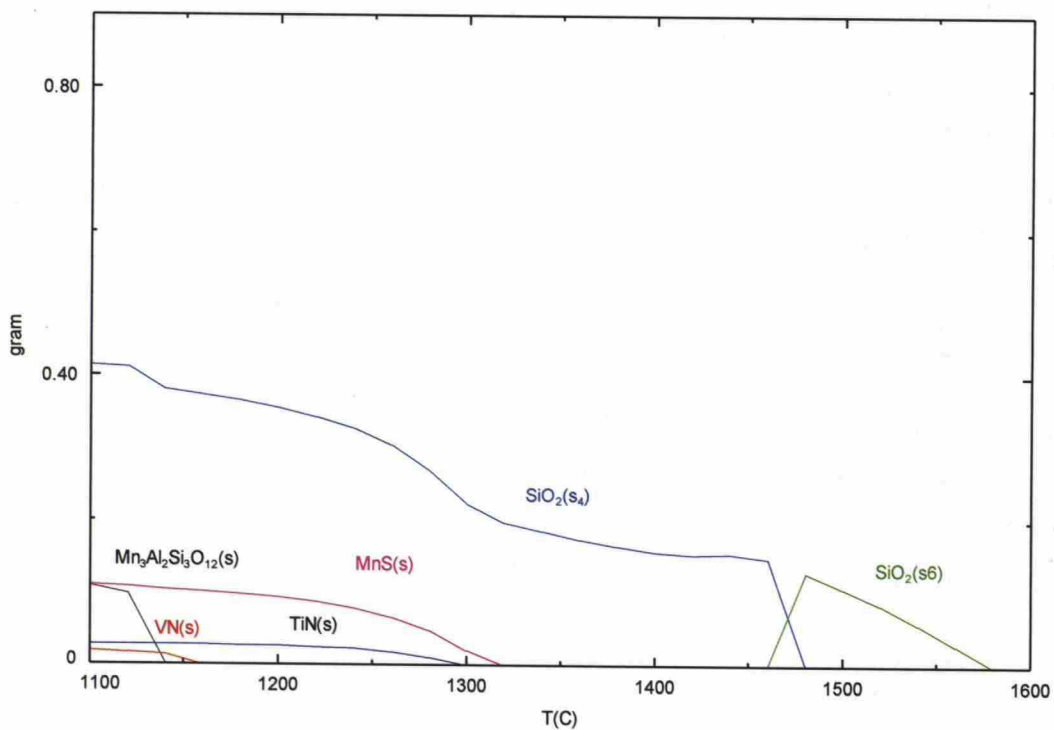


Figure B 7: 0,5 wt-% addition of SiO_2

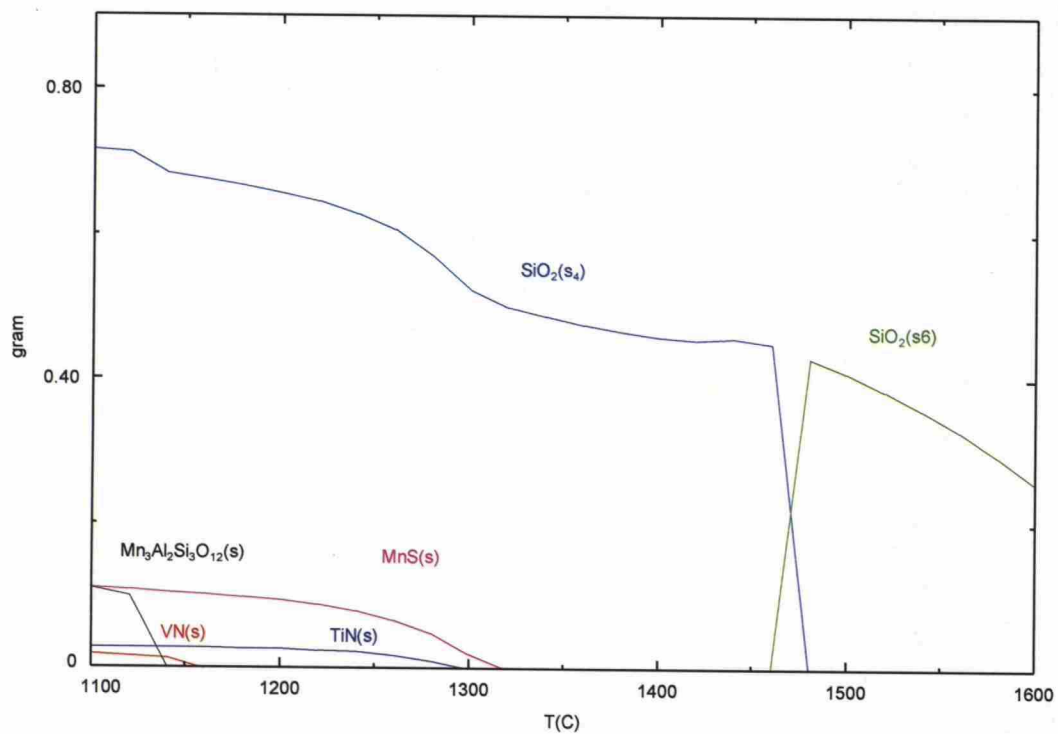


Figure B 8: 0,8 wt-% addition of SiO_2

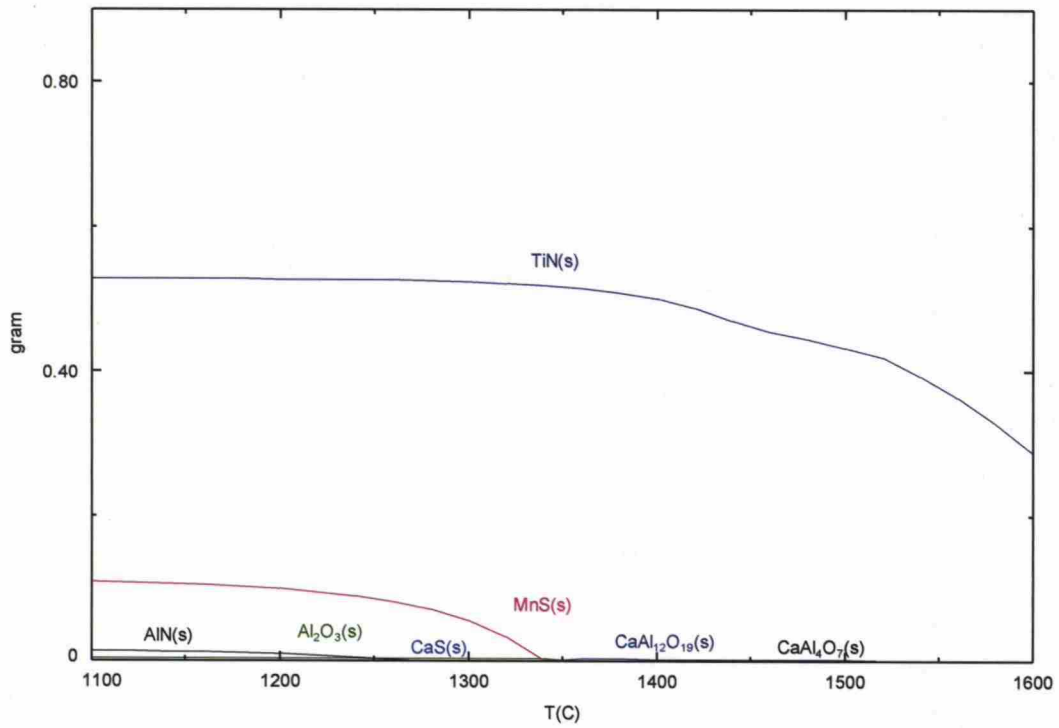


Figure B 9: 0,5 wt-% addition of TiN

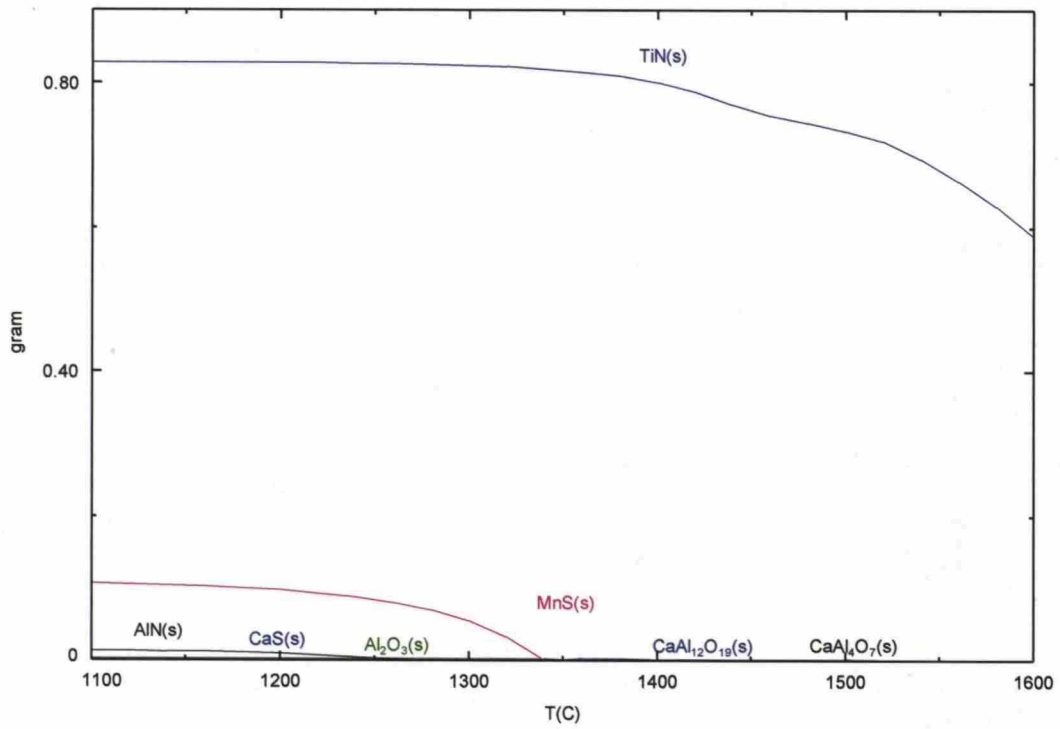


Figure B 10: 0,8 wt-% addition of TiN

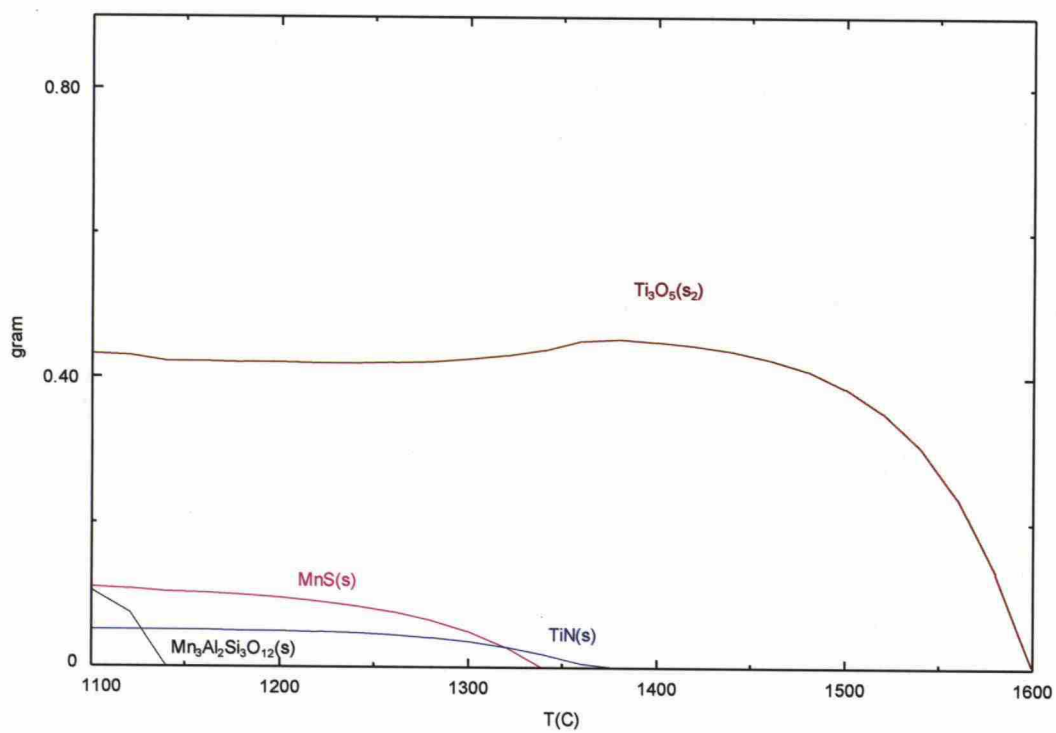


Figure B 11: 0,5 wt-% addition of TiO_2

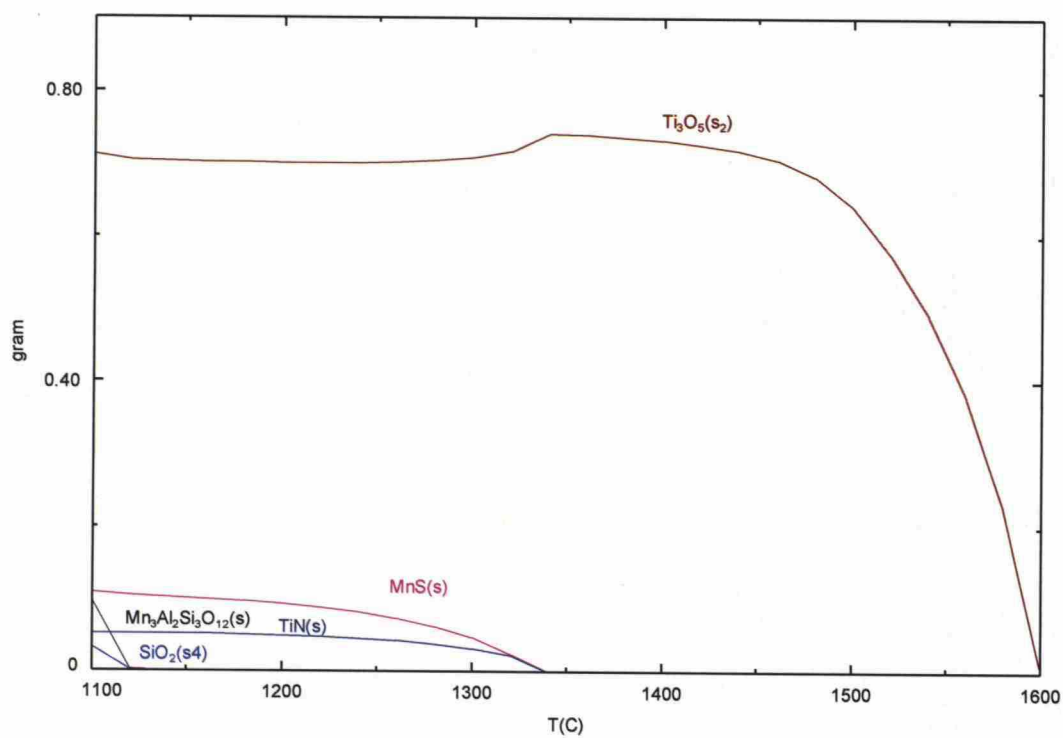


Figure B 12: 0,8 wt-% addition of TiO_2

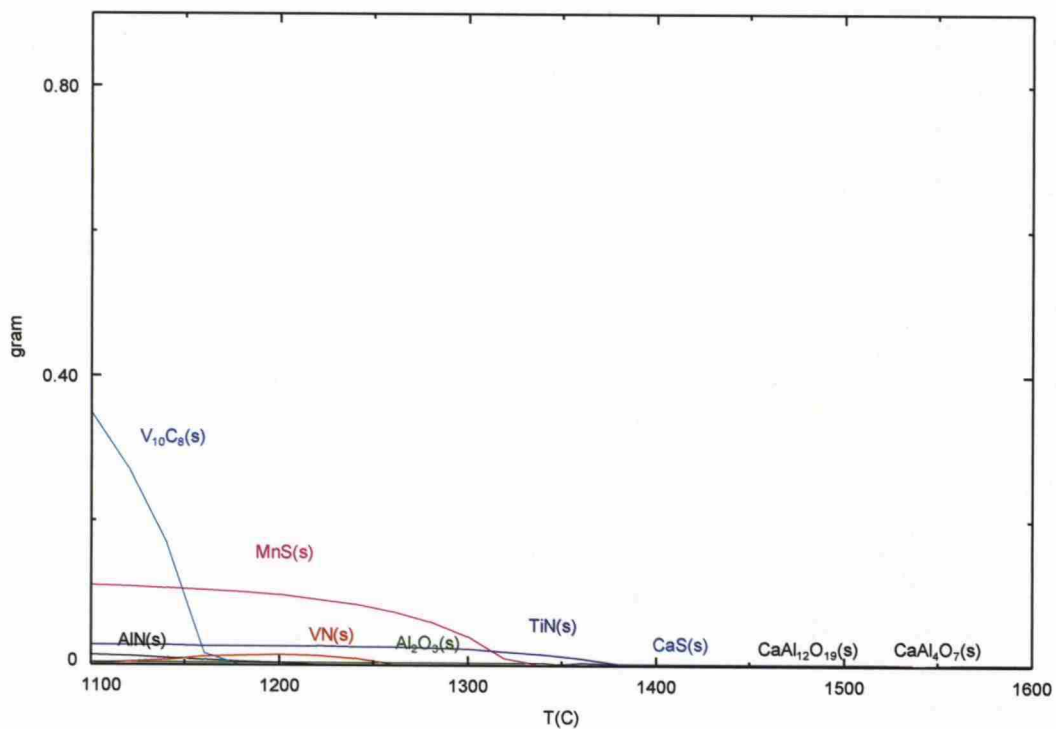


Figure B 13: 0,5 wt-% addition of VC

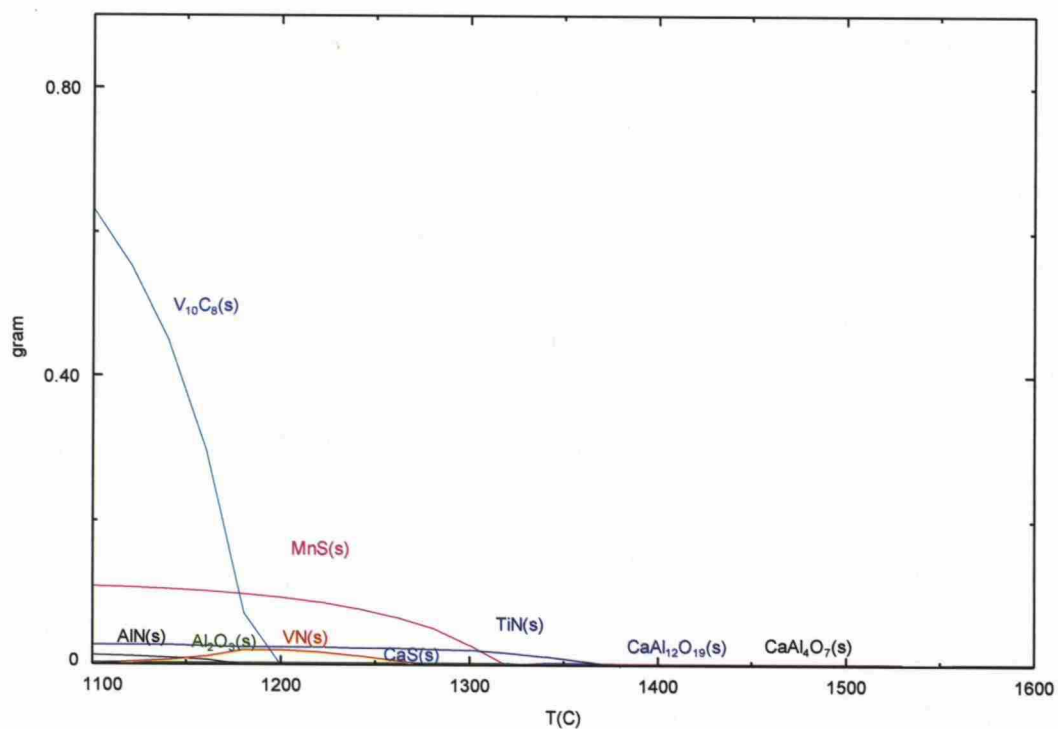


Figure B 14: 0,8 wt-% addition of VC

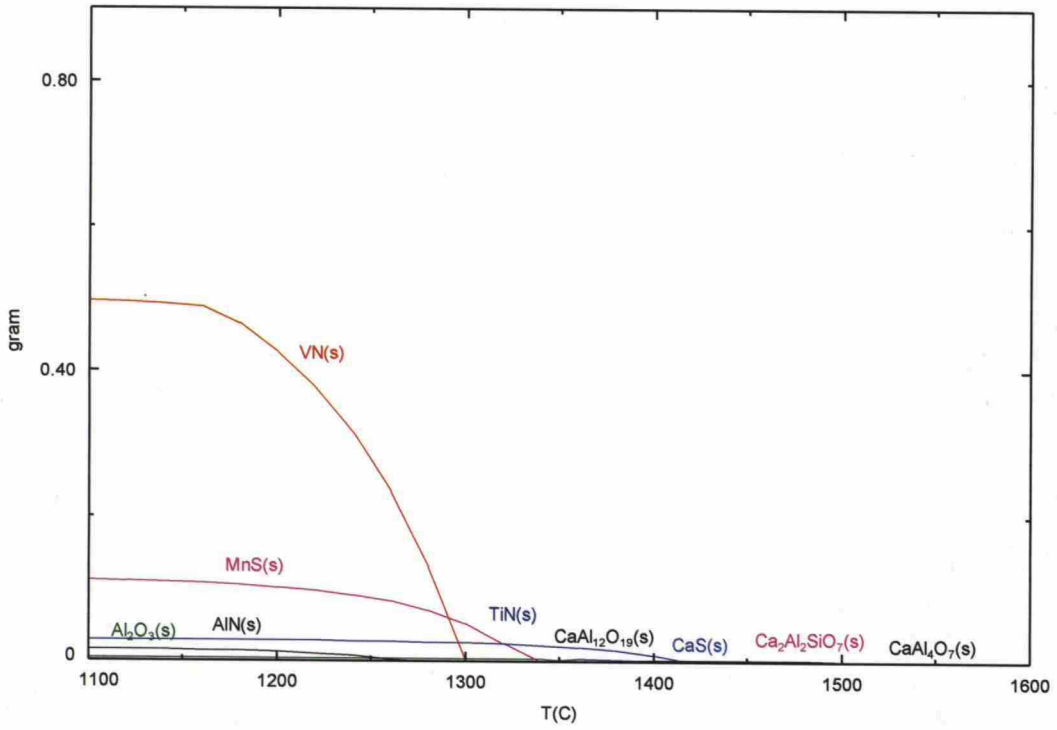


Figure B 15: 0,5 wt-% addition of VN

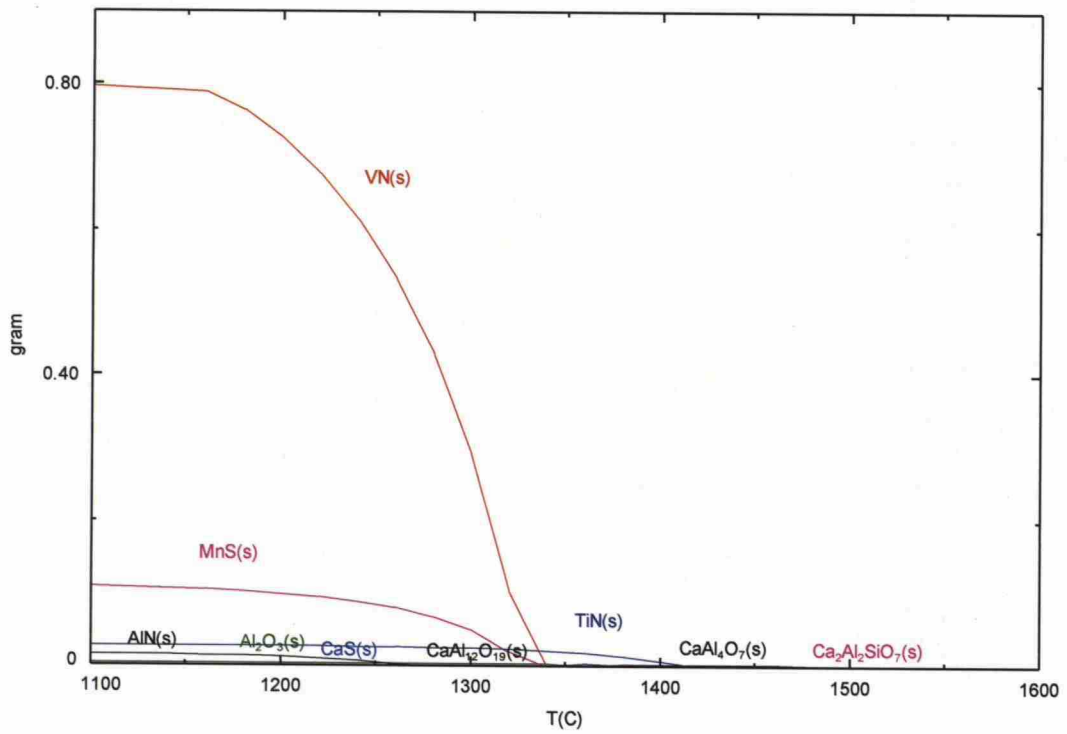


Figure B 16: 0,8 wt-% addition of VN

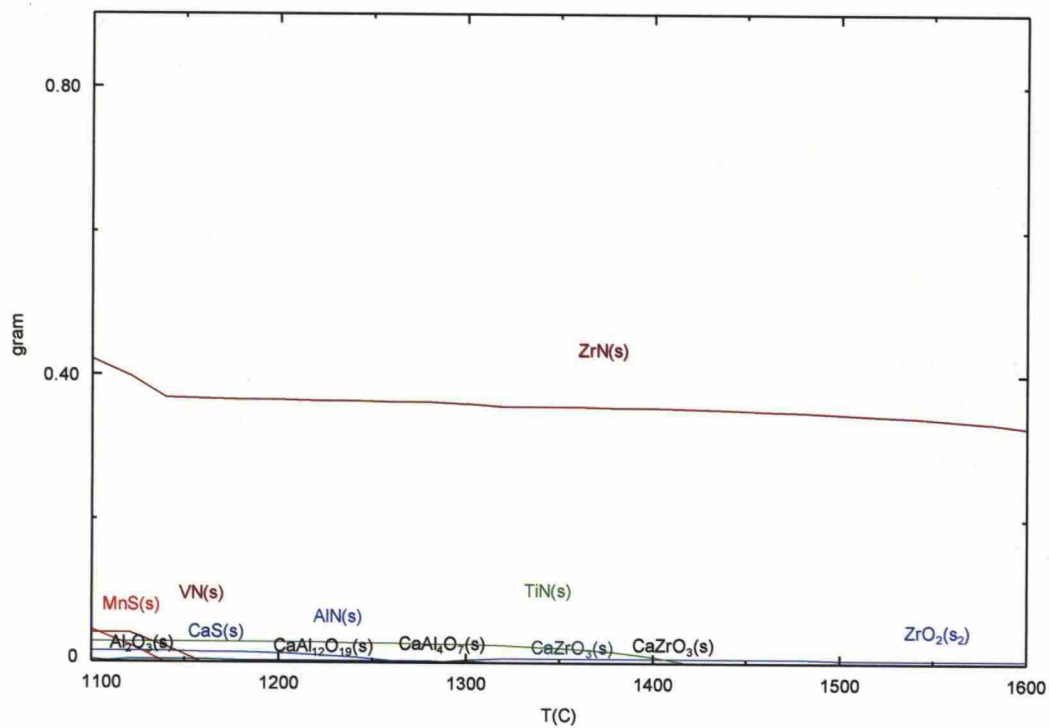


Figure B 17: 0,5 wt-% addition of ZrN

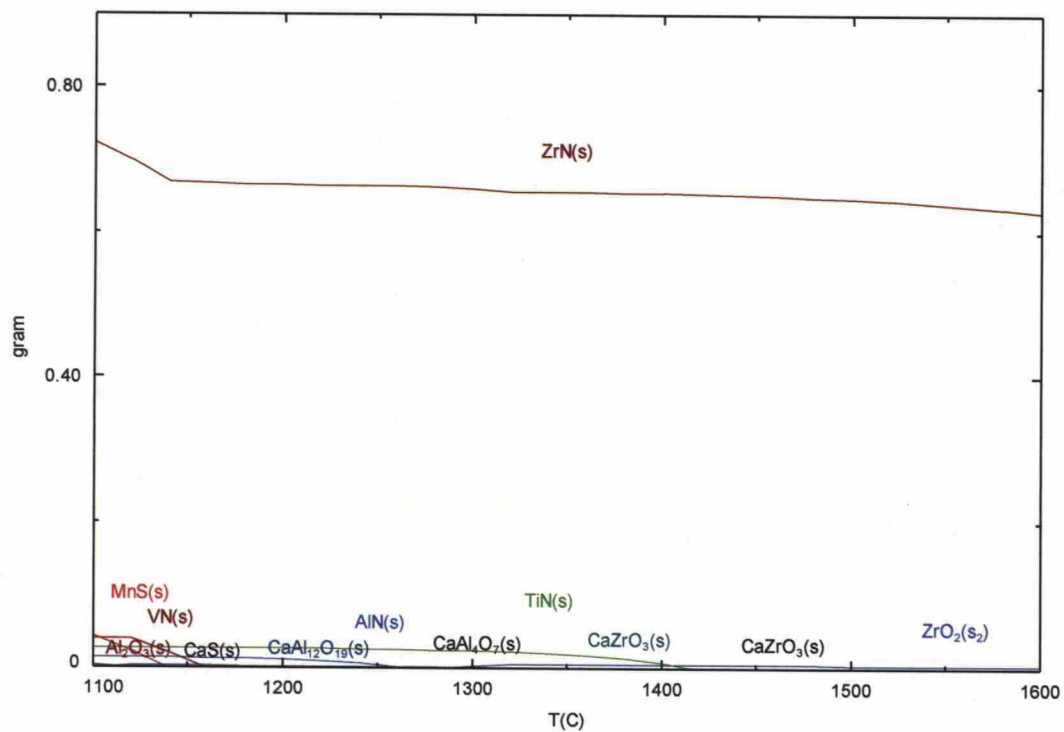


Figure B 18: 0,8 wt-% addition of ZrN

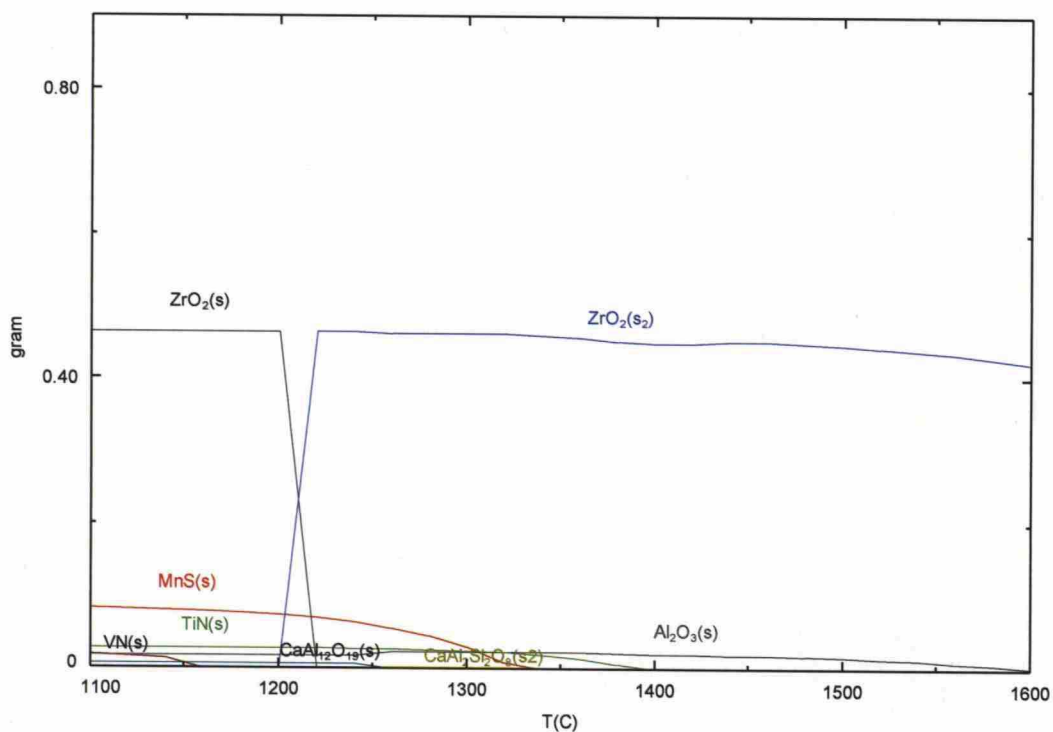


Figure B 19: 0,5 wt-% addition of ZrO_2

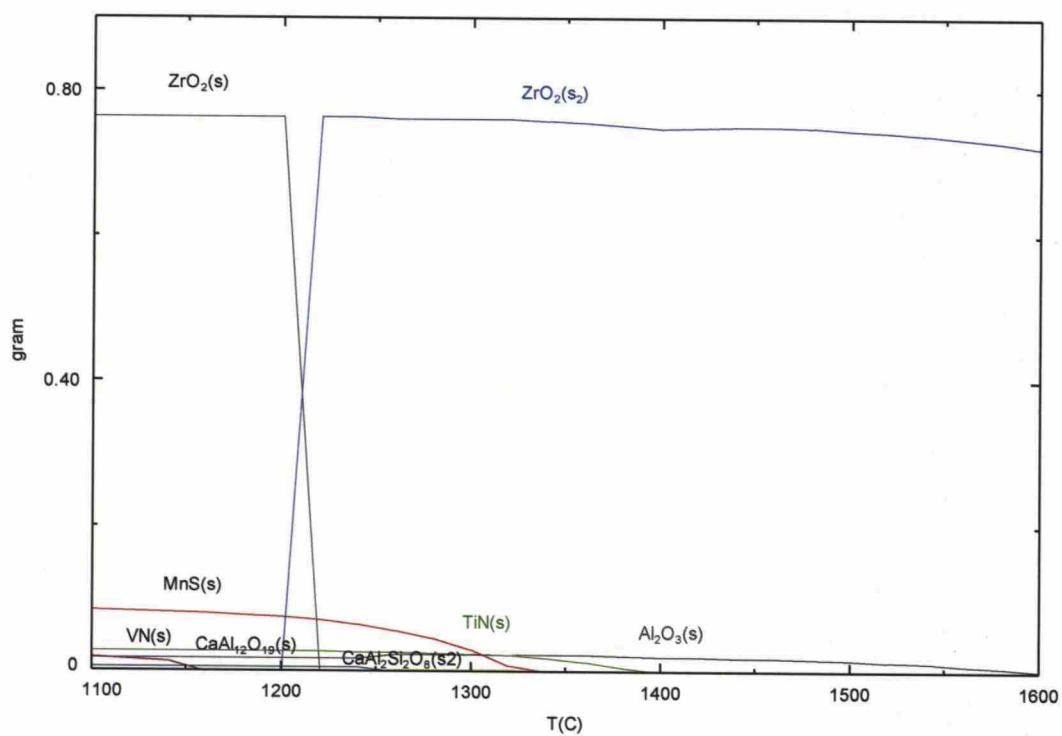


Figure B 20: 0,8 wt-% addition of ZrO_2

~~Aalto-yliopisto
Kemian tekniikan korkeakoulu
Puunjalostustekniikan kirjasto~~

MT