

EFFECT OF THE RARE-EARTH ELEMENTS
Ce, La, Nd AND Pr ON THE MORPHOLOGY
OF EUTECTIC CARBIDES IN TOOL STEELS:
EXPERIMENTAL AND MODELLING
APPROACHES

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Doctoral Dissertation
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VPLIV ELEMENTOV REDKIH ZEMELJ Ce, La, Nd IN
Pr NA MORFOLOGIJO EVTEKTIČNIH KARBIDOV V
ORODNIH JEKLIH: EKSPERIMENTALNI IN MODELNI
PRISTOPI

Doktorska disertacija

Supervisor: Assist. Prof. Dr. Matjaž Godec

Ljubljana, Slovenia, March 2018

To my wonderful wife Valentina

"V dimu in pepelu."

Acknowledgments

First, I would like to express my sincere gratitude to my advisor Assist. Prof. Dr. Matjaž Godec for his continuous support of my Ph.D study and research. His guidance helped me throughout the time of my research and while writing this thesis.

Besides my advisor, I would like to thank the rest of my thesis committee: Assoc. Prof. Dr. Monika Jenko, Assoc. Prof. Dr. Bojan Podgornik, and Assist. Prof. Dr. Sanja Šolić, for their insightful comments and suggestions.

My sincere thanks also go to all my colleagues and lab-mates, who contributed to this thesis. Without their support it would not be possible to conduct this research.

I also want to thank Slovenian research agency (ARRS) for financial support of my investigation with the young researcher scholarship as well as research program group ARRS - P2 0132.

Last but not the least, I would like to thank my family and friends for their moral support. Special thanks go to my wife Valentina Ivanovska Zelič. Without her the realization of this thesis would be impossible.

Abstract

The morphology of the eutectic chromium carbides in the microstructure of as-cast AISI D2 tool steel was modified by adding small amounts of the rare-earth elements (REEs) Ce, La, Nd and Pr to the melt. As a result of these REE additions, the eutectic carbide morphological type was changed from lamellar to globular. Similar phenomena have already been reported for various tool steels, but no complete theoretical explanation has been provided. In this thesis the successful experimental modification of the eutectic carbide morphology in AISI D2 tool steel by the REEs Ce, La, Nd and Pr is described. Further, we propose a new model that is derived from first-principles thermodynamic calculations based on the phase-field modeling of the eutectic reaction. Using this new approach, where the decomposition of the phase-boundary surface-energy term is divided into the isotropic and anisotropic parts, we were able to account for the transition from a lamellar to a globular eutectic morphology in REE-modified (Ce, La, Nd and Pr) AISI D2 tool steel. From the comparison of the experimental and modeling results we were able to explain the origins of the differences between the REE-modified and non-modified steel. We showed that the modification of the non-metallic inclusions in REE-modified steel does not influence the heterogeneous nucleation of eutectic carbides. Furthermore, we theoretically explained mechanism that governs the morphological evolution of the eutectic carbides and explains the observed differences.

Povzetek

Morfologijo evtektičnih kromovih karbidov v liti mikrostrukturi orodnega jekla AISI D2 smo uspeli modificirati z dodajanjem elementov redkih zemelj Ce, La, Nd in Pr v talino. Evtektični krbidi so se zaradi dodatkov redkih zemelj strdili v globularno obliko namesto lamelarne. Podobni vplivi redkih zemelj na orodna jekla so bili že večkrat navedeni v literaturi, kljub temu pa še ni bila izdelana podrobna teoretična razlaga za vpliv modifikacije redkih zemelj na strjevanje evtektičnih karbidov v orodnih jeklih. V doktorski dizertaciji je opisan uspešno izveden eksperiment modifikacije jekla z redkimi zemljami Ce, La, Nd in Pr. Dalje predstavljamo nov model, izpeljan iz osnovnih termodinamskih pristopov. Evtektična reakcija je bila modelirana s pristopom faznega polja. Uporabili smo nov pristop separacije člena površinske proste energije fazne meje na izotropni in anizotropni del. To nam je omogočilo uspešen opis prehoda lamelarnih evtektičnih karbidov v globularne, v orodnem jeklu AISI D2, zaradi modifikacije z redkimi zemljami Ce, La, Nd in Pr. S primerjavo eksperimentalnih in modelskih rezultatov smo uspeli podati razlago za spremembe pri modifikaciji. Pokazali smo, da modifikacija nekovinskih vključkov v jeklu modificiranem z redkimi zemljami ne vpliva na heterogeno nukleacijo evtektičnih karbidov. Preučili smo tudi mehanizem spreminjanja morfologije evtektičnih karbidov ki dobro razloži vse opažene razlike.

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Abbreviations

REE ...	Rare Earth Element
RE ...	Rare Earth
SEM ...	Scanning Electron Microscope
BEI ...	Backscattered-Electron Imaging
SEI ...	Secondary-Electron Imaging
EDS ...	Energy-Dispersive X-ray Spectroscopy
EBSD...	Electron-Backscatter Diffraction
FCC ...	Face-Centered Cubic
PDE ...	Partial Differential Equation

Symbols

a	... parameter of the model
a_γ	... austenite crystal lattice parameter
A_{xz}	... surface area of the boundary between control volumes in y direction
A_{yz}	... surface area of the boundary between control volumes in x direction
$\hat{a}_c$	... lattice parameter of hexagonal Cr_7C_3
$\hat{a}_\gamma$	... lattice parameter of the FCC austenite
α	... temperature crystallinity gradient coefficient
$\tilde{\alpha}$	... linear thermal expansion coefficient of the AISI D2 tool steel
$B(\mathbf{n})$	... Orientation dependency of strain magnitude
β	... logarithmic term magnitude
c	... non-dimensional carbon concentration
c_c	... non-dimensional carbon concentration Cr_7C_3 carbide
C_{ijkl}	... stiffness tensor
$c_{j,k}$	... non-dimensional carbon concentration in control volume indexed by j,k
$\bar{c}$	... average concentration
$\hat{c}_c$	... lattice parameter of hexagonal Cr_7C_3
$\tilde{c}_c$	... carbon molarity in Cr_7C_3 carbide in mol/m^3
$\tilde{c}_\gamma$	... carbon molarity in austenite mol/m^3
$\tilde{c}_L$	... carbon molarity in melt
c_δ	... non-dimensional carbon concentration value in first solid phase
c_γ	... non-dimensional carbon concentration value in second solid phase (austenite)
c_L	... non-dimensional carbon concentration in liquid phase
Δt	... non- dimensional time step length
ΔT	... temperature difference
ΔT_{UG}	... temperature difference between T_E and temperature of under-cooling at phase transition
Δx	... length of one control volume
Δy	... height of one control volume
Δz	... depth of one control volume
ε	... parameter of the model
ϵ_{ij}	... strain tensor
ϵ_{ij}^0	... misfit between austenit and carbide
f	... free energy density
f_s	... surface free energy density
$f_{s,a}$	... anisotropic part of surface free energy density
$f_{s,i}$	... isotropic part of surface free energy density
F	... total free energy
Φ	... right-hand sided vector
j	... index of discretization in x direction
$\mathbf{J}$	... Jacobian matrix
k	... index of discretization in y direction

k_b	... Boltzmann constant
κ	... gradient penalty coefficient
M	... mobility
M_c	... mobility of carbon in austenite
M_C	... molar mass of carbon
M_γ	... molar mass of austenite
M_θ	... average mobility of particles in melt
μ	... chemical potential
$\mu_{j,k}$	... value of chemical potential in control volume indexed by j,k
$\mathbf{n}$	... unit vector
N	... number of control volumes each one dimension
N_a	... Avogadro constant
Ω	... solid solution parameter
ψ	... order parameter
ρ	... specific density
ρ_{20}	... specific density of AISI D2 tool steel at 20 °C
ρ_E	... specific density of AISI D2 tool steel at eutectic temperature T_E
σ_{ij}^0	... stress on the phase boundary
T	... temperature
T_E	... eutectic temperature
θ	... non-dimensional crystallinity
θ_L	... value of non-dimensional crystallinity in liquid phase
θ_S	... value of non-dimensional crystallinity in solid phases
$\theta_{j,k}$	... value of non-dimensional crystallinity in control volume indexed by j,k
V	... volume
V_c	... Hexagonal Cr_7C_3 crystal lattice unit cell volume
V_γ	... FCC austenite crystal lattice unit cell volume
$V_{j,k}$	... volume of one control volume
x	... mass fraction in wt%
$\mathbf{X}$	... state vector
x_E	... mass fraction of carbon at eutectic composition in wt%

Chapter 1

Introduction

The investigation and control of steel quality is a very popular topic in material science, since it has a serious industrial application. Improved mechanical properties for steel is the goal of such investigations. Since the mechanical properties of steel depend on the steel microstructure, most studies of steel quality improvement are based on microstructural change [1]. Because the procedure of steel making involves many different thermodynamic processes, the final microstructure of steel depends on numerous different parameters and can therefore be changed in many different ways [2]. The most precise technique for steel microstructure evolution control is powder metallurgy, but due to the high cost this is not always the preferred option [3]. Ingot or continuous casting are much more common procedures of steel making but they do not allow the full control over the final microstructure [4]. In order to control and manage microstructure of cast steel many different techniques are used. Steel post-processing methods (rolling and forging) as well as different heat treatments of the steel are very efficient for obtaining the desired final microstructure of the steel [1], [5]. Nevertheless, it is important to perform such processes on well designed cast material since severe problems in the microstructure after casting still affect the final steel properties [6]. All steps in the production of the final steel should be optimized in order to get the best quality products at the end. Microstructure design begins at the chemical composition of the steel [6]. By altering the content of each individual chemical element inside the steel severe differences in microstructure can be obtained. Microstructure after casting (as-cast microstructure) is not equally sensitive to the alternation of each present element content. Some elements have the ability to change the as-cast microstructure even if real small alternation in their content is made. Such elements are usually added to the molten steel in very small amounts (trace amounts) for their desired strong influence on the as-cast microstructure [6]. A common example of such practice is deoxidation of the steel melt [7]. Besides deoxidation two other processes exist that are also based on small additions to the molten steel. These are modification and micro-alloying. The procedure of deoxidation, modification and micro-alloying are similar to each other but the purpose of each is different as well as the mechanisms that lead to the as-cast microstructural change [8].

1.1 Modification, Microalloying, Deoxidation

Modification, micro-alloying and deoxidation are the simplest, least expensive and effective methods to improve the mechanical, structural and service properties of steels [8]. Although the three processes all include addition of small amounts ($\sim 0,1 \text{ wt\%}$) of wisely chosen elements or compounds to the molten steel the purpose of the addition is different for every process.

Micro-alloying is a process where a small amount of metallic element is added to steel in order to exploit the ability of the added element to boundary segregate and precipitation harden the steel. In this way the hardness of steel can be greatly improved. The most common element for micro-alloying is Nb.

Modification is the term that in steel making means the improvement of steel's as-cast microstructure by small additions of elements called modifying agents. By modification, the microstructure of steel is refined and the inclusion size, composition and distribution can be changed. The most commonly used modifying agents are Al and Ti, as well as different rare earth elements (REEs).

Deoxydation is a common practice where additions of small amount of elements with a high affinity for oxygen are added to steel. Deoxydation is made in order to remove the harmful oxide inclusions from the steel. The most used deoxidisers are Ca and Al.

In this thesis we will focus on the modification and partially on the deoxydation of the steel. The micro-alloying will not be discussed. Figure 1.1 schematically shows the effect of chemical elements on the deoxydation, modification, and micro-alloying of steel.

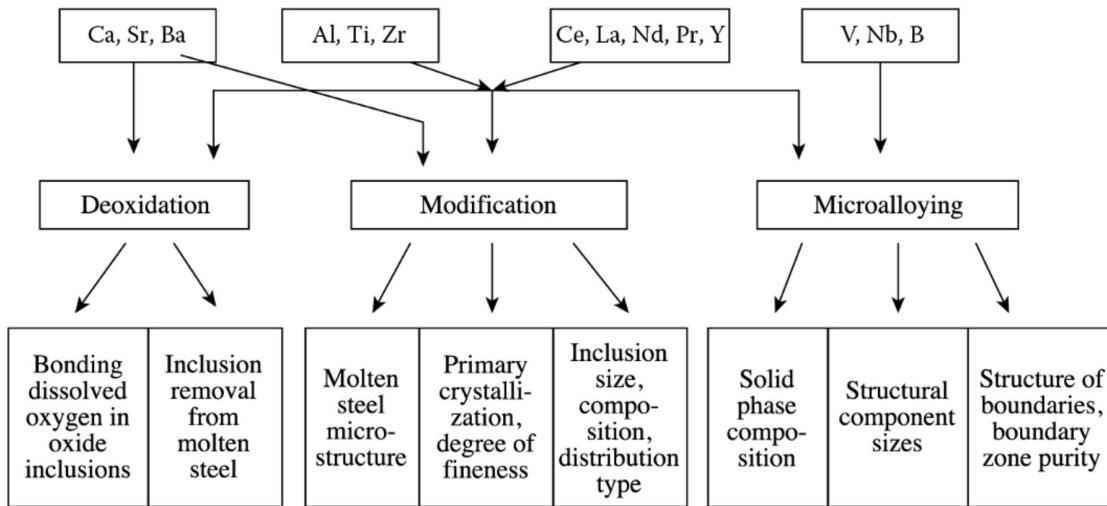


Figure 1.1: The effect of chemical elements on deoxydation, modification, and microalloying of steel [8]. Image was reused with the permission of copyright owner.

1.2 Gray Cast-Iron Modification

Gray cast-iron modification is one of the most common applications of the modification process. In order to obtain nodular cast iron (ductile iron) different modifying agents are added to the melt. Due to the modification the plate-like graphite in the microstructure of gray cast iron is transformed to the shape of nodules. That way ductility of material is increased [9]. The mechanism that governs the transition from plate like to nodular graphite morphology is not clear though. There are a few different possible explanations given in the literature [10]:

- The graphite theory: According to Boyles [11] graphite grows from already present small sizes crystalline graphite in the melt.
- The gas bubble theory: According to Karasay [12] graphite can only crystallize on a boundary such as gas bubble of CO .

- The salt-like carbide theory: Lux [13] proposed for the first time that different modifiers (Ca, Sr, Ba, Ce) form salt-like carbides which show low misfits with the graphite crystal lattice and thus act as effective nucleation sites.
- The silicon carbide theory: Wang and Fredriksson [14] developed a theory that explains nodularisation of graphite due to heterogeneous nucleation triggered by existence of local supersaturation of melt by C and Si.
- The oxide/sulfides theory: Kusakawa [15] proposed, that oxides and sulfides that occur in the melt due to modification act as heterogeneous nuclei for the graphite which leads to nodularisation.

None of these theories was proven beyond doubt [10].

The most commonly used modifying agents used in the case of gray cast-iron modification are Mg and Ce, which belongs to the group of REEs. The idea for the investigation of rare earth element (REE) Ce, La, Nd and Pr modification of AISI D2 tool steel came from analogy to gray cast iron. Since AISI D2 tool steel's carbon content is high (high above ledeburite point), we anticipated some similarities to the cast iron. The carbides in the as-cast microstructure were the target of our modification, similar to the plate-like graphite in the gray cast iron.

1.3 AISI D2 Tool Steel

AISI D2 ledeburitic steel belongs to the group of cold-work tool steels. These types of steels are used for tooling applications where wear resistance is important, such as blanking or forming dies and thread rolling dies, cutting tools, stamping, woodworking and molding tools for plastics [16]. Due to the high wear resistance, high compressive strength, and high hardness after hardening AISI D2 tool steel is the most commonly used high-carbon and high-chromium cold-work tool steel [17]. Composition requirements for this type of steel are presented in Table 1.1.

Table 1.1: Composition specifications for AISI D2 tool steel.

Element	Content[wt%]
C	1.40 - 1.60
Mn	0.60
Si	0.60
Co	1.00
Cr	11.00 - 13.00
Mo	0.70 - 1.20
V	1.10
P	0.03
Ni	0.30
Cu	0.25
S	0.03

As it can be seen from Table 1.1, the main characteristic of AISI D2 tool steel is very high content of carbon (above the ledeburite point) and high amount of carbide forming elements *Cr*, *Mo* and *V*. Due to high chromium content this type of steel is sometimes called semi-stainless steel. Nevertheless chromium is not added to AISI D2 for corrosion resistance purposes. The main target of high chromium content in connection to high

carbon content is evolution of eutectic primary carbides that bring high hardness and high wear resistance of steel in the cold work environment. These two mechanical properties are essential for the AISI D2 tool steel that is usually involved in die applications. *Mo* and *V* are used for the same purpose (high affinity to form carbides). Beside carbide formation *Mo* ensures the reduction of embitterment that is brought by high chromium content. The addition of *Co* increases hardness and promotes greater wear resistance by forming solid solution with ferrite. *Mn* is present in moderate amount for deep hardening. This is important since high concentrations of strong carbide formers are present, that withdraw carbon from solid solution, thereby reducing hardenability [1], [18], [19].

Detailed insights into the solidification process and resulting microstructure of the steel are essential for understanding modification.

1.3.1 Solidification of AISI D2 tool steel

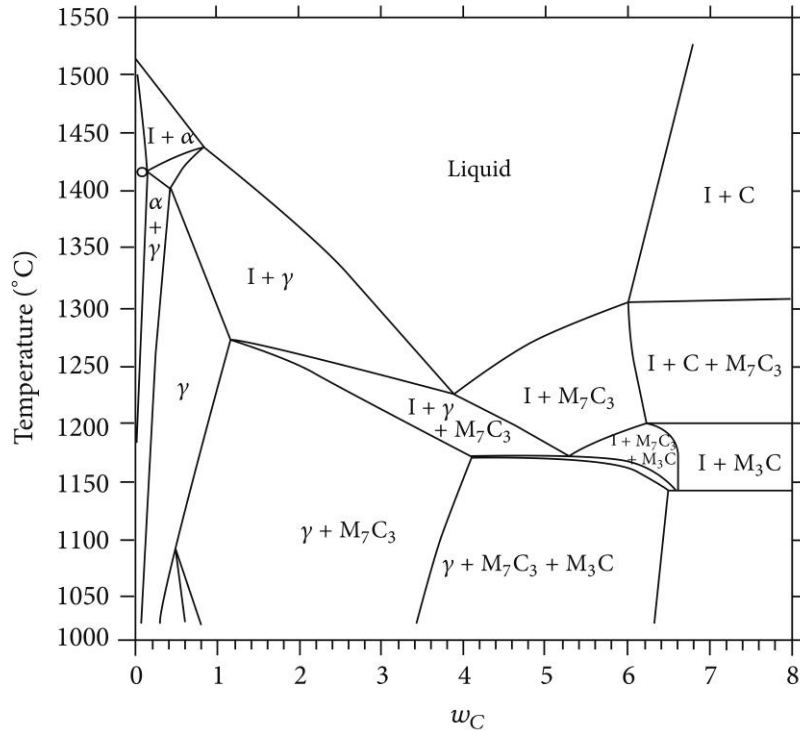


Figure 1.2: Binary phase diagram of AISI D2 tool steel with the variable carbon content, calculated with ThermoCalc [17] for composition 10.00 wt% *Cr*, 0.81 wt% *W*, 0.3 wt% *Mn*, 0.2 wt% *Si*, 0.6 wt% *Mo* and 0.8 wt% *V*.

Figure 1.2 shows the binary phase diagram of AISI D2 tool steel with variable carbon content. Phases present in phase diagram are liquid, α -ferrite, γ -ferrite and two carbides, M_7C_3 and M_3C . At the carbon composition 1.40–1.60wt% only the M_7C_3 eutectic carbides grow. Since chromium has by far the highest content among the carbide-forming metals in AISI D2 steel, eutectic carbides are of the type Cr_7C_3 . Different phases in solidification process are clearly seen on the phase equilibrium diagram in Figure 1.3, that shows the weight fraction of each phase dependency on temperature during equilibrium cooling. In combination with Figure 1.4 that schematically shows the microstructure evolution during solidification we can understand the as-cast microstructure of AISI D2 tool steel.

From Figure 1.3 it can be seen that the austenite phase is first nucleated from the melt

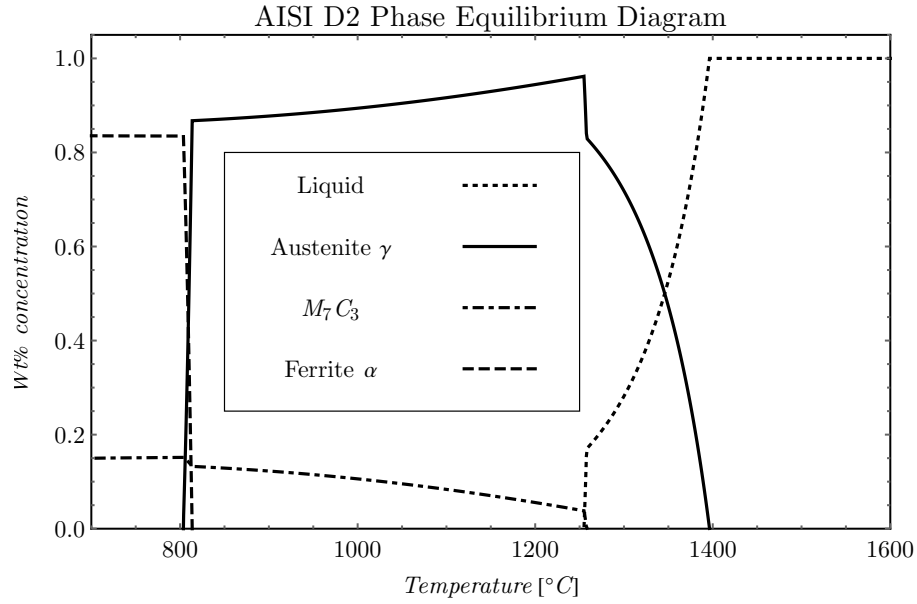


Figure 1.3: Temperature dependent phase equilibrium diagram for AISI D2 tool steel, calculated with ThermoCalc software for one mole of material at the pressure 101,325kPa and chemical composition as presented in Table 3.3, ingot #2. Ingot #2 composition was chosen as reference non-modified material since all the results for non-modified material in Chapter 4 are shown for ingot #2.

at 1396° C (Figure 1.4 (a) and (b)). The crystallization of the austenitic phase from the melt is strongly anisotropic [21]. This results in a dendritic growth of austenite (Figure 1.4 (b) - (e)). As dendrites grow the weight fraction ratio between austenite and liquid phase continuously increases, as can be seen from Figure 1.3. Since the overall carbon content in AISI D2 tool steel is larger than the solid solubility of carbon in austenite, carbon segregates to the remaining melt in this stage of solidification. In this way the carbon concentration in the melt rises. With the decreasing temperature the solubility of carbon in austenite rises (Figure 1.2). This results in a chemical inhomogeneity that can be seen later in the final as-cast microstructure as the chemical composition gradient along the primary dendrite arms. Segregation of carbon to the melt continues since eutectic temperature is met (1258° C), where the eutectic reaction happens in the remaining melt. This can be seen from Figure 1.3 as a sharp drop in the liquid phase fraction, sharp raise of austenite fraction and appearance of M_7C_3 carbide. Liquid phase is decomposed to lamellarly structured eutectic, composed of M_7C_3 and austenitic lamellas (Figure 1.4 (d) and (e)). At this point all the melt is solidified and only solid phases exist. Solidification is at the end but the microstructure evolution still continues. At the temperature of 814° C the α ferrite phase appears. In very narrow temperature interval all the austenite is transformed to the α -ferrite. Weight fraction of chromium carbide is slightly raised during this transformation since the solubility limit of carbon in austenite is higher than in α -ferrite and secondary carbides precipitate from the matrix at this point. From the Figure 1.3 it can be seen that these carbides are also M_7C_3 type. Further cooling results in a continuous decrease in carbon solubility in α -ferrite. This leads to further precipitations of carbides from the matrix. It was calculated with ThermoCalc that at the temperatures below 664° C another carbide ($M_{23}C_6$ type) appears at the equilibrium cooling. But since conditions in our experiment were far from equilibrium cooling this did not happen. That is also the reason why Figure 1.3 and Figure 1.2 are plotted only for the high temperatures.

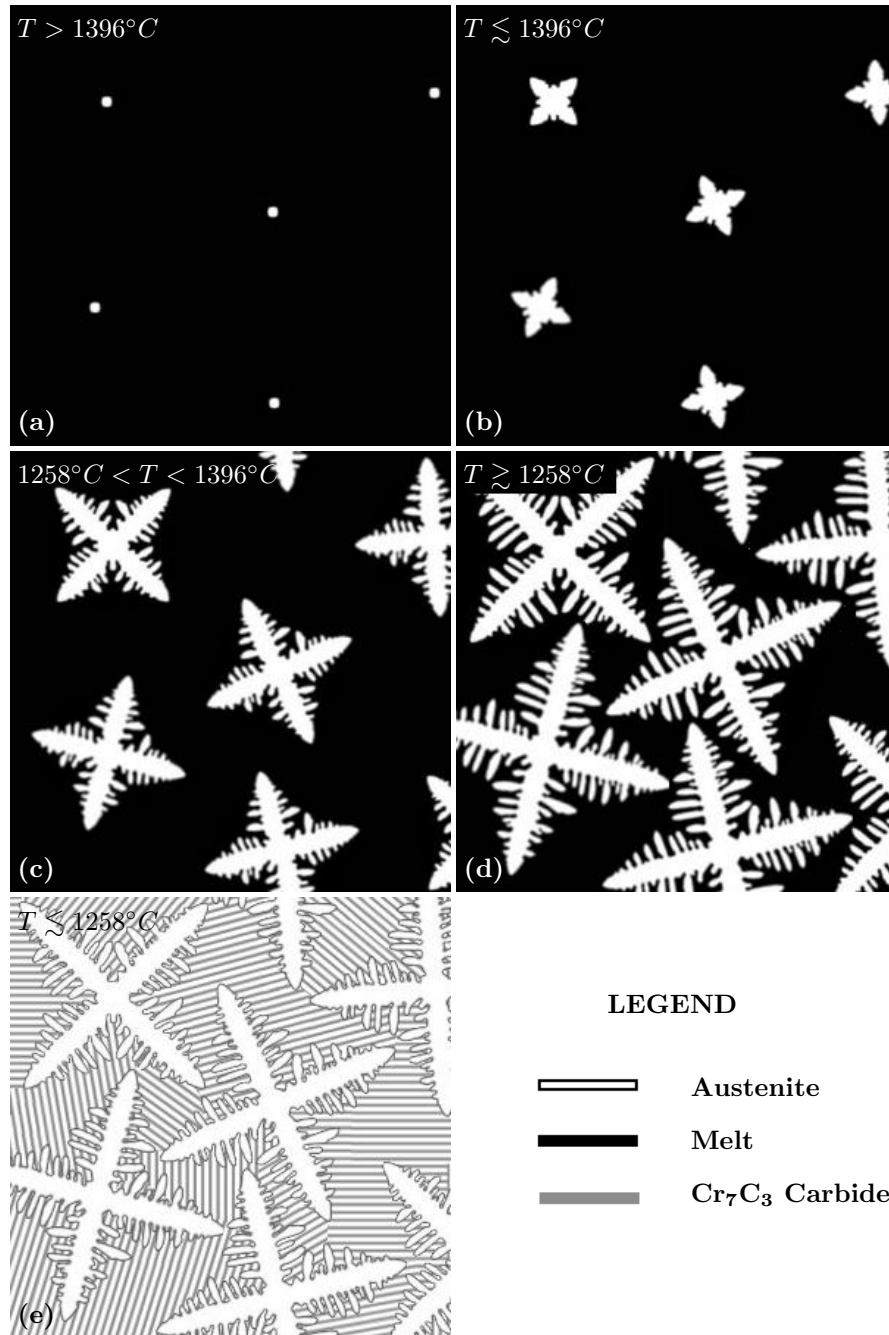


Figure 1.4: Schematic representation of microstructure evolution during solidification. Black color represents liquid phase (melt), white color is austenite and gray color Cr_7C_3 carbide. Volume fractions of different phases in the figure are not exact since this is not the real simulation but only a didactic representation. The temperature decreases from figures (a) to (e). Figure was made by author of this thesis with the parts of the images taken from reference [20].

1.3.2 As-cast microstructure of AISI D2 tool steel

The as-cast microstructure of AISI D2 tool steel is presented on Figure 1.5.

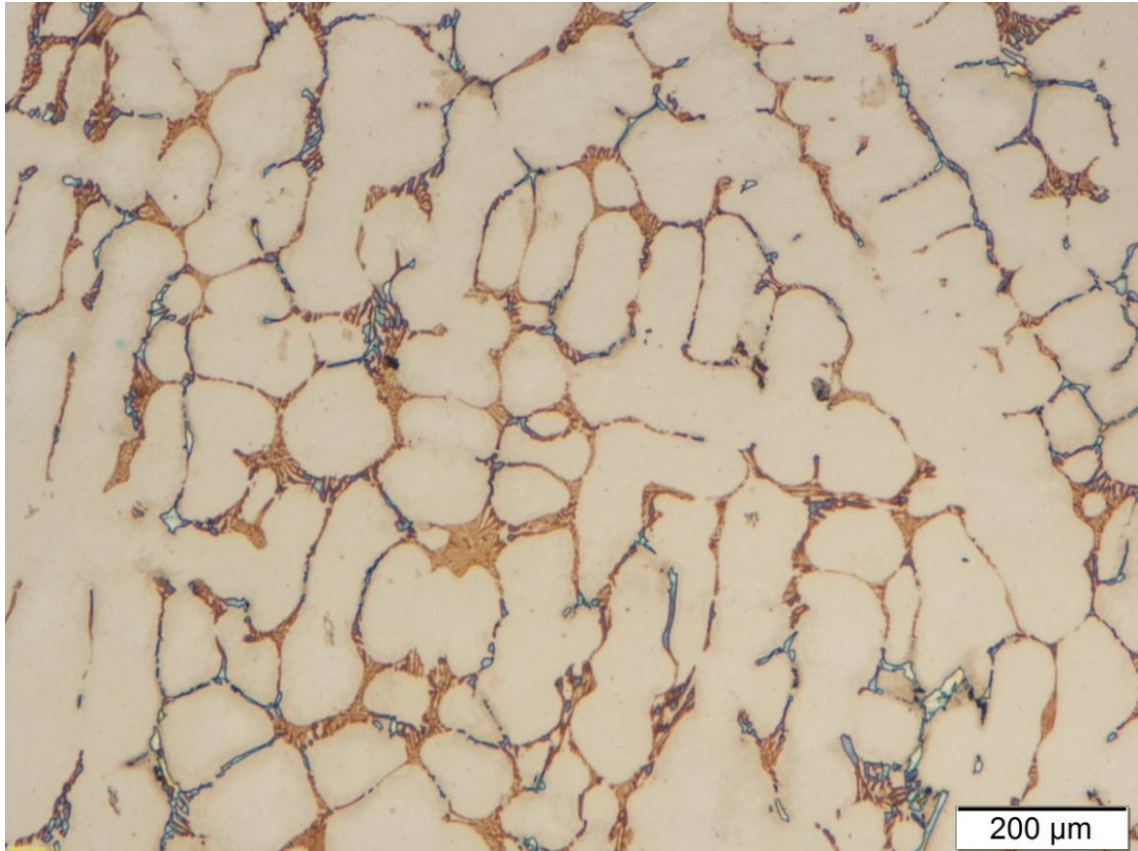


Figure 1.5: As-cast microstructure of AISI D2 tool steel. Light microscopy image.

Lighter areas on the figure represent the ferritic matrix and darker areas are ledeburite eutectic carbides. Many processes described in subsection 1.3.1 can be seen from this figure. The dendritic structure is very clearly seen. On the right side of the figure dendrite was cut along the primary dendrite arm and secondary arms are clearly seen. Among the secondary dendrite arms the eutectic is positioned. The eutectic phase forms connected network that wraps the dendritic grains. This shows that the eutectic was the last solidified phase in the interdendritic regions. The lamellar nature of the eutectic regions can only be seen at higher magnifications. In Figure 1.6 a typical lamellar eutectic carbide from AISI D2 tool steel is shown.

The lamellar structure of the eutectic region is the most common form of eutectic carbide. It is a result of different growth rates in different crystallographic directions of both phases forming the eutectic [1]. The detailed explanation of lamellar growth can be found in Chapter 5.

The morphological features of the eutectic phase as well as dendritic grains stay unchanged from the point of their formation even though austenite later undergoes the phase transformation to α -ferrite. They are a direct consequence of the melt solidification path. Therefore, a change in morphological features in the as-cast microstructure will be the primary goal of the modification by rare earth elements that can actively influence the path of solidification.

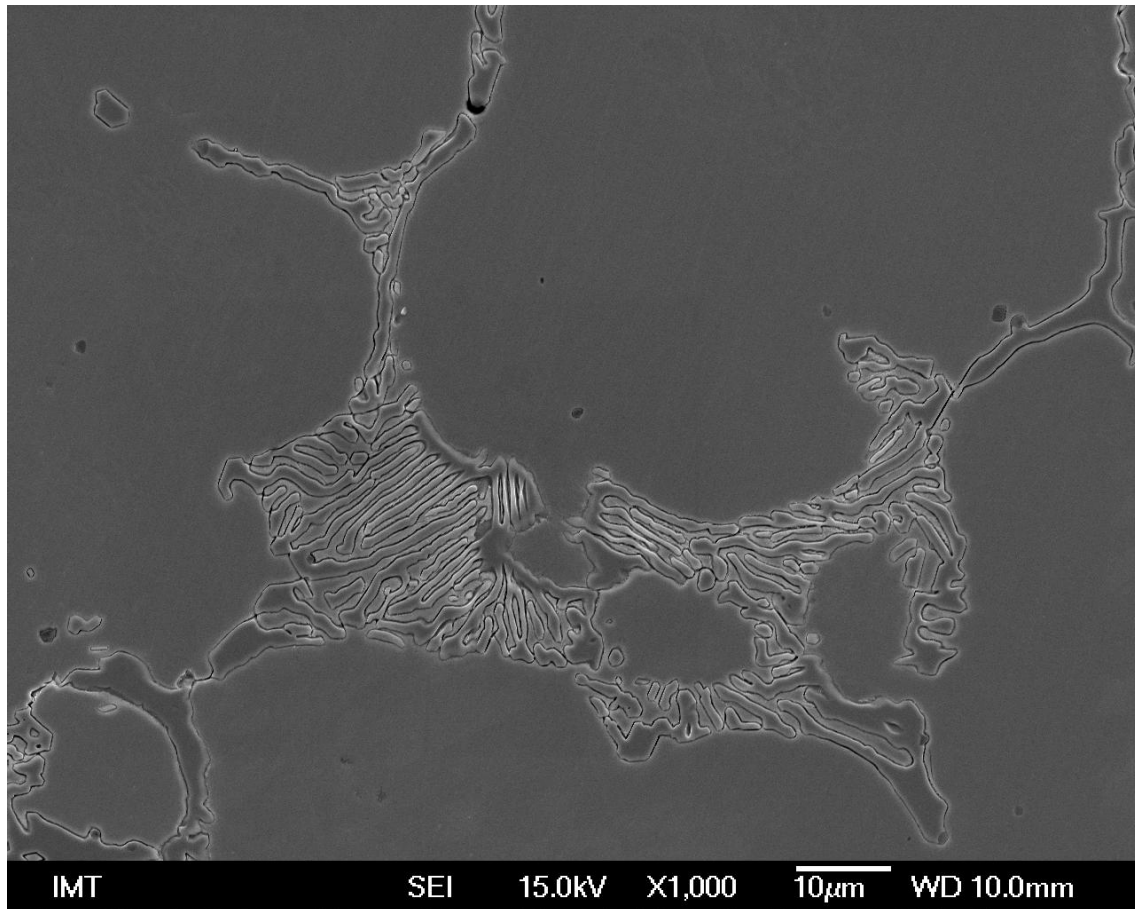


Figure 1.6: As-cast microstructure of AISI D2 tool steel. Scanning electron microscopy secondary electron image.

1.4 Modification of Steel with Rare Earth Elements

1.4.1 Rare Earth Elements (REEs)

Rare earth elements (also rare earth metals) is the term used to indicate the set of seventeen elements from the third group of the periodic system. REE group of elements consists of fifteen lanthanides as well as scandium and yttrium. Fifteen lanthanides are the elements from atomic number 57 through 71, from lanthanum through lutetium. Figure 1.7 shows the position of all seventeen REEs in the periodic table [22]. All but three REEs (lutetium, scandium and yttrium) are f-block elements, corresponding to the filling of the 4f electron shell. Lutetium, scandium and yttrium are considered to be REEs due to their chemical similarity with the other fourteen [23].

1.4.2 Physical properties of REE

Several physical properties of REEs are presented in Table 1.2.

Melting and boiling points of REEs in comparison to iron differ so much that the problems with dissolution or vaporisation are not likely to occur during the addition of REEs to molten steel. Also the low vapor pressure at steel making temperatures and infinite solubility of REEs in molten steel are the main advantages of REEs used as modifiers in comparison to the commonly used modifiers magnesium and calcium. Similar

1																	2	
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Lanthanides	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Actinides															
	Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		

Figure 1.7: Periodic table of elements with REEs indicated in yellow [22] (image found on Internet free from copyrights).

Table 1.2: Physical properties of several REEs, in comparison to iron [24].

Element	Melting Point [$^{\circ}\text{C}$]	Boiling Point [$^{\circ}\text{C}$]	Density [kg/m^3]
Fe	1538	2862	7874
Ce	795	3443	6770
La	920	3464	6162
Nd	1024	3074	7010
Pr	935	3130	6770

to the Mg and Ca, the solubility of REEs in solid steel is very low. This can be seen from the Fe - Ce phase diagram in Figure 1.8.

1.4.3 Function of REEs in Steel

REEs are added to steel for a few different reasons. The functions of REEs in steels can roughly be divided into three categories, described in this section.

1.4.3.1 Purification of the steel

The most frequent use of REEs in steel making is the process of purification (deoxidation and desulfurization) [26]. The suitability of several REEs for these two processes can be seen from Table 1.3 that shows the melting points and densities of most stable REE compounds in comparison to the other most common oxides, sulphides and nitrides found in steel.

From the high affinity of the REEs for oxygen and sulfur as well as the high melting points of RE oxides and sulfides it seems likely that REE oxides and sulfides as well as complex oxysulfides $\text{RE}_2\text{O}_2\text{S}$ will form immediately upon adding of REEs to molten steel. The Gibbs free energies of REE nitride formation are much lower than those of oxides, sulphides and oxysulphides. That is why we do not expect the REE nitrides to occur inside REE-treated steel. The same goes for carbides. The Gibbs free energies of

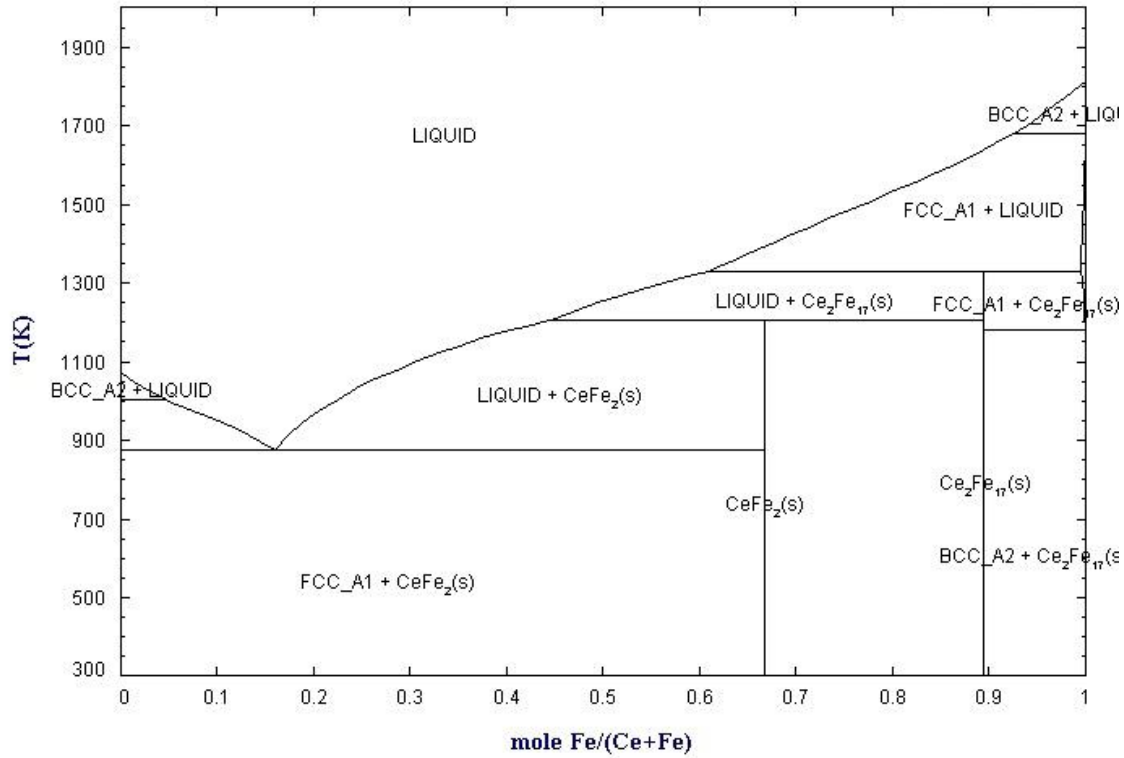


Figure 1.8: Binary phase of cerium and iron, calculated with ThermoCalc [25].

formation of carbides for the majority of the potential carbide formers (W, V, Ti, Cr) are much more negative than the Gibbs free energy of any REE carbide [35], [36].

1.4.3.2 Inclusion Control

Inclusion control is the process of steel modification that ensures control over the non-metallic inclusion type, size and distribution in the melt, during steel solidification [37]. REEs are frequently used for that purpose in many different steel grades. Precise control over the non-metallic inclusions in steel is important since the final properties of the steel greatly depend on it via three different effects:

1. The type of inclusion determines the efficiency of the inclusion as the heterogeneous nucleus for the solidifying steel. The misfit between the crystal lattice of the solidifying steel matrix and the non-metallic inclusion is the governing parameter that determines the efficiency of inclusion as a heterogeneous nucleus. According to the generally accepted Bramfitt planar disregistry theory the misfit between the nucleating crystal lattice and the nuclei crystal lattice should not be greater than 6% for heterogeneous nucleation to occur [38].
2. grain growth suppression occurs by pinning the austenitic grain boundary during recrystallization on different non-metallic inclusions [39]. The efficiency of the pinning depends on the non-metallic inclusion type and size [40].

Table 1.3: Physical properties of most stable REE compounds (oxides, sulphides, oxysulphides and nitrides) in comparison to some other common oxides, sulphides and nitrides found in steel. / sign in table means that compound does not exist [23], [27]–[35].

Compound	Melting Point [$^{\circ}C$]	Density [kg/m^3]
Oxides		
CeO_2	2400	7650
Ce_2O_3	2230	6200
La_2O_3	2305	6510
Nd_2O_3	2320	7240
Pr_2O_3	2300	6900
Al_2O_3	2054	3950
CaO	2900	3340
Sulfides		
CeS	2445	5900
Ce_2S_3	2450	5000
LaS	2300	5610
La_2S_3	/	/
NdS	2207	7000
Nd_2S_3	1760	5100
Pr_2S_3	1610	4000
Oxysulfides		
Ce_2O_2S	1949	6000
La_2O_2S	1993	5800
Nd_2O_2S	1988	6300
Pr_2O_2S	1965	6200
Nitrides		
CeN	2557	7900
LaN	/	/
TiN	3290	5430
ZrN	2960	7090
AlN	3000	3255

- Some non-metallic inclusions can act as the heterogeneous nuclei for the other inclusions that otherwise would never be nucleated (i.e., sulfides, nitrides and carbides). In this way segregations of sulfur, nitrogen and carbon can be controlled. Anticipations of the modification in such cases can be calculated by the Bramfitt planar disregistry theory, similar to the case of grain refinement due to increased heterogeneous nuclei in the melt.

The first two processes result in refined steel microstructure and consequently the toughness and the strength of the steel are improved. The third process is sophisticated purification by inclusion control. Therefore, it brings all the benefits of the of steel purification.

The REEs in steel form several complex compounds with oxygen and sulfur. In order to understand and plan the inclusion control by REEs it is essential to know the phase-equilibrium diagram of the different non-metallic REE-containing inclusions. Wilson et al.

[36] calculated an inclusion-precipitation diagram for the iron - cerium - oxygen - sulfur, presented in Figure 1.9

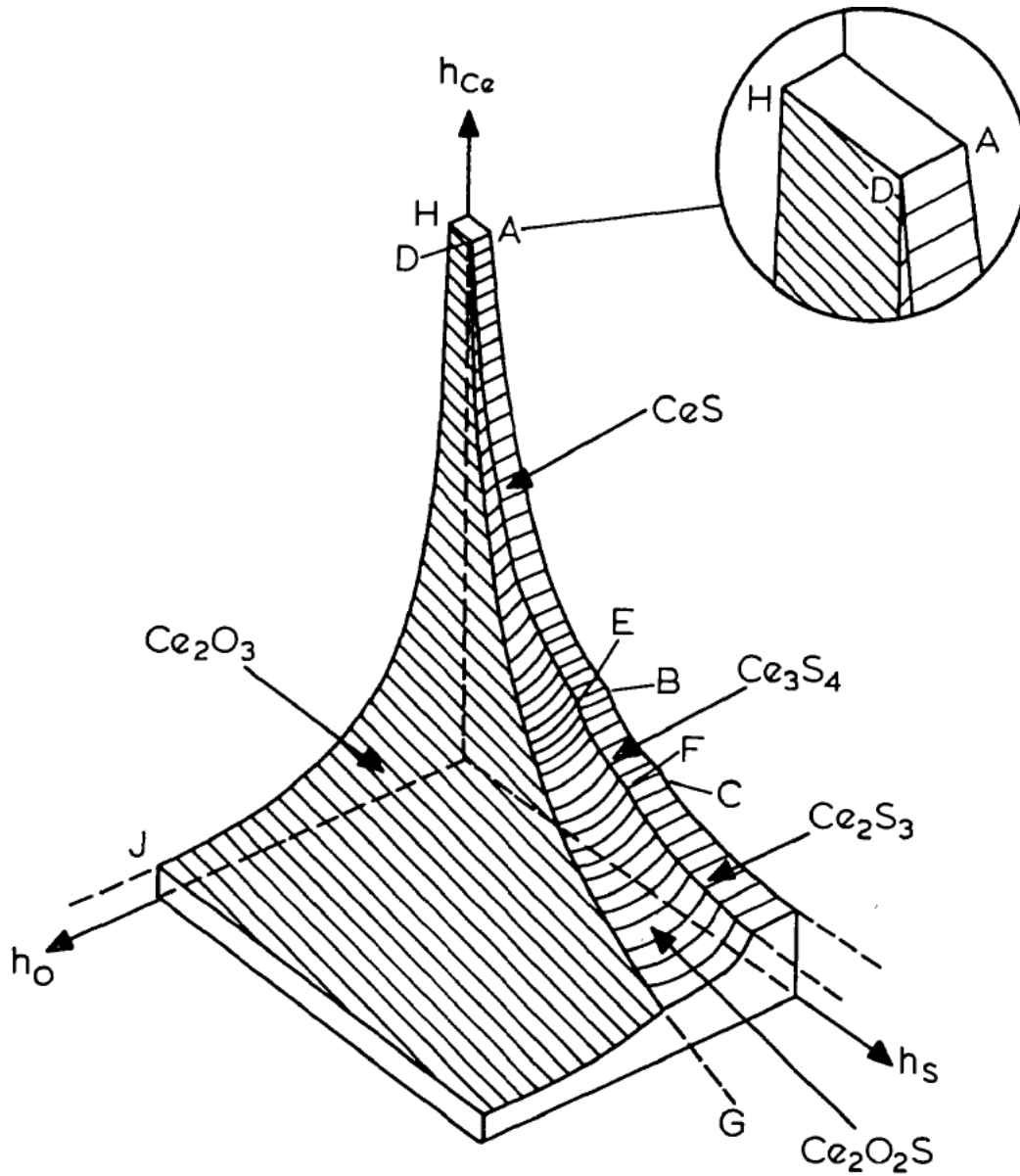


Figure 1.9: iron - cerium - oxygen - sulphur precipitation diagram [36]. h_{Ce} , h_S and h_O represent the activities of cerium, sulfur and oxygen.

From the precipitation diagram we can see that the type of inclusions that precipitate inside iron, mainly depends on the ratio between the initial activities (concentrations) of the oxygen and sulfur at a fixed cerium concentration. If the initial concentration of oxygen is less than ten times the concentration of sulfur, the Ce_2O_3 oxide precipitates. This precipitation lowers the activity of oxygen (consumes the oxygen and lowers its concentration in melt). When the concentration of oxygen falls under ten times that of the sulfur, the oxysulfide Ce_2O_2S starts to form (DG line on the diagram). This precipitation spends two times more oxygen than sulfur (in *at%*) and the ratio between both elements is still being changed. When the ratio between the concentrations of sulfur and oxygen rises to approximately 100 the sulfide starts to form (DEF line on diagram). The type of sulfide

that starts precipitating at this point is dependent on the amount of cerium in the melt. For the high cerium concentration CeS sulfide forms (above the BE line on diagram) and at the low concentrations Ce_2S_3 forms (below CF line). In the narrow region between both the Ce_3S_4 precipitate (between lines BE and CF). The oxysulfide Ce_2O_2S and one of the cerium sulphides precipitate simultaneously so that the ratio between the sulfur and the oxygen stays constant. The path of the reaction follows the equipotential plane that separates the oxysulfide and sulfide regions of the diagram. The amount of precipitated oxysulfide in comparison to the cerium sulfide in this regime is dependent on the stoichiometric oxide/sulfide ratio in both precipitates. In the ideal case this regime continues until the melt is completely depleted of oxygen. After that only the sulfide precipitation takes place. If the initial ratio between the sulfur and oxygen was above a value of ten, the path of precipitation would start in the region of oxysulfide. Similarly, if the initial sulfur/oxygen ratio was above 100, the precipitation would start in the sulfide region. Thus, the wanted performance of the modification can be controlled by the initial oxygen and sulfur contents. The diagram constructed by Wilson et al. [36] was obtained by theoretical thermodynamic calculations and not from the experimental data. The effects of additional alloying elements in different grades of steels can change the described reaction path, but the fact that the ratio between the oxygen and sulfur dictates the type of the precipitates stays unchanged.

1.4.3.3 Micro-alloying

The micro-alloying of steel can be achieved by REE additions to the melt. The atomic radii of REEs are between 0.164 nm (*Sc*) and 0.204 nm (*Eu*), which is large in comparison to the iron atom radius of 0.128 nm. That is the reason for the very low solubility of REEs in crystal iron (austenite or ferrite). REE atoms form a substitutional solid solution with the crystal lattice of iron with a very low solubility limit of around $10^{-5} - 10^{-6}$ ppm [41], due to the large differences between the atomic radii of the solvent and the solute. Every REE atom substitutionally inserted in the iron crystal lattice causes a high local lattice strain due to the iron and REE atom radius difference. Therefore, the integration of REEs into iron crystal lattice is energetically unfavorable and the solubility is low. The solubility of REEs in iron increases with the temperature, which leads to a process of precipitation during the heat treatment. Precipitates obtained by heat treatment (precipitation hardening) as well as local crystal lattice strain around individual RE atoms interact with moving dislocations in the crystal lattice. Interaction energy of expanded crystal lattice strain field around RE atoms with the dislocation is in average negative. Therefore dislocations bound to RE atoms and the motion of dislocations is blocked. Since dislocations are the dominant carriers of plasticity of material this serves to harden the material. Yield strength of the steel can be greatly improved by solid solution straightening as well as precipitate hardening [42].

Another beneficial effect of REEs in steel that can be classified as micro-alloying is the segregation of REE atoms to the phase boundaries due to low solubility in the steel matrix. With the segregation on grain boundaries REEs eliminate the local weaknesses due to sulfur and phosphor atoms in steel. This improves the shock resistance as well as the strength of the grain boundaries [43]–[46].

1.5 Tool-Steel Modification by REEs

Not all physico-chemical processes explained in section 1.4.3 (roughly divided in categories of purification, inclusion control and micro-alloying) were reported in the field of tool steels.

Most investigations of tool steel REE modification that are found in literature deal with either grain size refinement or eutectic carbide type, size and morphology modification. Both observed effects of REEs in tool steels can be explained by the inclusion control process, which is in general by far the most exploited process that REEs offer in steel.

1.5.1 Grain Size Refinement

In the field of tool steels Gao et al. showed a nice implementation of inclusion control by REEs on AISI H13 tool steel and offered a consistent explanation of the grain refinement that they measured. Figure 1.10 shows the results of Gao et al.'s investigation. Refinement in as-cast microstructure is clearly seen. Gao et al. explained grain refinement by Bramfitt

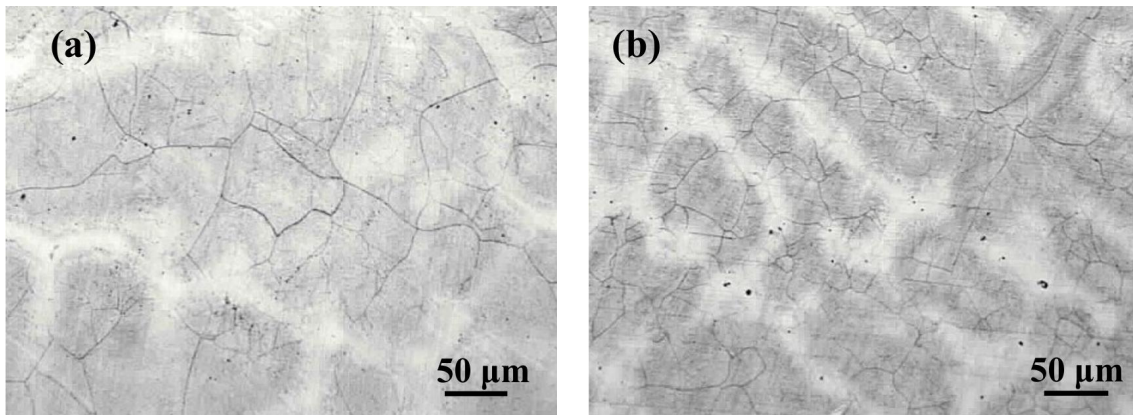


Figure 1.10: Example of grain refinement by REEs addition inclusion control in AISI H13 tool steel, published by Gao et. al. [47]. Figure (a) shows as-cast microstructure of non-modified AISI H13 steel. Figure (b) shows as-cast microstructure of AISI H13 steel modified by 0.025% REEs.

planar disregistry theory and also showed that in this kind of steel grain boundary pinning during recrystallization does not occur. Purification of the steel melt as well as micro-alloying mechanisms are not observed nor discussed in this study.

The refinement of the grain size in the as-cast microstructure of different tool-steel grades due to REE-modified non-metallic inclusions was also reported by the authors of the studies in references [48]–[52]. Their results are shown in Figure 1.11. Images of the non-modified microstructures are on the left-hand side and REE modified on the right-hand side of the figure. Details about each steel can be found in the caption of the figure. All the steels in Figure 1.11 are high-carbon, high-chromium tool steels and therefore all the microstructures are similar. The solidification paths are very similar to AISI D2 tool steel, described in Section 1.3.1. The as-cast microstructures consist of a dendritically solidified ferritic matrix and eutectic carbides on the boundaries between the dendrites. A comparison of the left to right column of images in Figure 1.11 shows that the refinement of the grain size happens in REE-modified tool steel.

1.5.2 Eutectic Carbide Modification

Even more important than several times proven grain refinement is the fact that all of mentioned authors reported some effect of REEs on the eutectic carbides in the tool steels as-cast microstructure. The effect of REE modification on eutectic carbides was also observed sometimes in the absence of grain size refinement [53]–[55]. They found that REEs in tool steels can modify shape [48]–[53], [55], size [52], morphology [49], [51], [54] and type

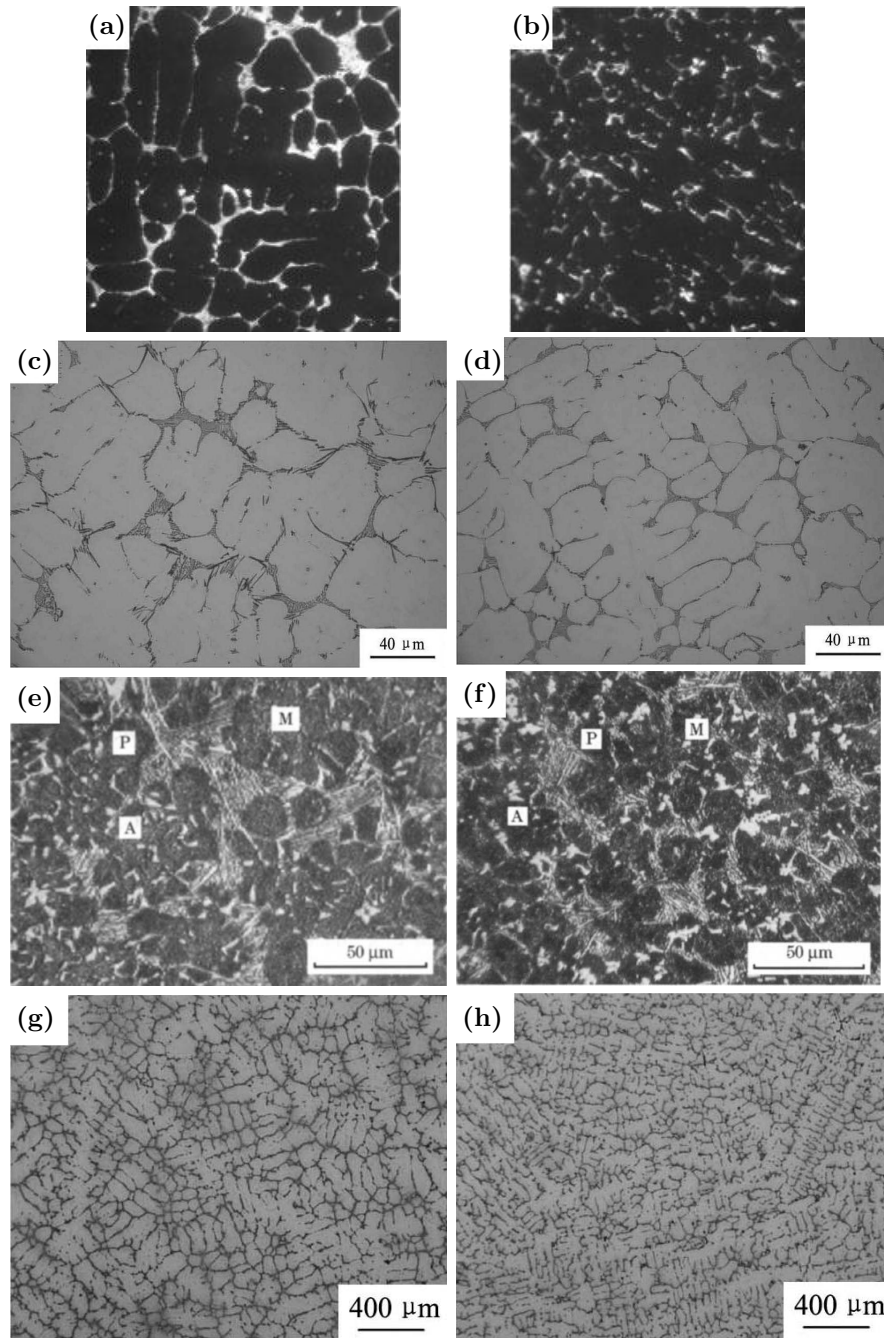


Figure 1.11: Refinement of as-cast microstructure by REEs. Non-modified (left - (a), (c), (e) and (g)) and RE modified (right - (b), (d), (f), (h)) as-cast microstructures of different tool steels from references [48]–[51]. Tool steel grades in figure are: (a) AISI M2 [50], (b) AISI M2 modified with 0.25 *wt%* *Ce* and 0.12 *wt%* *La* [50], (c) AISI M2 [51], (d) AISI M2 modified by 0.8 *wt%* *RE*, where *RE* represents the mix of *Ce*, *La*, *Nd* and *Pr* in the ratio decried in Table 3.1 [51], (e) HCHSS similar to AISI M35 [48] (f) HCHSS similar to AISI M35 modified with 0.09 *wt%* *Ce*, (g) AISI M2 [49], (h) AISI M2 modified with 0.2 *wt%* mostly *Ce* [49].

[49], [51], [54] of eutectic carbides. Contrary to grain size refinement, which is well understood, the effect of REEs on eutectic carbides in tool steels was not yet fully explained.

There are at least three different attempts of explanation of effects of REEs on eutectic carbides in tool steels.

1. First possible explanation was proposed by Li et al. [53] and later used again in references [50] and [51]. According to this explanation the segregations of REEs from solidifying solid phase to melt are responsible for the eutectic carbide shape change. Since REEs solubility limit in austenite is extremely low, segregation happens that enriches the melt in front of the advancing dendrite. This enrichment will cause high compositional supercooling, which promotes the branching of dendrites and consequently decreases the secondary dendrite arm spacing [56]. The residual space among the dendrite arms filled with melt at the time of eutectic reaction is thus refined and much smaller carbides are nucleated in the refined inter-dendritic regions.
2. Second possible explanation was also proposed by Li et al. [53] and states that the interaction between carbon and REEs in the enriched melt is responsible for the changed eutectic carbides. REEs (in original reference [53] *Ce*) decrease the activity of carbon in the melt. Due to the strong segregation of REEs to the melt during solidification, this effect can be non-negligible. The eutectic reaction caused by segregated carbon and carbide-forming metals in the melt must take place at a higher solid (austenite) fractions. In this way the inter-dendrite spaces are reduced and consequently eutectic carbides are refined and the overall volume of eutectic is decreased.
3. Third explanation is the most commonly accepted due to the fact that it is also capable of explaining carbide type change due to REE modification besides size, morphology and amount. The reason for the modified eutectic carbides are modified non-metallic inclusions that represent the heterogeneous nuclei for the eutectic reaction. Depending on the type of inclusions, different types of eutectic carbide can be nucleated in the as-cast microstructure. The amount and distribution of such nuclei (non-metallic inclusions) determine the size, distribution and morphology of the resulting eutectic carbides. Since REEs are efficient non-metallic inclusion modifiers it is highly possible that in this way several characteristics of eutectic carbides can be changed [49], [52].

1.5.3 REE modification of AISI D2 tool steel

A lot of experiments with REE modification were made on high-speed tool steels, especially on AISI M2 steel grade (as can be seen from cited references in the previous section). Not much was made on cold-work tool steels. Since the morphology, size, distribution and amount of eutectic carbides in cold-work tool steel as-cast microstructure strongly influence the post-processing procedure [57] (in case of AISI D2 forging), modification of eutectic carbides could beneficially affect AISI D2 production process as well as final mechanical properties of steel [52]. The only study of AISI D2 steel grade modification with REEs reported in literature was performed by Hamidzadeh et al. [52]. This study shows spectacular results. This was one of the reasons for the choice of material for our investigation. Figure 1.12 shows the comparison between the as-cast microstructure of the non-modified and REE-modified AISI D2 tool steel as measured by Hamidzadeh et al. [52].

The differences between the compared microstructures in Figure 1.12 are very significant. The eutectic carbide net among the dendrites is broken, eutectic carbides are refined and overall amount of eutectic is drastically reduced. According to explanation of Hamidzadeh et al. [52] the differences in microstructure are caused by heterogeneous nucleation of carbides on REE-modified non-metallic inclusions. They calculated crystal

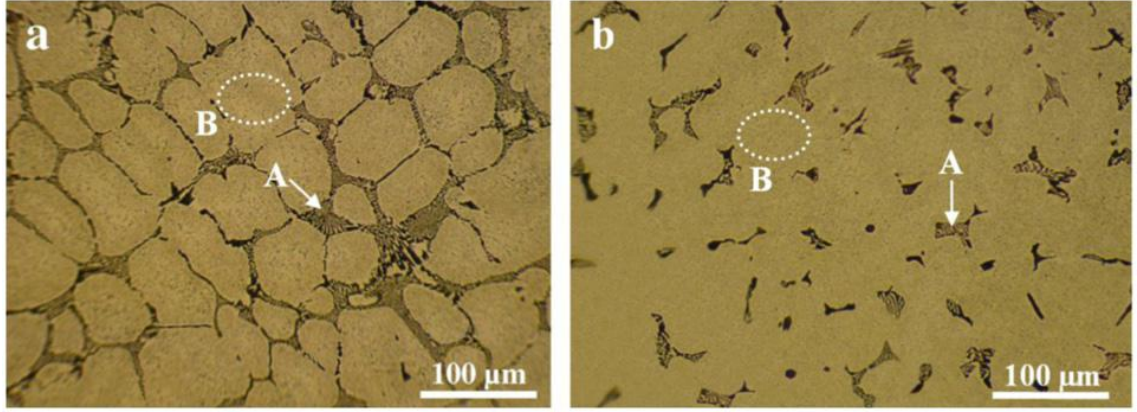


Figure 1.12: Light micrograph comparison of non-modified and RE Modified AISI D2 microstructure [52]. Composition of the material is almost identical to ours (Table 3.3). For RE modification 0.03 *wt%* of modifier was added, which included approximate 65% *Ce* and 35% *La*.

lattice misfit between RE_2O_2S type of non-metallic inclusion (found in modified steel) and Cr_7C_3 eutectic carbide. The match between both crystal lattice is high enough for inclusions to efficiently nucleate carbides.

Study of Hamidzadeh et al. [52] was a great motivation for our study since results are very promising. Since all investigations mentioned in the last section use *Ce*, *La* or *Ce*-mischmetal (Table 3.1) for the modification due to low price and accessibility of these materials, we decided to use the same modifiers in our study. In the experimental part of this thesis we will describe the successful modification of AISI D2 tool steel by the REEs *Ce*, *La*, *Nd* and *Pr*, that resulted in eutectic carbide morphology change from lamellar to globular.

1.6 Modeling

In the Section 1.5.2 we listed three different possible explanations for the modification of eutectic carbides in tool steel that are found in literature. The last of the three listed explanations is by far the most used one since it is capable of also explaining the carbide type change besides morphology, size and amount. Nevertheless, there is no general consent on which of the three explanations is true. That is why we decided to devote the second part of my thesis to the construction of a eutectic reaction model that would help us propose the right theoretical explanation of eutectic carbides modification. Eutectic solidification can be mathematically described as transport phenomena with transport of mass and heat across phase boundary interface [58]. Transport phenomena can be described with diffusion partial differential equations and the phase boundary interface is taken into account by one of the boundary conditions. Traditional modeling approach to the solidification problems [58] includes numerical solving of dynamic equation system by most appropriate numerical method (finite element, finite differences, finite volume method [59]). With the use of a phase-field modeling approach the boundary condition on the phase boundary interface is no longer needed and the complexity of dynamic equation system is reduced [60]. Since introduced concept of continuous phase field with high gradients demands fine discretization of the calculation domain as well as robust methods of solving equations, this modeling technique demands high computational power [61]. From the middle 1990s when personal computers became quite powerful and most of all inexpensive and accessible, phase-field

modeling is the only approach that is used for solidification problems (eutectic reaction among them) [62].

1.6.1 Phase-Field Modeling

Phase-field modeling is a special mathematical approach to solve the inter-facial problems. Rather than determining the boundary condition on the interfaces inside the system, interfaces are described by a rapid but continuous change in phase field. Variable determining the phase field value is called the order parameter and occupies distinctive values in each of two phases forming the interface. The exact position of the interface is defined by the interception of phase field with the predetermined threshold value that is usually the average of the order parameters values in both phases. The phase field modeling approach is not only capable of exact interface position calculation but inherently contains the phase boundary thickness, which is in many cases a very relevant physical quantity. Beside excluding inter-facial boundary conditions, this is the main advantage of phase-field modeling in comparison to traditional differential equation solving.

1.6.1.1 Landau Theory

Landau theory is the basis for the phase-field modeling of the phase transitions [63]. It is phenomenological thermodynamic theory, that offers precise description of first and second order phase transformations [64]. Many fundamental physical phenomena were first explained by Landau theory. The basic idea of the theory is to find the dependency of the free energy potential on the so-called order parameter. Minimization of the free energy determines the value of order parameter which describe the state of the system [64]. The order parameter is a quantity, that changes significantly during the phase transformation. The choice of order parameter of the system is essential and unique for any given system. In the case of describing liquid solidification to crystalline solid, which is one of the most well known Landau theory applications [64], crystallinity is usually used as order parameter [65]. This is the parameter that is severely changed during the phase transformation and therefore good phase transition monitoring parameter. The dependency of the free energy potential on the order parameter is minimized by the total free energy functional minimization and in this way stationary states of the system are obtained in relation to the parameters of the system [66]. The most demanding part of the whole process is to estimate the free energy dependence on the order parameter. In many cases it can be derived from physical first principles. For the systems where this is not the case, free energy functional dependency on the order parameter can be approximated by polynomial ansatz that describes the potential minimums position and depth well. For the first-order phase transitions (phase transitions where latent heat is generated) there are three usual choices. The non-symmetrical fourth-order polynomial double-well potential (equation 1.1), the logarithmic symmetric double well potential (equation 1.2) and the sixth order symmetric polynomial with the negative quadratic term (equation 1.3) [67]–[70].

$$f_1 = f_{1,0} + \gamma\psi + \frac{1}{2}\alpha\psi^2 + \frac{1}{4}\beta\psi^4 \quad (1.1)$$

$$f_2 = f_{2,0} + \alpha[\psi\ln(\psi) + (1 - \psi)\ln(1 - \psi)] - |\beta|\psi(1 - \psi) \quad (1.2)$$

$$f_3 = f_{3,0} + \frac{1}{2}\alpha\psi^2 - \frac{1}{4}|\beta|\psi^4 + \frac{1}{6}\gamma\psi^6 \quad (1.3)$$

f_1 , f_2 and f_3 are three different shapes of free-energy density, ψ is order parameter, α , β and γ are phenomenological parameters of the theory and $f_{1,0}$, $f_{2,0}$ and $f_{3,0}$ are energy constant terms of energy offset. Figure 1.13 shows the plot of two most commonly used Landau

free energy forms (f_1 and f_3). Figure 1.13(a) shows the asymmetric potential form, where two minimums are present. There are two stationary values of order parameter that define what phase system occupies. Figure 1.13(b) shows the symmetric potential, with three minimums. The order parameter in one phase can occupy two different values (usually with equal absolute values) and the second phase with the order parameter value 0.

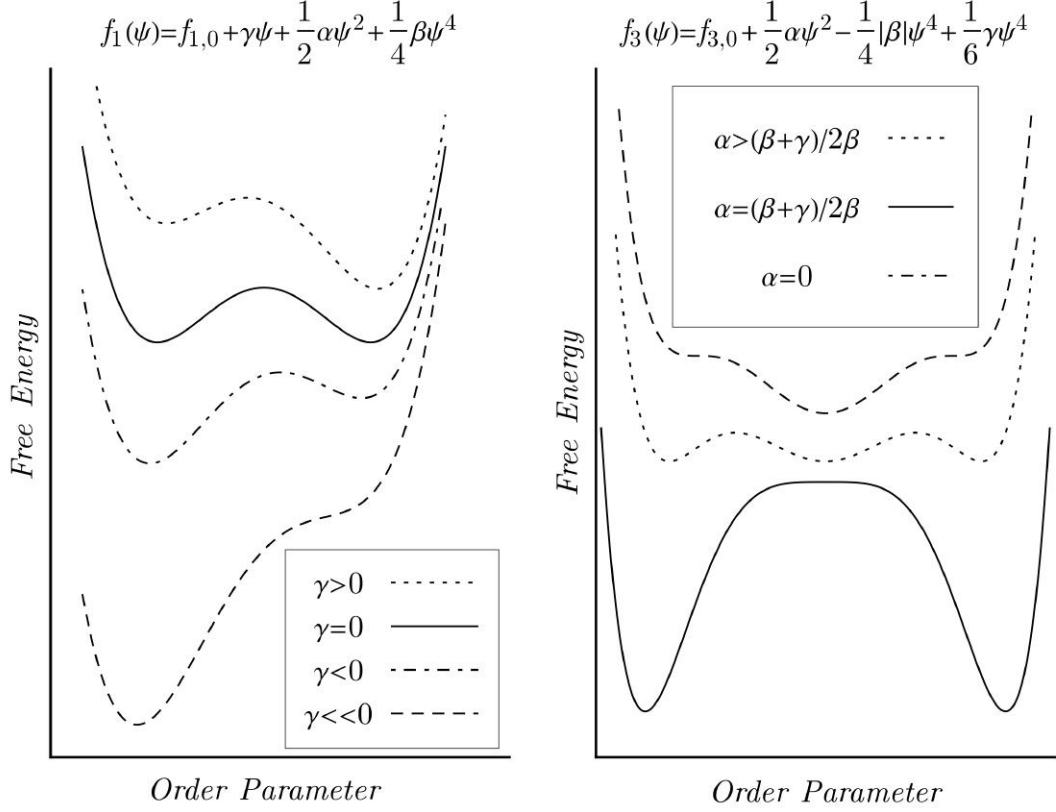


Figure 1.13: Two most common forms of Landau free energy dependences on order parameter.

After determination of local free energy density f , total free energy functional F can be written as volume integral of f over volume of the system.

$$F(\psi) = \int_V [f(\psi) + \kappa(\nabla\psi)^2] dV \quad (1.4)$$

$\kappa(\nabla\psi)^2$ is called gradient penalty term and represents the phase boundary surface energy. This is the term that replaces inter-phase boundary conditions from traditional approach and introduce the finite thickness of the phase boundaries in to the model. The addition of this term under the integral, determining total free energy is direct consequence of inherent order parameter non-homogeneity. The total derivation of gradient penalty term can be found in reference [71].

Dynamic equations of the system can be obtained from the total free energy expression by minimization of integral in Equation 1.4. The total free energy functional minimization is performed by Lagrange calculus of variation (Equation 1.5) [72].

$$\frac{\partial \mathcal{L}}{\partial \psi}(\mathbf{r}, \psi(\mathbf{r}), \nabla\psi(\mathbf{r})) - \nabla \frac{\partial \mathcal{L}}{\partial \nabla\psi}(\mathbf{r}, \psi(\mathbf{r}), \nabla\psi(\mathbf{r})) = 0 \quad (1.5)$$

Where $\mathcal{L}$ is Lagrange function and can be written as $\mathcal{L} = f(\psi) + \kappa(\nabla\psi)^2$.

From the solution of Lagrange equation (Equation 1.5) we obtain dynamic equations of the system together with the boundary conditions. These are partial differential equations that governs the dynamics of phase field. Solution of obtained dynamic equation system gives us time and space dependency of the order parameter, which is the solution of phase field model.

1.6.1.2 Phase-Field Modeling of Eutectic Reaction

Many different phenomena (phase transitions) can be modeled using phase-field modeling [63]. Eutectic solidification modeling is one of the most common cases of use of phase field method. Many papers were published lately about the phase field modeling of the eutectic reaction during steel solidification [69], [70], [73]–[75].

We used the novel principle first published by Ghosh et al. [76] to model the eutectic reaction in AISI D2 tool steel. The phase-field model includes the decomposition of the phase-boundary surface-energy term into the isotropic and anisotropic parts. A similar approach was reported in the phase-field modeling of spinodal decomposition [77] and eutectic reaction modeling in the Ag-Cu system [78]. Such a principle turns out to be essential for describing the transition from lamellar to globular eutectic carbide morphology, during REE modification. More can be found in Chapter 3 where the phase-field theory is applied to the case of the eutectic solidification of carbides in AISI D2 tool steel.

Chapter 2

Aims And Hypothesis

The solidification of eutectic carbides depends on many different chemical and thermodynamic properties of the solidifying steel. The aim of this doctoral thesis is to examine the parameters that influence the path of solidification, both experimentally and theoretically. The experimental results will be used as a proof that the REE-modification of the eutectic carbide morphology in AISI D2 steel is possible as well as to determine the parameters of the model. The model will theoretically explain why the change in the eutectic carbide's morphology occurs after the addition of REEs to the melt. We designed three hypothesis for this thesis that summarize the aim of our work.

The three hypothesis of this thesis are:

1. Hypothesis one: REE-modification of AISI D2 tool steel can lead to a change in the morphology, type, size and distribution of ledeburite eutectic carbides in the as-cast microstructure.
2. Hypothesis two: The reason for the eutectic carbide's morphology change in AISI D2 tool steel, modified by REEs, is the modified non-metallic inclusions that act like heterogeneous nucleation sites for the chromium carbide.
3. Hypothesis three: The reason for the eutectic carbide's morphology change in AISI D2 tool steel, modified by REEs, is the change in the ratio between the isotropic and anisotropic parts of the surface energy of the phase boundary between the austenite and the carbide.

All three hypotheses were constructed on the basis of the published work of others and our preliminary experimentation. In the literature many different effects of REE-modification were reported for different steel grades. The first hypothesis includes the most commonly observed effects that were measured in different tool-steel grades modified by REEs. We verified the validity of the first hypothesis with the experimental part of our work. The hypothesis is very broad as it includes four different effects that can be measured (change in morphology, type, size and distribution of eutectic carbides). Therefore, we expected only a partial confirmation of this hypothesis. The second and third hypotheses exclude each other, i.e., one of those two hypotheses is wrong. The modeling and simulation will validate these two hypothesis.

One fourth of the first hypothesis was validated at the end. Morphology of eutectic carbides was changed from lamellar to globular with the REE-modification. This was proved by scanning electron and light micrographs where morphological difference between both carbides is well seen. Same micrographs were used to estimate eutectic distribution differences between REE-modified and non-modified material and no differences in distribution were observed. Type of carbides was investigated by electron backscattered diffraction

(EBSD) on scanning electron microscope (SEM) and proved to be unchanged. Comparison between volume fractions of eutectic carbides in REE-modified and non modified steel was performed by image processing software that evaluates volume of carbides from light micrographs. No differences in volume fraction of eutectic carbides between REE-modified and non-modified material was observed.

Second hypothesis was disproved by the combination of measured and simulated results. RE-containing non-metallic inclusions appear bright on SEM BEI micrographs and therefore it was easy to observe their positions. No inclusions of this type were found inside eutectic regions which means that RE-containing non-metallic inclusions do not act as heterogeneous nuclei for eutectic carbides. This was also supported by simulation.

Last hypothesis was again investigated by combination of measurement and simulation. Hypothesis was proven by precise tuning of simulation parameters that showed clear dependency of carbide morphology type on ratio between isotropic and anisotropic surface energy magnitude.

Chapter 3

Methods

3.1 Experimental Methods

3.1.1 Sample Preparation

3.1.1.1 Casting

A total of 18 kg of AISI D2 tool steel from the Metal Ravne steel plant (with the commercial name OCR12) was remelted in an open induction furnace. It was cast to five metallic molds of the same shape at a temperature of about $1600^{\circ}C$. Approximately one-fifth of the melt was cast into each mold. In this way five different ingots were obtained with a comparable weight of around 3.6 kg. Before every cast the additional treatments of the melt were performed. First, a small portion of aluminum was added to the melt. The first fifth of the melt was poured into the first mold after that. The remainder of the melt was additionally treated by *CaSi* (30 %*Ca* and 70 %*Si*). Further, the second fifth of the melt was cast into the second mold. After the second casting we started adding REEs in the form of the Ce mischmetal (Table 3.1). REEs were added in small portions of 2.5 g to the remaining melt. After every addition of the REEs to the melt the casting was performed. Thus, the last three-fifths of the melt were cast with the increasing content of REEs. The procedure of casting and additives that were used for each individual ingot are presented in Table 3.2. The cast ingots were left to solidify and cool down.

Table 3.1: Chemical composition of Ce mischmetal in weight percent.

Element	Ce	La	Nd	Pr
Wt.%	45 - 55	20 - 35	15 - 20	5 - 8

Table 3.2: Additions to every ingot.

Ingot Number	#1	#2	#3	#4	#5
Additions	Al	Al, Ca-Si	Al, Ca-Si, Ce Mischmetal (2 g)	Al, Ca-Si, Ce Mischmetal (4.5 g)	Al, Ca-Si, Ce Mischmetal (6 g)

In the casting procedure we produced five different ingots. The first two ingots (#1 and #2) did not include any REEs. They were deoxidized by *Al* and *CaSi* in order to test whether deoxidation is the only process that influences eutectic carbides. If a modification similar to REEs was obtained with *Al* or *CaSi* we could conclude that the

depletion of oxygen from the melt is the governing mechanism of REE modification. REE modification in this case would be meaningless since the same results could be obtained with less-expensive additions.

The last three ingots (#3, #4 and #5) included different amounts of REEs. The amount of REEs in these ingots increased in proportion to the ingot number (ingot #3 - 0.016 wt%, ingot #4 - 0.021 wt% and ingot #5 - 0.026 wt% of REEs). The proportion between different REEs (*Ce*, *La*, *Nd* and *Pr*) in each of REE-modified ingots was the same as in mischmetal (Table 3.1). The detailed chemical composition of each ingot can be found in the next section (Table 3.3).

3.1.1.2 Microstructure Characterization

After the cast ingots cooled down, we took them out of the molds and cut out the samples for characterization. Samples were cut out of the of the ingots by water-jet slicer. Since no significant differences were observed between samples from the center of the ingot and samples from the ingot surface, we concluded that modification occurred across the whole volume of the ingot. That is why only central samples were used for comparison in chapter 4. Four samples from each ingot were used for the representation of results. The approximate dimensions of samples were $1\text{ cm} \times 1\text{ cm} \times 0.5\text{ cm}$ which is the most appropriate sample size for light as well as electron microscopy. Figure 3.1 shows the cross-section of the cylindrical ingot along the cylinder axis. The dashed lines show the position from where four samples were cut.

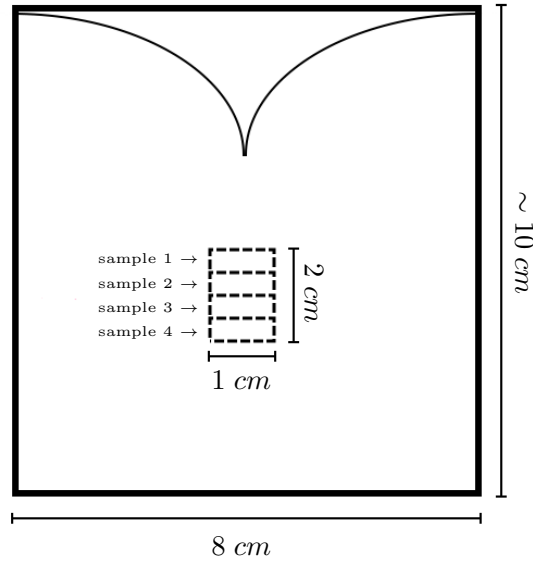


Figure 3.1: Schematical representation of cylindrical ingot cross-section along the cylinder axis. Dashed lines show the position from where all four samples were cut out.

Samples were prepared for micrographic characterization by a standard procedure of grinding, polishing (using Struer devices) and etching. Samples were first ground with different grindstone papers. After grinding, samples were polished by microfiber and diamond paste with the diamond particle sizes of $1\text{ }\mu\text{m}$. For light and electronic microscopy, polished samples were etched with Nital (mixture of $\text{C}_2\text{H}_6\text{O}$ and HNO_3). For the EDS analysis samples were only polished with a fine fiber with $1\text{ }\mu\text{m}$ polishing diamond paste. For the EBSD measurements the samples were prepared by polishing with $9\text{ }\mu\text{m}$ and $3\text{ }\mu\text{m}$ dia-

mond particle containing lubricant (5 min each size). Samples were further oxide polished by Struers 40 nm SiO_2 OP-S.

3.1.2 Characterization

The chemical composition of the samples was determined by classic chemical analysis. The results of the analysis are presented in Table 3.3, where the chemical compositions of all five ingots are shown. Microstructure investigations were performed with a Nikon Mi-

Table 3.3: Chemical composition of five ingots. Ingots number 3, 4 and 5 contain different amount of rare earth elements.

Element	C	Si	Mn	Cr	Cu	Ni	Mo	V	Ce	La	Nd	Pr	Fe
Ingot #1	1,43	0,19	0,21	10,4	0,08	0,17	0,60	0,83	0,00	0,00	0,00	0,00	bal.
Ingot #2	1,42	0,23	0,21	10,1	0,08	0,17	0,60	0,75	0,00	0,00	0,00	0,00	bal.
Ingot #3	1,41	0,23	0,22	9,8	0,08	0,18	0,59	0,70	0,007	0,004	0,004	< 0,002	bal.
Ingot #4	1,43	0,22	0,22	10,2	0,08	0,17	0,62	0,78	0,011	0,006	0,004	< 0,002	bal.
Ingot #5	1,41	0,22	0,21	10,3	0,08	0,17	0,59	0,80	0,013	0,008	0,005	< 0,002	bal.

crophot light microscope and Jeol JSM - 6500F field emission scanning electron microscope (SEM) with secondary and backscattered electron detectors. The chemical micro analysis were performed by energy-dispersive X-ray spectroscopy (EDS) and electron backscattered diffraction (EBSD) techniques on the SEM. The EDS analytic method was used to characterize the non-metallic inclusion in the steel. The EBSD measurements were used to determine the crystallographic type of eutectic carbide in the steel microstructure.

For the quantification of the results from back-scattered electron imaging (BEI), image-processing software was used, which quantifies the anisotropy of surface feature and therefore can distinguish between lamellar and globular eutectic carbides. The used technique, based on the linear-interception method, was developed within this thesis and can be found in Appendix A

3.2 Modeling Methods

3.2.1 Eutectic Reaction Modeling

The eutectic reaction can be modeled in terms of the Landau theory (Chapter 1). Since three phases are present in the system at the eutectic reaction the two-dimensional free-energy potential is needed for the description. Two one-dimensional decompositions are coupled with two different order parameters [69]. The free-energy potential can be written as

$$f(\theta, c) = \frac{a}{4}\theta^4 - \frac{|r|}{2}\theta^2 + (\alpha\Delta T + \Omega c(1 - c) - \varepsilon)\theta + \beta[c\ln(c) + (1 - c)\ln(1 - c)] \quad (3.1)$$

Where the two order parameters are the non-dimensional crystallinity θ and the non-dimensional concentration c . a and r are parameters of the solidification theory, α is the temperature crystallinity gradient coefficient, β is the logarithmic term strength factor and Ω is the so-called regular solution parameter that determines the strength of the interaction between chemical species particles that determine the concentration c . The parameter ΔT denotes the difference between the temperature of the phase transition and the absolute temperature of the system. For the solidification part the asymmetric polynomial potential

(Equation 1.1) was chosen, and for the eutectic decomposition of two solid phases the logarithmic potential (Equation 1.2) was used. Coupling of both phenomena occurs in the regular solution term, where the product of both order parameters takes place. The non-dimensional order parameter crystallinity θ is defined so that it is positive in both solid phases and negative in the liquid phase. At the phase boundary between solid and liquid order parameter θ equals 0. This characteristics of θ describes the transition from liquid to solid. close to the phase-transition temperature where $(\alpha\Delta T - \Omega c(1-c))/2a \ll (r/3a)^{3/2}$, both values of θ can be written as:

$$\theta_S = \sqrt{\frac{r}{a}} - \frac{1}{2r}(\alpha\Delta T + \Omega c(1-c)) \quad (3.2)$$

$$\theta_L = -\sqrt{\frac{r}{a}} - \frac{1}{2r}(\alpha\Delta T + \Omega c(1-c)) \quad (3.3)$$

where θ_S is the average crystallinity order parameter value of both solid phases and θ_L is the crystallinity order parameter value in the liquid phase. Both values are obtained by derivation of free-energy expression by θ and finding two minimums of the function in the direction along the coordinate θ . The non-dimensional concentration order parameter occupies three different values. All three values can be obtained by solving the Equation 3.4

$$\beta \ln\left(\frac{c}{1-c}\right) + \Omega(1-2c) = 0 \quad (3.4)$$

The equation cannot be solved analytically. But all three solutions are very well seen from the graph in Figure 3.2 The solution with the value $c_L = 0.5$ corresponds to the liquid

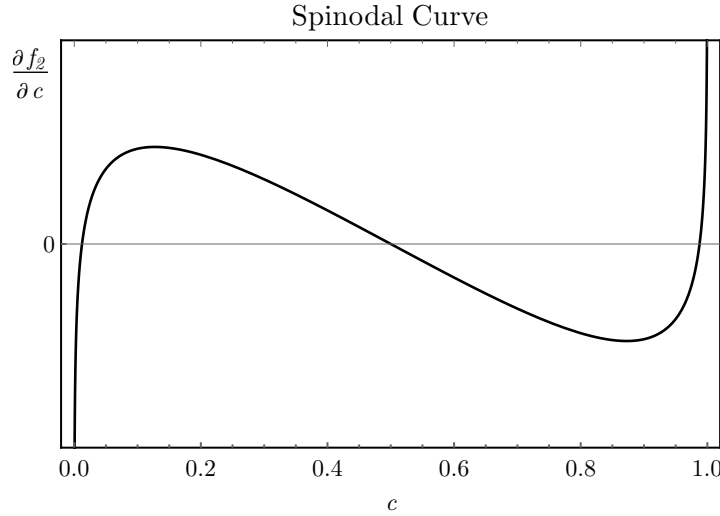


Figure 3.2: Spinodal curve. Derivation of free energy f_2 (Equation 1.2) plotted versus c . c is non-dimensional and therefore defined on domain from 0 to 1 and the values of function $\frac{\partial f_2}{\partial c}$ are in arbitrary units.

phase, where no phase separation is present and the concentration is equal to the average concentration of the chosen species. In the solid phase parameter c can occupy two different values, one corresponding to high concentration $c_\delta \approx 1$ and the second corresponding to low concentration phase $c_\gamma \approx 0$. With the indexes γ and δ we denoted two different solid phases that are present in the system.

The function $f(\theta, c)$ (Equation 3.1) can be plotted in two dimensions. Figure 3.3 shows the contour plot of the function f at the temperature of the phase transition ($\Delta T = 0$).

All three minimums are clearly seen on the figure (darker blue areas) and the value of the function at all three minimums is equal because at the temperature of the phase transition all three phases coexist and have exactly the same free-energy density value. $f(\theta_S, c_\delta) = f(\theta_S, c_\delta) = f(\theta_L, c_L)$. By changing parameter ΔT the asymmetry is added to

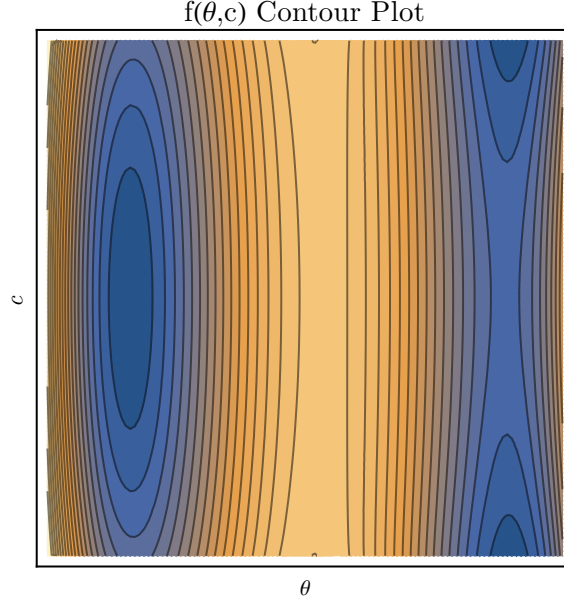


Figure 3.3: Contour plot of the function $f(\theta, c)$. Light areas represent higher values of the function. Function is plotted in arbitrary units.

the system and the values of the function in the minimum are not equal any more. Under the temperature of phase transition the minimums on the right (Figure 3.3) are deeper in comparison to the one minimum on the left ($f(\theta_S, c_\delta) = f(\theta_S, c_\delta) < f(\theta_L, c_L)$). Above the temperature of phase transition $f(\theta_S, c_\delta) = f(\theta_S, c_\delta) > f(\theta_L, c_L)$ nonequivalence holds. This temperature-dependent asymmetry of the free energy potential is the driving force for the reaction.

3.2.2 Eutectic reaction in AISI D2 tool steel

According to the solidification sequence in AISI D2 tool steel described in Chapter 1, Section 1.3.1, we applied the general eutectic reaction phase-field model (Section 3.2.1) to AISI D2 tool steel by determining the model parameters.

3.2.2.1 Determination of the model parameters

There are eight different parameters in the model including two non-dimensional order parameters that play the role of the variables in the model. These are ΔT , Ω , a , r , α , β , θ and c . In order to solve the model all the values of the parameters need to be determined. The first parameter to be determined will be ΔT .

3.2.2.1.1 ΔT determination

Parameter ΔT denotes the difference between the temperature of the phase transition (eutectic reaction temperature) T_E and the absolute temperature of the system at the given moment T .

$$\Delta T = T - T_E \quad (3.5)$$

The eutectic temperature T_E can be determined from the phase diagram. From Figure 1.3 we can see that $T_E = 1258,4^\circ\text{C}$ according to ThermoCalc software calculation. The absolute temperature parameter T will remain undetermined and will be varied during the simulation on the interval $[T_E + 2^\circ\text{C}, T_E - 10^\circ\text{C}]$ in order to obtain the temperature-dependent dynamics of the system. Parameter ΔT is positive above the phase-transition temperature T_E and negative below this temperature.

3.2.2.1.2 α determination

Coefficient α in the equation is the multiplication factor of the parameter ΔT and determines how strong the effect of temperature on the crystallinity θ is. The term in the Equation 3.1 that includes parameter α is $\alpha\Delta T\theta$. This term represents the linear correction to θ due to changing temperature and the parameter α therefore is linear thermal crystallinity coefficient ($\frac{\partial\theta}{\partial T}$). Since T_E is the temperature of the phase transition where the crystallinity θ change is severe the linear approximation of crystallinity changes the dependency on temperature is a wild guess. Nevertheless, the relationship holds well under the phase-transition temperature. The phase transition itself is described by discontinuity in θ that changes the sign during the phase transition. That is way the discrepancy of the linearized crystallinity temperature dependence during the phase transition in comparison to the real scenario does not affect the result seriously.

Since the determination of the linear thermal crystallinity coefficient at the temperature of the phase transition T_E is the task worth its own thesis, we did not carried it out. We rather estimate the coefficient from the temperature range of the simulation and estimated values for θ_L and θ_S . $\alpha = (\theta_S - \theta_L)/\Delta T = 3,1179$.

3.2.2.1.3 β determination

Parameter β is the easiest to determine, since we have one free parameter inside our model. The only demand that has to be fulfilled for the parameter β is the right choice of units. Since the parameter defines the free-energy potential function it has to be in the units of energy. For the convenience parameter β is set to the value of the thermal energy $\beta = k_b T$, where k_b is Boltzmann's constant and T is the absolute temperature of the system.

3.2.2.1.4 Ω determination

Ω is the so-called solid solution parameter. It measures how strong is the interaction between the particles of the same diffusing species in the material. In the case of AISI D2 tool steel the diffusing species of interest is carbon, since carbon content is chosen for the order parameter. The shape of the free-energy density is defined so that the negative values of the Ω parameter represent the repulsive interaction and positive values represents the attractive interaction. Uphill diffusion that is the driving mechanism of eutectic reaction occurs for attractive interactions, for values of Ω above $2k_b T$. k_b denotes the Boltzmann constant and T absolute temperature. The effect of the Ω parameter on the system dynamics can be clearly seen from the plot of the free-energy density function concentration derivative at the constant crystallinity θ , as it represents the chemical potential of the system (Equation 3.23). The chemical potential trends at the fixed crystallinities θ are presented on the Figure 3.4. Four functions are plotted. The curve for $\Omega/k_b T = 0.5$ is a monotone function with no extremes. Such a shape of chemical potential dependency on c will never lead to uphill diffusion and phase separation. At the value of $\Omega/k_b T = 2.0$ the plotted function shows the plateau around the values of the concentration $c = 0.5$. This is the boundary case between classic Fick and uphill diffusion. Plots with the $\Omega/k_b T = 3$ and $\Omega/k_b T = 4.5$ show the spinodal curve shape with the attractive forces between carbon

atoms. These two functions are non-monotone. The negative-sloped middle part of the curve is responsible for the uphill diffusion effect, that occurs in the systems with such chemical potential dependency on concentration. Since the spinodal decomposition is the

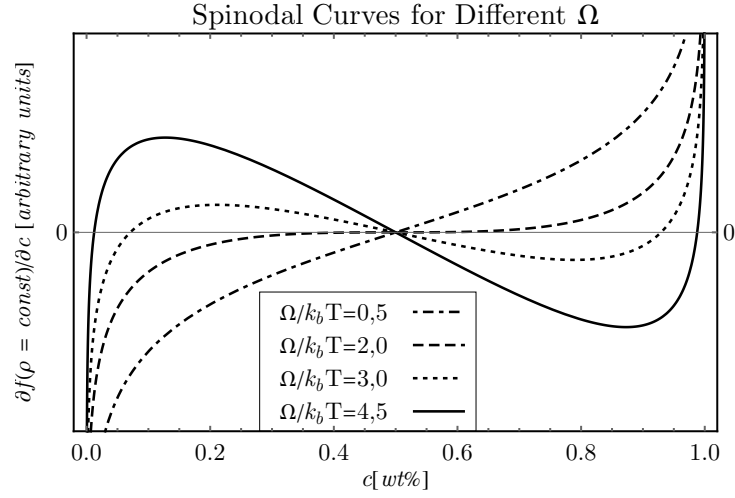


Figure 3.4: Spinodal curves for different values of Ω .

case during the eutectic reaction in AISI D2 tool steel, parameter Ω will necessarily be greater than $2k_bT$. The exact value of parameter Ω is determined from the depth of the free-energy minimums on the positive side of the variable θ (two minimums). Since the depth of the minimums also depends on the parameters a and r these three parameters must be determined together. They can be determined from the equation system presented in subsection 3.2.2.1.5. The value of the Ω parameter that solves the system is $\Omega = 4.5k_bT$.

3.2.2.1.5 a and r determination

Parameters a and r determine the dependency of the free energy of the system on the crystallinity θ . a and r have no impact on the carbide Cr_7C_3 and austenite decomposition. The relationship between a and r can be determined from the fact that the free-energy value at the three minimums (Figure 3.3) at the $\Delta T = 0$ are equal. Furthermore, the absolute values of both parameters are obtained by considering the highest possible under-cooling degree, that would occur in the thermodynamically equilibrium cooling. These two criteria completely characterize the shape of the polynomial part of the free energy potential f . The mathematical formulation of the first criterion (equality of minimum values at $\Delta T = 0$) first demands finding minimums of the function f (Equation 3.1). The point (θ_{min}, c_{min}) represents the minimum of the two variable function f if and only if $f_\theta = 0$ and $f_c = 0$ and $f_{\theta\theta}f_{cc} - f_{\theta c}^2 > 0$ and $f_{\theta\theta} > 0$ and $f_{cc} > 0$ [79], where the index θ represents the derivation by θ and the index c derivation by variable c . If all the derivatives are calculated and all six equations are formed, the system of nonlinear algebraic equations is obtained. The solution of the system in the point (θ_{min}, c_{min}) gives us the relationship between a and r . Furthermore, the absolute values of a and r are calculated from the second criterion. This criterion demands parameters that exceed the inflection point inside the f function at the constant value of $c = c_L$, in the direction of θ at the temperature of under-cooling (ΔT_{UC}). The mathematical formulation of the inflection point calculation in one direction is $f_\theta(c_L) = 0$ and $f_{\theta\theta}(c_L) = 0$. $f_\theta(c_L)$ and $f_{\theta\theta}(c_L)$ are the first and second derivatives of the function f in the θ direction at constant $c = c_L$. The degree of under-cooling at the eutectic reaction (value of ΔT) was estimated on the grounds of the DTA

measurements from Bombač et al. [57]. The second criterion brings us two more equations that in connection to the six from the first criterion give us the values of a , r and Ω . The analytical solution of the full system of all eight equations does not exist. That is why we solved the equations numerically. The obtained numerical values are

$$a = 0.7143k_bT \quad \text{and} \quad r = 7,4029k_bT$$

Both parameters are expressed in the units of thermal energy, since later on the non-dimensionalized form of the equation will be obtained by dividing the free-energy expression by the thermal energy k_bT .

3.2.2.1.6 Non-dimensional form of c

The concentration c inside the function $f(\theta, c)$ (Equation 3.1) is in non-dimensional form so that it can take the values between 0 and 1. Values of the non-dimensional concentration of two solid phases in equilibrium (c_γ and c_c) can be calculated from Equation 3.4. The values are $c_\gamma = 0.0123$ and $c_c = 0.9877$. The third solution of the equation gives us the parameter $c_L = 0.5$, which represents the non-dimensional value of the carbon concentration in the melt. Non-dimensional values should be connected to the real values of the concentrations in the material. Since the mass percentage concentration is not an absolute quantity and depends on the state of whole system the molarity (number of particles per volume - mol/m^3) is chosen as the concentration measure.

The molarity of the carbon inside the Cr_7C_3 carbide can be calculated from its crystal lattice parameters that are explained in detail in Section 3.2.4.1. There are twelve carbon atoms ($N = 12$) in the hexagonal unit cell of Cr_7C_3 with crystal parameters $\hat{a}_c = 0.691nm$, $\hat{c}_c = 0.4495nm$ [80]. The molar concentration of carbon inside the Cr_7C_3 can be calculated from this data:

$$\tilde{c}_c = \frac{N}{N_a V_c} = 52,593mol/l \quad (3.6)$$

$\tilde{c}_c$ denotes the molar concentration of carbon in Cr_7C_3 , V_c is the volume of the unit cell of Cr_7C_3 that can be calculated as $V_c = \frac{\sqrt{3}\hat{a}_c^2\hat{c}_c}{4}$ and N_a is Avogadro's constant.

The same procedure is repeated for the carbon concentration in austenite. From the phase diagram of AISI D2 tool steel we see that the solid-solution limit of carbon in austenite expressed as a mass fraction is $x = 1,15 wt\%$. Combined with the fact that the face-centered cubic crystal system of austenite unit cell parameter at temperature T_E is approximately $\hat{a}_\gamma = 0.362 nm$, we again can calculate the molar concentration of carbon. This time in the austenite. There are four ($N = 4$) iron atoms in the austenite unit cell.

$$\tilde{c}_\gamma = \frac{M_\gamma N x}{M_C N_a V_\gamma} = 6,4071mol/l \quad (3.7)$$

$\tilde{c}_\gamma$ represents the molar concentration of carbon in austenite, M_C and M_γ are molar masses of carbon and austenite and V_γ is the volume of the unit cell of austenite and can be calculated as $V_\gamma = \hat{a}_\gamma^3$.

In the melt the molar concentration ($\tilde{c}_L$) can be calculated from the specific density of the material at the temperature T_E . The specific density of the steel at the temperature T_E can be calculated from the known data of the specific density at $20^\circ C$ (ρ_{20}) where the density of AISI D2 tool steel is $\rho_{20} = 7.70 kg/l$ (data was obtained by steel manufacturer [81]). The density (ρ_E) at temperature T_E can be written as

$$\frac{1}{\rho_E} = \frac{1}{\rho_{20}}(1 + \tilde{\alpha}\Delta T) \quad (3.8)$$

Table 3.4: The measured dependency of the linear thermal expansion coefficients $\tilde{\alpha}$ of AISI D2 tool steel for different temperature ranges.

T rage [$^{\circ}C$]	20-100	20-200	20-300	20-400	20-500	20-600	20-700	20-800
$\tilde{\alpha}[10^{-6} \times ^{\circ}C^{-1}]$	9,8	11,7	12,1	12,8	12,9	13,0	13,2	13,3

The parameter $\tilde{\alpha}$ represents the linear thermal expansion coefficient of the AISI D2 tool steel. $\tilde{\alpha}$ was determined from published data, measured at the lower temperatures and then extrapolated. We used the data from the manufacturer of the steel (Metal Ravne steel plant) [81]. The linear thermal expansion coefficients for different temperature ranges are presented in Table 3.4

The data presented in Table 3.4 were used for the extrapolation of the linear thermal expansion coefficient so that value of $\tilde{\alpha}$ at temperature T_E was calculated. The extrapolation of data is presented in Figure 3.5

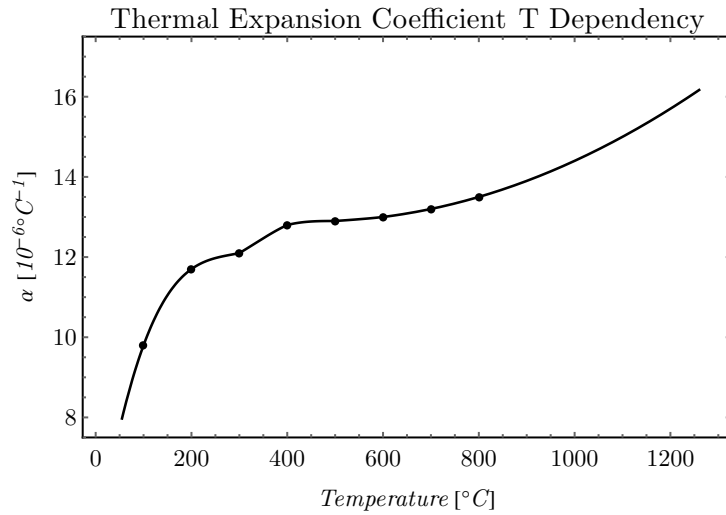


Figure 3.5: Linear thermal expansion coefficient $\tilde{\alpha}$ dependency on temperature. Dots represent the measured values 3.4. Line represent the extrapolation of the trend that measured data determine.

The value of parameter $\tilde{\alpha}$ obtained by extrapolation is $\tilde{\alpha} = 16.1551 \times 10^{-6} K^{-1}$. With estimated linear thermal expansion coefficient we were able to calculate the density of the steel at the temperature T_E , from Equation 3.8. The obtained value of the density is $\rho_E = 7.5489 kg/l$. The molar concentration of the material $\tilde{c}_L$ can be calculated from the density ρ_E .

$$\tilde{c}_L = \frac{x_E \rho_E}{M_C} = 24.889 mol/l \quad (3.9)$$

Where $x_E = 3,88 wt\%$ is the mass fraction of carbon at the eutectic composition, which was calculated with ThermoCalc software. M_C is the molar mass of carbon.

The equilibrium molar concentration values of both solid phases ($\tilde{c}_\gamma$ and $\tilde{c}_c$) determines the transformation function that transforms the molar concentration to non-dimensional concentrations used in simulations. The transformation function should satisfy the transformations:

$$\begin{aligned} \tilde{c}_\gamma &\rightarrow c_\gamma \\ \tilde{c}_c &\rightarrow c_c \end{aligned}$$

Since we only have two points of the function defined the only possible way is to define the linear function. The function that transforms the molar concentration values to the non-dimensional concentration values of our model is:

$$c = \frac{c_c - c_\gamma}{\tilde{c}_c - \tilde{c}_\gamma} \tilde{c} + \frac{c_\gamma(\tilde{c}_c - \tilde{c}_\gamma) - \tilde{c}_\gamma(c_c - c_\gamma)}{\tilde{c}_c - \tilde{c}_\gamma} \quad (3.10)$$

The values of the coefficient can be calculated and we obtain the transformation function

$$c = 0.02112 \text{ l/mol} \times \tilde{c} - 0.123 \quad (3.11)$$

The solutions of the model will be presented in the non-dimensional quantities. If the results want to be seen in molar concentrations, they need to be multiplied by the inverse of the function in Equation 3.11.

We can now calculate the value of the non-dimensional eutectic concentration c_L , that should be somewhere between the values of c_γ and c_c . If we put the value of $\tilde{c}_L$ (Equation 3.9) we obtain the value of non-dimensional $c_L = 0.41197$ the obtained non-dimensional concentration should exactly define the volume ratio of austenite to carbide inside the ledeburite region. To validate the credibility of the calculated C_L value, we inspected the micrographs of the ledeburite regions with the analyzing tool that measures the area of the carbide in the image. The measured area tells us the volume fraction of the carbide in the material. The measured values match the calculated values inside the standard deviation. The analyzing tool that was used for the micrograph processing was developed within this thesis .

3.2.3 Decomposition of the gradient penalty term

For the construction of the dynamic equations (Section 3.2.4) we need to insert the constructed free-energy density f (Equation 3.1) in equation for total free energy (Equation 3.12). The total free-energy of the system therefore can be written as:

$$F(\theta, c) = \int_V [f(\theta, c) + \frac{1}{2}\kappa_\theta(\nabla\theta)^2 + \frac{1}{2}\kappa_c(\nabla c)^2]dV \quad (3.12)$$

Where the term $\frac{1}{2}\kappa_\theta(\nabla\theta)^2$ describes the free-energy density of the phase boundaries between liquid and solid parts of system $\frac{1}{2}\kappa_c(\nabla c)^2$ describes the surface free-energy density on the phase boundary between two different solid phases (austenite and Cr_7C_3 carbide). The gradient penalty parameters κ_θ and κ_c that determine the magnitude of the surface energy of the phase boundaries must be determined in order to solve the system. κ_θ and κ_c are in principle tensors. The tensor nature of both parameters is necessary to describe the surface energy dependence on the orientation of phase boundary. Since the eutectic solidification reaction occurs at a fixed temperature and not on the wide range of temperatures we can assume that κ_θ is scalar (no orientation dependencies). Otherwise we would get dendritic growth of the solid phase from the liquid, which is not the case for the eutectic reaction. The same assumption cannot be made for the κ_c which describes the surface energy of the phase boundary between two crystal solid phases (carbide and austenite). The orientation-dependent surface energy in that case is inherent, since the different orientation relationship between crystal lattices of both solid phases results in different degrees of misfit and consequently different surface strain energies. The tensor shaped κ_c parameter is inconvenient for the strain energy description and that is why we have decomposed the surface energy term into two. The isotropic and anisotropic terms. The first term describes only the chemical contribution to the surface energy of the phase boundary between solid

phases and is therefore isotropic. It can be simply written as the gradient penalty term with the scalar pre-factor κ_c (Equation 3.13).

$$f_{s,i} = \frac{1}{2}\kappa_c(\nabla c)^2 \quad (3.13)$$

Where $f_{s,i}$ denotes the isotropic part of the phase-boundary contribution to the free-energy density. The anisotropic term that describes the contribution of the crystal lattice strain surface energy of the phase boundary between solid phases can be written in terms of elasticity theory.

$$f_{s,a} = \frac{1}{2}C_{ijkl}\epsilon_{ij}\epsilon_{kl} \quad (3.14)$$

where $f_{s,a}$ is the anisotropic value of the phase-boundary contribution to the free-energy density, ϵ_{ij} is the strain tensor and C_{ijkl} is the stiffness tensor. $f_{s,a}$ can be simplified by only considering the first term in the Taylor series [82].

$$f_{s,a} = \frac{1}{2}C_{ijkl}\epsilon_{ij}\epsilon_{kl} \approx \frac{1}{2}B(\mathbf{n})(c - \bar{c})^2 \quad (3.15)$$

$\bar{c}$ denotes the average concentration, $\mathbf{n}$ is a unit vector normal to the phase boundary and $B(\mathbf{n})$ is the function that determines the magnitude of the strain energy of the phase boundary in dependence of the phase-boundary orientation. It can be written as

$$B(\mathbf{n}) = \frac{1}{2}C_{ijkl}\epsilon_{ij}^0\epsilon_{kl}^0 - \mathbf{n}_i\sigma_{ij}^0\Omega_{ji}(\mathbf{n})\sigma_{lm}^0\mathbf{n}_m \quad (3.16)$$

ϵ_{ij}^0 is the misfit between the austenite and eutectic carbide crystal lattice, σ_{ij}^0 is the stress on the phase boundary due to the lattice misfit and Ω_{ij} is defined as $\Omega_{ji}^{-1}(\mathbf{n}) = C_{ijkl}\mathbf{n}_k\mathbf{n}_l$ [77]; The total free energy can now be written as:

$$F(\theta, c) = \int_V [f(\theta, c) + \frac{1}{2}\kappa_\theta(\nabla\theta)^2 + \frac{1}{2}\kappa_c(\nabla c)^2 + B(\mathbf{n})(c - \bar{c})^2]dV \quad (3.17)$$

3.2.3.1 $B(\mathbf{n})$ determination from crystallography

In order to implement Equation 3.17 in the model we need the estimation for the parameter $B(\mathbf{n})$. For the different crystallographic orientations of phase boundary forming austenite and Cr_7C_3 , $B(\mathbf{n})$ can be calculated from Equation 3.16. If we know the misfits, stresses and strains of the phase boundary. All the tensors needed for the calculation of $B(\mathbf{n})$ can be calculated from crystallographic data of both participating phases (austenite and Cr_7C_3). Austenite possesses FCC crystal (space group $Fm\bar{3}m$) and Cr_7C_3 carbide has a hexagonal crystal lattice (space group $P6_3cm$). Misfits and strains on the phase boundary were calculated for every possible phase boundary for Miller indices up to ten. Lattice parameters were needed for both crystal structures in order to perform such a calculation. For the austenite lattice parameter $a_\gamma = 0.367nm$ was used, based on the reference [83]. For the Cr_7C_3 lattice parameters $a_c = 0.691nm$ and $c_c = 0.4495nm$ [80]. Figure 3.6 shows unit cells of crystal lattices of austenite and Cr_7C_3 carbide.

All existing crystallographic plane Miller indices were calculated for both crystals and further written on the basis of the austenite cubic system with the orthogonal base vectors of the length a_γ . The calculation for each crystal was done by three for loops, each running across one Miller index (h, k and l) in the basis of the primitive Bravais vectors of the addressed crystal lattice. On each step of for loops base vectors were multiplied by coinciding the Miller index and than summing up. The obtained vector represents the normal to one existing crystal plane. Crystallographically identical planes (planes of the

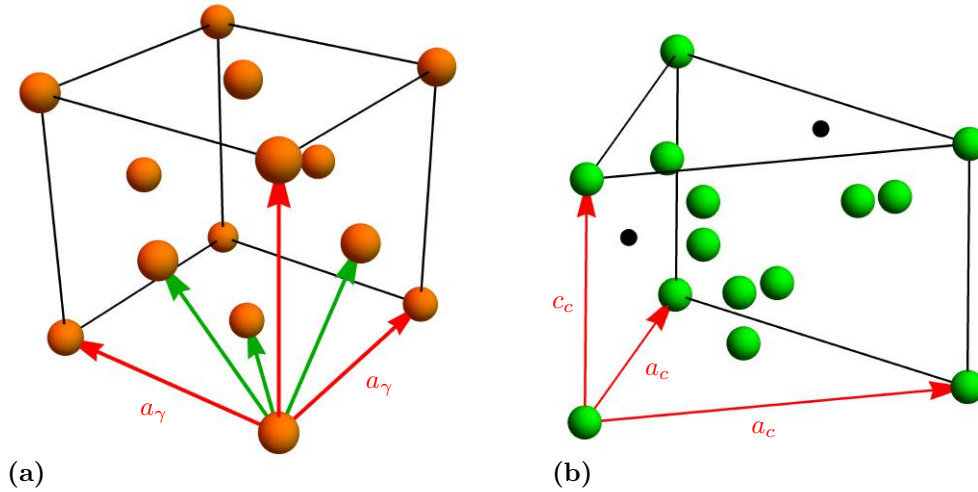


Figure 3.6: Unit cells of crystal structures of (a) austenite and (b) Cr_7C_3 . Orange spheres represent iron atoms, green spheres chromium atoms and black spheres carbon atoms. On figure (a) basis of the primitive unit cell of austenite FCC crystal is denoted by green vectors. Red vectors on in Figure (a) denotes the orthogonal basis of cubic unit cell. In Figure (b) red vectors show the non-orthogonal basis of primitive unit cell of hexagonal carbide lattice.

same crystallographic family) were taken into account only once. After calculating all the vectors normal to all existing crystal plane families, two base vectors defining each crystallographic plane were calculated in the same basis as normals to the planes (FCC cubic basis - red vectors in Figure 3.6(a)). Base vectors pairs for each plane were calculated from two conditions. First, both vectors have to be perpendicular to the plane normal vector (dot product must equal zero) and second both vectors must be Bravais vectors of the addressed crystal (linear combination of primitive basis vectors). Since the system of equations obtained from both conditions was predetermined (due to the large number of normals belonging to the crystallographically identical planes) estimating of the results was performed in four for loops, running across different primitive Bravais vectors of the crystal that must form the calculated two plane vectors. The obtained pairs of planes base vectors gave us distances and angles between atoms laying in all crystallographic planes for austenite and carbide. From these two geometric parameters for both lattices the strains and misfits were easily calculated from the displacement of coinciding atoms on the phase boundary surface between the austenite and carbide. Each crystal plane of austenite was matched with each plane of carbide to obtain the full orientational dependency of the misfit and strain tensors. From the obtained tensors numerical values for $B(\mathbf{n})$ were calculated by Equation 3.16 for each orientation and type of phase boundary. It was found that the lowest possible misfit occurs when both crystals meet with faces $\{11\bar{2}0\}$ (hexagonal carbide lattice) and $\{730\}$ (FCC austenite lattice). This is the phase boundary with the lowest possible surface free energy and therefore the realized phase boundary in the case of the lamellar eutectic. A few other phase boundaries with a slightly higher surface free energy (higher misfits) were found in the calculation. Particularly interesting was the phase boundary $\{1\bar{1}00\}$ (carbide) stacked to $\{941\}$ (austenite), which have the special property, i.e., when rotated by 120° we obtain the same boundary with the same misfit. The coincidence that both crystal lattices have a crystal plane family with the members (planes) 120° rotated to each other and low misfit between such crystal plane families of

both crystals enables the growth of a globular eutectic instead of lamellar in some cases (the detailed explanation can be found in Chapter 5).

3.2.4 Dynamic Equations

With the minimization of the total free energy (Equations 1.5 and 3.17) we obtain dynamic equations of the system that determine the system's time evolution. Since the free-energy potential (Equation 3.18) depends on two different order parameters we obtain a system of two separate dynamic equations (Equations 3.18 and 3.19).

$$\frac{\partial \theta}{\partial t} = M_\theta \frac{\delta F}{\delta \theta} = M_\theta \left(\frac{\partial f}{\partial \theta} - \nabla \frac{\partial f}{\partial \nabla \theta} \right) = M_\theta \mu \quad (3.18)$$

$$\frac{\partial c}{\partial t} = \nabla M_c \nabla \frac{\delta F}{\delta c} = \nabla M_c \nabla \left(\frac{\partial f}{\partial c} - \nabla \frac{\partial f}{\partial \nabla c} \right) = \nabla M_c \nabla \mu \quad (3.19)$$

M_θ denotes the average mobility of particles in the melt. The M_c denotes the carbon mobility in the austenite. The first equation that describes the solidification of the melt is the so-called Langevin equation [84]. The second equation that describes the decomposition to austenite and Cr_7C_3 carbide just after the liquid phase was solidified is called the Cahn-Hilliard equation [84]. Both equations are non linear partial differential equations (PDE). The system of both PDEs should be solved in order to simulate the eutectic reaction. The first step to solving both equations is to insert the chemical potential expression in both equations (from Equation 3.17). After insertion the system of equation looks like:

$$\frac{\partial \theta}{\partial t} = M_\theta [a\theta^3 - |r|\theta + \alpha\Delta T + \Omega c(1 - c)] + \kappa_\theta \nabla^2 \theta \quad (3.20)$$

$$\frac{\partial c}{\partial t} = \nabla \left(M_c \nabla \left[\beta \ln \left(\frac{c}{1 - c} \right) + \Omega(1 - 2c)\theta + \kappa_c \nabla^2 c + B(\mathbf{n})(c - \bar{c}) \right] \right) \quad (3.21)$$

Equation 3.20 is a second-order PDE and Equation 3.21 is PDE of the fourth order. To simplify the solving procedure we divided Equation 3.21 into two separate PDEs of the second order that can be written as:

$$\frac{\partial c}{\partial t} = \nabla M_c \nabla \mu \quad (3.22)$$

$$\mu = \beta \ln \left(\frac{c}{1 - c} \right) + \Omega(1 - 2c)\theta + \kappa_c \nabla^2 c + B(\mathbf{n})(c - \bar{c}) \quad (3.23)$$

The mathematical principle of introducing a new variable was used, to lower the order of the differential equation. The chemical potential μ is the obvious choice of the new variable. In this way our system of dynamic equations transformed to three PDE of the second order. The whole system of dynamic equations consist of Equations 3.20, 3.22 and 3.23. The dynamic equations were solved numerically in two dimensions on the square domain. The size of the domain represent $4\mu m \times 4\mu m$ of the real system. The solving procedure is described in Section 3.2.5

3.2.4.1 Boundary Condition

The boundary conditions for all three variables (θ , c and μ) are needed on the boundaries of the domain. Since we are modeling the small part of the continuous media ($4\mu m \times 4\mu m$) periodic boundary conditions make sense for all three variables. If the origin of the Cartesian coordinate system is placed in the center of the square domain (all three

variables are functions of x and y coordinates) and the length domain boundary is denoted by $2l$, the boundary conditions can be written as:

$$\begin{aligned}\theta(-l, y) &= \theta(l, y) & \theta(x, -l) &= \theta(x, l) \\ c(-l, y) &= c(l, y) & c(x, -l) &= c(x, l) \\ \mu(-l, y) &= \mu(l, y) & \mu(x, -l) &= \mu(x, l)\end{aligned}$$

3.2.5 Solving the Dynamic Equations

The dynamic equations (Equations 3.20, 3.22 3.23) do not have an analytic solution and that is why they were solved numerically. The equations were solved in two dimensions for periodic boundary conditions. First, the method of finite volumes was used to discretized the system of equations on the pre-determined two-dimensional square mesh, indexed with two indexes. The system of non-linear ordinary algebraic equations was obtained by discretization, that was further solved using the Newton-Raphson method for root finding [85].

3.2.5.1 Discretization

Discretization of the equations was made using the finite-volume method on a square two-dimensional mesh of 50×50 control volumes size. For the control volume indexing we used two-dimensional indexing with two indexes. Index j denotes the column (x direction) and index k denotes the row in the mesh (y direction). Both indexes start in bottom left corner of the mesh, with the value of 1. An illustrative example of indexing for 10×10 square mesh is presented in Figure 3.8. Every control volume was used to track three different variables θ , c and μ . All three variables are set constant inside one control volume and evaluated at the center of the control volume. Fluxes that correspond to the variables and gradients of the tracked variables are calculated on the control volumes boundaries. Control volume boundaries are indexed with the half indexes. The discretized form of equations was obtained by integration of the dynamic equation through one control volume and one time step. Since second-order derivatives appear in the dynamic equation, nearest-neighbor control volumes will influence the dynamics of the observed control volume.

3.2.5.1.1 Bulk Dynamics

If we perform the integration on an arbitrary control volume that does not lay on the boundary of the domain, we obtain a system of discretized dynamic equations for the bulk of the system. All the variables of the chosen control volume will be denoted by index j, k . The variables of the four nearest-neighbor control volumes will be denoted by indexes $j, k + 1$ (east neighbor), $j, k - 1$ (west neighbor), $j + 1, k$ (north neighbor) and $j - 1, k$ (south neighbor). Variables on the boundaries between control volume j, k and all nearest-neighbor control volumes will be denoted by the half indexes $k, j + 1/2$ (east), $j, k - 1/2$ (west), $j + 1/2, k$ (north) and $j - 1/2, k$ (south) (Figure 3.7). First equation 3.20 is integrated.

$$\begin{aligned}& \int_{\Delta t} \int_{V_{j,k}} \frac{\partial \theta_{j,k}}{\partial t} dV dt = \\ &= \int_{\Delta t} \int_{V_{j,k}} [a\theta_{j,k}^3 - |r|\theta_{j,k} + \alpha\Delta T + \Omega(c_{j,k} - c_L)(1 - c_{j,k} + c_L) + \kappa_\theta \nabla^2 \theta_{j,k}] dV dt \quad (3.24)\end{aligned}$$

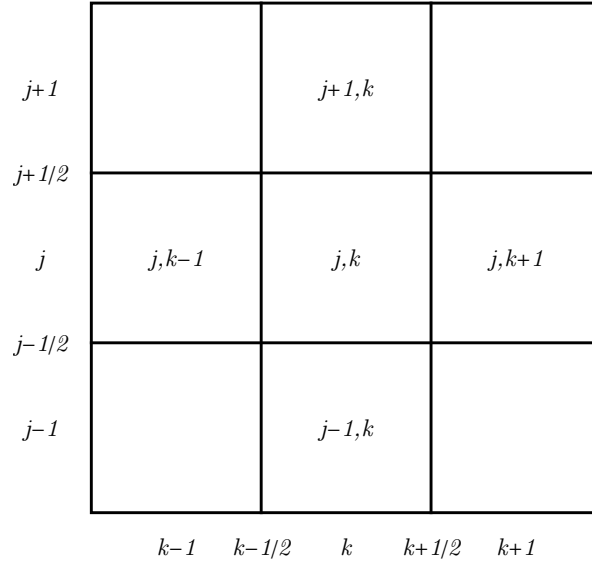


Figure 3.7: Nine control volumes. Central control volume was chosen for integration in order to obtain discretization of system bulk. Values of the variables in this control volume are denoted by index j, k . Indexes $j, k + 1$ (east), $j, k - 1$ (west), $j + 1, k$ (north) and $j - 1, k$ (south) denote the neighbor control volumes. Half indexes denotes boundaries between control volumes.

$V_{j,k}$ is volume of the control volume and can be written as $V_{j,k} = \Delta x \Delta y \Delta z$ where Δx and Δy are the dimensions of the control volume in the x and y directions and Δz is a fictive value of the height of the two-dimensional domain. Δt is the length of the time step. $\theta_{j,k}$ and $c_{j,k}$ are values of variables θ and c in control volume j, k . Since the variables $\theta_{j,k}$ and $c_{j,k}$ are constant on whole control volume $V_{j,k}$ and whole time step Δt integration of all terms is trivial ($\int_{V_{j,k}, \Delta t} \text{Const} dV = \text{Const} V_{j,k} \Delta t$) except gradient penalty term, that includes the Laplace operator. The Gauss divergence theorem is used on this term to simplify the integration.

$$\int_{\Delta t} \int_{V_{j,k}} \kappa_{\theta} \nabla(\nabla \theta_{j,k}) dx dy dz dt = \int_{\Delta t} \left(\oint_{A_{yz}} \kappa_{\theta} \nabla \theta_{j,k} dx dz + \oint_{A_{xz}} \kappa_{\theta} \nabla \theta_{j,k} dy dz \right) dt \quad (3.25)$$

where we wrote the Laplace operator as the divergence of gradient $\nabla^2 \theta = \nabla(\nabla \theta)$. The volume integral was reduced to the integral through the cyclic area of the $A_{xz} = \Delta y \Delta z$ and $A_{yz} = \Delta x \Delta z$. A_{xz} and A_{yz} denotes the areas of the boundaries between control volumes with the normal vector in the x and y directions. Both spatial integrals can be evaluated.

$$\oint_{A_{yz}} \kappa_{\theta} \nabla \theta_{j,k} dx dz = (\nabla \theta|_{j,k+1/2} - \nabla \theta|_{j,k-1/2}) \Delta x \Delta z \quad (3.26)$$

Where $\nabla \theta|_{j,k+1/2}$ and $\nabla \theta|_{j,k-1/2}$ denote values of gradients of the variable θ evaluated at control volume boundaries $j, k + 1/2$ and $j, k - 1/2$. The gradients of the θ are constant in the direction parallel to the control-volume boundaries inside one control volume. The equivalent expression could be written for the second right-hand term from Equation 3.25. The gradient of the variable θ on the control-volume boundary can be evaluated with the finite difference.

$$\nabla \theta|_{j,k+1/2} = \frac{\theta_{j,k+1} - \theta_{j,k}}{\Delta x} \quad (3.27)$$

$\theta_{j,k+1}$ is value of the variable θ in control volume $j, k+1$. The equivalent form of the gradient could be written for all four boundaries that enclose control volume j, k . Equation 3.25 in that case reads:

$$\begin{aligned} \iint_{\Delta t V_{j,k}} \kappa_\theta \nabla(\nabla \theta_{j,k}) dx dy dz dt = \\ = \kappa_\theta \left(\frac{\theta_{j,k+1} - 2\theta_{j,k} + \theta_{j,k-1}}{\Delta x} + \frac{\theta_{j+1,k} - 2\theta_{j,k} + \theta_{j-1,k}}{\Delta y} \right) \Delta t \end{aligned} \quad (3.28)$$

Using this equality in Equation 3.24 with the fact that the time derivative can be written as $\partial \theta_p / \partial t \approx (\theta_{j,k,t} - \theta_{j,k,t-1}) / \Delta t$ we successfully discretized the first PDE of the system of dynamic equations (Equation 3.18). The third index was added (index t), which denotes the time step (discretization of time). $\theta_{j,k,t}$ denotes value of variable θ at the control volume j, k at time step t and $\theta_{j,k,t-1}$ is value of the same variable at the same mesh site (j, k) but one time step back. The final form of Equation 3.20 integrated through the j, k control volume can be written as:

$$\begin{aligned} \frac{\theta_{j,k,t} - \theta_{j,k,t-1}}{\Delta t} = a\theta_{j,k,t}^3 - |r|\theta_{j,k,t} + \alpha\Delta T + \Omega(c_{j,k,t} - c_L)(1 - c_{j,k,t} + c_L) + \\ + \kappa_\theta \left(\frac{\theta_{j,k+1,t} - 2\theta_{j,k,t} + \theta_{j,k-1,t}}{\Delta x^2} + \frac{\theta_{j+1,k,t} - 2\theta_{j,k,t} + \theta_{j-1,k,t}}{\Delta y^2} \right) \end{aligned} \quad (3.29)$$

The same way we can integrate Equations 3.22 and 3.23. Terms in both equations that include the second-order derivative are solved by the Gauss divergence theorem the same way as this is done in equation 3.25. Obtained equations read:

$$\begin{aligned} \frac{c_{j,k,t} - c_{j,k,t-1}}{\Delta t} = \left(1 - \frac{c_{j,k,t} + c_{j,k+1,t}}{2} \right) \frac{c_{j,k,t} + c_{j,k+1,t}}{2} \frac{\mu_{j,k+1,t} - \mu_{j,k+1,t}}{\Delta x} + \\ + \left(1 - \frac{c_{j,k,t} + c_{j,k-1,t}}{2} \right) \frac{c_{j,k,t} + c_{j,k-1,t}}{2} \frac{\mu_{j,k,t} - \mu_{j,k-1,t}}{\Delta x} + \\ + \left(1 - \frac{c_{j,k,t} + c_{j+1,k,t}}{2} \right) \frac{c_{j,k,t} + c_{j+1,k,t}}{2} \frac{\mu_{j+1,k,t} - \mu_{j,k,t}}{\Delta y} + \\ + \left(1 - \frac{c_{j,k,t} + c_{j-1,k,t}}{2} \right) \frac{c_{j,k,t} + c_{j-1,k,t}}{2} \frac{\mu_{j,k,t} - \mu_{j-1,k,t}}{\Delta y} \end{aligned} \quad (3.30)$$

$$\begin{aligned} \mu_{j,k,t} = \beta \ln \left(\frac{c_{j,k,t}}{1 - c_{j,k,t}} \right) + \Omega(1 - 2c_{j,k,t})\theta_{j,k,t} + \\ + \kappa_c \left(\frac{\theta_{j,k+1,t} - 2\theta_{j,k,t} + \theta_{j,k-1,t}}{\Delta x^2} + \frac{\theta_{j+1,k,t} - 2\theta_{j,k,t} + \theta_{j-1,k,t}}{\Delta y^2} \right) + B(\mathbf{n})(c_{j,k,t} - \bar{c}) \end{aligned} \quad (3.31)$$

3.2.5.1.2 Indexing

Equations 3.29, 3.30 and 3.31 represent a system of $3 \times N \times N$ non-linear algebraic equations, where N is the dimension of the domain and represents the number of control volumes along one dimension (number of all control volumes on the mesh is $N \times N$). Since the system of the equations was solved in matrix form, the state vector of all the variables needed to be created. For the creation of the state vector one-dimensional indexing of the mesh was needed. Variables were arranged in the vector so that groups of three variables representing the same control volume were placed one after another in the order θ , c and μ . index l , representing the number of control volume was defined so that it starts with value

1 in the bottom left corner and increment in the direction of x (east/right direction). After the end of the row is met, index l incrementation continuous on the left edge of the above row (Figure 3.8). Index l is determined by $l = N(j-1) + k$, where N is the dimension of the

$j=10$	$l=91$	$l=92$	$l=93$	$l=94$	$l=95$	$l=96$	$l=97$	$l=98$	$l=99$	$l=100$
$j=9$	$l=81$	$l=82$	$l=83$	$l=84$	$l=85$	$l=86$	$l=87$	$l=88$	$l=89$	$l=90$
$j=8$	$l=71$	$l=72$	$l=73$	$l=74$	$l=75$	$l=76$	$l=77$	$l=78$	$l=79$	$l=80$
$j=7$	$l=61$	$l=62$	$l=63$	$l=64$	$l=65$	$l=66$	$l=67$	$l=68$	$l=69$	$l=70$
$j=6$	$l=51$	$l=52$	$l=53$	$l=54$	$l=55$	$l=56$	$l=57$	$l=58$	$l=59$	$l=60$
$j=5$	$l=41$	$l=42$	$l=43$	$l=44$	$l=45$	$l=46$	$l=47$	$l=48$	$l=49$	$l=50$
$j=4$	$l=31$	$l=32$	$l=33$	$l=34$	$l=35$	$l=36$	$l=37$	$l=38$	$l=39$	$l=40$
$j=3$	$l=21$	$l=22$	$l=23$	$l=24$	$l=25$	$l=26$	$l=27$	$l=28$	$l=29$	$l=30$
$j=2$	$l=11$	$l=12$	$l=13$	$l=14$	$l=15$	$l=16$	$l=17$	$l=18$	$l=19$	$l=20$
$j=1$	$l=1$	$l=2$	$l=3$	$l=4$	$l=5$	$l=6$	$l=7$	$l=8$	$l=9$	$l=10$
	$k=1$	$k=2$	$k=3$	$k=4$	$k=5$	$k=6$	$k=7$	$k=8$	$k=9$	$k=10$

Figure 3.8: Example of the 10×10 mesh indexing with two dimensional indexes j and k and one dimensional index l .

domain (number of control volume in one direction). State variables can now be indexed with only two indexes l and t as $\theta_{j,k,t} = \theta_{N(j-1)+k,t} = \theta_{l,t}$ (c and μ equivalently). The constructed state vector of all the state variables was denoted by $\mathbf{X}$ and can be written as:

$$\mathbf{X} = [\theta_{1,t}, c_{1,t}, \mu_{1,t}, \theta_{2,t}, c_{2,t}, \mu_{2,t} \dots \theta_{l,t}, c_{l,t}, \mu_{l,t} \dots \theta_{N,t}, c_{N,t}, \mu_{N,t}]$$

Index i will be used to refer to the i -th element in the state vector $\mathbf{X}$. Index i is therefore exactly $i = 3l$.

3.2.5.1.3 Discretized Boundary Conditions

The boundary conditions for the set of dynamic PDEs that describes the system are explained in Section 3.2.4.1. If we chose the arbitrary control volume on the square mesh (denoted with index k and j - Figure 3.7) that lays on the boundary of the domain we can write the periodic boundary conditions in the discretized form.

$$\theta_{j,N+1,t} = \theta_{j,1,t} \quad \theta_{j,0,t} = \theta_{j,N,t} \quad \theta_{N+1,k,t} = \theta_{1,k,t} \quad \theta_{0,k,t} = \theta_{N,k,t}$$

$$c_{j,N+1,t} = c_{j,1,t} \quad c_{j,0,t} = c_{j,N,t} \quad c_{N+1,k,t} = c_{1,k,t} \quad c_{0,k,t} = c_{N,k,t}$$

$$\mu_{j,N+1,t} = \mu_{j,1,t} \quad \mu_{j,0,t} = \mu_{j,N,t} \quad \mu_{N+1,k,t} = \mu_{1,k,t} \quad \mu_{0,k,t} = \mu_{N,k,t}$$

All twelve boundary conditions can be rewritten to the boundary condition for state vector $\mathbf{X}$, written in one-dimensional indexing i .

South boundary ($j = 1$)

$$\begin{aligned} \mathbf{X}_{3k-3N,t} &= \mathbf{X}_{3N(N-1)+3k,t} & \mathbf{X}_{3k-3N-1,t} &= \mathbf{X}_{3N(N-1)+3k-1,t} \\ \mathbf{X}_{3k-3N-2,t} &= \mathbf{X}_{3N(N-1)+3k-2,t} \end{aligned}$$

West boundary ($k = 1$)

$$\begin{aligned} \mathbf{X}_{3N(j-1),t} &= \mathbf{X}_{3Nj,t} & \mathbf{X}_{3N(j-1)-1,t} &= \mathbf{X}_{3Nj-1,t} \\ \mathbf{X}_{3N(j-1)-2,t} &= \mathbf{X}_{3Nj-2,t} \end{aligned}$$

East boundary ($k = N$)

$$\begin{aligned} \mathbf{X}_{3N(j-1)+3(N+1),t} &= \mathbf{X}_{3N(j-1)+3,t} & \mathbf{X}_{3N(j-1)+3(N+1)-1,t} &= \mathbf{X}_{3N(j-1)+2,t} \\ \mathbf{X}_{3N(j-1)+3(N+1)-2,t} &= \mathbf{X}_{3N(j-1)+1,t} \end{aligned}$$

North boundary ($j = N$)

$$\begin{aligned} \mathbf{X}_{3NN+3k,t} &= \mathbf{X}_{3k,t} & \mathbf{X}_{3NN+3k-1,t} &= \mathbf{X}_{3k-1,t} \\ \mathbf{X}_{3NN+3k-2,t} &= \mathbf{X}_{3k-2,t} \end{aligned}$$

3.2.5.2 Solving Discretized System by Newton-Raphson Method

Now that we have fully discretized the system of the dynamic PDE we can solve the system. The vector $\mathbf{X}$ is the variable that will be evaluated by the system's solution. The system of equations that determine $\mathbf{X}$ (Equations 3.29, 3.30 and 3.31) is implicit. The implicit Newton-Raphson method [85] was used in order to find the solutions of the system. First, Equations 3.29, 3.30 and 3.31 were rewritten in the form with the zero on the right-hand side (the right-hand of equation was divided from the whole equation). The left hand side from the obtained result was further proclaimed function Φ_i . Since these are the equations that govern the dynamics of our system, root finding of the functions Φ_i will give us the result for $\mathbf{X}$. The functions Φ_i were placed in the vector Φ , the same way that was done for vector $\mathbf{X}$. The implicit root finning was performed by Jacobian matrix of the equation system written in functions Φ_i . The solution (vector $\mathbf{X}$) was obtained by solving the matrix equation system:

$$\mathbf{J}\mathbf{X} = \Phi \quad (3.32)$$

where $\mathbf{J}$ denotes the Jacobian matrix of the system. The elements of the Jacobian system can be written as $J_{pq} = \frac{\partial \Phi_p}{\partial X_q}$. The system is solved iteratively by inverting the Jacobian matrix at every step with the LU decomposition and back-substitution [85] and then multiplying the vector Φ by the inverse $\mathbf{J}^{-1}$. With this procedure the equilibrium form of variables θ , c and μ are obtained for the calculated time step. After the procedure the values of $\theta_{l,t}$, $c_{l,t}$ are saved as $\theta_{l,t-1}$, $c_{l,t-1}$ and used in next step time step, where the same procedure is repeated. In this way the time dependency is obtained.

Chapter 4

Results

4.1 Experimental Results

Samples from all five ingots (Table 3.3) were investigated by light microscopy and SEM. There were no differences between samples from ingot #1 and #2. That is why samples from ingot #2 were chosen as a reference non-modified material. All the images of non-modified material in the Results chapter are from the ingot #2. All the REE-modified samples (samples from ingots #3, #4 and #5) showed the same differences in eutectic carbide morphology from the reference non-modified material (ingot #2). The differences of the eutectic carbides in ingot #5 from the reference material were by far most significant since the average carbide in the samples from ingot #5 was strongly refined in comparison to the carbides in samples from ingots #1 and #2. The carbide morphology from ingots #1 and #2 was not found in ingot #5. All the carbides in ingot #5 were modified. Refinement of the eutectic carbides in the samples from ingots #3 and #4 was much less severe than in ingot #5. Parts of the carbides in the samples from ingots #3 and #4 showed the same morphology as the carbides from ingots #1 and #2. We attributed these differences between the carbides in ingots #3, #4 and #5 to the different contents of the REEs. The refinement of eutectic carbides was the highest in the ingot with the highest content of REEs (ingot #5). That is why all the results of the modification showed in the following section are from the samples from ingot #5 (REE-modified material in the Results chapter) except Figure 4.2 where the comparison of samples from ingot #2, #4 and #5 is shown. In that figure we can see that morphological type of carbides in ingot #2 (Figure 4.2 (a) and (b)) and #5 (Figure 4.2 (e) and (f)) are different (refined carbides in #5). In sample from ingot #4 (Figure 4.2 (c) and (d)), both morphological types of carbides are present. No further investigation of the dependency of the modification on the REEs content was performed.

4.1.1 Eutectic carbides

The main difference between non-modified and REE-modified AISI D2 tool steel was the change in the eutectic carbides. Few different characteristics of the eutectic carbides were measured: type, volume, shape and size. All four parameters were investigated using the light microscope and SEM. In this sub-section we will investigate the first hypothesis of this thesis. It will be concluded that the first hypothesis can only be partly verified, since it is true that the eutectic carbide morphology in AISI D2 steel is changed by REE modification, but no change in carbide type as well as carbide volume was measured.

4.1.1.1 Carbide shape and size

On the basis of the literature [52] we anticipated severe changes in eutectic carbide shape after the modification (Chapter 1). We did not measure any effect of REE modification on the shape of the eutectic carbide net (Figure 4.1).

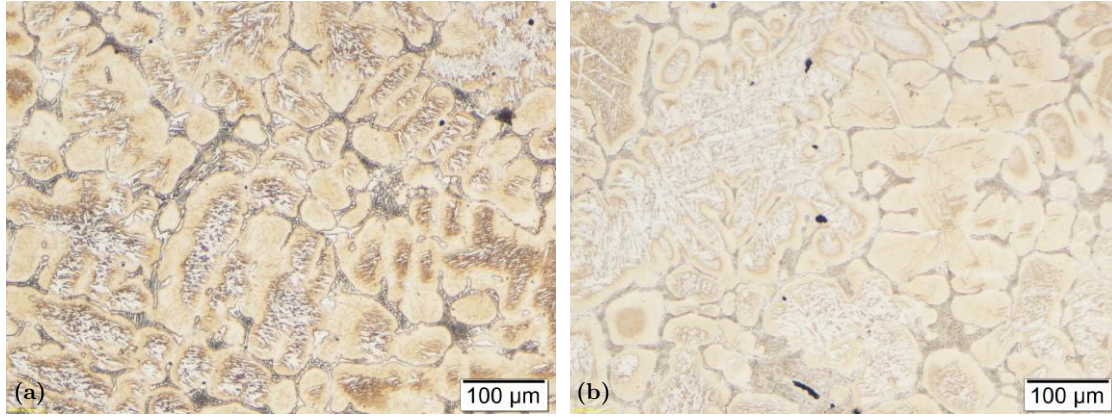


Figure 4.1: Comparison of light micrographs of (a) non-modified and (b) RE modified as-cast microstructures of AISI D2 tool steel. Samples were polished and etched by Nital. Dark areas represents the eutectic Cr_7C_3 carbide. Lighter areas represent the matrix - ferrite and martensite.

It can be seen from the Figure 4.1 that the shape of the eutectic carbide net remains unchanged after modification. Nevertheless, the internal morphology of the eutectic carbide is changed drastically. The individual Cr_7C_3 carbides that form the eutectic are refined by the modification and the size of the individual carbide inside the eutectic is drastically reduced. This fact can be seen from the light and SEM micrographs and at higher magnifications (Figure 4.2).

From the Figure 4.2 it can be seen that the internal structure of eutectic in the REE-modified samples (Figure 4.2 (c) - (f)) is refined in comparison to the non-modified sample (Figure 4.2 (a) and (b)). The degree of modification in dependency of the REEs content can be seen from a comparison of the images in Figure 4.2 (c), (d) and (e), (f). Refinement is more severe in the REE sample with the higher content of REEs (Figure 4.2 (e) and (f)) than in (Figure 4.2 (c) and (d)). Part of the eutectic carbide in Figure 4.2 (c) (lower right part of image) and (d) (left part of image) show the same morphology as the eutectic carbide from the non-modified sample in Figure 4.2 (a) and (b). The modification is not complete. In the sample from Figure 4.2 (e) and (f) only the refined morphological type of carbides were found. From this point, phrase "REE-modified sample" will refer only to material from Figure 4.2 (e) and (f) (ingot #5) since the effects of modification are the most notable in this material and all the further examples and results of REE modification are shown on samples from this ingot.

The experimentation was not performed on the material with the higher amount of REEs. Amounts of RE additions were based on the study of Hamidzadeh et. al. [52]. The trend can be seen in our results, that implies that higher contents of REEs bring better results (higher refinement of carbides). From our study it is impossible to give any conclusions what would happen to the steel microstructure at the RE contents above that of ingot #5. Nevertheless many papers report diminishing of REEs beneficial effects to steel at higher contents. If the amount of REEs added to steel exceeds the value needed

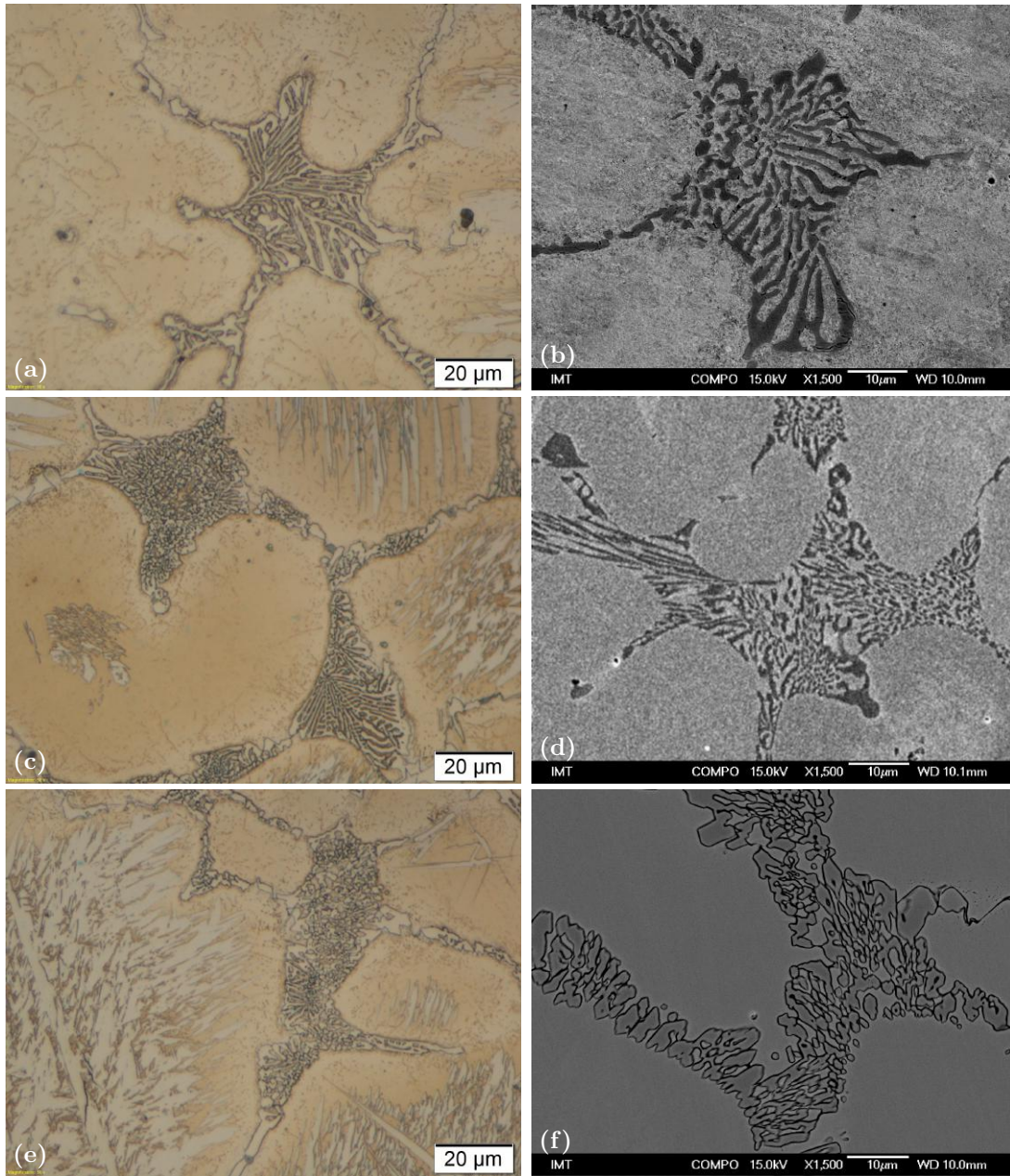


Figure 4.2: Comparison of light micrographs ((a), (c), (e)) and SEM BEI ((b), (d), (f)) micrographs of non-modified - ingot #2 (a) and (b), RE modified - ingot #4 (c) and (d) and RE modified - ingot #5 (e) and (f) as-cast microstructures of AISI D2 tool steel. Dark areas represents the eutectic Cr_7C_3 carbide. Lighter areas represent the matrix.

for efficient modification the Fe - Ce eutectic forms (Figure 1.8) that is undesirable due to the harmful effect to the material mechanical properties. Many experiments were made and reported on different steel grades with the excessive amount of REE added. The Ce - Fe eutectic point is at $641\text{ }^{\circ}C$, that is below the primary rolling temperature. During hot rolling the problems with hot-shortness are experienced [86]. Luyckx et. al. [87] was one of the first that reported the maximum amount of REEs in different grades of steels for efficient modification without impact on hot rolling performance. The measured upper limit of REEs in different steel grades was reported to be between 0,1 and 0,2 wt% [87]. In

the field of tool steels, two studies show rapid drop in wear resistance and impact toughness due to excessive REEs content, above 0.05 *wt%* [50], [88].

The eutectic carbide in non-modified material has the typical shape of a lamellar eutectic carbide. On the other hand, the eutectic in REE-modified samples has the morphology of a globular eutectic, where individual carbides (separate parts of eutectic) have the shape of globules. This can even better be seen in SEM BEI micrographs (Figure 4.3 and Figure 4.4). Similar micrographs were measured at several different spots at two different samples of each kind. All the micrographs show the same morphological differences between the non-modified and REE-modified carbides. This way we systematically proved that a difference exists for more than one case. The series of 14 different SEM BEI images of carbides of each kind are shown in Figures 4.5 - 4.18. Images were made on 8 different spots in two different samples of each kind (non-modified and REE-modified). Measurement spots were randomly selected on 1 *cm*² sample surface so that good statistical representation is obtained of carbide morphology across the whole sample.

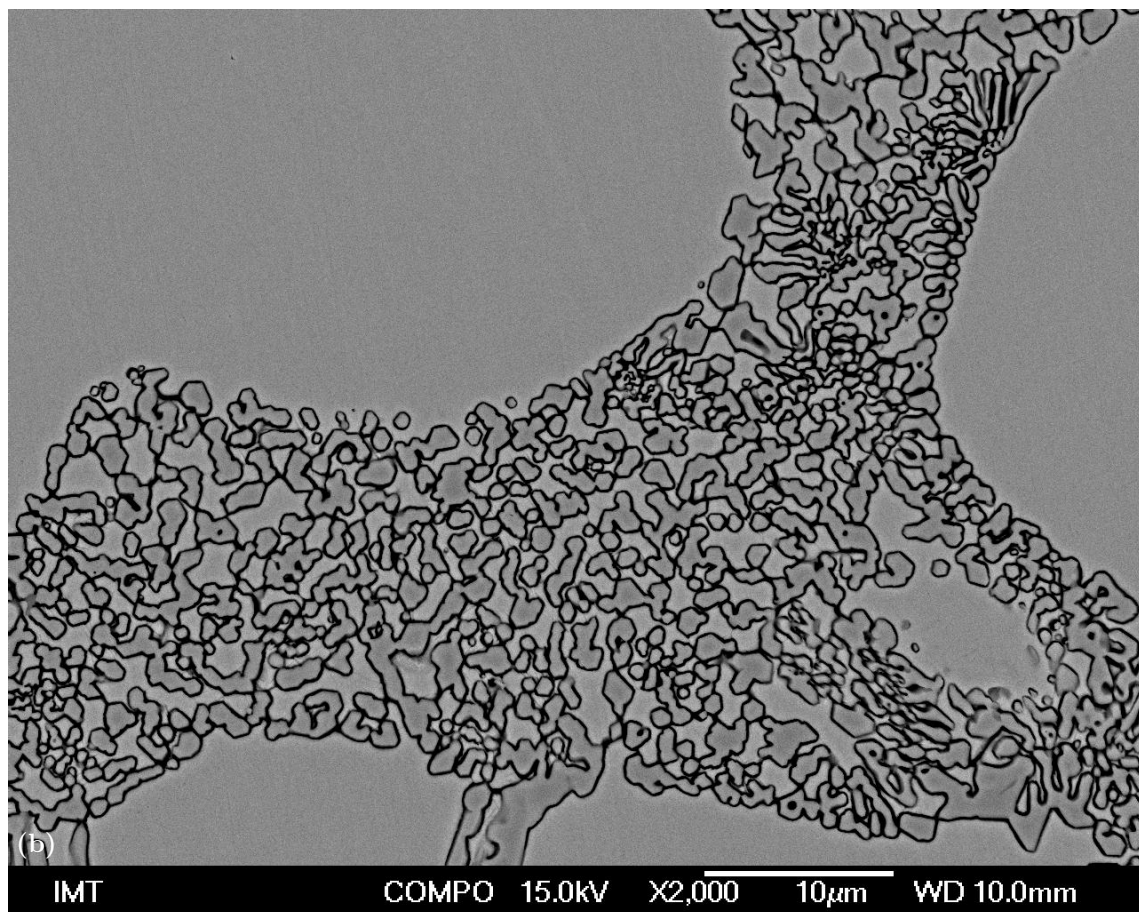
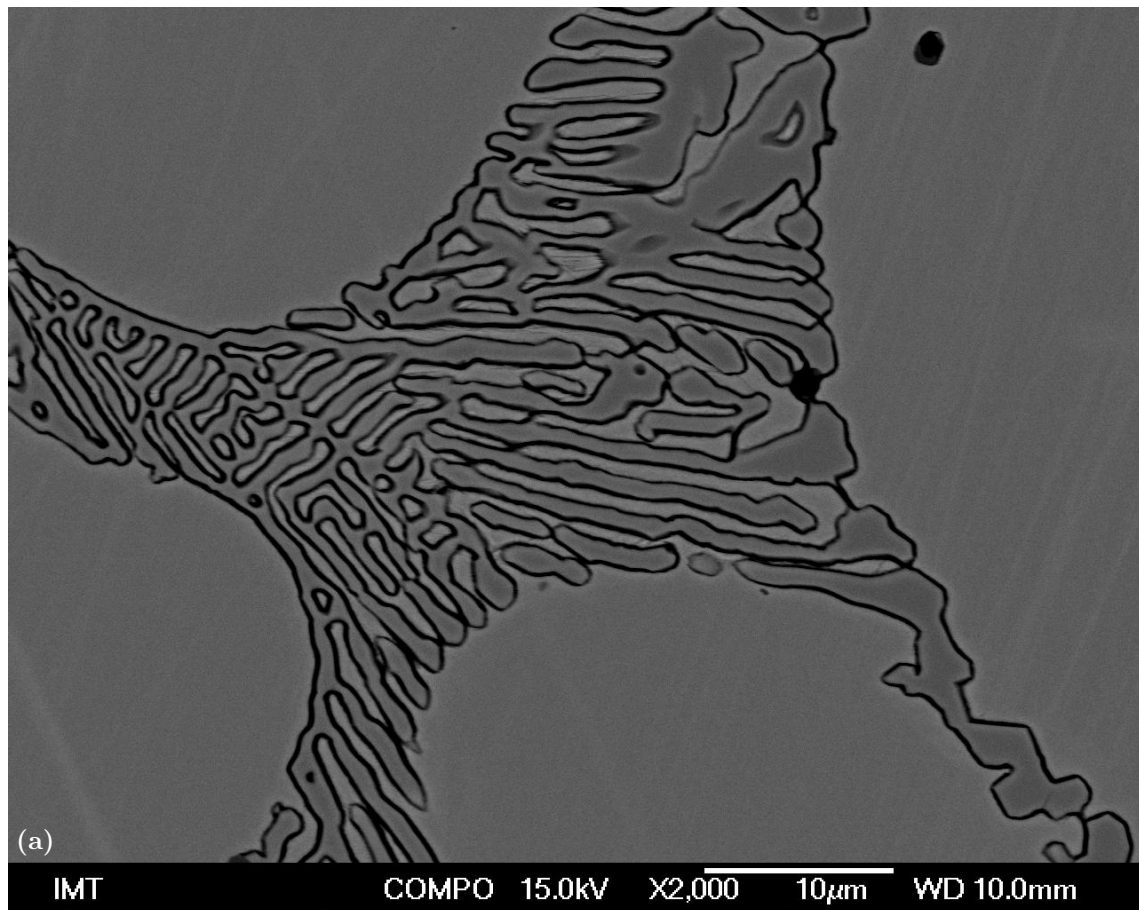


Figure 4.3: Comparison of SEM BEI of (a) non-modified and (b) REE modified as-cast microstructures of AISI D2 tool steel on low magnification. Dark areas represents the eutectic Cr_7C_3 carbide. Lighter areas represent the matrix.

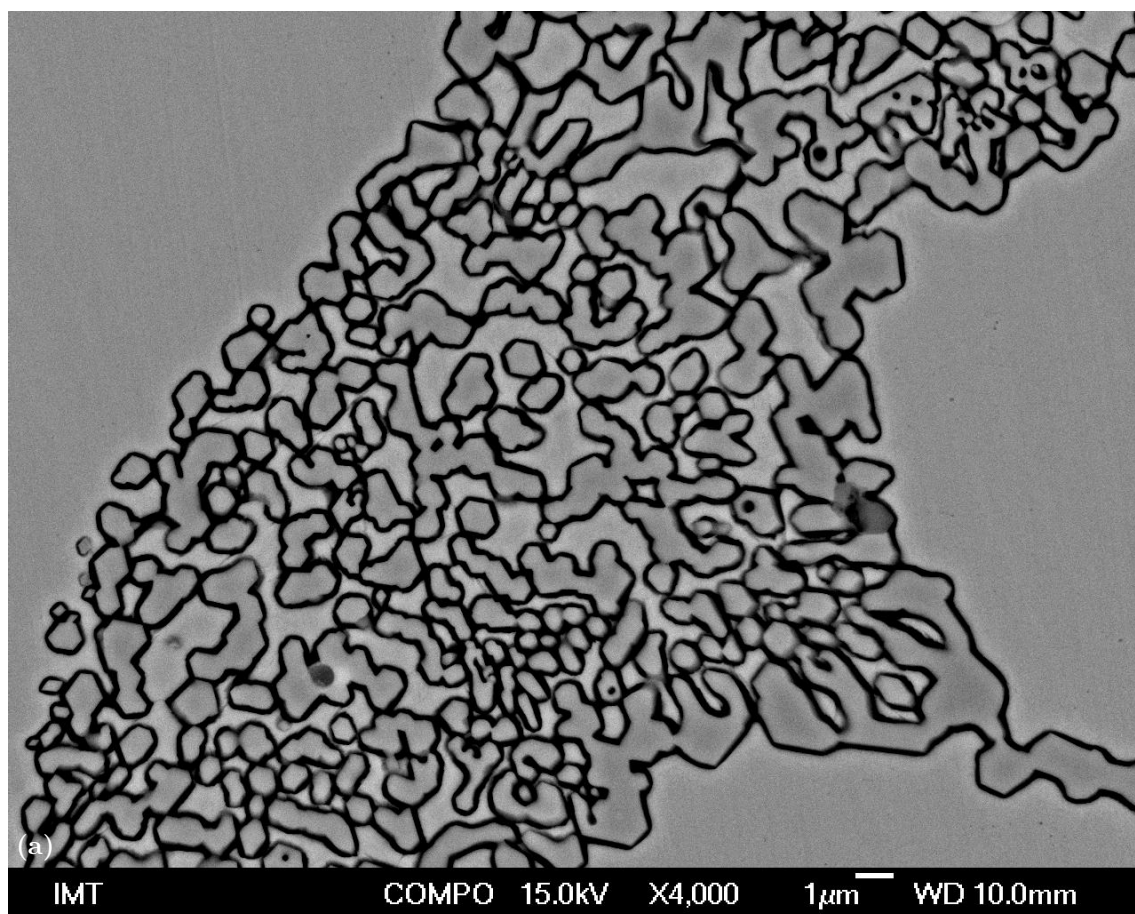
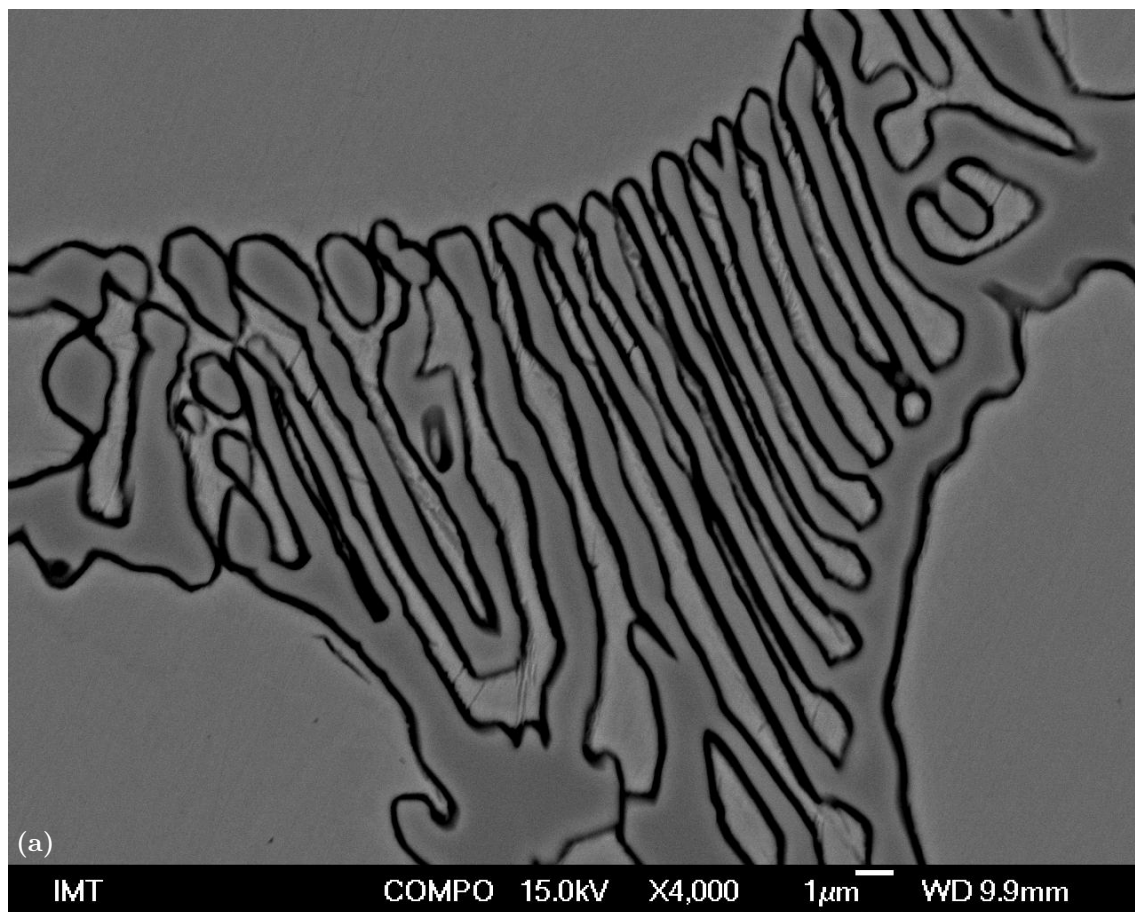


Figure 4.4: Comparison of SEM BEI of (a) non-modified and (b) REE modified as-cast microstructures of AISI D2 tool steel on high magnification. Dark areas represents the eutectic Cr_7C_3 carbide. Lighter areas represent the matrix.

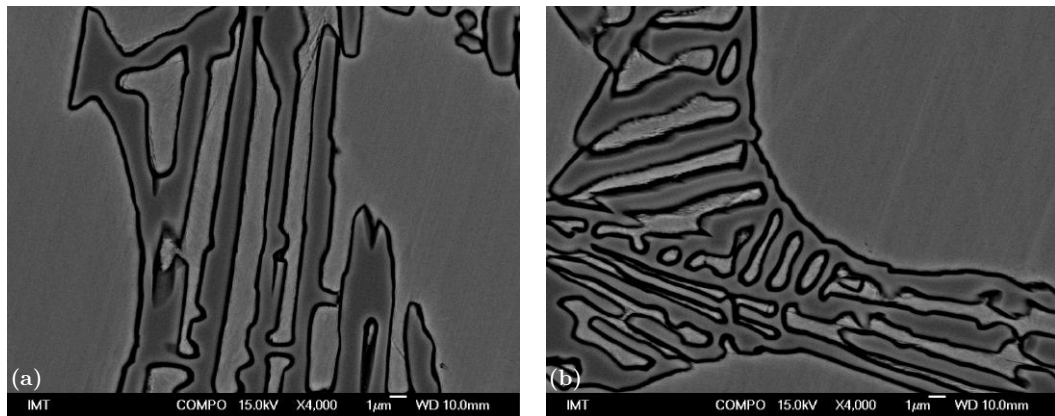


Figure 4.5: SEM BEIs of eutectic carbides in non-modified AISI D2 tool steel made on first sample on (a) spot 1 and (b) spot 2.

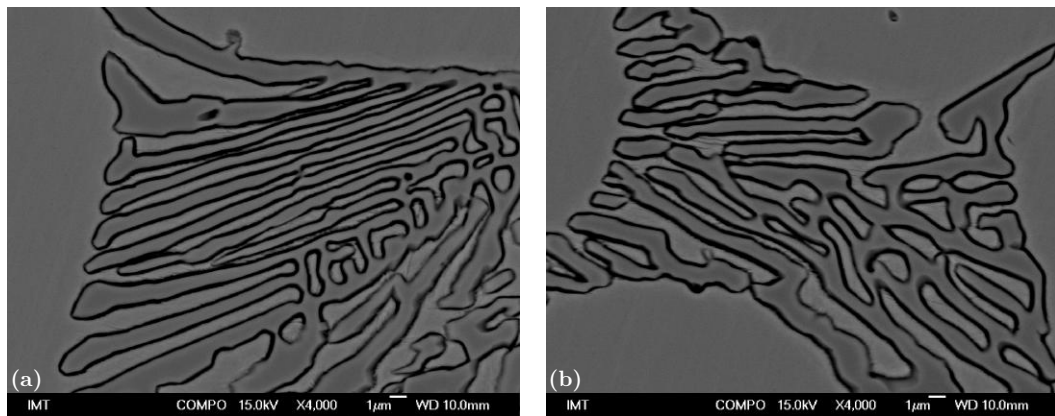


Figure 4.6: SEM BEIs of eutectic carbides in non-modified AISI D2 tool steel made on first sample on (a) spot 3 and (b) spot 4.

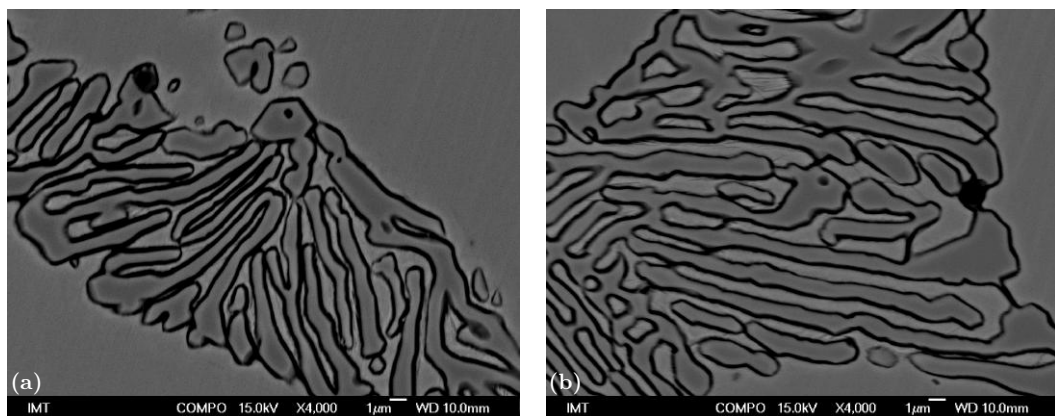


Figure 4.7: SEM BEIs of eutectic carbides in non-modified AISI D2 tool steel made on first sample on (a) spot 5 and (b) spot 6.

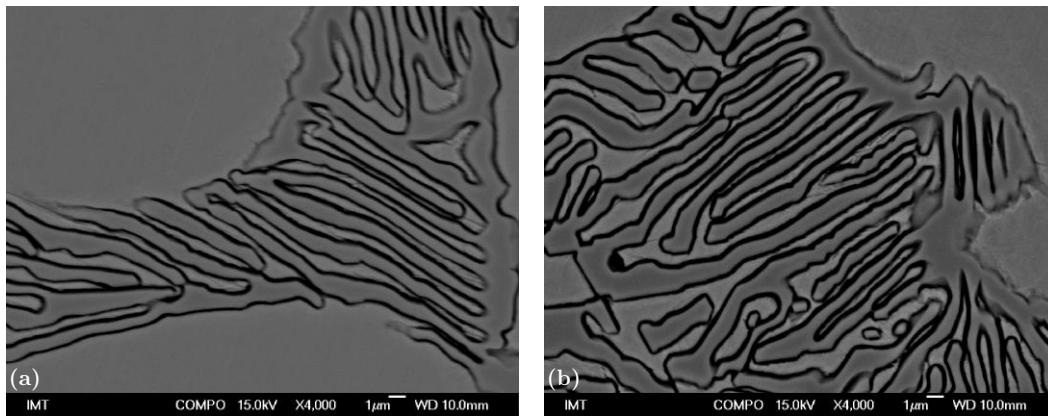


Figure 4.8: SEM BEIs of eutectic carbides in non-modified AISI D2 tool steel made on second sample on (a) spot 1 and (b) spot 2.

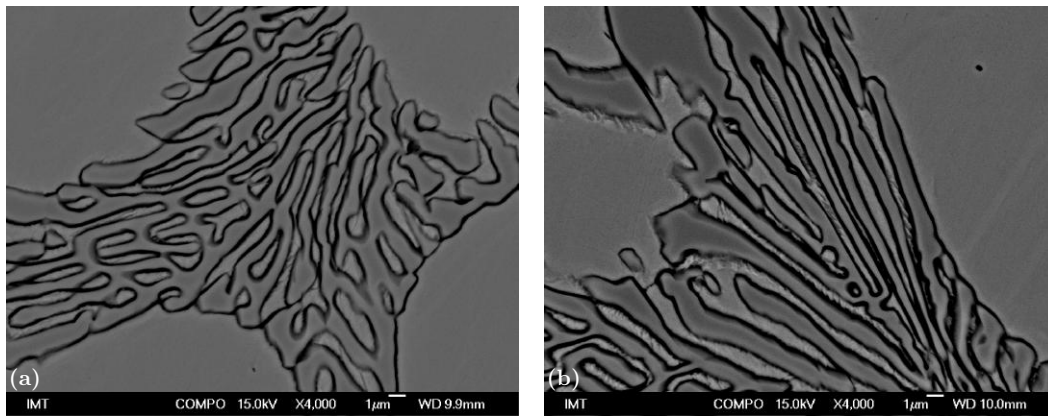


Figure 4.9: SEM BEIs of eutectic carbides in non-modified AISI D2 tool steel made on second sample on (a) spot 3 and (b) spot 4.

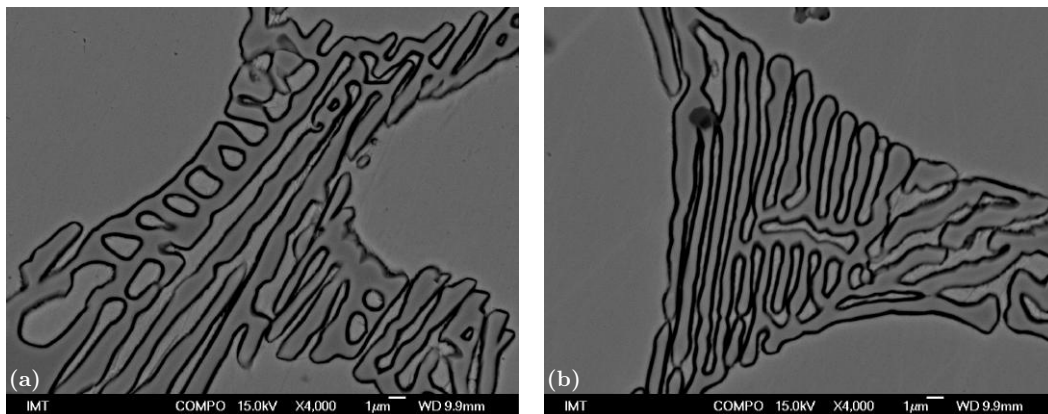


Figure 4.10: SEM BEIs of eutectic carbides in non-modified AISI D2 tool steel made on second sample on (a) spot 5 and (b) spot 6.

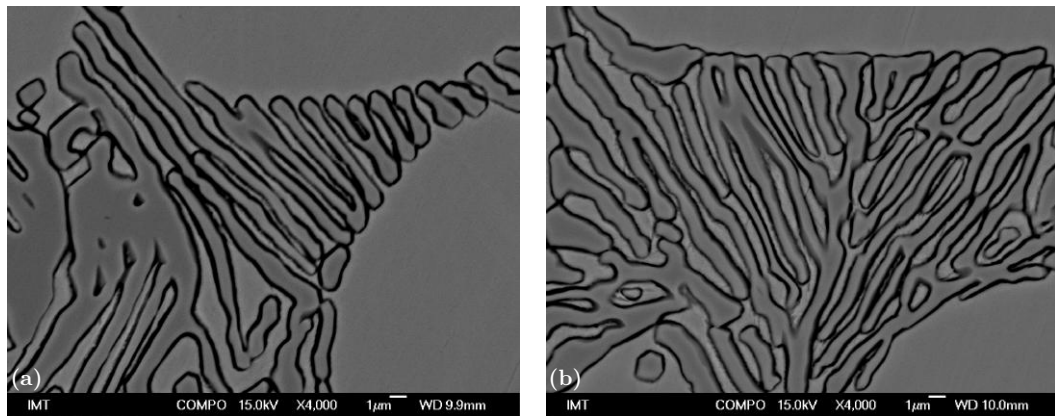


Figure 4.11: SEM BEIs of eutectic carbides in non-modified AISI D2 tool steel made on second sample on (a) spot 7 and (b) spot 8.

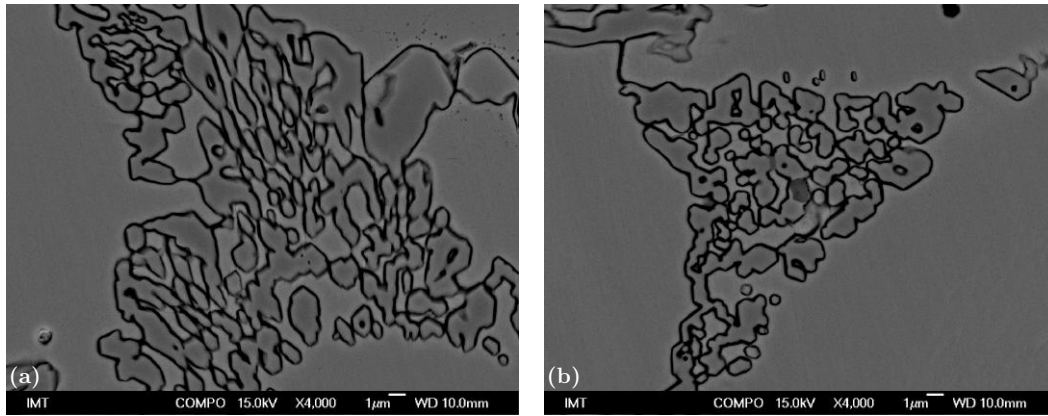


Figure 4.12: SEM BEI of eutectic carbides in RE modified AISI D2 tool steel made on first sample (a) spot 1 and (b) spot 2.

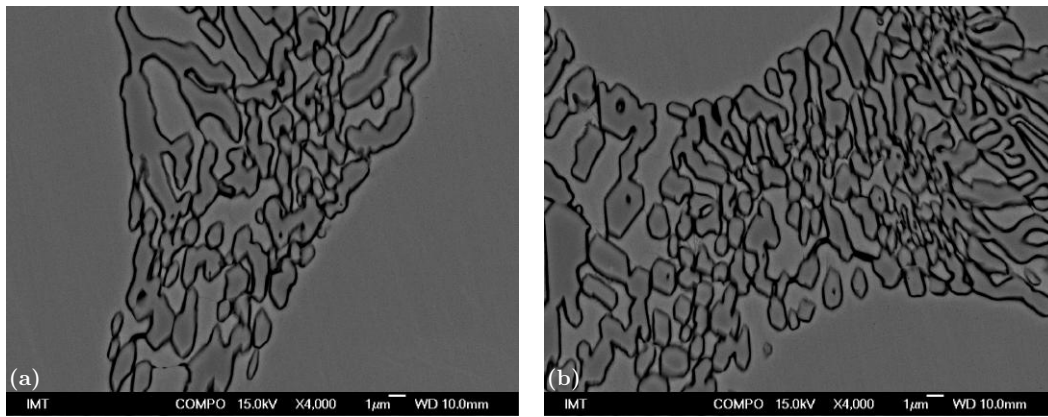


Figure 4.13: SEM BEI of eutectic carbides in RE modified AISI D2 tool steel made on first sample (a) spot 3 and (b) spot 4.

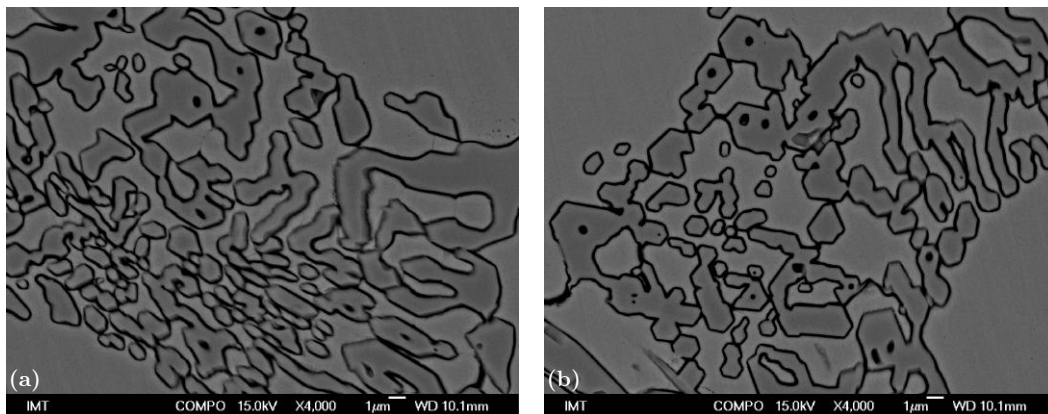


Figure 4.14: SEM BEI of eutectic carbides in RE modified AISI D2 tool steel made on first sample (a) spot 5 and (b) spot 6.

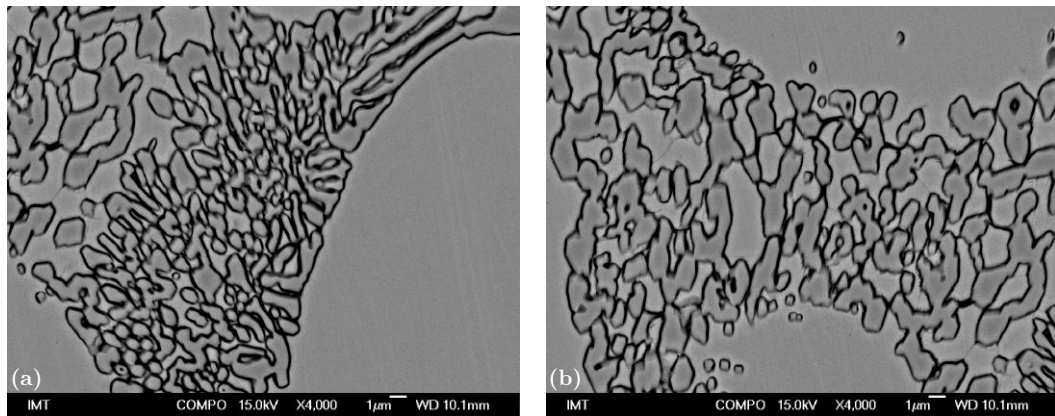


Figure 4.15: SEM BEI of eutectic carbides in RE modified AISI D2 tool steel made on first sample (a) spot 7 and (b) spot 8.

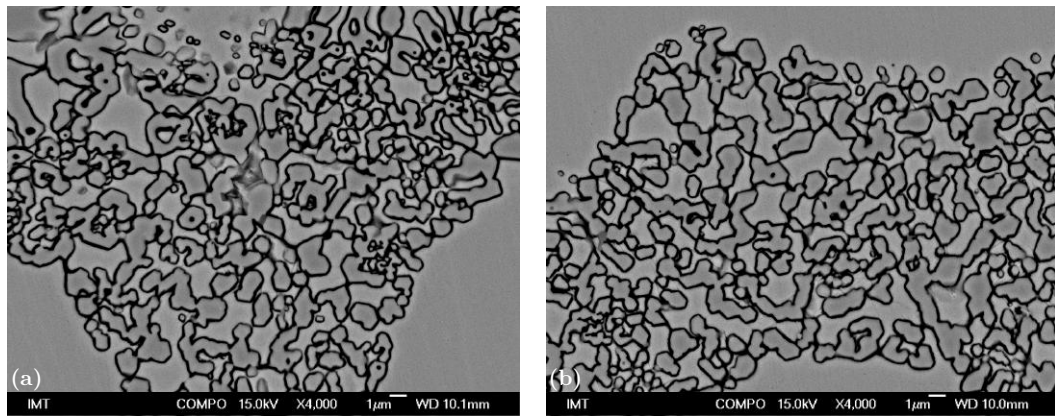


Figure 4.16: SEM BEI of eutectic carbides in RE modified AISI D2 tool steel made on second sample (a) spot 1 and (b) spot 2.

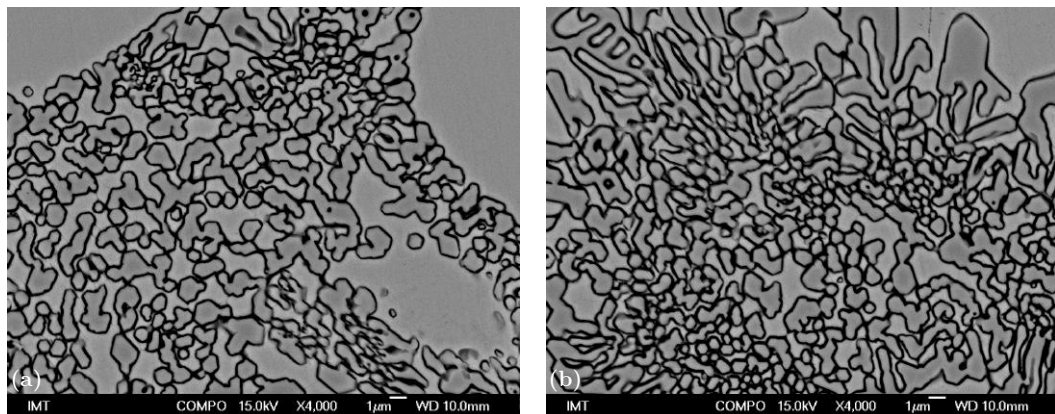


Figure 4.17: SEM BEI of eutectic carbides in RE modified AISI D2 tool steel made on second sample (a) spot 3 and (b) spot 4.

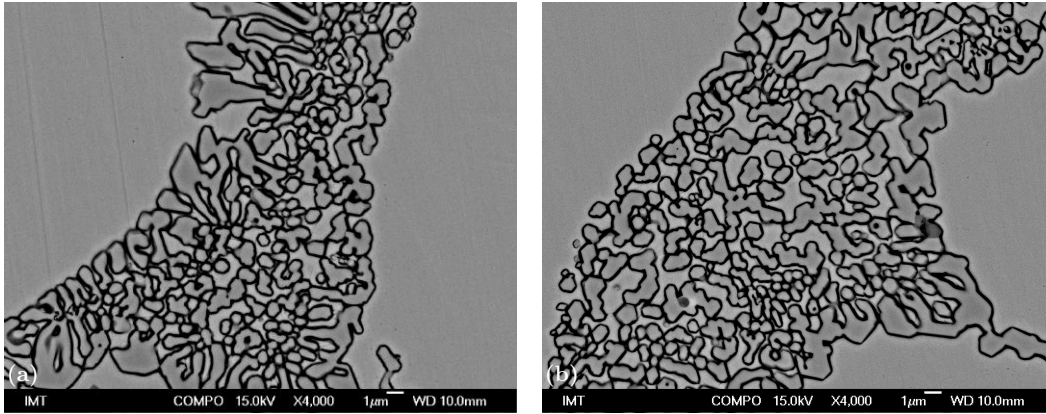


Figure 4.18: SEM BEI of eutectic carbides in RE modified AISI D2 tool steel made on second sample (a) spot 5 and (b) spot 6.

Even though the differences in morphology between the carbides from both samples are well seen we wanted some quantification to analytically prove the effect of REE modification on the morphology of the eutectic carbides. Quantification of the morphological differences was obtained by analyzing micrographs with a metallographic image-recognition tool that evaluates the elongation of the surface features on the micrographs. The analyses were made on 38 different micrographs of each kind of samples (non-modified and REE-modified) in order to obtain good statistics. The results clearly show that major differences exist in the morphology of the carbides. The carbides inside the REE-modified samples are in average completely isotropic (inside the standard deviation) - globular eutectic morphology. The carbides in the non-modified samples are anisotropic (elongated) - lamellar eutectic morphology. The non-modified carbides are on average four times longer than they are thick. The analyzing tool that was used for the quantification of the carbide elongation was developed in our laboratory as part of this thesis. The details about the analyzing tool can be found in Appendix A. The measured differences in the morphology of eutectic carbides between non-modified and REE-modified AISI D2 tool steel samples partially validate the first hypothesis of this thesis.

From Figure 4.3 and Figure 4.4 more than just the morphological difference between the non-modified and REE-modified samples can be seen. The shapes of globular carbides in RE modified samples are not spherical but polygonal. In order to investigate the shape of the REE-modified carbides we made SEM micrographs at high magnifications. Figure 4.19 shows the eutectic carbide from the REE-modified sample at a magnification of 60,000. From this figure we can see that globular carbides actually have the shape of hexagonal prisms. This fact can be seen especially well on the small carbide marked with the red circle. This carbide that fell out of the matrix during the etching shows us the true morphology of the carbides in the REE-modified samples. The hexagonal morphology of the eutectic carbides is not surprising since eutectic carbides are of the type Cr_7C_3 with a hexagonal crystal structure, as will be discussed in the next section.

4.1.1.2 Carbide type

The effect of REE modification on the carbide type in the AISI D2 tool steel's as-cast microstructure was determined by EDS and EBSD measurements on the SEM. There are six chemically different types of carbides existing inside tool steels. MC , M_2C , M_3C , M_6C , M_7C_3 and $M_{23}C_6$ [16], where M denotes the carbide-forming metals. Table 4.1

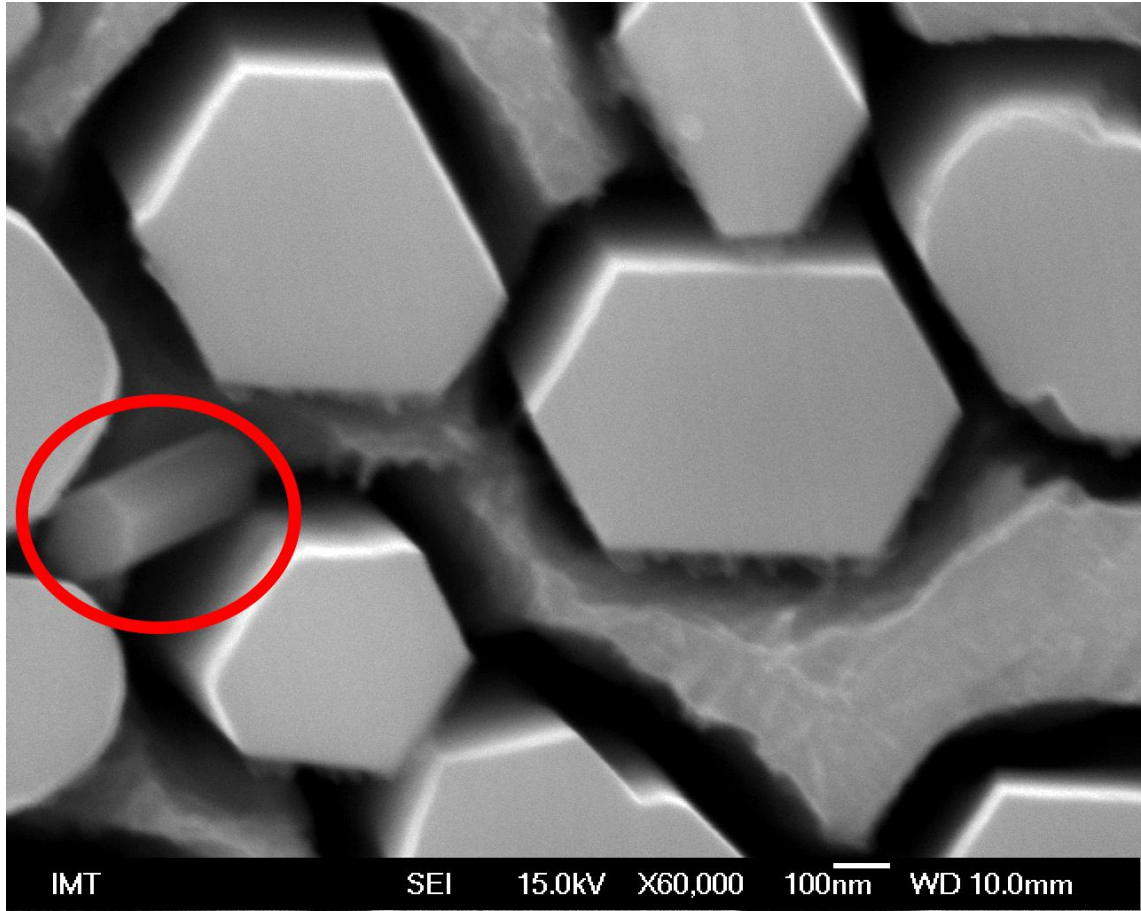


Figure 4.19: SEM secondary electron image (SEI) micrograph of eutectic carbide in RE modified sample on magnification of 60000.

shows the characteristics of all six types.

Table 4.1: All existing types of carbides in tool steels. First column shows the chemical formula for the carbide. M represents the carbide-forming elements. Second column shows the crystal structure type and the third column shows which are the most common carbide-forming metals that form this type of carbide.

Type of Carbide	Lattice type	Elements present
MC	FCC	V
M_2C	Hexagonal	W, Mo
M_3C	Orthorombic	Fe, Mn, Cr
M_6C	FCC	W, Mo
M_7C_3	Hexagonal	Cr
$M_{23}C_6$	FCC	Cr

From Figure 4.3, Figure 4.4 and Figure 4.19 we deduced that the eutectic carbides in the REE-modified samples have a hexagonal crystal structure. The same deduction can be made for the non-modified samples if a detailed examination of the carbides in Figure 4.3, Figure 4.4 and Figures 4.5 - 4.18 is performed. Even more precise hexagonal nature of eutectic carbides in non-modified samples can be seen from Figure 4.20. The end parts of

the individual lamellas in non-modified carbides always form 120° angles, which is unique for crystals with hexagonal crystal lattice.

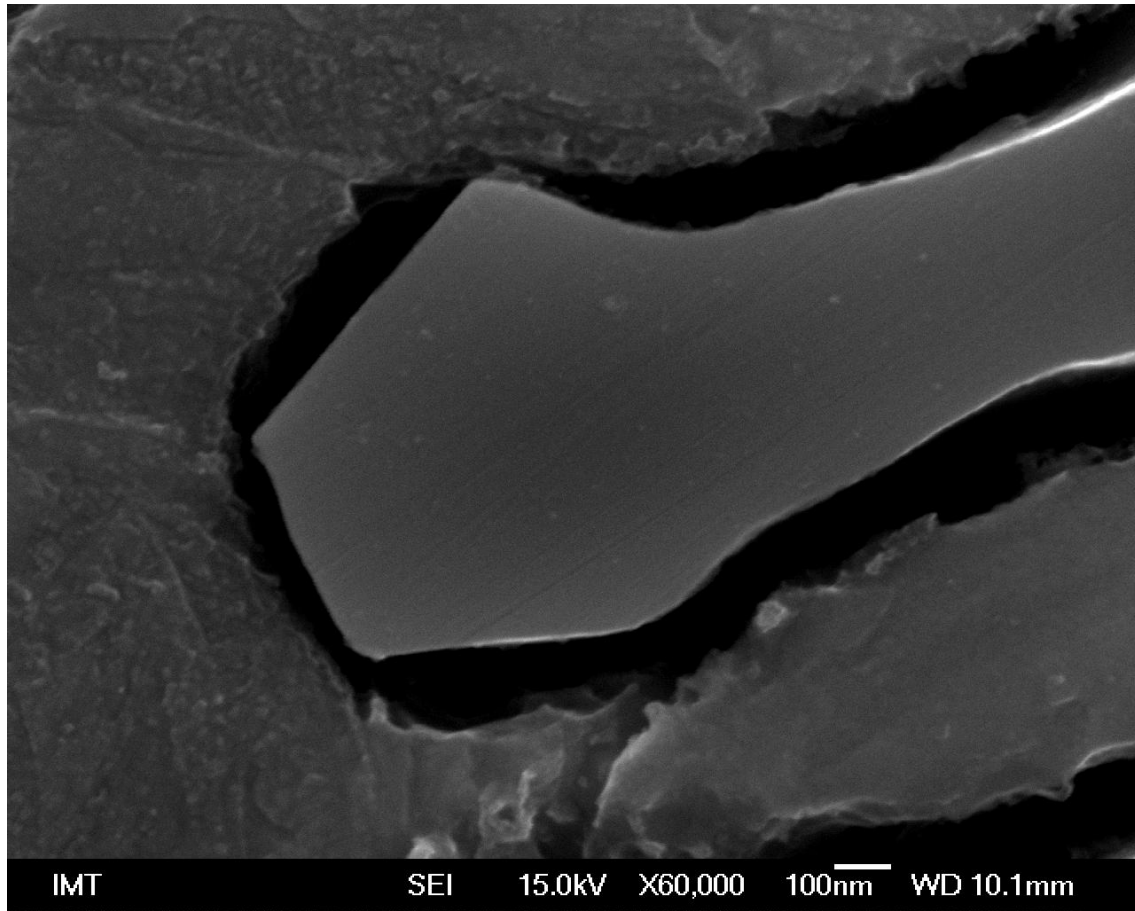


Figure 4.20: SEM secondary electron image (SEI) micrograph of eutectic carbide in non-modified sample on magnification of 60000. 120° angles at the end of eutectic carbide lamella are well seen.

In this way we can anticipate that only M_2C or M_7C_3 carbides are candidates for the chemical type of carbides in our samples, since only these two carbides crystal lattices are hexagonal (Table 4.1). Furthermore, we expected that a much more probable carbide type is M_7C_3 because of the large amount of chromium that is present in our steel grade (Table 3.3). All the assumptions that were made on the basis of the SEM images and the chemical composition of the material were proven with electron-backscatter diffraction (EBSD) measurements on the SEM. Figure 4.21 shows the result of the EBSD measurement. EBSD mappings in Figure 4.21 show that the whole of the eutectic carbide is of the same crystallographic type. From the comparison of solved Kikuchi band patterns in Figure 4.22 it can be seen that the type of eutectic carbides in non-modified and REE-modified samples is the same. An automatic comparison of both patterns to the database showed that this type is hexagonal Cr_7C_3 .

It was proven that the only type of carbides that exist in the non-modified as well as REE-modified samples is the Cr_7C_3 carbide. The type of carbide is not changed by REE modification of the AISI D2 tool steel. This partially invalidates the first hypothesis of this thesis.

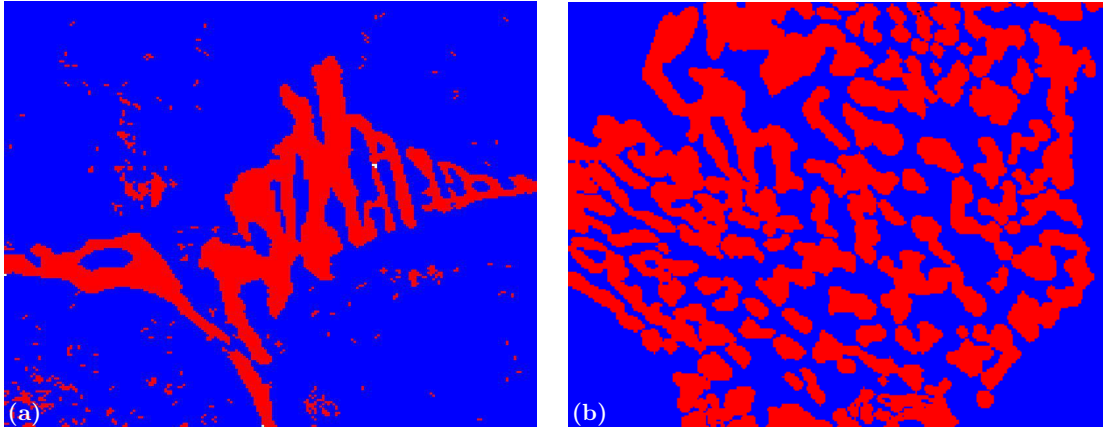


Figure 4.21: EBSD mapping of eutectic carbide from (a) non-modified and (b) RE modified AISI D2 tool steel.

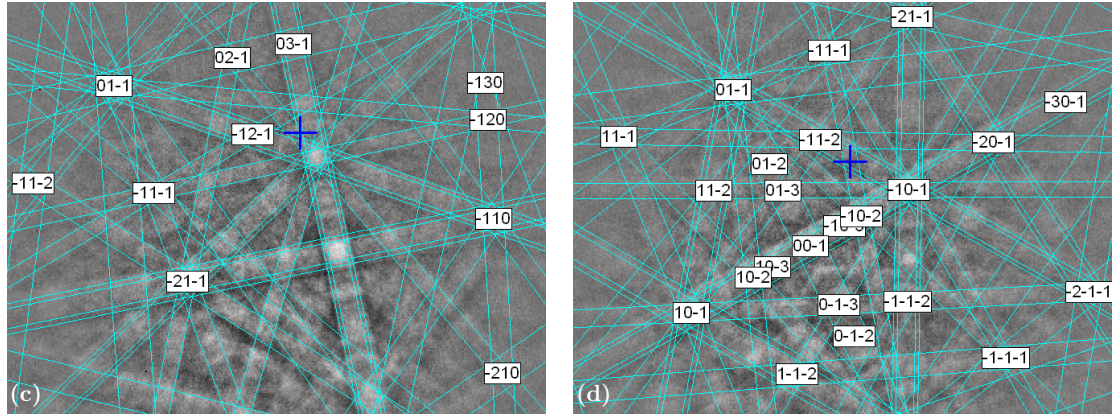


Figure 4.22: Kikuchi band patterns from EBSD measurements on eutectic carbide from (a) non-modified and (b) RE modified AISI D2 tool steel.

4.1.1.3 Carbide volume

The total volume of eutectic carbide depends on many different chemical and thermodynamic parameters. In some tool-steel grades the eutectic carbide volume was changed by REE modification, as discussed in Chapter 1. That is why we wanted to compare the volume fraction of the eutectic carbide in the non-modified samples to REE-modified samples. The volume fraction of eutectic carbides was estimated from the light micrographs at low-magnification made on the samples etched using Groesbeck reagent ($KMnO_4$, $NaOH$ and H_2O) (Figure 4.23). Carbides in the micrographs of samples etched with Groesbeck reagent appear much darker than the steel matrix. Besides that the boundary between the carbide and the matrix is clear and well defined. These two characteristics make the Groesbeck-etched-sample micrographs perfect for use with analyzing softwares that estimate the total area of carbide on the micrograph. From the measured area the total volume fraction of eutectic carbide can be concluded. The image-recognition software that was used for the volume ratio of eutectic carbides estimation was developed and coded in our laboratory as part of this thesis. The figures were binarized (Figure 4.24) and trans-

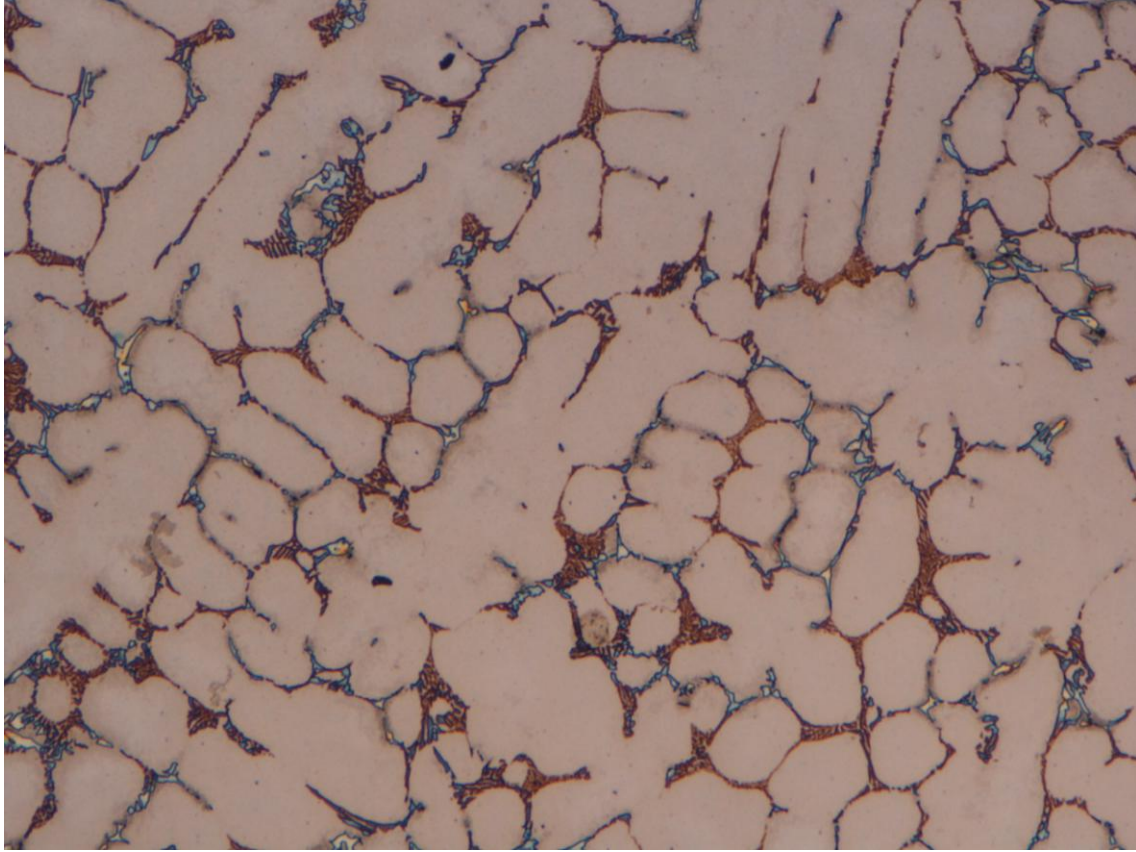


Figure 4.23: Light micrograph of non-modified sample of as-cast AISI D2 tool steel. Sample was polished and etched by Groesbeck reagent. Dark regions represent eutectic carbides. Light region is matrix. There is no scale bar on the image since image was further processed with software that determines the volume fraction of carbides.

formed to a matrix of zeros and ones. One representing black and zero representing white. The total area of the carbide was measured by counting all the ones in matrix by walking across matrix in two for loops. This type of analysis was performed on ten different figures of both types of samples (non-modified and REE-modified). For the analysis two samples of each kind were analyzed (samples 2 and 3). No difference in the volume ratio of eutectic carbides between non-modified and REE-modified samples was obtained (inside standard deviation). The average result from all ten images from non-modified sample accounts for (29.20 ± 1.12) vol%. The same average result from the modified sample is (28.60 ± 1.33) vol%. Both results are in reasonable agreement with the approximate calculation of the volume fraction of both phases (Equation 4.1).

$$\rho_{\gamma}w_{\gamma}\bar{x}_{\gamma} + \rho_Ew_Ex_E = \rho_Mx_M \quad (4.1)$$

where ρ_i denotes the densities, w_i the volume fraction of the i -th phase and x_i the average concentration of carbon in the i -th phase. γ denotes the austenite, E the eutectic phase and M is the melt. The average concentration of carbon in austenite was obtained by integration of the liquidus line in the phase diagram from the liquidus to the eutectic temperature. x_M is the measured average concentration in the material and x_E is the carbon concentration in the melt at the eutectic point. The densities of all three phases were obtained from the literature. The estimated volume fraction of the eutectic carbides is 28.2, which is compatible with the values measured by our software (inside standard

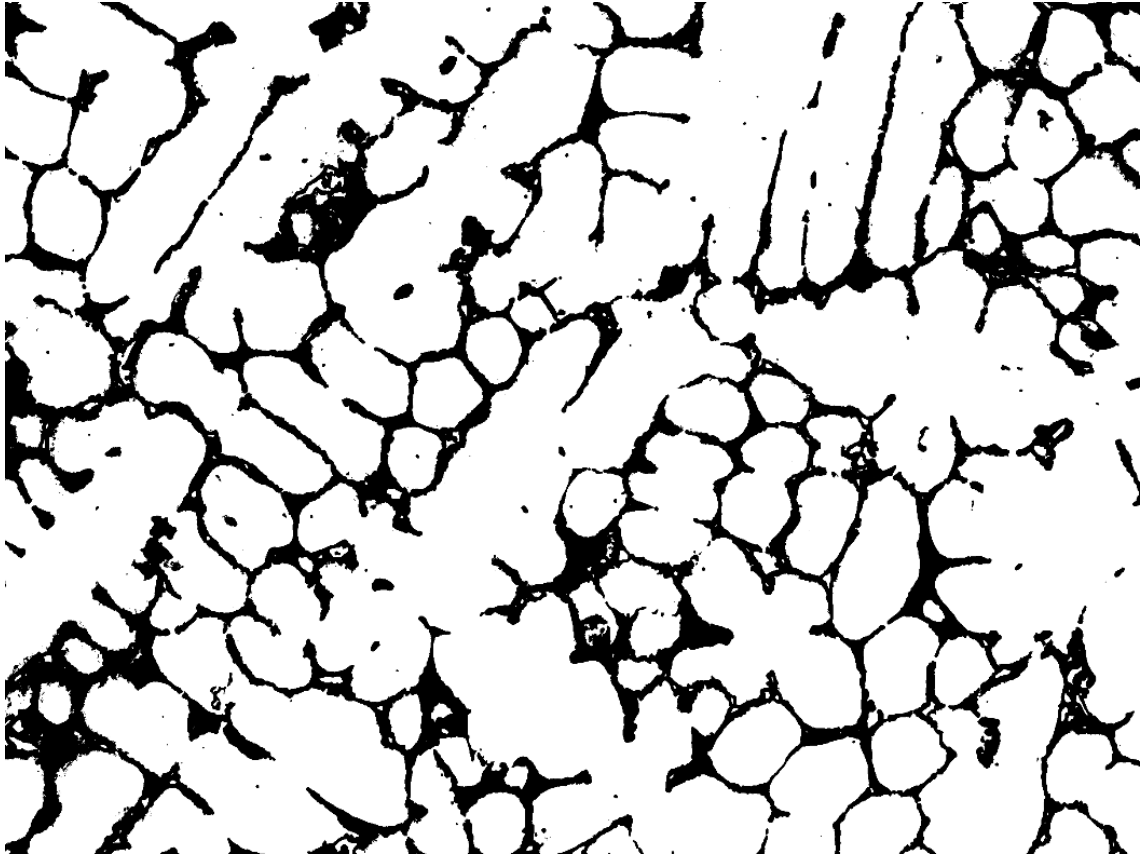


Figure 4.24: Binarization of Figure 4.23. Binarization was made in GNU Octave with the Matlab function `im2bw`.

deviation).

We concluded that the volume ratio of eutectic carbides cannot be changed by the REE modification of AISI D2 tool steel. This fact partially invalidates the first hypothesis of this thesis

4.1.2 Modification by non-metallic inclusions

The effect of REEs on the non-metallic inclusions in AISI D2 tool steel was investigated by micro-chemical EDS point analysis. In this way the second hypothesis of this thesis was investigated. The second hypothesis was partially disproved by the experimentation described in this sub-section. The full disproving of the second hypothesis was achieved in connection with the simulation results, which are described in next section.

In order to test the second hypothesis we wanted to find out whether any of the REEs-containing inclusions are found inside the eutectic carbide region. In order to observe REEs-containing inclusions we performed BEI on SEM. Due to the high atomic weights of the REEs and consequently the high scattering cross-sections for electrons, REEs on SEM BEI appear much brighter than any other element present in the steel. This fact was first proved with the point EDS examination of several inclusions that appeared bright on SEM BEI images. Our anticipation turned out to be correct. REEs containing non-metallic inclusions were by far the brightest objects on the SEM BEI micrographs. EDS analysis of one of such inclusions can be seen in Figure 4.25. For the clarity Figure 4.25 shows only parts of the EDS spectrum that contain informations about REEs and oxygen (parts of

the spectrum between $0.175 - 0.275 \text{ nm}$ and $1.85 - 2.60 \text{ nm}$). Since the bright inclusions in the SEM BEI micrographs were smaller than the EDS beam interaction volume, a large part of the result of inclusion EDS measurement (Figure 4.25) was contributed by the steel matrix. The high content of cerium, lanthanum and oxygen in the analyzed inclusion is obvious if we compare the EDS analysis of the matrix (Figure 4.26) to the EDS analysis of the inclusion (Figure 4.25).

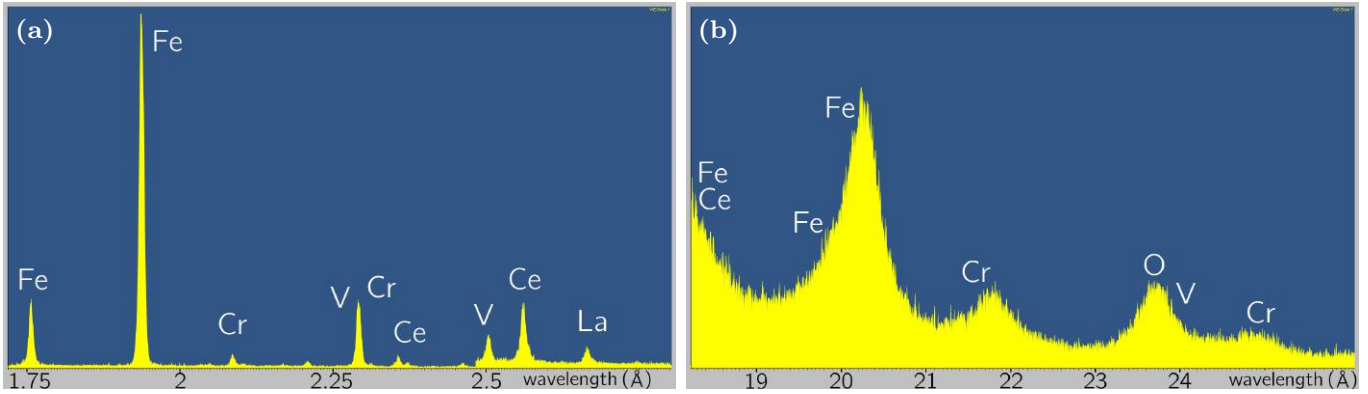


Figure 4.25: EDS spectrum of non-metallic inclusion containing REEs (measured on spot 1 in Figure 4.27). Only parts of spectrum where *Ce*, *La* and *O* peaks are present are shown. These are $0.175 - 0.275 \text{ nm}$ (Figure (a)) and $1.85 - 2.60 \text{ nm}$ (Figure (b)).

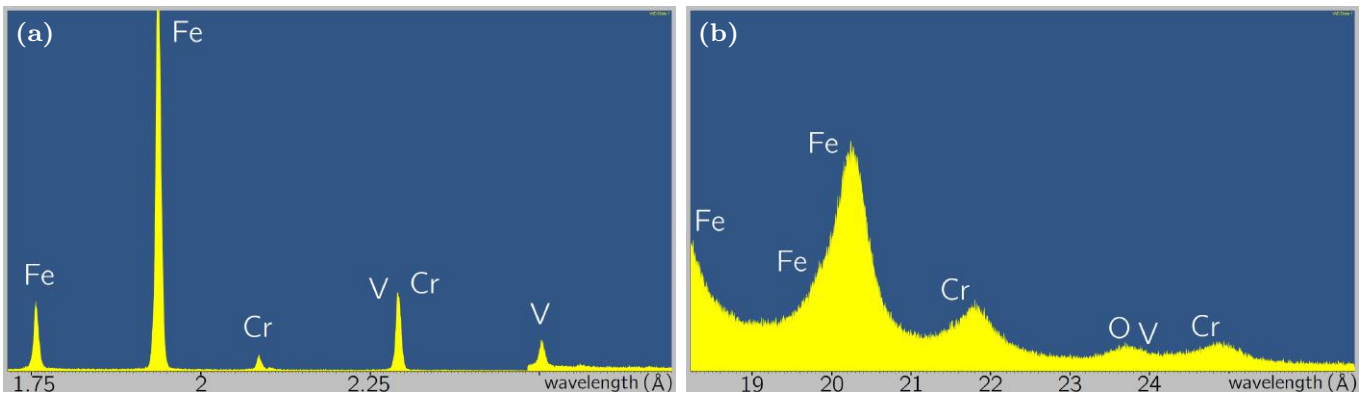


Figure 4.26: EDS spectra of RE modified steel matrix (measured on spot 2 in Figure 4.27). Only parts of spectrum where *Ce*, *La* and *O* peaks are present are shown. These are $0.175 - 0.275 \text{ nm}$ (Figure (a)) and $1.85 - 2.60 \text{ nm}$ (Figure (b)).

The only major differences between both spectra are the peaks of *Ce*, *La* and *O* that are present in EDS spectrum of the inclusion, but not in the EDS spectrum of the matrix. From the stoichiometric ratio between *Ce*, *La* and *O* we could determine the type of analyzed inclusion but due to the EDS insensitivity to lighter elements (*O* and *S*), such determination would be questionable. Nevertheless, presence of *Ce*, *La* and *O* in the analyzed inclusion was proven and the conclusion can be made, that REEs containing non-metallic inclusion are the bright spots on the SEM BEI micrographs, which was the only purpose of EDS analysis. The procedure was repeated on several different spots. After proving that the bright spots on the SEM BEI micrographs are REEs-containing non-metallic inclusions we performed an examination of the typical position of such inclusions by BEI. On the

SEM BEI micrographs in Figure 4.28 and Figure 4.29 we can clearly see bright spots that represent the REEs-containing non-metallic inclusions.

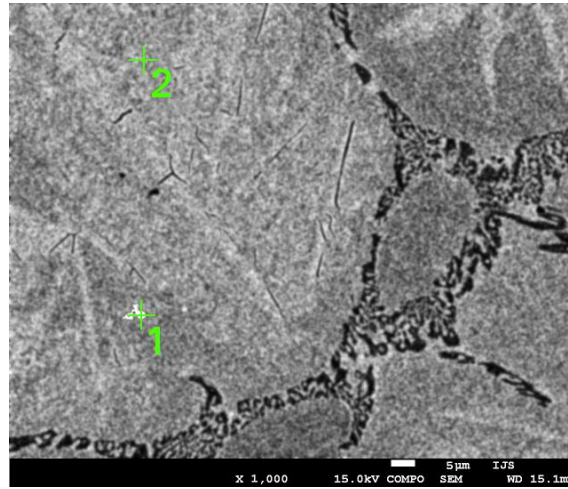


Figure 4.27: SEM BEI of microstructure of REE-modified AISI D2 tool steel with marked EDS measurement spots. Spot 1 is on the inclusion that appear bright in BEI. Spot 2 is on the matrix of steel.

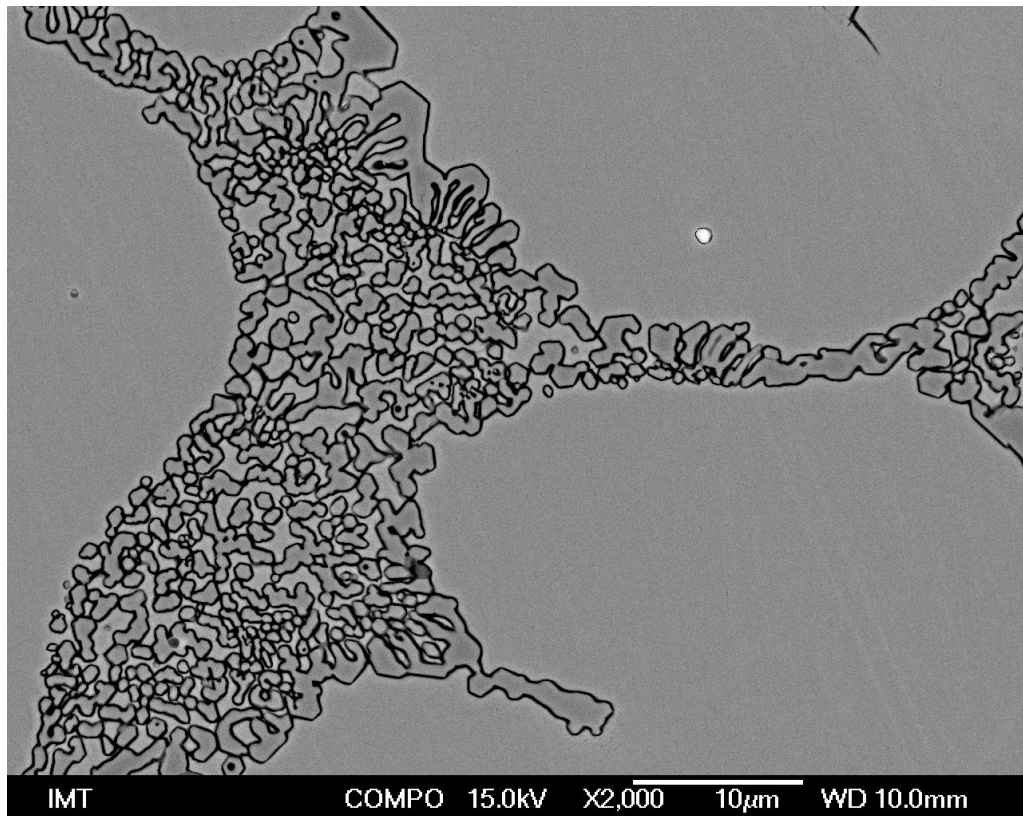


Figure 4.28: SEM BEI of microstructure of REE-modified AISI D2 tool steel on higher magnification. Bright spots on the figure represents REE containing non-metallic inclusions.



Figure 4.29: SEM BEI of microstructure of REE-modified AISI D2 tool steel on lower magnification. Bright spots on the figure represents REE containing non-metallic inclusions.

All three REEs-containing non-metallic inclusions are inside the steel matrix and there are no such inclusions inside the eutectic carbides. A detailed SEM examination of several different REE-modified samples proved that this is a general rule since REEs-containing non-metallic inclusions were not found in any investigated eutectic carbide. On the basis of this result we decided that REEs-containing non-metallic inclusions were not the nucleation sites for the eutectic chromium carbide. This disproves the second hypothesis of this thesis.

4.2 Modeling results

Simulations of the eutectic carbide solidification were made using the modeling principles described in Chapter 3. The results of the simulation in connection with the experimental results represent a good basis for the verification of the second and third hypotheses.

The model validation was made by monitoring the solid phase ratio in the simulation. The parameters of the test simulation were set to the values explained in Chapter 3 except κ_c and $B(\mathbf{n})$. Those two parameters were varied. The dependency of the phase ratio on the temperature was monitored for the different κ_c and $B(\mathbf{n})$. Since those two parameters only affect the internal distribution of the solid phases they do not affect the solid phase ratio during solidification. This was proved without a doubt since the obtained phase ratio - temperature dependencies were identical. Figure 4.30 shows the solid phase ratio dependency on temperature. From the figure under-cooling is clearly seen, since the rapid appearance of the solid phase occurs well under the liquidus temperature of 1396°C . The dashed line, fitted to the linear part of simulated data, shows that very well since it intercepts the temperature axis at the liquidus temperature. After the nucleation, the linear

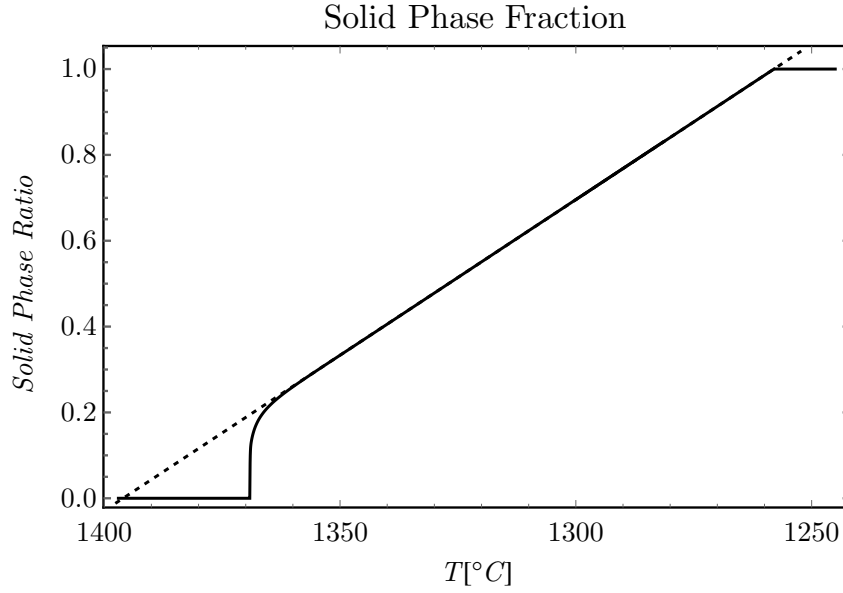


Figure 4.30: Solid phase ratio obtained by simulation (solid line). Dashed line represent linear fit to calculated data in order to show the under-cooling.

dependency of the solid phase ratio is a consequence of the linearly changing temperature.

The results of the simulation are presented as 50×50 pixel images of the calculation domain of the $4 \mu m \times 4 \mu m$ size. Calculated two-dimensional phase fields for both order parameters (non-dimensional crystallinity and carbon concentration) were plotted on the domain in different colors (white - melt, red - Cr_7C_3 carbide, blue - austenite). The results for both the REE-modified and non-modified material solidification were simulated for two different types of heterogeneous nucleation sites that initiate the solidification. The first type of nucleation sites used in the simulation exhibits a smaller crystal-lattice misfit with the Cr_7C_3 hexagonal lattice than the austenite FCC crystal lattice and the second type was the opposite. Figure 4.31 shows the results of simulation for non-modified material solidification. Figure 4.32 shows the time evolution of the REE-modified material solidification.

The time evolution in Figure 4.31 and Figure 4.32 goes from top to bottom. The simulation results for different simulation times are plotted. The solidification of the eutectic in CASE 1 and CASE 3 started on heterogeneous nucleus that exhibits low lattice misfits with Cr_7C_3 . Eutectic solidified in CASE 2 and CASE 4 heterogeneously nucleated on the nucleus that shows low misfits with the austenite crystal lattice. We can see that in both cases for non-modified steel the result of the simulation is a lamellar eutectic. In both cases for REE-modified steel the results are globular carbides. The difference in both simulations was the choice of the ratio between the isotropic and anisotropic parts of the surface energy. It turns out that sharp transition from lamellar to globular eutectic morphology occurs at the value of ratio $B(\mathbf{n}_x)/\kappa_c = 2500$. Simulations in Figures 4.31 and 4.32 are made for ratios of 2000 and 3000.

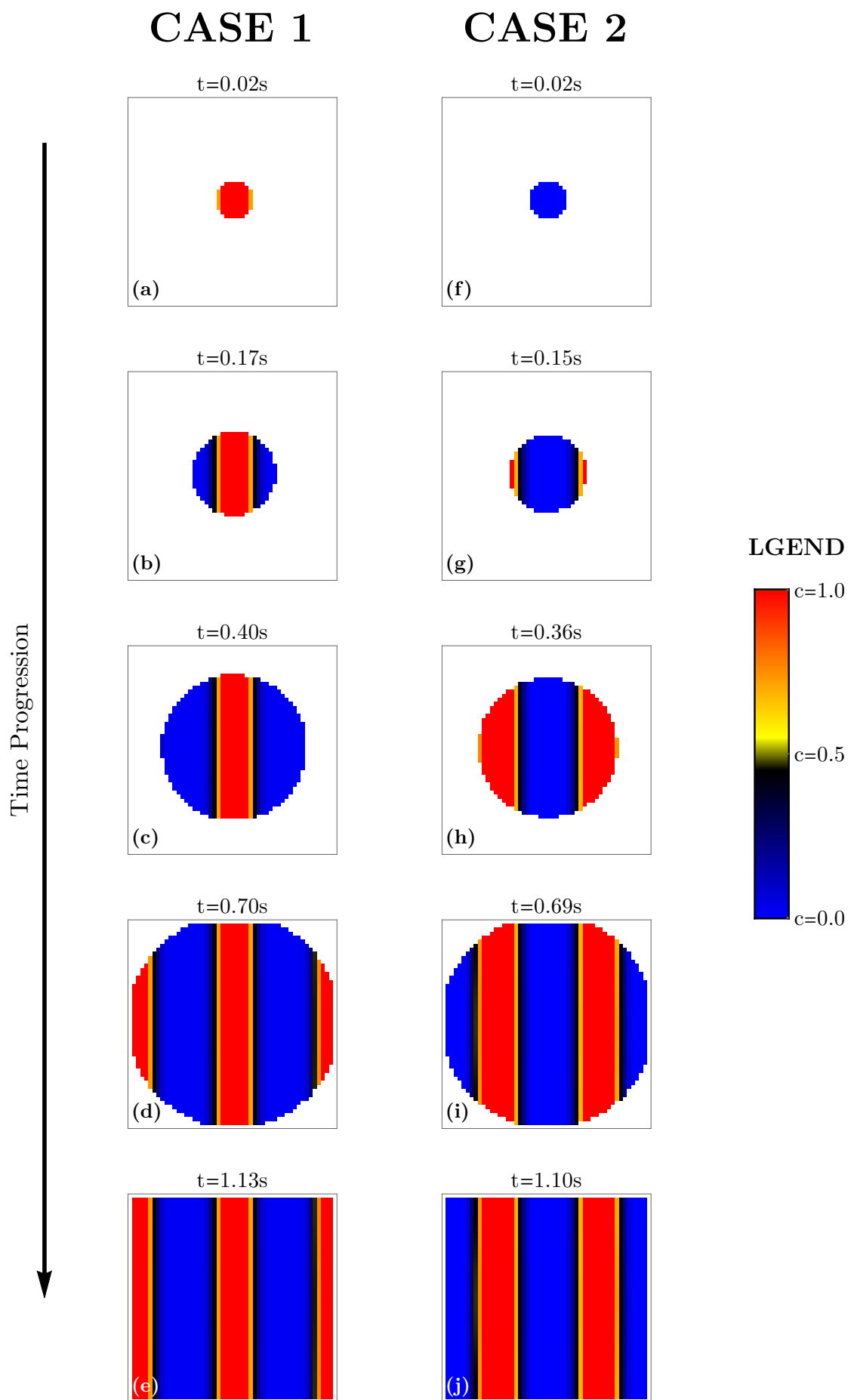


Figure 4.31: Results of simulation for non-modified AISI D2 steel. Values of phase field are represented by different colors (white - melt, blue - austenite, red - Cr_7C_3 carbide). Time evolution goes from top to bottom. Case 1 (figures (a) - (e)) show solidification that started on Cr_7C_3 compatible nucleus. Case 2 (figures (f) - (j)) show solidification that started on austenite compatible nucleus.

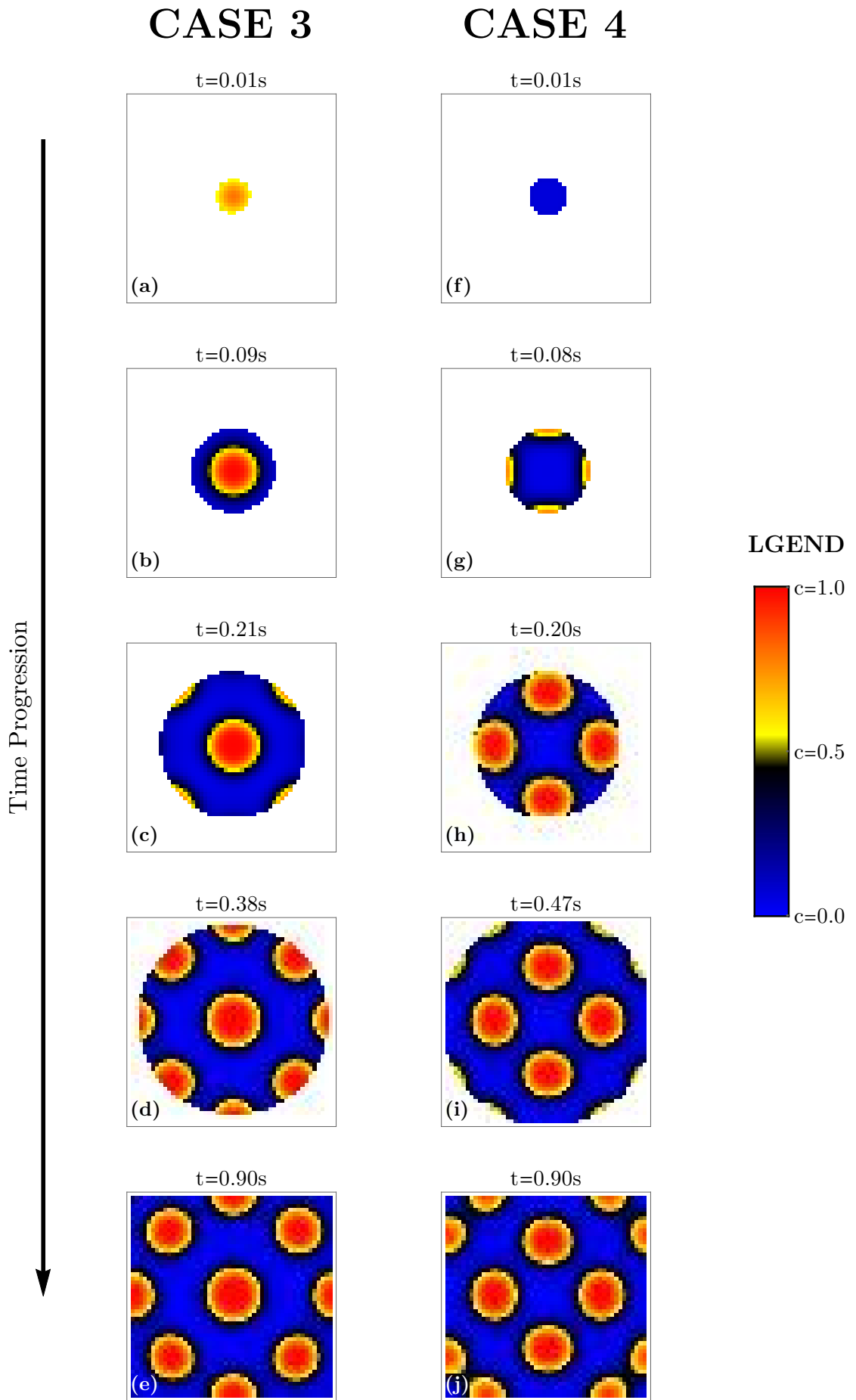


Figure 4.32: Results of simulation for RE modified AISI D2 steel. Values of phase field are represented by different colors (white - melt, blue - austenite, red - Cr_7C_3 carbide). Time evolution goes from top to bottom. Case 3 (figures (a) - (e)) show solidification that started on Cr_7C_3 compatible nucleus. Case 4 (figures (f) - (j)) show solidification that started on austenite compatible nucleus.

Besides the general transition from lamellar to globular eutectic morphology, due to REE modification, our model is capable of describing some smaller morphological features found in the REE-modified samples. Figure 4.33 and Figure 4.34 show very specific shapes of the individual globules of the eutectic carbides in the REE-modified samples. Globular carbides have the shape of a toroid with the small amount of austenitic phase in the middle of carbide globule. The same feature can be seen in several globules of eutectic carbide if the figures 4.12 to 4.18 are carefully inspected.

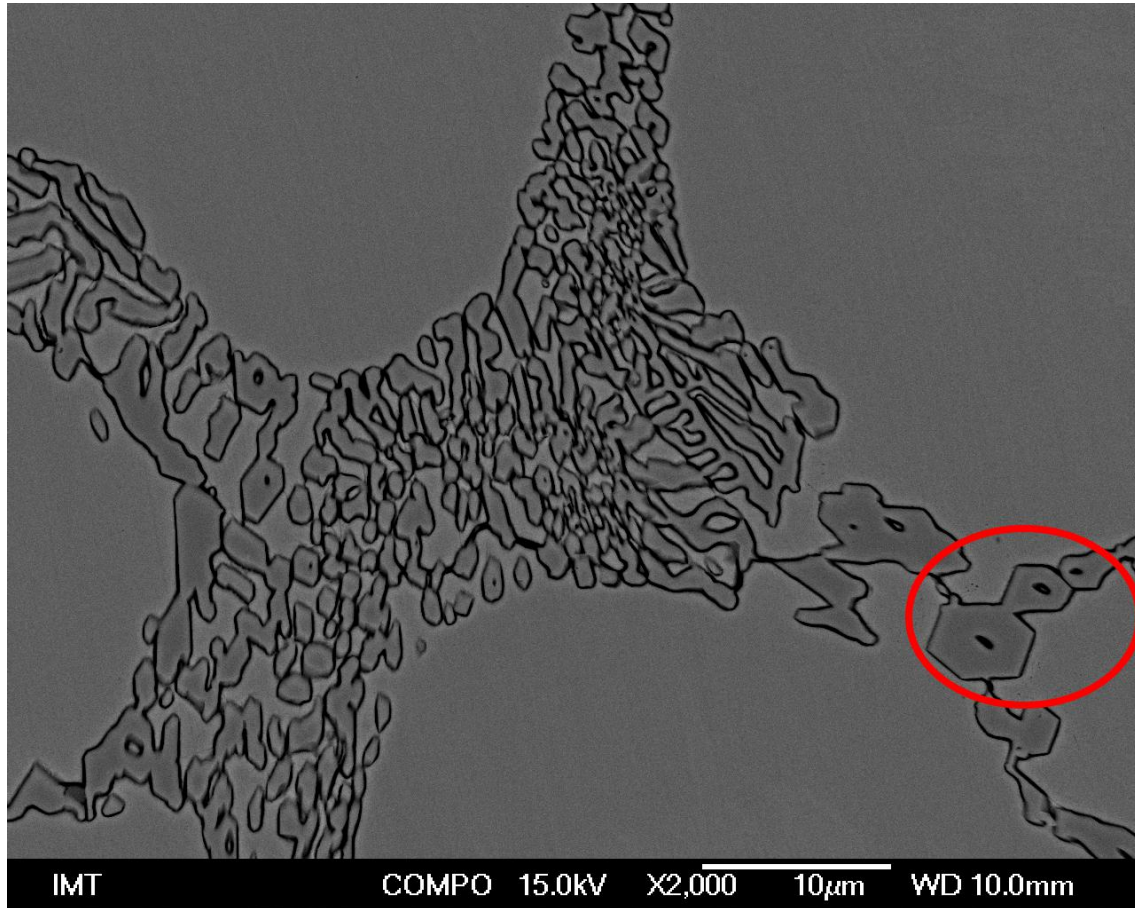


Figure 4.33: SEM BEI micrograph of eutectic carbide in REE-modified sample. Eutectic carbide globules with the austenitic phase in the center are clearly seen on the right-hand side of the image (marked with red circle).

Using the proposed model we were able to simulate the growth of the eutectic carbide globule with the austenitic phase in the core [89]. The simulation was made on the smaller domain ($1\ \mu\text{m} \times 1\ \mu\text{m}$) and the temperature reduction rate was raised by 20%. For the initiation of the reaction a heterogeneous nucleation seed was used with the crystal lattice similar to the austenite. The result of the simulation for the described conditions is presented in Figure 4.35. The slight asymmetry of the result is the consequence of an even number of control volumes in the simulation, thus it is impossible to start the nucleation in the geometric center of the domain.

All the results of the simulations additionally disprove our second hypothesis, since it is clear that no matter what type of inclusion is introduced to the system as heterogeneous nucleus, both type of carbides are possible.

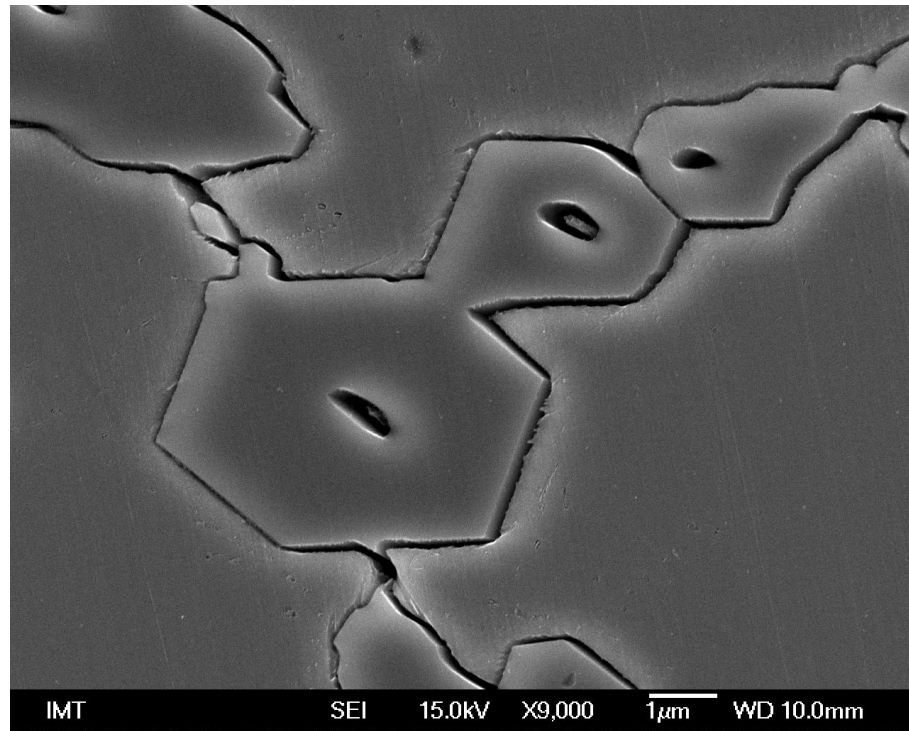


Figure 4.34: SEM BEI micrograph of eutectic carbide in REE-modified sample. Zoom of the eutectic carbide globules with the austenitic phase in the center.

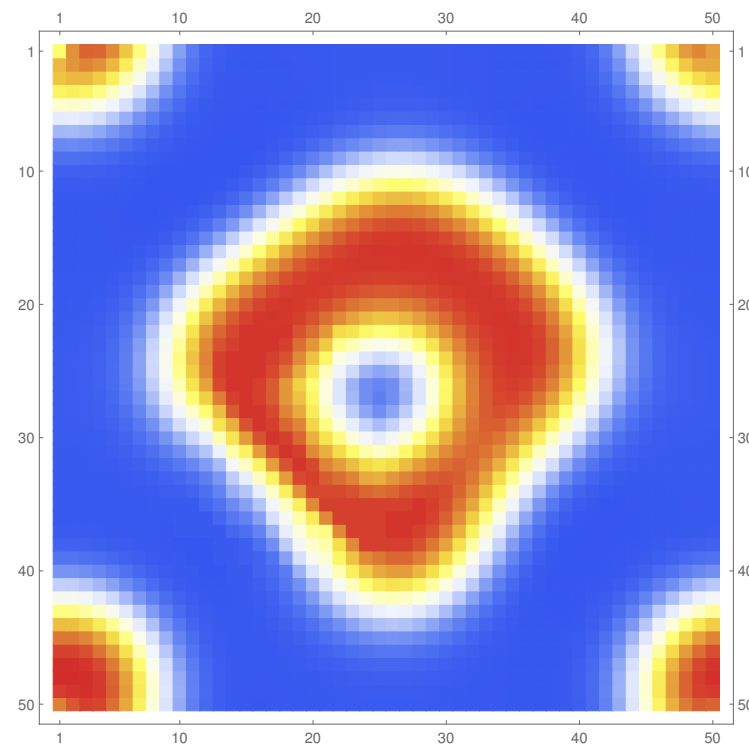


Figure 4.35: Result of simulation for REE-modified steel solidification on smaller domain ($1 \mu\text{m} \times 1 \mu\text{m}$) and 20% increased cooling rate. Blue color represents austenite and red color is Cr_7C_3 carbide. Colors yellow and white represent the phase boundary between both phases.

Chapter 5

Discussion

In Chapter 4 many results of the experiment and simulation are presented as well as a short interpretation of each individual result. In Chapter 5 we will discuss the results of the experiment in connection to the simulation results. The discussion consists of three different parts, each of which refer to one of the hypothesis.

5.1 First Hypothesis

REE-modification of AISI D2 tool steel can lead to a change in the morphology, type, size and distribution of ledeburite eutectic carbides in the as-cast microstructure.

First hypothesis of the thesis is very broad and therefore we did not expected to fully verify it. The hypothesis focuses on four different characteristics of eutectic chromium carbides: morphology, type, size and distribution. The hypothesis was fully tested only by experimental part of our work. One of the four eutectic carbide properties that were included in the hypothesis turned out to be changed by REE modification. It is the morphology of the eutectic carbides. We can conclude that only one fourth of the hypotheses was proved. Nevertheless, it was proved that the difference in eutectic carbides due to REE modification exists, which is the major finding of this thesis.

5.2 Second Hypothesis

The reason for the eutectic carbide's morphology change in AISI D2 tool steel, modified by REEs, is the modified non-metallic inclusions that act like heterogeneous nucleation sites for the chromium carbide.

The second hypothesis was tested in experiment as well as by simulation. It was composed on the basis of previous similar experiments, that were found in the literature. It is generally understood that non-metallic inclusions modified by REEs represent good nucleation sites for the eutectic carbide and thus carbides with a modified morphology evolve in the REE-modified steel [47], [52]. However, we found this to be highly unlikely, since during a detailed examination of the SEM BEI images of the modified samples no REE-containing modified inclusions of any type were found inside the Cr_7C_3 carbides. If the morphology of the eutectic was changed from lamellar to globular due to efficient heterogeneous nucleation of carbides on non-metallic inclusions, every globule of the eutectic had its own nucleus inside. Independent of the orientation of the cross section of observed sample some of the nucleus would be surely seen on BEI SEM micrographs since the number of globules

in every image is large. From SEM BEI images in Chapter 4 it is clear that this is not true. This was the first experimental proof that the second hypothesis is wrong.

Further, we tested same hypothesis by simulations. It is clear from Figure 4.32 that only one nucleation site is needed for the whole region of the eutectic to solidify in the decomposed final state. A single nucleation site is sufficient for the number of lamellae (Figure 4.31) or globules (Figure 4.32) to grow. In addition to that numerous individual carbides can be formed from a nucleation site that does not even exhibit compatibility of the crystal lattice with the carbide (high misfits). Figure 4.32 CASE 4 shows the time evolution of the solidification that started on the nucleation site compatible with an austenite FCC crystal lattice and nevertheless twelve globular eutectic carbides grew on the $4\ \mu\text{m} \times 4\ \mu\text{m}$ domain. That clearly shows that the globularisation of the eutectic carbides has a different origin than the heterogeneous nucleation of the eutectic on the REE-containing inclusions. The simulation results additionally disprove the second hypothesis.

The hypothesis was finally rejected when in addition to the first two findings we calculated the misfits for all the lowest-index crystal faces of all the inclusions that were found on the EDS mapping with the crystal lattice of the Cr_7C_3 carbide. None of the inclusions showed a misfit small enough to represent an efficient nucleation site for the carbide. Calculations of the misfits were done in the same way as the calculations of the misfits between carbide and austenite described in Chapter 3.

5.3 Third Hypothesis

The reason for the eutectic carbide's morphology change in AISI D2 tool steel, modified by REEs, is the change in the ratio between the isotropic and anisotropic parts of the surface energy of the phase boundary between the austenite and the carbide.

The third hypothesis was tested by comparison of experimental and modeling results. The hypothesis states that the reason for the different morphologies of the eutectic carbides is the anisotropy of the surface energy of the phase boundary between the Cr_7C_3 carbide and the austenite. By the simulation this was analytically proven. Large anisotropies result in a lamellar structure, since the carbide growth is energetically preferable in the directions parallel to the phase-boundary orientation with the lowest free energy. In the case of the globular eutectic there is no anisotropy of the phase-boundary surface energy and thus the carbide growth velocity is equal in all directions. The result is globular carbides.

The magnitude of anisotropic part of surface energy ($B(\mathbf{n})$ in equation 3.23) is the parameter that governs the directions of the eutectic carbide growth. The high anisotropy of $B(\mathbf{n})$ results in a lamellar carbide morphology, while a low anisotropy of $B(\mathbf{n})$ leads to globular eutectic growth. $B(\mathbf{n})$ can be calculated from the crystallographic properties of the carbide and the austenite. From the SEM micrographs and the crystallographic calculations we determined that the hexagonally structured chromium carbide and FCC austenite crystals meet with faces $\{11\bar{2}0\}$ (hexagonal lattice) and $\{730\}$ (FCC lattice). The function $B(\mathbf{n})$ in this case shows a high anisotropy, since all possible perpendicular phase boundaries exhibit much larger misfits. This results in a lamellar eutectic growth. After the modification the hexagonal carbide and the FCC austenite are stacked with $\{1\bar{1}00\}$ and $\{941\}$ planes. This stacking has only a slightly higher strain energy than $\{11\bar{2}0\}$ to $\{730\}$, but it has a special property, i.e., when rotated by 120° we obtain the same boundary with the same misfit. For the hexagonal symmetry of the chromium carbide this means an equal growth rate in even the lowest crystallographic direction and, consequently, carbides in the shape of hexagonal globulas. The transition from one regime to another due to REE modification was investigated by varying the different parameters in the model. It was

found that the ratio between the isotropic and anisotropic parts of the surface energy is the crucial parameter that dictates the realization of two different regimes, i.e., the globular and the lamellar.

In the first regime (before modification) the contribution of the isotropic part (κ_c) to the surface energy is small in comparison to the anisotropic part ($B(\mathbf{n}_x)$). The phase boundaries with the smallest possible misfit are realized, which minimizes the total free energy, even though the ratio between the areas of the phase-boundary surfaces versus the volume of carbide is large (lamellae). In the second regime (after modification) the isotropic part becomes non-negligible in comparison to the anisotropic part. The isotropic contribution to the surface energy favors the evolution of globules (spheres), since this morphology shows the lowest carbide area-to-volume ratio and consequently the smallest contribution of the isotropic surface energy. The compromise is made in the anisotropic part where the phase boundaries do not have the smallest possible misfit, but exhibit the lowest possible anisotropy in order to enable the globular growth and this way to minimize the total free energy.

We assume that the change in the ratio between the isotropic and anisotropic parts of the surface energy is a direct consequence of the REE addition. REEs have a very strong affinity for oxygen and sulfur. After the addition of the REE to the melt, complex oxysulfide non-metallic inclusions (REE_2O_2S) occur [52] that tend to deplete the melt of sulfur and oxygen. These two elements are known to segregate to the grain boundaries during the solidification due to the low solid solubility of austenite [90]–[92]. Since the casting was conducted in an open induction furnace the levels of oxygen and sulfur in our material are high. In the case of the non-modified material large amounts of those two elements can be found at the grain boundaries, including the boundaries between the carbides and the austenite. In the case of the REE-modified steel the oxygen and sulfur segregate to the grain boundaries to a much lower extent since most of oxygen and sulfur are found in non-metallic inclusions. The amount of oxygen and sulfur that segregate to the boundaries between the carbide and the austenite changes the surface energy of such a boundary [93]. The coherency of the phase boundary is reduced due to the segregations and the number of dislocations is increased [94], [95]. The anisotropic part of the surface energy is increased in comparison to the isotropic part when segregations are present. This is the reason why the ratio between the isotropic and anisotropic parts of surface energy of the phase boundary between the carbide and austenite differs between the REE-modified and non-modified material.

Quantitatively, this is shown in the simulation presented in Figure 4.28 and Figure 4.29. The reason for the change in the carbide morphology was the altered ratio between κ_c and the parameter $B(\mathbf{n}_x)$. The function $B(\mathbf{n})$ was simplified in our model so that the hexagonal anisotropy was approximated by isotropy, due to the long computational times. The results of the model therefore show spherically shaped carbides instead of hexagonal types in the case of the REE-modified steel, but in comparison to the lamellae they prove the concept. It turns out that a relatively sharp transition from the lamellar to the globular regime occurs at the value of the non-dimensional expression $\frac{B(\mathbf{n}_x)}{\kappa_c} = 2500$. In Figure 4.29 we can see that value of $\frac{B(\mathbf{n}_x)}{\kappa_c} = 2000$ leads to a globular eutectic, while the value of 3000 leads to a lamellar eutectic. This proves that the oxygen and sulfur contents, controlled by REE additions, can lead to the transition from a lamellar to a globular eutectic in AISI D2 tool steel. The third hypothesis was proved.

Chapter 6

Conclusions

The aim of the thesis was to investigate the effect of REE modification on the evolution of the microstructure of AISI D2 cold work tool steel. The differences in microstructure between non-modified and REE-modified samples were found in the morphology of the eutectic carbides. Cr_7C_3 eutectic carbides morphology was changed from lamellar to globular eutectic morphology due to REE modification. The difference in eutectic carbide morphology was measured on a few different samples on several different spots and quantified by a metallographic image-processing tool. That way the existence of difference between non-modified and REE-modified samples was proven with good statistics.

Further, we focused on the mechanism that is responsible for the change of eutectic morphology due to REE modification. First we tested the most commonly used theoretical explanation of the eutectic carbide REE modification in tool steel, that is well explained in reference [52]. It says that REE-modified non-metallic inclusions in steel can act as heterogeneous nuclei for the Cr_7C_3 carbide and thus the eutectic carbide is refined. From a detailed inspection of light and SEM micrographs as well as calculation of crystal lattice misfits between non-metallic inclusions and Cr_7C_3 we concluded that this theoretical explanation is highly unlikely.

Due to the lack of a theoretical explanation for the REE modification of tool steels in the literature the third part of thesis is dedicated to an investigation of modification mechanisms. Eutectic solidification of the Cr_7C_3 carbides in AISI D2 steel was modeled for this purposes. The model was based on the phase-field modeling approach with an additional term in total free-energy expression that describes the anisotropic part of the surface free energy, due to the phase boundary crystal lattice misfit. Such a model was able to simulate the transition from lamellar to globular eutectic due to REE modification. In connection with the experimental results we found that the decreased ratio between the isotropic and anisotropic parts of the phase-boundary surface free energy leads to a globular eutectic morphology instead of a lamellar type. The decrease in the ratio between the isotropic and anisotropic parts of the phase-boundary surface energy is a consequence of the altered amounts of oxygen and sulfur that segregate to the phase boundaries, which was caused by the REE additions.

Relevant scientific contribution was made by our investigation with the impact on different fields. It offers first successfully conducted repetition of eutectic carbides modification by REEs in AISI D2 tool steel. For the first time it was observed that in this steel grade REE-modification brings transition of eutectic carbide morphology from lamellar to eutectic. Further thesis includes detailed theoretical explanation of modification that is unique, never proposed or published before and firmly supported by experimental as well as modeling results. Last but not least we successfully modeled eutectic reaction during steel solidification with the innovative approach of phase-boundary surface-energy decom-

position on isotropic and anisotropic part. Since our phase field model is very general, such modeling approach can be applied to many different systems, even outside the field of material science.

Appendix A

Modified Mean-Linear-Intercept Method

A new, quantitative metallographic method has been developed to distinguish the morphology of lamellar from globular eutectic carbides across a range of steel samples [96]. The distinction is based on the degree of anisotropy of the surface features (referred to as the surface texture) determined from micrographs of the eutectic carbides. The method is based on the mean-linear-intercept method [97], [98], but modified for use with eutectic carbides. A small feature is added to the method so as to enable the user to uniquely specify the investigated image region. It was used to distinguish a lamellar eutectic from a globular eutectic. But it can also be used for many other applications where the degree of anisotropy needs to be determined from the surface features of the micrograph. The method is based on the commonly used intercept method [99] that is normally used for grain-size determinations in metallic materials [100]. By obtaining the azimuthal dependence of the intercept number we can estimate the degree of surface texture. The Mean-Linear-Intercept Method uses a principle that is similar to that used for bone-tissue anisotropy determinations [101]. The method was applied to images of four different surfaces. Two of them are computer-generated test images that prove the functionality of the method. The other two images were scanning electron micrographs of real samples of an AISI D2 tool steel's as-cast microstructure. These two samples included two morphologically different types of eutectic carbides: a lamellar and a globular eutectic. The difference between the lamellar and globular eutectic carbides can be seen by eye from a picture (Figure A.1(a) and A.1(b)). With the developed method we can analytically prove that a difference exists and estimate its extent by monitoring the anisotropy parameter (AP).

A.1 Method

Our new method uses a standard intercept technique to measure how many grain boundaries are intercepted if a straight line is drawn on the image [99]. The anisotropy is estimated by performing numerous intercept methods on the same image and then measuring the radial dependency of the intercept number [97], [98]. In our case we chose a point on the image (the intercept point) and then a family of lines were drawn to intercept the chosen point so that the lines are rotated by a fixed angle relative to each other (Figure A.2). In this way the user has some degree of freedom in comparison to the mean-linear-intercept method as the intercept point can be chosen. The intercept point should not be put outside the region of the eutectic carbide or on the edge of an image, as could easily occur if the method was fully automatic. For a representative result the intercept point must be placed in the middle of the eutectic carbide region of the micrograph.

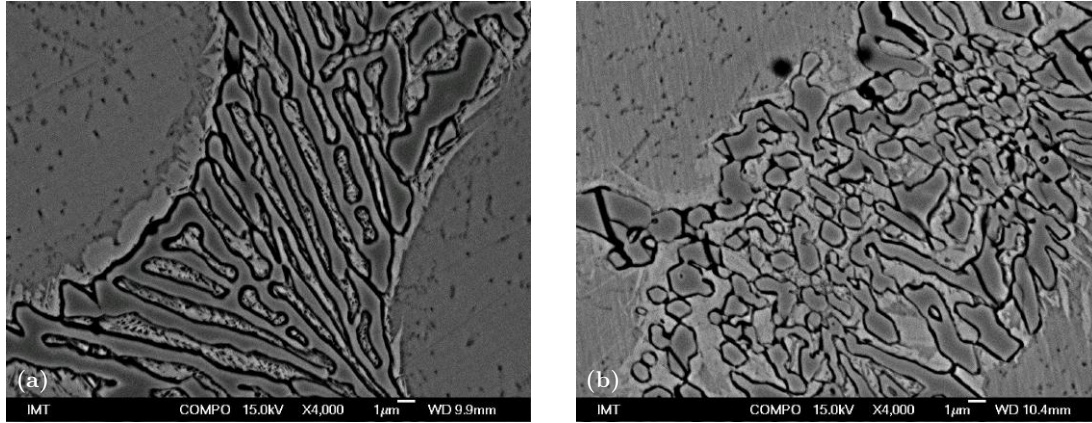


Figure A.1: Comparison between micrographs of lamellar (a) and globular (b) eutectic Cr_7C_3 carbides in as-cast AISI D2 tool steel. The images were made on a scanning electron microscope (SEM) using a backscattered-electron detector.

This is the main difference compared to the well-known mean-linear-intercept method that is commonly used for an anisotropy determination from micrographs.

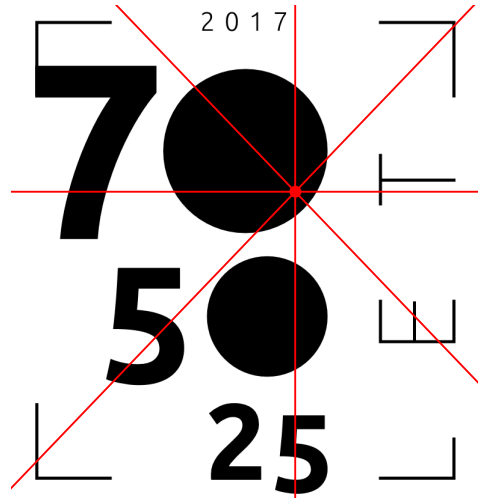


Figure A.2: Shows the concept of our method. The intercept point is placed on the desired spot in the image and the anisotropy of the surroundings is evaluated. Background image was reused with the permission of copyright owner.

A schematic demonstration of the method is shown in Figure A.2. There are 6 lines that cross the image in different directions and meet at the intercept point. By counting the intercept number for each line and then plotting the radial dependence of the intercept number, we can estimate how anisotropic the image is. The real algorithm includes many more intercept lines. They are one angular degree apart so that every image is processed by 360 lines. In this way the angular dependence of the intercept number is sufficiently smooth.

The intercept method was applied to processed micrographs. The images were first

binarized and then processed by a filter that replaces the value of each pixel with the most common pixel value from its surroundings. This type of filtering turned out to be the most efficient for revealing the phase boundaries between the carbide and the austenite. Figure A.3 shows the images of the lamellar eutectic carbide before and after the image processing.

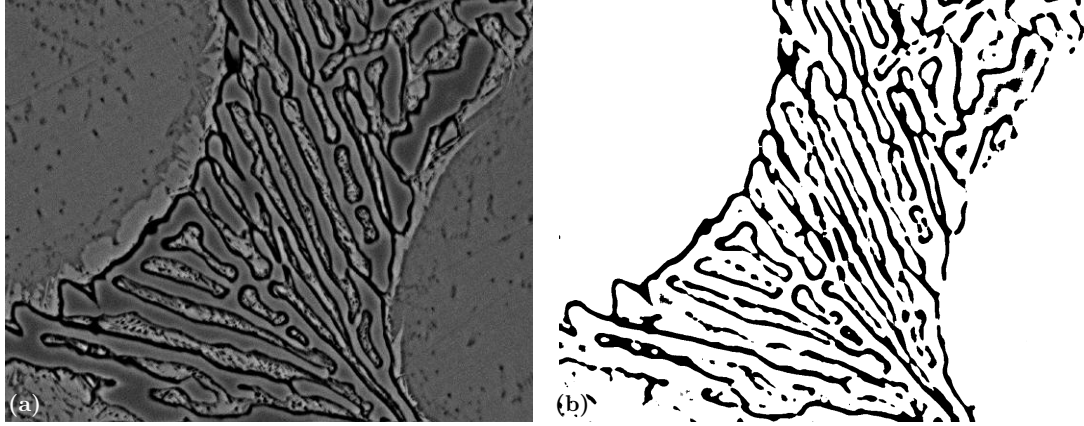


Figure A.3: Comparison between original SEM micrograph (a) and processed SEM micrograph (b). Binarization and filtration were performed on the micrograph.

The texture of the eutectic carbide is clearly seen on the filtered image, as we obtained only the image of the boundaries between the carbide and austenite phases. The image was subsequently transformed into a 1280x1024 matrix of ones and zeros (depending on the colors of the pixels). The intercept method was applied for 360 different azimuthal angles by walking across the matrix in two for loops. Every change from zero to one (from black to white) was stored as an intercept. At the end the density of the intercepts in every direction was calculated by considering the size of the carbide in different azimuthal directions. This size was determined by saving the first and the last intercepts for a given azimuthal angle. The difference between both gives us the size of the carbide in terms of pixels. Next, the number of intercepts per micrometer depending on the azimuthal angle was calculated and averaged with a moving average to reduce the noise. The moving-average step size was set to 5% of the whole range. After averaging, the intercept density was plotted versus the azimuthal angle. The image processing and the analysis were made with the open-source GNU Octave program.

A.2 Results of the Method

The results are obtained in the form of the angular dependence of the intercept density .

In order to prove the functionality of our new algorithm, it was first tested on two computer-generated images (Figure A.4(a) and A.4(b))

Figure A.4(a) shows a perfect lamellar structure (parallel stripes). It is the most anisotropic texture that can exist. We expect that there will be no intercepts in the direction parallel to the lamellas (black stripes). Figure A.4(b) includes randomly distributed, approximately circular dots of random size. No anisotropy exists in this image, so we expect no periodicity and high levels of noise in the dependence of the number of intercepts on the azimuthal angle. All our expectations were met when the analysis was

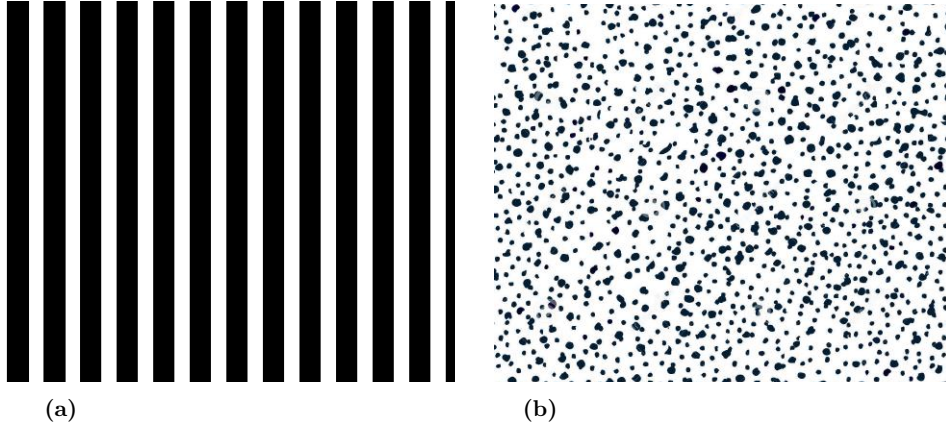


Figure A.4: test image "Stripes" (a) and test image "Random dots" (b).

performed on figures Figure A.4(a) and A.4(b), which proves that the method works. Figure Figure A.5(a) shows the results of the analysis of the image in Figure A.4(a), and the result in Figure A.5(b) corresponds to the image in Figure A.4(b).

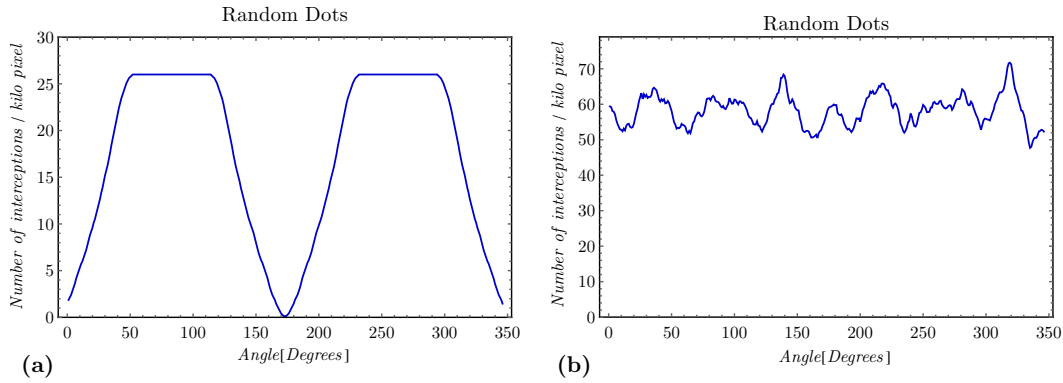


Figure A.5: Results of algorithm performed on test images "Stripes" (a) and test image "Random dots" (b).

After proving the functionality of the algorithm, it was run on the real micrographs of the eutectic carbides in Figure Figure A.1. Figure A.6 shows the comparison between the results for the lamellar (a) and globular (b) eutectics.

The difference between the two graphs is obvious. In Figure A.6(a) we can see the drop in the intercept density at an angle of 170 degrees. This corresponds to the intersection method performed in the direction parallel to the eutectic lamellas. Also, the periodicity is very obvious. The two peaks at approximately 80 and 260 degrees correspond to the large density of the phase boundaries in the direction perpendicular to the eutectic lamellas. The anisotropy clearly exists in the sample and we can also determine the direction of the texture.

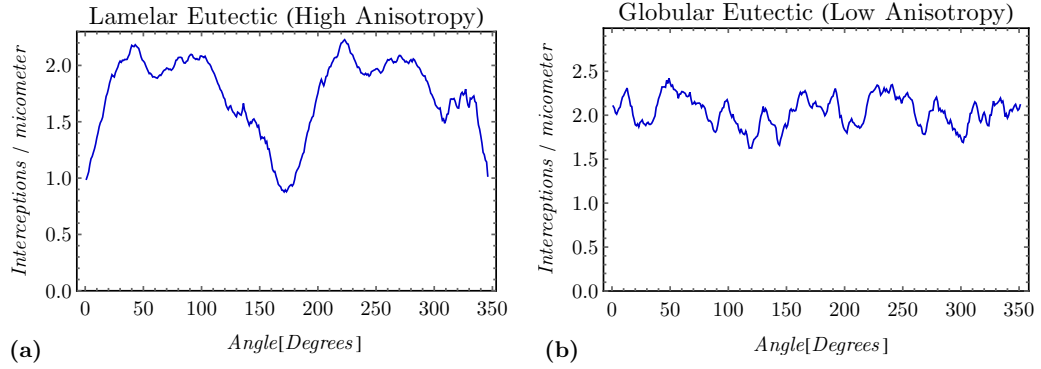


Figure A.6: Angular dependence of the intercept length for a lamellar eutectic (a) and a globular eutectic (b).

Figure A.6(b), on the other hand, shows no periodicity and the amplitude of the fluctuations cannot be distinguished from the noise (note that two maxima and two minima are always obtained in the 360-degree range if anisotropy is present - no more or less than this is theoretically possible). The constant density of the intercepts (inside the standard deviation) in Figure A.6(b) shows us that the analyzed features are isotropic.

For the full quantification we used the anisotropy parameter (AP). The AP is a numerical value that tells us how anisotropic the investigated surface features are. The amplitude of the intercept density's angular dependence can be used as the AP, but due to the noise and non-sinusoidal shape it is hard to estimate without large deviations. In analogy with the mean linear method we plotted the inverse of the intercept density data parametrically and then fitted the parametric plot with an ellipse. This procedure is an exact equivalent of fitting a sinusoidal wave to the Cartesian plot, but fitting the ellipse to a cloud of points in a polar coordinate system is much more elegant. Figure A.7 shows the comparison between two polar plots for the lamellar (a) and globular (b) eutectics. The semi-major and semi-minor axes of the ellipse indicate the direction of the largest and smallest intercept densities. The quotient between the lengths of the semi-major and semi-minor axis is used as the anisotropy parameter. We calculated the AP for both cases. For the lamellar eutectic $AP_L = 3.00$ and for the globular eutectic $AP_G = 1.39$. In the case of the lamellar eutectic the average feature in the direction of the semi-minor axis is, on average, three times longer than the average feature in the direction of the semi-major axis. In the case of the globular eutectic this ratio is only 1.39.

A.3 Conclusions

Our new method for distinguishing lamellar from globular eutectic carbides using micrographs is a fully quantitative approach. The distinguishing is based on the anisotropy of the eutectic carbide. The software output is an anisotropy parameter (AP). If the AP value is 1 (inside the standard deviation) the analyzed features are isotropic (globular eutectic). Any other value of the AP between one and infinity shows that the investigated surface features are anisotropic, i.e., a lamellar eutectic. The method is very efficient for the boundary cases where we have both types of carbides in the same image. Sometimes one

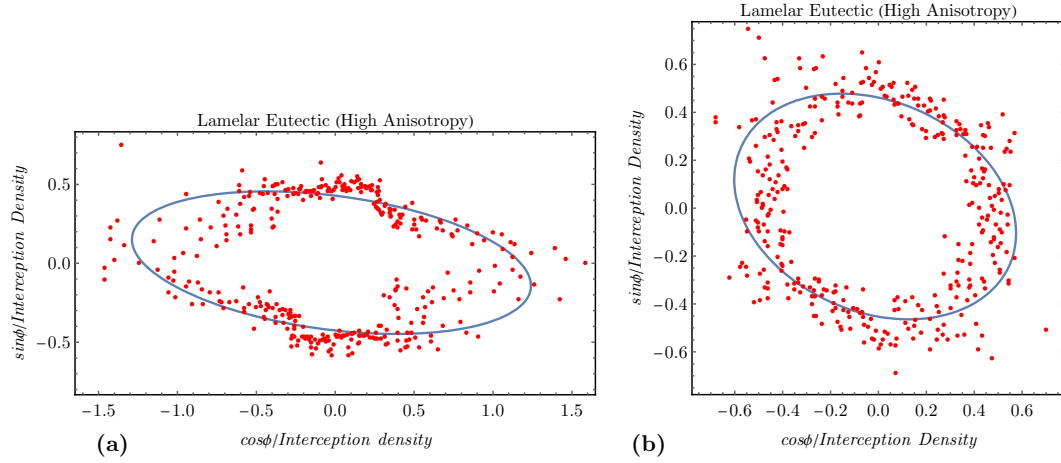


Figure A.7: Polar plot of inverse intercept density's angular dependence for a lamellar eutectic (a) and a globular eutectic (b) using an elliptical fit.

eutectic carbide can be divided into two regions of different morphological carbide types. The main feature of our method in comparison to existing ones is the degree of freedom that the user has. By selecting the intercept point the user can choose the investigated area and in this way our algorithm becomes useful for distinguishing between a lamellar and globular eutectic morphology. The code of the software is open source and can be obtained by contacting the author of this thesis.

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Publications Related to the Thesis

Journal Articles

- K. Zelič and M. Godec, "A modified mean-linear-intercept method for distinguishing lamellar and globular eutectic carbides in metallographic samples," *Materials and technology*, vol. 52, no. 1, 2018. DOI: 10.17222/mit.2017.17.
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- K. Zelič, J. Burja, F. Tehovnik, B. Šetina Batič, and M. Godec, "Microstructural changes of ocr12 tool steel modified by rare earth elements," in *Program in knjiga povzetkov = Program and book of abstracts, 22. mednarodna konferenca o materialih in tehnologijah*, Portorož, Slovenia: Inštitut za kovinske materiale in tehnologije, 2014.
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