



**THE LAVES PHASE EMBRITTLEMENT OF FERRITIC STAINLESS STEEL  
TYPE AISI 441**

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**THE LAVES PHASE EMBRITTLEMENT OF FERRITIC STAINLESS STEEL  
TYPE AISI 441**

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## PREFACE

This dissertation is submitted for the degree of Doctor of Philosophy at the University of Pretoria. The research described herein was conducted under the supervision of Professor W. Stumpf in the department of Materials Science and Metallurgical Engineering, University of Pretoria.

Except where acknowledgements and references are made to previous work, this work is, to the best of my knowledge, original. This dissertation is the result of my own work and includes nothing of which is the outcome of work done in collaboration with others except where specifically indicated in the text. Neither this, nor any substantially similar dissertation has been, or is being submitted to my knowledge for any other degree, diploma, or other qualification at any other university.

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Maitse P. Sello

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## TYPE AISI 441

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### **Synopsis**

The effect of Laves phase ( $\text{Fe}_2\text{Nb}$ ) formation on the Charpy impact toughness of the ferritic stainless steel type AISI 441 was investigated. The steel exhibits good toughness after solution treatment at 850 °C, but above and below this treatment temperature the impact toughness decreases sharply. With heat treatment below 850 °C the presence of the Laves phase on grain boundaries and dislocations plays a significant role in embrittlement of the steel whereas above that temperature, an increase in the grain size from grain growth plays a major role in the impact embrittlement of this alloy. The toughness results agree with the phase equilibrium calculations made using Thermo–Calc® whereby it was observed that a decrease in the Laves phase volume fraction with increasing temperature corresponds to an increase in the impact toughness of the steel. Annealing above 900 °C where no Laves phase exists, grain growth is found which similarly has a very negative influence on the steel's impact properties. Where both a large grain size as well as Laves phase is present, it appears that the grain size may be the dominant embrittlement mechanism. Both the Laves phase and grain growth, therefore, have a significant influence on the impact properties of the steel, while the Laves phase's precipitation behaviour has also been investigated with reference to the plant's manufacturing process, particularly the cooling rate after a solution treatment.

The microstructural analysis of the grain size shows that there is a steady increase in grain size up to about 950 °C, but between 950 °C and 1000 °C there is a sudden and rapid 60 % increase in the grain size. The TEM analysis of the sample that was annealed at 900 °C shows that the Laves phase had already completely dissolved and cannot, therefore, be responsible for “unpinning of grain boundaries” at temperatures of 900 °C and higher where this “sudden” increase in grain size was found. The most

plausible explanation appears to be one of Nb solute drag that loses its effectiveness within this temperature range, but this probably requires some further study to fully prove this effect.

During isothermal annealing within the temperature range of 600 to 850 °C, the time – temperature – precipitation (*TTP*) diagram for the Laves phase as determined from the transformation kinetic curves, shows two classical C noses on the transformation curves. The first one occurring at the higher temperatures of about 750 to 825 °C and the second one at much lower temperatures, estimated to possibly be in the range of about 650 to 675 °C. The transmission electron microscopy (TEM) analyses show that there are two independent nucleation mechanisms that are occurring within these two temperature ranges. At lower temperatures of about 600 °C, the pertaining nucleation mechanism is on dislocations and as the temperature is increased to above 750 °C, grain boundary nucleation becomes more dominant. Also, the morphology of the particles and the misorientation with the matrix changes with temperature. At lower temperatures the particles are more needle-like in shape, but as the temperature is increased the shape becomes more spheroidal.

The effect of the steel's composition on the Laves phase transformation kinetics shows that by lowering the Nb content in these type 441 stainless steels, had no significance effect on the kinetics on precipitation of the Laves phase. However, a Mo addition and a larger grain size of the steel, retard the formation of the Laves phase, although the optimum values of both parameters still need further quantification.

The calculation made for the transformation kinetics of the Laves phase, using the number density of nucleation sites  $N_0$  and the interfacial energy  $\gamma$  as the fitting parameters in this work, demonstrated a reasonable agreement with experimental results.

Keywords: Laves phase ( $\text{Fe}_2\text{Nb}$ ), titanium niobium carbonitrides (Ti,Nb)(C,N), impact embrittlement, grain size, ductile-to brittle transition temperature (DBTT), Laves phase transformation kinetics, Cottrell approach to grain size, Smith model of brittle grain boundary phases, Thermo- Calc®.

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Figure 7.3. Optical micrographs of the specimens from steel B in the (a) as received plant hot rolled condition and (b) to (d) after being annealed at different temperatures from 850 to 950°C for 30 minutes followed by water quenching.

Figure 7.4. Effect of annealing temperature on the room temperature Charpy impact energy of the laboratory hot rolled materials. The samples were annealed for 30 minutes at different temperatures and then water quenched: Steel C (Nb-Ti alloy); Steel D (Nb-Ti-Mo alloy) and Steel E (Type 444 alloy).

Figure 7.5. The microstructure of the laboratory hot-rolled experimental steels, showing different grain size distributions if compared to those of the commercial Steels A and B: (a) Steel C; (c) Steel D; and (d) Steel E.

Figure 8.1. The Laves phase volume fraction – temperature/time curves during isothermal annealing in the temperature range 600 °C to 850 °C.

Figure 8.2. The Laves phase transformation curves according to the Johnson–Mehl–Avrami–Kolmogorov (JMAK) type of equation.

Figure 8.3. A time – temperature – precipitation (TTP) diagram for the Laves phase formation in Steel A.

Figure 8.4. Effect of the grain size on the Laves phase kinetics transformation in Steel A. The specimens were annealed first at 850 and 950°C respectively to set different grain sizes and were then annealed both at 750 °C for different annealing periods.

Figure 8.5. Effect of the steel's composition on the Laves phase transformation kinetics. The specimens from these steels were all annealed at 750 °C for different annealing periods.

Figure 8.6. TEM micrographs of the specimen of Steel A annealed at 600 °C; (a) a low magnification micrograph shows coarse grain boundary Laves phase precipitates, and (b) the same area but at a high magnification, showing Laves phase precipitates nucleated on subgrain boundaries and dislocations.

Figure 8.7. TEM micrographs of the specimen of Steel A annealed at 750 °C; (a) a low magnification micrograph showing grain and subgrain boundary Laves phase



precipitates, and (b) at a high magnification, showing Laves phase precipitates nucleated on the subgrain boundaries.

Figure 8.8. TEM micrographs of the specimen annealed at 750 °C; (a) at a low magnification, showing grain boundary Laves phase precipitates, and (b) at a higher magnification showing Laves phase precipitates nucleated on the subgrain boundaries.

Figure 8.9. Transmission electron micrographs and corresponding selected area diffraction (SAD) pattern from Steel A annealed at 600 °C.

Figure 8.10. Transmission electron micrographs and corresponding selected area diffraction (SAD) pattern from Steel A annealed at 750 °C.

Figure 8.11. Transmission electron micrographs and corresponding selected area diffraction (SAD) pattern from Steel A annealed at 800°C.

Figure 9.1. TEM micrograph shows the presence of the  $M_6C$  or  $(Fe_3Nb_3C)$  type carbide in the subgrain structure from Steel A. Note that the specimen was annealed at 700 °C for 30 minutes and other fine particles were determined to be  $Fe_2Nb$  Laves phase particles.

Figure 9.2. Comparison between experimental and Thermo-Calc® calculated weight fractions of Laves phase in Steel A. The points and dotted line represent the experimental results while the full line is as predicted by Thermo-Calc® for this steel.

Figure 9.3. The effect of grain size on the yield strength of Steel A.

Figure 9.4. A room temperature tensile test of the specimen of Steel A that was annealed at 850 °C for 30 minutes and then water quenched.

Figure 9.5. High resolution field emission scanning microscope image showing the cracking of  $(Ti,Nb)(C,N)$  particles after impact testing the specimen at room temperature. This specimen of Steel A was annealed at 850 °C followed by quenching in water.

Figure 9.6. The plot of transition temperature versus  $\{\ln d^{1/2}\}$  of 441 ferritic stainless steel, Steel A.

Figure 9.7. Effect of annealing temperature above 850 °C on the grain size for the AISI type 441 stainless steel, Steel A.

Figure 9.8. TEM micrographs of the microstructures of the specimens from Steel A that were annealed at (a) 850 °C and (b) 900 °C. Note that with the specimen that was annealed at 900 °C, there were no grain boundary Laves phase precipitates.

Figure 10.1. The relationship between  $\ln x_{Nb}^{\alpha\beta}$  and  $T^{-1}$  for AISI type 441 ferritic stainless steel.

Figure 10.2. Comparison between the experimental data and calculated isothermal transformation curves for the Laves phase's precipitation at 700 °C in the AISI type 441 ferritic stainless, with  $N_o = 4.3 \times 10^{14} \text{ m}^{-3}$  and  $\gamma = 0.331 \text{ Jm}^{-2}$ .

Figure 10.3. Comparison between the experimental data and calculated isothermal transformation curves for the Laves phase precipitation at 800 °C in the AISI type 441 ferritic stainless, with  $N_o = 2.9 \times 10^{13} \text{ m}^{-3}$  and  $\gamma = 0.331 \text{ Jm}^{-2}$ .



## NOMENCLATURE

$\alpha_3$	is the three-dimensional parabolic rate constant	$c_r^{\alpha\beta}$	solute concentration in the $\alpha$ matrix that is in equilibrium with a spherical particle of $\beta$ and $r$ is the radius of curvature
$\beta^*$	atomic impingement rate	$c^{\alpha\beta}$	equilibrium solute concentration in the $\alpha$ matrix at which $r \rightarrow \infty$
$\delta$	volume misfit of the precipitate in the matrix	$c^{\beta\alpha}$	corresponding concentration in the $\beta$ which is in equilibrium with $\alpha$ ,
$\delta_{disl}$	effective diameter of dislocation	$c_i$	mole fraction of species $i$
$\delta_{gb}$	width of the grain boundary	$c_j$	mole fraction of species $j$
$\gamma$	interfacial surface energy per unit area associated with the interface of the two phases	$d$	grain size
$\gamma_f$	effective surface energy of ferrite	$D$	diffusion coefficient of the rate controlling solute atoms in the matrix
$\gamma_s$	surface energy of the exposed crack surface	$D_{disl}$	diffusion coefficient down a dislocation
$\gamma_T$	true surface energy	$D_{gb}$	diffusion coefficient along the grain boundary
$\sigma_i$	friction stress	$E$	Young's elastic modulus
$\sigma_y$	yield strength	$f_{GB}$	fraction of potential grain boundary sites filled by solute
$\nu$	Poisson's ratio	$G_m$	shear modulus of the matrix
$\nu^\alpha$	lattice spacing of the matrix	$G_r$	growth rate
$\nu^\beta$	lattice spacing of the precipitate phase	$\Delta G$	molar free energy change of the precipitate reaction
$\nu_b$	mobility rate	$\Delta G_v$	Gibbs chemical free energy released per unit volume of new phase
$\tau$	incubation time	$\Delta G_\epsilon$	misfit strain energy per unit volume
$\tau_e$	effective shear stress	$\Delta G^*$	known as the activation energy
$\tau_i$	lattice friction shear stress	$G^\circ$	Gibbs energy due to the mechanical mixing of the constituents of the phase
$\tau_N$	shear stress for crack nucleation	${}^{id}G_{mix}$	ideal mixing contribution
$\tau_y$	yield shear stress	${}^{xs}G_{mix}$	excess Gibbs energy of mix (the non-ideal mixing contribution)
$\nu^\beta$	molar volume of the phase $\beta$ ,	$\Delta G_\epsilon$	strain energy
$\tau_s$	shear stress	$G_m - H_m^{SER}$	Gibbs energy relative to a standard element reference state (SER)
$\Phi$	extent of the reaction parameter	$h$	Planck constants
$\theta$	contact angle	$H_m^{SER}$	enthalpy of the element in its stable state
$a$	mean atomic lattice distance of the matrix phase		
$b$	Burgers vector		
$\bar{c}$	average concentration of the solute in the matrix alone		
$c_\alpha$	equilibrium solute composition within the matrix		



$k$	Boltzman constant	$\Delta p_{ppt}$	retarding force exercised by particles on the grain boundary
$k_y^s$	Hall – Petch constant for shear	$Q$	activation energy for diffusion
$L_{gb}$	length of grain boundary per unit volume	$r^*$	critical radius
$L_{i,j}^k$	binary interaction parameter between species $i$ and $j$	$r_0$	initial average particle radius
$M_0$	intrinsic grain boundary mobility in pure material	$R$	gas constant
$M_T$	overall mobility due to intrinsic plus solute drag	$S_{gb}$	surface area of grain boundary per unit volume
$M_B$	mobility in the presence of solute drag elements	$t$	time
$n$	number of dislocations in the pileup	$T$	absolute temperature
$\dot{N}$	nucleation rate	$V'$	instantaneous volume fractions of alloy precipitates
$N'$	number of dislocations that meet each particle	$V^{eq}$	equilibrium volume fractions of alloy precipitates
$N^*$	concentration of critical – sized nuclei	$V^\beta$	instantaneous fraction
$N_c$	density of the grain boundary corners	$V^{\beta\alpha}$	maximum fraction of a given phase
$N_0$	initial number density of nucleation sites per unit volume	$V^{i\alpha}$	maximum volume fraction of the $i^{th}$ phase
$p_d$	driving force for the grain boundary mobility	$X_s$	atom fraction of solute in the bulk metal
		$z$	coordinate normal to the interface with the value $z^*$