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 (Fe_2Nb) 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_o and the interfacial energy γ as the fitting parameters in this work, demonstrated a reasonable agreement with experimental results.

Keywords: Laves phase (Fe_2Nb), 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®.

TABLE OF CONTENT

α_3	is the three-dimensional parabolic rate constant
β^*	atomic impingement rate
δ	volume misfit of the precipitate in the matrix
δ_{disl}	effective diameter of dislocation
δ_{gb}	width of the grain boundary
γ	interfacial surface energy per unit area associated with the interface of the two phases
γ_f	effective surface energy of ferrite
γ_s	surface energy of the exposed crack surface
γ_T	true surface energy
σ_i	friction stress
σ_y	yield strength
ν	Poisson's ratio
ν^α	lattice spacing of the matrix
ν^β	lattice spacing of the precipitate phase
ν_b	mobility rate
τ	incubation time
τ_e	effective shear stress
τ_i	lattice friction shear stress
τ_N	shear stress for crack nucleation
τ_y	yield shear stress
υ^β	molar volume of the phase β,
τ_s	shear stress
Φ	extent of the reaction parameter
θ	contact angle
$\boldsymbol{a}$	mean atomic lattice distance of the matrix phase
$\boldsymbol{b}$	Burgers vector
$\bar{c}$	average concentration of the solute in the matrix alone
c_α	equilibrium solute composition within the matrix

$c_r^{\alpha\beta}$	solute concentration in the α matrix that is in equilibrium with a spherical particle of β and r is the radius of curvature
$c^{\alpha\beta}$	equilibrium solute concentration in the α matrix at which $r\rightarrow\infty$
$c^{\beta\alpha}$	corresponding concentration in the β which is in equilibrium with α;
c_i	mole fraction of species i
c_j	mole fraction of species j
d	grain size
D	diffusion coefficient of the rate controlling solute atoms in the matrix
D_{disl}	diffusion coefficient down a dislocation
D_{gb}	diffusion coefficient along the grain boundary
E	Young's elastic modulus
f_{GB}	fraction of potential grain boundary sites filled by solute
G_m	shear modulus of the matrix
G_r	growth rate
ΔG	molar free energy change of the precipitate reaction
ΔG_v	Gibbs chemical free energy released per unit volume of new phase
ΔG_ε	misfit strain energy per unit volume
ΔG^*	known as the activation energy
$G°$	Gibbs energy due to the mechanical mixing of the constituents of the phase
$^{id}G_{mix}$	ideal mixing contribution
$^{xs}G_{mix}$	excess Gibbs energy of mix (the non-ideal mixing contribution)
ΔG_ε	strain energy
$G_m - H_m^{SER}$	Gibbs energy relative to a standard element reference state (SER)
h	Planck constants
H_m^{SER}	enthalpy of the element in its stable state

k	Boltzman constant	Δp_{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
		R	gas constant
M_0	intrinsic grain boundary mobility in pure material	S_{gb}	surface area of grain boundary per unit volume
M_T	overall mobility due to intrinsic plus solute drag	t	time
		T	absolute temperature
M_B	mobility in the presence of solute drag elements	V'	instantaneous volume fractions of alloy precipitates
n	number of dislocations in the pileup	V^{eq}	equilibrium volume fractions of alloy precipitates
$\dot{N}$	nucleation rate	V^{β}	instantaneous fraction
N'	number of dislocations that meet each particle	$V^{\beta\alpha}$	maximum fraction of a given phase
N^*	concentration of critical – sized nuclei	$V^{i\alpha}$	maximum volume fraction of the ith phase
N_c	density of the grain boundary corners	X_s	atom fraction of solute in the bulk metal
N_0	initial number density of nucleation sites per unit volume	z	coordinate normal to the interface with the value z^*
p_d	driving force for the grain boundary mobility		