Metallurgical reliability: Ensuring integrity of steels for hydrogen pipelines

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Objective of the work

Continuous energy sector developments → steels with superior properties and performance.

To fulfill these requirements → understanding of the composition-processing -microstructure-property relationship, is needed.

Objective: to define the best practice for the production of steel for application in hydrogen high content pipelines.

Background: different forms of cracking...

HIC: hydrogen induced cracking

SSC: sulphide stress cracking

SOHIC: strain oriented hydrogen induced cracking

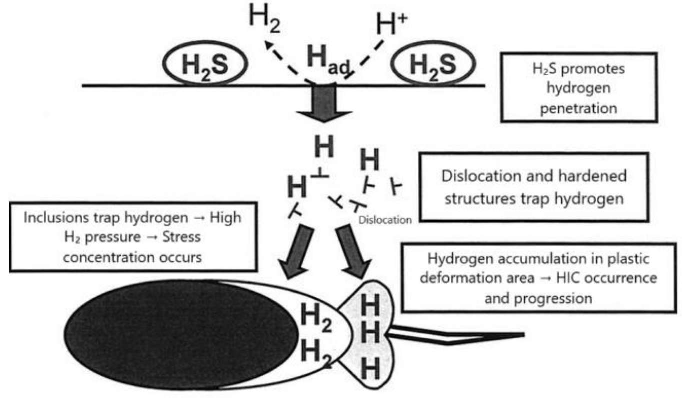


Figure 4. Material factos affecting hydrogen- induced cracking (HIC)

Cracking resistance depends on both on reduction of the **initiation** sites and on reduction de factors that contribute to the **propagation** of hydrogen-induced cracking.

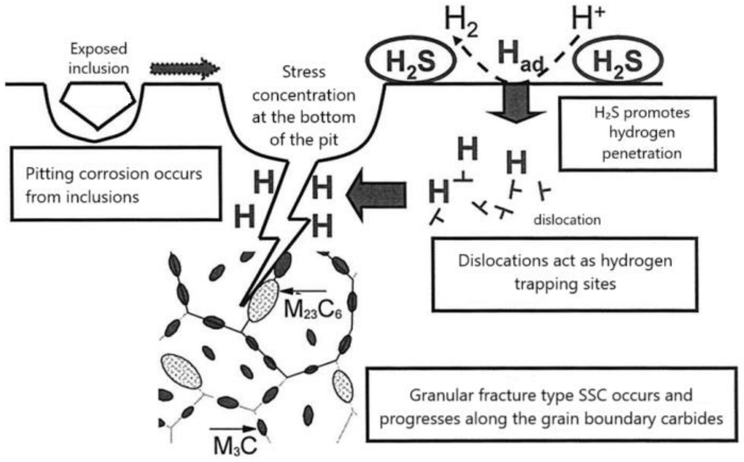
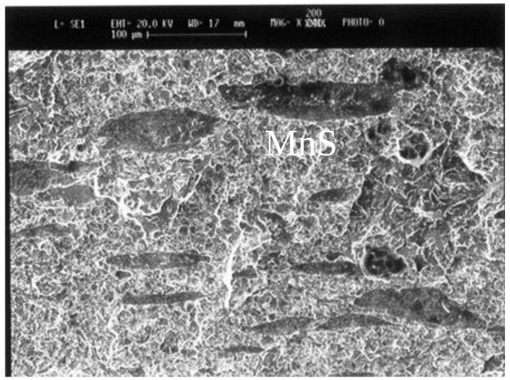


Figure 3. Material factors affecting sulfidee stress cracking (SSC)

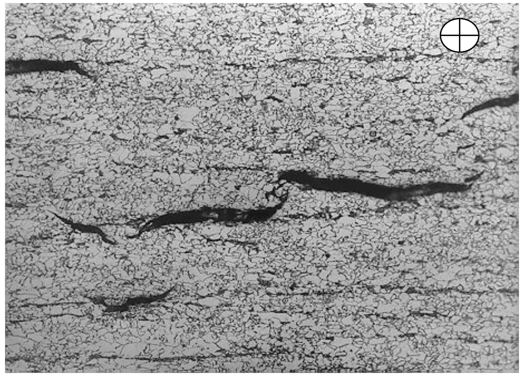
Source: Adaptation from Hydrogen Embrittlement of OCTG and Linepipes -Tomohiko Omura and Kenji Kobayashi (2011)

Metallurgical factors for HIC resistance

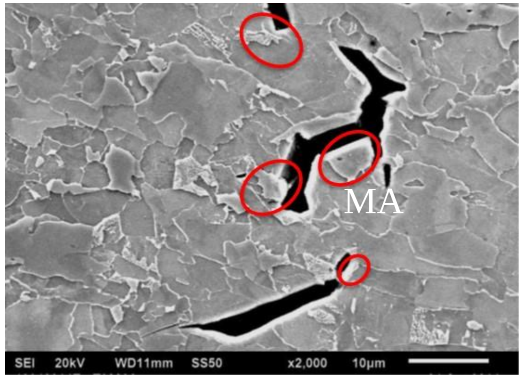
KILLING DEFECTS	IMPACT AND RISKS	TARGETS REGARDING MICROSTRUCTURE
NMI - Oversize	Hydrogen trap sites Stress raisers	Control severity of MnS, Al2O3 , calcium oxysulfide CaAl(OS) Inclusion modification and shape control. Oversize control
Coarse precipitates	Initiation sites and propagation of hydrogen-induced cracking	Nano-precipitates of TiN , TiNb(C,N)
Banded microstructure	Nucleation and propagation of step cracks Welded defects (hook cracks)	Mainly fine FP/ NPF
MA particles	Crack propagation along interphase MA / matrix Impact properties highly reduced	Fine/isolated particles of martensite- austenite (MA).



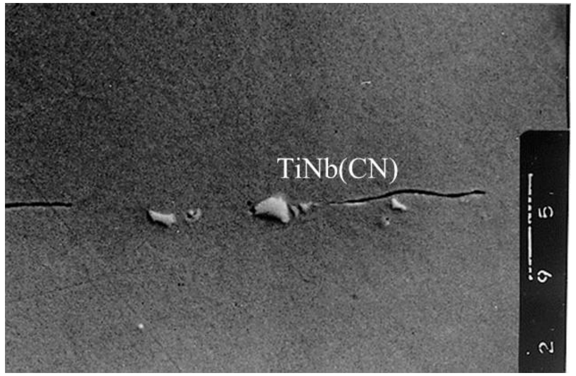
MnS on the fracture surface
API X52



HIC step cracks



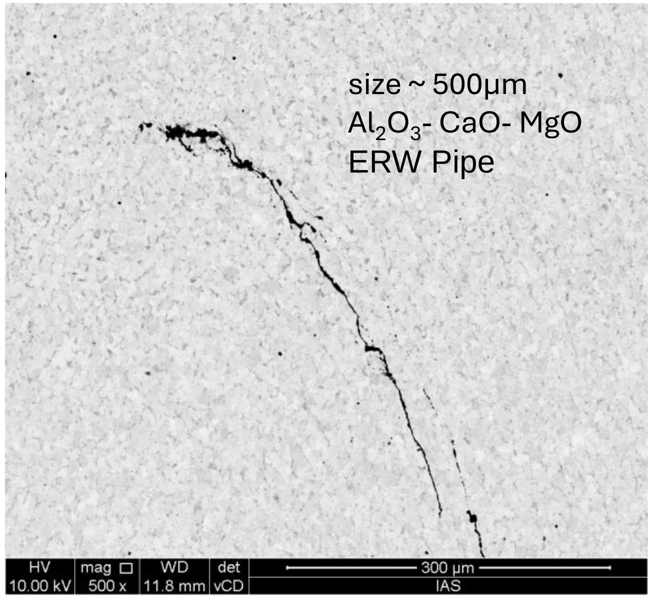
Cracks along interphase MA/ matrix
API X70



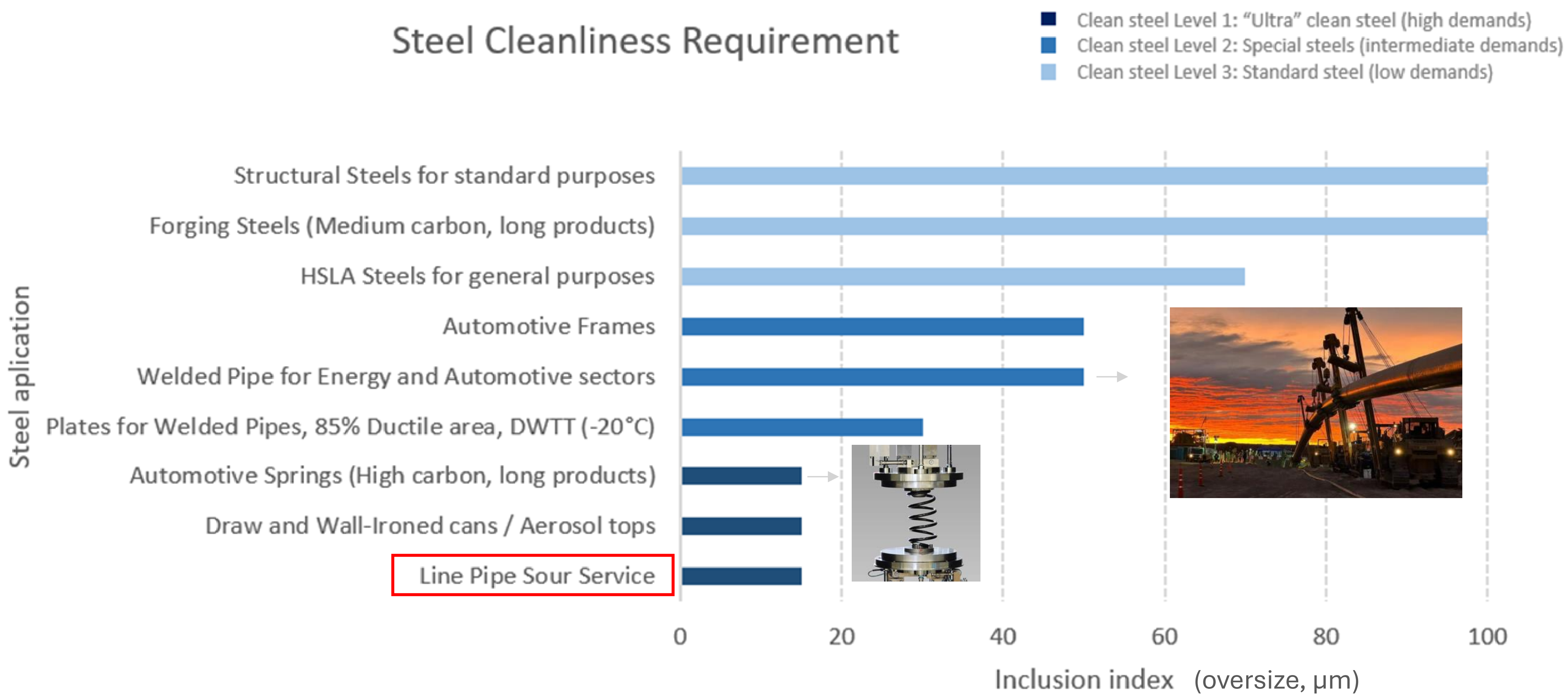
Coarse precipitates contribute to the propagation of HIC

Background: the origin of NMIs

- **Origin**
  - **Indigenous:** deoxidation products, precipitated (cooling and solidification)
  - **Exogenous:** refractory, ladle/ tundish slags, re-oxidation products
- **Chemical composition**
  - **Oxides**
  - **Sulphides**
- **Critical size**
  - **Macro-inclusions:** big enough to cause immediate failure while processing or using the steel
  - **Micro-inclusions**



Steel cleanliness demand by product application

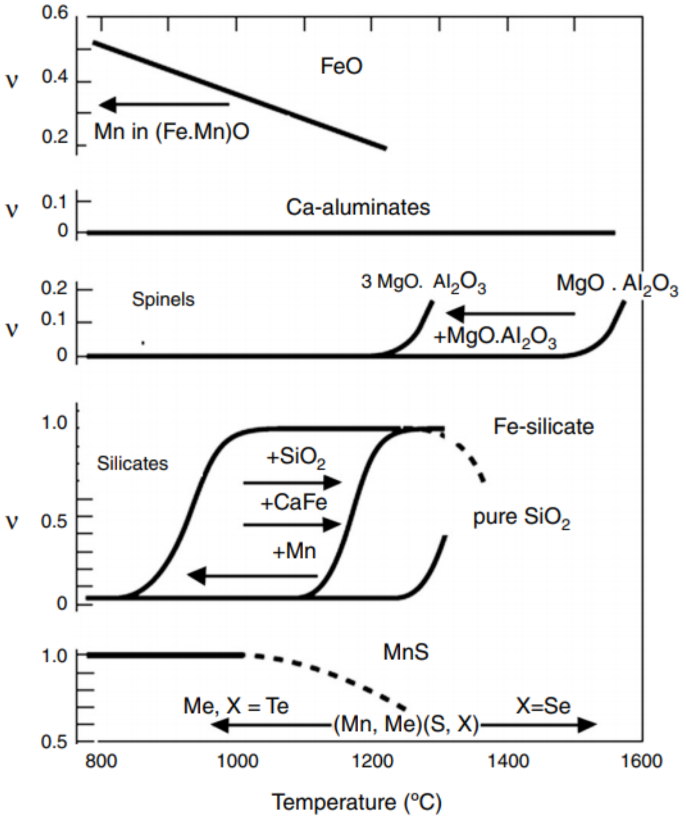


Source: Clean steels for more reliable and cost-effective steel products, F, Actis, R. Bruna, AISTECH (2024)

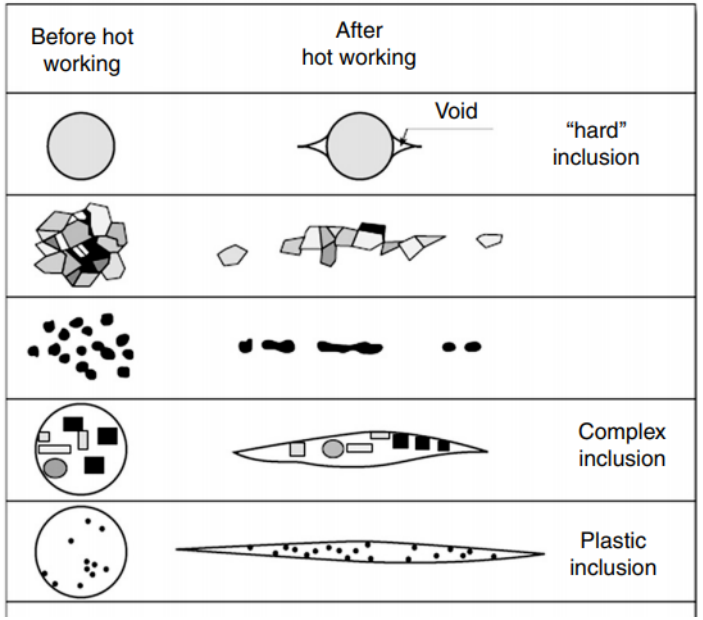
Relevant properties of NMIs

Relative plasticity $v = \frac{\varepsilon_1}{\varepsilon_2}$

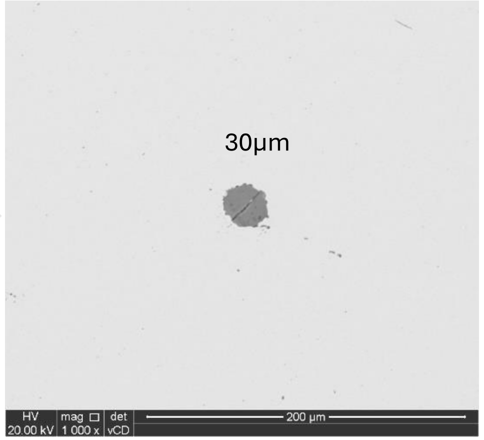
ε_1 true elongation of the NMI, and
ε_2 true elongation of the Steel matrix



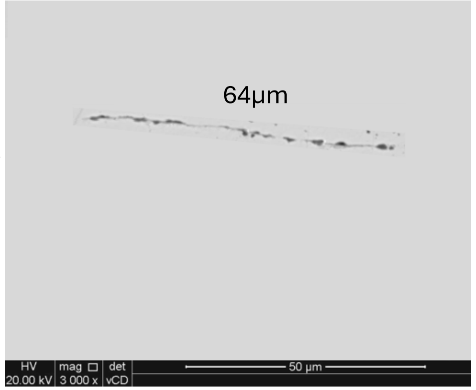
Effect of temperature on relative plasticity of NMIs, depending on their chemical composition. The curves are of semi-quantitative natura .
Vasconcellos da Costa e Silva (2019)



Schematic illustration of the behaviour of NMIs after thermomechanical treatment depending on their relative plasticity at the working temperatures.
Vasconcellos da Costa e Silva (2019)



Ca-Mg aluminate: 60% Al_2O_3 - 31% CaO - 7% MgO - 1% MnO - 2% S



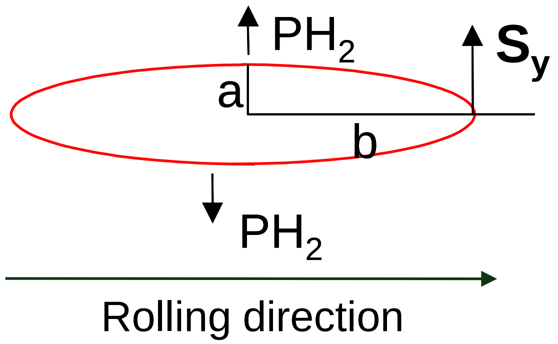
Manganese sulfide
70% Mn – 30% S

Stress concentration on trap sites

Hydrogen Traps	Binding energy (eV)
Grain boundary	0,19
Cementite	0,19
Intertitials	0,25
Dislocations	0,26 - 0,32
MnS	0,75
Al_2O_3	0,82
TiC	0,90

Ascending effect

1 Elliptical section:



S_y =Stress concentration on the tip

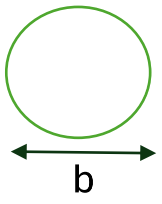
PH_2 = internal pressure of H_2

When a/b = 0,1

S_y/PH_2 = **16**

$$S_y = \frac{PH_2}{(a/b)^{1,2}}$$

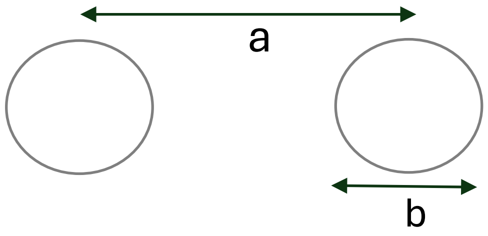
2 Round section:



In this case a = b

S_y/PH_2 = **1**

3 Influence of inter-particle distance:



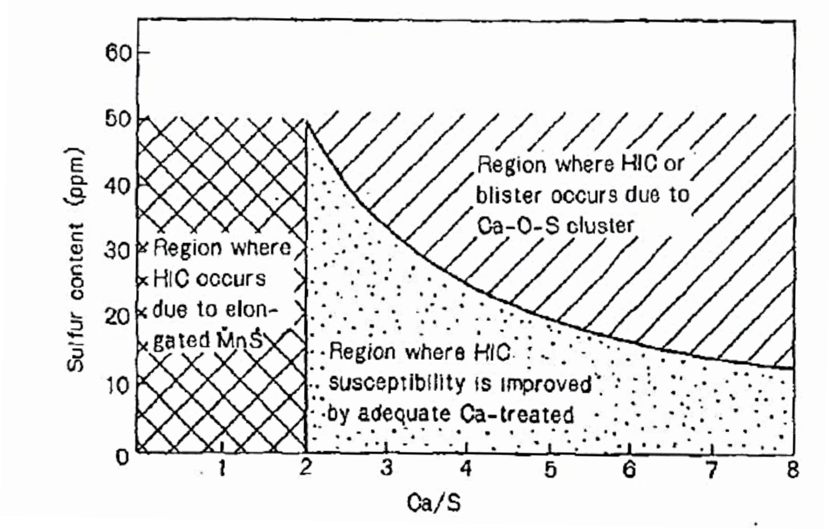
Stress concentration factor= 1,85

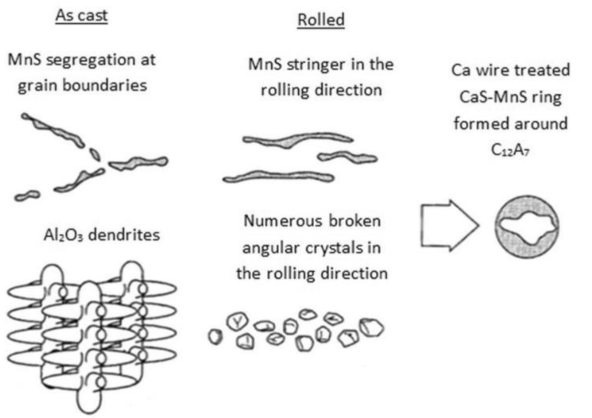
a = 2.b

source: R. Ratnapulli, ABM (2007)

Inclusion modification and shape control

Influence of Ca/S ratio and sulfur content on improving the HIC resistance of a calcium-treated steel tested in solution of a0,5% acetic acid – 5% NaCl and H_2S
A. Ikeda *et al*. Sumitomo Search, N°26 (1981)





Schematic illustration of inclusion morphology with calcium- treated steel.
Turkdogan, Fundamentals of Steelmaking, The Institute of Materials (1996).

HIC resistance:

Morfology and shape control of Al2O3 and MnS, Ca/S > 2

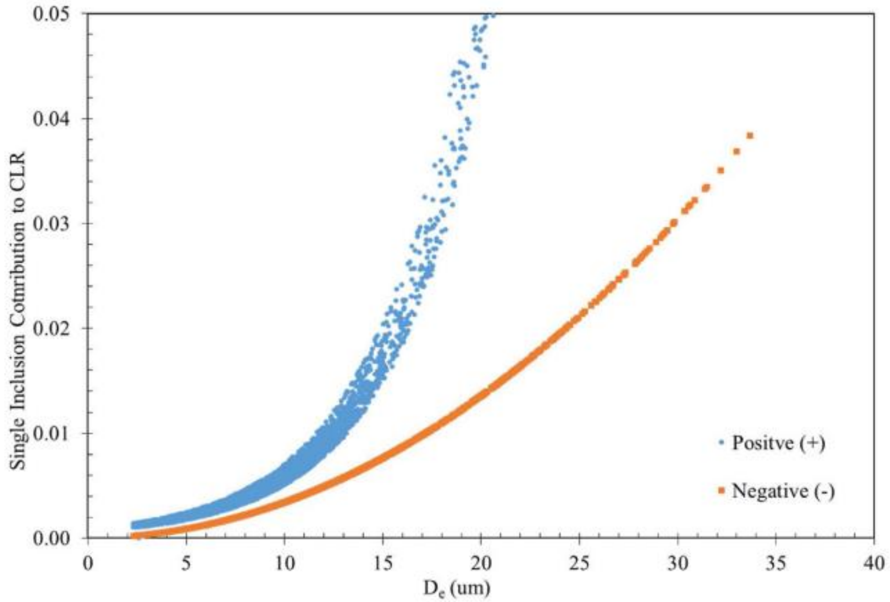
Globulization index (ACR) = $Ca_{eff.}/Ca_{combined\ with\ S}$ = $Ca_{eff.}$ *1,25.S

$Ca_{effective} = Ca_{total} – Ca_{calcium\ oxide}$

S < 0,002% (aim < 10ppm)

O < 30 ppm (aim < 20 ppm)

OS (De) < 15µm



Effect of Oxide De on increasing CLR and decreasing CLR (trapping term) for a single inclusion. Ouhiba et al (2023)

Identification of key process parameters

PRIMARY METALLURGY → SECONDARY METALLURGY → CONTINUOUS CASTING

Pre-desulfurization

- Hot metal sulphur pre treatment

Laddle Condition

- Number of previous heats
- Thermal status
- MgO projection
- Residence time of steel in ladle from tapping to CCM
- Porous plugs performance

BOF/EAF

- Primary desulphurization
- Charge mix
- Tapping temperature
- Transit time from tapping to secondary treatment
- Deoxidants, ferroalloys, fluxes additions practice
- Bubbling time in laddle after tapping

LF/AHF/Vacuum treatment

- Arrival temperature
- Upstream oxidation
- Previous desulphurization
- Ferroalloys and fluxes additions practice
- Top slag adjustment
- Total addition of aluminum (tapping+ secondary treatment)
- Heating control
- Vacuum time/pressure specification

Stirring Control

- Stirring time after tapping
- Argon stirring on heating process
- Red zone (Soft stirring)

  - Killing time (VTD/RH)

  - Time from end of heating to end of treatment, no additions (LF)
- Flotation of inclusions

Reoxidation conditions

- Total Al drop
- Total N pick up
- Ca drop
- Alox (Total aluminum – Soluble aluminum)
- Aluminum ratio (Soluble aluminum/ Total aluminum)

CCM / Inspection

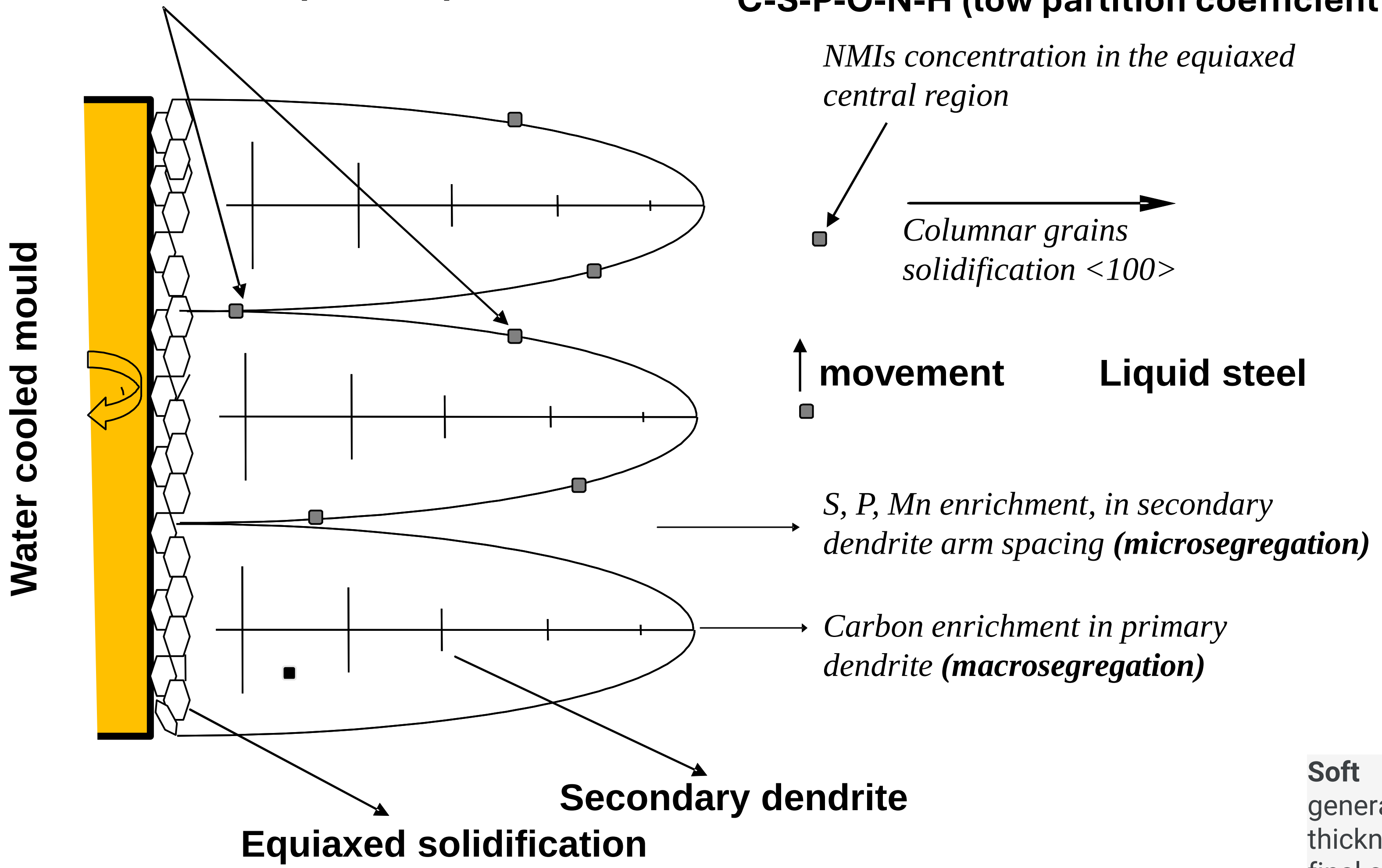
- Steel weight in tundish
- Variation of Steel level in mould
- SEN inmersión depth in mould
- Superheat
- Use of EMS/Soft reduction
- Slabs rejection due to events with quality impact
- Internal soundness by macroetching check

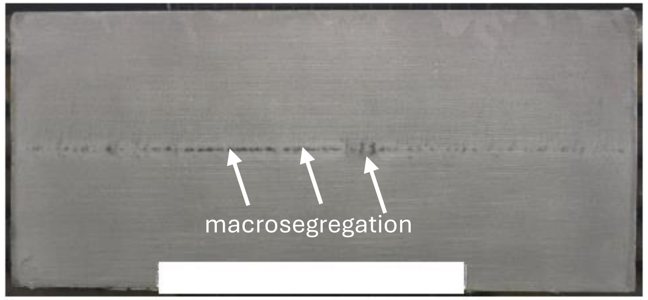
References:
BOF: Basic Oxygen Furnace
EAF: Electric Arc Furnace
LF: Laddle Furnace
AHF: Aluminum Heating Temperature
VTD: Vacuum Tank Degasser
RH: Rurhstahl Heraeus Degasser

Source: Clean steels for more reliable and cost-effective steel products, F, Actis, R. Bruna, AISTECH (2024)

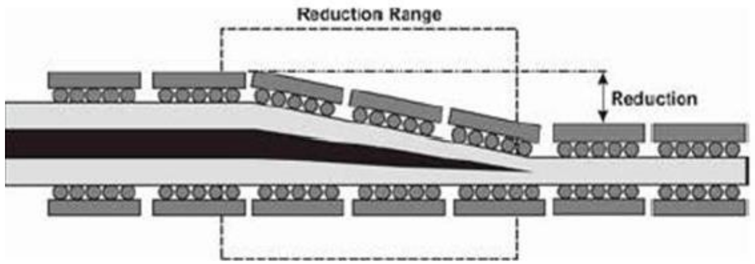
Schematic ilustration of solidification [1]

Elements conducive to microsegregation:
C-S-P-O-N-H (low partition coefficient values)





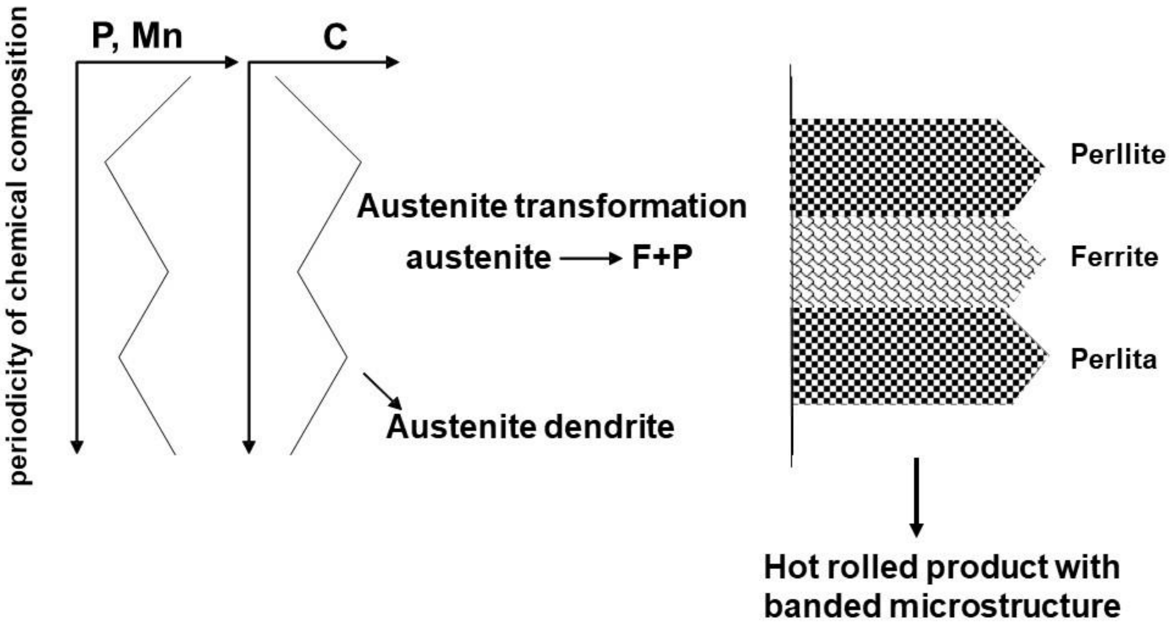
Macroetching – 20% ammonium persulfate

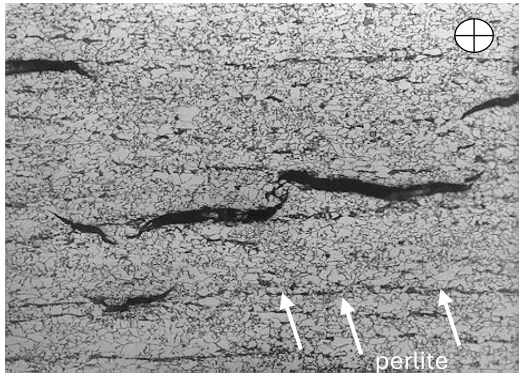


Soft reduction (SR): established technology and is generally understood as a reduction (~2% of the thickness) of the cross-section of the strand (near to the final solidification point)

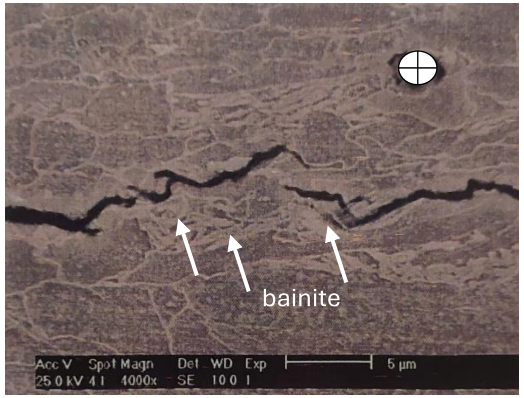
[1] Adapted from R. Ratnapulli, ABM (2007)

Microsegregation and banding





HIC step cracks

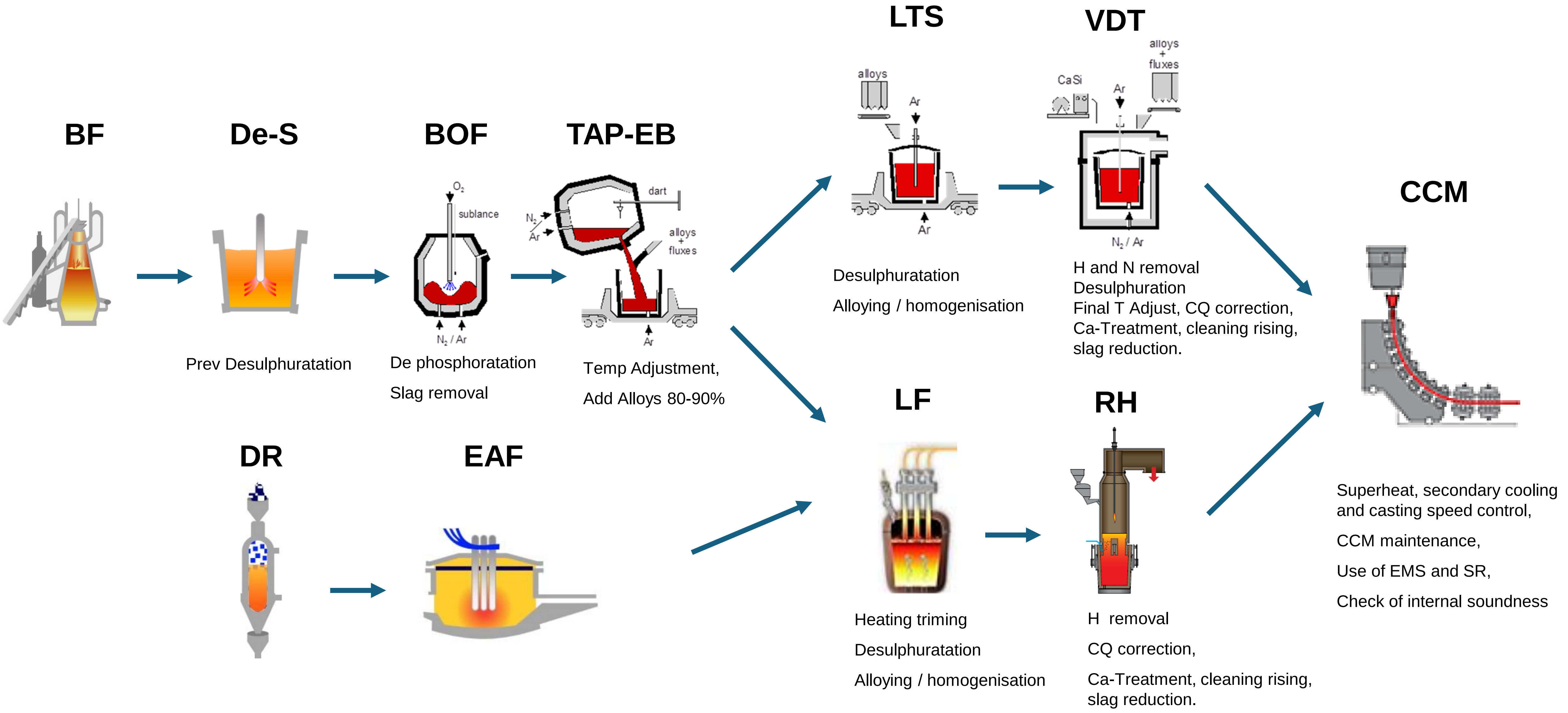


Crack propagation in mixed softer ferrite (180HV) and bainite (> 210HV)
API X60, NbTiCuNi

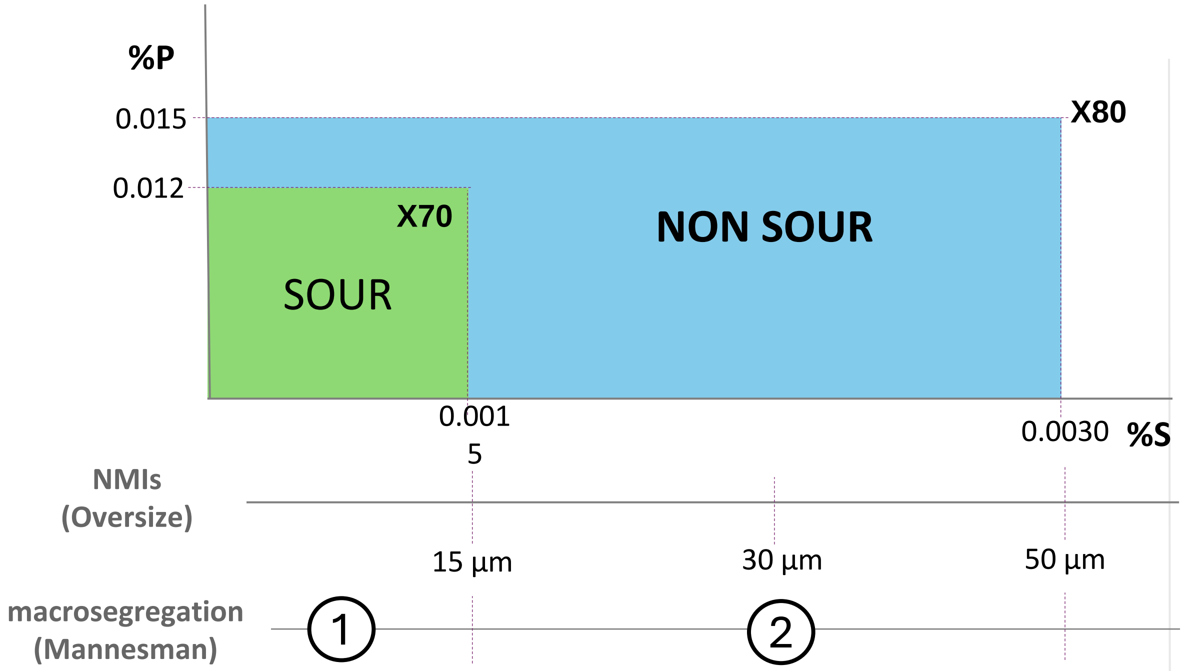
Minimization of banding severity

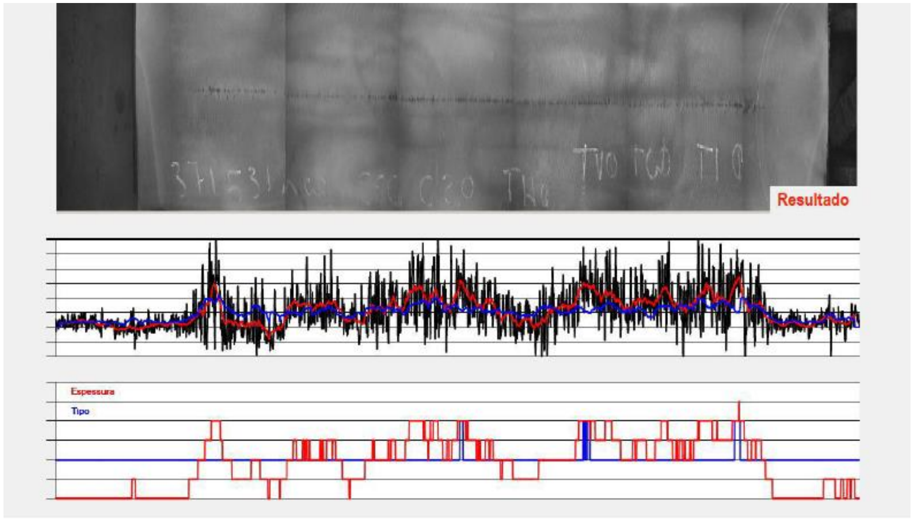
- Reduction of C, Mn and P contents
- Control of continuous casting parameters (superheat, secondary cooling, use of EMS and SR)
- Redistribution of C with acelerated cooling after hot rolling

Technical approach : steelmaking overview

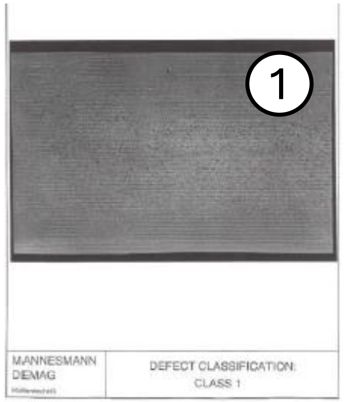


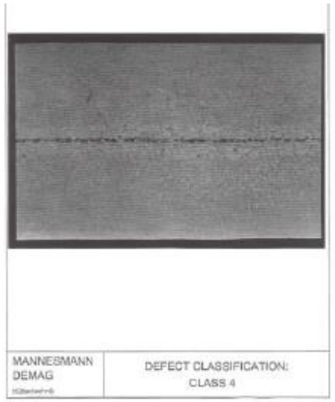
Residuals, steel cleanliness and soundness

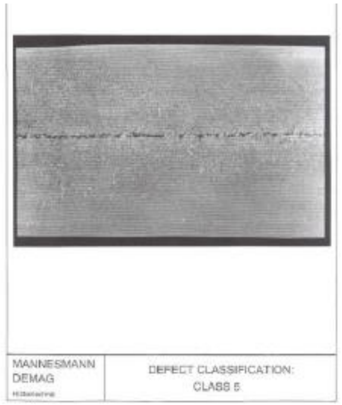




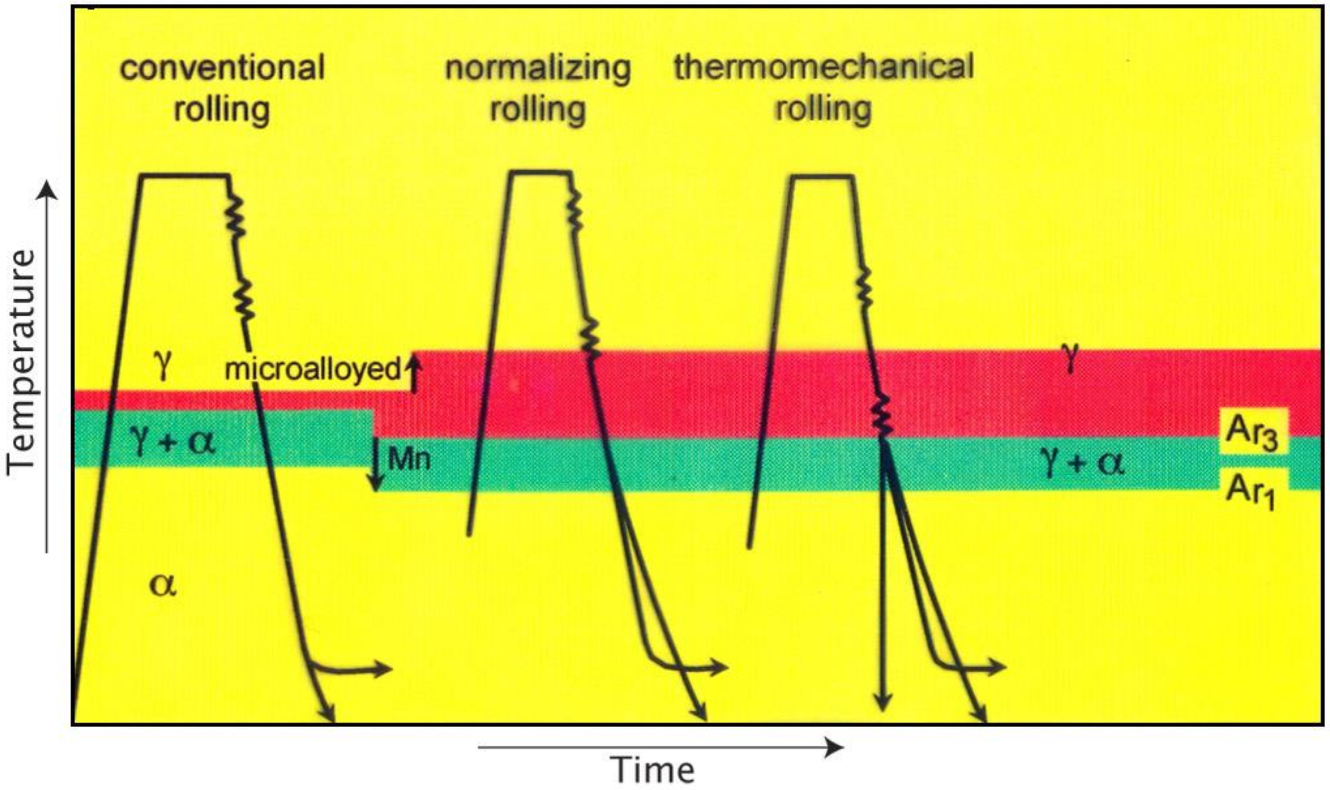
Source: F. Ramstorfer et al. - COMPUTATIONAL CLASSIFICATION OF CENTRAL SEGREGATION OF PLATES BY IMAGE PROCESSING OF BAUMANN PRINTS, ABM Proceedings (2014)

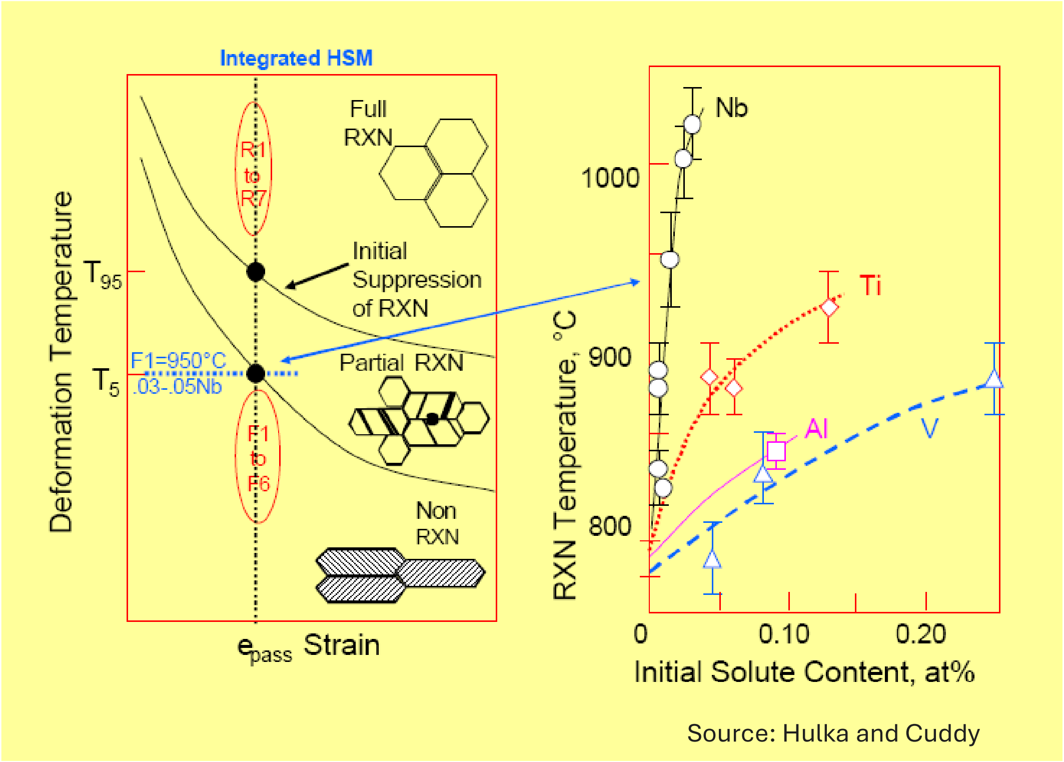






Thermomechanical processing (TMP)

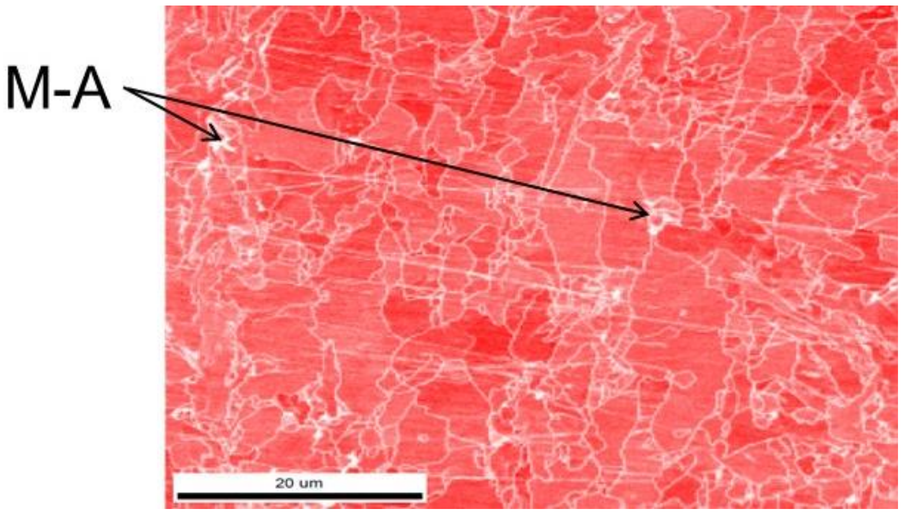




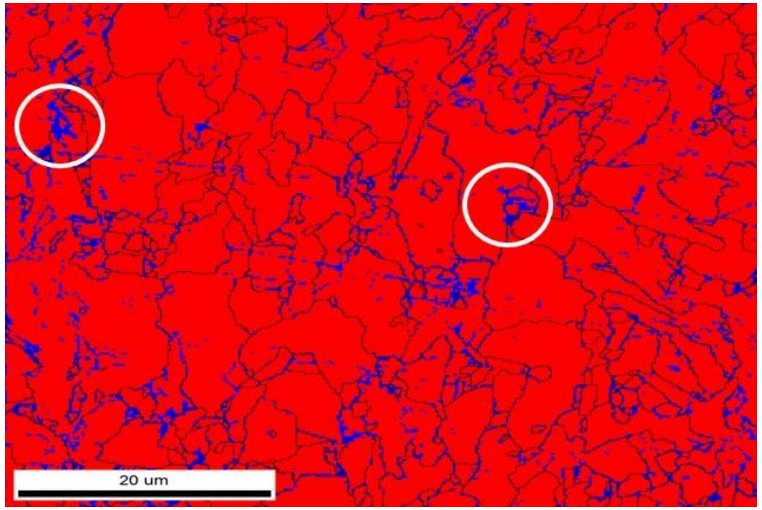
Goal of the TMP: fine grain, isolated MA constituent

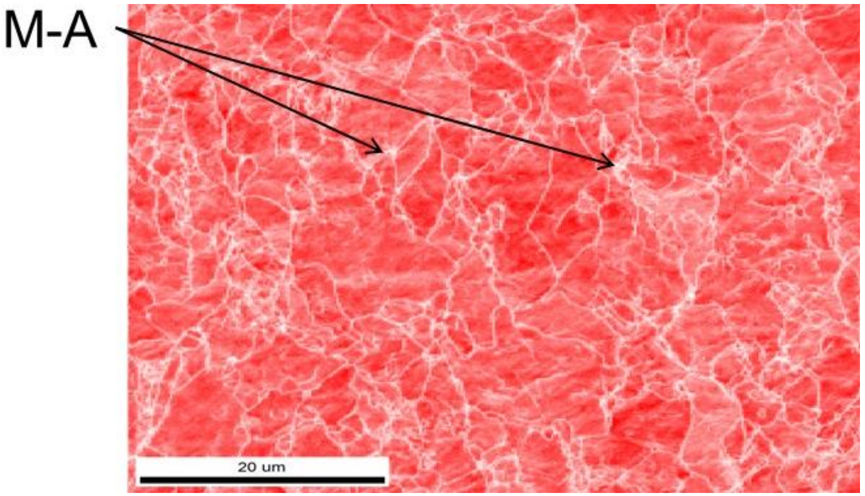
- Proper alloy design to increase the processing window as defined by T_{nr} and T_{ar3},
- Processes conditions control during hot rolling,
- Transformation control

MA control by TMCP, API X70 (t=12.7mm)

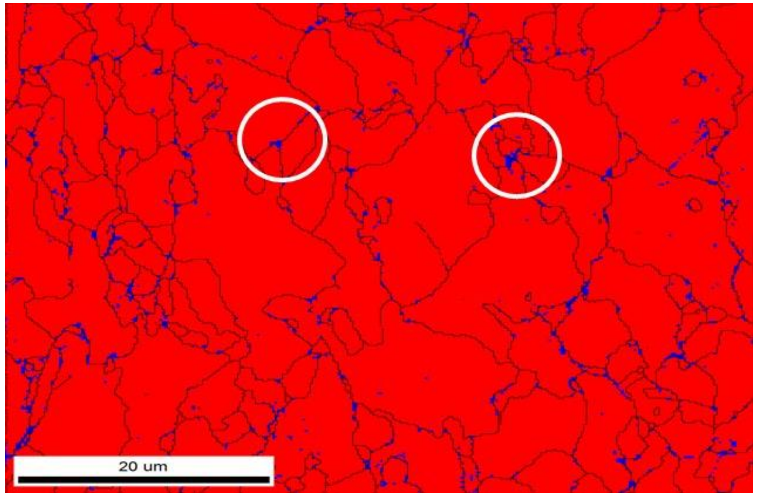


5.7% MA
DA < 85%
-20° C





1.2% M-A
DA = 100%
-40° C

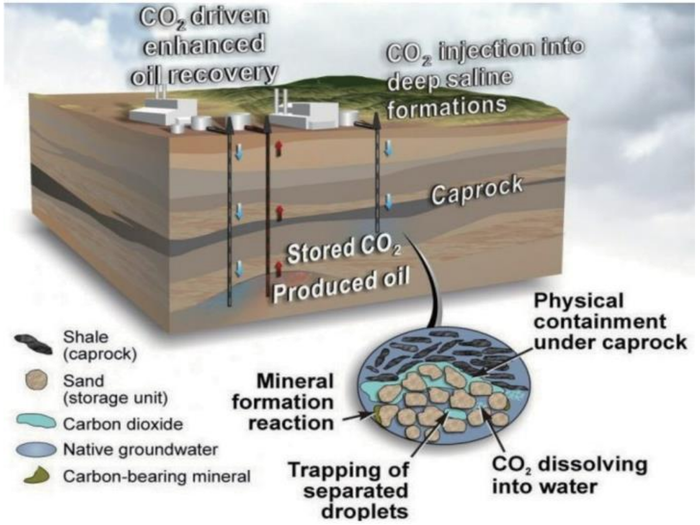


Source: Advanced Microstructural Characterization of a X-70 Microalloyed Steel for the Oil& Gas Industry. T. Perez, I. García, R. Bruna (2015)

Metallurgical factors to be controled: resume

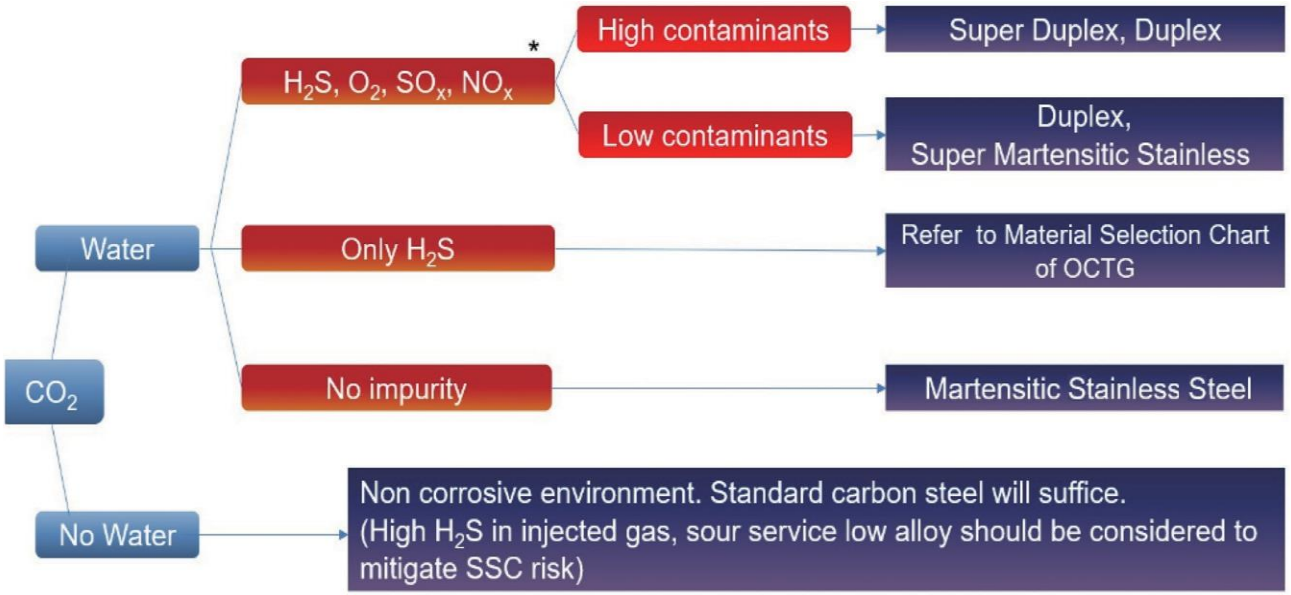
KILLING DEFECTS	TARGETS REGARDING MICROSTRUCTURE	SOLUTIONS & CHALLENGES
NMI - Oversize	Control severity of MnS, Al_2O_3 , calcium oxysulfide CaAl(OS) Inclusion modification and shape, maximum oversize (OS) control	***Best practice for production of ultra-clean steels*** (low S, H contents, Ca-treated steels) OS < 15µm, globular oxide type (avoid sulfides and alumina types).
Coarse precipitates	Nano-precipitates of TiN , TiNb(C,N)	Low Nitrogen steels, Ti/N= 2.5-3.0 (sub-stoicheiometric ratio), mean particle size: 100nm Use of Electromagnetic stirring (EMS) and Sof reduction (SR) at the CCM
Banded microstructure	Mainly fine FP/ NPF	***Steel design*** : reduction of P, Mn and C contens. ***Best practice* for the casting high quality of slabs**: - Superheat, secondary cooling and casting speed control, - Position control and alignment of the CCM equipment, - Use of EMS and SR reduction in strand to reduce micro &macrosegregation, - Chek of internal soundness (Mannesmann 1 maximum severity). ***Best practice for termomechanical rolling of microalloyed steels:*** *proper alloy design, processes conditions during hot rolling and transformation control* - Select alloy elements (Nb, Ni, …) → Reduce austenite/ ferrite starting temp. (Tar3) - Increase reduction rate in last pases → Reduce final effective austenitic GS, big ΔT (Tnr-Tar3) - Reduce finishing temperature. Acelerated cooling → redistribution of carbon during transformation - Hardness < 210 HV (hard spot control)
MA particles	Fine/isolated particles of martensite- austenite (MA).	

Corrosion in CO_2 enviroment (CCS)



Schematic image of CCS process

Component	Corrosion effects
CO_2	• Balance Gas pH drop out
O_2	• Oxidant: risk of localized corrosion • Elemental Sulfur (S_0) produced by reaction with H_2S. → risk of localized corrosion
SO_2	• Sulfuric acid (H_2SO_4) produced. → pH drop out
NO_2	• Possibility of producing Nitric acid (HNO_3) → pH drop out • Oxidant: risk of localized corrosion
H_2S	• Risk of Hydrogen Embrittlement because H_2S acts as a poison in Hydrogen penetration



Source: Nippon Steel's Corrosion Resistant Alloy for CCS Application (2023)

Conclusions:

- Research today focuses on overcoming technical concerns related to pipeline transmission, including the potential for hydrogen to embrittle the steel and welds used to fabricate the pipeline
- To fullfill this requeriments a **proper balance** of toughness, mechanical strength, weldability and resistance cracking of the pipe in the field is needed.
- Cracking resistance depends on both on reduction of the **initiation** sites and on reduction de factors that contribute to the **propagation** of hydrogen-induced cracking.
- By adopting and implementing a **tailor-made Best Practice** at the steelmaking and hot rolling processes steel suppliers can produce significant cleaner steels with the necessary microstructure
    - Due attention must be given for improving **steel cleanliness** and reducing the **macro and microsegregation** of elements such as S, P, O, N and H, in order to improve the behavior of the base metal and the welded joint.
    - **Advanced process control** of key process variables by using IA, ML, expert-system are highly recomended for quality prediction of the Steel supplied.
- This leads to an improved hydrogen pipelines with a novel approach based on **metallurgical reliability.**