The Thermodynamic Evaluation and Modeling of Grade 91 Alloy and its Secondary Phases through the CALPHAD Approach

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Outline

- Purpose of Study / Objectives
- Main Problems & Observed Failure Mechanisms
  - Type IV Cracks
  - Secondary Phases
  - Formation of the Heat-Affected-Zone
  - Short-Term Creep Failure
  - Long-Term Creep Failure
- Results
- Conclusion

Purpose of Study / Objectives

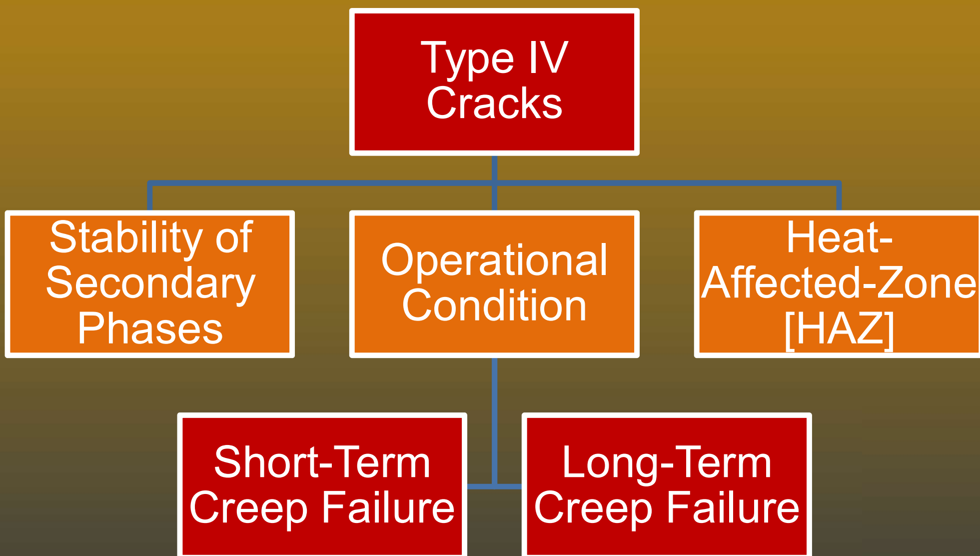
Purpose of Study

- Provide a clear Computational Thermodynamic understanding of Gr.91.

Objectives

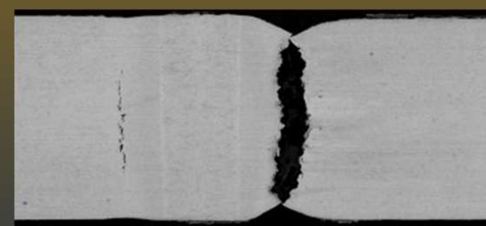
- Provide simulations that thermodynamically accurate.
- Develop a model based on those simulations.
- Improve Creep Resistance for High-Chromium Ferritic and Martensitic Steels.

Type IV Cracks

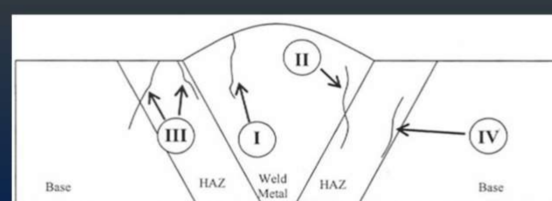


Type IV Cracks

- Main observed failure during creep.
- Mostly been observed along the outer edge of the HAZ, more specifically in the Fine-Grain HAZ (FGHAZ) and Intercritical HAZ (ICHAZ).
- The exact mechanism which leads to its critical failure along the HAZ are still unknown.



D. J. Abson and J. S. Rothwell 2013



J. M. Brear and A. Fleming 2004

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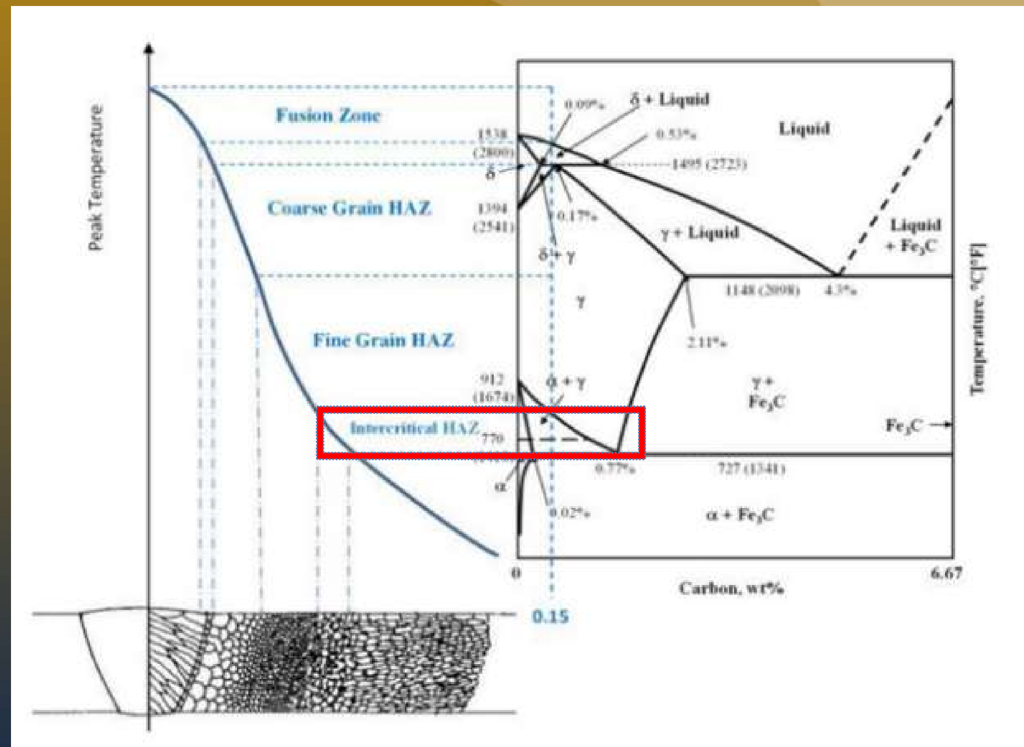
Formation of the Heat-Affected-Zone (HAZ)

Heat-Affected-Zone

- Contains 3 subzones which have been observed in the HAZ:
  1. Coarse-grain HAZ (CGHAZ)
  2. Fine-grain HAZ (FGHAZ)
  3. Intercritical HAZ (ICHAZ)
- 3 main factors are involved in the formation of the HAZ and its subzones:
  1. Peak welding temperatures
  2. Ac1 and Ac3 temperatures
  3. Formation and dissolution of $M_{23}C_6$ carbides.



Lippold J.C 2015

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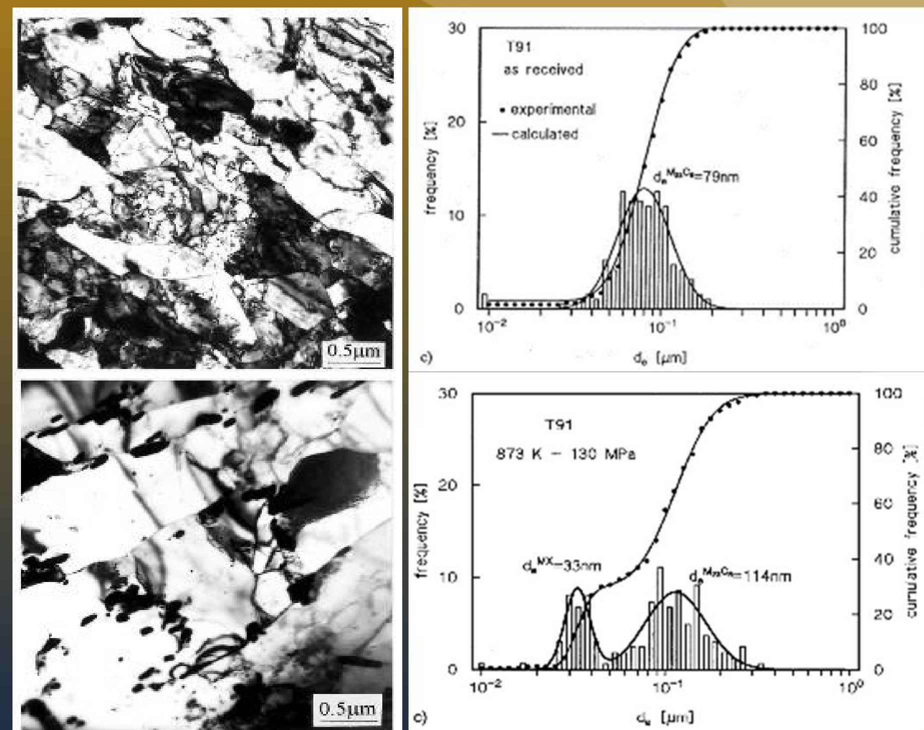
Short-Term Creep Failure

Short-Term Creep

- Speed up failure creep tests.
- Can vary depending on parameters:
  - 100-1,000 total testing hours
  - Temperatures between 575C-650C
  - Stresses between 100MPa-200MPa
- Main observation is the increase and the coarsening of $M_{23}C_6$ particles which influences the microstructure in the HAZ that can lower the creep resistance.



E. Cerri 1997

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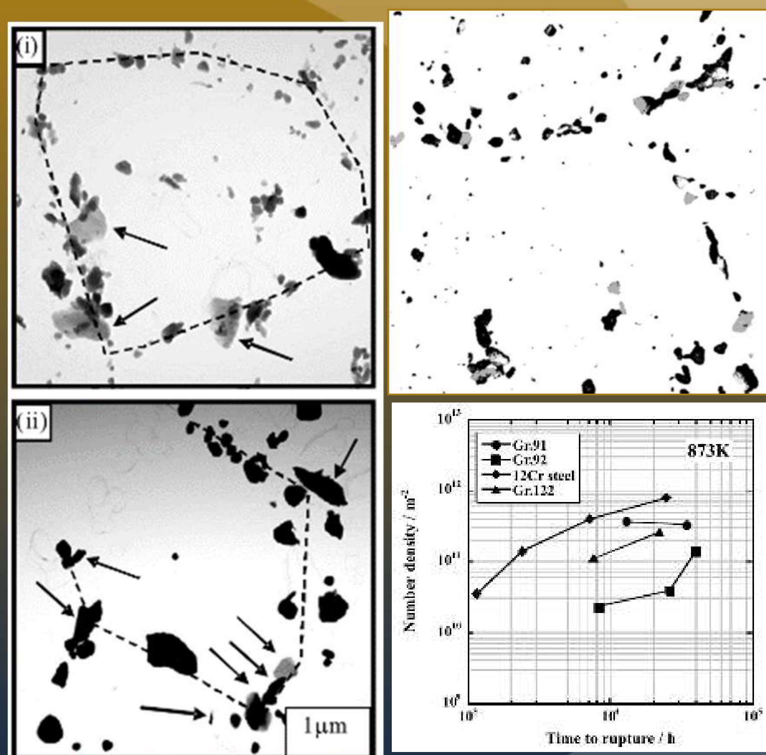
Long-Term Creep Failure

Long-Term Creep

- Failure creep tests over a long period of time.
- Can vary depending on parameters:
  - 100,000 or above total testing hours
  - Temperatures as low as 550°C
  - Stresses below 100MPa
- It has been observed that Z-phase will eventually form and reduce the creep resistance of the material through the dissolution of fine MX carbonitrides (M(C,N)) and disappearance of Nb rich (NbX) MX phases.



K. Sawada 2009

Creep Failure Solution

Observed Problems

- Type IV Cracks
  - FGHAZ
  - ICHAZ
- Short-Term Creep Failure
  - $M_{23}C_6$ Coarsening
- Long-term Creep Failure
  - Z-phase Formation
  - Dissolution of beneficial MX Phase

Solution - Adjust Ac Temperatures and further optimize composition.

- Tuning HAZ Microstructure
  - Change behavior of creep failure

Short-Term Creep Failure

- Destabilize $M_{23}C_6$ carbides
- Reduce recovery

- Long-term Creep Failure
  - Destabilize Z-phase
  - Promotion of MX phase

Approach of Study

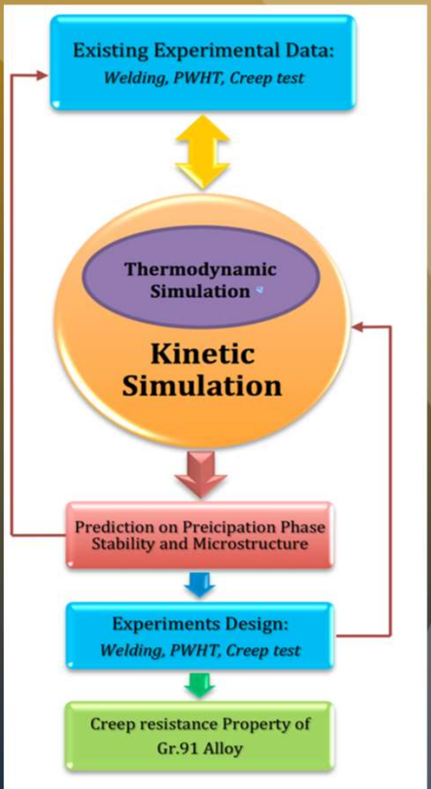
1st Set of Results – Baseline Study

- Isopleth Diagrams
- Ac1 and Ac3 Temperatures
- Equilibrium & Scheil Simulations

2nd Set of Results – Compositional Changes

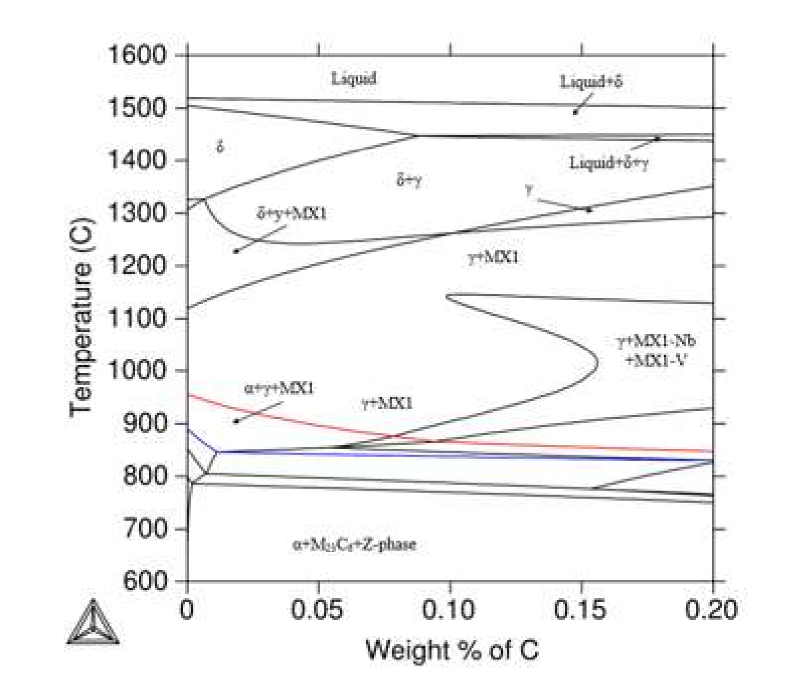
- Additional Alloying Element = Mn, Ni, & Ti.
- 3 Different Compositional Changes = V, Nb, & N.

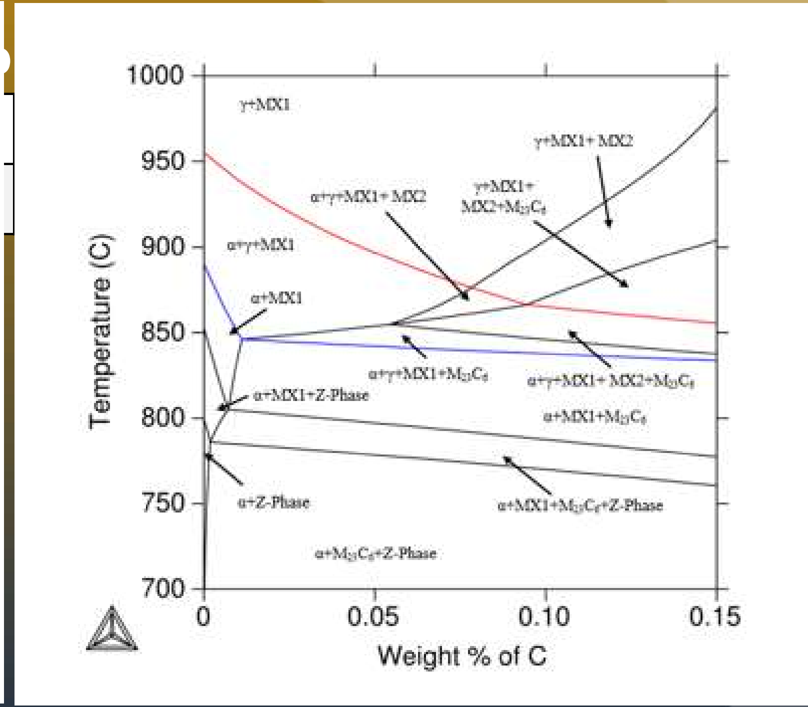
ICME Approach Diagram



Results – Baseline Gr.91 System

Isopleth Diagrams





Establishing Location of Ac1 (Blue) and Ac3 (Red) Temperatures

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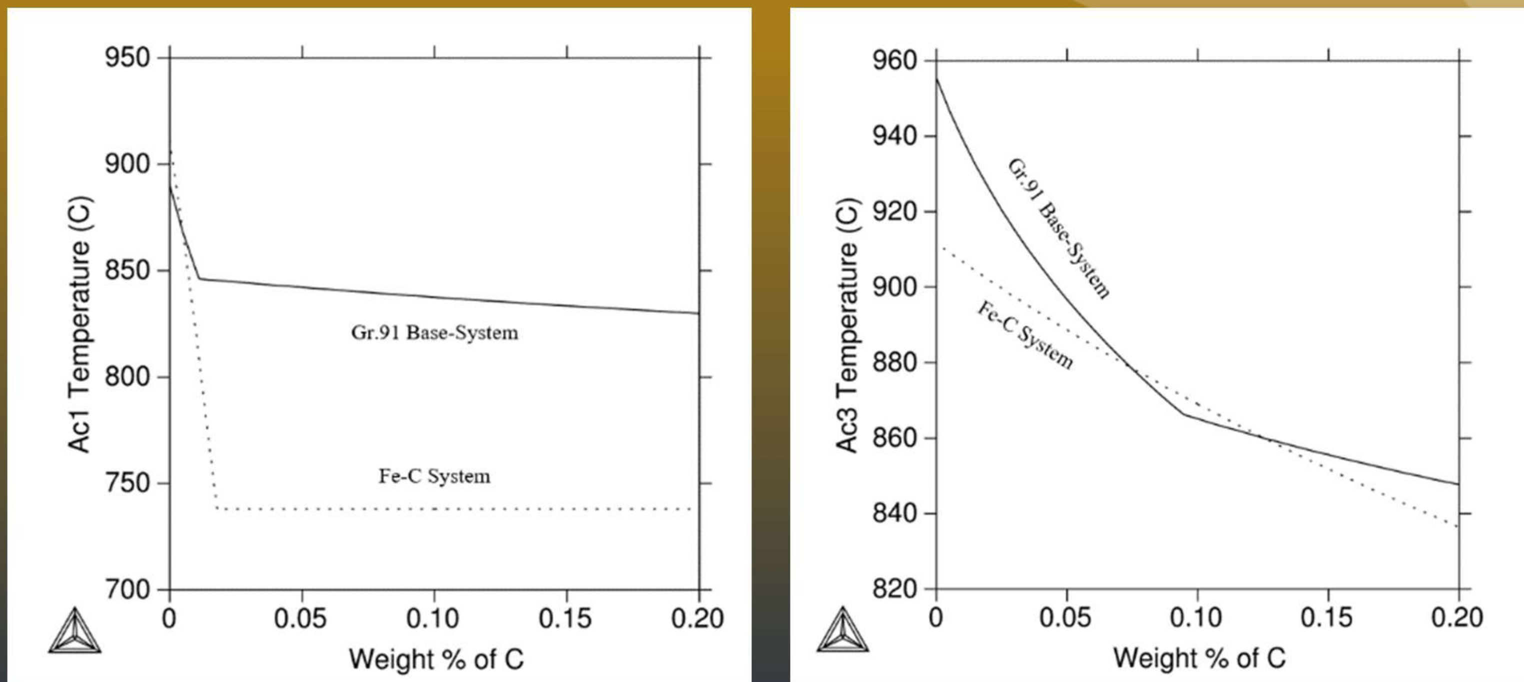
Results – Baseline

Ac Temperatures Vs. Fe-C System



Relate the baseline Ac temperature profile with an existing known binary system.

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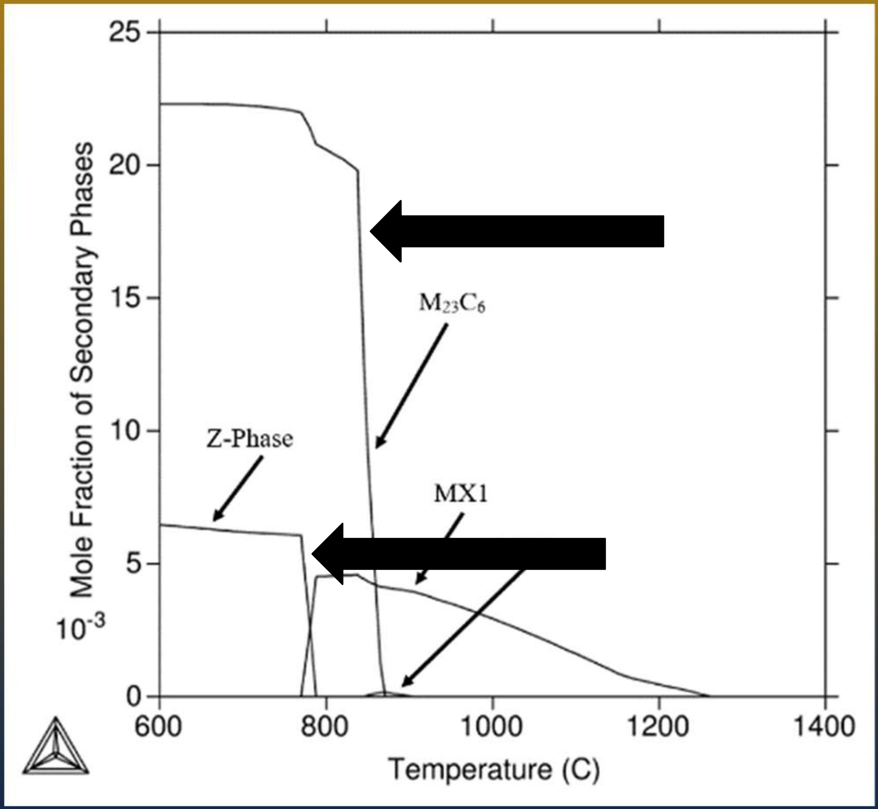
Results – Baseline

Molar Fraction of Secondary Phases



$M_{23}C_6$

- Most dominate secondary phase
- 600°C - 870°C

Z-Phase

- Stable nitrite in lower temperature regions
- 600°C - 770°C

MX Phases

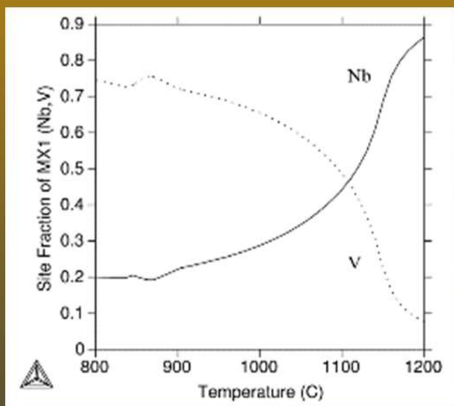
- MX1 and MX2

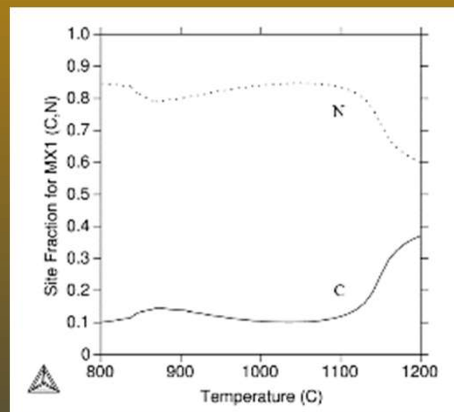
Goal

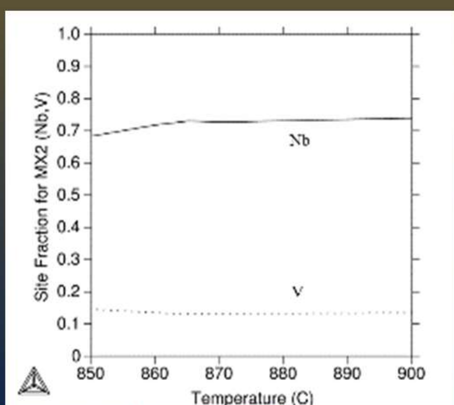
- Suppression of $M_{23}C_6$ and Z-phases.
- Increasing MX phases.

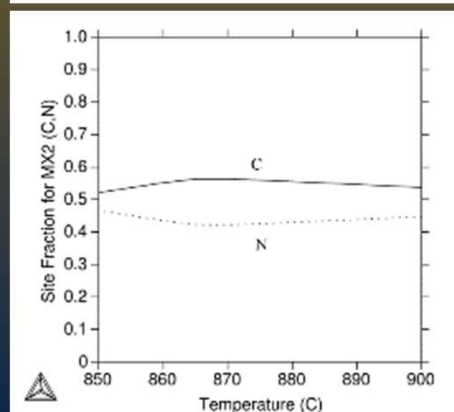
Results – Baseline

Site Fraction of MX1 and MX2









MX1

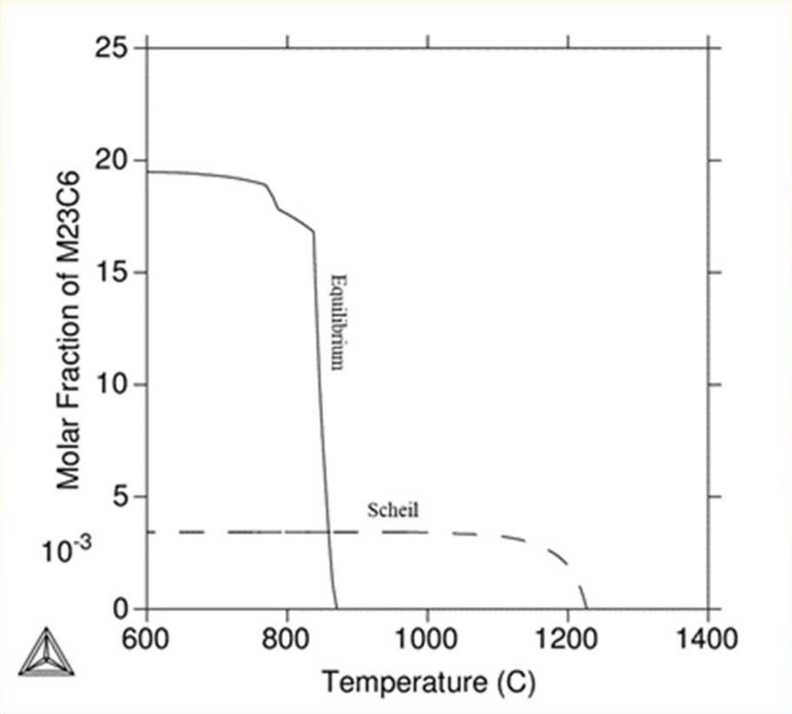
- NbN dominate at higher temperatures
- VN dominate at lower temperatures

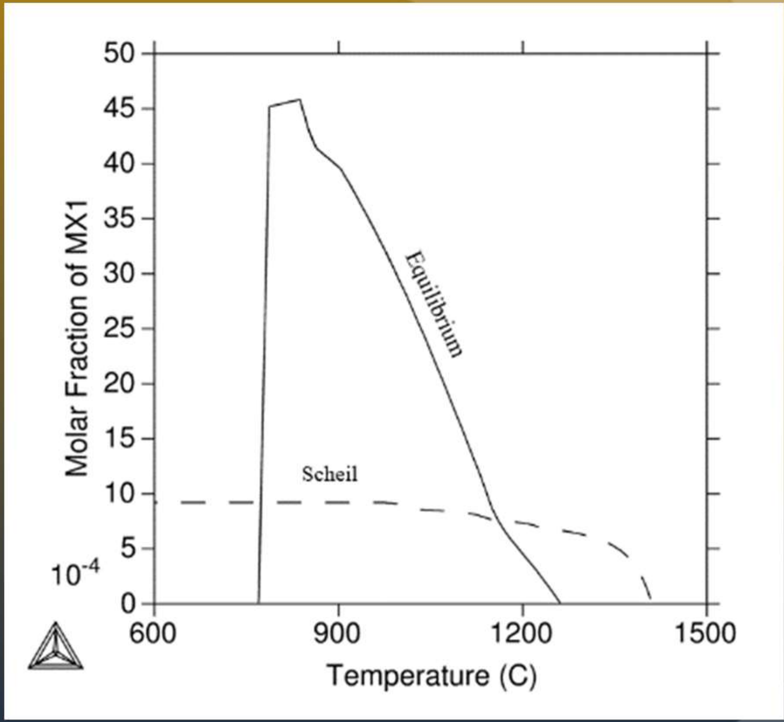
MX2

- Mostly NbC formation
- Very small stable temperature region

Results - Baseline

Scheil Vs. Equilibrium





Establish the boundary conditions of $M_{23}C_6$ and MX1 Phases

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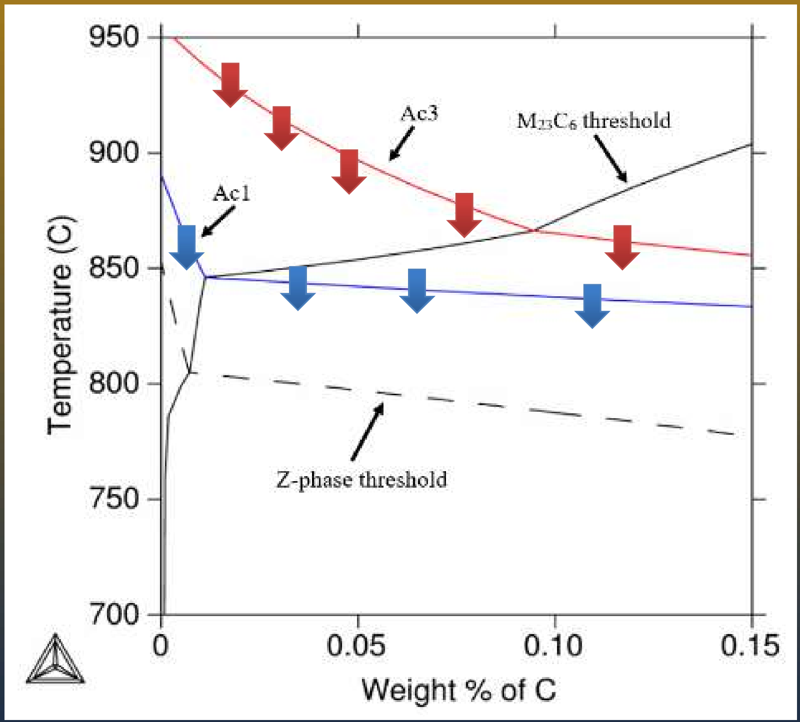
Results - Baseline

Threshold Temperatures



Established Threshold Temperatures

- $M_{23}C_6$
- Z-Phase
- Ac1 Temperature
- Ac3 Temperature

Goal

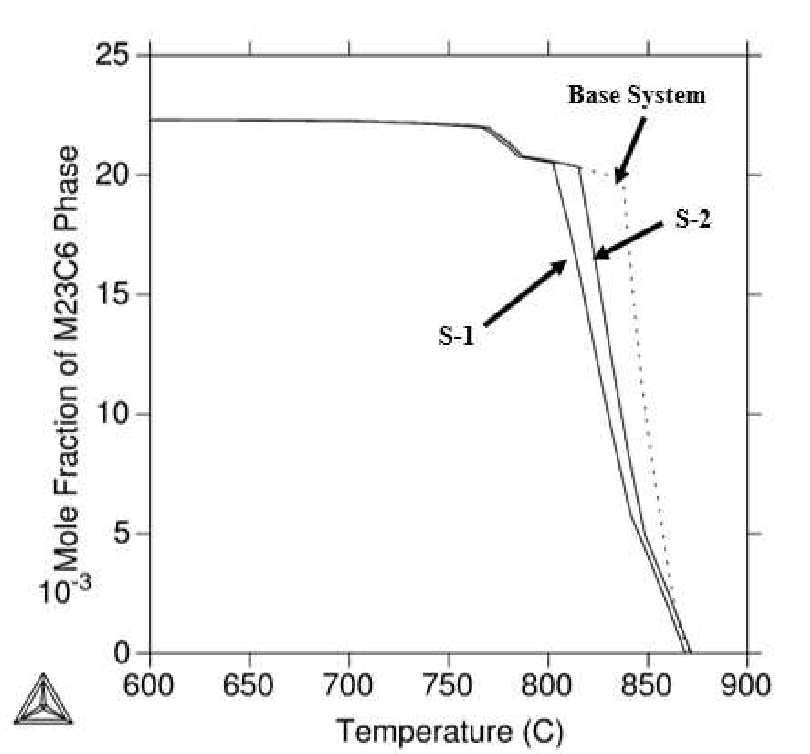
- Lower Ac Temperatures
  - Change HAZ Microstructure
  - Destabilize $M_{23}C_6$

Results – Modified Gr.91

Effects of Increased Concentration of Mn and Ni

Material Composition for Gr.91 with added alloying elements

Elements (wt.%)	Cr	C	V	Nb	Mo	N	Mn	Ni	Ti
ASME standard	7.90-9.60	0.06-0.15	0.16-0.27	0.05-0.11	0.80-1.10	0.025-0.08	0.25-0.66	0.43 (max)	0.01 (max)
Gr.91 Baseline	8.75	.10	.215	.08	.95	.05	-	-	-
Simulation 1 (S-1)	8.75	.10	.215	.08	.95	.05	0.66	-	-
Simulation 2 (S-2)	8.75	.10	.215	.08	.95	.05	-	0.43	-
Simulation 3 (S-3)	8.75	.10	.215	.08	.95	.05	-	-	.01



Summary

0.66wt.%Mn (S-1) showed most effective when compared with the 0.43wt.%Ni (S-2) to destabilize $M_{23}C_6$

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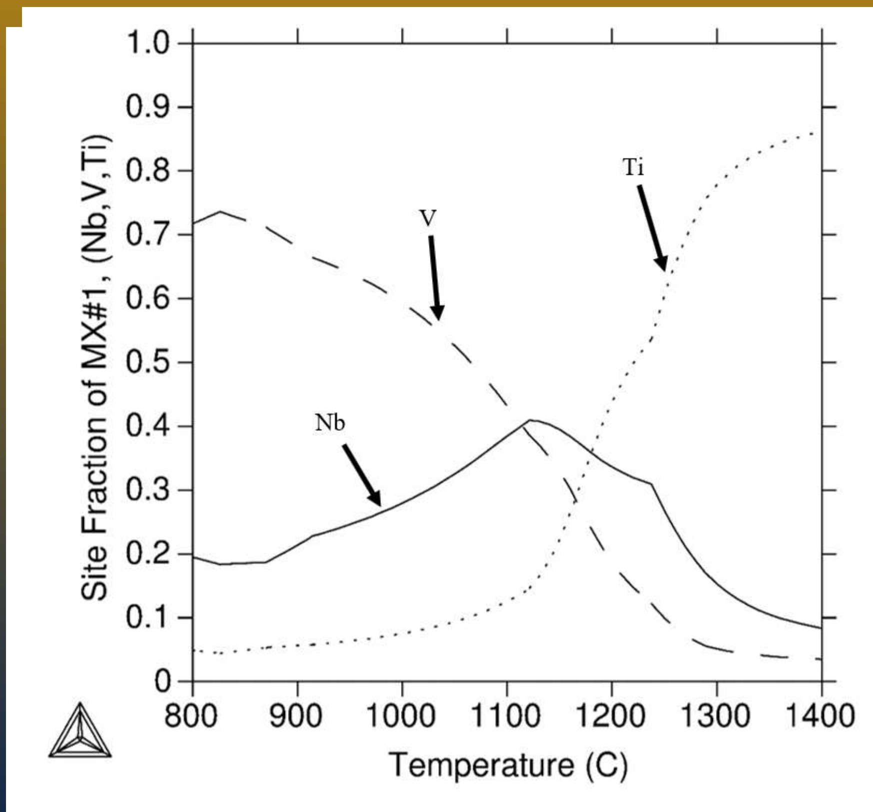
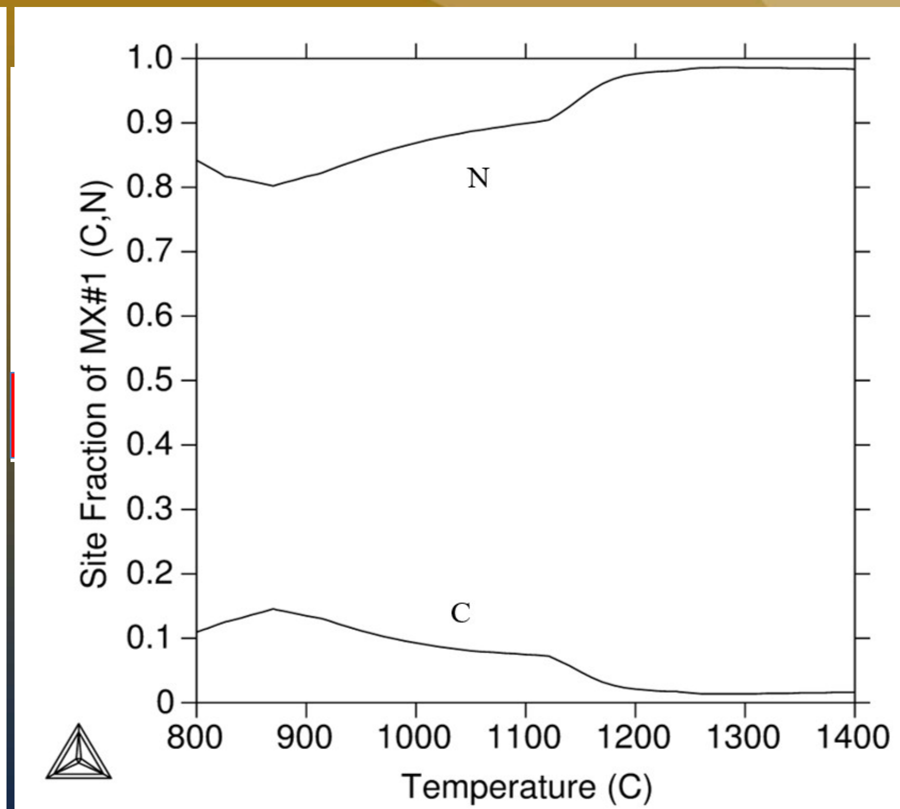
Results – Modified Gr.91

Effects of Increased Concentration of Ti





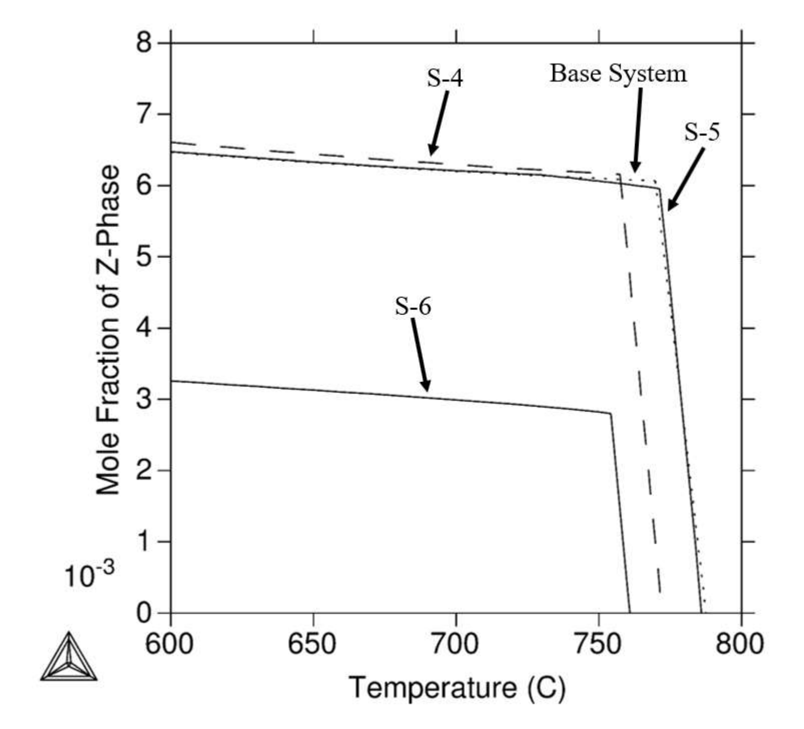
ents

Ti
0.01 (max)
-
-
-
.01

of

Results – Modified Gr.91

Z-Phase Stability Changes



Adjustment to Gr.91 Composition

Elements (wt.%)	*Cr*	*C*	*V*	*Nb*	*Mo*	*N*	*Mn*	*Ni*	*Ti*
ASME standard	*7.90-9.60*	*0.06-0.15*	*0.16-0.27*	*0.05-0.11*	*0.80-1.10*	*0.025-0.08*	*0.25-0.66*	*0.43 (max)*	*0.01 (max)*
Gr.91 Baseline	*8.75*	*.10*	*.215*	*.08*	*.95*	*.05*	-	-	-
Simulation 4 (S-4)	*8.75*	*.10*	*.27*	*.08*	*.95*	*.05*	-	-	-
Simulation 5 (S-5)	8.75	.10	.215	.11	.95	.05	-	-	-
Simulation 6 (S-6)	*8.75*	*.10*	*.215*	*.08*	*.95*	*.025*	-	-	-

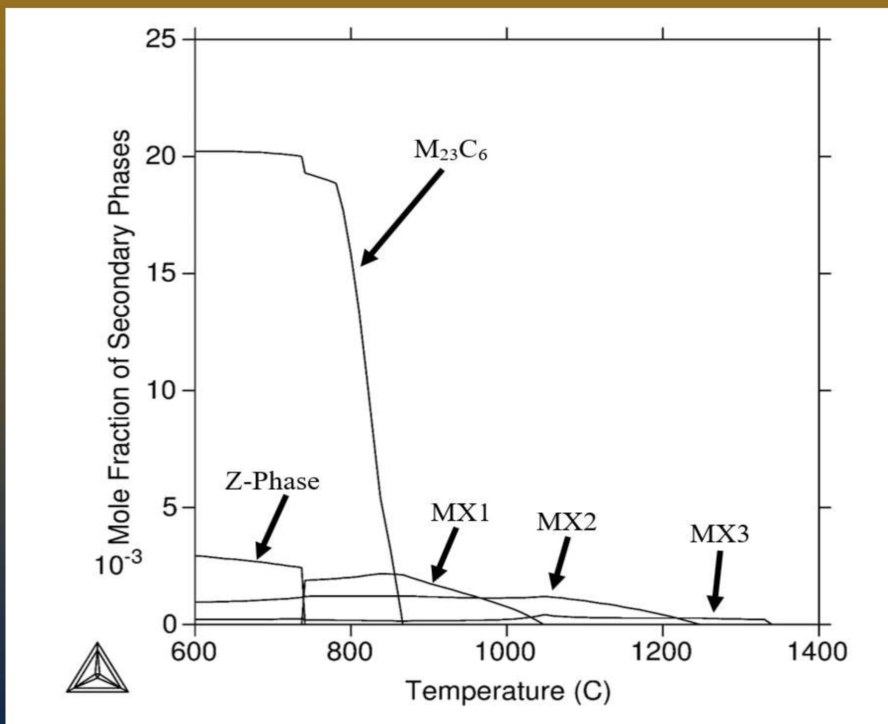
Summary

- S-6 for 0.025wt.%N showed greatest change to Z-phase stability.
- S-4 for 0.27wt.%V showed no change to total volume, only stability temperature.
- S-5 for 0.11wt.%Nb showed no change to Z-phase stability.

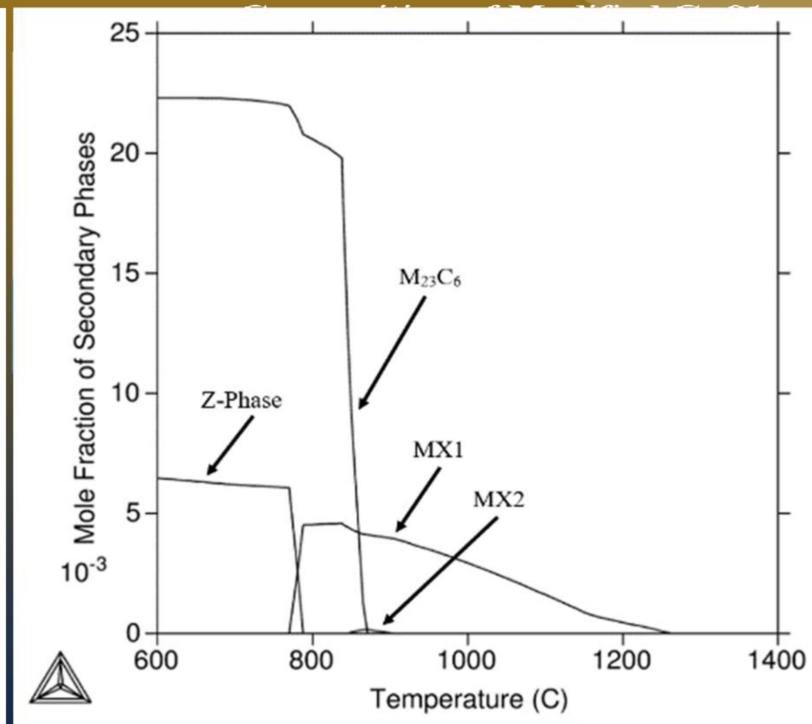
Results – Modified Gr.91

Mole Fraction and Threshold Temperatures for Modified Gr.91

Modified Gr.91 Alloy



Baseline Gr.91 Alloy



i	Al	Ti
8-6	0.02 (max)	0.01 (max)
	-	-
	-	.01

Conclusion

- The CALPHAD approach was utilized to perform basic precipitation phase stability.
- Provided Isopleth diagrams, Ac temperatures, equilibrium and scheil simulations.
- Mn and Ni concentration have destabilized $M_{23}C_6$, while lowering N has destabilized Z-phase and Ti has increased the beneficial MX phase.
- Modified Gr.91 resulted in stable MX carbide (NbC) and nitride (TiN) formation.
- Focus on carbide and highly stable nitride formation.

Acknowledgements

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Questions?