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


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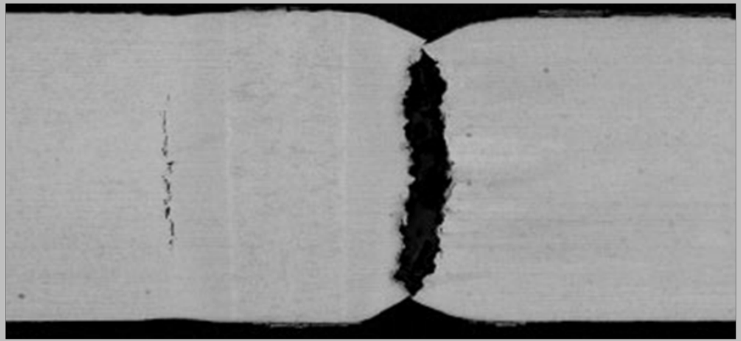
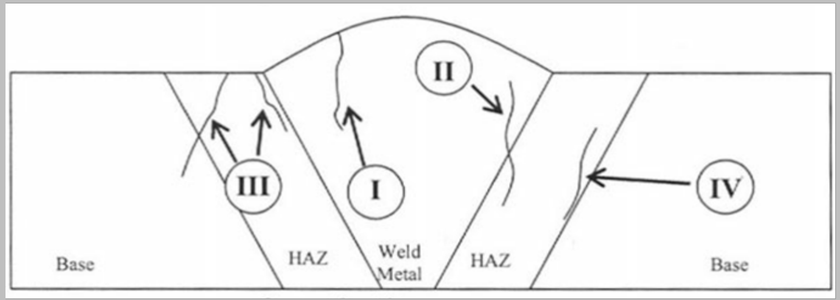
# Outline

- ***Creep Resistance--Type IV Cracks***
- ***Microstructure***
- ***Critical Secondary Phase Formations***
- ***Short-Term and Long-Term Creep***
- ***Simulation Results***
  - ***Baseline***
  - ***Modified Composition***
- ***Conclusion***

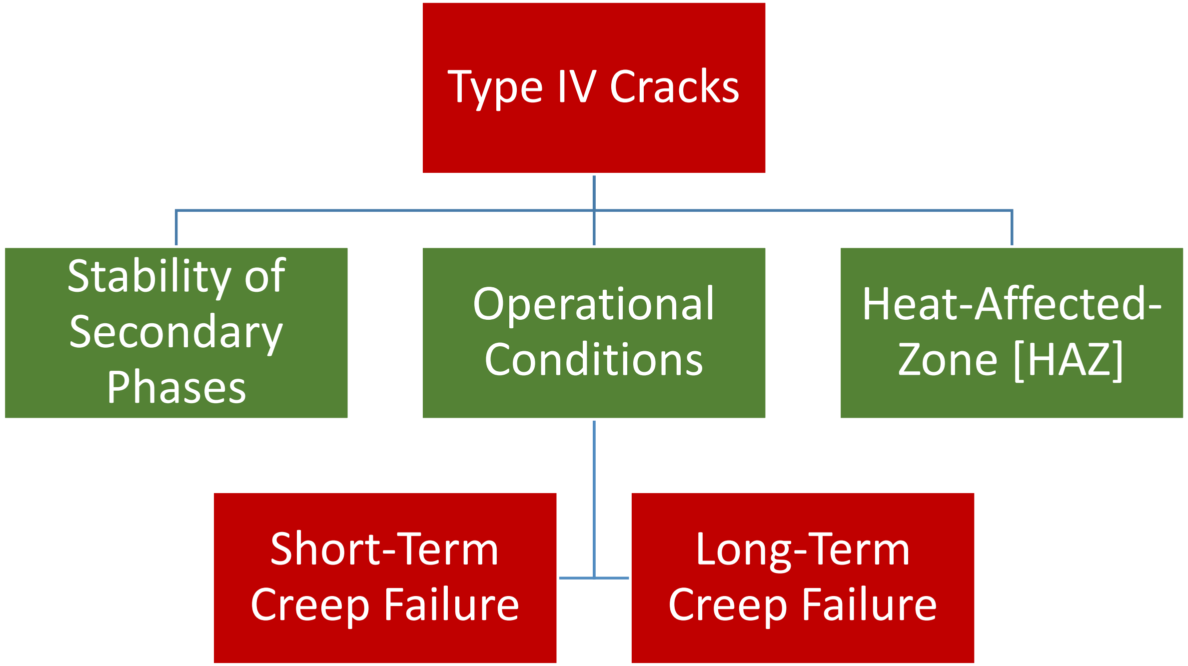
# Creep Failure for Gr.91



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




*J. M. Brear and A. Fleming 2004*



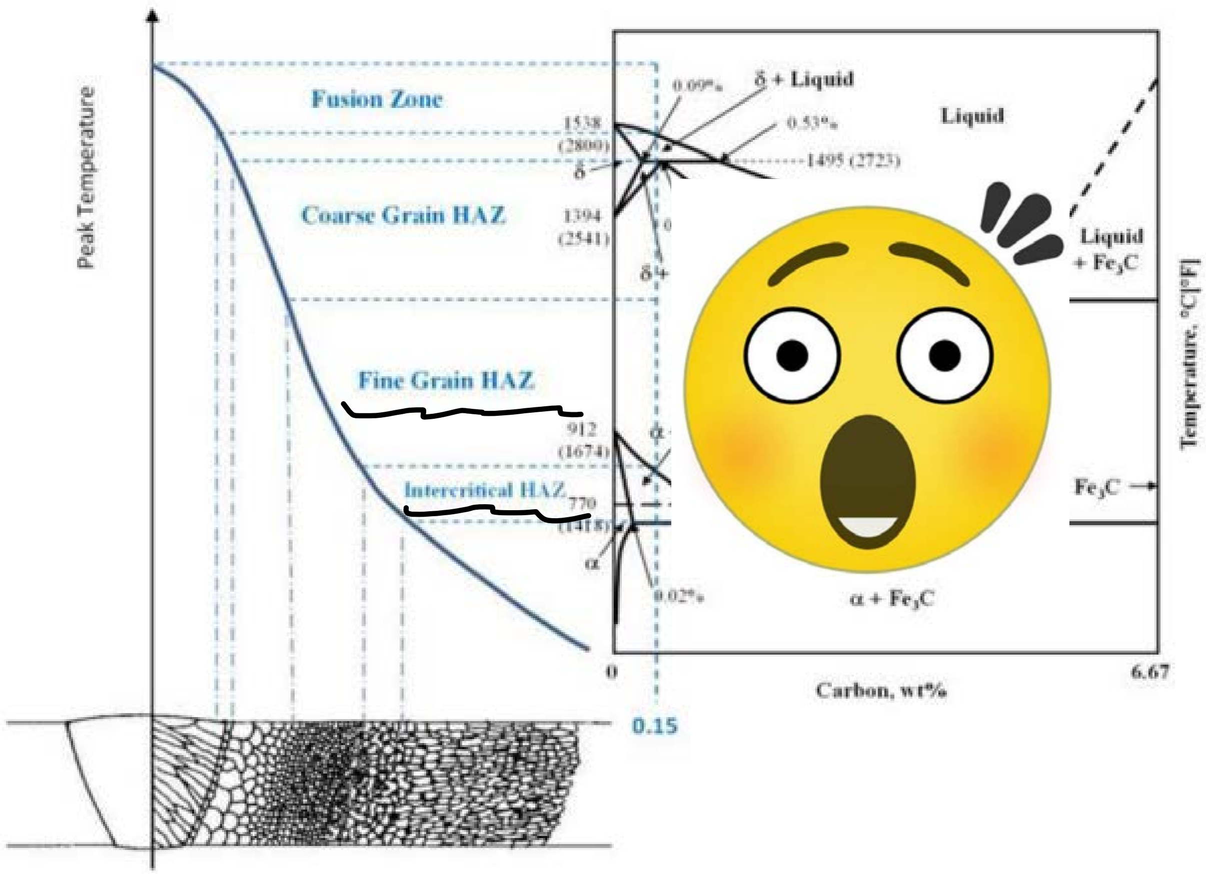

- Extensive Experiments and Modeling effort
- **Anything further help from Thermodynamics?**

# Microstructure

***3 Subzones:***

- Coarse-grain HAZ (CGHAZ)
- Fine-grain HAZ (FGHAZ)
- Intercritical HAZ (ICHAZ)

Most investigation relied on carbon steel phase diagrams?!




*Lippold J.C 2015*

# Critical Secondary Phases

## *$M_{23}C_6$ Precipitates*

M = Cr, Fe, and Mo, Coarsening during operation

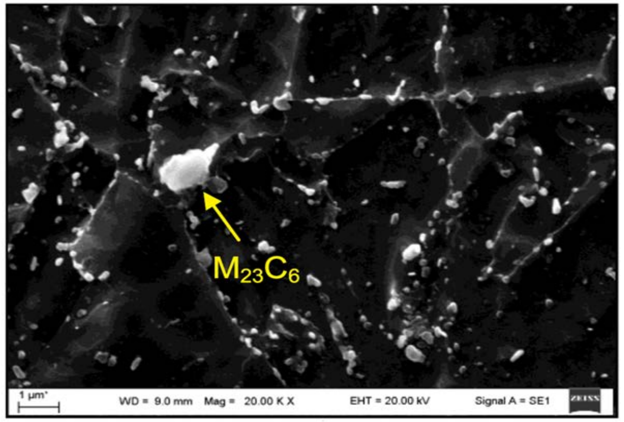
## *MX Precipitates*

FCC structure, M = V/Nb, X = C/N. Very small and low coarsening rate.

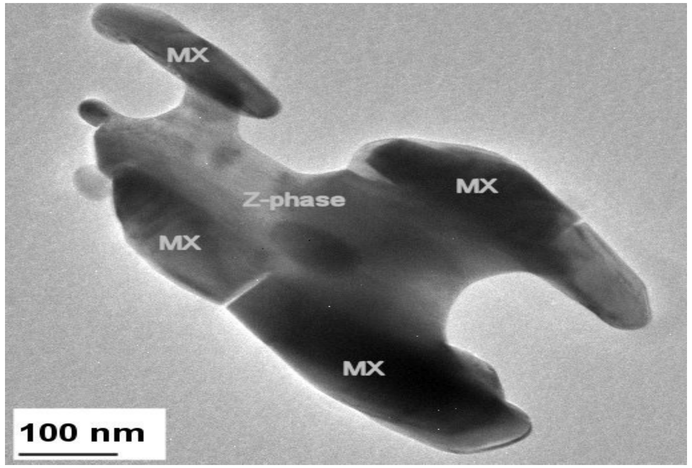
## *Z-Phase*

Cr(V,Nb)N, detrimental to creep resistance, long term operation.

How to control their stabilities?




*A. Grybėnas 2017*




*H.K. Danielsen 2008*

# Questions Related to Thermodynamics

- Creep mechanisms at different conditions?
- Thermodynamics vs. HAZ microstructures?
- The role of elements inside Gr.91?
- Any better creep resistant alloys?
- Choice of processing parameters?

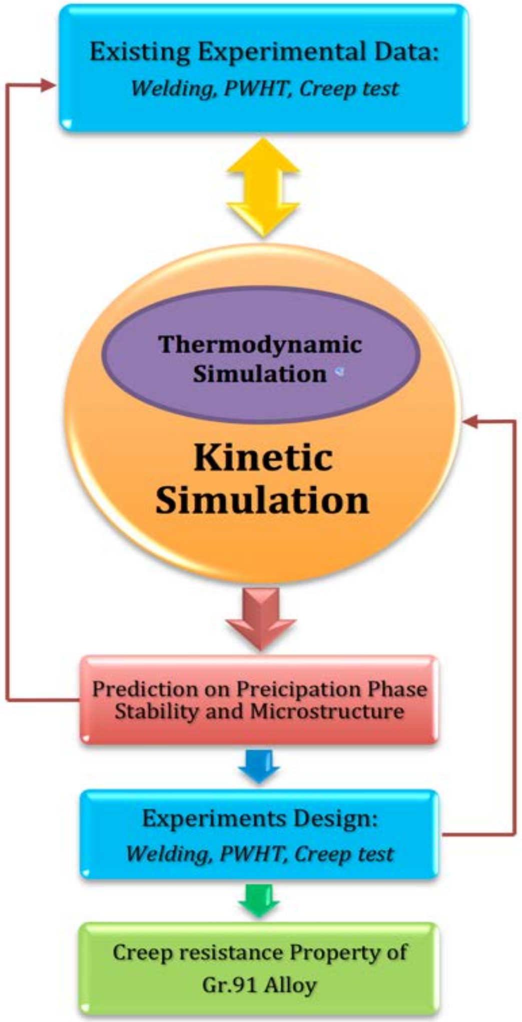
# Approach of Study

*1st Set of Results – Baseline Study (Gr.91)*

- 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.

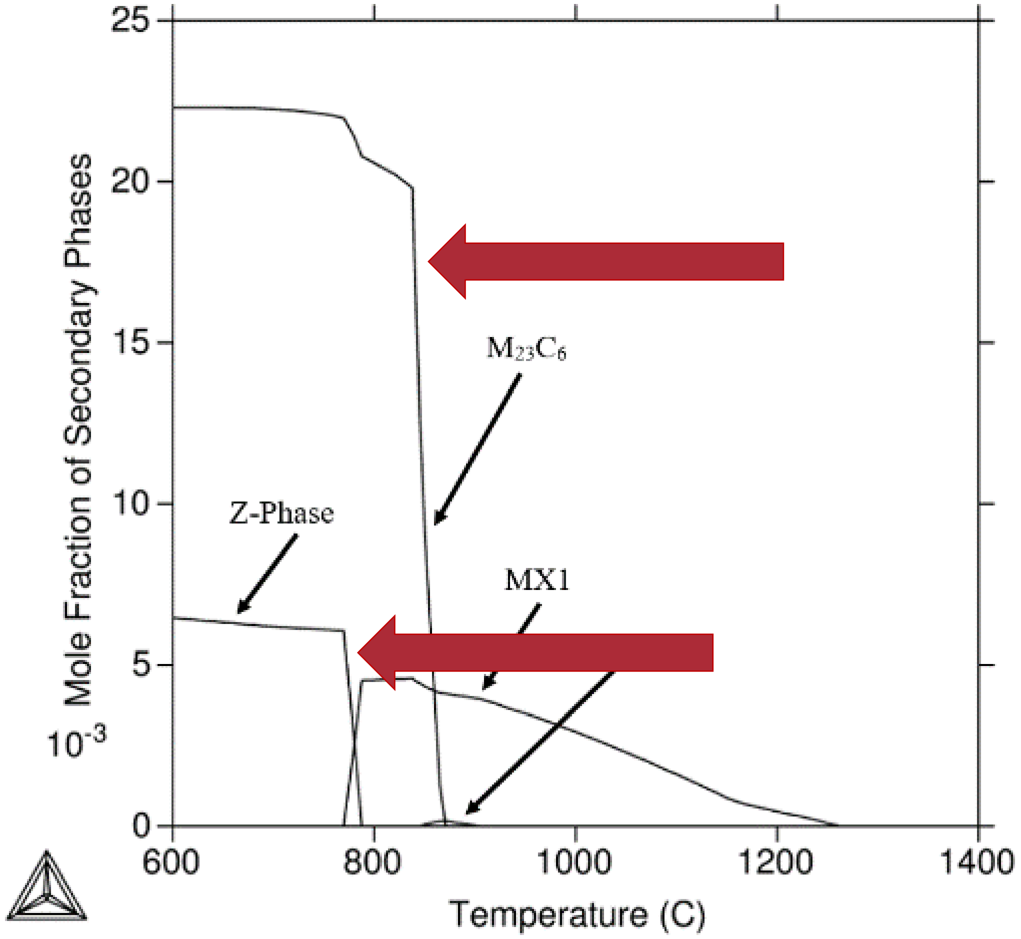


# Part I

- **Baseline Study**
  - *Factors affecting creep resistance?*
  - *Possible ways to improve creep resistance?*
  - *Any criteria?*

# Results – Baseline

## Molar Fraction of Secondary Phases




$M_{23}C_6$

- Most dominate secondary phase
- <870°C

Z-Phase

- Stable in lower temperature regions
- <770°C

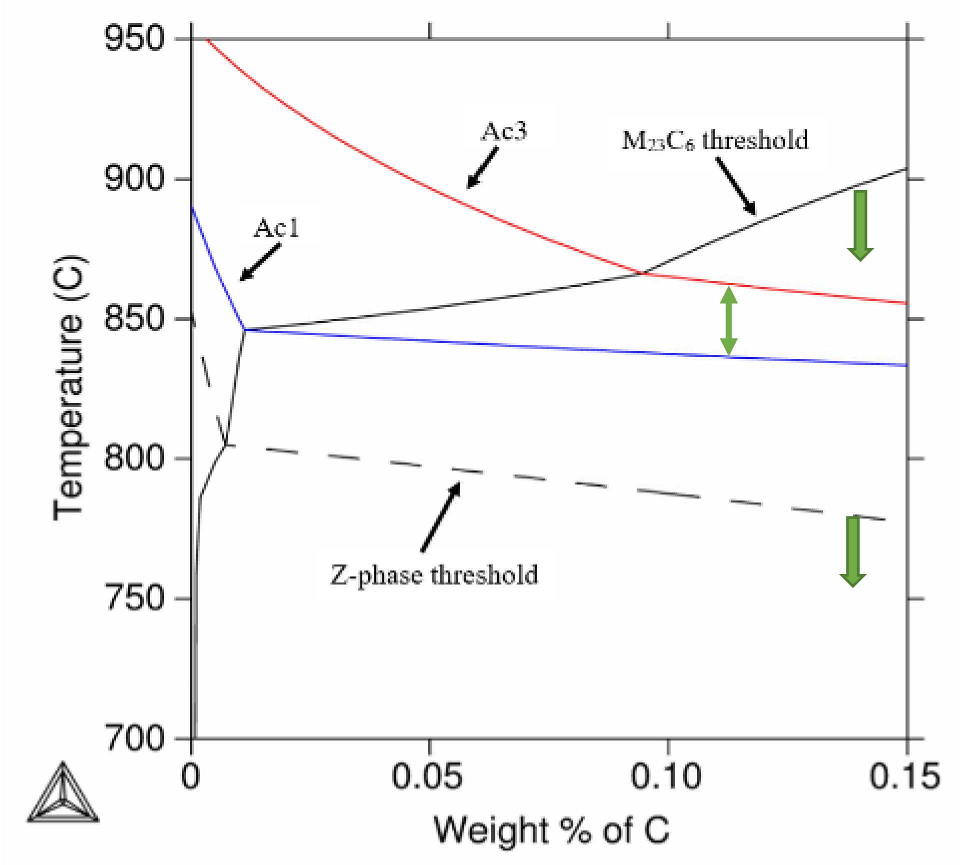
MX Phases

- MX1 and MX2

**Goal**

- **Suppress $M_{23}C_6$ and Z-phases.**
- **Stabilize MX phases.**

# Microstructure




## Threshold Temperatures

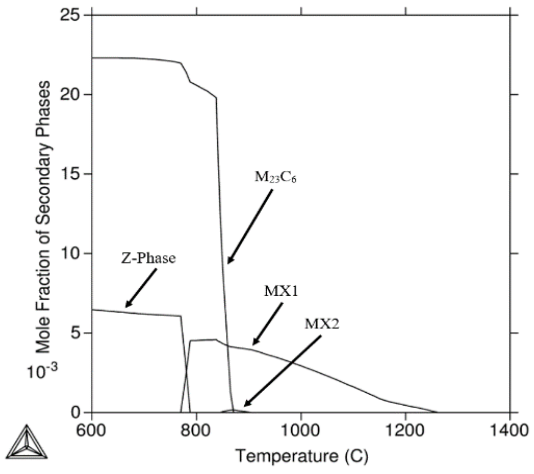
- $M_{23}C_6$ (the lower the better)
- Z-Phase (the lower the better)
- Ac1 Temperature
- Ac3 Temperature

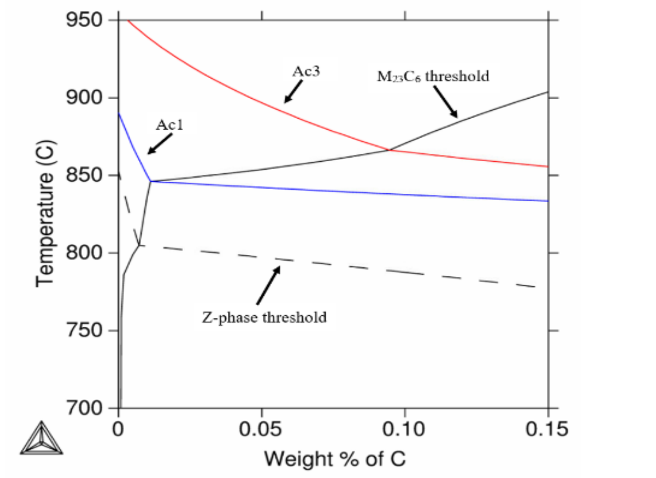
## Goal

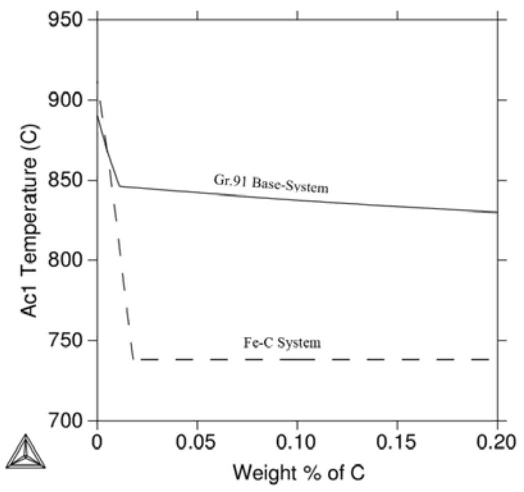
- Change HAZ Microstructure
- Destabilize $M_{23}C_6$
- Destabilize Z phase

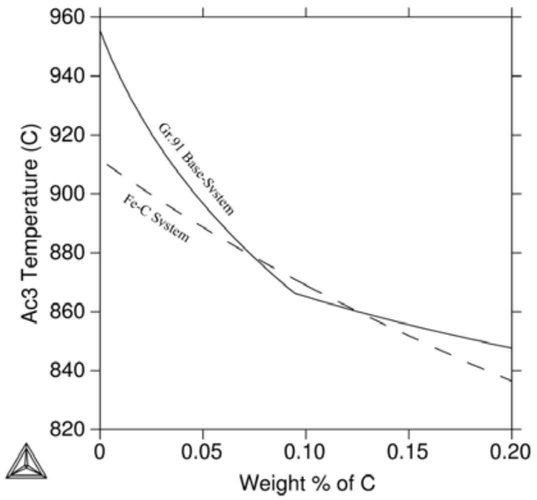
# Baseline Results

- Z phase, M23C6, MX1 and MX2 are the critical phases
- Ac1, Ac3, M23C6 and Z phase thresholds are critical temperatures and may affect the HAZ microstructure.
- There are both good and bad effects of changing C concentrations.
- Alloying elements greatly changed the Ac1 temperature.




***Baseline Composition***

| *Elements* (wt.%) | *Cr* | *C* | *V* | *Nb* | *Mo* | *N* | *Mn* | *P* | *S* | *Si* | *Al* | *Ti* | *Zr* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ASME standard | 7.90-9.60 | 0.06-0.15 | 0.16-0.27 | 0.05-0.11 | 0.80-1.10 | 0.025-0.080 | 0.25-0.66 | 0.025 (max) | 0.012 (max) | 0.18-0.56 | 0.02 (max) | 0.01 (max) | 0.01 (max) |
| Simulation | 8.75 | .10 | .215 | .08 | .95 | .05 | - | - | - | - | - | - | - |

# Part II

- **Steel Compositions**
  - *Role of each element*
    - *Cr, V, Nb, N, Mn, Ni*
  - *Any better compositions?*

# Compositional Changes

**compositional changes:**

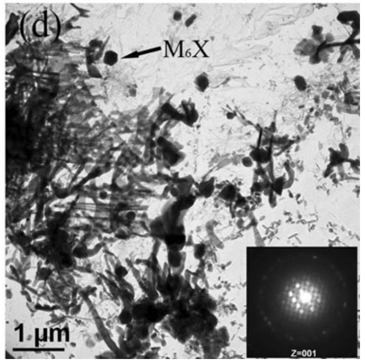
- Cr = 7.0 - 11.0wt.%
- V = .01 - .50wt.%
- Nb = .05 - .25wt.%
- N = .025 - .24wt.%
- Mn = 0.0 - .80wt.%
- Ni = 0.0 - .80wt.%

*Simulation Setup Part 1*

| *Elements (wt.%)* | *Cr* | *C* | *V* | *Nb* | *Mo* | *N* | *Mn* | *Ni* |
|---|---|---|---|---|---|---|---|---|
| ASME standard | *7.90-9.60* | 0.06-0.15 | *0.16-0.27* | *0.05-0.11* | *0.80-1.10* | *0.025-0.080* | *0.25-0.66* | *0.43(max)* |
| Modified Simulation 1 | *7.0-11.0* | *.10* | *.215* | *.08* | *.95* | *.05* | - | - |
| Modified Simulation 2 | *8.75* | *.10* | *.01-.50* | *.08* | *.95* | *.05* | - | - |
| Modified Simulation 3 | *8.75* | *.10* | *.215* | *.05-.25* | *.95* | *.05* | - | - |
| Modified Simulation 4 | *8.75* | *.10* | *.215* | *.08* | *.95* | *.025-.24* | - | - |
| Modified Simulation 5 | *8.75* | *.10* | *.215* | *.08* | *.95* | *.05* | *0.0-.80* | - |
| Modified Simulation 6 | *8.75* | *.10* | *.215* | *.08* | *.95* | *.05* | - | *0.0-.80* |

# Cr’s Role (Exp)

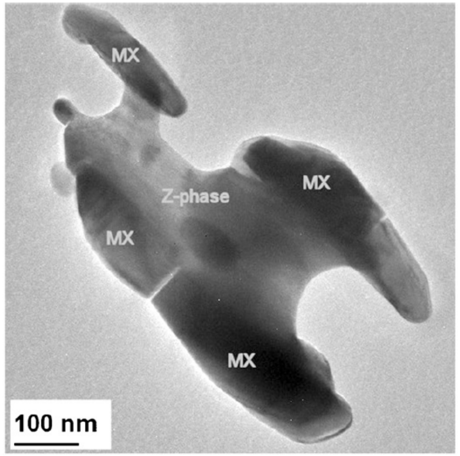
- Prevent oxidation and corrosion
- Formation of $M_{23}C_6$ & Z-Phase
  - $Cr_6C$ forms at lower wt.%, $Cr_{23}C_6$ forms at higher wt.%.
  - More Z-Phase is observed at higher wt.%Cr *(Sawada, K.,2008)*

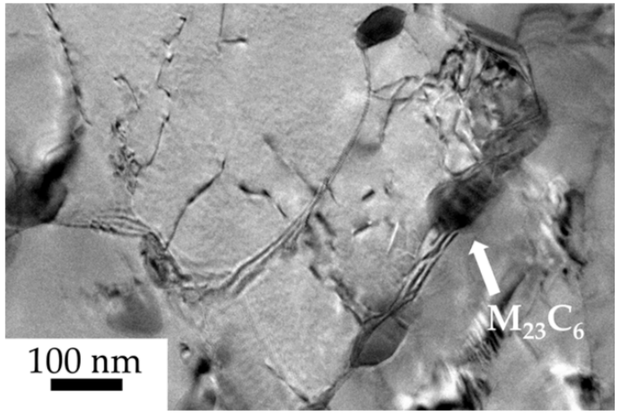



Yong Yang, 2010

2.25wt.%Cr
Gr.22

Danielsen 2009



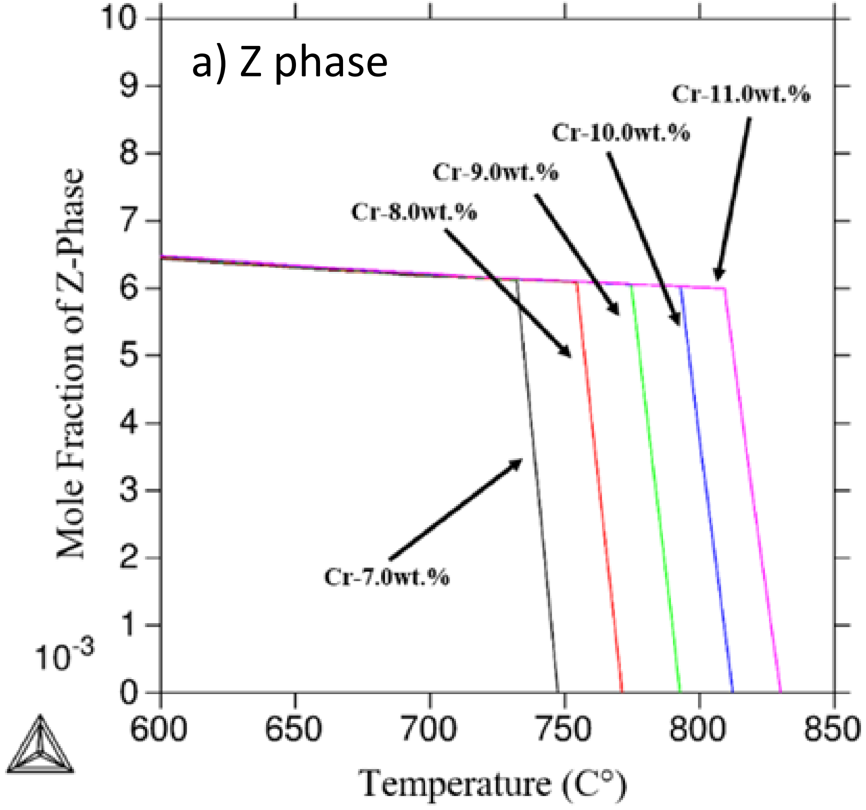



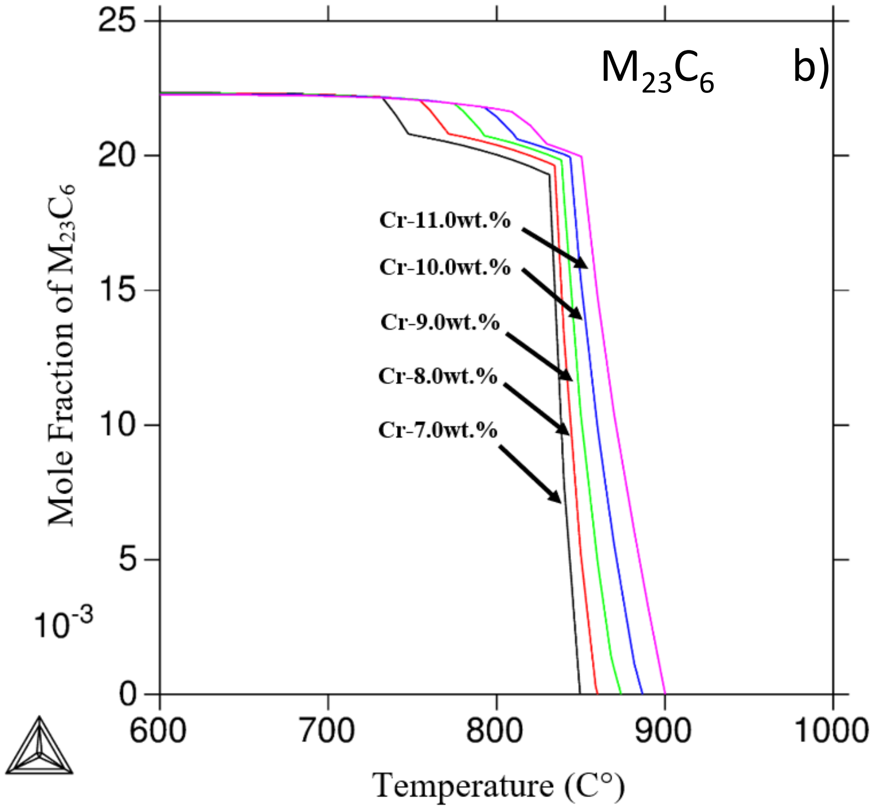

Javier Vivas, 2017

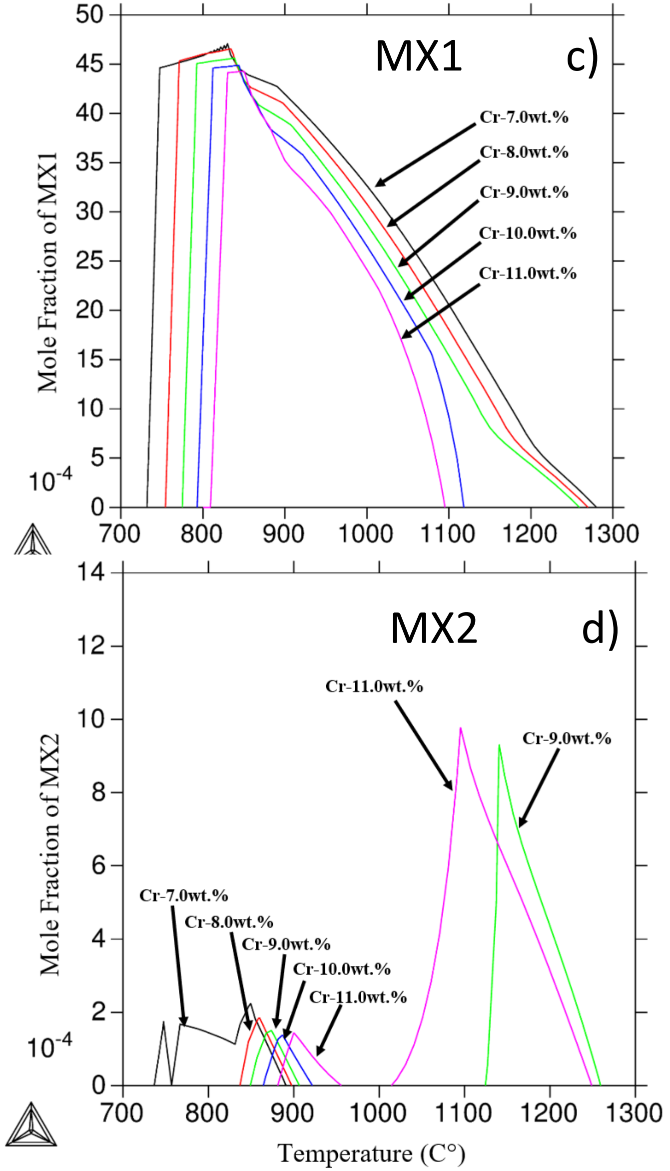
9wt.%Cr
Gr.91

# Cr's Role (Simulation)

## Mainly affect the Z phase formation



# V & Nb's Role (Exp)

***Vanadium (V)***

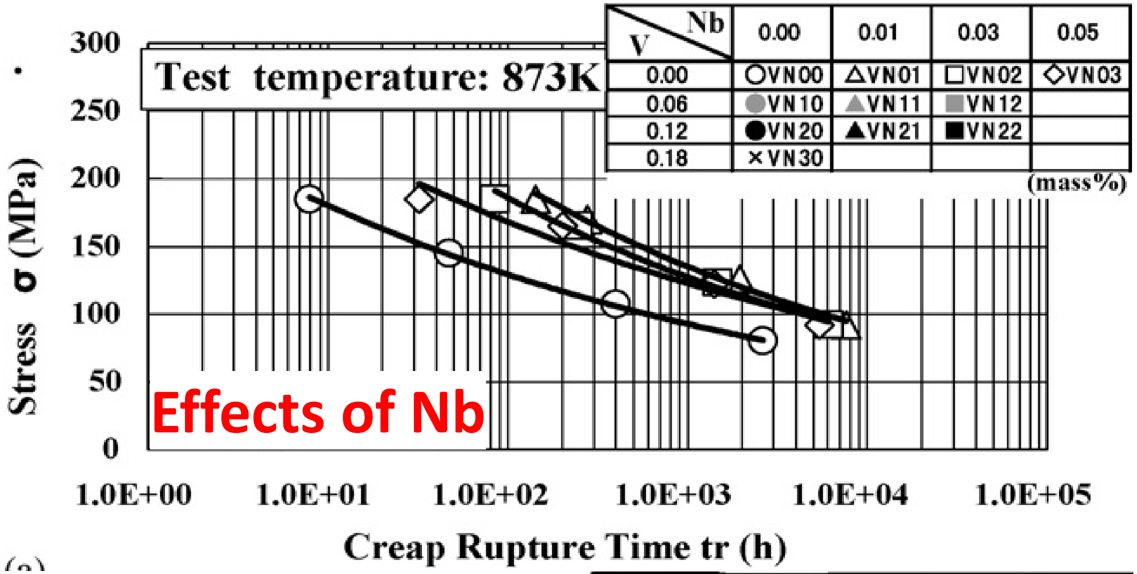
- MX Phase V(C,N) (MX1)

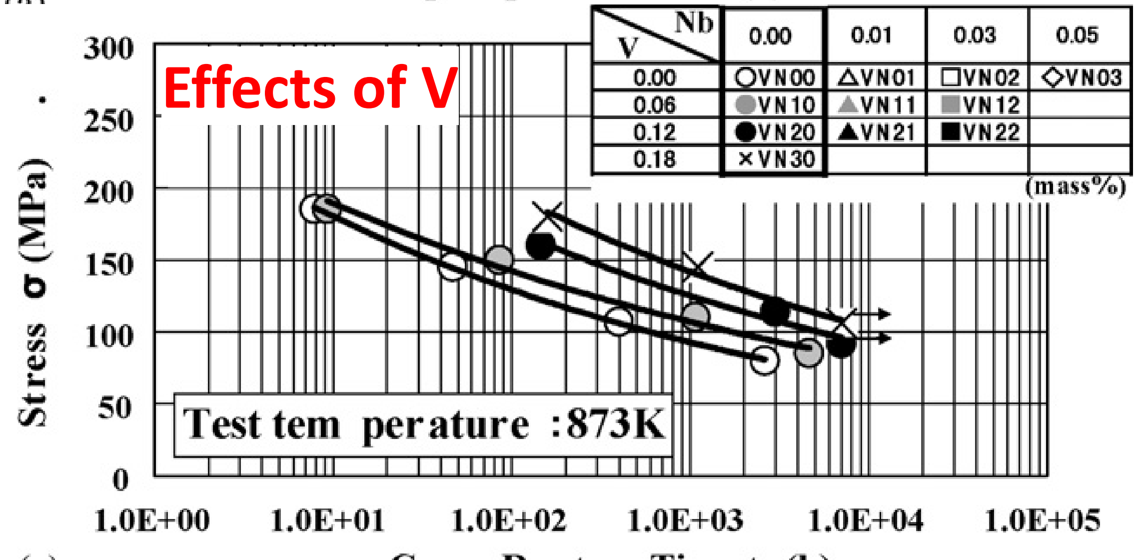
***Niobium (Nb)***

- MX Phase Nb(C,N) (MX2)

***Both***

- increase in creep life and MX density in matrix.
- reduce $M_{23}C_6$ coarsening with increased wt.%V
  - by replacing Mo and W (Yuantao Xu, 2016)



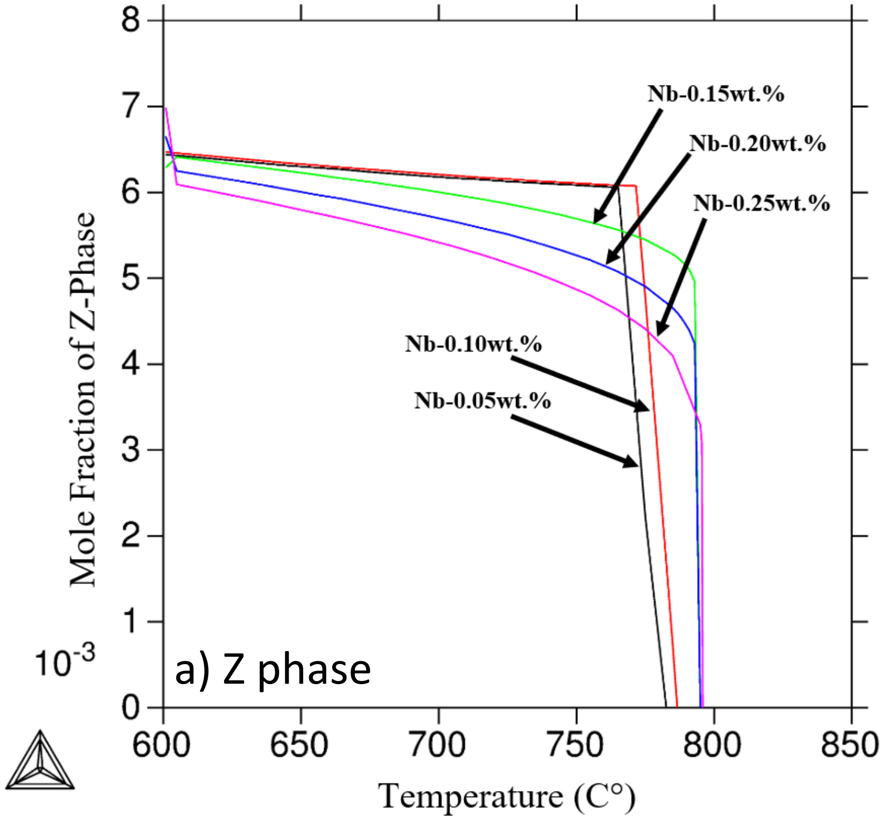

(a)

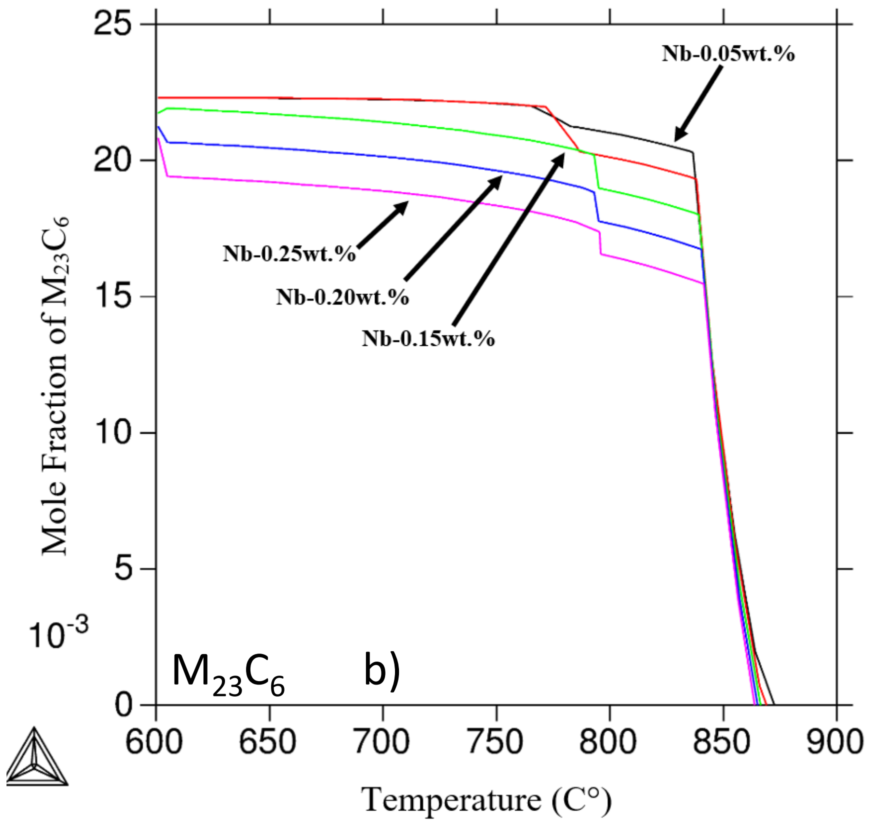
Takashi Onizawa, 2006

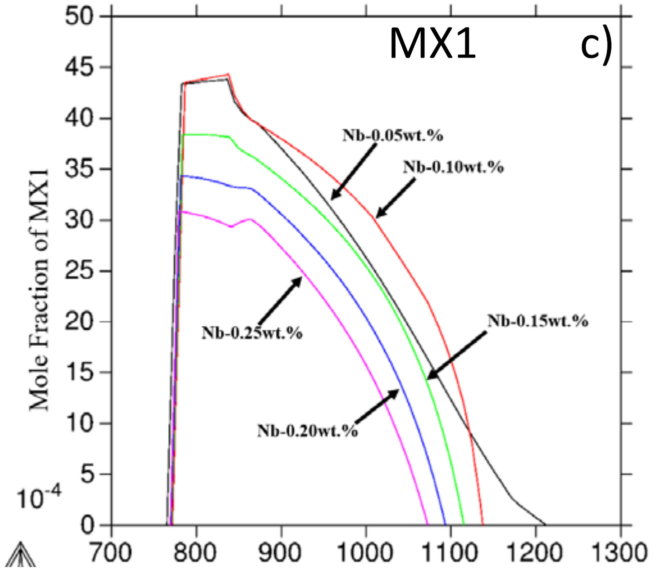
# Nb's Role (Simulation)

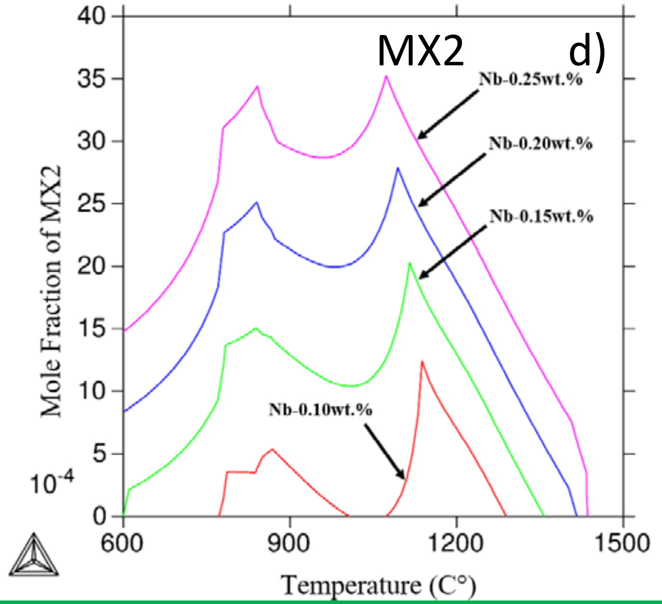
**With the increase of Nb:**

- M23C6 is less stable
- MX2 phases become more stable at lower T



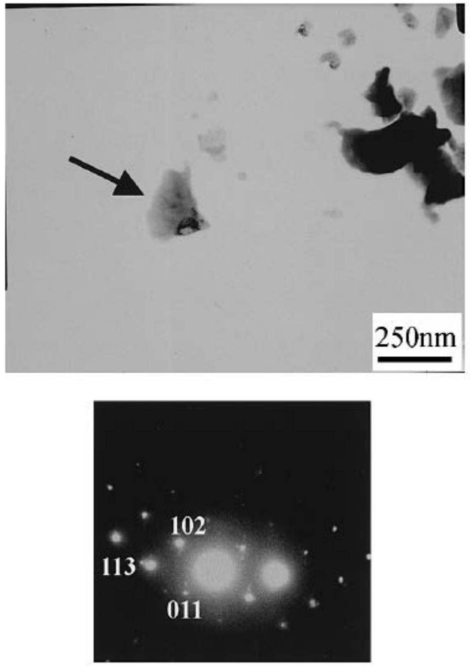
# N's Role (Exp)

## *Nitrogen (N)*

- Nitrogen helps the formation of MX and Z-phase formation

- Increasing N (up to 0.07wt.%N) helps **short-term creep tests** with more MX nitrides *[Vaclav]*

- increasing N is detrimental to For **long-term creep tests** as it helps the precipitation of Z-phase and $Cr_2N$ *[Sawada]*




B=[211]

Fig. 10. TEM image of carbon extraction replica in 7N steel and electron diffraction pattern from Z-phase. Arrow indicates Z-phase. The replica was obtained from specimen crept for 1 187 h at 923 K.

Kota Sawada, 2004

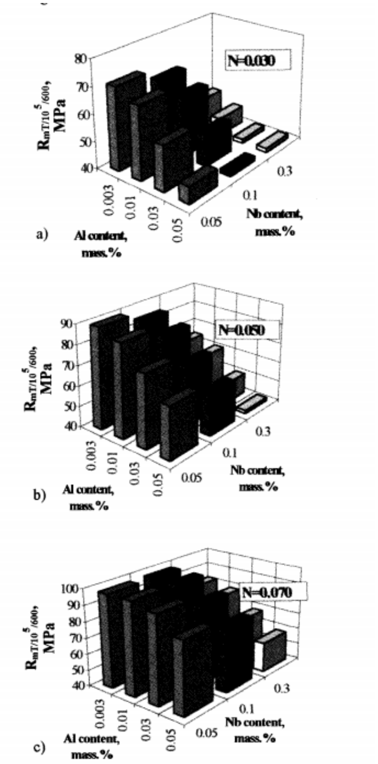
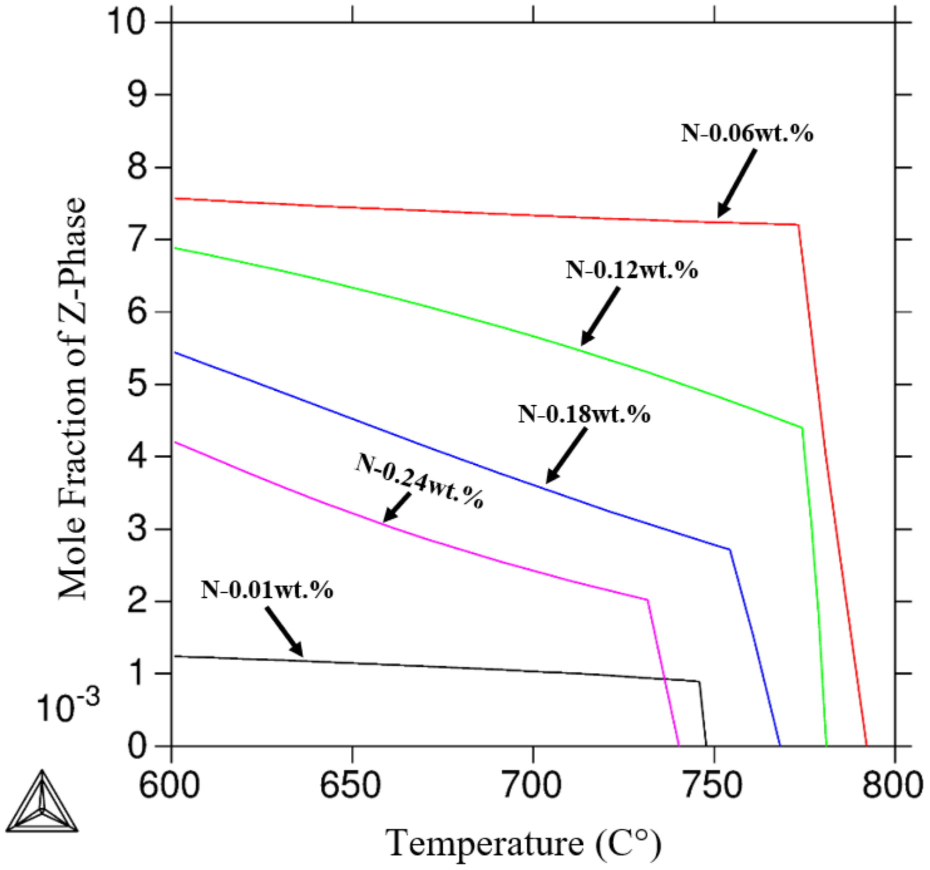


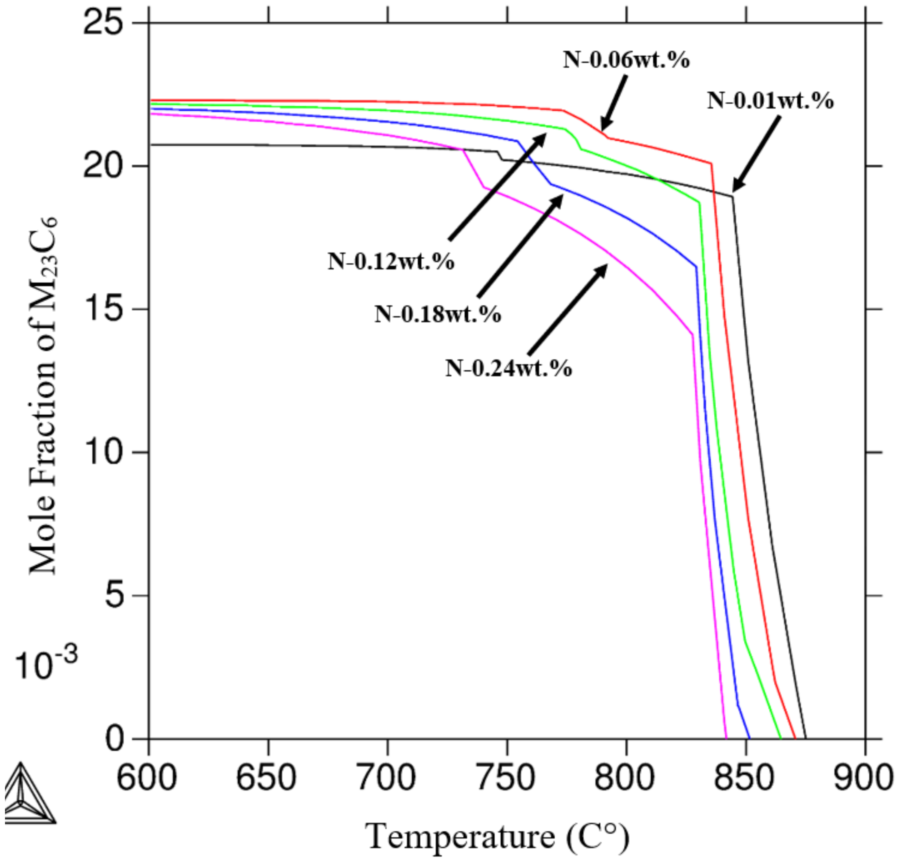

Fig. 1: Creep rupture strength of the model 0.10C-9Cr-1Mo steel in dependence on nitrogen, aluminium and niobium contents
a) for N=0.030%
b) for N=0.050%
c) for N=0.070%

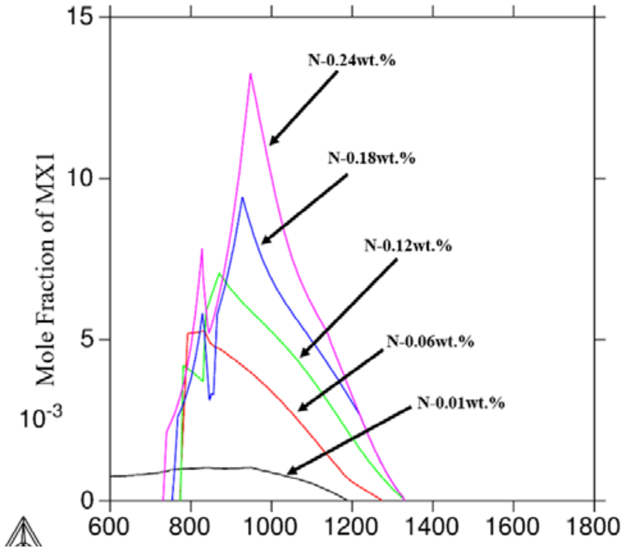
Vaclav Foldyna, 2001

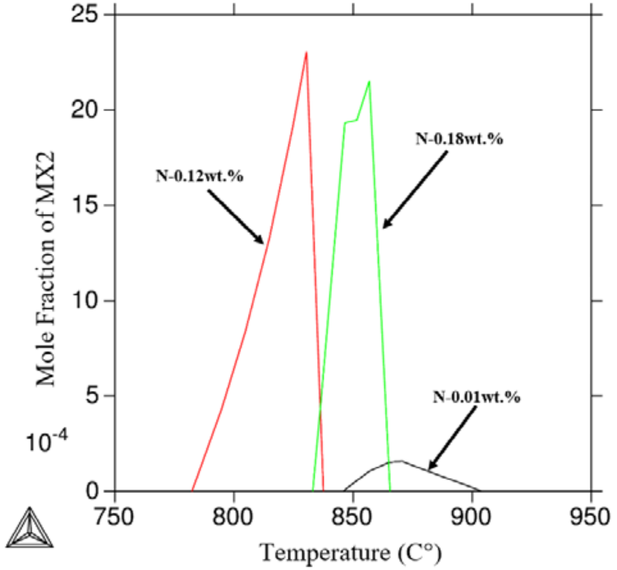
# N's Role (Simulation)

Extremely low N is beneficial to reduce the formation of Z phase
Extra addition of N will cause the formation of detrimental Hcp (Cr2N)



# Compositional Changes – Simulation Setup Part 2

### *Optimized Simulation*

- To give an optimized version of Grade 91 based on results and ***within the parameters***.
  - Min Cr
  - Max V, Nb, Mn, and Ni

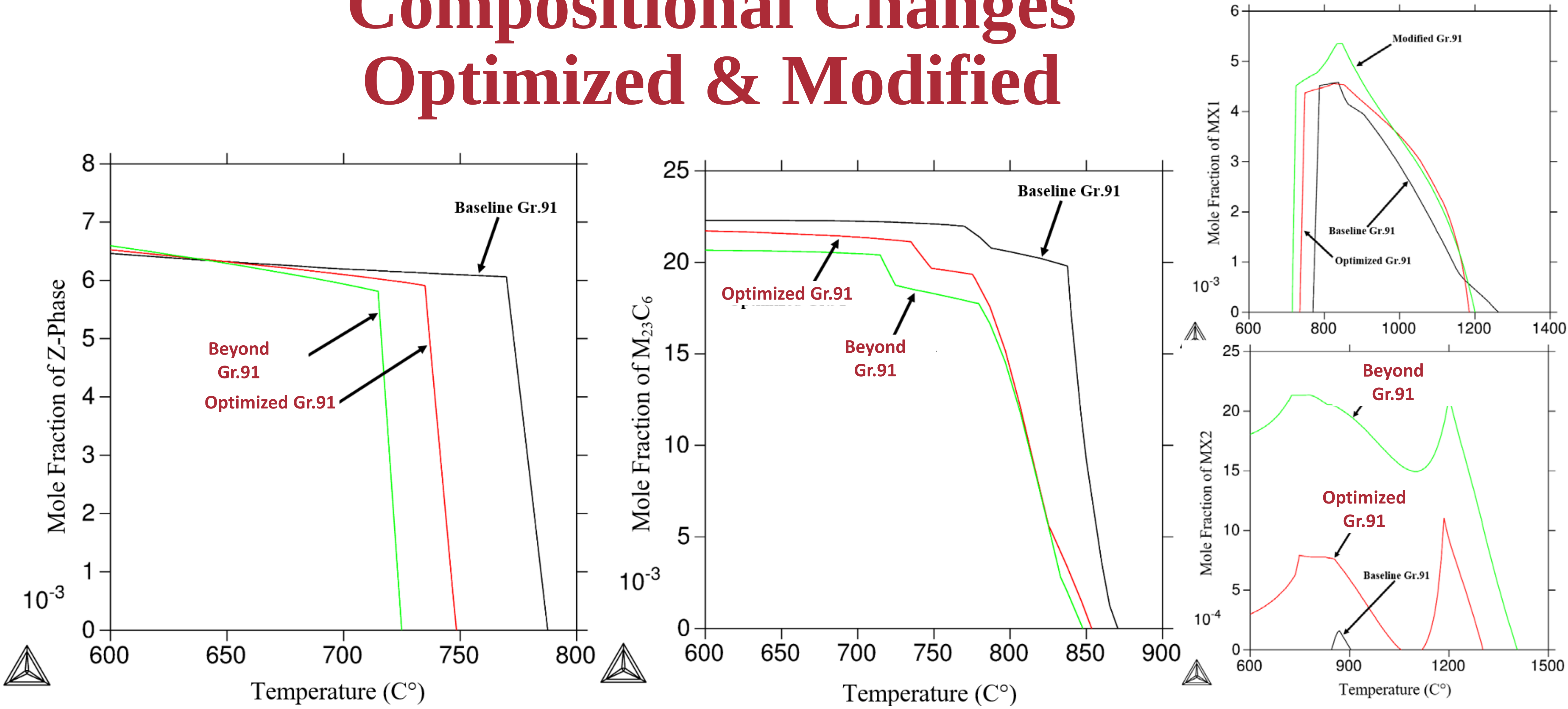
### *Modified Simulation*

- To give an optimized version of Grade 91 based on results and ***outside the parameters***.
- This is to established that certain elements in the system, when increased, suppress certain secondary phases establishing a pattern.

### *Simulation Setup Part 2*

| Elements (wt.%) | Cr | C | V | Nb | Mo | N | Mn | Ni |
|---|---|---|---|---|---|---|---|---|
| ASME standard | 7.90-9.60 | 0.06-0.15 | 0.16-0.27 | 0.05-0.11 | 0.80-1.10 | 0.025-0.080 | 0.25-0.66 | 0.43(max) |
| Baseline Simulation | 8.75 | .10 | .215 | .08 | .95 | .05 | - | - |
| Optimized Gr.91 | 7.9 ↓ | .10 | .27 ↑ | .11 ↑ | .95 | .05 | .66 ↑ | .43 ↑ |
| Beyond Gr.91 | 7.9 ↓ | .11 | .40 ↑ | .20 ↑ | .95 | .05 | .66 ↑ | .43 ↑ |

# Compositional Changes Optimized & Modified



# Part III

- **Experimental Investigation**
  - *Processing Parameter Design*
  - *Real creep test*
  - *Microstructure analysis*

# Conclusions

From the optimized version of Gr.91:

- V & Nb = Increase MX
- Mn & Ni = decrease Ac temperatures

- It is clear that V & Nb play an important role in the stability of MX phases, however it decreases the overall ductility and toughness of the steel due to previous works.
- Decreasing Cr seems to be beneficial for the creep resistance of Gr. 91 alloy, however, this can affect other properties like oxidation resistance.

# Acknowledgements

*Department of Energy (DOE)*

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- Program manager Karol Schrems

*Ohio State University (OSU)*

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