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Award No. DE-FEOO08719

Synergistic Computational and Microstructural Design of Next-Generation High-Temperature Austenitic Stainless Steels

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Department of Material Science and Engineering
Department of Mechanical Engineering
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Team's past work

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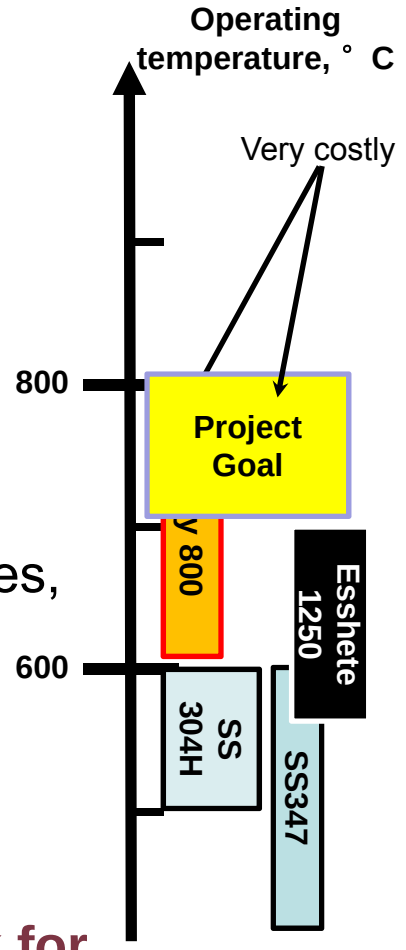
- Microstructure – property relationships in low stacking fault energy austenitic steels (Karaman)
- Microstructure design in materials that demonstrate deformation twinning and martensitic transformation, texture and grain size control (Karaman)
- Integrated computational materials engineering (Arroyave)
- Computational materials design using genetic algorithms and multi-objective design optimization, data mining (Arroyave)
- Combined computational and experimental design of materials that show twinning and martensitic transformation (examples: TRIP steels, high temperature shape memory alloys) (Arroyave, Karaman)

❖ Project Goal

- Design new austenitic stainless steels (ASS) for advanced ultra supercritical combustion coal-fired power systems
  - ✓ High temperature strength
  - ✓ High ductility
  - ✓ Good creep resistance
  - ✓ Good high temperature oxidation/corrosion resistance
- Design of micro-alloying additions, heat treatment schedules, and microstructure
  - Cost-effective alternatives to Ni-base superalloys
  - Higher-temperature alternatives to ferritic steels
- **Develop a robust ICME design/optimization framework for high temperature ASS.**



❖ Computational/Microstructural Design Framework
TRIP Steel Design

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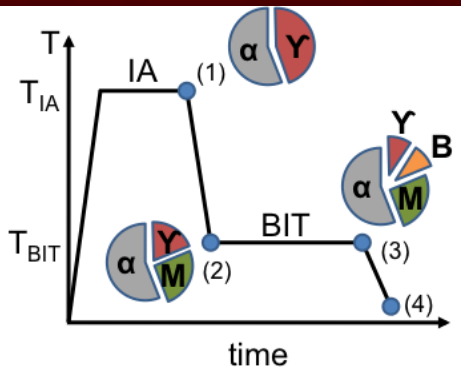
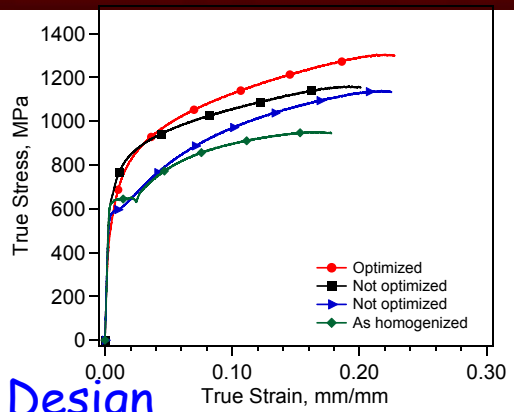
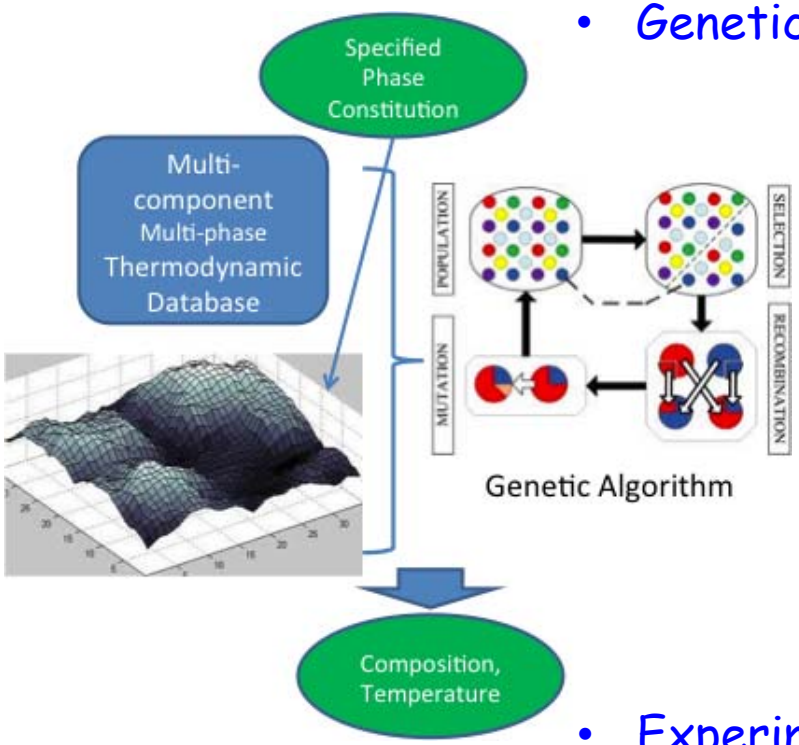
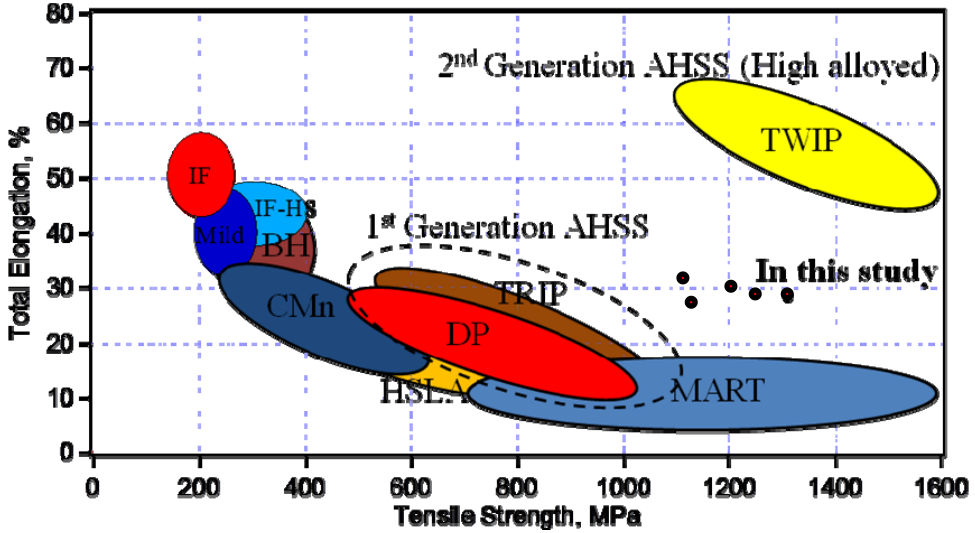


- Heat Treatment Design

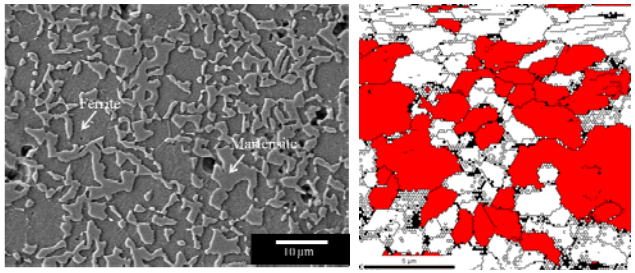


- Genetic Algorithm-based Alloy Design





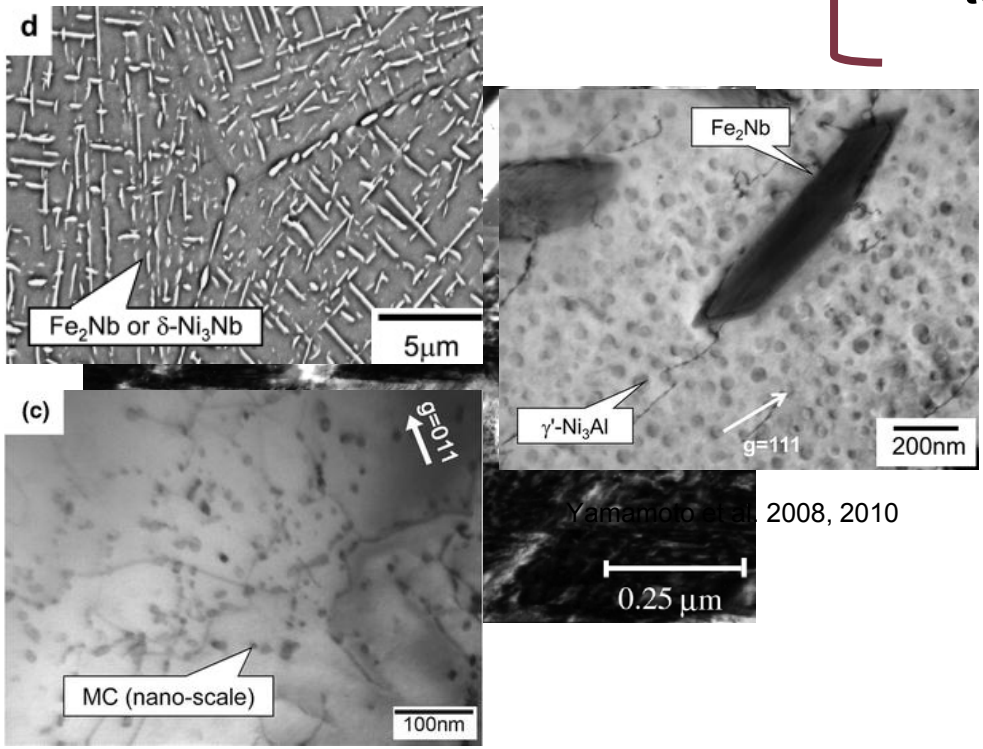
- Experimental Characterization



❖ Approach

Alloy + Microstructure Design

- Austenitic structure
- High density of low energy grain boundaries or nano-twin boundaries
- Nano-scale precipitates, intermetallics, laves phases stable at high temperature

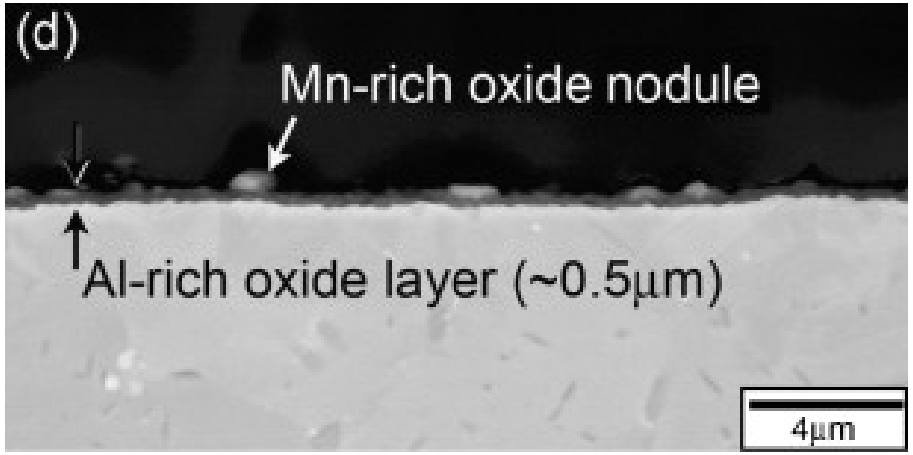


Yamamoto et al. 2008, 2010

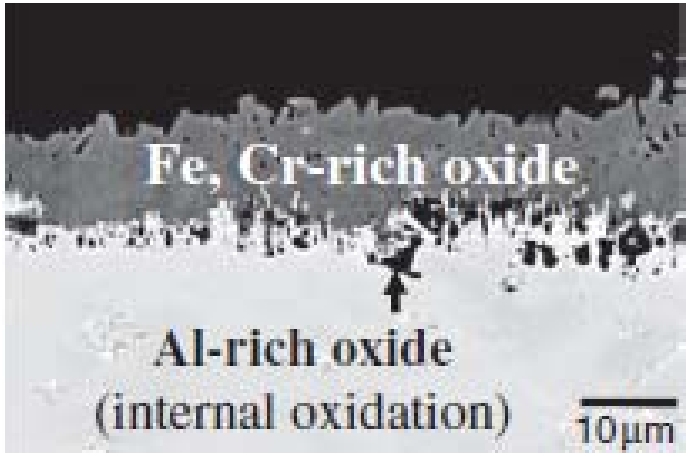
❖ Approach

Alloy + Microstructure Design

- Austenitic structure
- High density of low energy grain boundaries or nano-twin boundaries
- Nano-scale precipitates, intermetallics, laves phases stable at high temperature
- Formation of alumina surface oxide



Yamamoto et al. 2009



Yamamoto et al. 2007

❖ Approach

Alloy + Microstructure Design

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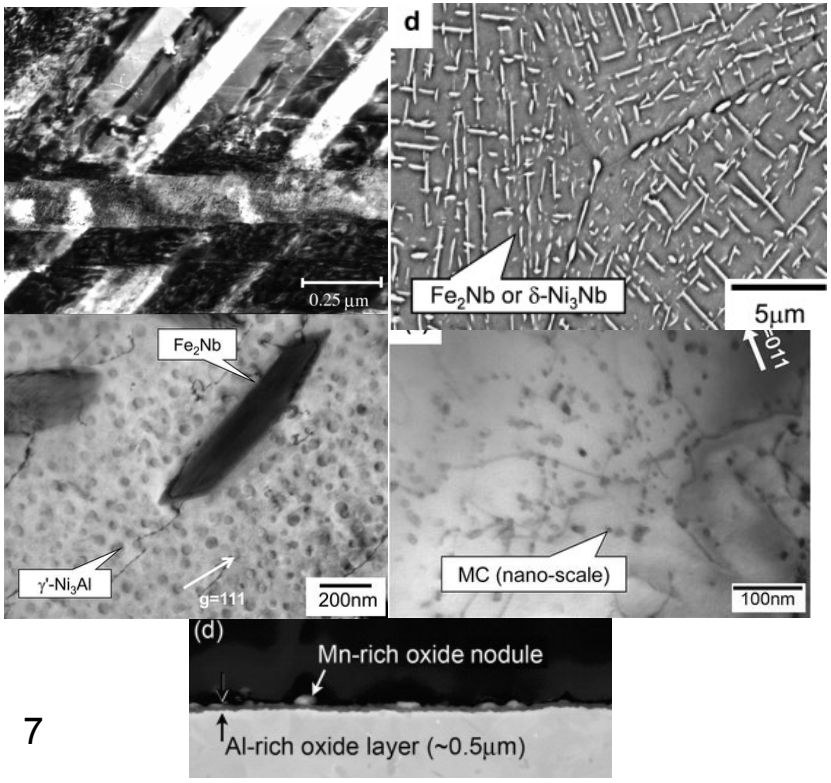
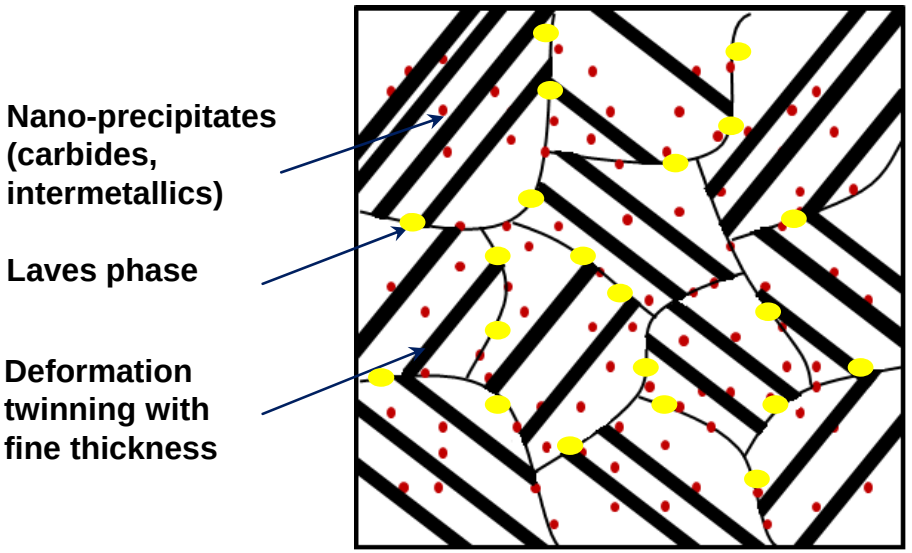
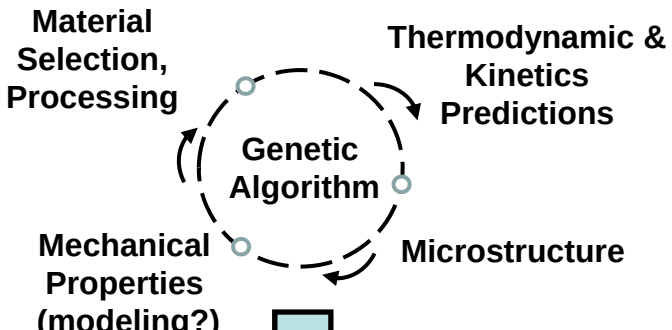


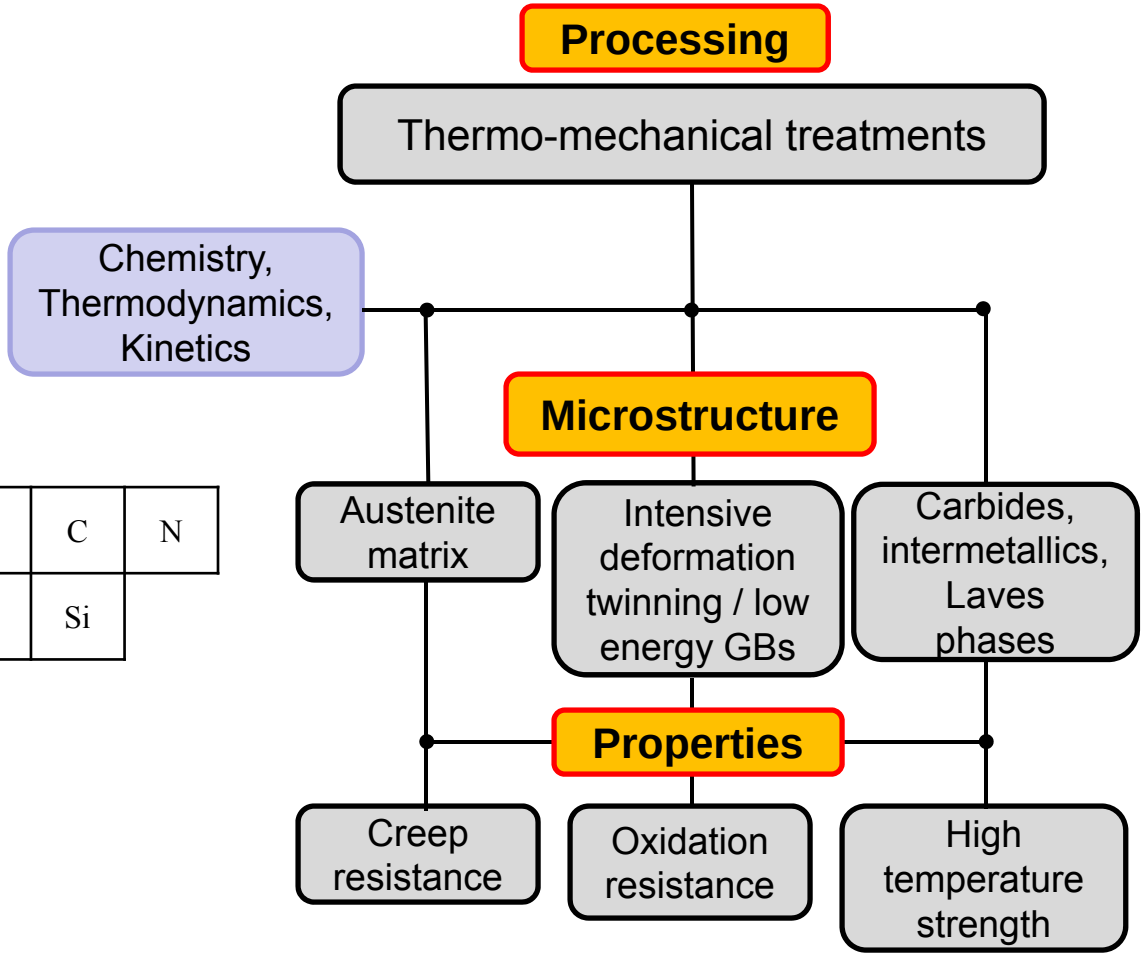


❖ Strategy--Computational Alloy Design

- ICME---Integrated Computational Materials Engineering
- Multi-objective optimization through Generic Algorithms



												B	C	N			
												Al	Si				
Ti	V	Cr	Mn		Co	Ni	Cu										
Zr	Nb	Mo															
	Ta	W															



❖ Strategy--Computational Alloy Design

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- Optimization of micro-alloying additions for desired microstructure and given performance criteria (?)
  - Single bulk phase, i.e. austenite
  - Lower SFE and enhanced twinning ability
  - Alumina formation
  - Dissolvable carbides/carbonitrides (welding issue?)
  - MC instead of $M_{23}C_6$
  - High temperature intermetallics and laves phases
  - Very fine particles (control MC size with Nb, Ti, Zr, V, etc., nucleation at dislocations and twin boundaries)
- Prediction of twinning ability
- Transformation kinetics of precipitate phases

❖ Strategy--Microstructure Design

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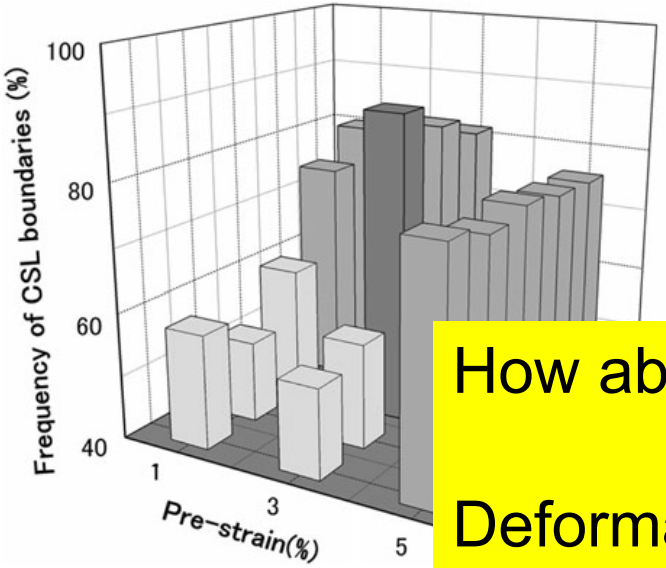
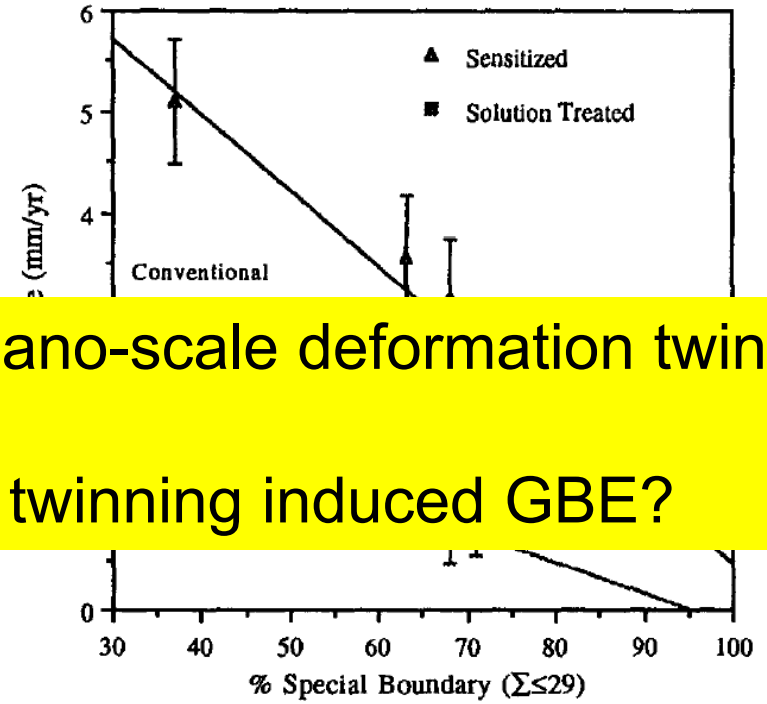
- Twinning induced Grain Boundary Engineering (GBE)



Effects of pre-strain and annealing temperature on the frequency of CSL boundaries in thermomechanically processed 321 austenitic stainless steel, cited from Kurihara et al.



How about nano-scale deformation twins?

Deformation twinning induced GBE?

References

Lin, P., G. Palumbo, U. Erb, and K. Aust, Scripta Materialia, 1995. 33(9): p. 1387-1392.

Kurihara, K., H. Kokawa, S. Sato, Y. Sato, H. Fujii, and M. Kawai, Journal of Materials Science, 2011: p. 1-6.

❖ Strategy--Microstructure Design

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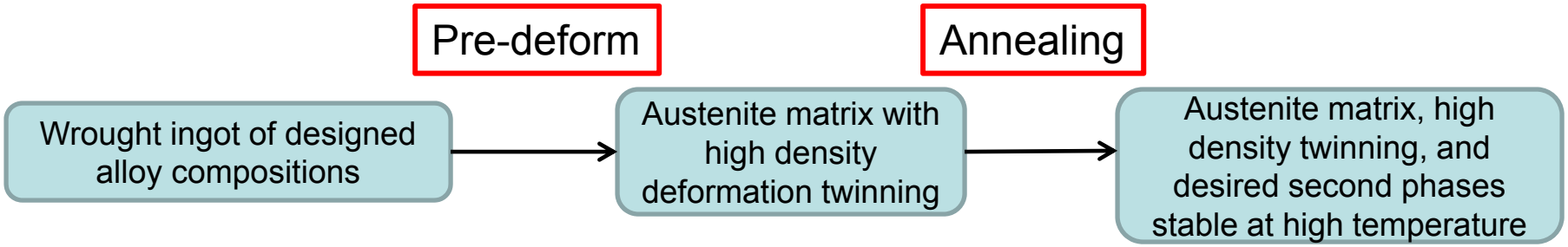
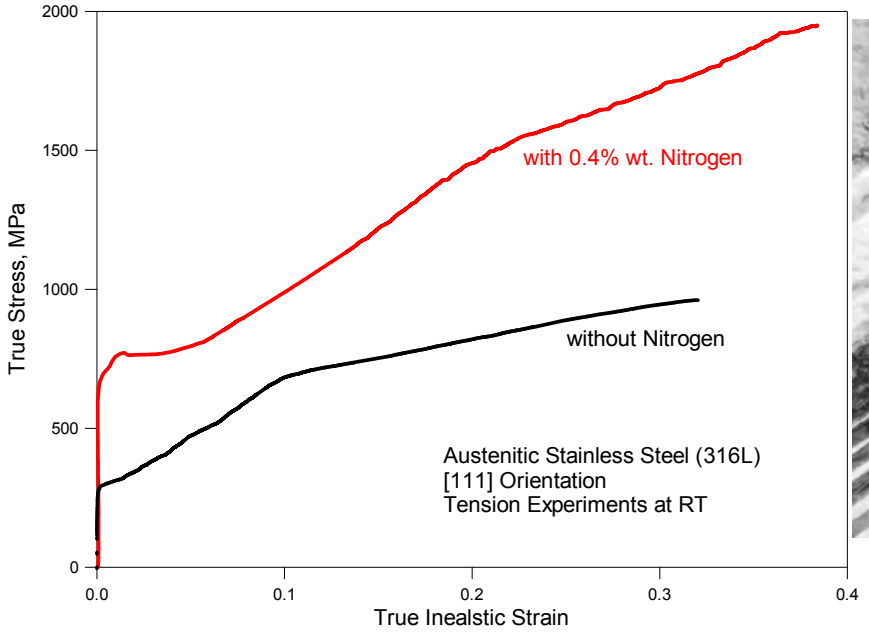
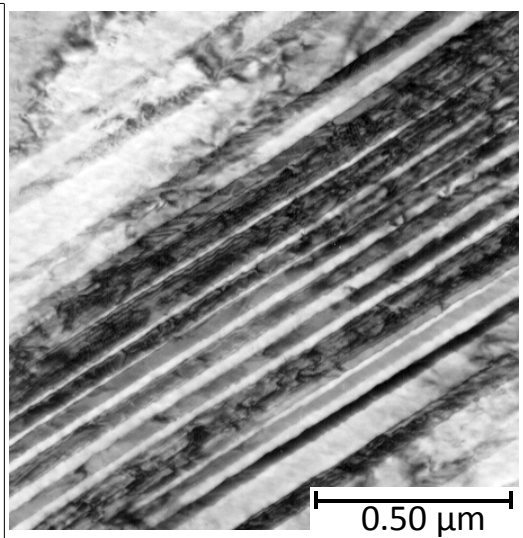
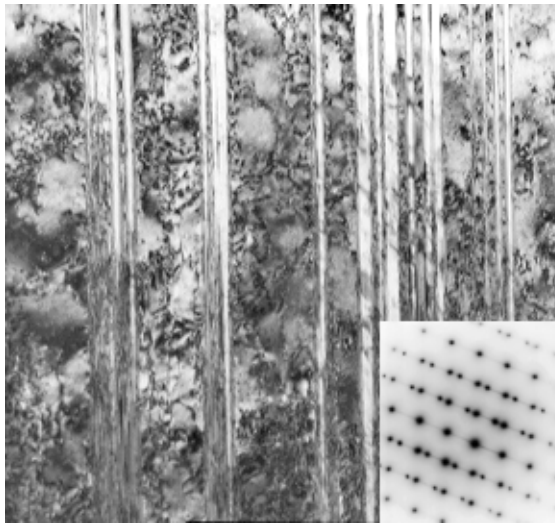
- Simple thermo-mechanical processing







With Nitrogen
15% strain



Without Nitrogen
15% strain

❖ Questions and Challenges

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- Fundamental study of recovery and recrystallization (ReX) of deformation twins in low SFE steels in the presence of various densities of dislocations.
  - In single crystalline Fe-Mn-C and 316L SS
  - In baseline and designed polycrystals
- Role of in-situ carbides and nitrides of Nb, Ta, V, W, Cr during recovery and ReX in the presence of deformation twins? What is the optimum thermo-mechanical processing path?
- Control of particle size and distribution with micro-alloying control
- Multi-objective alloy optimization using genetic algorithms
- The role of deformation twins, laves phases, nano carbides, and intermetallic particles on creep and stress rupture behavior of designed steels.

❖ Year 1 Milestones

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Proposed Milestones	Year 1											
	Quarter 1			Quarter 2			Quarter 3			Quarter 4		
	08/2012	09/2012	10/2012	11/2012	12/2012	01/2013	02/2013	03/2013	04/2013	05/2013	06/2013	07/2013
1.1 Fabrication and wrought processing of baseline material												
1.2 Uncertainty quantification of thermodynamic database												
1.3 Investigation of phase stability of carbides												
1.4 Study of the nano-precipitation behavior of the baseline material												
1.5 Fabrication of single crystalline samples												
1.6 Investigation of phase stability of intermetallic strengthening phases												
1.7 Development of Phase 1 of Genetic Algorithm												
1.8 Alloy optimization GA and phase stability of strengthening phases												
1.9 Room temperature microstructural and mechanical characterization of the polycrystalline baseline material												
1.10 Room temperature microstructural and mechanical characterization of the baseline single crystalline material												
1.11 High temperature mechanical response of both single and polycrystalline baseline material												
1.12 Study of oxidation behavior of the baseline material in air and steam												
1.13 Development of master phase stability maps for strengthening phases with different Cr contents												
1.14 Study of corrosion response of the baseline material												
1.15 Characterization of creep and creep rupture behavior of the poly and single crystalline baseline material												

❖ Materials studied so far

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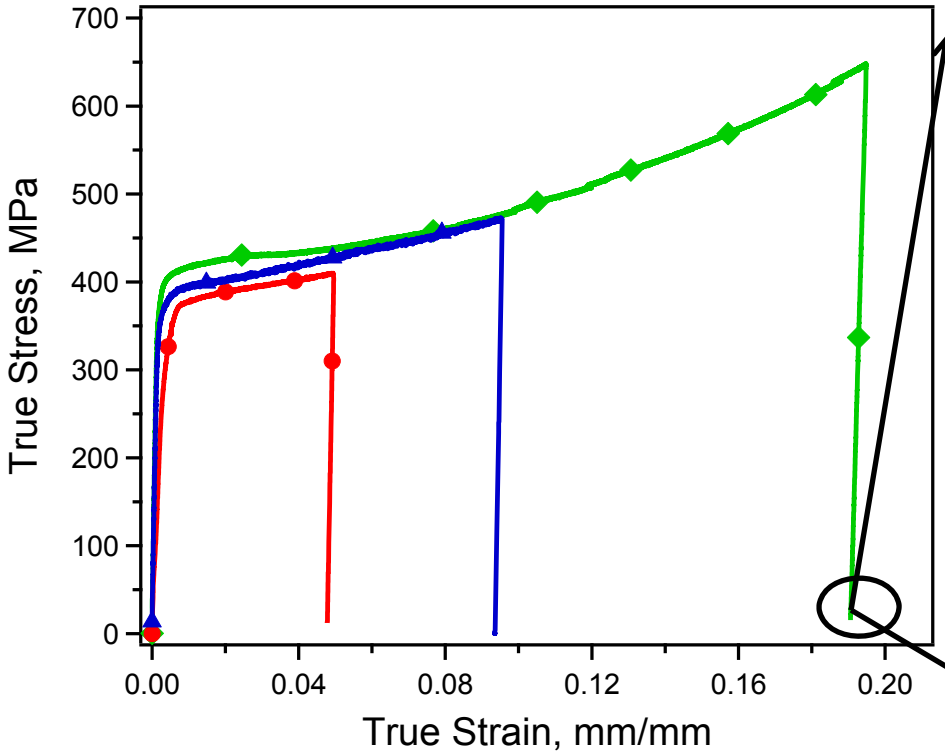
		Fe	Ni	Cr	Mn	Nb	Si	Al	Ti	Mo	V	C	N	B
Single crystals*	**Fe-Mn-C**	Ba.			13							1.1		
	316 LN	Ba.	11.8	17.7	1.1		0.44			2.3		0.08	0.2	
Poly crystals	**Alloy 1****	Ba.	20	14	2	0.86	0.15	2.5		2.5		0.08		0.01
	Alloy 2***	Ba.	12	14	10	1	0.2	2.5	0.3	2.5	0.5	0.08	0.01	
	Alloy 3***	Ba.	17	14	10	1	0.2	2.5	0.3	2.5	0.5	0.08	0.01	

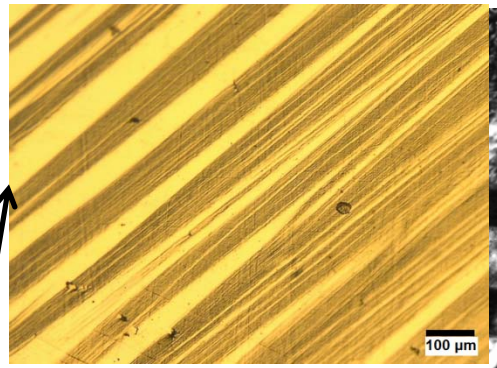
*: For single crystals, [111], [110] and [123] orientation have been grown
**: Vacuum induction melted and hot forged
***: Vacuum arc melted

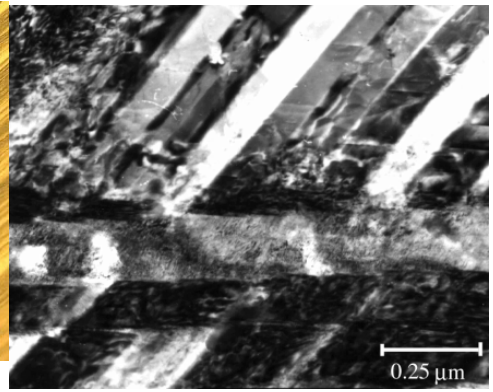
- Rationale for the selection of Alloys 1 through 3:
  - Need to validate the predictive power of thermodynamic databases and models developed (oxidation, twinning ability). Selected based on the material developed by Yamamoto et al., at ORNL
  - Form alumina at the surface instead of Cr_2O_3
  - Austenite structure that can exhibit deformation twinning
  - Small Laves phase and NbC carbide particles for increased alloy strength and creep resistance
- Issues encountered
  - Formation of undesired AlN
  - Dual phase structure, BCC and FCC
  - Relatively large NbTiC

❖ Twinning in Single Crystals

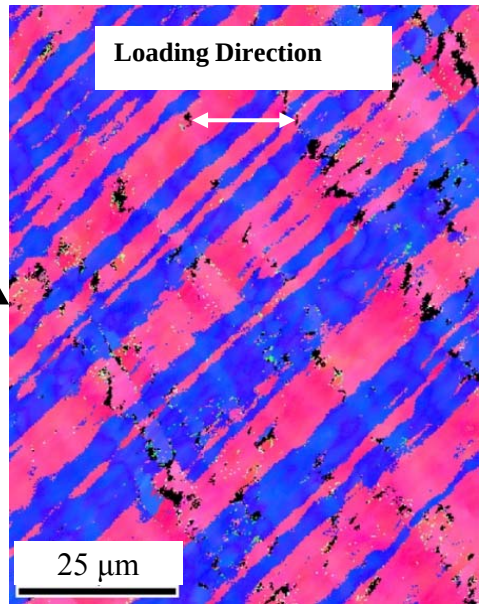
Fe-Mn-C, [111] single crystals, Tension at RT

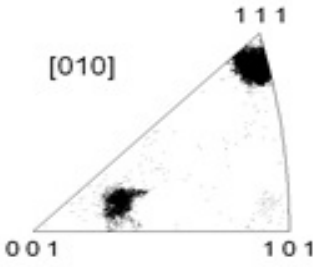






Large volume fraction of deformation twins, dislocation density is relatively low

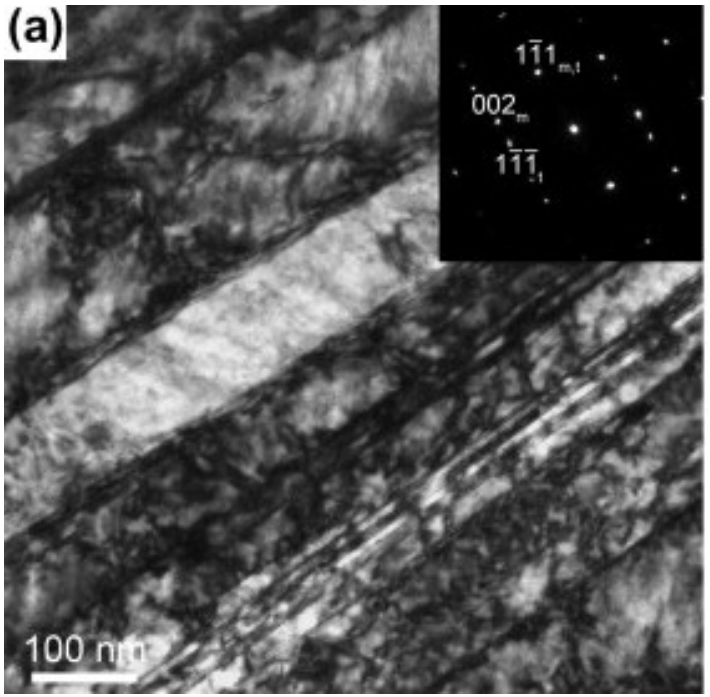




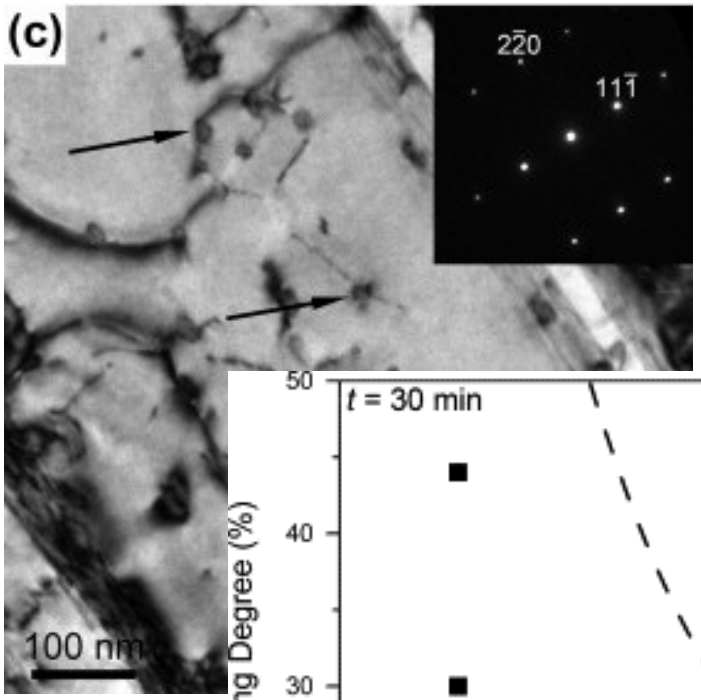
What is the influence of these twins in recrystallization behavior?

❖ Thermal stability of deformation twins

Fe-24Mn-0.7C-1Pd

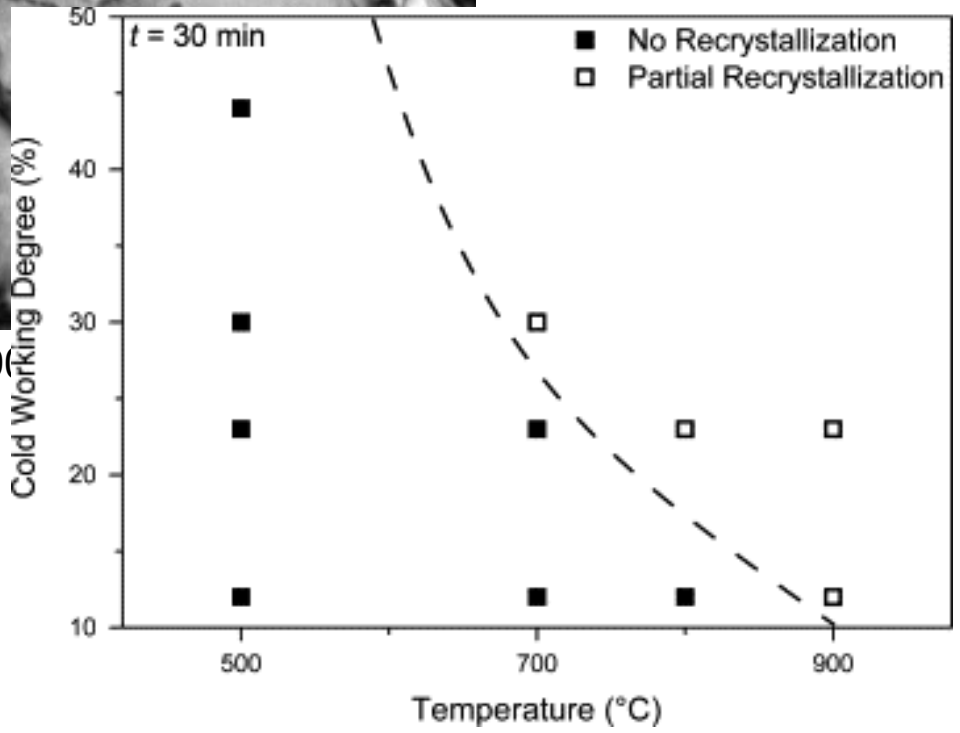


23% CW, 700°C – 30 min annealed



12% CW, 9

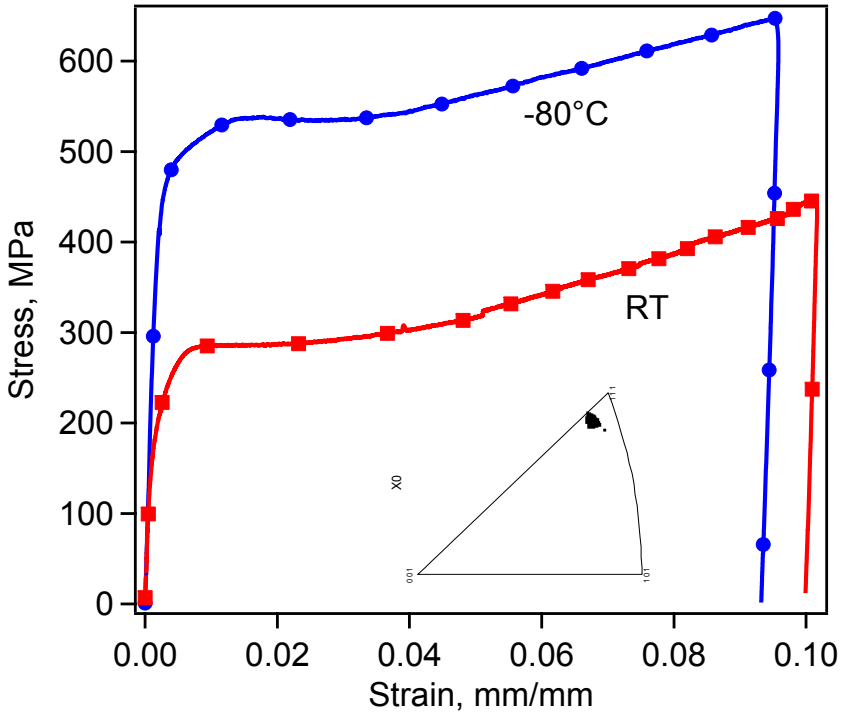
Pd-rich particles

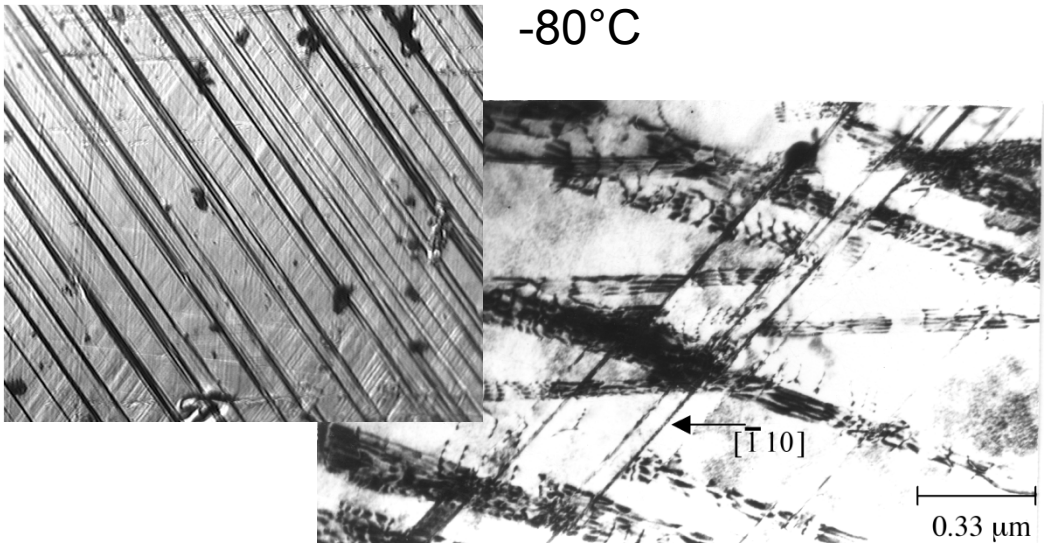


Schinhammer et al, Acta Mat. 2012

❖ Twinning in Single Crystals

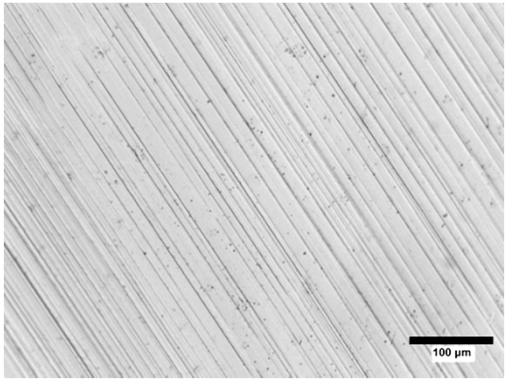
316 LN SS, [111] orientation, 10% pre-deformed



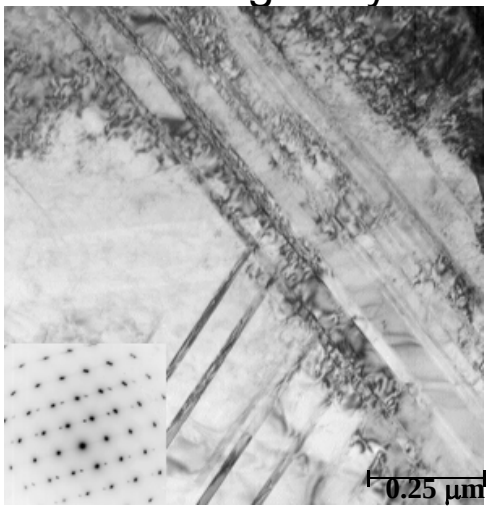


316L SS single crystal

Room temperature



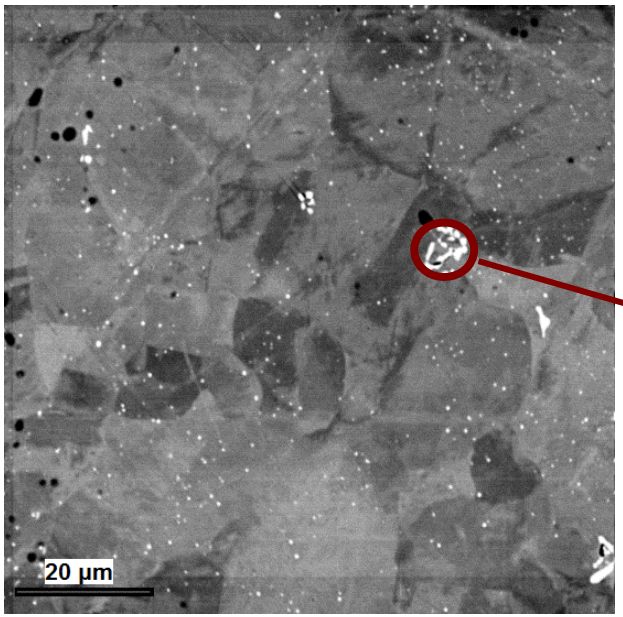
Deformation twins?



- Deformation twins exist
- Increasing nitrogen content first increases and then decreases SFE.

❖ Phase stability, Alloy 1

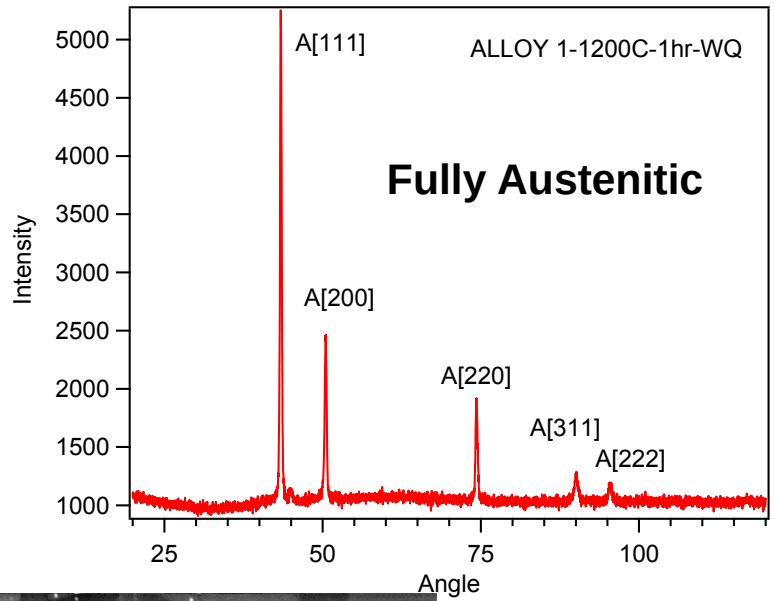
wt%	Fe	Ni	Cr	Mn	Nb	Si	Al	Mo	C	B
Alloy 1	Ba.	20	14	2	0.86	0.15	2.5	2.5	0.08	0.01



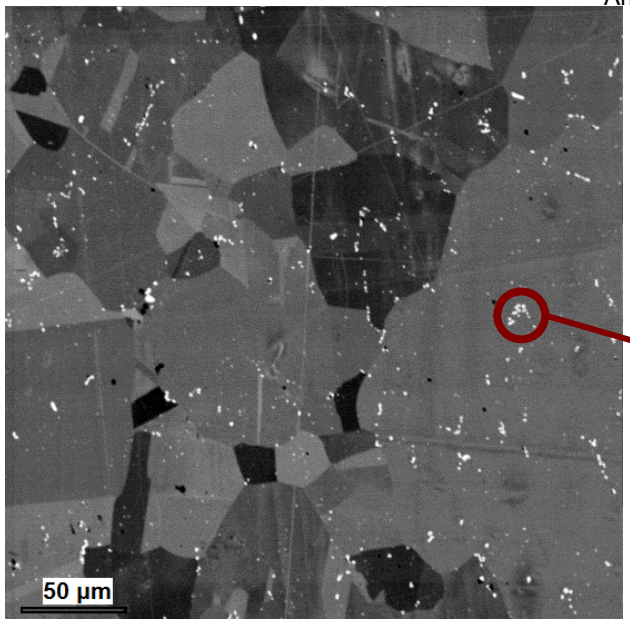
Grain size ~ 10 µm
Particle volume fraction ~ 5%

NbC

As-Forged



- NbC clusters are clear after forging
- 1200°C, 1 hr heat treatment did not dissolve NbC, but the clusters are smaller and less
- Predictions suggest to dissolve them above 1300°C



Grain size ~ 60 µm
Particle volume fraction ~ 4%

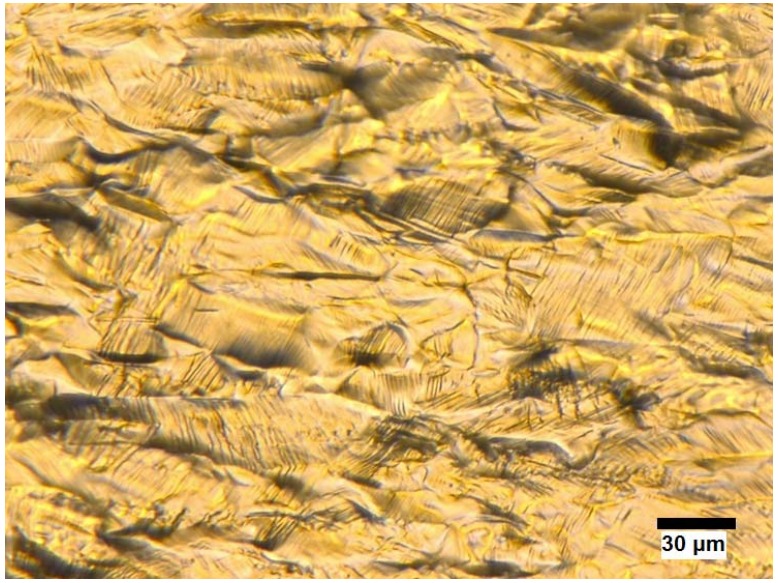
NbC

1200°C, 1 hr

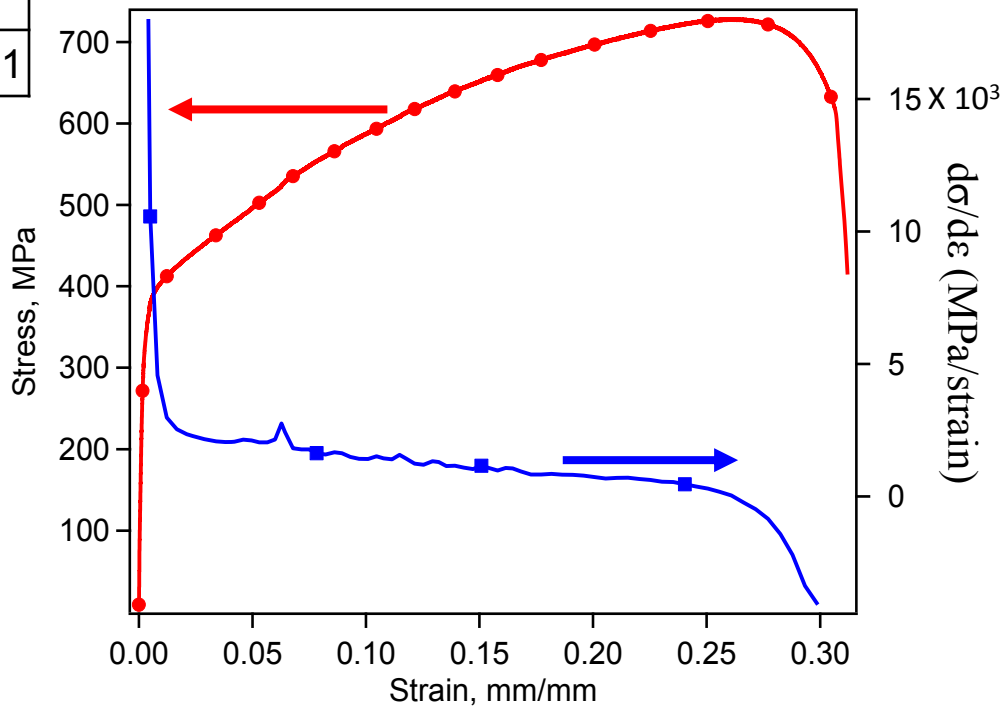
❖ Deformation Behavior, Alloy 1

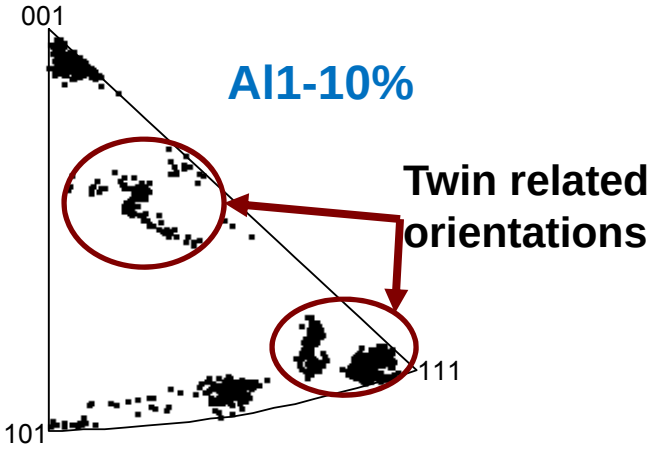
wt%	Fe	Ni	Cr	Mn	Nb	Si	Al	Mo	C	B
Alloy 1	Ba.	20	14	2	0.86	0.15	2.5	2.5	0.08	0.01

Alloy 1, wrought condition, Until failure



Tension direction



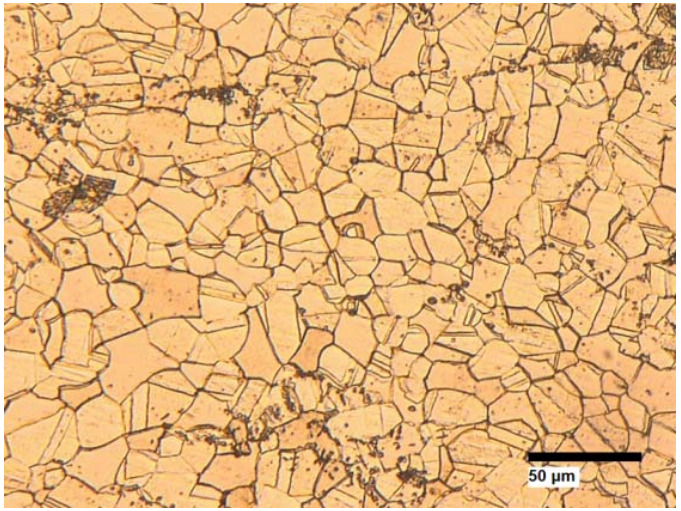


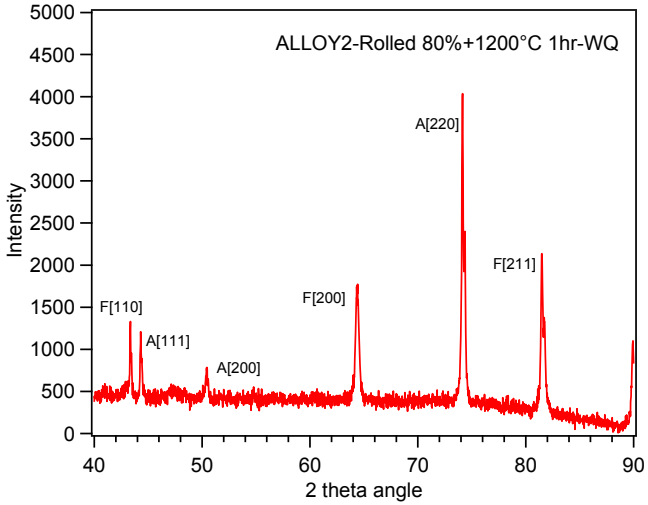
EBSD and Texture analysis are ongoing
Experimental and computational work will continue on this polycrystalline alloy

❖ Phase stability, Alloy 2

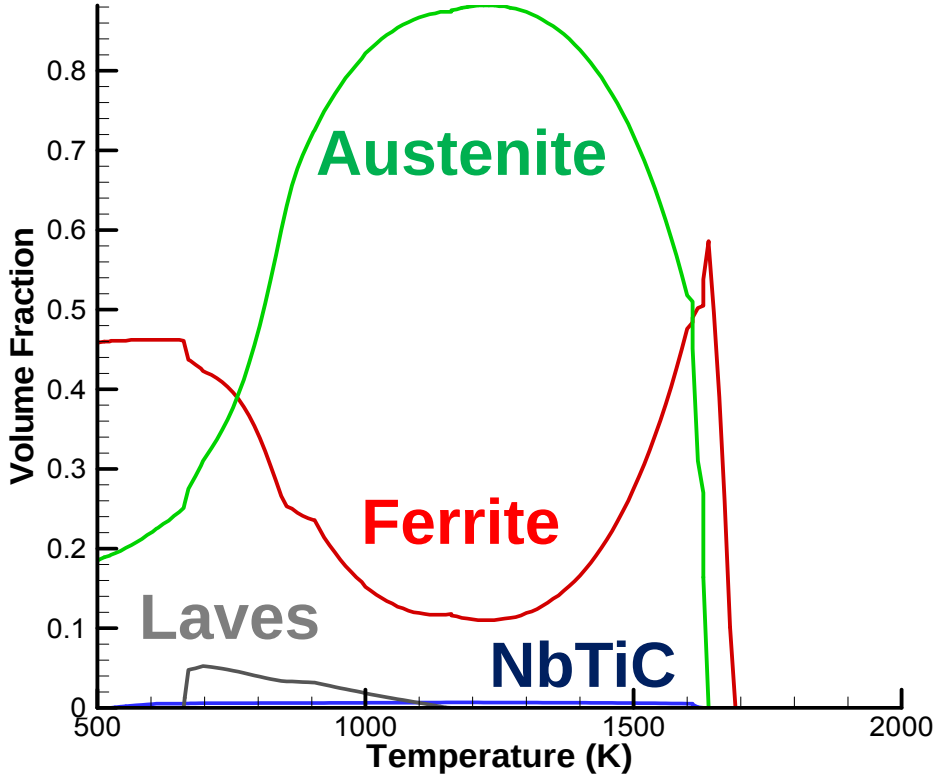
wt%	Fe	Ni	Cr	Mn	Nb	Si	Al	Ti	Mo	V	C	N
Alloy 2	Ba.	12	14	10	1	0.2	2.5	0.3	2.5	0.5	0.08	0.01

Cold Rolled 80%+1200°C 1hr WQ





Ferrite and Austenite coexists

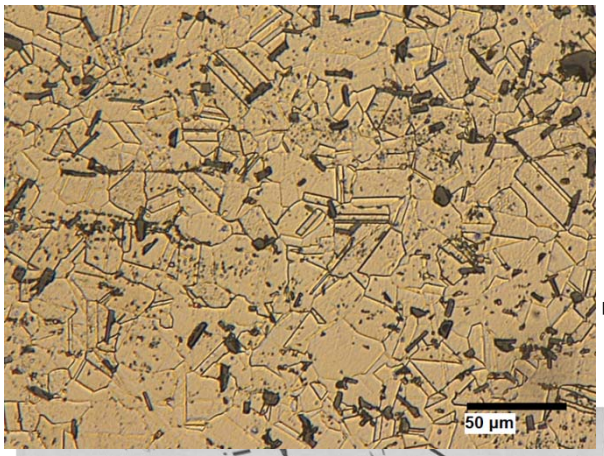


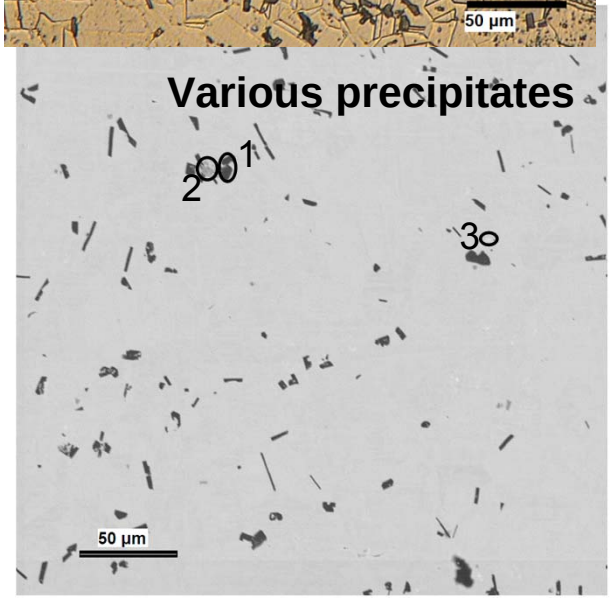
The prediction of the phase stabilities at high temperature

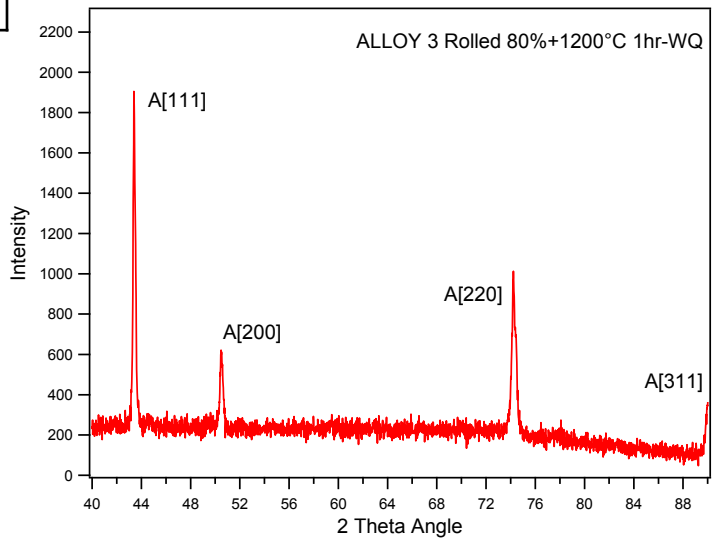
❖ Phase stability, Alloy 3

wt%	Fe	Ni	Cr	Mn	Nb	Si	Al	Ti	Mo	V	C	N
Alloy 3	Ba.	17	14	10	1	0.2	2.5	0.3	2.5	0.5	0.08	0.01

Cold Rolled 80%+1200°C 1hr WQ







AlN and NbTi(C,N)

- ThermoCalc predictions could not capture AlN formation

Region 1

- Aluminum Nitride particles, will negatively influence
  - Twinning ability due to nitrogen loss
  - Alumina formation due to Al loss

Region 2

- Complicated Nb-Ti Carbo-nitrides, may not be dissolvable

Region 3

- Complicated Nb-Ti Carbo-nitrides, may not be dissolvable. Less N and Ti as compared to region 2

21

❖ Computational Materials Work so far

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- The effect of alloying on
  - Phase stability (austenite, ferrite, Laves phases, carbides, intermetallics). Modification of the existing databases based on the experiments.

- Selecting/developing appropriate models for
  - stacking fault energy as a function of alloying
  - Twinning ability
  - Oxidation

- Setting up the criteria for GA optimization

❖ Effect of Ti, V and W on the austenite stability, Alloy 2

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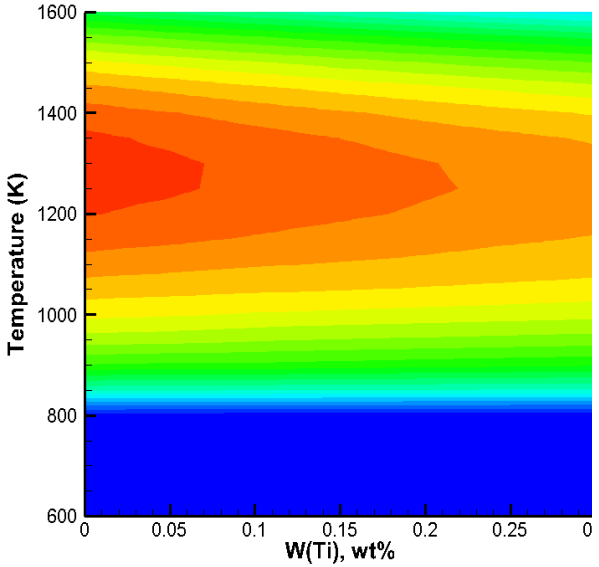
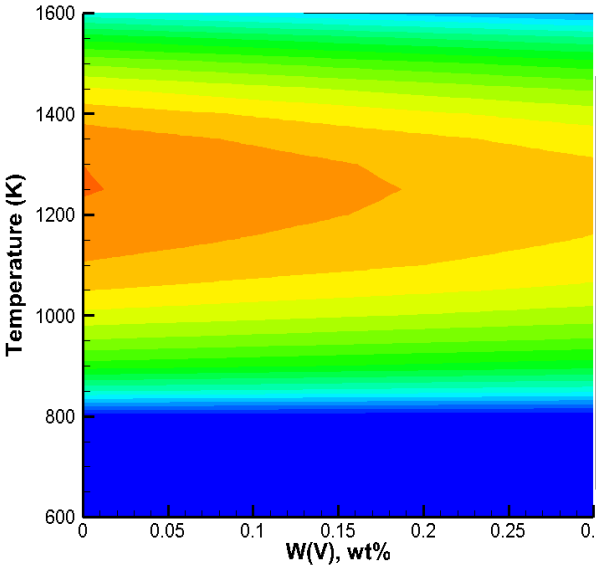
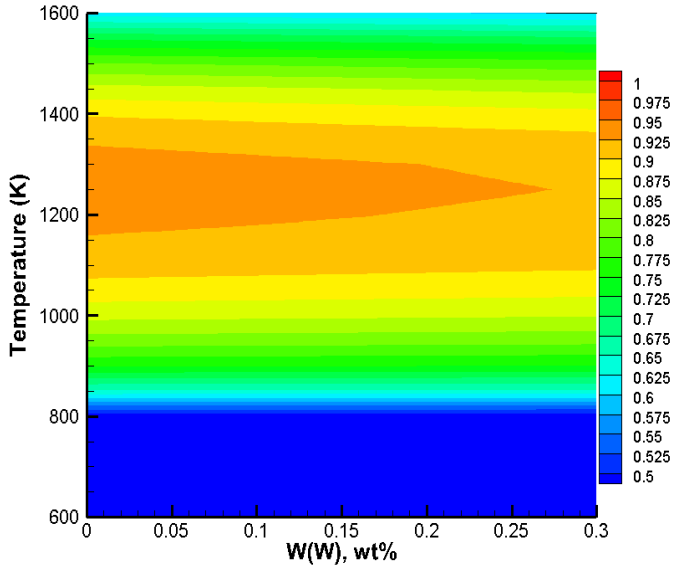
Ti case



V case

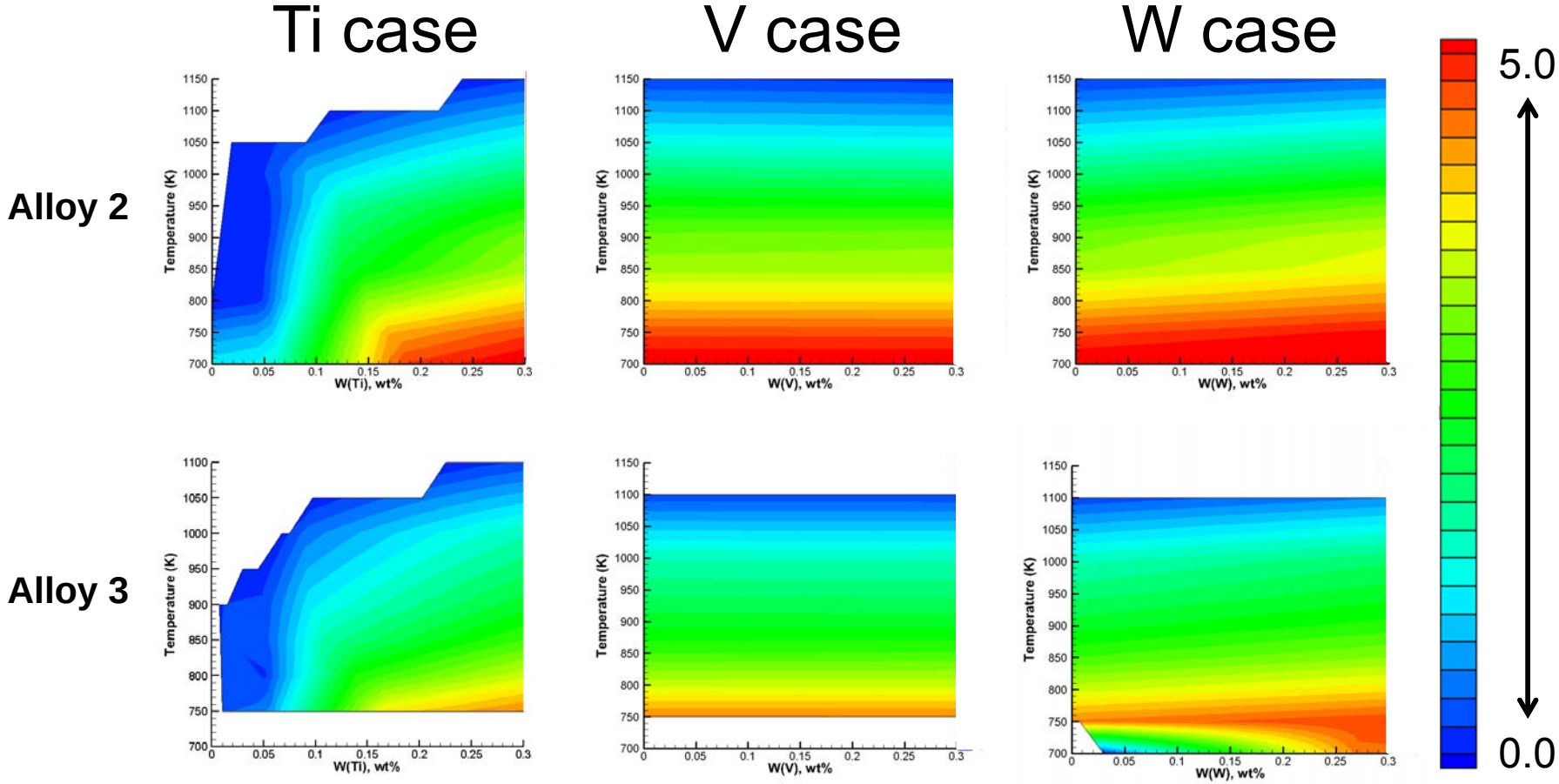


W case



- In general, austenite phase fraction in this alloy is expected to be higher than 50% while the temperature is between 800-1600 Kelvin.
- The results show that increasing the Ti, V, and W content decrease the austenite stability during the solution heat treatment

❖ Effect of Ti, V and W on the formation of Fe_2Nb Laves phase



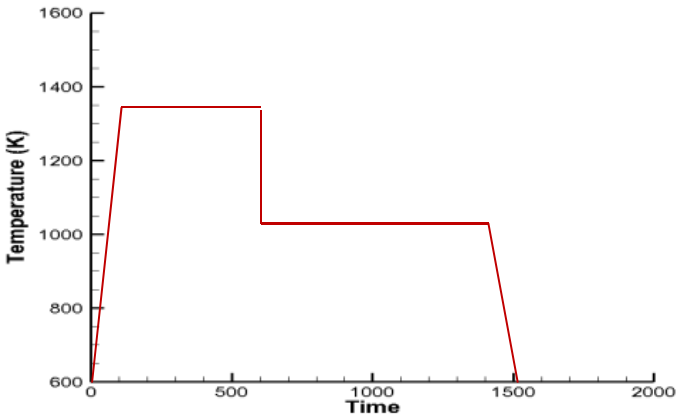
- The predicted volume fraction of the Laves phase after the second step heat treatment.
- Alloy 2 has a wider range of stability for Fe_2Nb Laves Phase
- The results show that Ti has a strong effect on the phase stability of the Fe_2Nb Laves phase. Next question is the kinetics!

❖ Alloy Design with GA

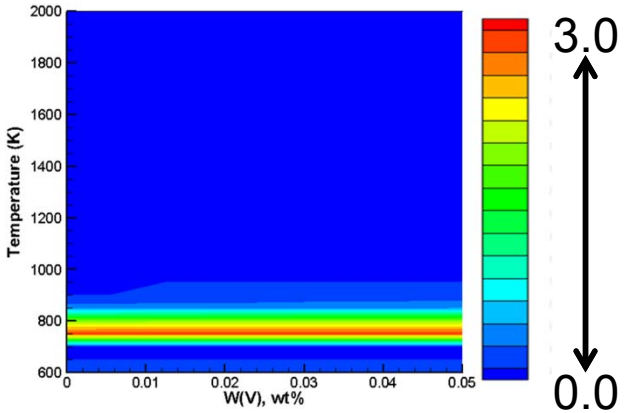
- Preliminary tests are being performed with a reduced based alloy with only 8 components.
- Alloy base composition:

(Fe-20Ni-14Cr-10Mn-0.86Nb-2.5Al-0.5V-0.08C)

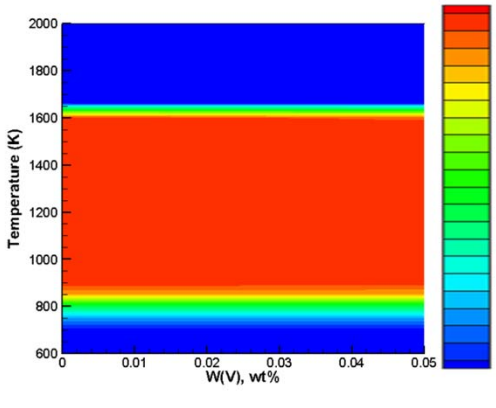
- GA will be used to find a 2 step heat treatment process for a demonstration alloy.
  1. Maximize FCC phase and minimize BCC phase
  2. Maximize Laves and NbC and minimize BCC and other phases, excluding FCC.



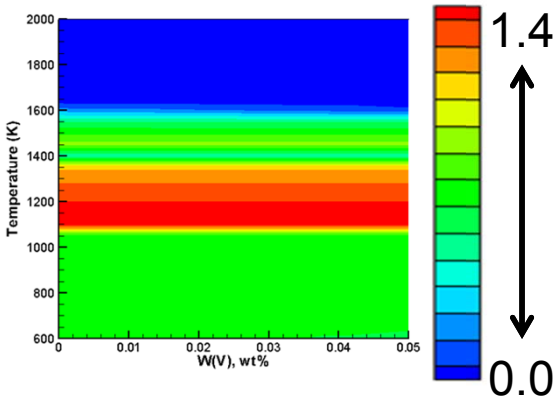
Ferrite



Austenite



NbC

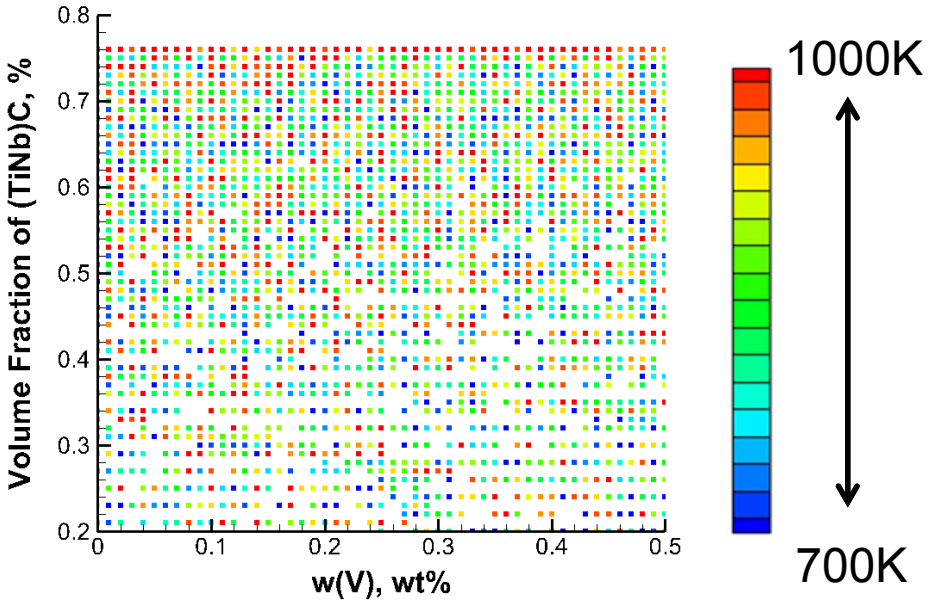


❖ Second Step Heat Treatment - GA

Second step heat treatment (Fe-20Ni-14Cr-10Mn-0.86Nb-2.5Al-0.5V-0.08C)

1. The optimum heat treatment temperature is in the range of 700-1000 K after the first heat treatment.

2. The predictions with V addition to find out the optimum heat treatment temperature to maximize the NbC.



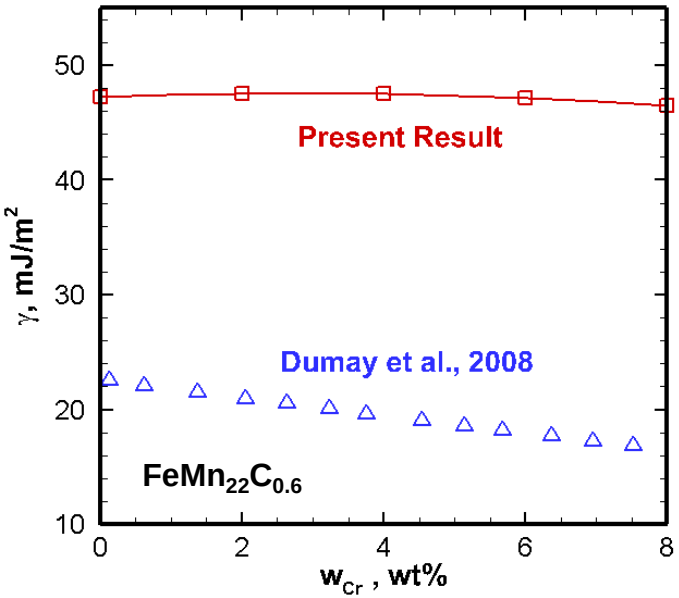
- The color stands for the selected heat treatment temperature.
- The results shows that the maximum NbC content is about 0.8%. The selection of the optimum temperature can be done based on this kind of diagrams.

❖ Stacking Fault Energy

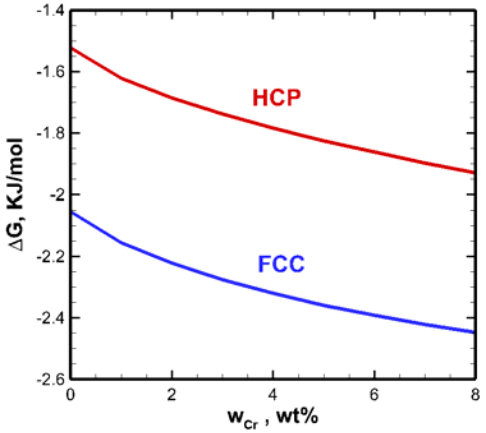
Calculation of the SFE

The SFE can be estimated according to the interfacial energy of austenite-HCP ($\sigma^{\gamma\to\varepsilon}$) using CALPHAD model [Dumay, 2008]:

$$\gamma = 2\rho\Delta G^{\gamma\to\varepsilon} + 2\sigma^{\gamma\to\varepsilon}$$



The results of the calculations using TCFE6 V6.2 database comparing to the experimental results [Dumay, 2008]



This model is not able to provide quantitative results. This may be because of the interfacial energy or the thermodynamic database. The next step is to use DFT calculation to estimate SFE [Vitos, 2006] using equation below:

$$\gamma = \frac{G_{SF} - G_0}{A} = \frac{G_{HCP} + 2G_{DHCP} - 3G_{FCC}}{A}$$

❖ Study of the oxidation formation

- **Alumina forming austenitic stainless steels**: Better high temperature oxidation (corrosion) limit, comparable to nickel-base alloys without abandoning the lower cost, formability, and weldability of conventional stainless steels.

- Criteria for alloying additions
  - Alloying additions that increase oxygen permeability or decrease Al diffusivity would raise the amount of Al needed for protective alumina scale formation.
  - Maintain austenitic structure (suppress δ and σ phase formation)
  - Internal oxidation vs. external oxidation

- In Fe-20Ni-14Cr-2.5Al-0.15Si-2Mn-2.5Mo-0.86Nb-0.08C-0.01B, 2.4% Al is sufficient to achieve good alumina scale between 650°C to 800°C

$$\Delta G = \Delta G^0 + RT \ln Q$$

At equilibrium

$$\Delta G = 0, Q = K$$

$$\Delta G^0 = -RT \ln K$$

$$\Delta G = -RT \ln K + RT \ln Q$$

$$\Delta G = RT \ln \frac{Q}{K}$$

$$k = \exp\left(\frac{-\Delta G^0}{RT}\right)$$

If $k > Q$ then forward reaction

$$4\,Al + 3\,O_2 \Rightarrow 2\,Al_2O_3$$

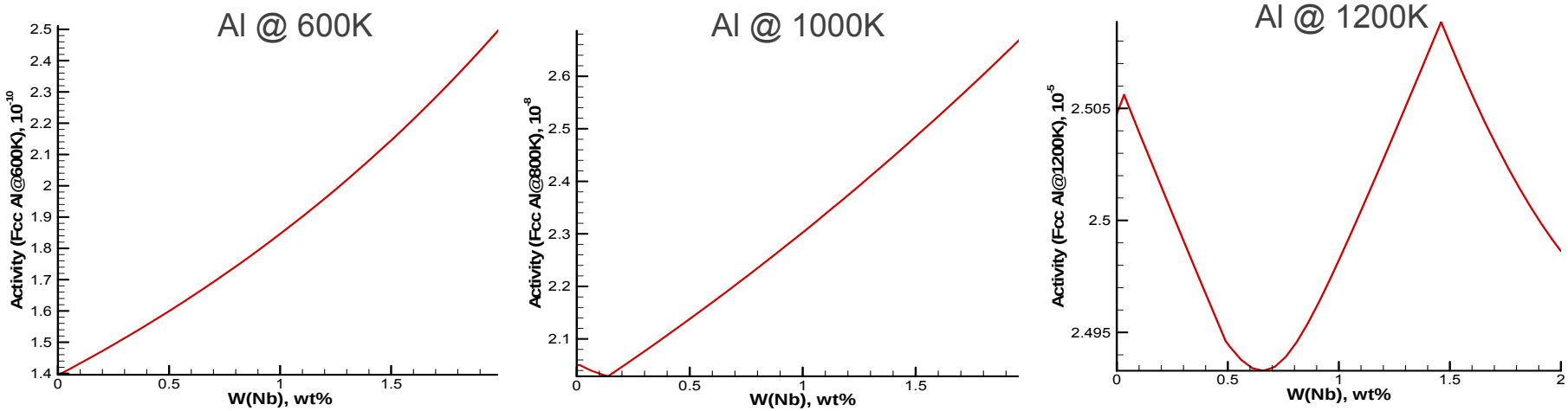
$$4\,Cr + 3\,O_2 \Rightarrow 2\,Cr_2O_3$$

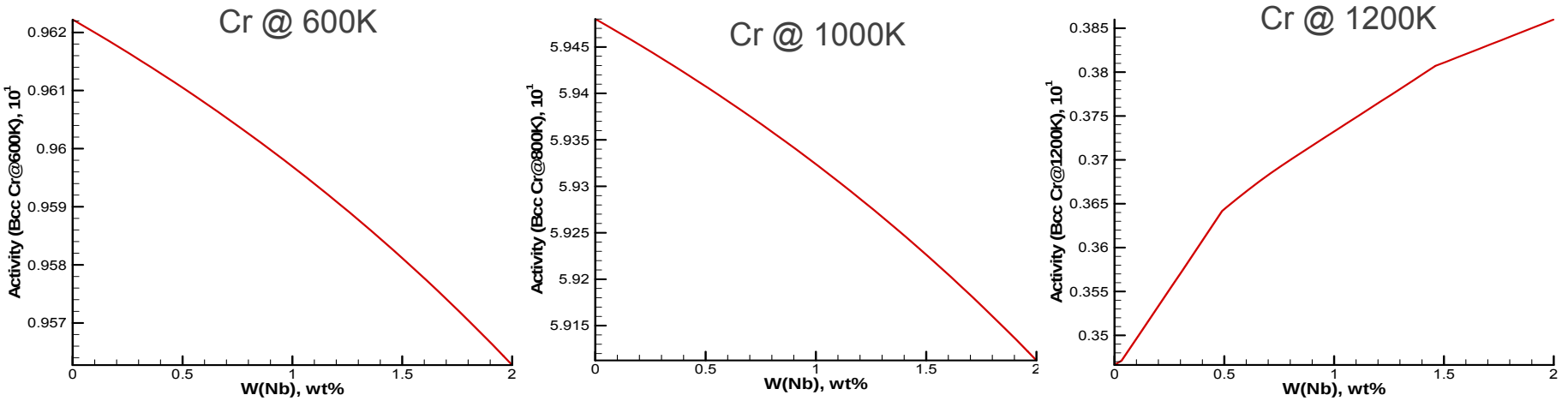
Ref: Y. Yamamoto *et al. Science*, 316 (5823): 433-436
Y. Yamamoto, et al Metal and mat trans A Vol 38, (2007) 2737

❖ Study of the oxidation formation

Fe - 20Ni -14Cr - 2.5Al - 0.15Si - 2Mn - 2.5Mo - 0.86Nb - 0.08C - 0.01B

Activities of Al and Cr at 600K, 1000K, and 1200K





- Calculated chemical activity values through Thermocalc and JANAF databases

❖ Study of the oxidation formation

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Using the JANAF data shown in previous slide

Al2O3						
T/K	ΔG°	log a (al2o3)	a (al)	a (o)	q	k
600	-1.44E+03	1.26E+02	1.77E-10	8.61E-09	1.65E+98	3.43E+125
1000	-1.38E+03	9.03E+01	2.26E-08	2.28E-06	2.70467E+71	1.956E+90
1200	-1.26E+03	5.48E+01	2.50E-05	5.00E-04	8.38E+42	6.81E+54

$k > Q$ so forward reaction

Cr2O3						
T/K	ΔG°	log a (cr2o3)	a (cr)	a (o)	q	k
600	-9.72E+02	8.46E+01	9.60E-01	8.61E-09	9.83E+60	4.44E+84
1000	-9.20E+02	6.01E+01	5.93E+00	2.28E-06	3.02E+41	1.24E+60
1200	-8.18E+02	3.56E+01	3.71E-01	5.00E-04	1.73E+26	4.23E+35

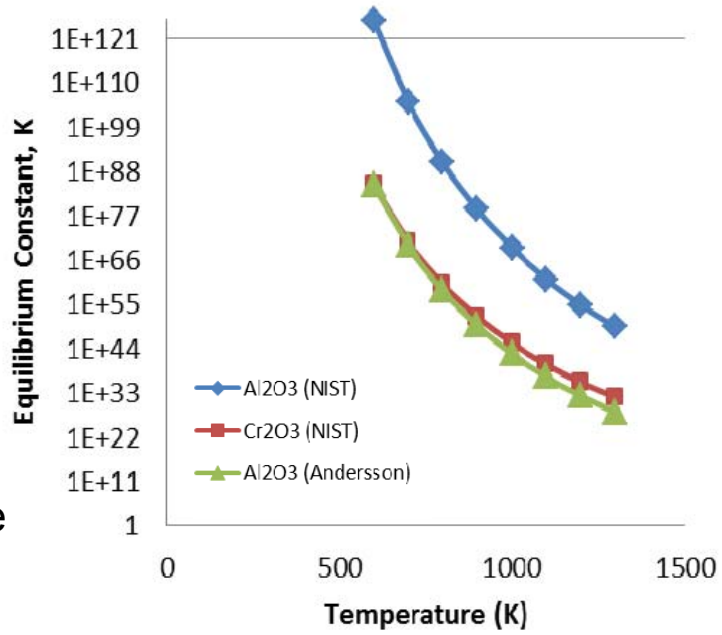
$k > Q$ so forward reaction

For both 600K, 1000K and 1200K,
Al_2O_3 and **Cr_2O_3** should form according to simulation

The empirical equation used by Andersson:

$$\Delta G^0 = -1205 + 0.387T$$

- The results obtained from this simulation agrees with the experiment completed by Y. Yamamoto et al.
- The equation used by Andersson shows the same trend



❖ Summary

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- A polycrystalline baseline material has been selected. Multiple custom compositions have been fabricated and the phase stabilities have been studied.

- Single crystals of two austenitic steels have been grown. High volume fractions of deformation twinning confirmed. Recovery, recrystallization study is ongoing. Deformation twins did not grow up to 600°C in FeMnC, however, pearlite phase has nucleated.

- In the baseline material, it was found that NbC is not easily dissolvable and hard to manipulate. N addition with Al led to nitride formation.

- The use of computational thermodynamics has enabled the study of the phase stability in three different alloys. The calculations agree with the observed microstructures but some modifications in the database is needed. More systematic work will be performed.

- Developed a preliminary alloy design framework through the use of Genetic Algorithms.

❖ Ongoing and Future Work

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- Further develop models to describe twin formation using DFT calculations, coupled to the CALPHAD method
- Develop alloy criteria to determine transition between internal oxidation vs formation of oxide passivating layer
- Recovery/Recrystallization of deformation twins in single crystals and the baseline alloy.
- Computationally design MC carbides or complex carbonitrides that are dissolvable at high temperature, without suppressing alumina scale formation and deformation twinning.
- Develop models for precipitation kinetics of carbides, Laves phases, and intermetallic particles.
- Incorporate alloy design criteria to GA alloy optimization framework. Design a set of first generation steels. Fabricate and characterize few.
- Conduct high temperature mechanical and creep tests on the baseline and first generation designed steels.
- Study the high temperature oxidation behavior in air and steam.

❖ Year 1 Milestones

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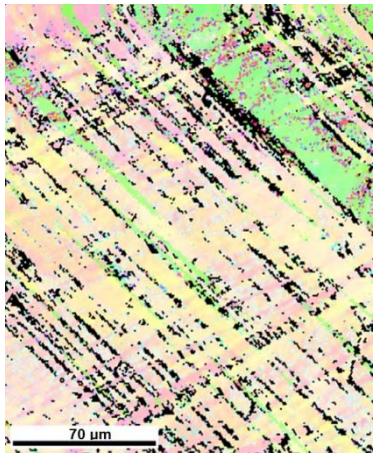
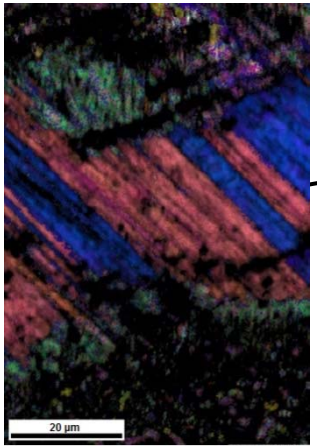
Milestone Title / Description (from the original PMP)	Comments
1.1 Fabrication and wrought processing of baseline material	The single crystalline 316LN stainless steel has been grown. Another baseline material is selected and processed
1.4 Study of the nano-precipitation behavior of the baseline material	We are currently studying the precipitation behavior in one of the baseline materials. Due to the delay in the selection and fabrication of the new wrought baseline material, this milestone was delayed.
1.6 Investigation of phase stability of intermetallic strengthening phases for the baseline material	Some of the newly designed alloys have demonstrated large second phase formations and thus, have not been investigated further.
1.7 Development of Phase 1 of Genetic Algorithm. Optimization based on volume fraction of likely strengthening phases as well as temperature stability ranges	The GA development attempts to maximize the volume fraction of discrete Laves phases at grain boundaries by optimizing heat treatments. More elements such as Nb, V, and Ti are taken into consideration for further strengthening through precipitation.
1.8 Alloy optimization GA and phase stability of strengthening phases and comparison with available literature. Report 1st generation candidate alloy	The development/adaptation of the models for estimating the phase stability and stacking fault energies in order to eventually incorporate them in GA for compositional optimization.
1.9 Room temperature microstructural and mechanical characterization of the baseline material in polycrystalline form.	We have started the characterization of the new baseline material and two designed alloys in polycrystalline forms. This characterization work is planned to be completed by July 2013.
1.10 Room temperature microstructural and mechanical characterization of the single crystalline baseline material	This task is almost completed for 316L and Fe-Mn-C single crystals. We will soon grow single crystals from the new baseline material.

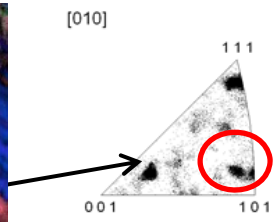
❖ Deformation twinning stability at high temperatures

450°C 1hr



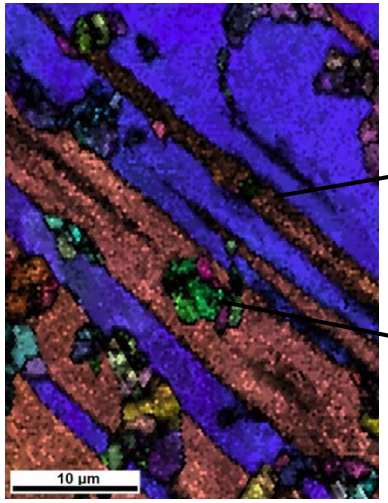
500°C 1hr

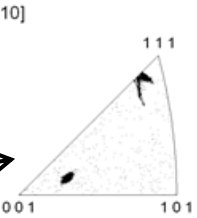


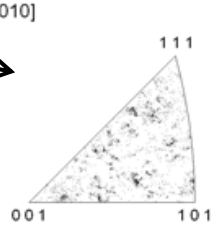


partial recrystalization

600°C 1hr

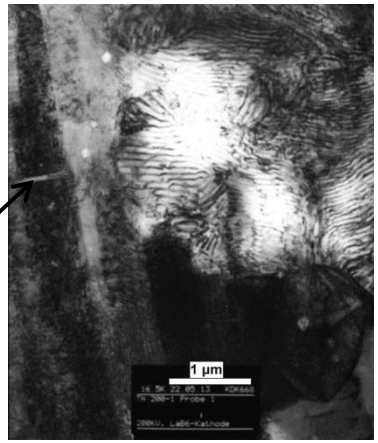






Recrystalized phase shows no texture!

Coarse Pearlite nucleated up to 500°C



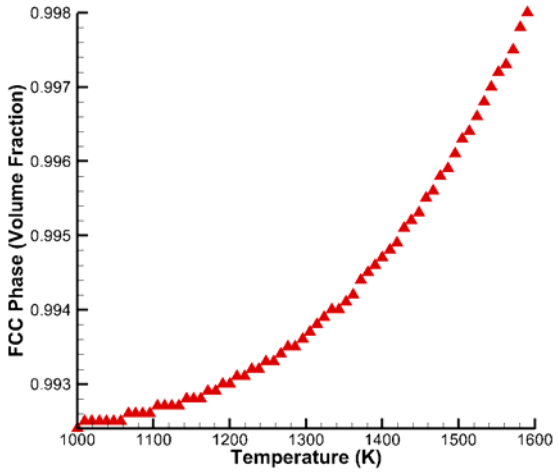
❖ First Step Heat Treatment - GA

First step heat treatment

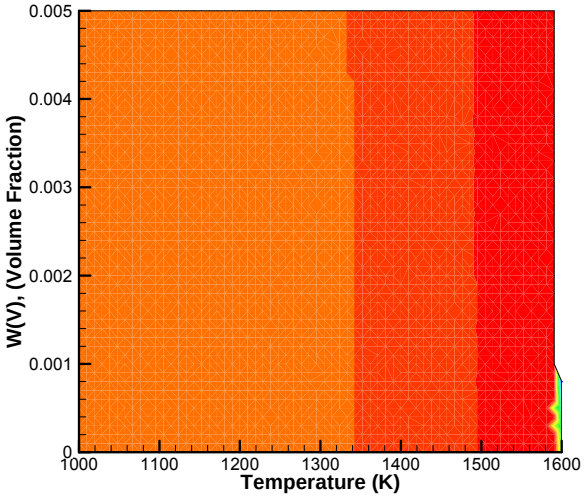
- Target: **Obtaining the lowest temperature for fully austenizing the alloy.**

$$1000K < T < 1600K$$

- Adding V as a variable to the composition does not affect the temperature for complete austenization



Variable T and Fixed Composition



Variable V and T

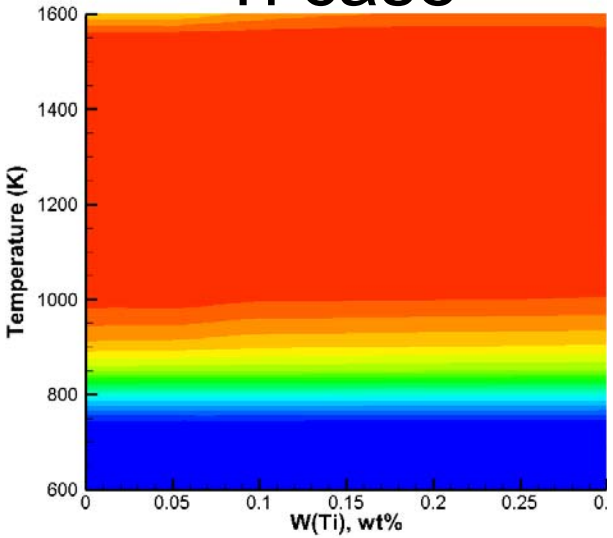
(Fe-20Ni-14Cr-10Mn-0.86Nb-2.5Al-0.5V-0.08C)

The predicted austenite fraction as function of temperature and V content

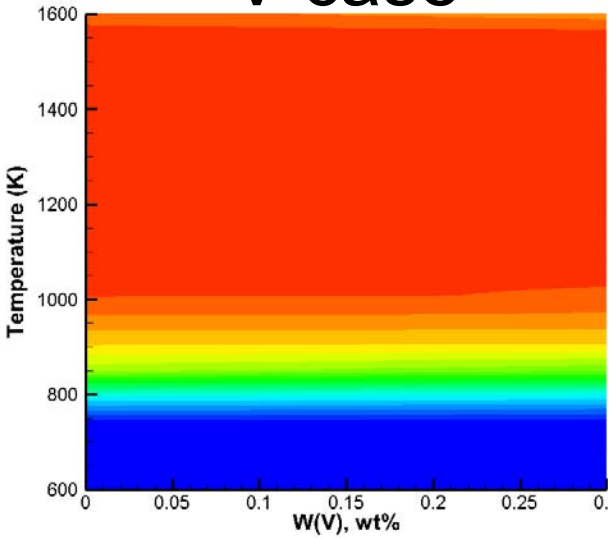
❖ Effect of Ti, V and W on the austenite stability, Alloy 3

wt%	Fe	Ni	Cr	Mn	Nb	Si	Al	Ti	Mo	V	C	N
Alloy 3	Ba.	17	14	10	1	0.2	2.5	0.3	2.5	0.5	0.08	0.01

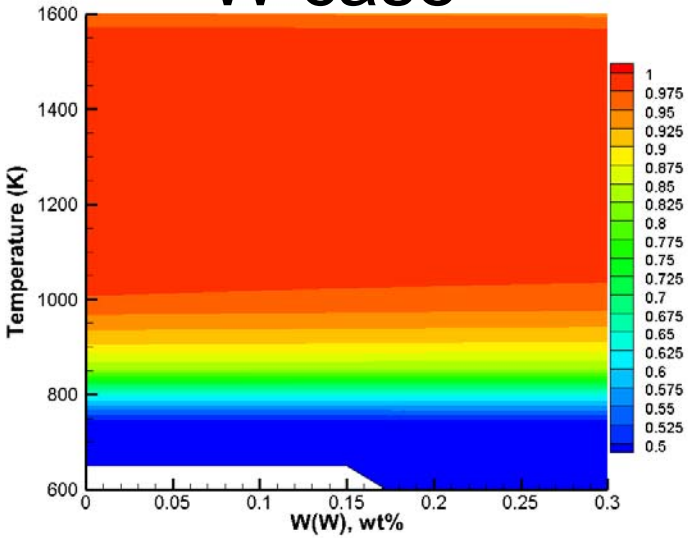
Ti case



V case



W case



- For this alloy, the effect of the Ti, V, and W on the phase stability of austenite is minor. This is mainly due to the increased Ni content (12 vs 17 wt.%)
- In this alloy, we have a wider range of temperatures for the solution heat treatment.