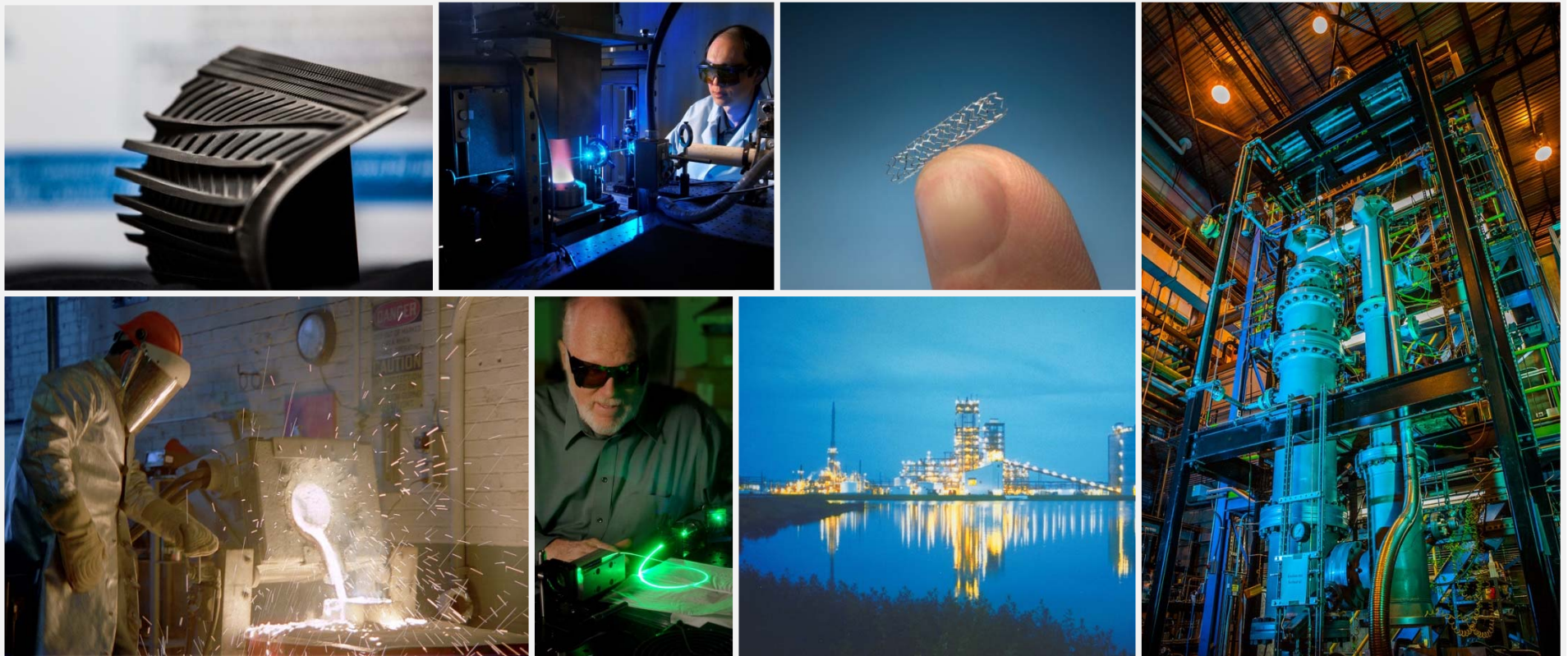




Driving Innovation ♦ Delivering Results



Creep Optimization in Haynes 282 Through Gamma Prime Coarsening Control: Preliminary Results

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Y. Wen & P.D. Jablonski



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Gamma Prime, Precipitate Strengthened Haynes 282 Ni-base superalloy



- Haynes 282 is one potential candidate alloy for A-USC and sCO₂ (boiler, turbine, and heat exchanger) components. Mechanical behavior and microstructure are being investigated, comparing the unstressed versus stressed states for a variety of environmental conditions.

	B	C	Al	Si	S	Ti	Cr	Mn	Fe	Co	Ni	Cu	Mo
H282	0.005	0.06	1.5	0.15 max	–	2.1	20.0	0.3 max	1.5 max	10.0	BAL	–	8.5

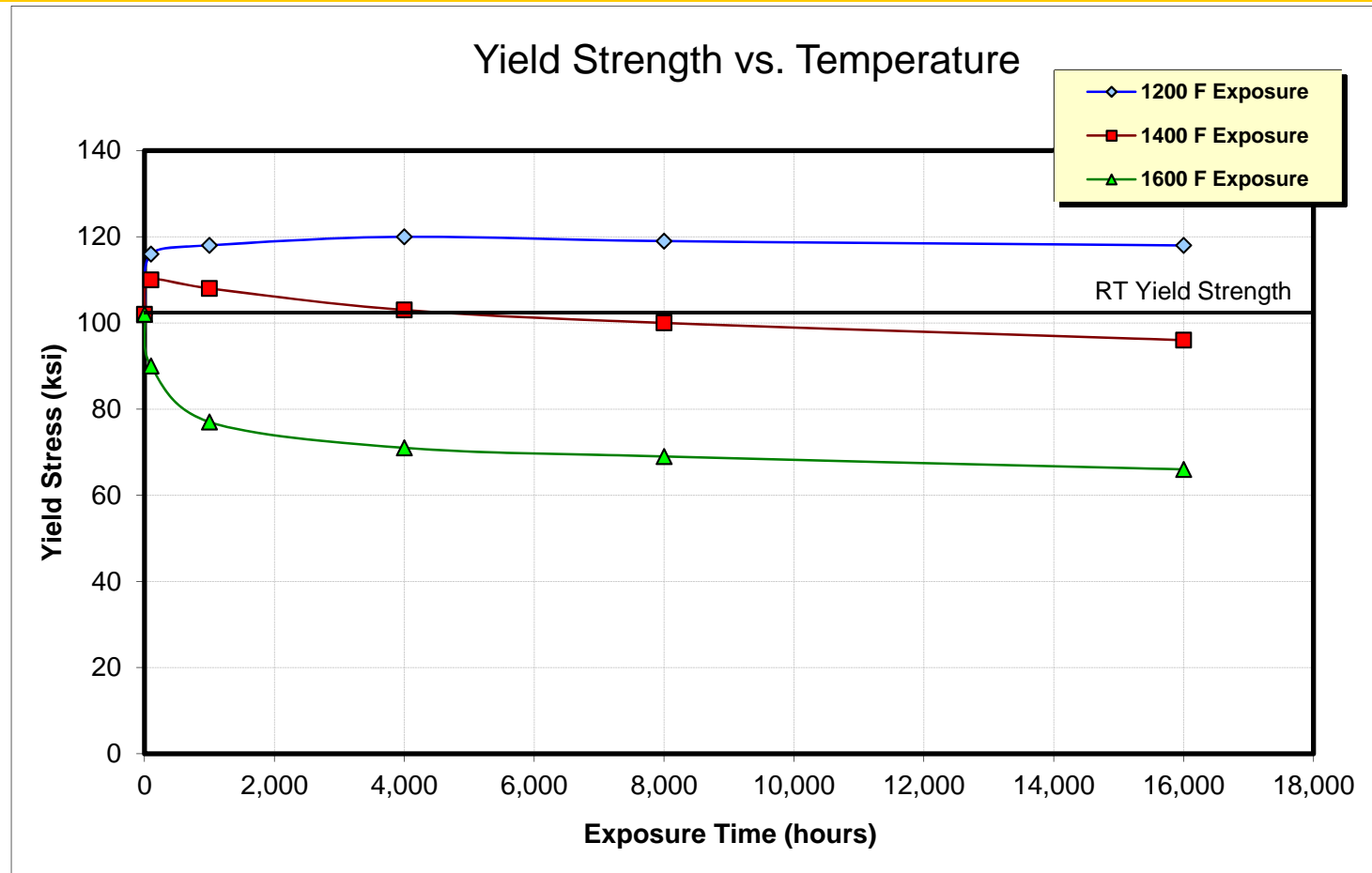
- High temperature FCC alloys typically use a combination of matrix strengthening precipitates (γ' for this alloy), carbides, and high dislocation density to impart strength.
- In Ni-base superalloys for use in advanced power plants at temperatures up to 760°C and beyond, the main strengthening phase is the γ' precipitate. Volume fraction and precipitate morphology are two important factors in alloy strength – both influence matrix strength and deformation behavior in the alloy.
- The character of grain boundaries and the phases found there are also important in generating high temperature creep strength and long-term microstructural stability.

Haynes 282: A-USC Candidate Alloy



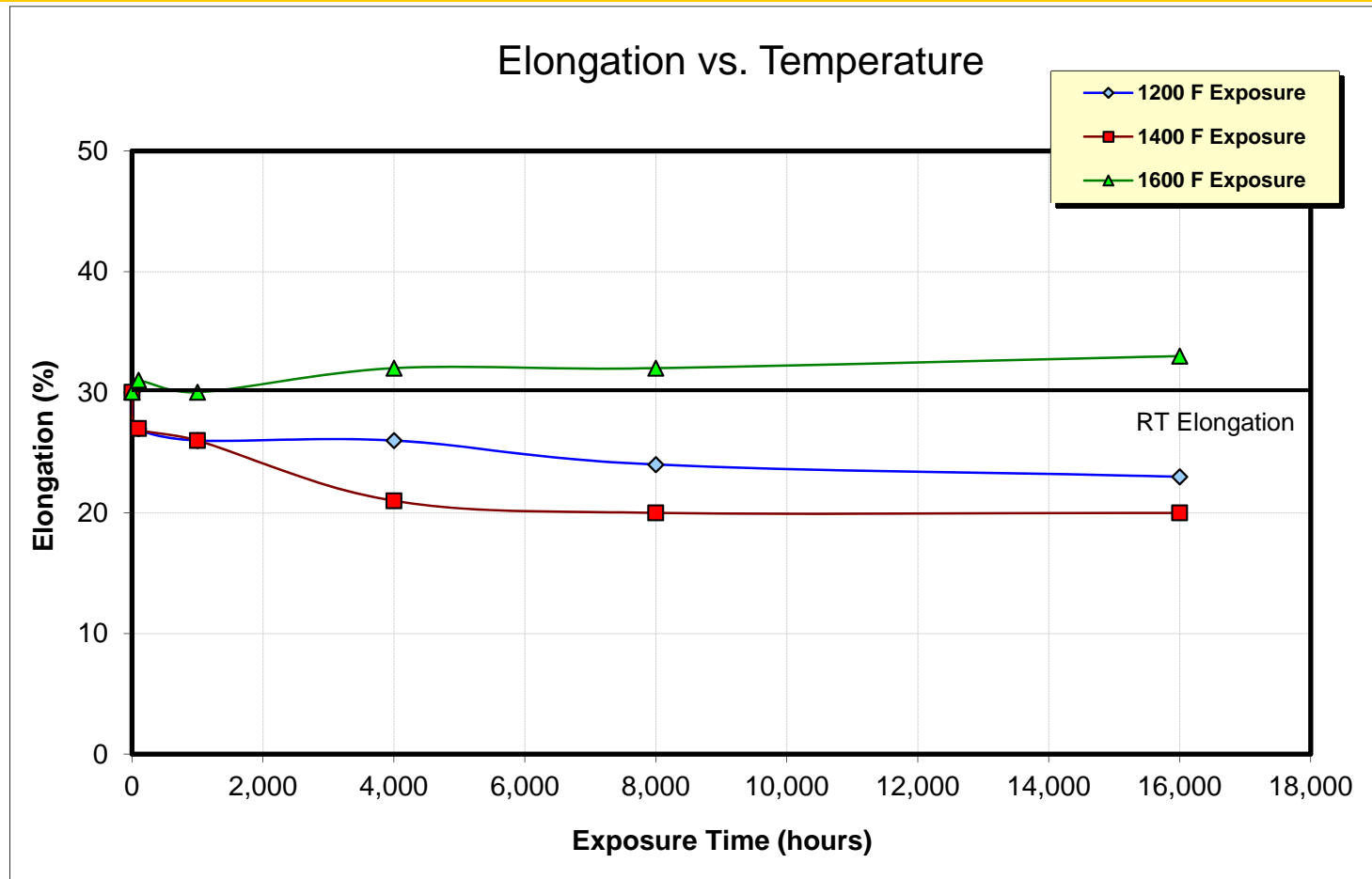
- Haynes 282 was selected as candidate alloy for DOE / NETL A-USC steam turbine for 760°C operation.
 - Gamma prime (γ') strengthened (16-18% by volume)
 - Very good creep strength for γ' precipitate volume fraction
 - Good tensile strength and ductility
 - Good low cycle fatigue strength
 - Good oxidation resistance in steam
- Previous Haynes research suggested retention of strength after long-term isothermal exposure at 1200 & 1400°F, with some reduction in strength after exposure at 1600°F for exposure times reaching 16,000 hours.
 - These results suggest that the alloy and γ' are relatively stable
 - Other deleterious changes, like reduced elongation, are minimal

Haynes 282 Yield Strength after Long-term Isothermal Exposure



L.M. Pike, "Long Term Thermal Exposure of Haynes 282 Alloys," 7th International Symposium on Superalloy 718 and Derivatives, Eds. E.A. Ott et al., TMS, 2010, pp. 645-660.

Haynes 282 Elongation after Long-term Isothermal Exposure



L.M. Pike, "Long Term Thermal Exposure of Haynes 282 Alloys," 7th International Symposium on Superalloy 718 and Derivatives, Eds. E.A. Ott et al., TMS, 2010, pp. 645-660.



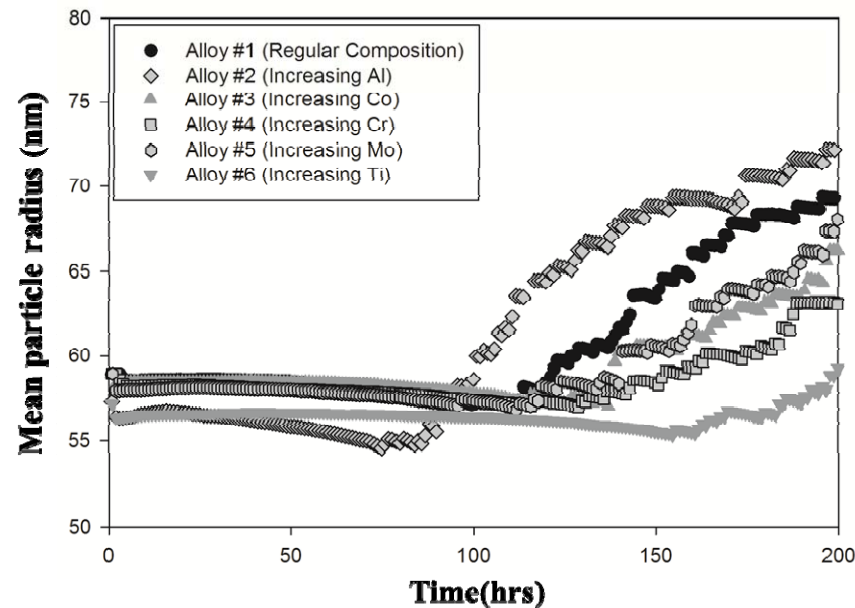
- Without performing extensive alloy design experiments, what is the best experimental approach to assessing changes in chemistry with corresponding effect on strength?
 - Phase field modeling of Haynes 282 major elements (Co, Cr, Mo, Ti, Al)
 - Co, Cr, Mo primarily affect solid solution strength and makeup of carbides; would also change interfacial energy between matrix and γ
 - Al, Ti affect γ precipitate superlattice structure
- Stepwise approach to chemistry changes were initiated, and coarsening simulations were run (short times) and compared to the nominal starting model chemistry.
 - Increasing Al relative to nominal level suggested a possible increase in the γ coarsening rate
 - Increasing the Ti content relative to the nominal level suggested a potential decrease in the γ coarsening rate

Simulated Alloy Compositions and Phase Field Coarsening Simulations



Alloy	Al	Co	Cr	Fe	Mo	Ti	Ni	Vol.% γ'
#1*	1.5	10.0	20.0	1.5	8.5	2.1	Bal	18.86
#2	<u>1.8</u>	10.0	20.0	1.5	8.5	2.1	Bal	21.08
#3	1.5	<u>11.0</u>	20.0	1.5	8.5	2.1	Bal	18.91
#4	1.5	10.0	<u>21.0</u>	1.5	8.5	2.1	Bal	18.97
#5	1.5	10.0	20.0	1.5	<u>9.5</u>	2.1	Bal	19.05
#6	1.5	10.0	20.0	1.5	8.5	<u>2.5</u>	Bal	21.62

#1* is the starting nominal composition for the phase field model



How do we test this?

Experimental Alloy Chemistry for H282-B / H282-C Were Designed & Manufactured



Alloy	Ni	Cr	Co	Mo	Ti	Al	Fe	Mn	Si	C	B#
Nominal	Bal	20.0	10.0	8.5	2.1	1.5	1.5*	0.3*	0.15*	0.06	50
H282-B	Bal	19.22	9.86	8.49	<u>2.22</u>	<u>1.27</u>		0.25	0.15	0.08	100
H282-C	Bal	19.19	9.85	8.50	<u>1.94</u>	<u>1.54</u>		0.25	0.14	0.08	100

PPM (parts per million)

* Maximum value

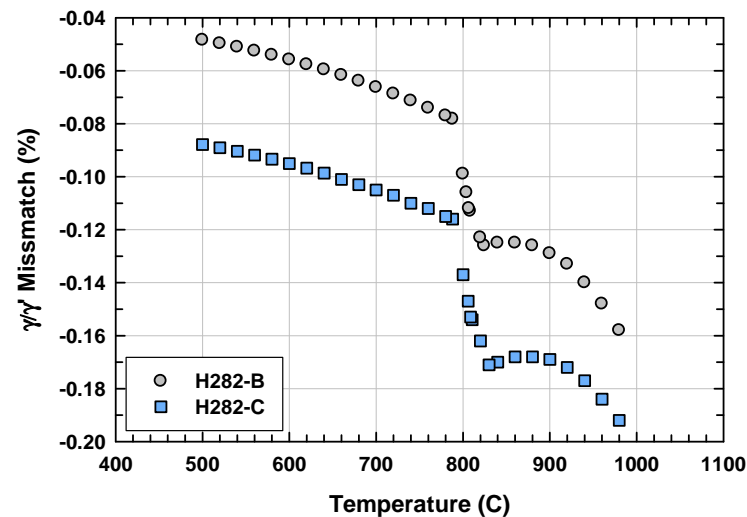
Two alloys based on Haynes 282 were designed (Ti/Al = 1.4, nominal):

- One alloy had increased Ti relative to Al: H282-B (Ti/Al = 1.75)
- One alloy had increased Al relative to Ti: H282-C (Ti/Al = 1.26)
- The γ precipitate volume fractions within the compositions of H282-B & H282-C were designed to be approximately the same
- Specimens were solution heat treated, quenched, and then aged at 760°C from 1 to 20,000 h - water quenched: γ size determined by TEM

Manufacturing Process Plan H282 (B-C)



- Two alloys based on Haynes 282 were designed via ThermoCalc.
- Alloys were formulated from *commercial* purity elements and compounds.
- Alloy melts were produced in VIM, homogenized, & TMP into plate.
- Alloys were solutionized/quenched to eliminate γ precipitates.
- Alloys were isothermally annealed at 760°C for various times/quenched.



Microscopy and Gamma Prime (γ') Measurements

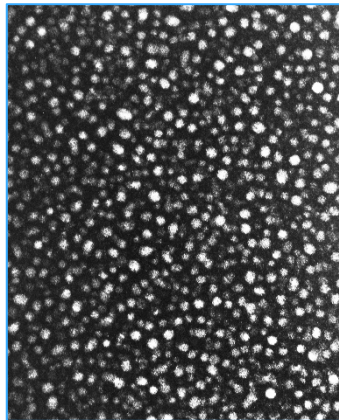


- Axial dark field (DF) imaging was used to reveal the γ' precipitates. Several imaging conditions were attempted, and some of the strongest DF contrast was found when using a 110 superlattice reflection with the γ matrix tilted just a few degrees from a $\langle 110 \rangle$ zone axis.
- Images were recorded on traditional cut film (wet chemical processing) over a range of magnifications from 20,000 to 150,000x. Image magnification was chosen to suit the sample's microstructure, where each recorded field of view incorporated a worthwhile number of γ' precipitates, but with those particles enlarged sufficiently to facilitate easy and accurate measurement.
- *ImageJ* was used to measure γ' precipitate features subsequent to further statistical correction for truncation due to TEM foil thickness / γ' precipitate size.

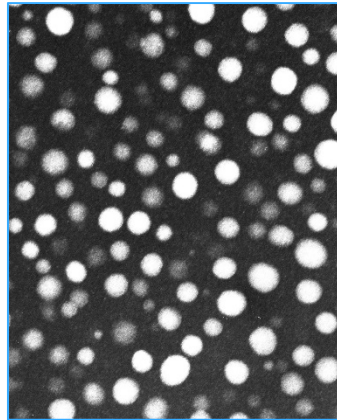
Gamma prime coarsening with isothermal exposure at 760°



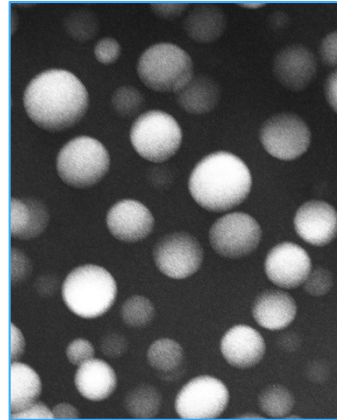
H282-B



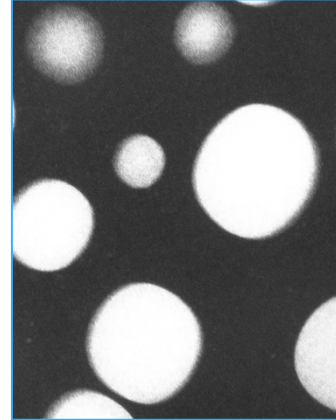
Aging Time (h): 10



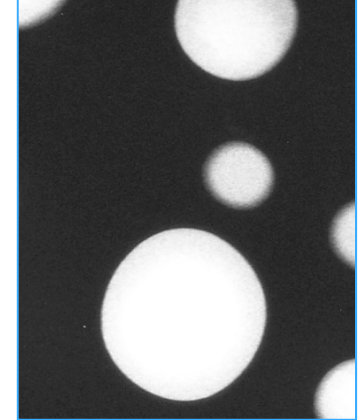
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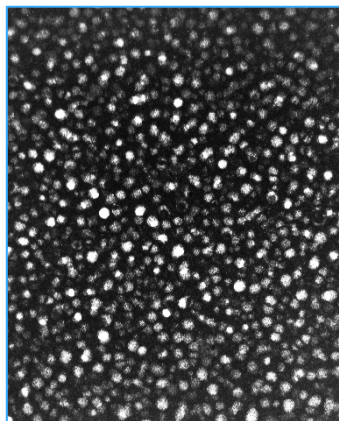
1,176



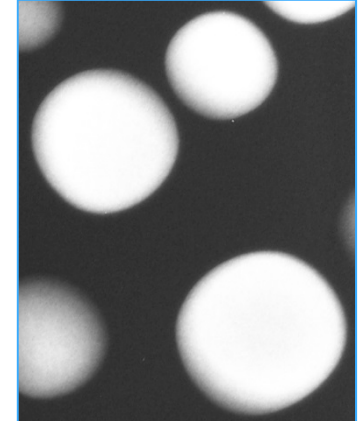
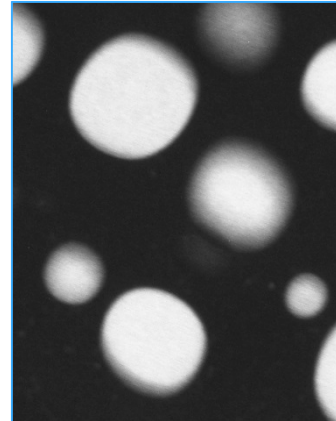
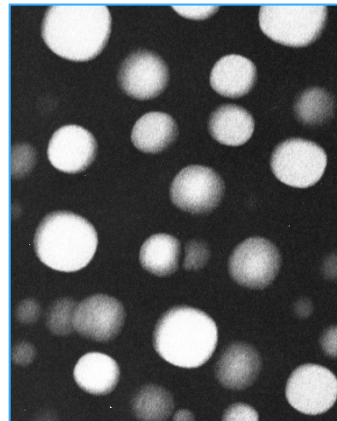
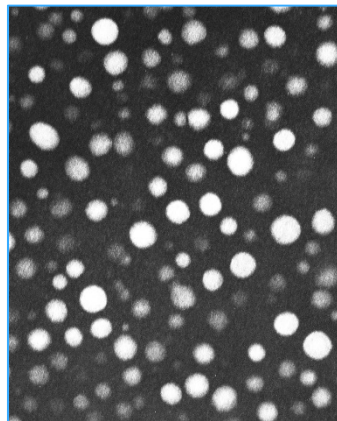
9,835



20,000



H282-C



Dark field images, all scaled to the same magnification: 200 nm



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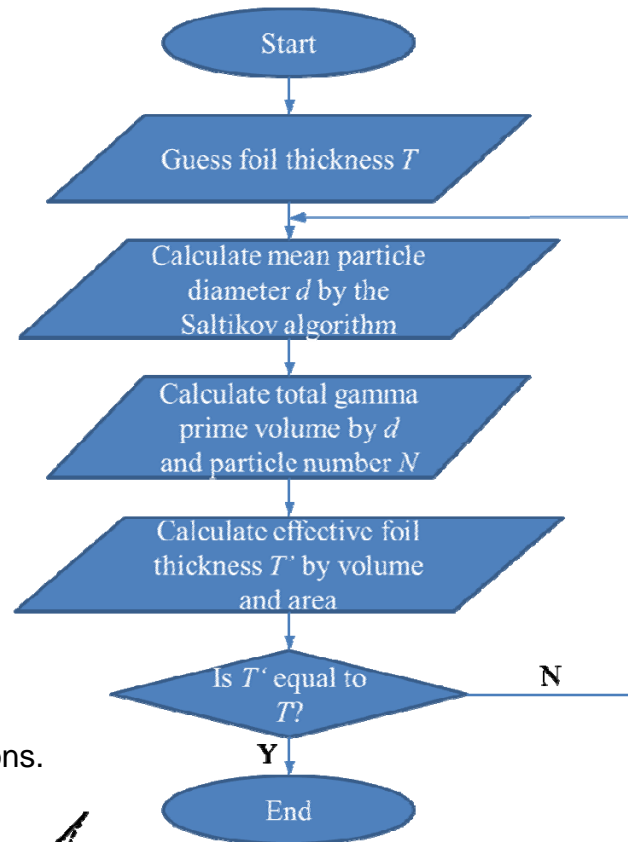
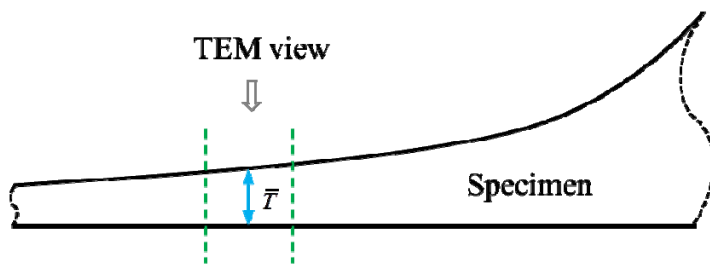
Gamma Prime Particle Size Determination and Correction



Thickness of TEM Foil

$$T = \frac{V}{A} = \frac{N\pi\bar{d}^3}{6Af}$$

Schematic: The effective thickness of the foil within the TEM view, T , varies from sample to sample for practical considerations.



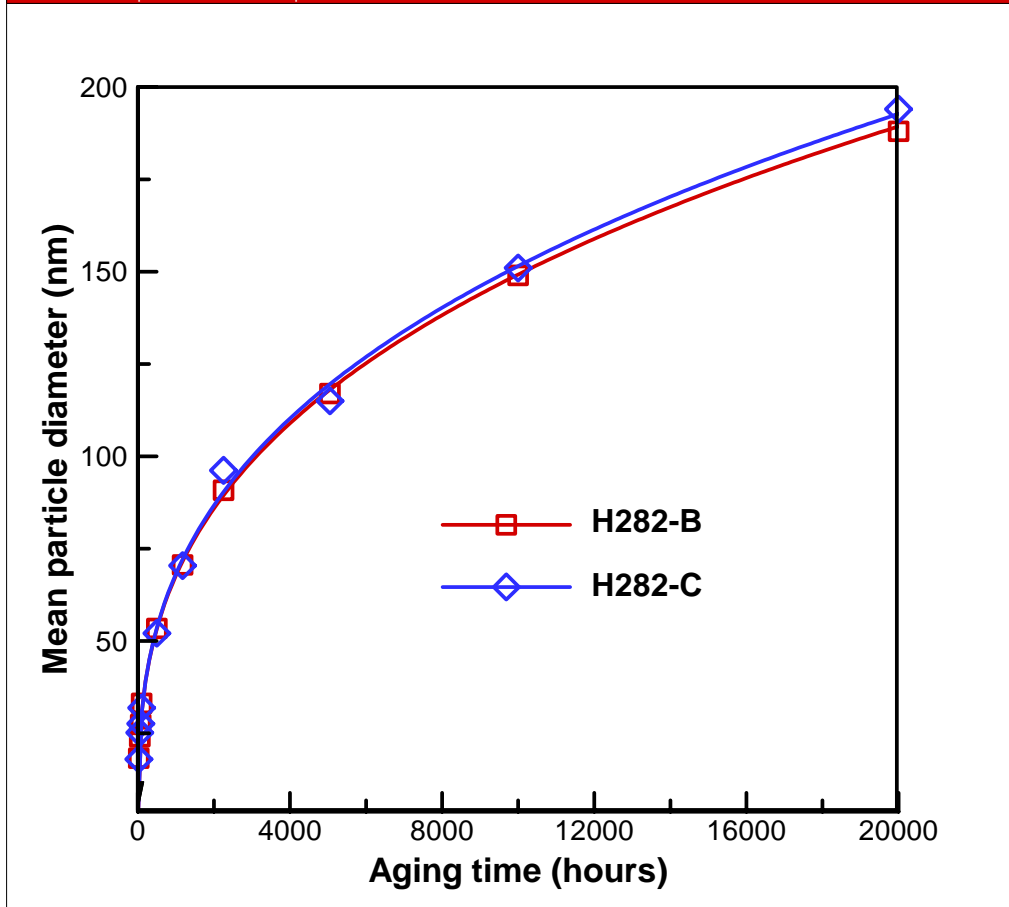
TEM used to image γ' and determine uncorrected particle size.

Iterative correction algorithm (ICA)

Gamma Prime Coarsening



Frame 001 | 21 Jan 2016



During ideal coarsening, the particle size distribution is self-similar at any time; the mean particle diameter should evolve with time by $d \sim t^{1/3}$; and the particle number density n should evolve by $n \sim 1/t$. It is expected that starting from time t_0 , the mean particle diameter d evolves following

$$\bar{d}^3 - \bar{d}_0^3 = k(t - t_0)$$

$$k = \left[\frac{8D_{eff} \sigma N_{\alpha} V_m}{9RT} \right]^{1/3}$$

Relationship of mean particle diameter and aging time for H282-B / H282-C during isothermal annealing. The two power fit curves are very close, except that starting from ~2500 hours, particles in H282-C are slightly bigger than H282-B.

Gamma Prime Coarsening (from 25 h)



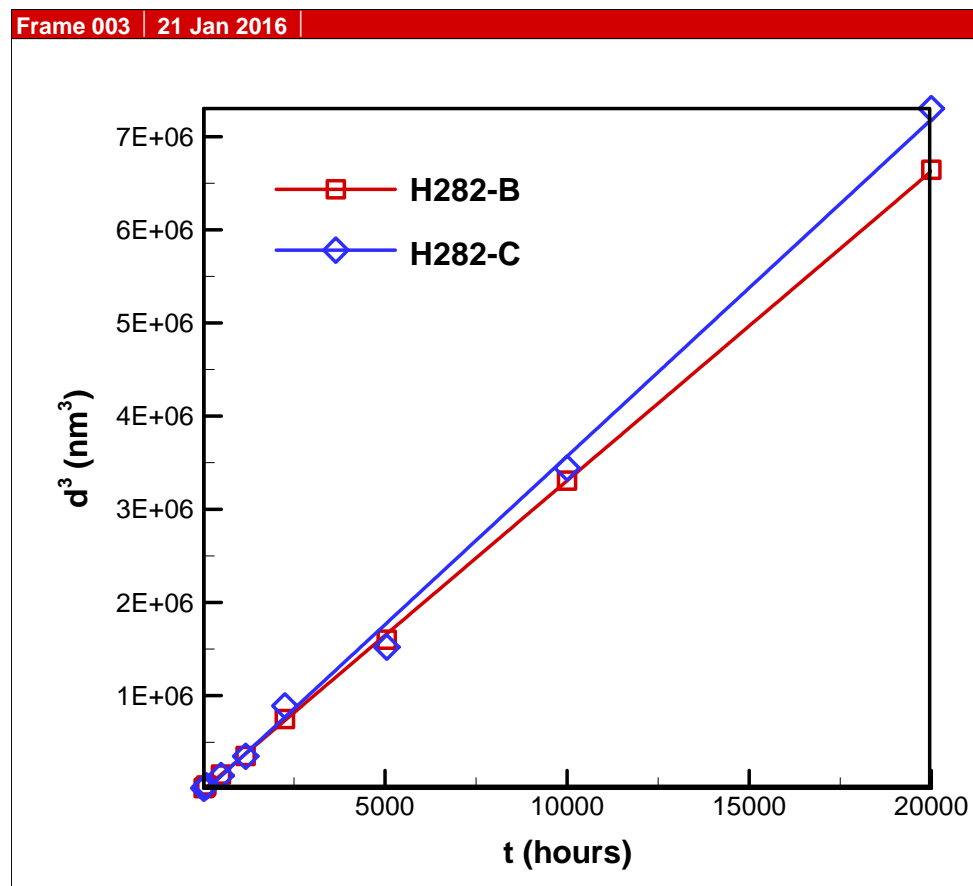
H282-B

$$\bar{d}^3 - 18.4^3 = 332.0(t - 25.0)$$

H282-C

$$\bar{d}^3 - 18.0^3 = 360.9(t - 25.0)$$

Up to and including 25 h of isothermal exposure, the diameters of H282-B / H282-C are very similar. Only after that time do they begin to diverge more significantly as indicated by the equations plotted in the graph.



Additional Clarifying Points on γ Precipitate Coarsening



- At the TMS Annual Meeting a question arose concerning standard error in precipitates measurements.
- Precipitate size was determined, on the one hand, as an exact average of the original particle size. These data were then used to construct histograms, which separated a range of particle sizes into “bins”. These histograms formed distributions, where the mean of the distribution was determined and then corrected for truncation error. This procedure produced a mean precipitate size (MPS) from the histogram distribution.
- In reality the mean apparent γ precipitate size (MAS) and the mean γ particle size (MPS) from the histogram distribution were very close.
- Subsequently, the mean particle size (MPS) was “consistently” corrected (CMPS) for foil thickness and the number density of particles consistent with the γ precipitate volume fraction for that time interval.
- From this a “standard error of the mean corrected size” was calculated:

$$\text{SEMCS} = \text{SEMAS} * (\text{CMPS}/\text{MPS})$$

Table of H282-B Particle Size Calculations



Time (hours)	25	50	75	100	500	1,176	2,252	5,051	9,835	20,000
Mean apparent particle size (exact, in nm)	16.9	21.5	24.2	29.5	48.1	63.5	79.5	102	131	161
Mean particle size (nm)	16.9	21.5	24.3	29.5	48.1	63.6	79.6	102	131	167
Number of particles	2192	1600	1300	1547	1020	536	902	728	676	1457
Standard error of mean apparent size(nm)	0.12	0.19	0.23	0.26	0.50	0.94	0.97	1.45	1.84	1.65
Consistent foil thickness (nm)	16.7	18.9	20.6	30.4	63.7	76.9	71.6	106	98.7	175
Consistently corrected mean size (nm)	18.4	24.1	27.4	33.1	53.4	70.6	90.8	117	149	188
Standard error of mean corrected size (nm)	0.13	0.21	0.26	0.29	0.56	1.05	1.11	1.66	2.09	1.93
Number density of particles (μm^{-3})	6.0e+04	2.7e+04	1.8e+04	1.0e+04	2.5e+03	1.1e+03	5.0e+02	2.3e+02	1.1e+02	5.6e+01

Summary of H282 Long-term Microstructural Features Observed

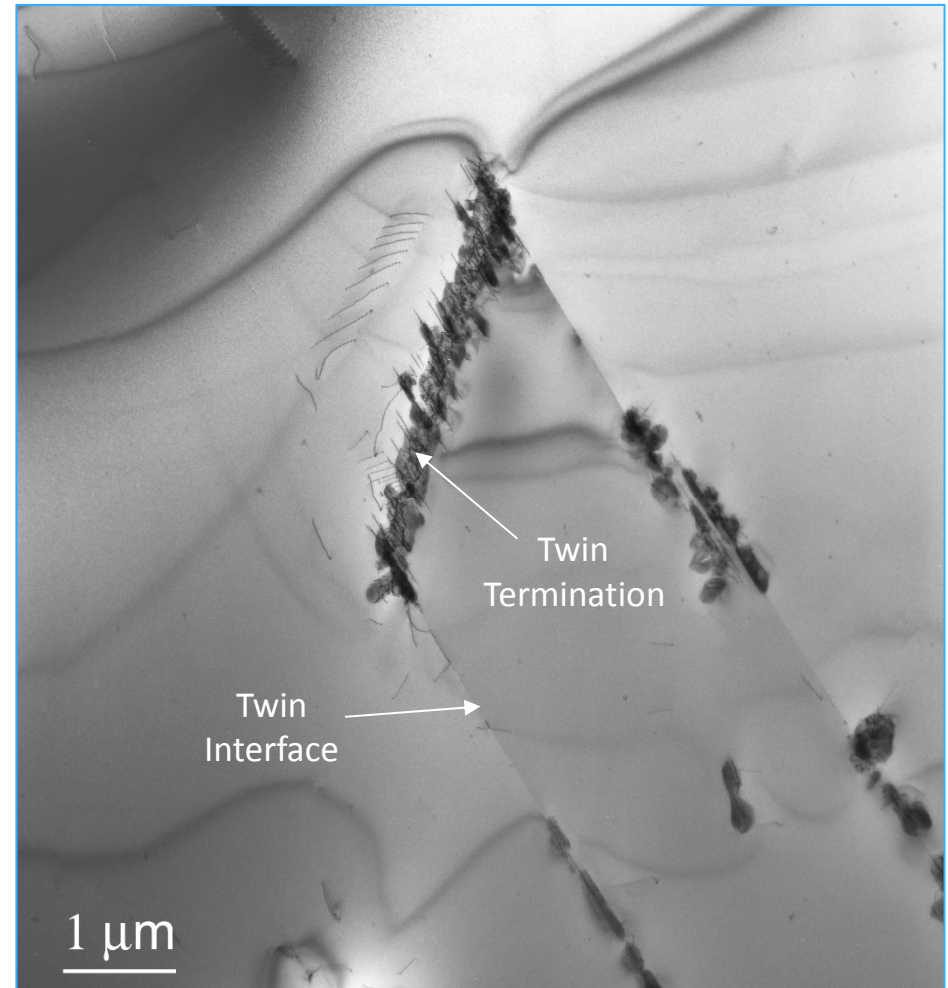
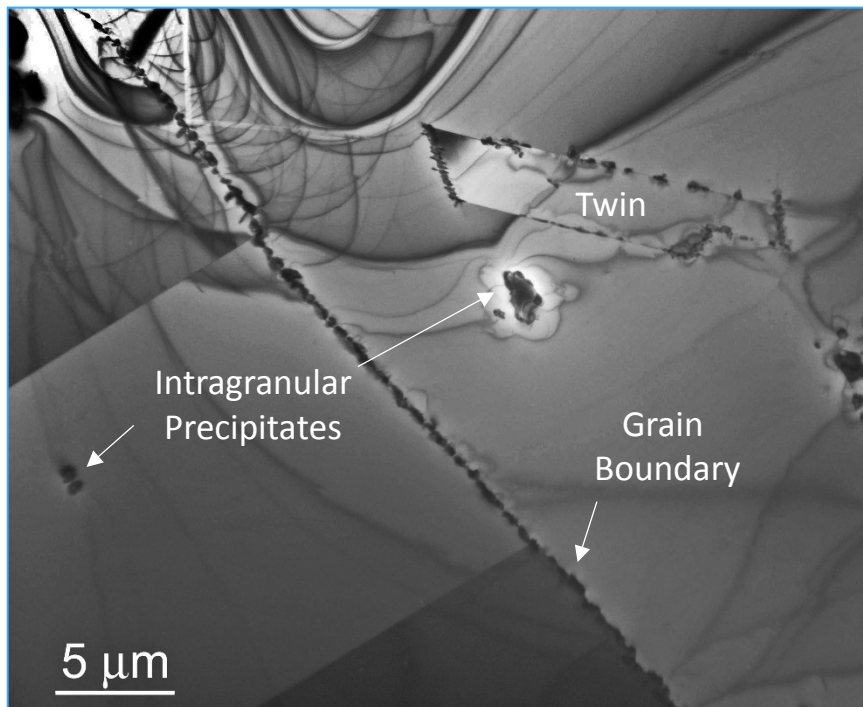


- Gamma prime coarsening was observed by measuring the change in the γ' precipitate diameters as a function of isothermal exposure time from 1 to 20,000 hours. The coarsening rate was influenced by the Ti/Al ratio.
- Additionally, characteristics of the grain boundaries (carbide type and chemistry) were surveyed as a function of time at temperature.
- Twin terminations were also observed relative to exposure time for changes in carbide type and size (not completely quantified).
- Any other characteristic change in features was also noted as well as when it occurred (roughly speaking).
- Remember, general alloy makeup the same for both B & C.

Twins, grain boundaries & intragranular precipitates



H282-C Aged for 1 hour at 760°C



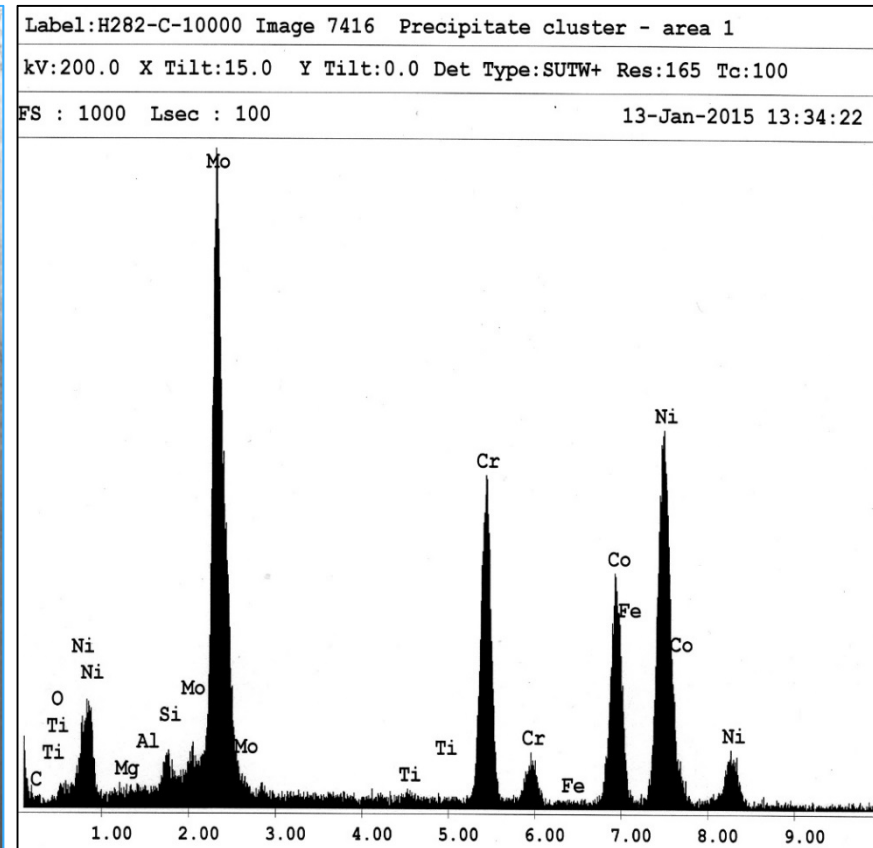
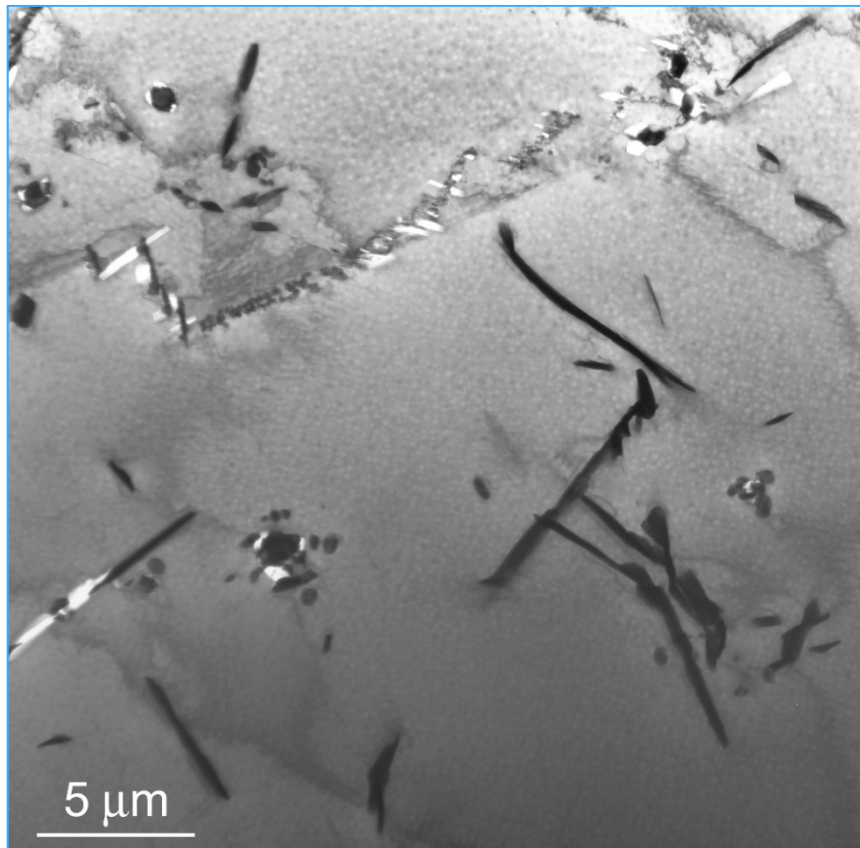
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Matrix Characteristics after 10,000 hours Exposure



H282-C Aged for 9,835 hours at 760°C

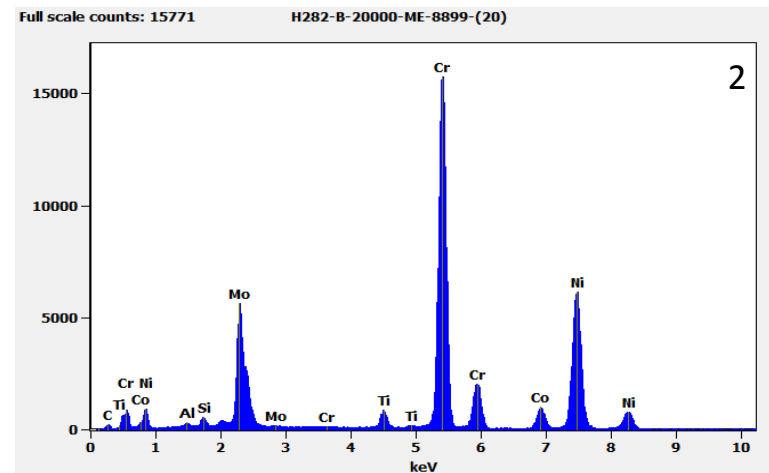
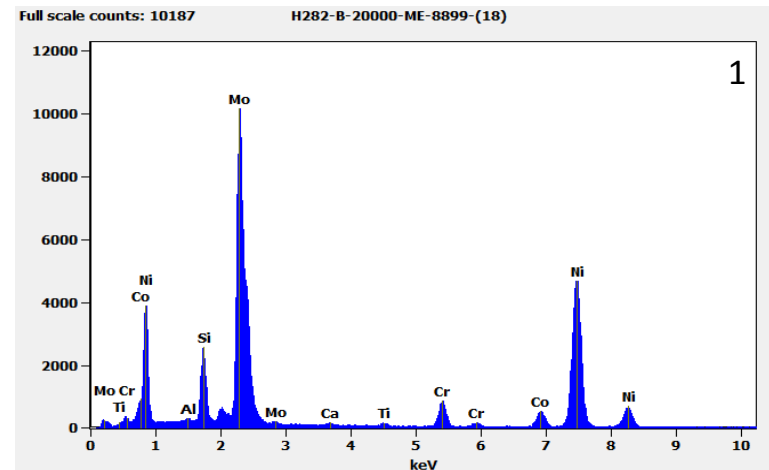
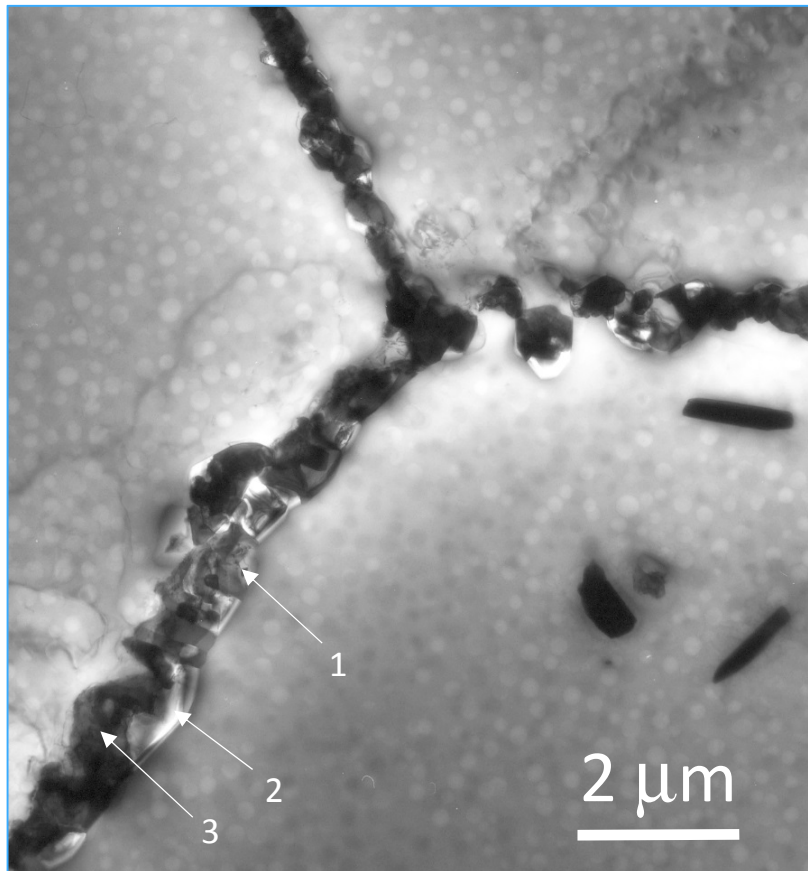


One of the more obvious microstructural changes occurring at longer aging times is the development of blade-like precipitates with a high Mo content, some Cr and some Co. The spectrum at the right illustrates the typical composition, but as always, includes some contribution from the metal matrix.

Matrix Characteristics after 20,000 hours Exposure



H282-B Aged for 20,000 hours at 760°C



The development of MoSi-rich phase begins at around 1,000 hours aging, and continues throughout longer aging times. Spectrum 1 is typical of carbide grains 1 & 2. Spectrum 2 is from grain 3, the common CrMo-rich carbide.



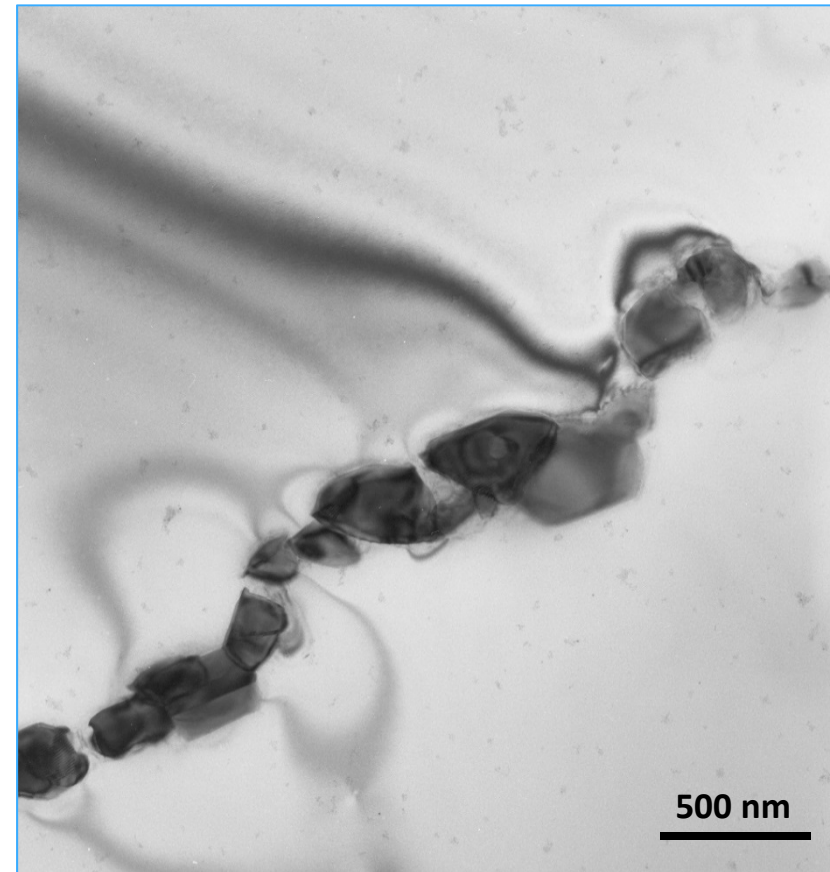
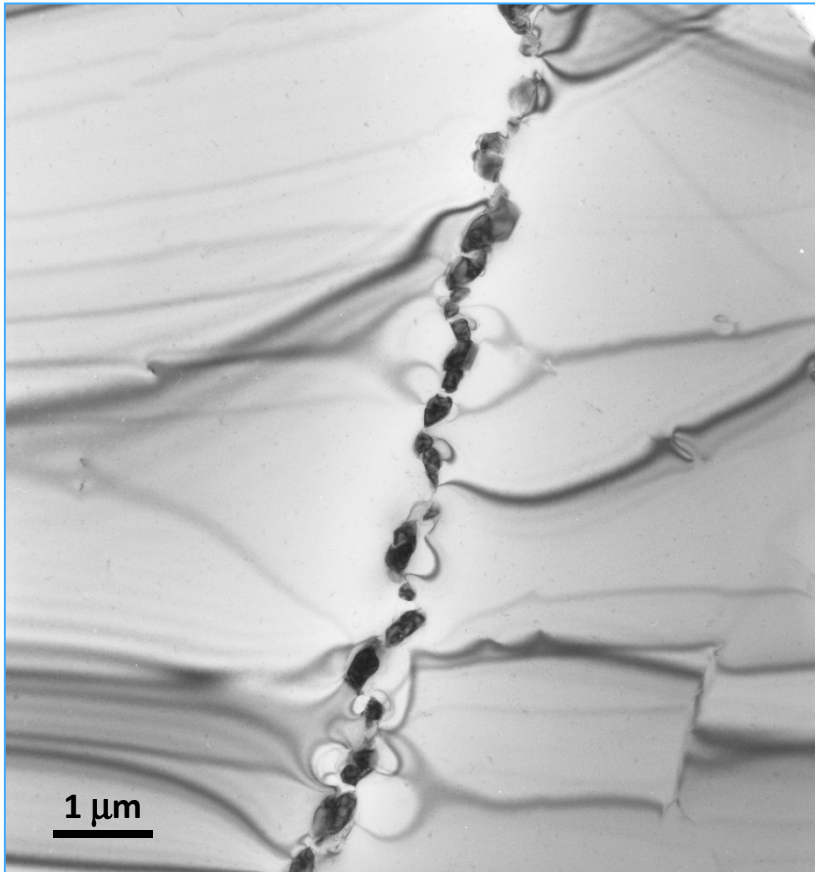
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Grain Boundary Nature and Carbides



H282-B Aged for 1 hour at 760°C

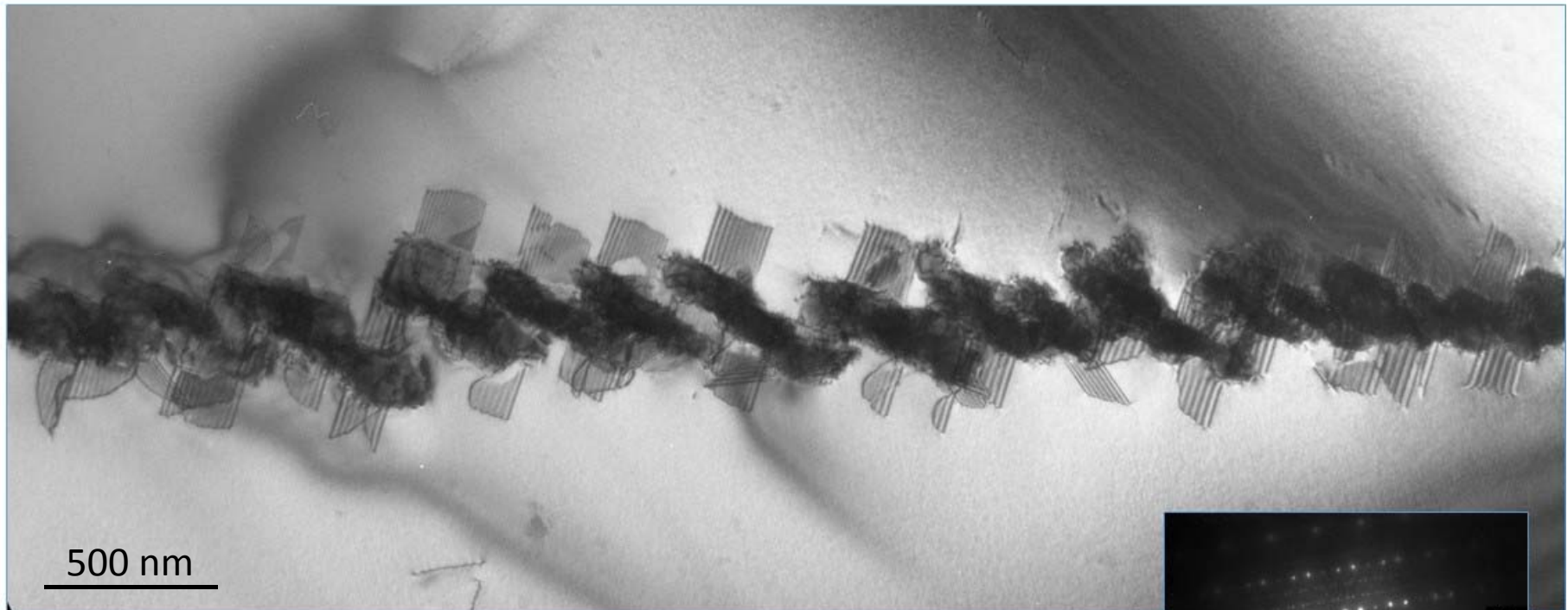


Carbide at a high angle grain boundary – the dominant composition being CrMo-rich.

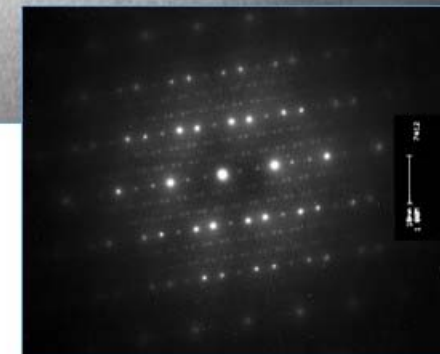
Twinning in Haynes 282 & Carbides on Twin Interfaces / Terminations



H282-B Aged for 1 hour at 760°C



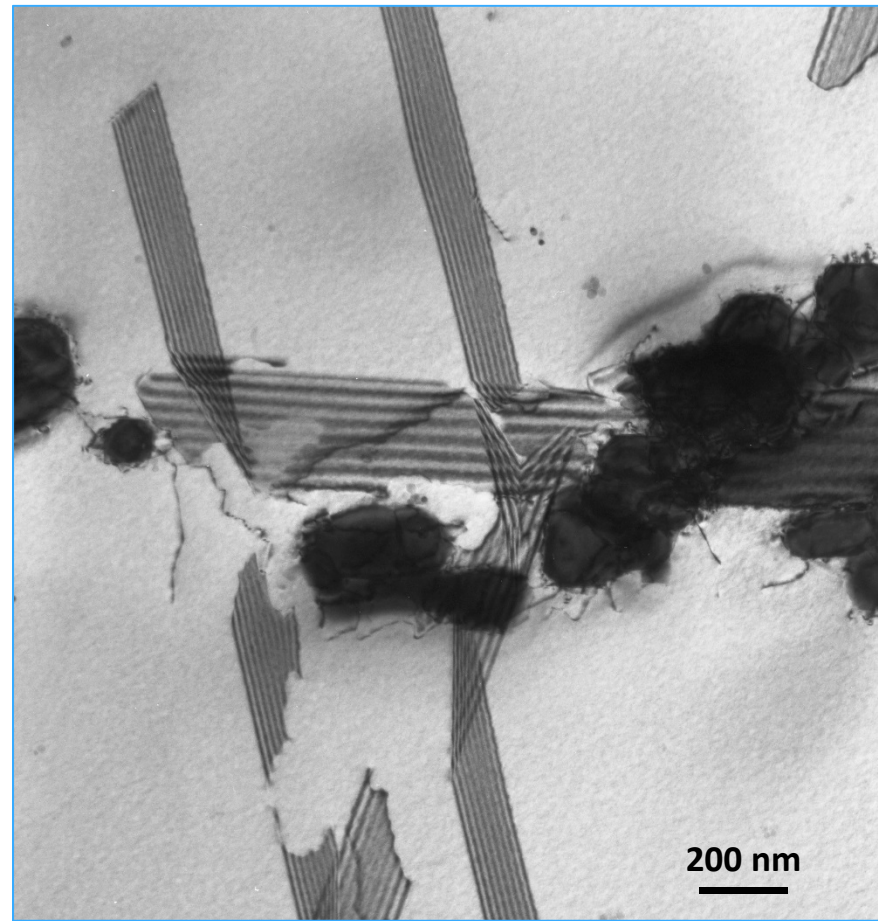
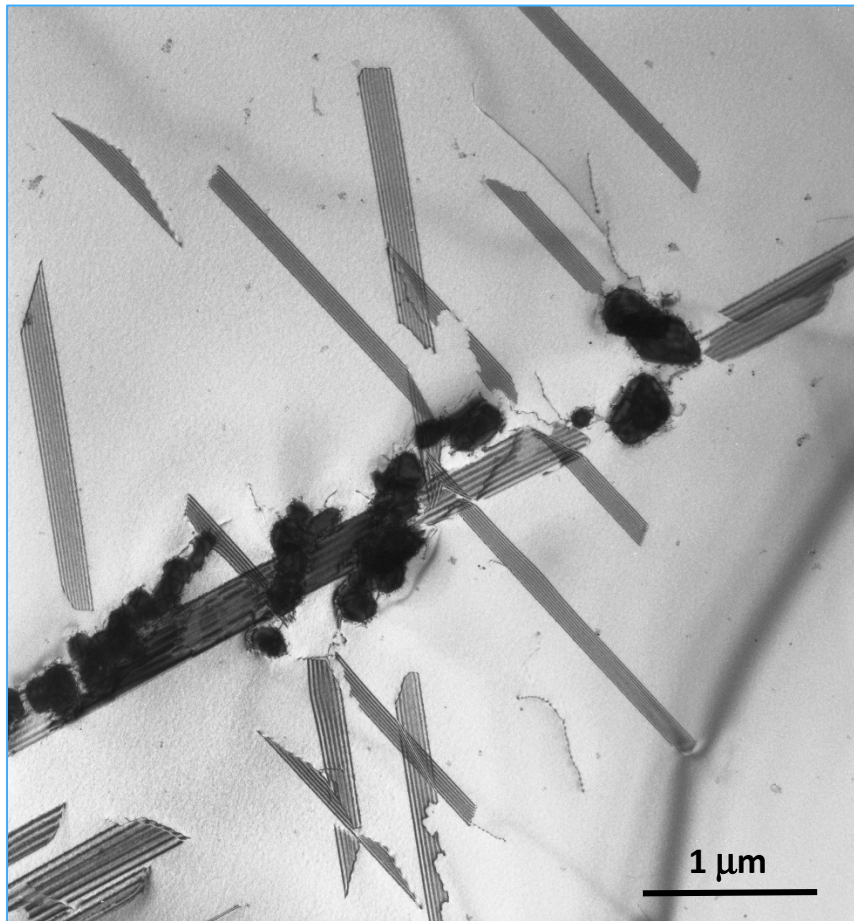
The DP from this twin termination area indicates the common twin relationship with both regions at a $\langle 110 \rangle$ zone axis orientation, and with a rotation of 70.5° across the interface. The weak spots that are readily visible originate from the carbide content. Spots arising from gamma prime are almost impossible to discern.



Carbide Formation on Internal Interfaces



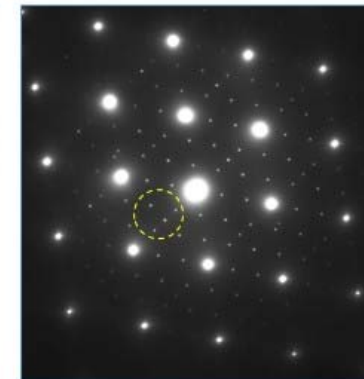
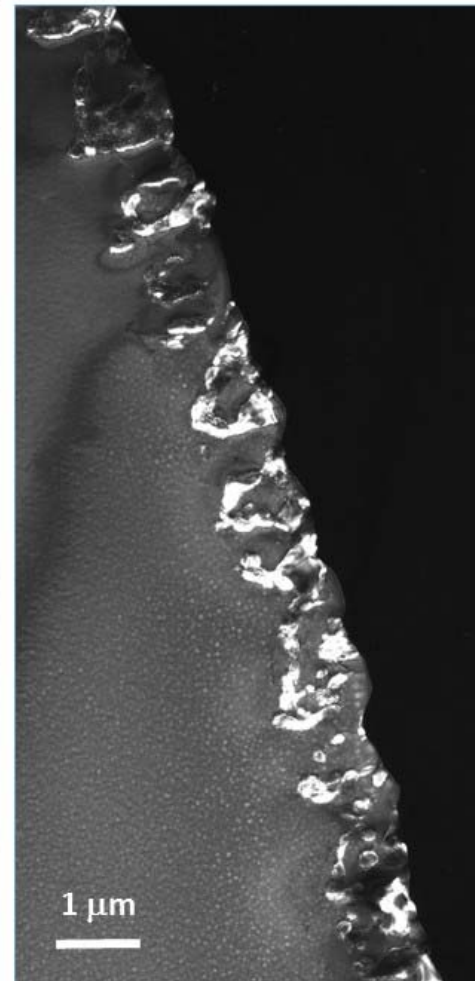
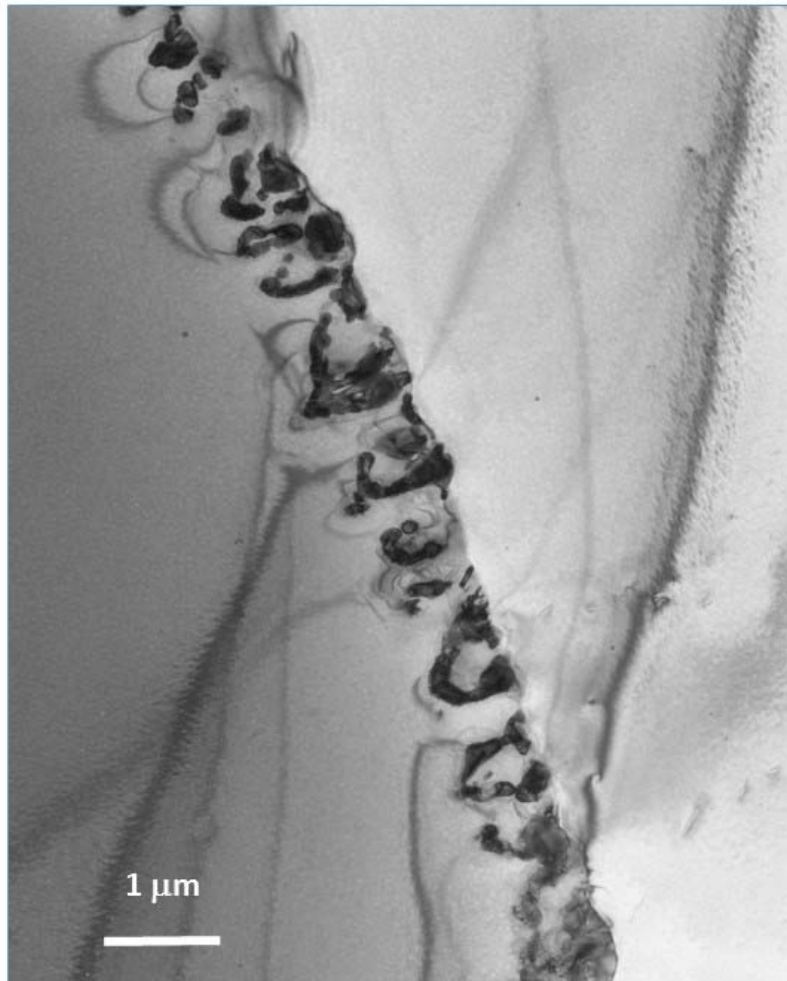
H282-C Aged for 10 hours at 760°C



Grain boundary Carbide, CrMo-rich, $M_{23}C_6$



H282-C Aged for 100 hours at 760°C

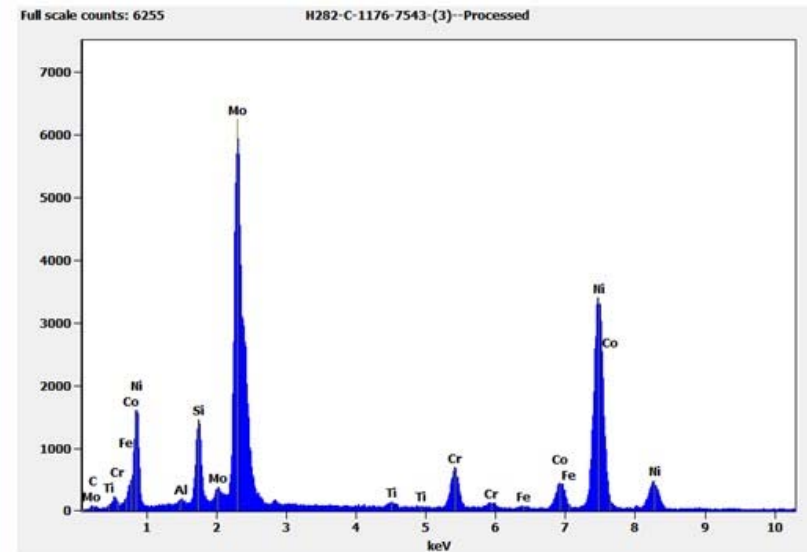
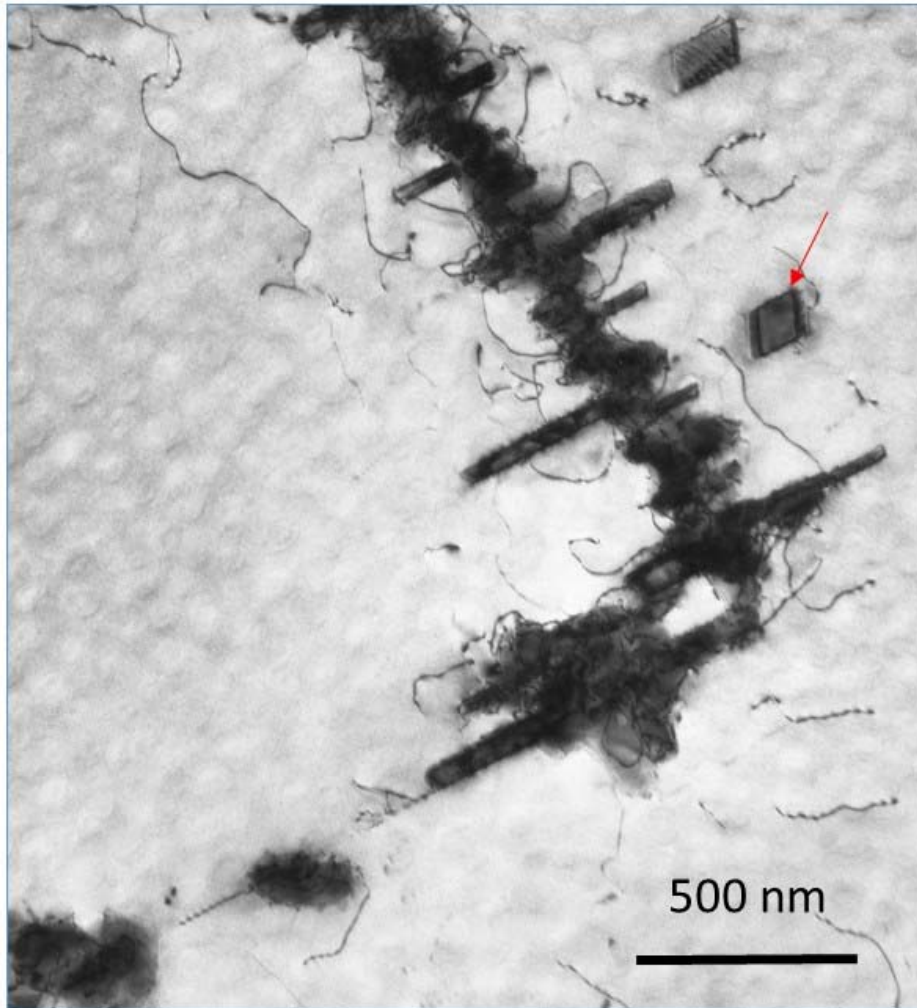


Dark field imaging with a collection of fine spots (but not including intensity from the metal matrix) reveals the coherent nature of this grain boundary phase; confirms its presence only in the left hand grain; and shows some of the gamma prime precipitates in the optimally-tilted region of the thin foil.

Gamma prime, Twin Carbides & Other Features



H282-C Aged for 1,176 hours at 760°C

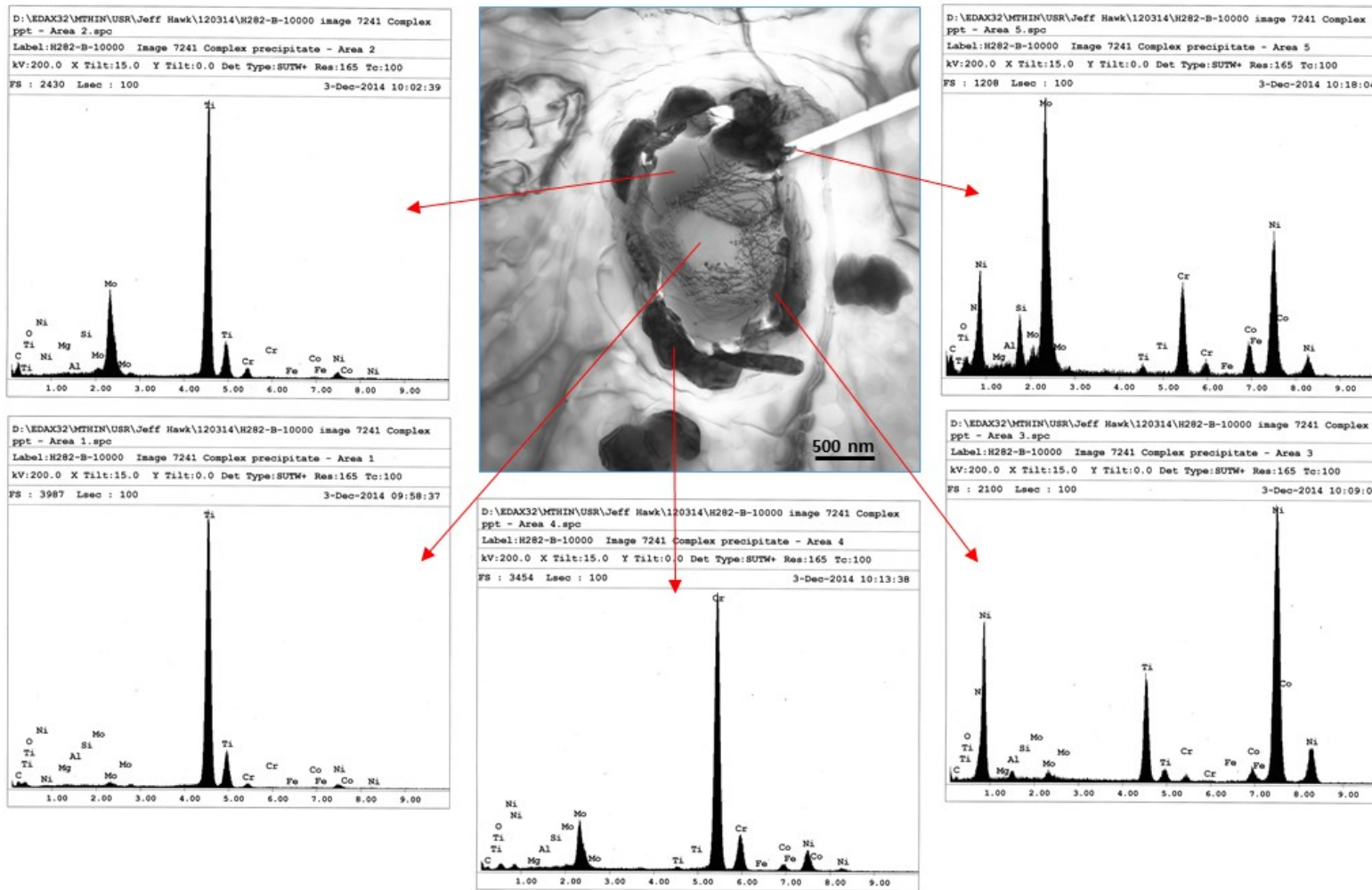


A MoSi-rich phase can be found in both compositions B and C, in a variety of locations, after about 1000 hours of aging – here, in the vicinity of a twin termination (arrowed).

Complex Intragranular Precipitates



H282-B Aged for 9,835 hours at 760°C



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Summary of Feature Evolution with Isothermal Exposure



Haynes 282 Microstructural Evolution During Aging at 760°C

Key:

- CrMo
- MoCr
- TiMo
- High-Mo (twinned/faulted)
- High-Mo (NOT twinned/faulted)
- AlMgTiO (core of complex ppt)
- AlMgO (core of complex ppt)
- MoSi
- High-Ti (carbide or nitride?)
- NiTi
- High-C, High-P

Aging Time	Alloy Designation	Location of Precipitates within the Microstructure			
		Grain Boundary	Intragranular	Twin Termination	Twin Interface
1	B	● ● ●	● ● ● ● ● ● ●	● ● ●	●
	C	● ● ● ●	● ● ● ●	● ●	● ● ● ●
10	B	● ● ●	● ● ● ●	●	●
	C	● ● ●	● ● ● ● ● ● ●	●	●
100	B	● ● ●	● ●	●	●
	C	● ● ●	● ● ● ● ●	●	●
1,176	B	● ●	● ● ● ● ● ●	● ●	●
	C	● ● ●	● ● ● ● ● ●	● ●	●
9,835	B	● ●	● ● ● ● ● ● ● ● ● ●	● ●	● ●
	C	● ● ● ●	● ● ● ● ● ● ● ●	● ●	●
20,000	B	● ● ● ●	● ● ● ● ● ● ● ● ● ●	● ●	● ●
	C	● ● ●	● ● ● ● ● ● ● ● ● ●	● ●	● ●

Precipitate's dominant elements, and the locations at which each variety has been found. The appearance of a MoSi-containing phase (●), beginning at around 1,000 hours is evident, as is the presence of an intragranular NiTi-rich precipitate (●) at around 10,000 hours.

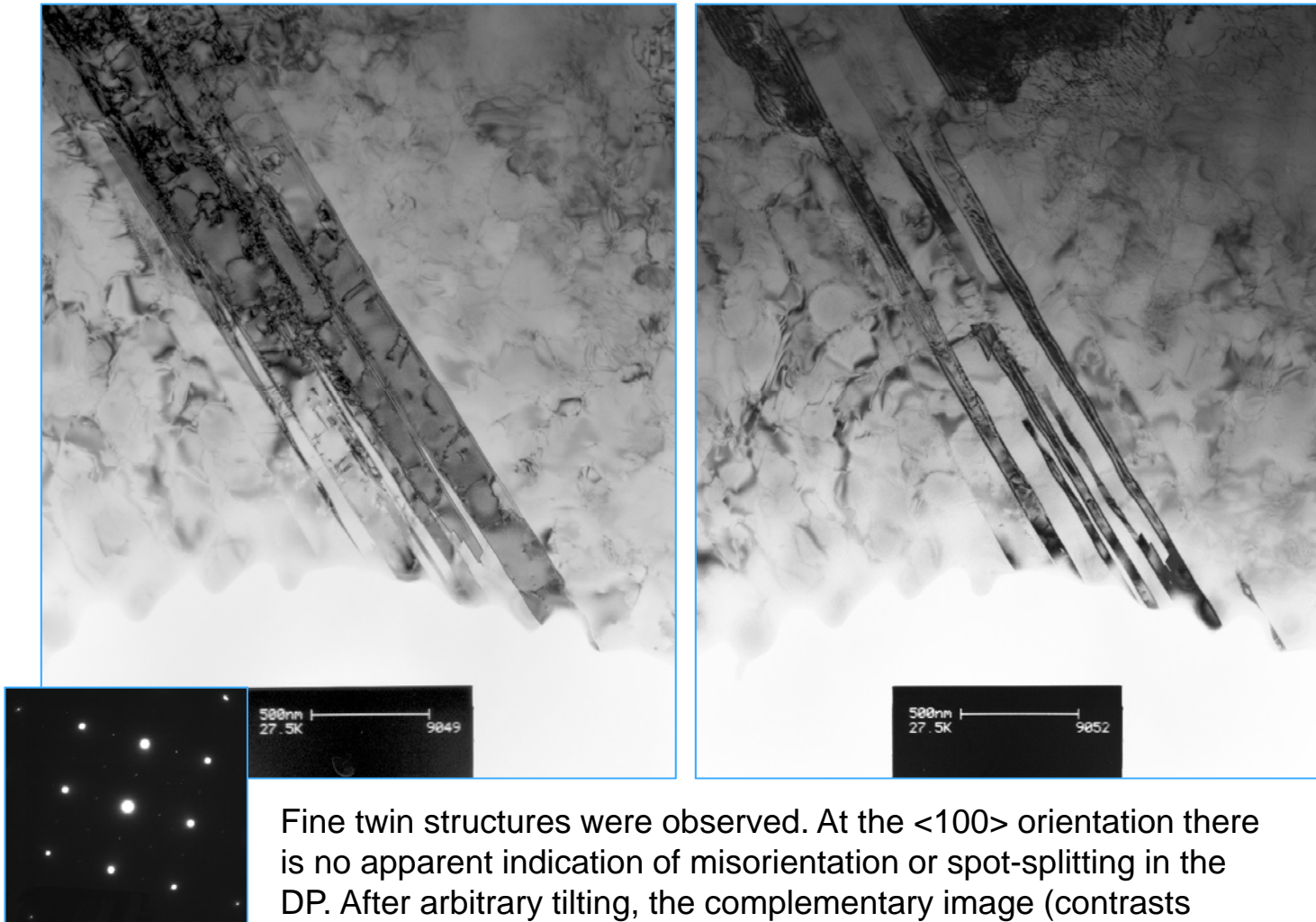
Gamma Prime Coarsening Effects on Creep



The γ' precipitate coarsening behavior of Haynes 282 has been studied from an isothermal perspective. However, what does that really mean in terms of creep? Accelerated creep testing of H282-B / H282-C is underway. The table shows the current status of those results.

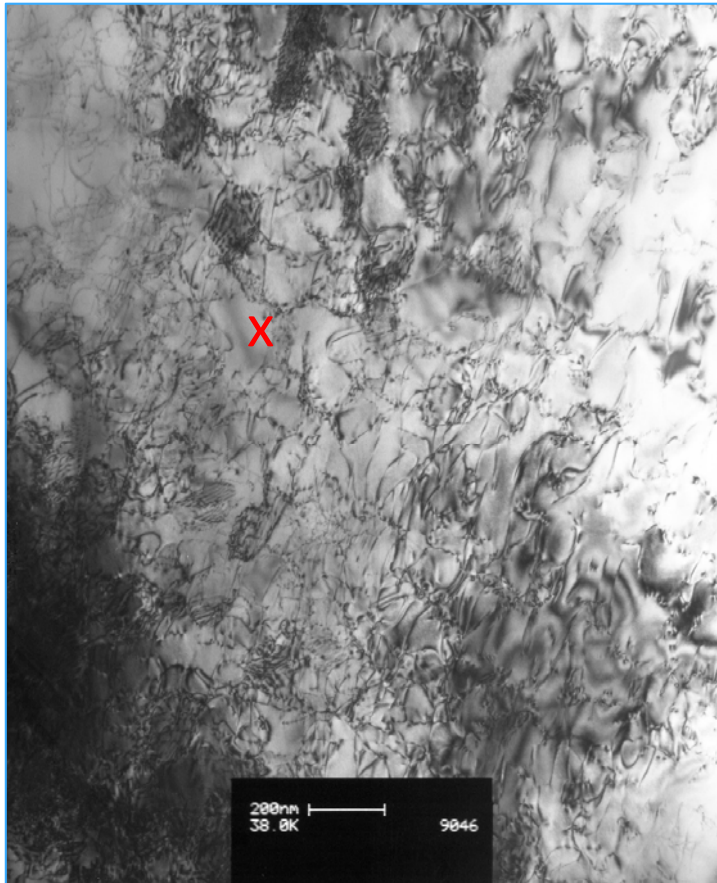
Creep Stress	Temperature	H282-B		H282-C	
		t_f (h)	ϵ_{creep} (%)	t_f (h)	ϵ_{creep} (%)
121	800	4,966	0.58	4,534	0.52
155	800	4,517	----	3,753	----
200	800	1,171	----	1,113	----
276	800	212	----	156	----
345	800	54	----	46	----
414	800	15	----	16	----

Gage Section of Crept H282-B after 1,171 h



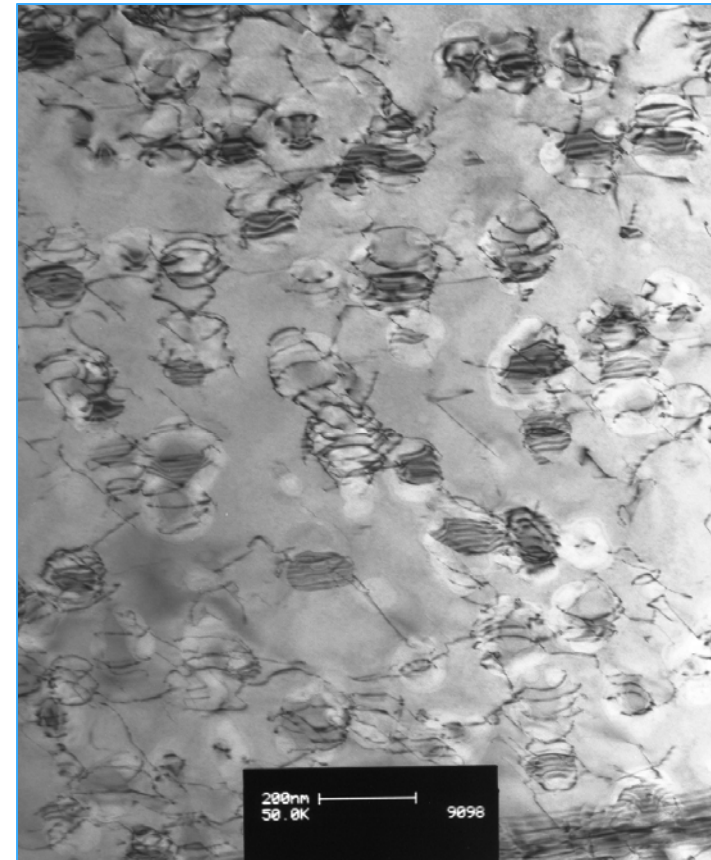
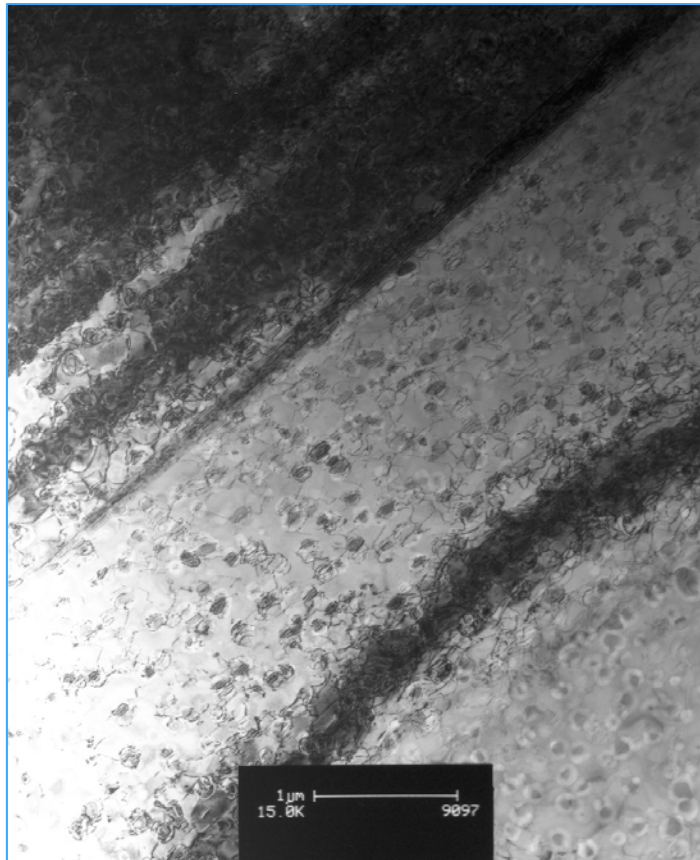
Fine twin structures were observed. At the $\langle 100 \rangle$ orientation there is no apparent indication of misorientation or spot-splitting in the DP. After arbitrary tilting, the complementary image (contrasts reversed) was obtained.

Gage Section of Crept H282-B after 1,171 h



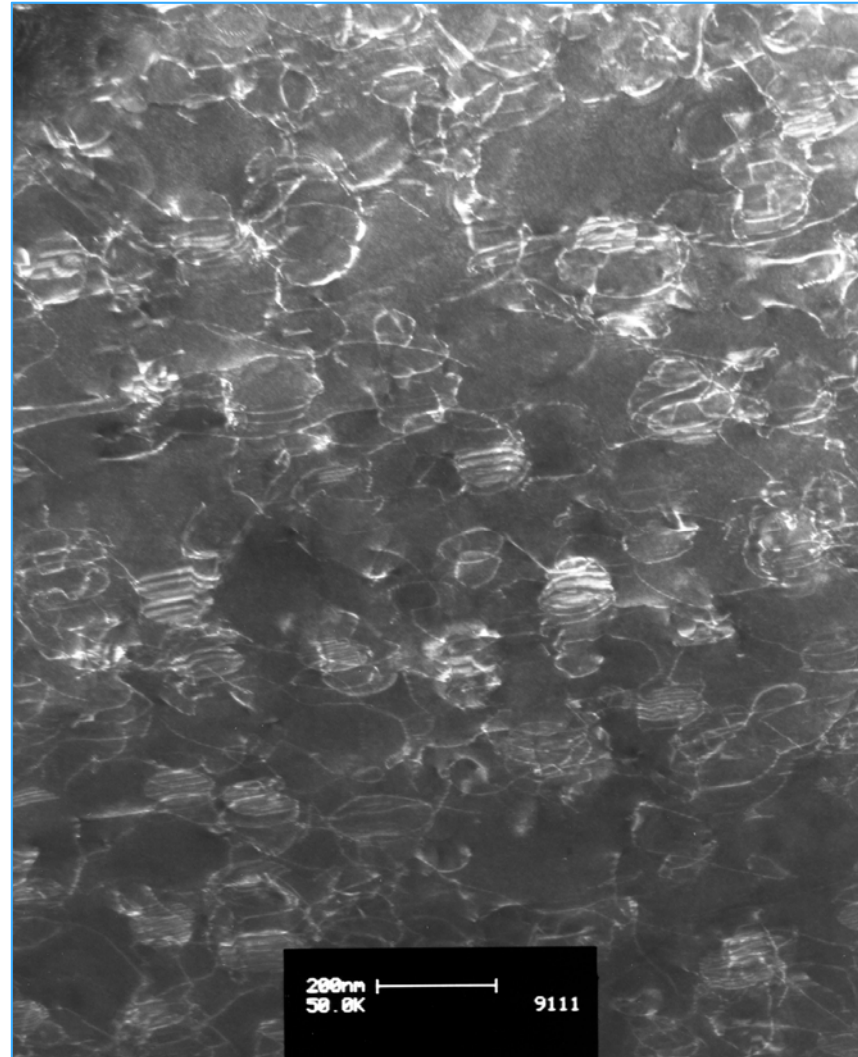
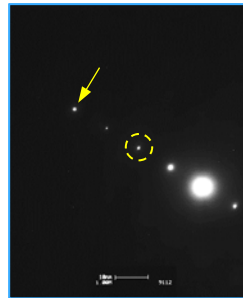
This pair of images from essentially the same region of the foil (with a common feature marked in both images) were recorded at slightly different tilt conditions, and illustrate the difficulty of obtaining a consistent diffraction condition over a broad area of the sample.

Gage Section of Crept H282-C after 1,113 h



Dislocations, imaged in BF mode with $g=111$ near a $\langle 110 \rangle$ zone axis. Whereas there are a few dislocations running across fairly broad regions of g matrix, the majority appear to be quite tightly wrapped around g' precipitates.

Gage Section of Crept H282-C after 1,113 h



A number of attempts at WBDF imaging were made using a variety of imaging conditions – most of them not very successful.

This result was obtained using a 2g/4g condition with a systematic 111 row close to a $\langle 110 \rangle$ zone axis.

Summary Results and Conclusions



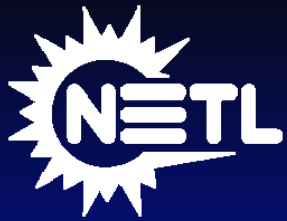
- Haynes 282 is a robust γ precipitate strengthened nickel superalloy. The combination of physical and mechanical properties makes it attractive for A-USC steam & sCO₂ turbine applications.
- Microstructural stability is very good in terms of alloy mechanical properties after long-term isothermal exposure. From a microstructure point of view, the alloy (depending on the specific Ti to Al chemistry) can possess good resistance against coarsening of the γ precipitate, thereby facilitating good creep strength.
- Microstructurally, the alloy is “relatively” simple in that it has γ precipitates and carbide (although there are a number of different carbides that form during isothermal exposure).
- From a structural perspective, the alloy is made up of grains strengthened by carbide as well as twins, which are also stabilized by carbide. This 3-D network provides creep capability not typically seen in nickel superalloys at such a low γ precipitate volume fractions.

Summary of Future Work



- Finish creep testing for 282B / 282C. Repeat creep tests as necessary. Assess creep performance relative to preferred Haynes 282 composition.
- Continue investigations of microstructures from grip and gage for creep tests at 800°C for 200, 155 and 121 MPa stress levels. Assess the γ precipitate size in each section (note that doing so in the gage will be challenging given the degree of strain from dislocations). Convert to equivalent time (via LMP) at 760°C and compared to expected γ precipitate size from isothermal coarsening study.
- Document other non- γ precipitates relative to isothermal annealing experiments as well as general differences between the creep deformed and non-stressed regions within the microstructure.
- Assess future potential of improving upon the creep capability of Haynes 282 close to the nominal composition range of the alloy.

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