Understanding kinetics of phase transformations in precipitation-strengthened low-alloy steels and its influence on mechanical properties

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Presentation Outline

- **Introduction to high-strength low-alloys (HSLA) steels used in U. S. Naval applications**
- **Development and implementation of HSLA-115: where 115 is the yield strength in ksi**
- **Mechanical properties and 3-D atom-probe tomography (APT) results for as-received HSLA-115**
- **3-D atom-probe tomography results for HSLA-115 aged at 550°C**
- **Mechanical properties of NuCu-140 steels: NuCu = Northwestern University Cu precipitation strengthened steels, where 140 is the yield strength in ksi.**

High-Strength Low-Alloy (HSLA) Precipitation Strengthened Steels: Naval Applications

HY (High Yield)

Carbon content

0.12-0.20 wt.%

Microstructure in heat-affected zone (HAZ) susceptible to hydrogen-induced cracking

High degree of preheat, post-weld heating, and stringent control requirements on welding processes increases processing costs

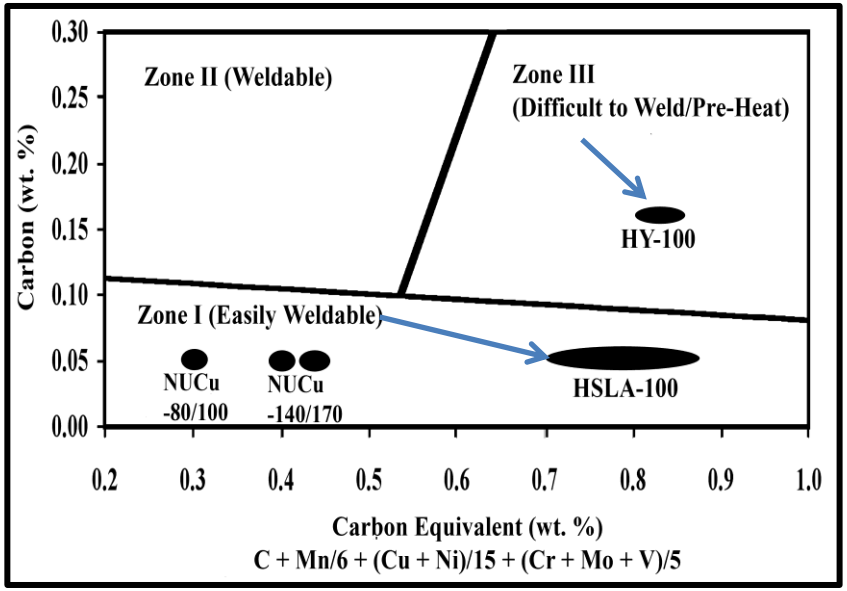
HSLA-100

Carbon content

<0.06 wt.%

Low-carbon concentration enhances weldability, but limits the strength

Cu addition is for precipitation strengthening provided by nanosize Cu-precipitates



Graville Diagram[1]

Development and Implementation of HSLA-115

- **Modified version of HSLA-100: Composition-3**
- **Objective is to increase the yield strength and concomitantly meet other property requirements**
- **Higher strength results in weight reduction and increases factor of safety for critical applications, where thickness reduction is not desired.**
- **Approved for plate production in January 2009; currently used for the flight deck of USS Gerald R. Ford carrier, CVN 78**
- **Development has been mostly empirical; no detailed investigations to date**

HSLA-100 (Comp-3)

Element	Comp (wt%)
C	0.06 max
Cu	1.15-1.75
Ni	3.35-3.65
Al	0.015 min
Mn	0.75-1.15
Si	0.40 max
Cr	0.45-0.75
Mo	0.55-0.65
Nb	0.02-0.06
P	0.02 max
S	0.004max

USS Gerald R. Ford (CVN 78)

Design Chemistry of HSLA-115

- ***Carbon*** **concentration is small to limit the preheating requirements during welding.**

- ***Copper*** **precipitation strengthening is utilized to meet the strength requirements.**

- **Alloying additions of *Cr and Mo* are for increasing hardenability, so that a lath martensitic/bainitic microstructure results on quenching.**

- **Microalloying additions of *Nb* are for refining the grain size during high-temperature rolling and solutionizing treatments**

- ***Nickel*** **addition improves the low-temperature impact toughness and prevents hot shortness that can result due to Cu-addition.**

- ***Mn*** **addition getters sulphur impurities, and provides solid-solution strengthening along with *Si.***

HSLA-100 (Comp-3)

Element	Comp (wt%)
C	0.06 max
Cu	1.15-1.75
Ni	3.35-3.65
Al	0.015 min
Mn	0.75-1.15
Si	0.40 max
Cr	0.45-0.75
Mo	0.55-0.65
Nb	0.02-0.06
P	0.02 max
S	0.004max

As-Received HSLA-115 from NSWC Carderock Division

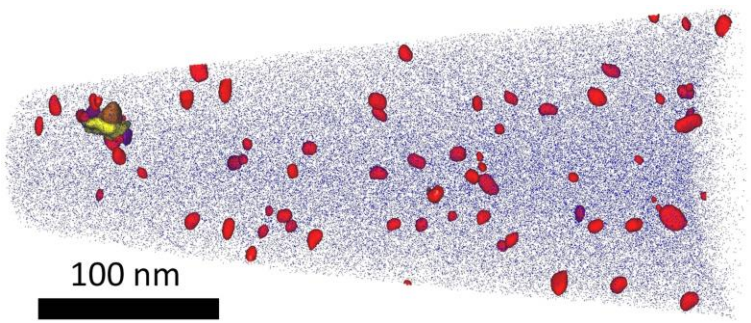
- **Heat Treatment**
  Solution-treated at 913°C by "double-austenitization" treatment and water quenched. Aged at 660°C for 49 minutes and air cooled.

- **3-D Atom-probe tomographic (APT) observations.**
  - **Over-aged Cu precipitates,**
    <R> = 4.36±2.05 nm
    N_v = 2.0±0.5 x 10^{22} m^{-3}

  - **M_2C precipitates were rarely observed**

- ***<u>Motivation to temper at 550°C</u>***

  - **Suitable tempering temperature to facilitate precipitation of M_2C (M = Mo, Cr, Fe) metal carbides along with Cu-precipitates**



3-D APT reconstruction of as-received HSLA-115[1]

Mechanical Properties of as-received HSLA-115	
Yield strength (YS)	806.23±9.55 (MPa) 116.93±1.38 (ksi)
Elongation to failure (%)	23.32±0.15
Impact Toughness	139.67±16.50 ft-lbs (-84.4°C)
	164.67±10.26 ft-lbs (-18°C)

Characterization of the nanostructure of HSLA-115 aged at 550°C using 3-D atom-probe tomography

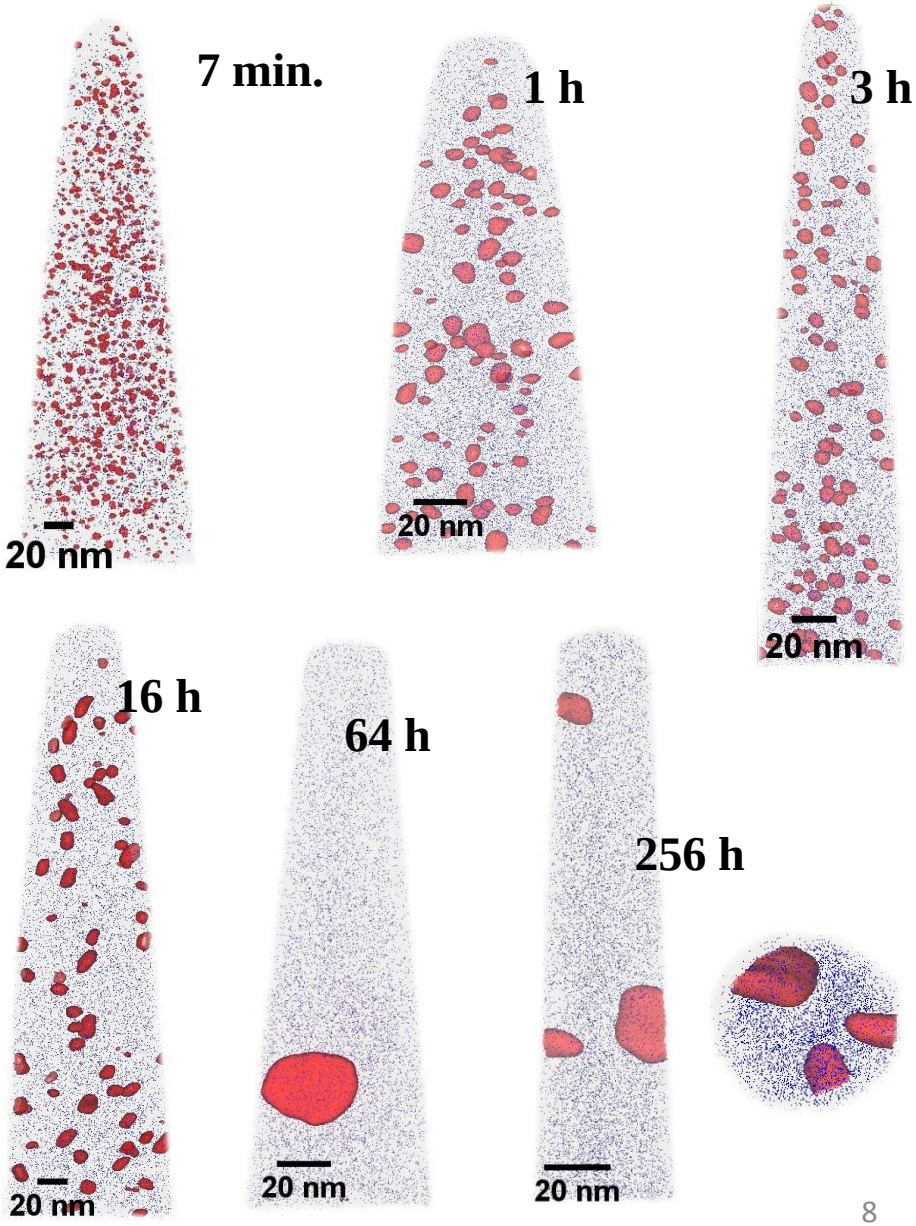
Aging study from 7 minutes to 256 h

- **Temporal evolution of copper precipitates at 550°C**
- **Temporal evolution of M_2C carbides at 550°C**
- **Niobium carbide precipitates observed in solutionized and as-quenched sample, and 16 h aged samples**
- **Coarse-cementite precipitates observed at 0.25 h of aging**
- **Colocated Cu precipitates and M_2C carbides observed at intermediate aging times of 0.25, 1, 3 and 16 h**

Temporal evolution of Cu-precipitates at 550°C

Cu precipitates are delineated by Cu-10 at. % iso-concentration surfaces (shown in red). Matrix Fe-atoms are shown in blue (only a fraction is displayed for clarity)

- **Cu-precipitates were *not* observed in the solutionized and as-quenched HSLA-115.**
- **Profuse Cu-precipitation occurs *after 7 minutes of aging.***
- **Cu-precipitates transform from spherical precipitates to ellipsoids, discs and rod-morphologies with increasing aging time**



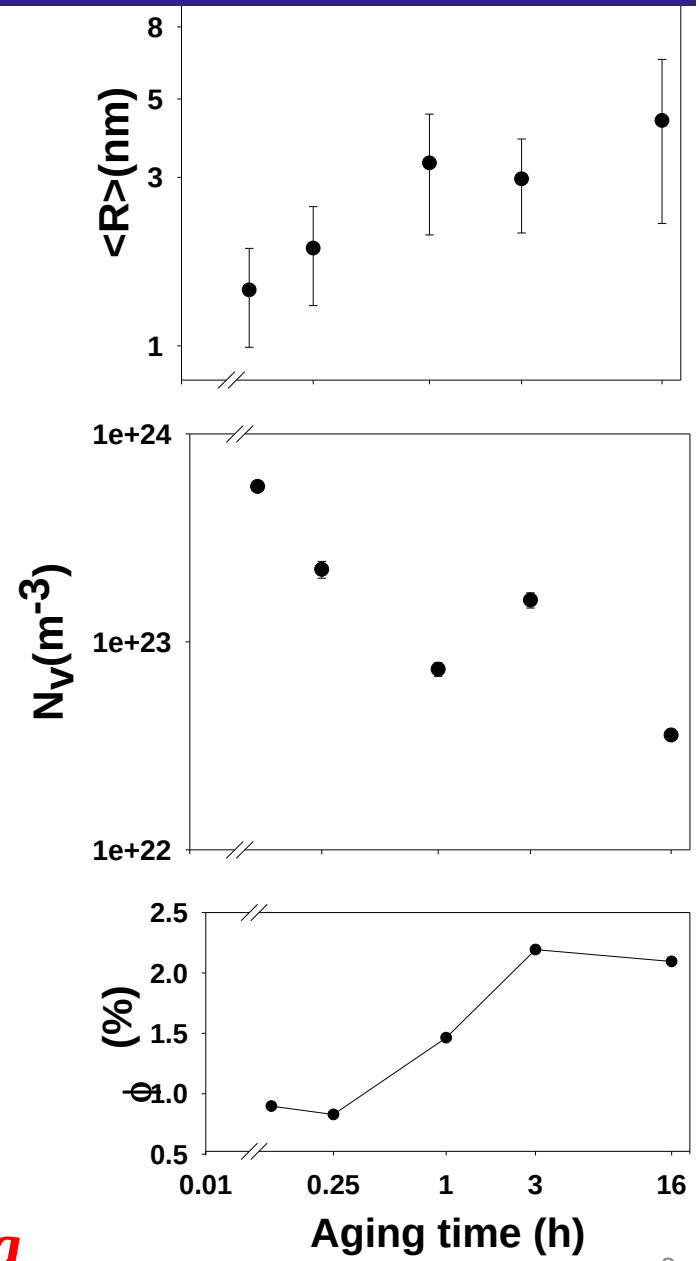
Temporal evolution of Cu-precipitates at 550°C

<R(t)>: Average radius (nm)

ϕ (t) %: Volume fraction

N_v(t): Number density (m^{-3})

- **Kinetics of Cu precipitation in HSLA-115 steel is complex.**
- **Evolution of Cu-precipitates is influenced by the co-located M_2C carbides at intermediate aging times, in particular from 1 h to 16 h**
- **<R(t)> is nearly the same at 1 and 3 h of aging, with a concomitant increase of N_v (t) and ϕ(t) indicating nucleation regime**
- **M_2C carbides and dislocations can be providing a reduced driving force for nucleation of Cu- precipitates, even with a significantly reduced supersaturation during this period.**

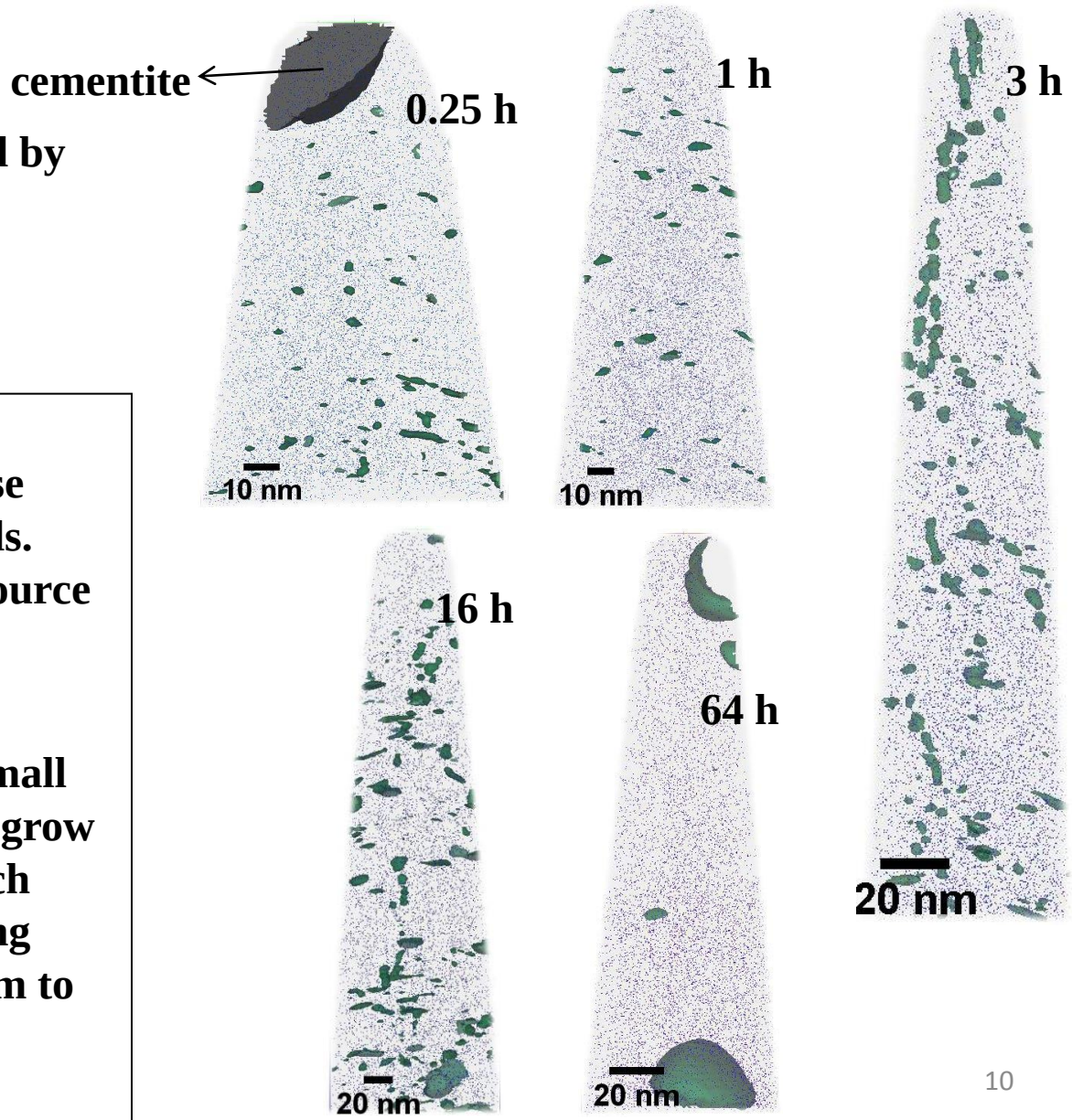


N_v(t) > 10^{23} m^{-3} even after 3 h of aging

Temporal evolution of M_2C carbides at 550 ^oC

M_2C carbides are delineated by 5 at.% (C + Cr + Mo) iso-concentration surfaces (displayed in dark green).

- **A fine dispersion of M_2C carbides replaces the coarse cementite as aging proceeds. Dissolving cementite is a source of carbon atoms for M_2C carbides.**
- **M_2C carbides nucleate as small spheroidal precipitates and grow as needles and/or rods, which thicken with increasing aging time. These finally transform to large irregular spheroids**



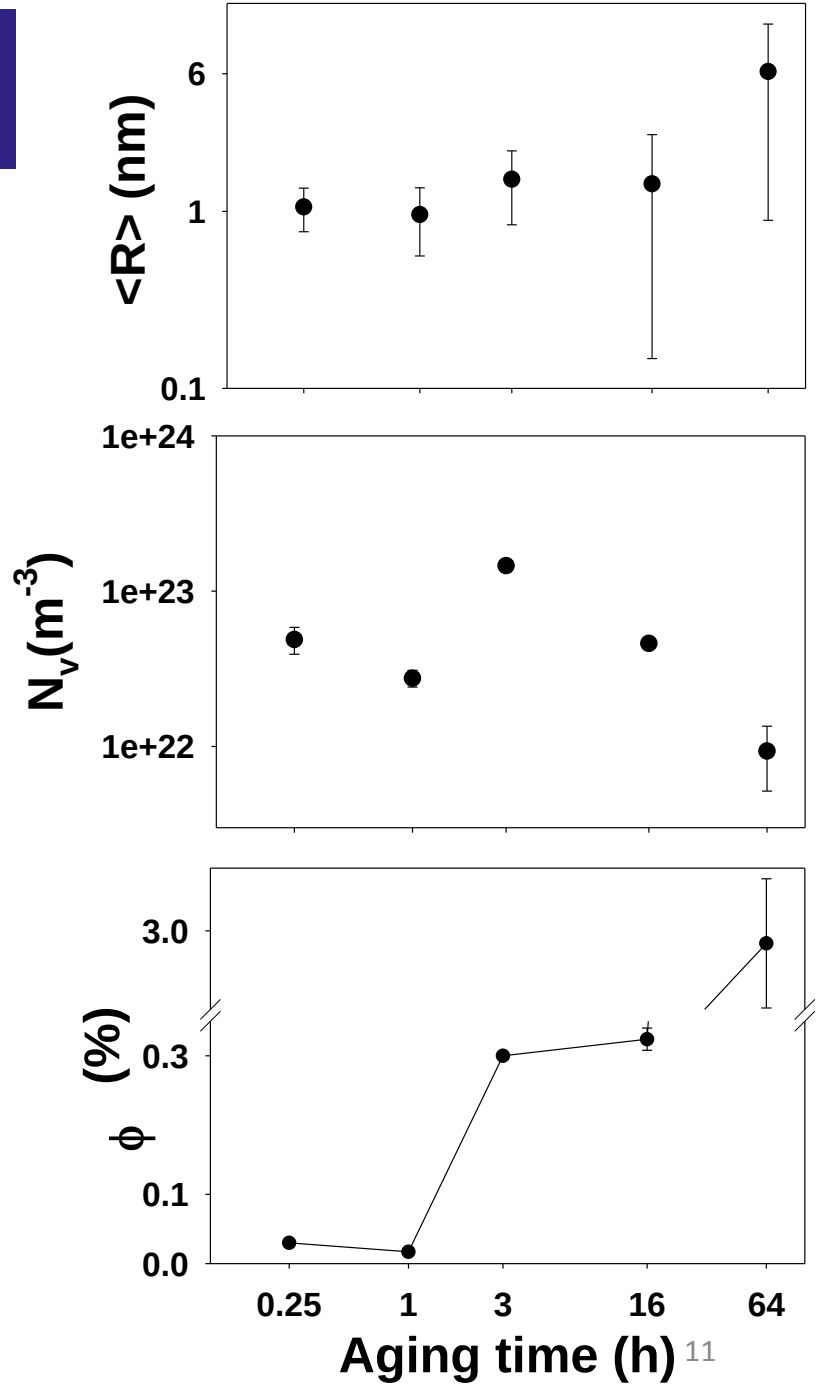
Temporal evolution of M_2C carbides at 550°C

<R(t)>: Average radius

ϕ (t)(%): Volume fraction

N_v(t): Number density

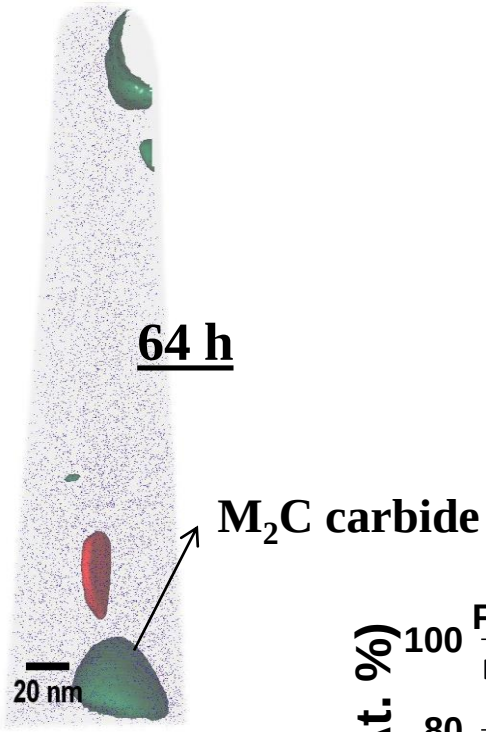
- **<R (t)> is nearly the same between 0.25 to 3 h of aging.**
- **N_v(t) increases significantly after 1 h of aging and has a maximum at 3 h.**
- **ϕ(t) increases from 1 to 3 h. This implies nucleation occurring until 3 h of aging**
- **ϕ(t) increases significantly after 16 h with a concomitant increase in <R (t)> and decrease in N_v(t), indicating the occurrence of growth and coarsening between 16 h and 64 h of aging**



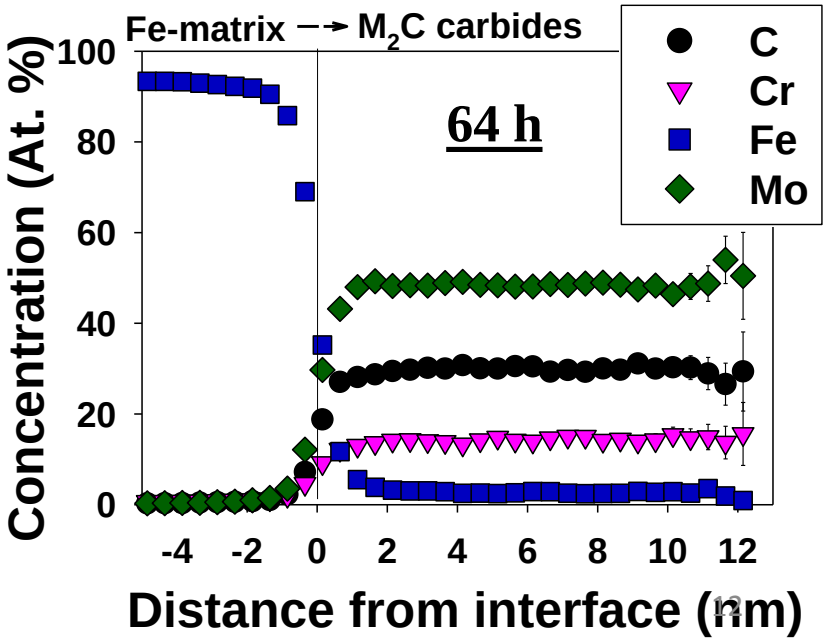
Composition of M_2C carbides: M = Mo, Cr, Fe

- **M_2C carbides at shorter aging times (< 3 h) are enriched in Fe, depleted in C and have nearly equal Cr and Mo concentrations.**

- **Composition at early aging times *may be affected* by local magnification effects, arising due to differences in the evaporation fields of the M_2C carbides and the matrix, Fe atoms**



At.%	Concentrations obtained from the proxigrams (±2σ)
Mo	48.4±0.3
Cr	14.2±0.2
Fe	2.8±0.1
Mn	3.2±0.1
C	30.0±0.3



- **At longer aging times (64 h), the Cr-to-Mo ratio as well as the Fe-concentration decreases significantly; the proxigram on the right-hand side displays the concentration profiles across the Fe/M_2C interface at 64 h of aging**

Other microstructural Observations

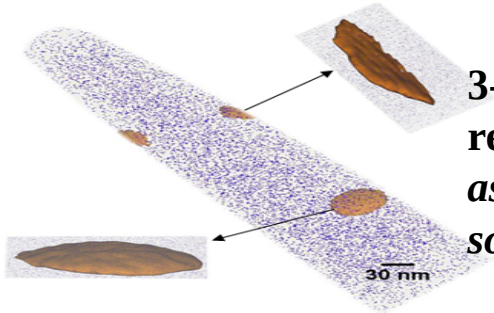
- **<u>Niobium carbide precipitates are observed in solutionized and quenched sample and 16 h aged samples:</u>**
  - **Microalloying additions of Nb to HSLA steels refine the grain size.**
  - **Number density observed of precipitates $<10^{21}$ m^{-3}**
  - **Significant concentrations of nitrogen and molybdenum in these precipitates**

- **<u>A coarse cementite precipitate is observed at 0.25 h of aging:</u>**
  - **Coarse morphology of cementite is deleterious to impact toughness.**
  - **Enrichment of Mn, Cr and Mo and depletion of Si occurs in the cementite phase.**

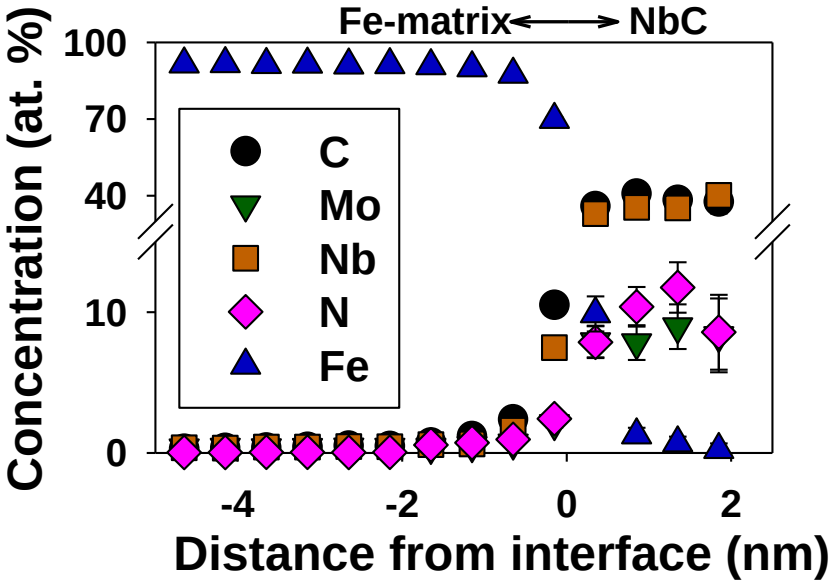
- **<u>Sequence of precipitation of Cu precipitates and M_2C carbides:</u>**
  - **Cu precipitates appear first at 7 minutes of aging while M_2C carbides are not observed at this aging time**
  - **M_2C carbides first appear at 0.25 h of aging time. They are observed to be co-located with Cu-precipitates at intermediate aging times of 0.25 1, 3 and 16 h**

Niobium carbide precipitates observed in solutionized and as-quenched sample and 16 h aged samples

- **NbC precipitates are delineated by Nb-3 at.% isoconcentration surfaces (displayed in brown).**
- **Cu precipitates are not observed in solutionized and as-quenched sample.**
- **Disc-shaped NbC precipitates are observed; they weren't dissolved during the solutionizing treatment at 912°C**
- **Number density observed is $<10^{21} m^{-3}$, though their detection in the 16 h aged sample suggest that these are present at all the aging times studied**



3-D APT reconstruction of *as-quenched solutionized sample*



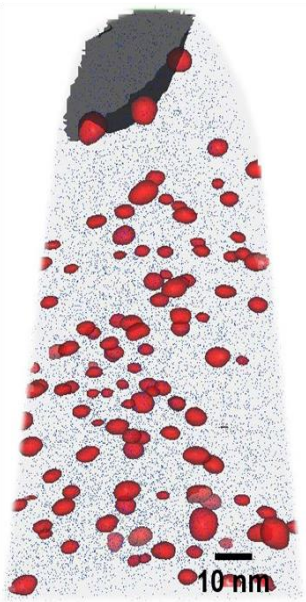
Core concentrations in niobium carbide

Element	Nb	Mo	C	N
At.% (±2σ)	36.0±1.7	8.3±1.0	40.1±1.7	10.4±1.1

Cementite in 0.25 h aged sample

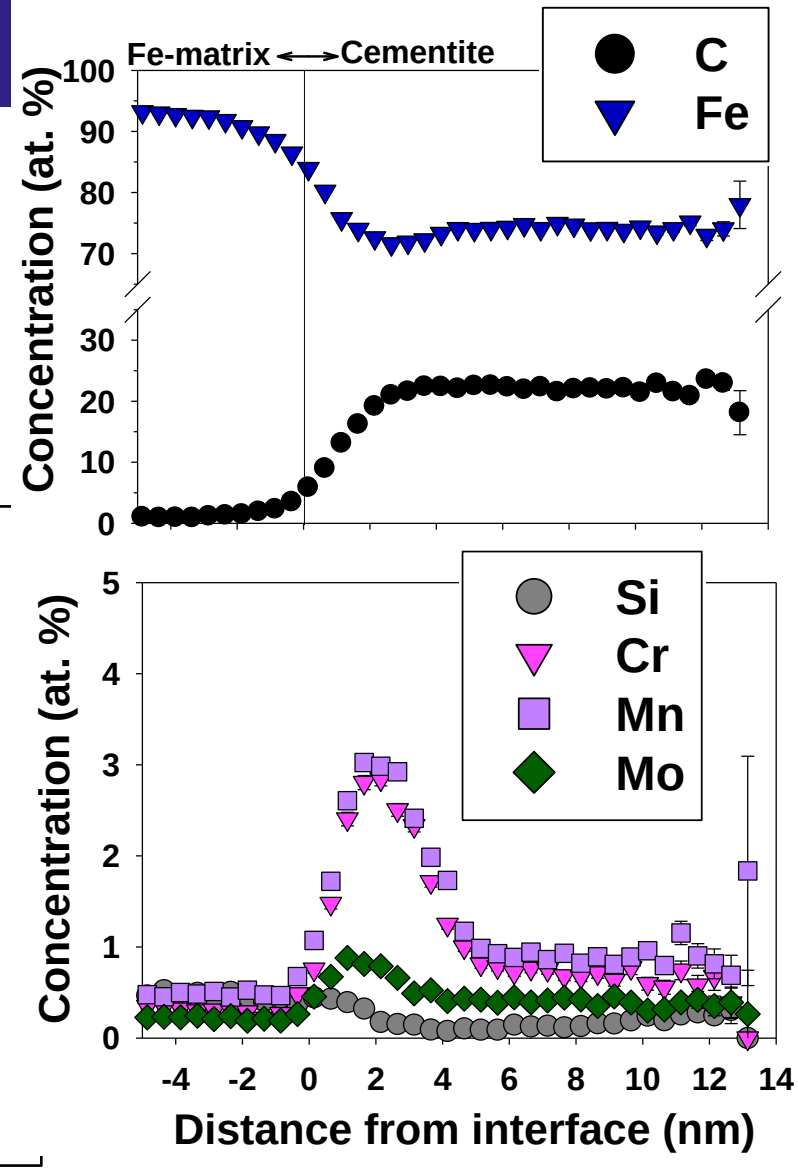
- Cementite is delineated by a C-5 at.% isoconcentration surface, shown in black in the 3-D atom-probe tomography reconstruction shown below

- To the right is displayed proxigram across the Fe/cementite interface



- There are localized concentration peaks of Mn, Cr and Mo observed near the interface on the cementite side of the precipitate

- Depletion of Si occurs in the core of the cementite precipitate.

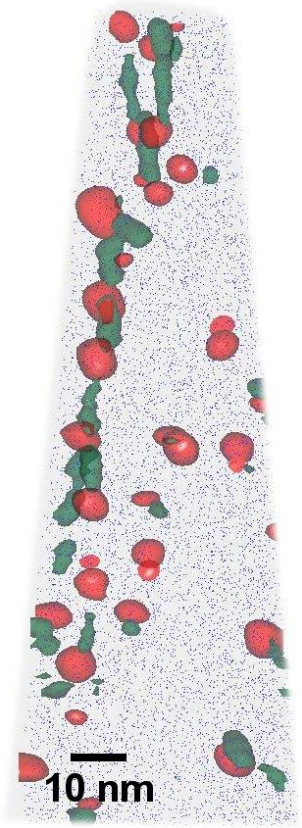


Chemical composition of the core of cementite precipitate

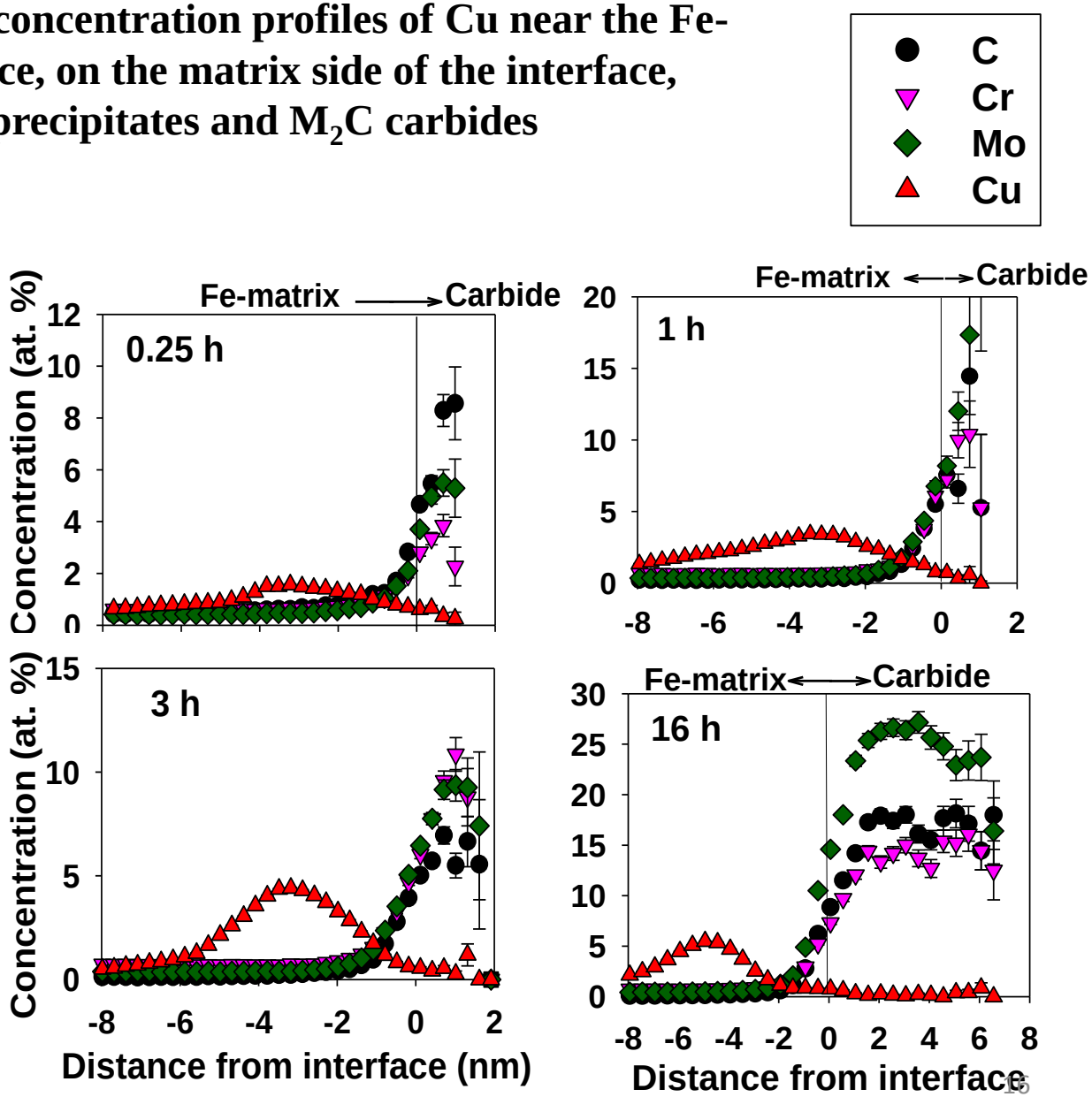
Element	Fe	C	Mo	Cr	Si	Mn	Ni
At.%(±2σ)	71.2±0.1	23.3±0.1	0.4±0.02	0.83±0.03	0.12±0.01	1.0±0.03	2.3±0.05

Co-location of Cu-precipitates and M_2C carbides

Localized enrichment in the concentration profiles of Cu near the Fe-matrix/Cu-precipitate interface, on the matrix side of the interface, indicating co-location of Cu precipitates and M_2C carbides



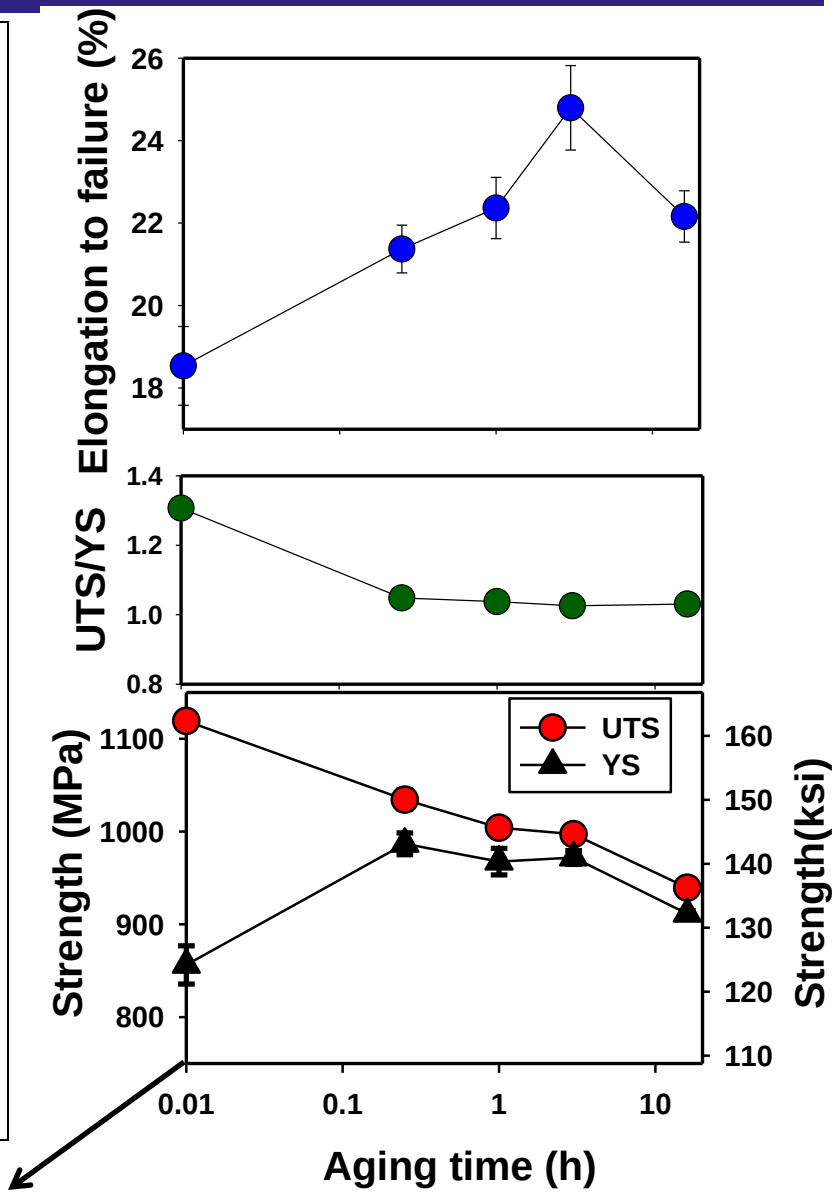
3-D atom-probe tomographic reconstruction of 3h aged sample



Mechanical Properties obtained for HSLA-115 aged at 550°C

Trends in the tensile properties of HSLA-115

- **UTS is a maximum for the solutionized and as-quenched HSLA-115, while the YS attains its maximum value at 0.25 h of aging**
- **Plateau region is observed for both the UTS and YS trends at intermediate aging times**
- **Negligible work-hardening except for the as-quenched sample**
- **Elongation to failure is minimum for the as-quenched sample. It increases with aging time and attains maximum at 3 h of aging**

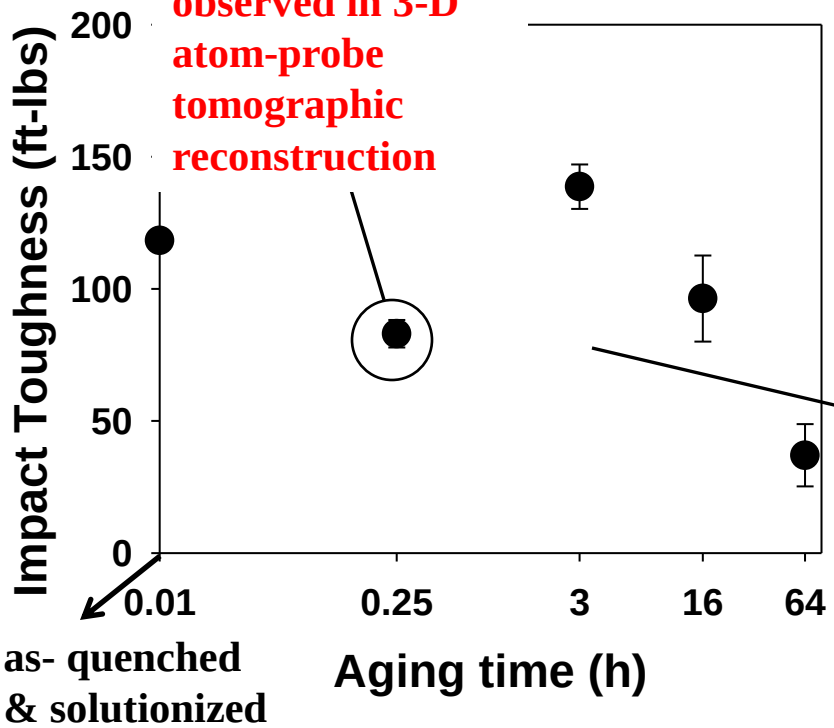


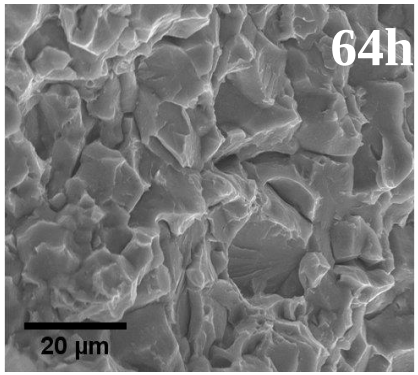
Solutionized & as- quenched

Charpy Impact Toughness at -18°C of HSLA-115

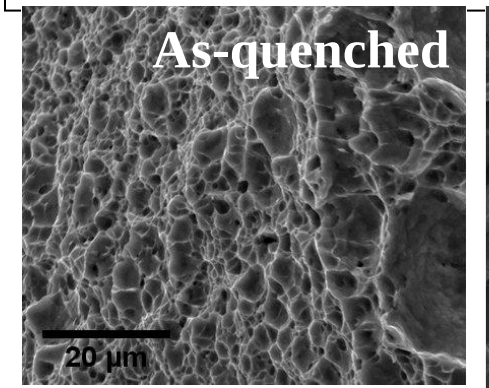
- **Toughness decreases significantly after 0.25 h of aging**
- **Maximum toughness at 3 h**
- **Prolonged aging at 64 h results in minimum toughness**
- **SEM fractographs in qualitative agreement with obtained toughness**

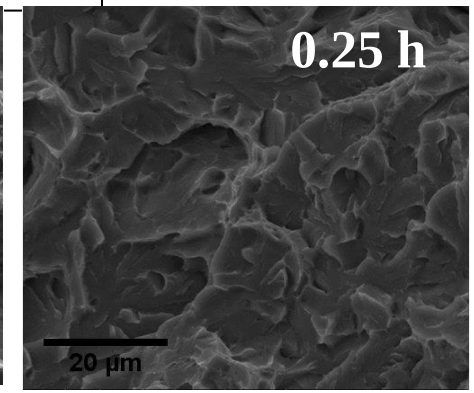
Coarse cementite observed in 3-D atom-probe tomographic reconstruction

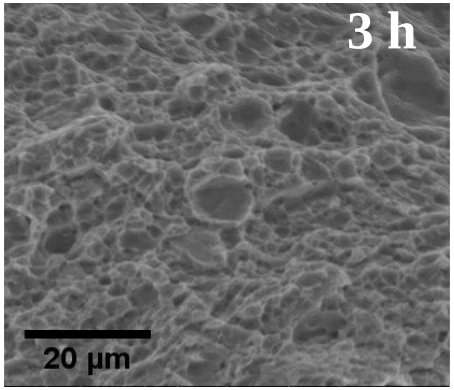


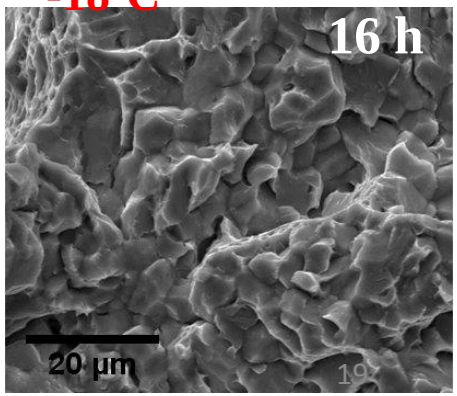


80 ft-lbs is the minimum impact toughness requirement of these steels for Naval applications at -18°C









Comparisions between the mechanical properties of HSLA-115 and NuCu-140 steels with sub-nanoscale microstructural information obtained using 3-D atom-probe tomography

(Both steels aged at 550ºC)

Chemical Composition (wt. %)

Elements	HSLA -115	NuCu-140
C	0.05	0.05
Cu	1.29	1.64
Ni	3.37	2.77
Al	0.02	0.59
Mn	0.97	0.48
Si	0.22	0.50
Nb	0.02	0.065
Cr	**0.69**	**0.02**
Mo	**0.33**	**-**

Comparison between HSLA-115 and NuCu-140

HSLA-115

- Addition of Cr & Mo increases hardenability, results in a predominantly lath martensitic/bainitic microstructure of the as-quenched sample
- Aging at 550°C facilitates co-precipitation of Cu-precipitates and M_2C (M = Mo, Cr, Fe) carbides
- Secondary-hardening provided by M_2C carbides and slower coarsening of Cu-precipitates maintains a high yield-strength at 3 h of aging time, where impact toughness improves

NuCu-140

- Mixture of ferritic lath and equiaxed ferrite microstructure in the as-quenched sample
- Does not form M_2C carbides. Cu-precipitates coarsen faster than in HSLA-115
- Significant decrease in strength at 3 h of aging time, where impact toughness improves

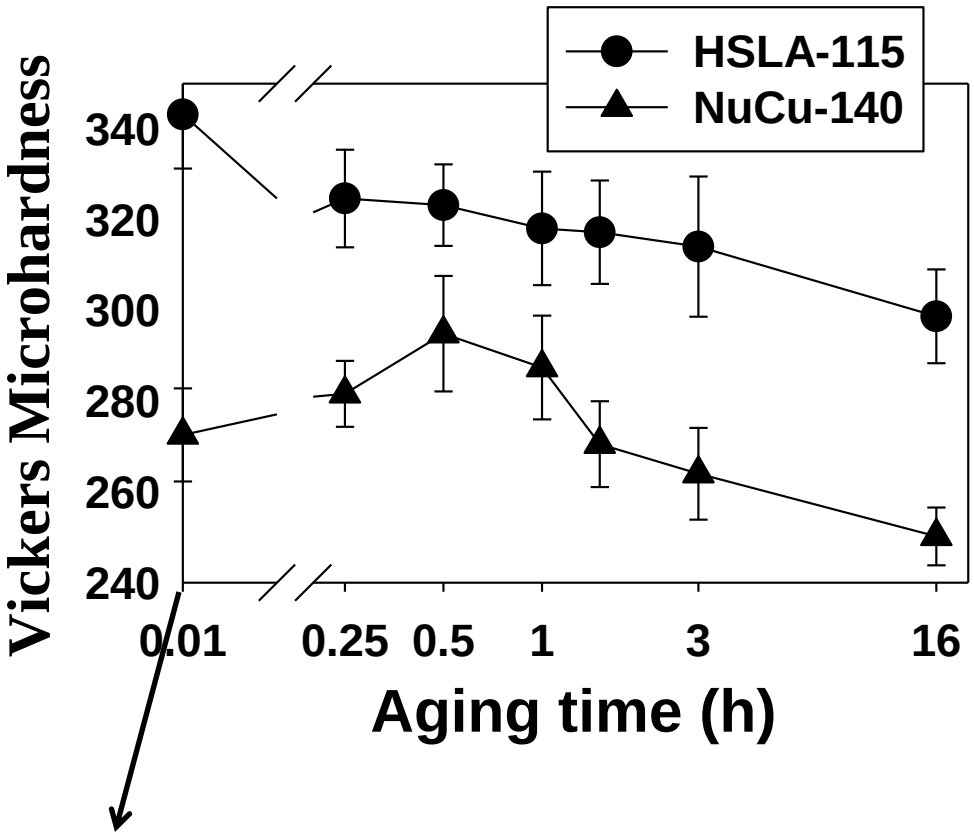
Chemical compositions

Elements (wt. %)	HSLA-115	NuCu-140
C	0.05	0.05
Cu	1.29	1.64
Ni	3.37	2.77
Al	0.02	0.59
Mn	0.97	0.48
Si	0.22	0.50
Nb	0.02	0.065
Cr	0.69	0.02
Mo	0.33	-

Maintenance of high strength at long aging times in HSLA-115

- **After aging for 3 h, microhardness decreases by 3.3% from its peak aged condition (1/4 h) in HSLA-115, while the decrease is 10.5% for NuCu-140 from its peak aged condition (0.5 h aging)**

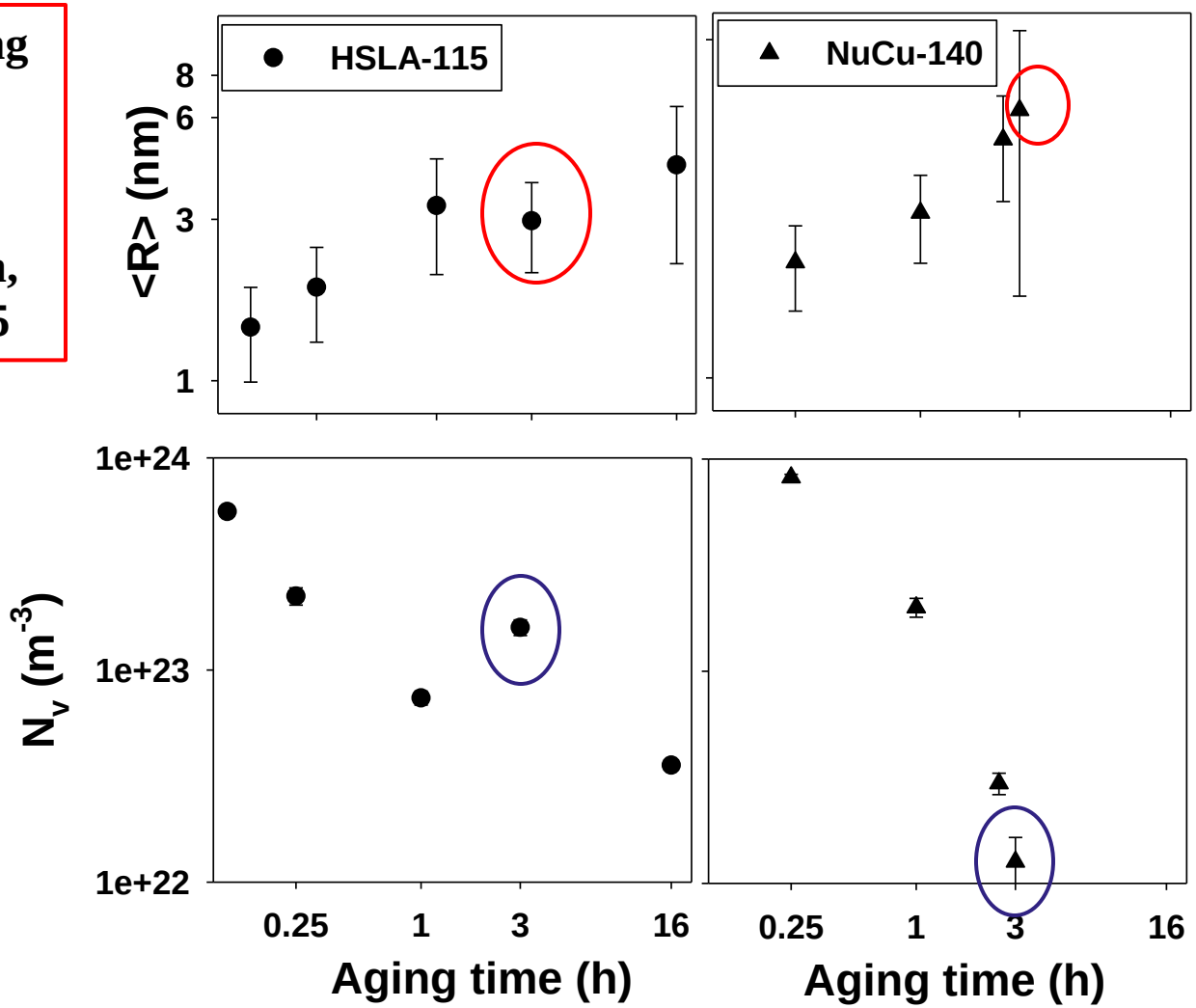
- **This is due to a combination of secondary-hardening provided by the M_2C precipitates in HSLA-115 and slower coarsening kinetics of Cu precipitates in HSLA-115.**



Slower coarsening of Cu-precipitates in HSLA-115 than in NuCu-140

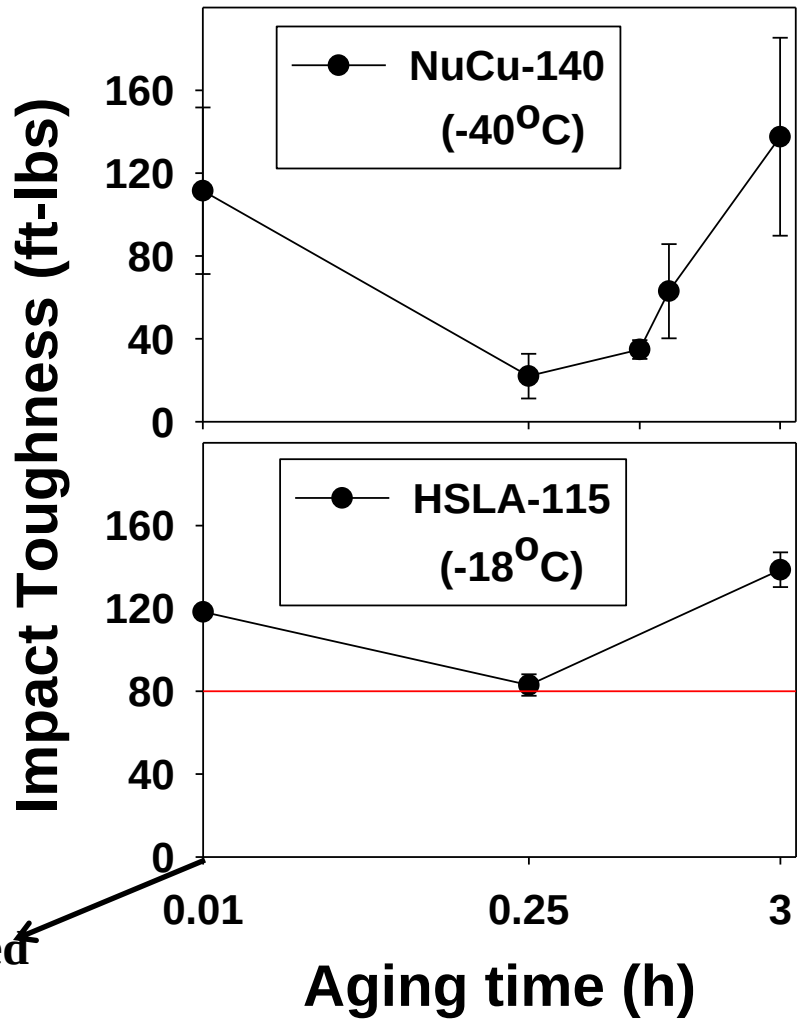
- **<R(t)> after 2.5 h of aging in NuCu140 is > 5 nm**
- **<R(t)> at 3 and16 h of aging is 2.97 and 4.35 nm, respectively, in HSLA-115**

- ***N_v after 3 h of aging is one order of magnitude greater in HSLA-115 than in NuCu-140.***
- ***Even after 16 h of aging, $N_v(t)$ in HSLA-115 is more than twice as large as in NuCu-140 at 3 h.***



Similar trend of sub-ambient impact toughness in both steels

- **Impact toughness decreases in both steels at 0.25 h from its solutionized and as-quenched value**
- **Impact toughness then increases to attain its maximum value at 3 h of aging in both steels**
- **Maintenance of high-strength at 3 h of aging in HSLA-115 is thus highly beneficial as it leads to a better combination of strength-impact toughness properties as compared to NuCu-140**



as- quenched solutionized

80 ft-lbs is the minimum impact toughness requirement of these steels for Naval applications at -18°C

Conclusions from the aging study of HSLA-115 at 550°C

- **Strength achieved at 550°C aging temperature is significantly greater than required by U.S. Naval specifications, and thus HSLA-115 with its current composition is a candidate for higher-strength applications.**
- **Bulk mechanical properties obtained for HSLA-115 and NuCu-140 are compared and correlated with microstructural and sub-nanoscale observations using 3-D atom-probe tomography**
- **A tempering temperature of 550°C facilitates co-precipitation of Cu precipitates and M_2C carbides in HSLA-115. Cu precipitates appear to serve as nucleating agents for M_2C nucleation because M_2C carbides are co-located on Cu precipitates.**
- **Kinetics of Cu-precipitation is also affected by the co-located M_2C carbides, which may inhibit Cu-diffusion resulting in the deceleration of the coarsening of Cu-precipitates in HSLA-115. Similar phenomena were also observed in BA-160 steels.[1]**
- **Unlike NuCu140, HSLA-115 tempered at 550°C, maintains its strength for long aging times.This result is significant as the desired toughness values are often obtained after significant tempering, which results in a loss of strength**

1. Mulholland, M. D., & Seidman, D. N. (2011). Nanoscale co-precipitation and mechanical properties of a high-strength low-carbon steel. *Acta Materialia*,*59*(5), 1881-1897.

Acknowledgements

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Welding Studies of NuCu-140 steels: Motivation

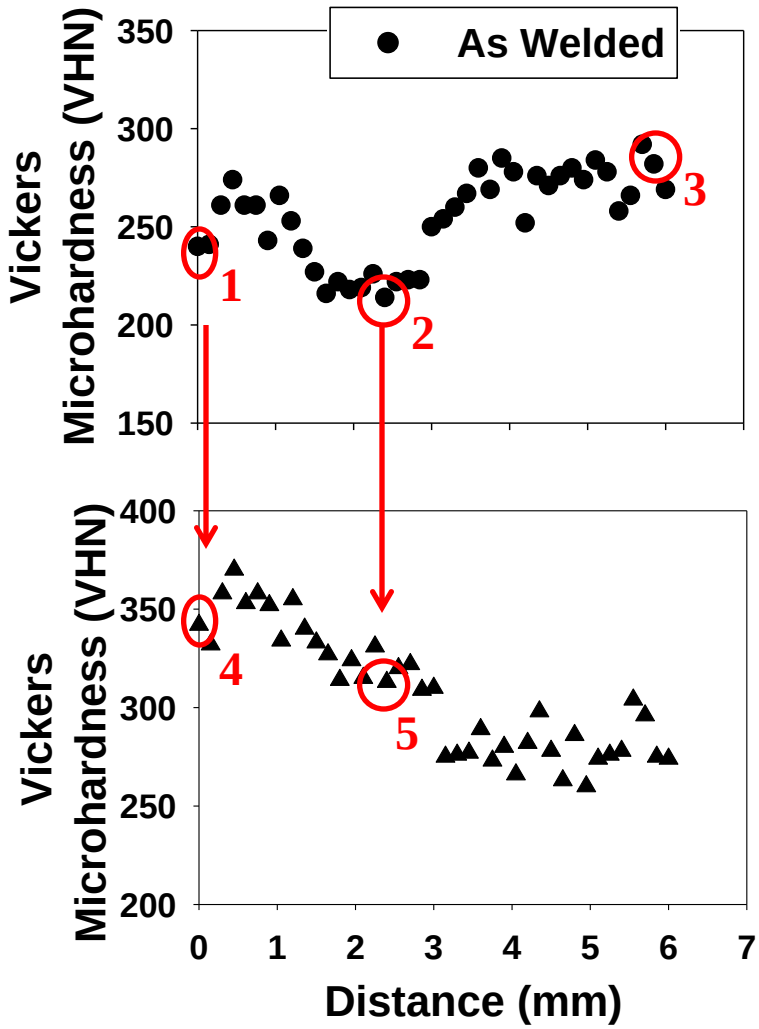
- **Welding of plate steels is the primary method of fabrication used by the U.S Navy for ship-construction.**
- **Large temperature gradients during the welding processes result in complex phase transformations and varied microstructures within a small volume of material**
- **High processing costs are a result of preheat and post-heat treatments, and inspection requirements during welding.**
- **There is, therefore, a need to understand the evolution of Cu-precipitates in the microstructures obtained after welding.**

Strength decrease in the fusion zone (1) and heat-affected (2) of the weldment

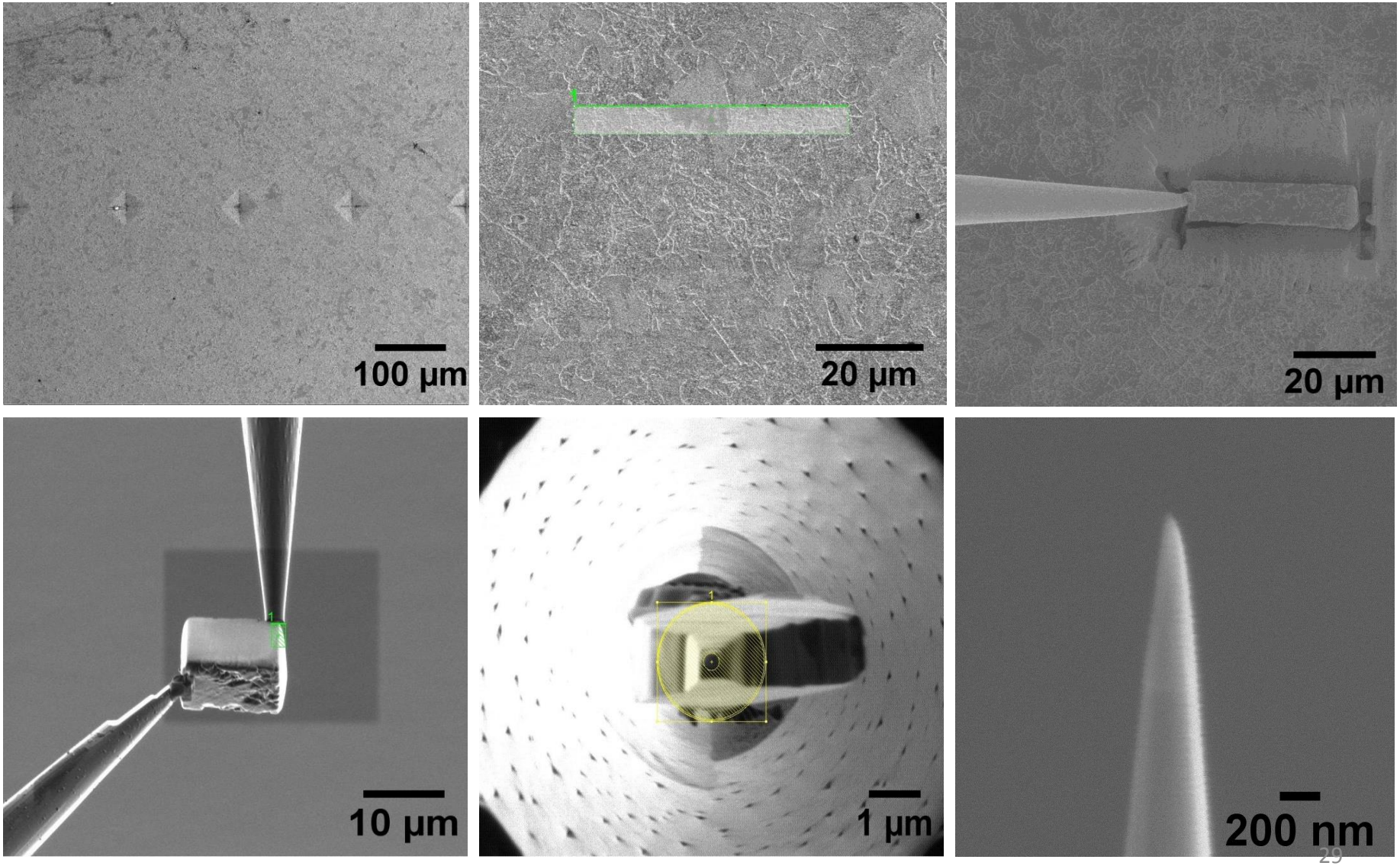
- **Microhardness decrease in the fusion zone (1) and heat-affected zone (2) of the as-welded sample is recovered by a simple direct-aging treatment without affecting the hardness in the base-metal region, BM (3).**

- **This can be understood by studying the evolution of Cu-precipitates in these zones using 3-D atom-probe tomography**

- **Site-specific samples for 3-D atom-probe tomography examination are prepared using a dual-beam focused-ion beam microscope.**



Site-specific 3-D atom-probe microtip preparation using dual-beam FIB microscope



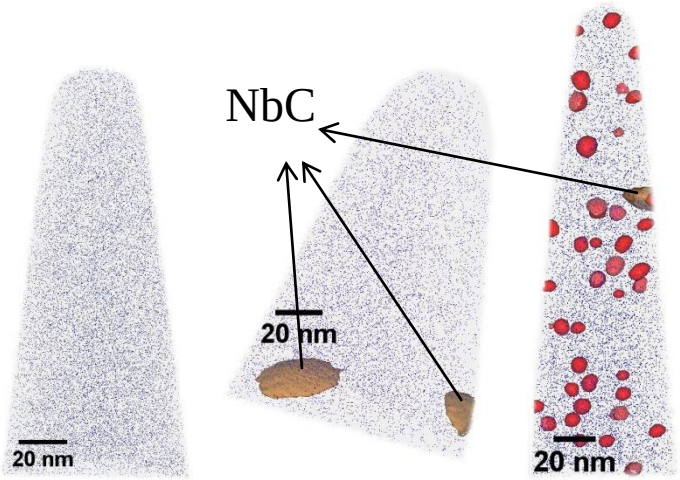
3-D atom-probe tomographic results and conclusions

Zone	<R> (nm)	Nv (m^{-3})	Vf %
Zone1_aswelded	*No Cu precipitates observed*		
Zone2_aswelded	*No Cu precipitates observed*		
BM_aswelded	3.54±1.05	(9.35±1.44)E+22	2.16±0.33
Zone 4_aged	2.39±0.75	(3.75±0.34)E+23	2.60±0.24
Zone 5_aged	2.38±0.68	(4.11±0.15)E+23	2.83±0.10

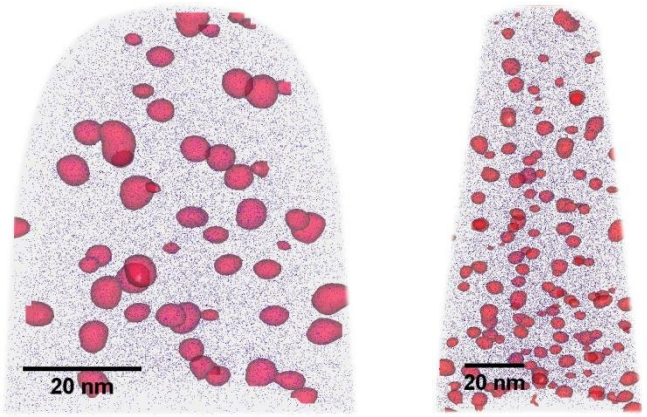
- N_v of Cu-precipitates in zones 4 and 5 of the directly aged sample is greater and <R> is smaller than in the base metal (BM) of the as-welded sample

- This implies that decrease in microhardness in fusion zone (Zone 1) and heat-affected zone (Zone 2) of the as-welded sample is primarily due to the dissolution of the Cu-precipitates and not due to their over-aging in these zones

- An economically efficient direct-aging treatment, without a prior solutionizing step, is, therefore, sufficient to recover the loss in strength



Zone 1 FZ | Zone 2 HAZ | Zone 3 BM



Zone 4 Directly-aged | Zone 5 Directly-aged

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