Precipitation of Topologically Close-Packed Phases and Thermodynamic Calculations for Alloy 22

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MS&T '03
Chicago, IL
November 9-12, 2003

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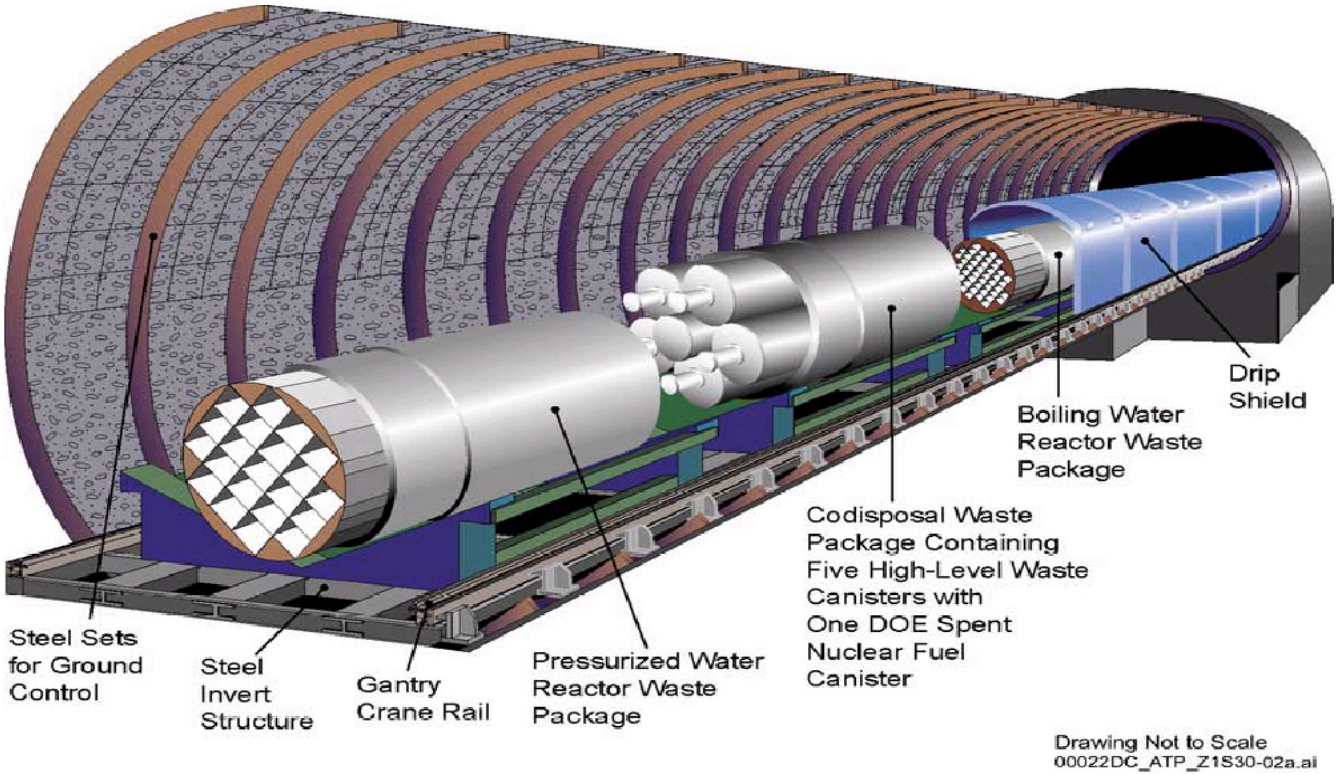
Objectives and Scope

- Evaluate the effects of thermal aging, solution annealing, and compositional variation on the microstructure of mill-annealed and welded Alloy 22
- Determine the microstructure and chemistry of heat treated and welded materials using analytical electron microscopy (AEM) and scanning electron microscopy (SEM)
- Model the phase stability of Alloy 22, as influenced by alloy compositional variation and element segregation in the weld, using thermodynamic calculations

Engineering Barrier System

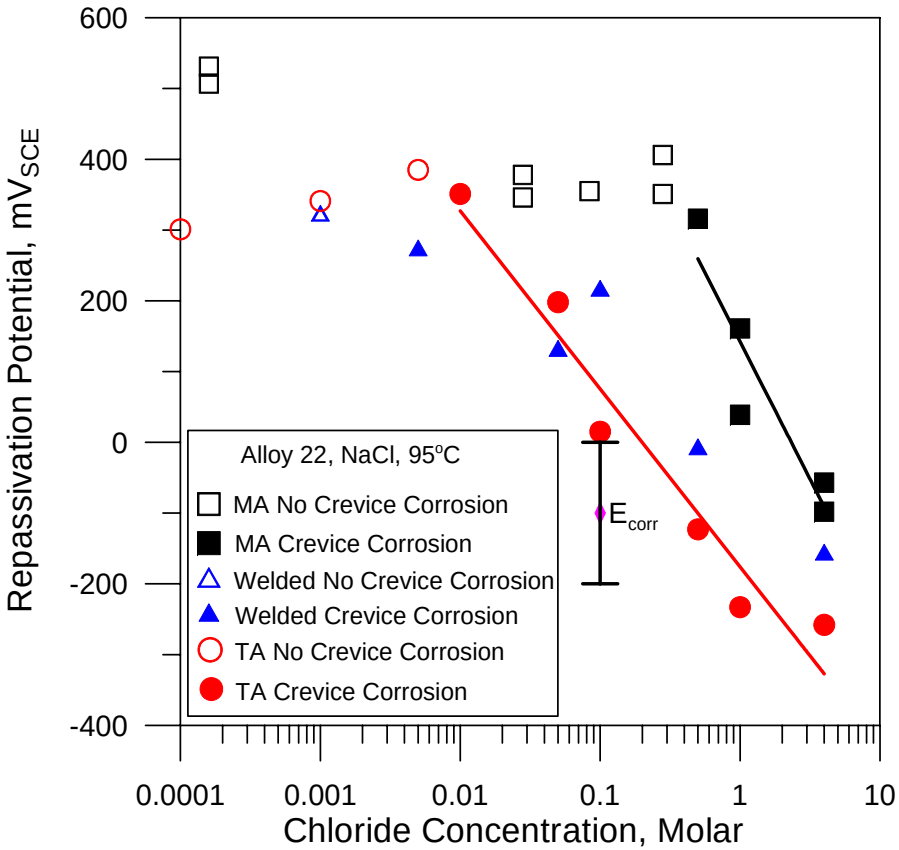


- Current waste package design: Alloy 22 (Ni-22Cr-13.5Mo-3W-3Fe) outer container for corrosion resistance, Type 316 SS inner container for structural support
- Microstructure of mill-annealed Alloy 22: single-phase, face-centered cubic solid solution

Phase Stability of Alloy 22

- Phase instability may not occur for the waste packages after emplacement because of slow kinetics of topologically close-packed (TCP) phase precipitation and long range ordering (LRO) at the expected repository temperatures
- Phase stability likely to be affected by fabrication and closure processes such as welding, postweld heat treatments, and stress mitigation operations
- DOE has focused its analysis on the low-temperature regime without appropriate consideration of the range of temperatures typical in fabrication processes

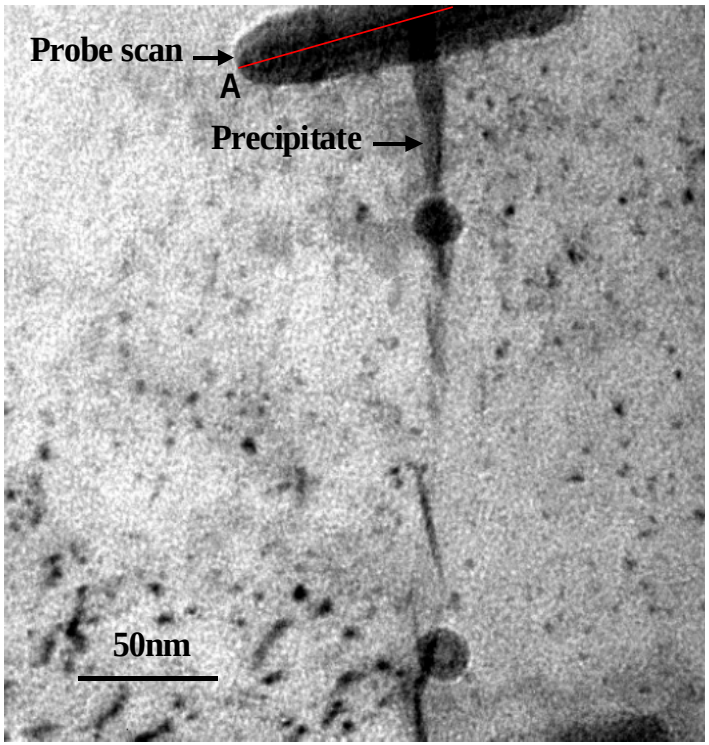
Effect of Fabrication Processes on Localized Corrosion of Alloy 22

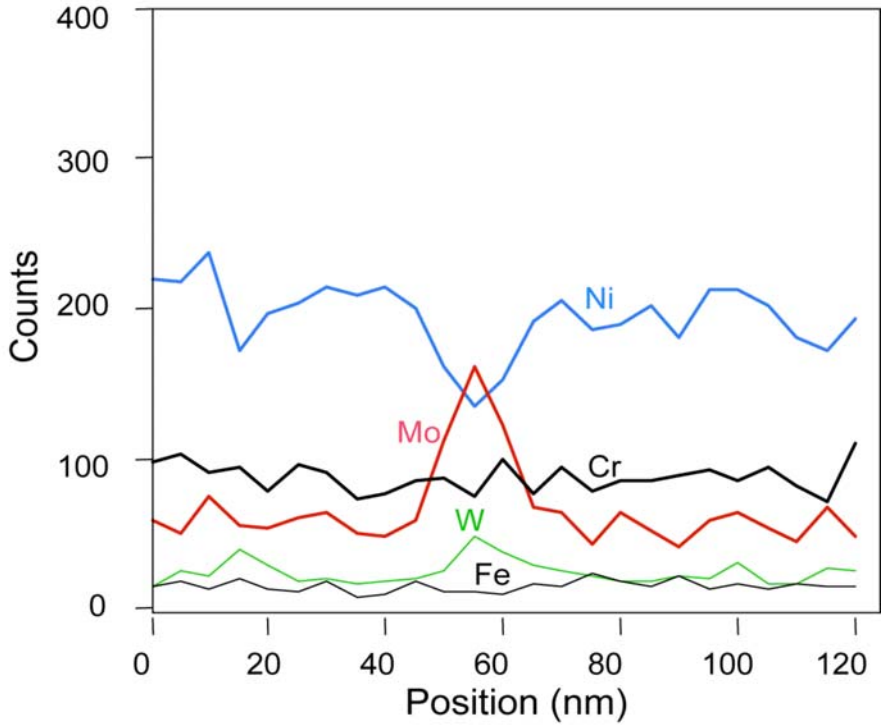


MA – Mill Annealed
TA – MA + Aged 5 minutes at 870 °C
Welded – MA + Welded

- E_{rcrev} parameter used as a lower bound for initiation of localized corrosion
- Slow cooling from annealing temperature during postweld operations could decrease E_{rcrev} significantly
- E_{rcrev} may become lower than E_{corr} as a result of such processes, potentially facilitating the occurrence of localized corrosion at Cl^- concentrations lower than those required for the MA alloy

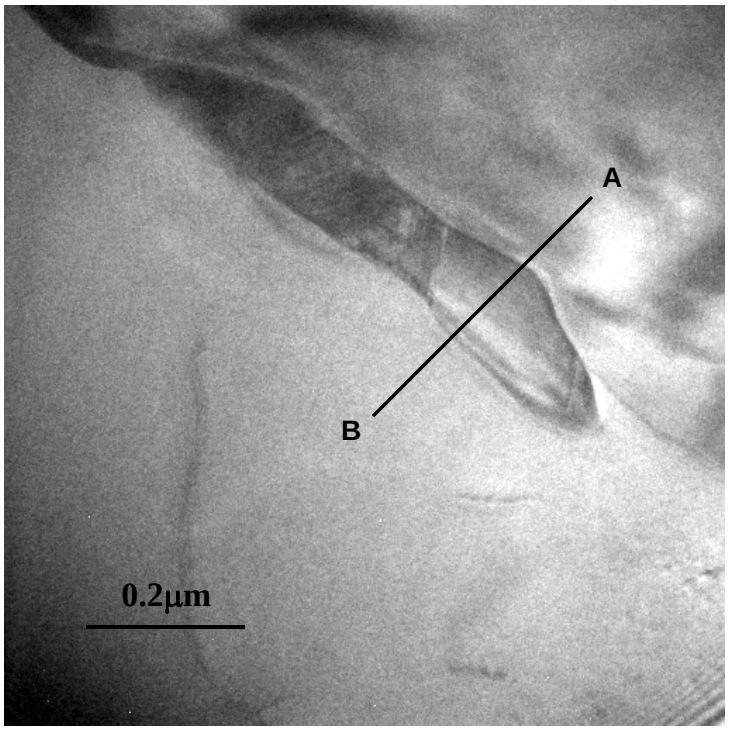
Grain-Boundary Microstructure and Chemistry (5 minutes at 870°C)

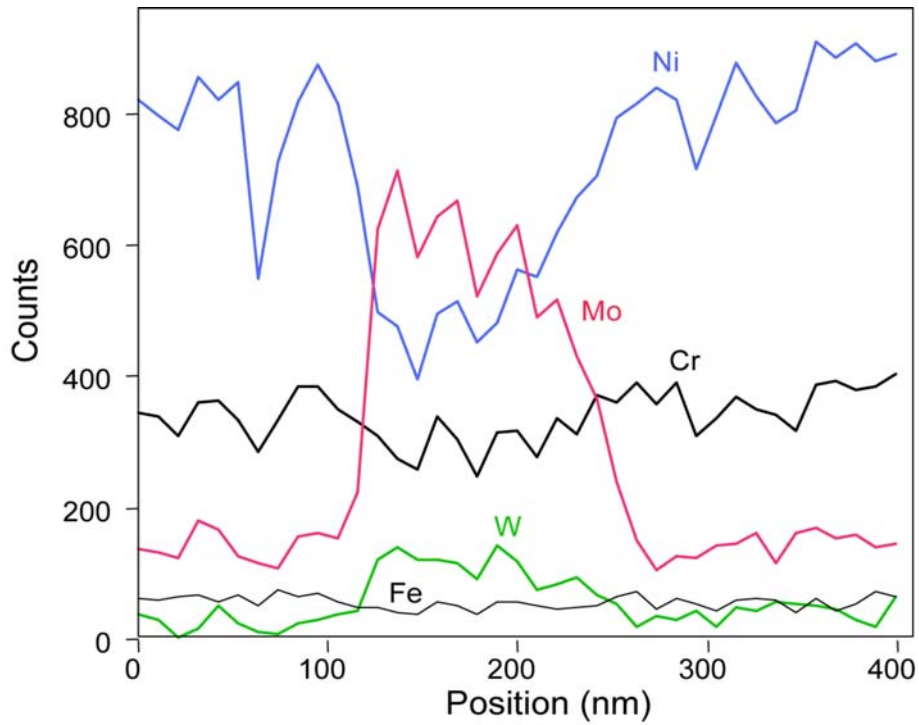




- Aging at 870°C for 5 minutes produced thin-film type, Mo and W-rich TCP precipitates at grain boundaries
- No detectable depletion of Mo and Cr across grain boundaries

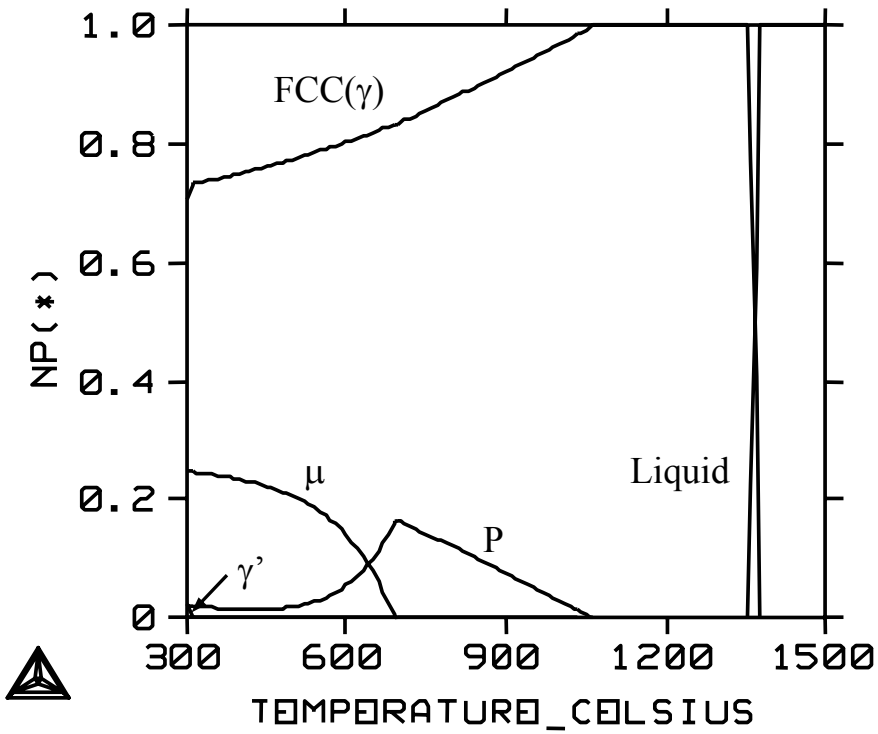
Grain-Boundary Microstructure and Chemistry (30 minutes at 870°C)

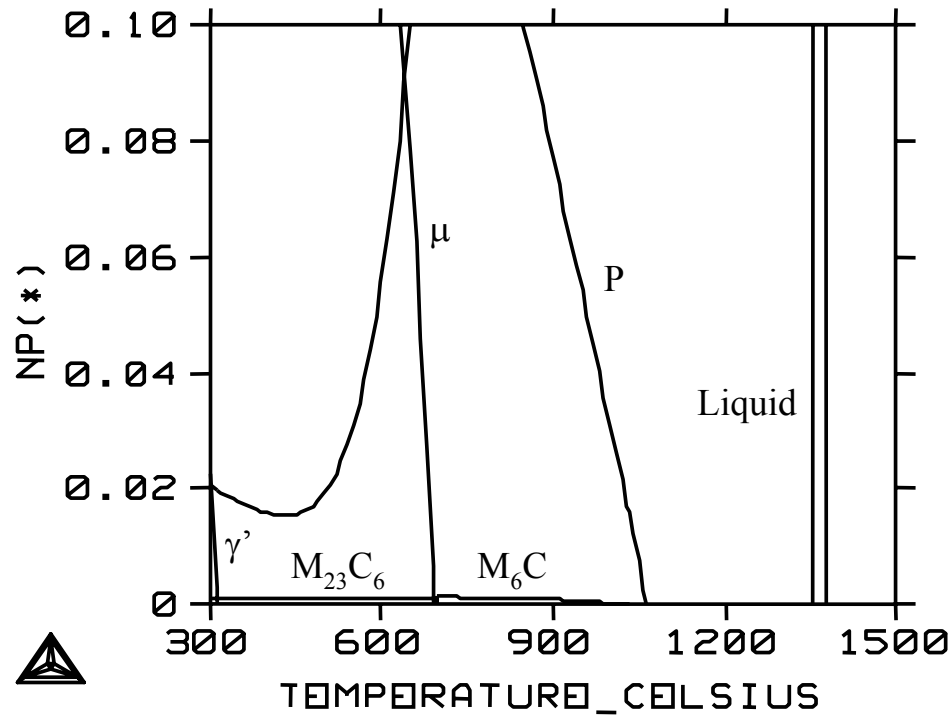




- Substantial increase in precipitate size after aging for 30 minutes
- No detectable depletion of Mo and Cr across matrix-precipitate interface

Calculated Equilibrium Phases and Their Mole Fractions





- Calculations conducted with Thermo-Calc Version N software and Ni-Data Version 5 database
- At 870°C, γ, P-phase and M_6C are present and P-phase is the only equilibrium TCP phase

Composition of Precipitates

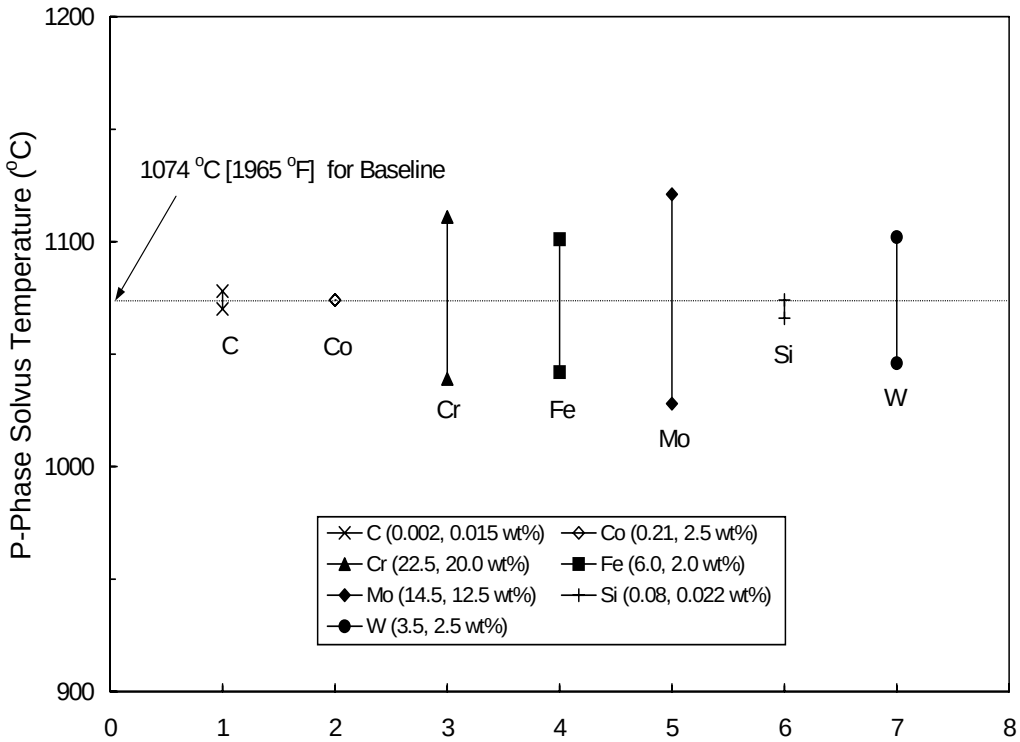
Chemical Composition of Grain Boundary Precipitates and the Vicinity (wt%)

Probe Location	Ni	Cr	Mo	W	Fe
Precipitate	26.53 ± 3.00	17.81 ± 3.81	44.33 ± 2.66	8.88 ± 1.17	2.34 ± 0.27
Adjacent to Precipitate	58.42 ± 0.15	22.43 ± 0.25	11.75 ± 0.38	2.54 ± 0.70	4.46 ± 0.15
Bulk Composition	57.8	21.40	13.60	3.00	3.08

Calculated phase compositions at 870 °C

Phase	Amount		Chemical Content (wt%)							
	wt%	mole%	Ni	Cr	Mo	W	Fe	Co	Si	C
γ	88.88	90.83	62.60	21.69	10.34	1.85	3.39	0.095	0.034	0.001
P	11.01	9.07	28.47	19.10	39.50	12.29	0.59	0.045	—	—
M_6C	0.11	0.10	25.08	14.47	52.12	4.80	0.93	0.016	0.001	2.58

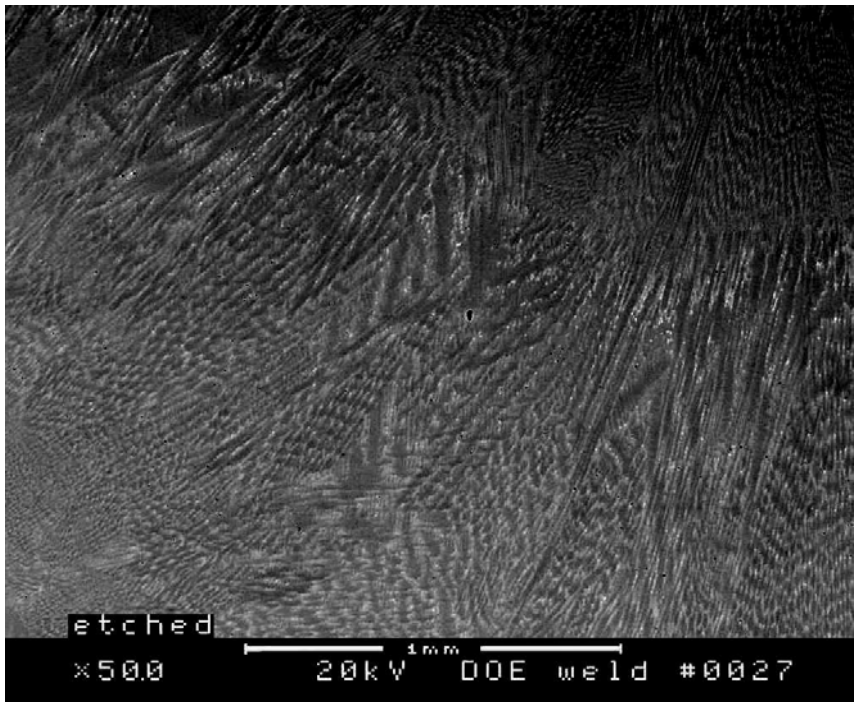
TCP Phase Stability vs. Alloy Compositional Variation

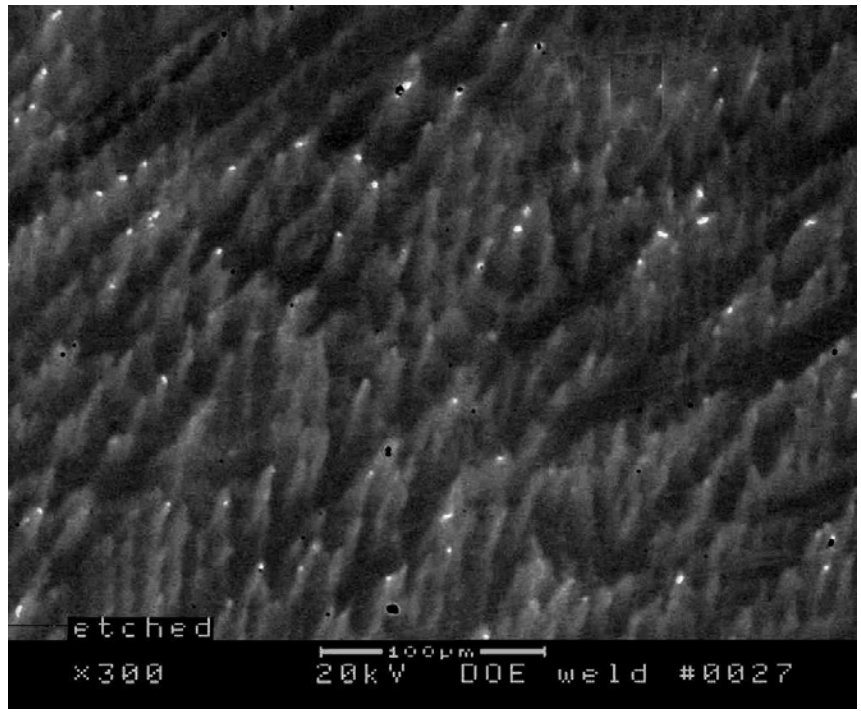


- Each element varies between its max and min limits specified in ASTM B575
- Mo, the major TCP phase forming element, exhibits the greatest sensitivity to the upper stability temperature of the P-phase

Heat-to-heat variation in alloy composition may have a significant influence on phase stability in Alloy 22

Microstructure of the Weld





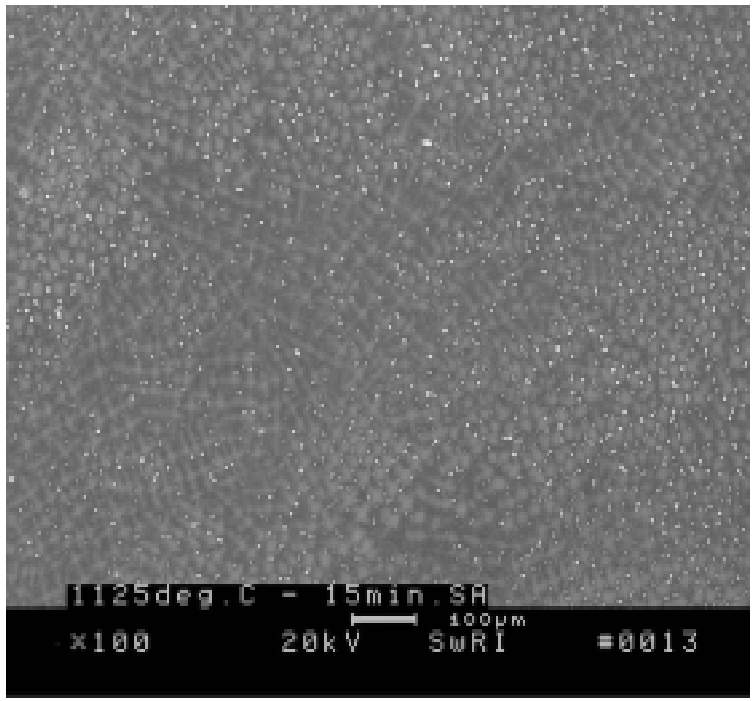
- Alloy 22 Gas Tungsten Arc Weld (GTAW)
- Mo-rich TCP precipitates in the as-welded condition

TCP Phase Stability in Weld Fusion Zone

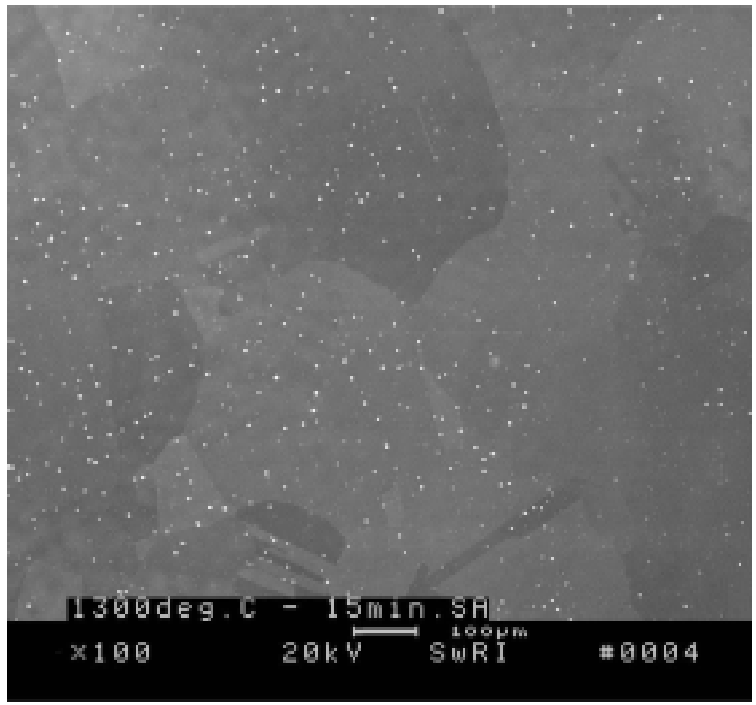
Location	Chemical Content (wt%)					P-Phase Solvus Temperature
	Ni	Cr	Mo	Fe	W	
Dendrite Core	59.8±1.3	21.8±0.4	13.0±1.1	2.75±0.11	2.60±0.09	1,024°C[1,875°F]
Interdendritic Region	54.4±1.6	22.6±0.2	18.0±1.6	2.48±0.07	2.48±0.06	1,271°C[2,320°F]
Alloy 22 Base Metal	60.64	20.44	12.80	2.63	3.08	1,026°C[1,879°F]
Alloy 622 Filler	59.89	20.41	13.99	2.46	2.96	1,066°C[1,951°F]

- Local compositions measured with energy-dispersive x-ray spectroscopy analysis
- Mo segregated to the interdendritic regions as a consequence of nonequilibrium solidification
- Thermo-Calc calculations predicted a solvus temperature for the P-phase at 1,271 ^{o}C in the interdendritic regions

Effect of Solution Annealing on Microstructural Changes in Alloy 22 Weld



1,125 °C/15 Minutes



1,300 °C/15 Minutes

- Residual precipitates observed for all solution annealing conditions
- Homogenization of fusion zone occurred at 1,125 ^{o}C, whereas abnormal grain growth at 1,300 ^{o}C
- Current solution annealing treatment at 1,121 ^{o}C for 20 minutes may be inadequate for Alloy 22 weld to form a single-phase solid solution

Summary

- Thermal aging of the mill-annealed Alloy 22 at 870 ^{o}C for only 5 minutes results in formation of TCP phases at grain boundaries and thus increases localized corrosion susceptibility
- Compositional variations in the base metal (heat-to-heat variation) and weld (filler metal composition and element segregation) may influence the formation and dissolution of TCP phases
- Results obtained from both experiments and theoretical calculations suggest that current solution annealing treatment for Alloy 22 weld could be inadequate to produce a homogeneous single-phase structure
- Additional evaluation is needed in assessing microstructural changes arising from fabrication processes and the consequences of phase instability of the Alloy 22 waste package outer container

Acknowledgments

This work was performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the U.S. Nuclear Regulatory Commission under Contract No. NRC–02–02–012 on behalf of the NRC Office of Nuclear Material Safety and Safeguards, Division of Waste Management

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