Phase Stability of Alloy 22 High-Level Waste Container Weldments: Experiments and Thermodynamic Calculations

Y.-M. Pan, D.S. Dunn, and G.A. Cragnolino
Center for Nuclear Waste Regulatory Analyses (CNWRA)
Southwest Research Institute
San Antonio, Texas, USA

CALPHAD XXXIII
Krakow, Poland
June 3, 2004

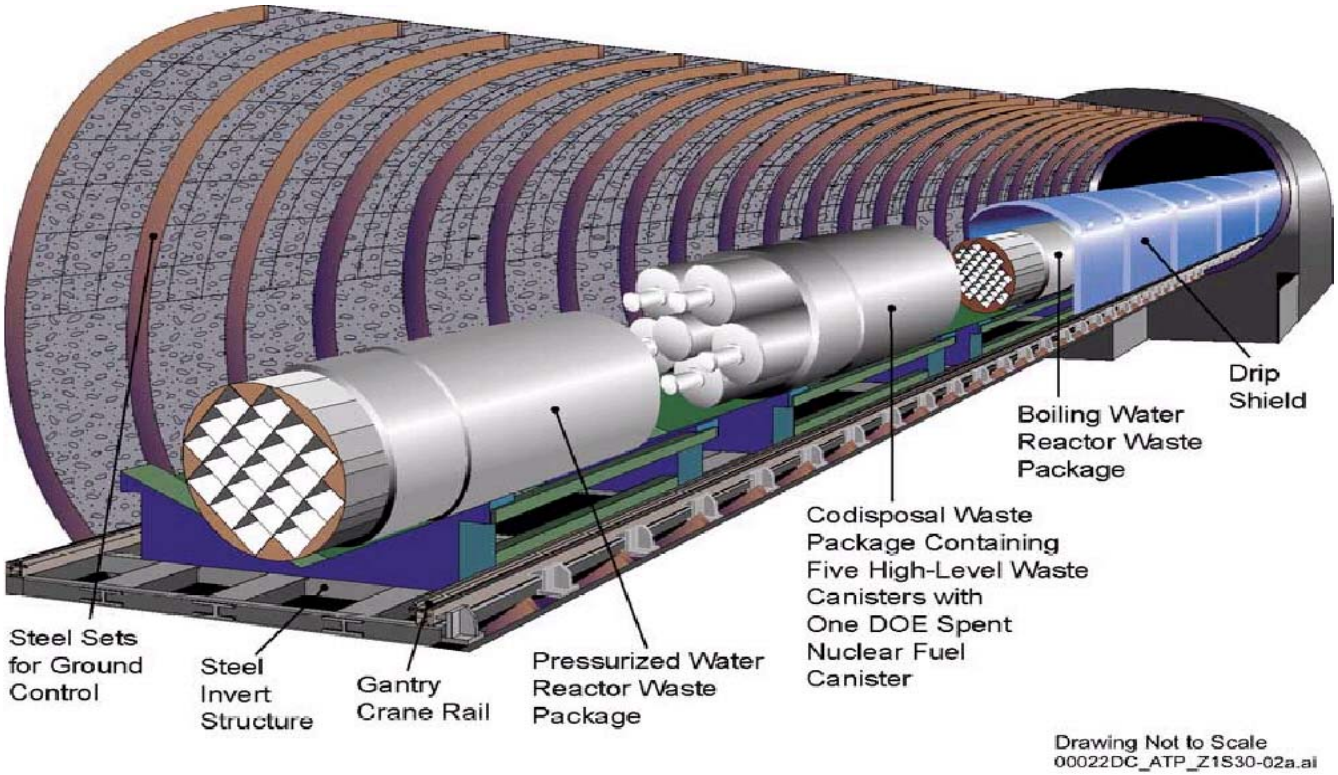
CNWRA
A center of excellence in earth sciences and engineering

SwRI®

Objectives and Scope

- Evaluate the effects of postweld heat treatment and element segregation on the phase stability of welded Alloy 22
  - Determine the microstructure of welded materials, as influenced by solution annealing and the subsequent thermal aging, using optical and scanning electron microscopy
  - Model the influence of alloy compositional variation on the stability of topologically close-packed (TCP) phases and solidification reactions using thermodynamic calculations

Engineering Barrier System

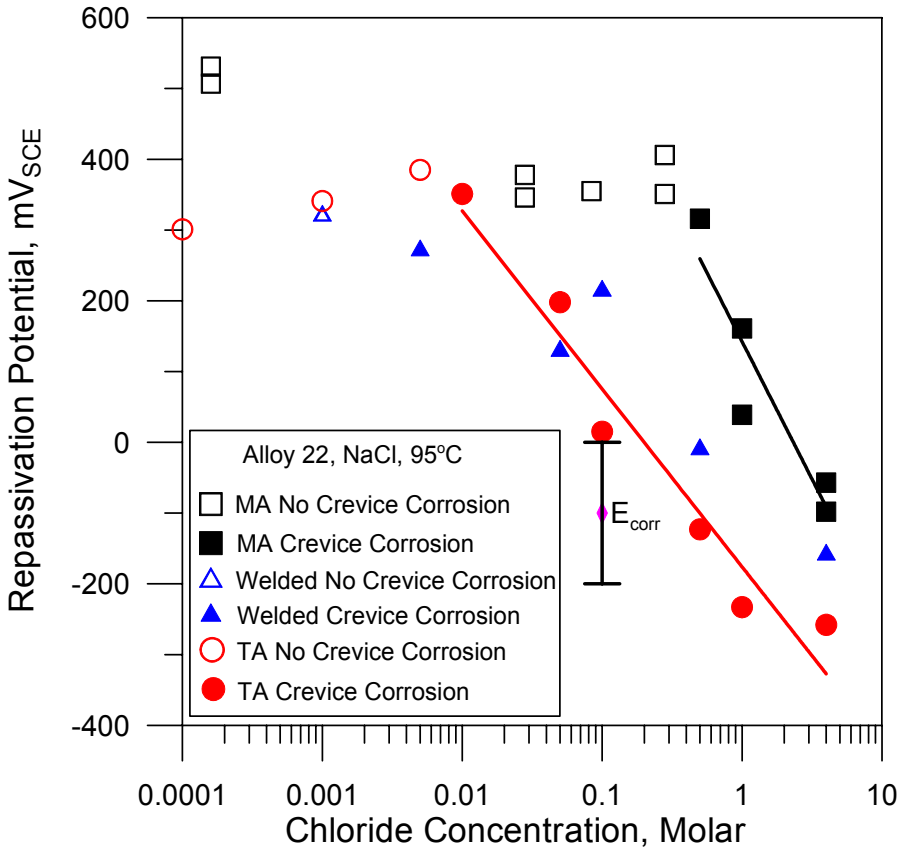


- Current waste package design: Alloy 22 (Ni-22Cr-13.5Mo-3W-3Fe) outer container for corrosion resistance, Type 316 SS inner container for structural support
- U.S. Department of Energy (DOE) proposes to use solution annealing to eliminate any detrimental phases resulting from fabrication processes

Phase Stability of Alloy 22

- Phase instability may not occur for the waste packages after emplacement because of slow kinetics of TCP phase precipitation at the expected repository temperatures
- Phase stability likely to be affected by fabrication and closure processes such as welding and postweld heat treatments
- Cold work from forming, machining, and residual stress mitigation methods such as laser peening and plasticity controlled burnishing may increase precipitation kinetics

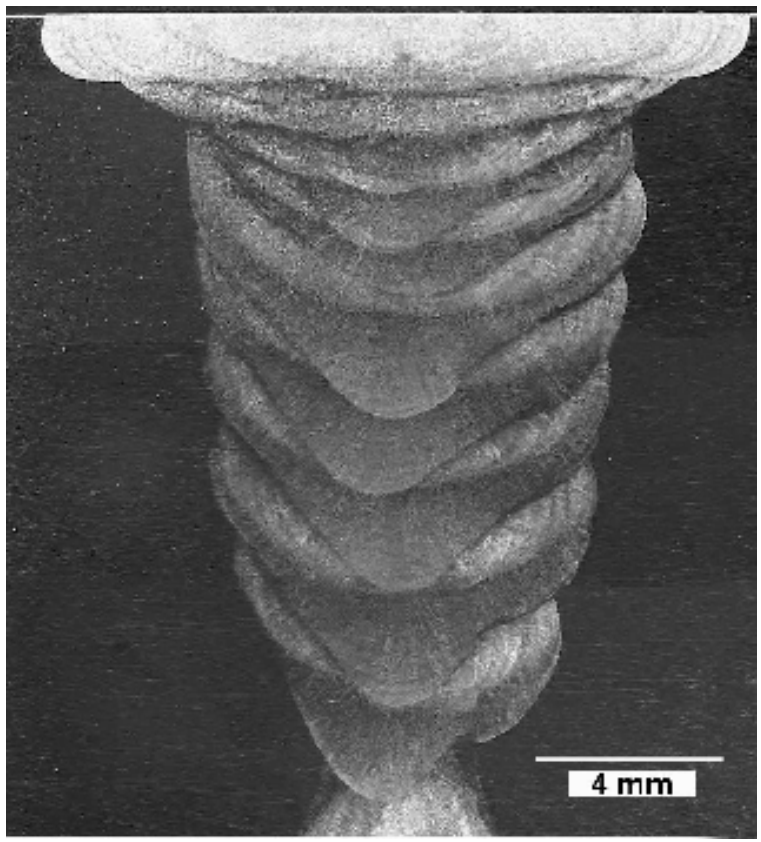
Effect of Fabrication Processes on Localized Corrosion of Alloy 22



Mill-Annealed (MA)
Thermally Aged (TA) – MA + Aged 5 minutes at 870 °C
Welded – MA + Gas Tungsten-Arc Weld

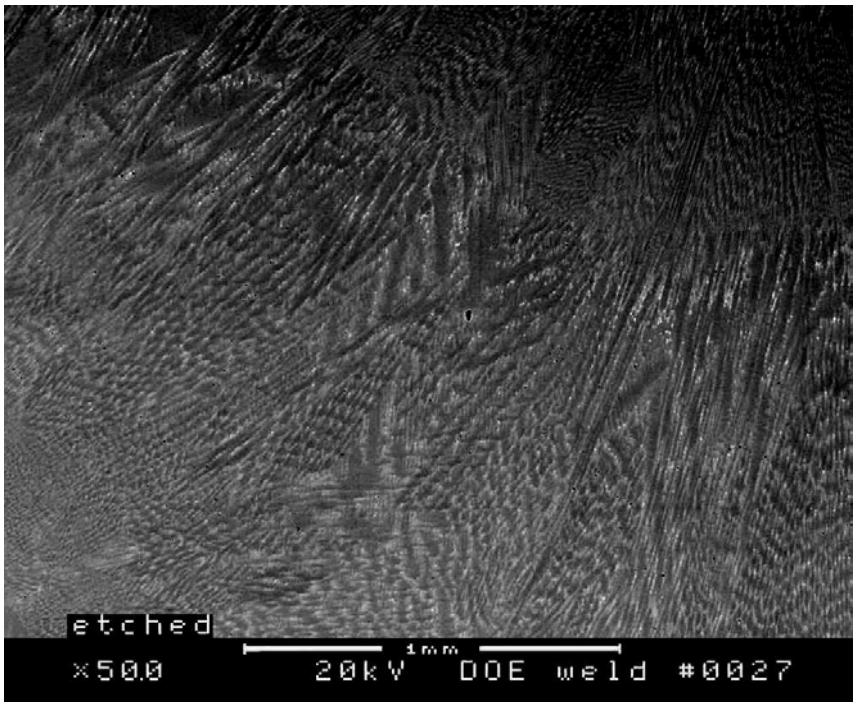
- The crevice corrosion repassivation potential (E_{rcrev}) is used as a lower bound parameter for the long-term initiation of localized corrosion
- Localized corrosion can occur if the corrosion potential (E_{corr}) is higher than E_{rcrev}
- Slow cooling from annealing temperature during postweld operations 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

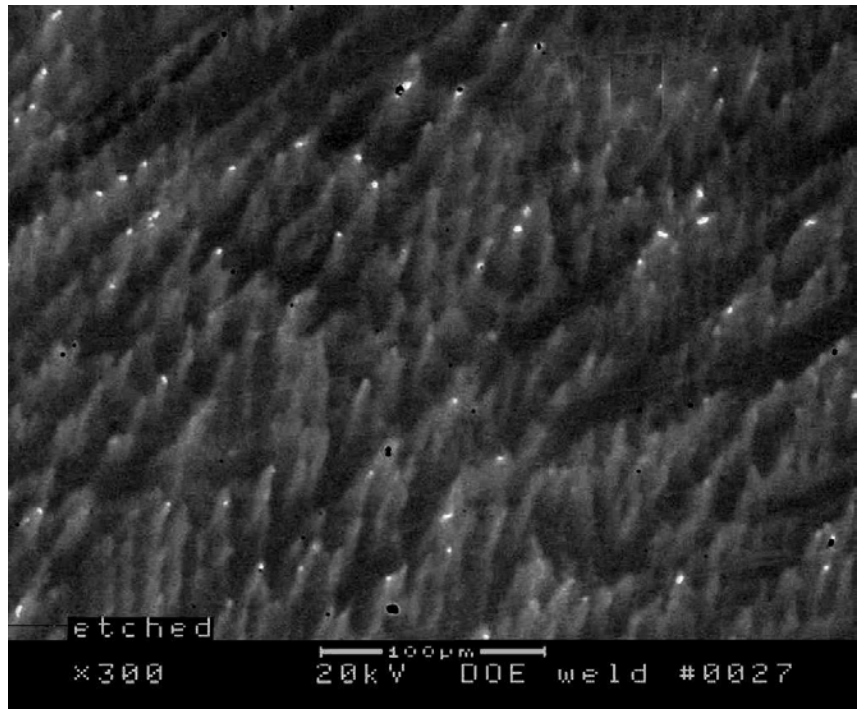
Weld Fusion Zone



- 38.1-mm [1.5-in] thick Alloy 22 plate welded by Framatome ANP, Inc. for the DOE
- Material provided to CNWRA at the request of the U.S. Nuclear Regulatory Commission (NRC)
- Gas Tungsten-Arc Weld
- Double U-groove joint geometry

Microstructure of the Weld





- Alloy 22 Gas Tungsten-Arc Weld with dendritic structure and precipitation of secondary phases
- Mo-rich TCP precipitates in the as-welded condition

Element Segregation in the Weld

Location	Chemical Content (wt%)				
	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
Interdendritic Region	54.4 ± 1.6	22.6 ± 0.2	18.0 ± 1.6	2.48 ± 0.07	2.48 ± 0.06
Alloy 22 Base Metal	60.64	20.44	12.80	2.63	3.08
Alloy 622 Filler	59.89	20.41	13.99	2.46	2.96

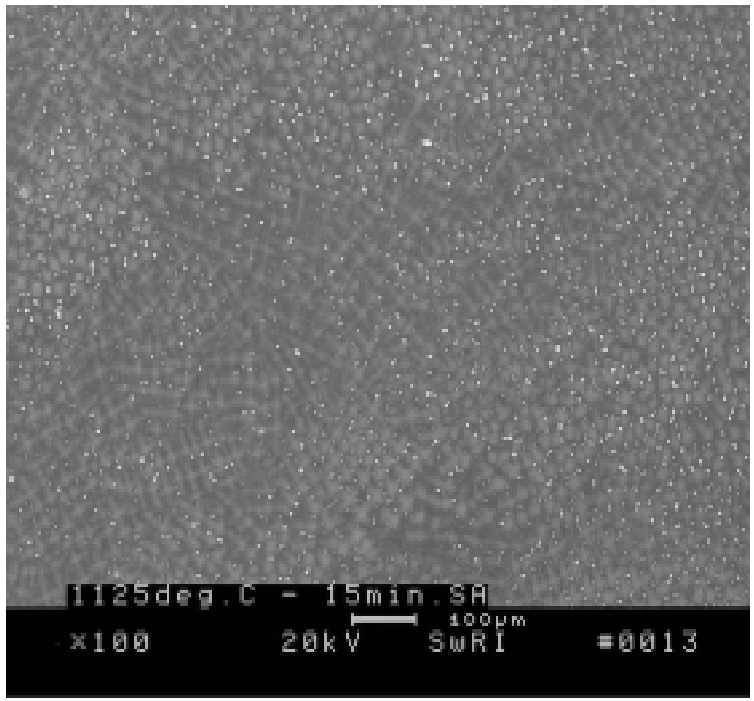
- Local compositions in dendrite core and interdendritic region measured with energy-dispersive x-ray spectroscopy analysis
- Segregation of Mo to the interdendritic regions as a consequence of nonequilibrium solidification

Effect of Heat Treatment on Volume Fraction of TCP Phases

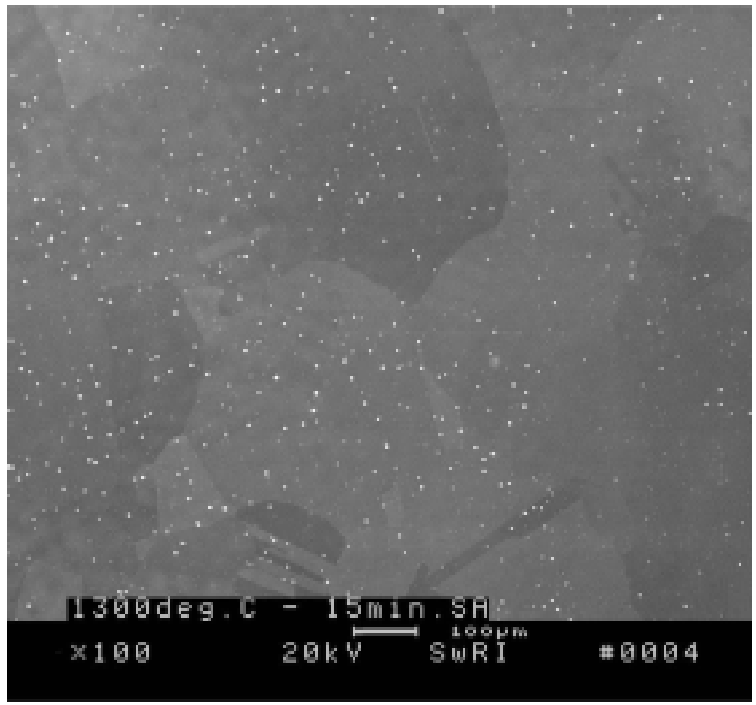
Heat Treatment Condition	Amount of Precipitates (vol%)
As-welded	0.42 ± 0.24
1125 °C/15 min	1.8 ± 0.4
870 °C/5 min	1.2 ± 0.2
870 °C/30 min	4.0 ± 0.9
870 °C/60 min	8.1 ± 1.6
870 °C/4 hr	10.8 ± 1.5

- Image analysis results of 20 measurements along the centerline of fusion zone
- All aging and solution annealing treatments enhanced precipitation of TCP phases
- The amount of precipitates increases with increasing aging time at 870 ^{o}C

Effect of Solution Annealing on Microstructural Changes in Alloy 22 Weld



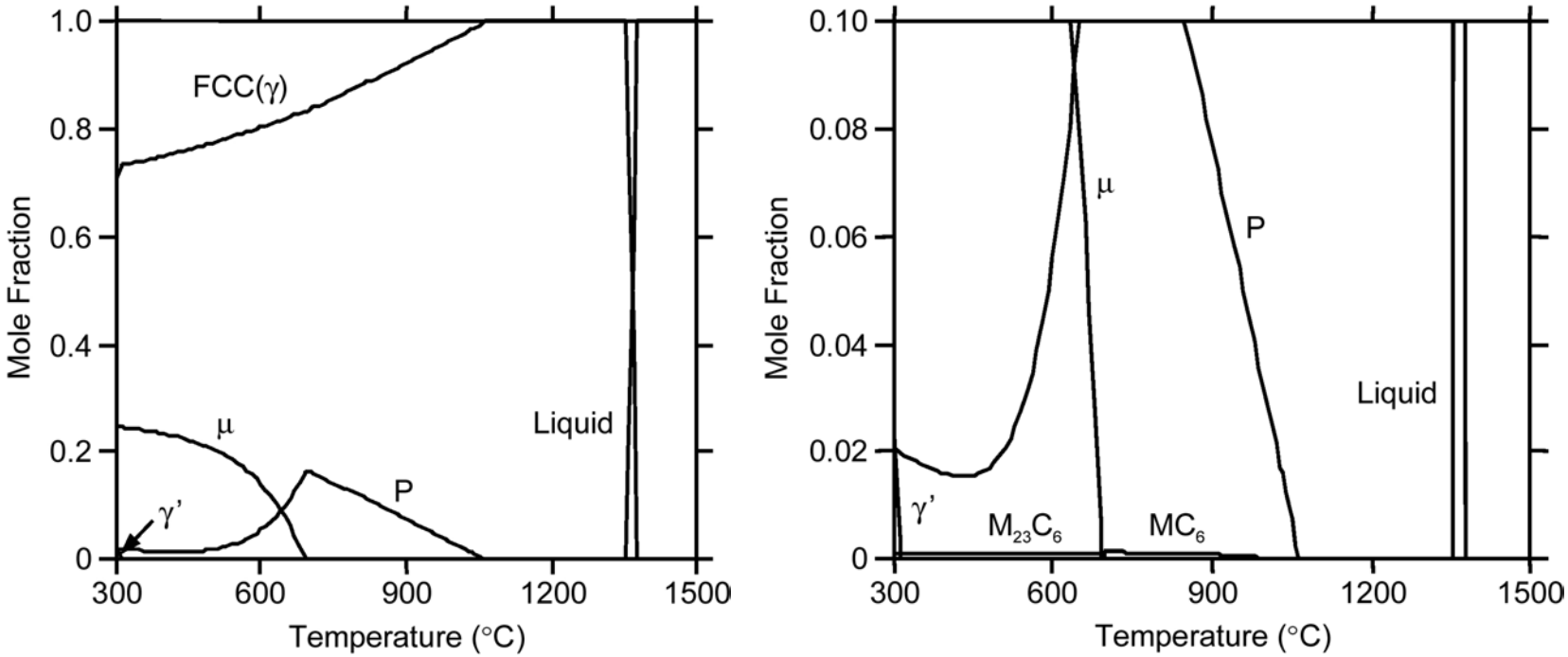
1,125 °C/15 Minutes



1,300 °C/15 Minutes

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

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 but P-phase is the only equilibrium TCP phase

Composition of Precipitates

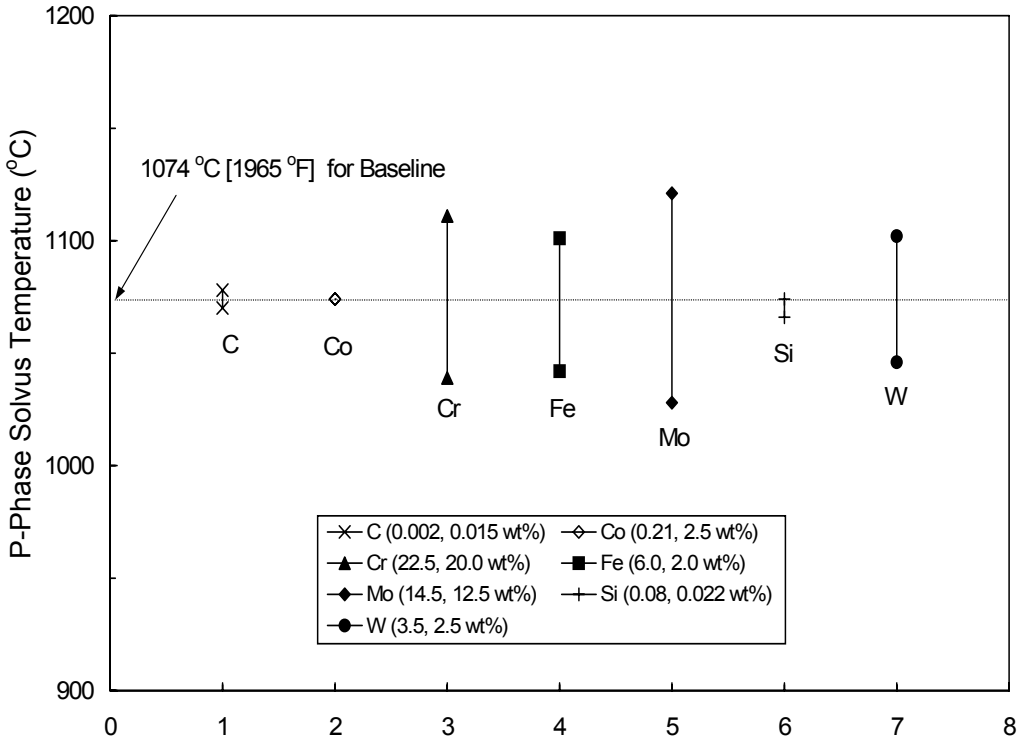
Chemical Composition of Grain Boundary Precipitates and the Vicinity (wt%)

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

Effect of Compositional Variation on Solvus Temperature for P-Phase



- Each element varies between its maximum and minimum 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 variations may affect TCP phase formation and dissolution

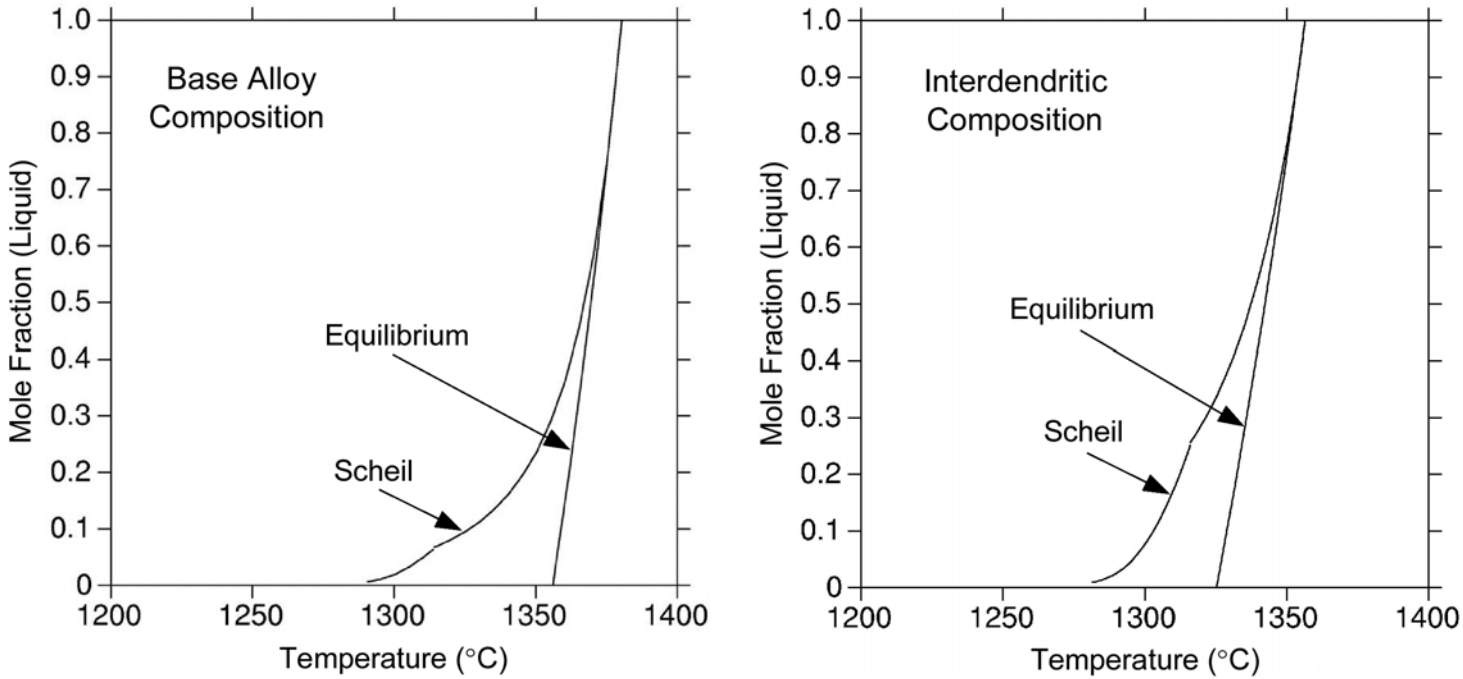
Baseline composition: Ni-21.1Cr-13.5Mo-4Fe-3W-2Co-0.08Si-0.01C

Effect of Element Segregation on Solvus Temperature for P-Phase

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	1024 °C
Interdendritic Region	54.4 ± 1.6	22.6 ± 0.2	18.0 ± 1.6	2.48 ± 0.07	2.48 ± 0.06	1271 °C
Alloy 22 Base Metal	60.64	20.44	12.80	2.63	3.08	1026 °C
Alloy 622 Filler	59.89	20.41	13.99	2.46	2.96	1066 °C

- Mo segregated to the interdendritic regions as a consequence of nonequilibrium solidification
- The equilibrium thermodynamic calculations predicted a solvus temperature for the P-phase at 1,271 ^{o}C in the interdendritic regions

Solidification Simulation of Alloy 22



- The equilibrium and Scheil solidification simulation profiles for the base alloy and interdendritic compositions under a 5 °C cooling step
- The Scheil model assumed complete liquid phase mixing and no back diffusion in the solidified phases
- The equilibrium simulation predicted complete solidification of liquid to γ-phase whereas P-phase formed near the end of solidification in the Scheil simulation

Calculation of the Liquidus, Solidus, and P-Solvus Temperatures for Alloy 22

Location	Equilibrium Simulation			Scheil Simulation		
	Liquidus	Solidus	P-Solvus	Liquidus	Solidus	P-Solvus
Dendrite Core	1382	1358	1018	1382	1292	1310
Interdendritic Region	1357	1325	1265	1357	1287	1316
Base Alloy	1380	1356	1062	1380	1291	1314

Note that all temperature values in ^{o}C

- The Scheil simulation predicted a high solvus temperature for the P-phase due to element partitioning and a low solidus temperature for the lack of back diffusion in the solid phase
- The equilibrium simulation predicted an accurate solidus temperature by reaching equilibrium at each cooling step
- Solidification simulations suggest a solution annealing temperature window ranging from 1316 to 1358 ^{o}C

Summary

- All aging and solution annealing treatments of the welded materials conducted in this study enhanced precipitation of the secondary phases due to a substantial increase in solvus temperature for P-phase as a result of solidification-induced Mo segregation
- 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 thermodynamic calculations suggest a solution annealing temperature window at higher temperatures than the currently proposed solution annealing temperature for Alloy 22 weld
- Additional evaluation is necessary to assess microstructural changes arising from fabrication processes and the effects of phase instability on localized corrosion and mechanical properties 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 High Level Waste Repository Safety

This work is an independent product of CNWRA and does not necessarily reflect the views or the regulatory position of the NRC