Coal-ash Corrosion of Alloys for Combustion Power Plants

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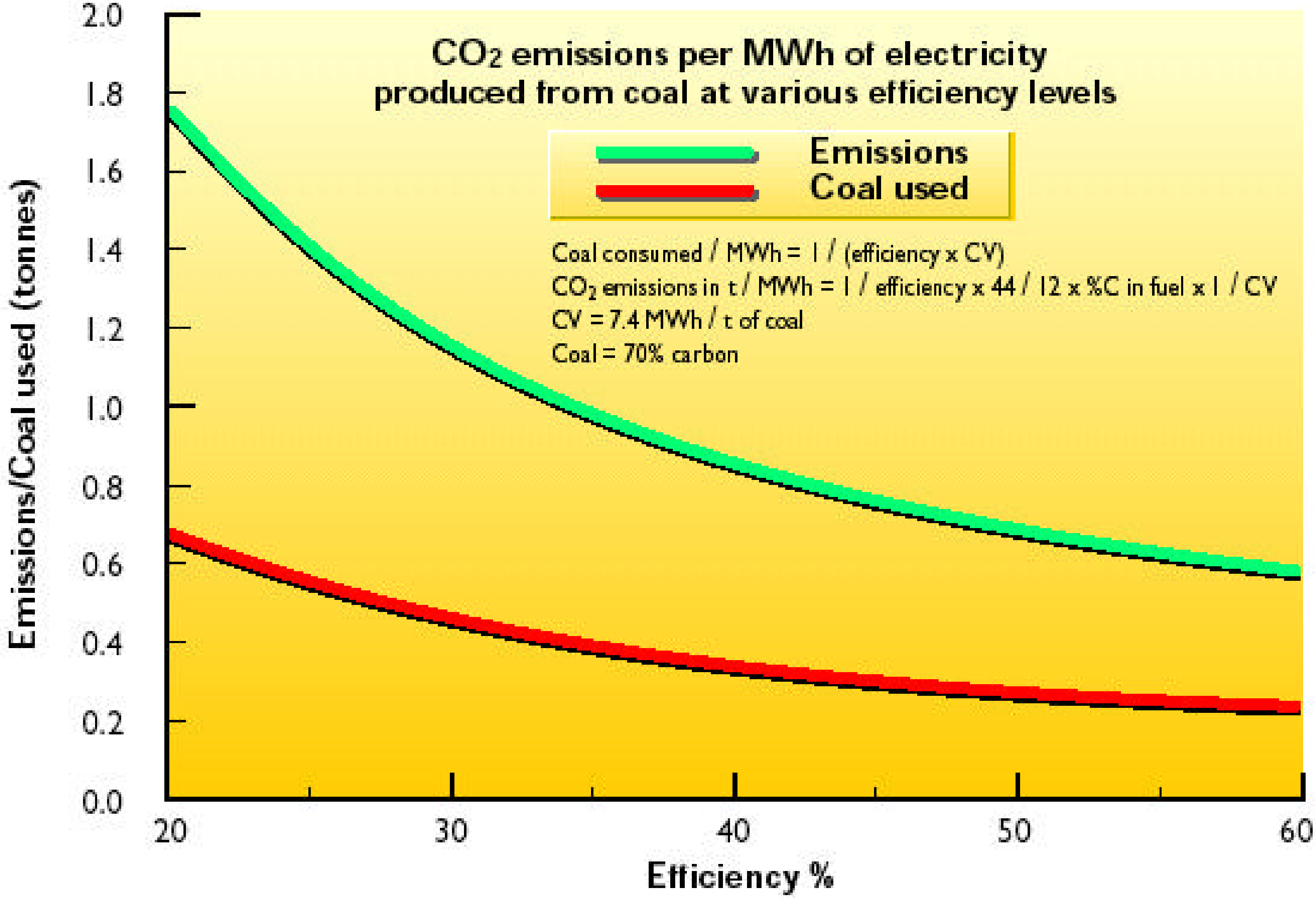
Rationale for Advanced Combustion Systems

- Global warming
- CO_2 generation
- Acid rain
- New source performance standards
- Environmental compliance -- Toxins
- Plant economics

Plants with higher thermal efficiency and lower impact on environment are needed

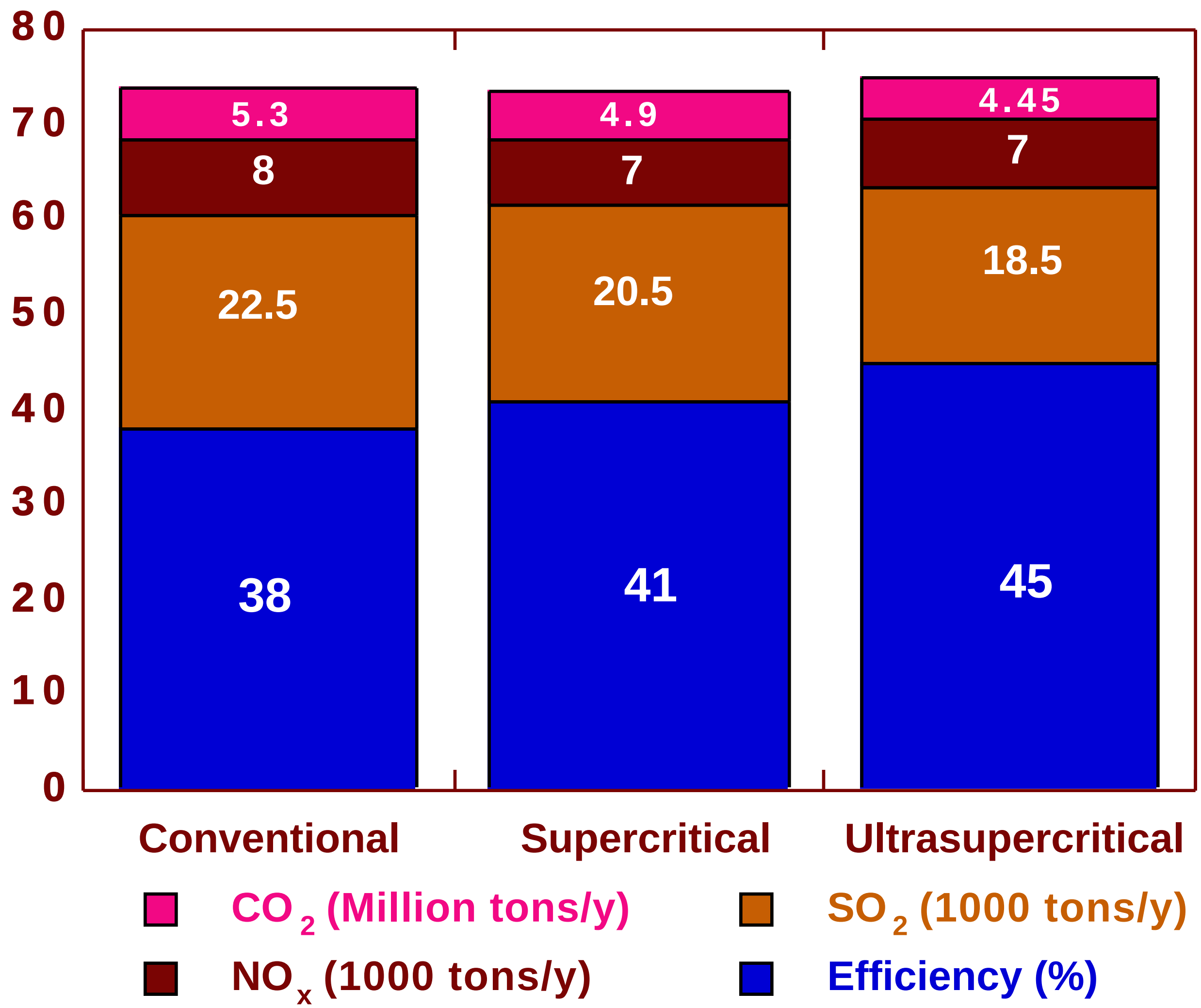
Efficiency vs. CO_2 Emissions



Comparison of Selected Coal Utilization Technologies

Technology	Unit size (Mwe)	Net efficiency (%)	Capital cost (US $/Kw)
Subcritical PC	50-1000	36-38	950-1300
Supercritical PC	50-1000	40-46	950-1600
PFBC	70-350	42-45	1000-1500
IGCC	100-320	43-45	1500-1600

Efficiency and Emissions for Coal-fired Boiler Technologies



Pulverized Coal-Fired Boilers

Goal is to develop advanced steam cycles

Current: 16.5-24 MPa (2,400-3,500 psig), 540°C (1000°F) steam

Near-Term Goal: 34.5 MPa (5,000 psig), 650°C steam

Long-Term Goal: 34.5 MPa (5,000 psig), 760°C steam

Waterwall corrosion:	**Formation of pyrosulfates, trisulfates**
Superheater corrosion:	**Formation of alkali-iron trisulfates** **Alkali sulfates/alkali chlorides induced corrosion** **Loss of mechanical properties**

Alloy Development

- High temperature creep strength
  - solution strengthening W, Mo
  - precipitation strengthening VN, Nb(C,N), etc.
  - stable long-term strength (Cu addition in ferritics)
- Weldability
- Toughness
- Corrosion resistance (T, design life, fireside environment)

Program Objectives

- **Evaluate fireside corrosion performance of metallic materials in coal-ash environments typical of advanced steam cycle systems**
- **Evaluate the role of alkali sulfates in the corrosion process**
- **Evaluate the role of alkali chloride in the corrosion process**
- **Establish the relative corrosion performance of off-the shelf and experimental alloys**
- **Perform comparative corrosion tests on candidate materials by exposures in coal- burning combustion test facility at NETL, Pittsburgh**

Laboratory Test Details

- **Key variables: temperature, time, alloy composition, deposit composition**
- **Materials: ferritics, austenitics, claddings**
- **Gas: 1 vol.% SO_2 in air (catalyzed)**
- **Test temperatures: 575, 650, 725, and 800°C**
- **Test times: 336 to 1868 h**
- **Specimen evaluation: weight change**
scanning electron microscopy
energy dispersive X-ray analysis
X-ray diffraction

Deposit chemistry

(a) $SiO_2 : Al_2O_3 : Fe_2O_3 = 1:1:1$

(b) $Na_2SO_4 : K_2SO_4 = 1:1$

(c) NaCl

Ash 1: 90 wt.% (a) + 10 wt.% (b)

Ash 2: 85 wt.% (a) + 10 wt.% (b) + 5 wt.% (c)

Ash 3: 89 wt.% (a) + 10 wt.% (b) + 1 wt.% (c)

Alloy Selection for Corrosion Tests

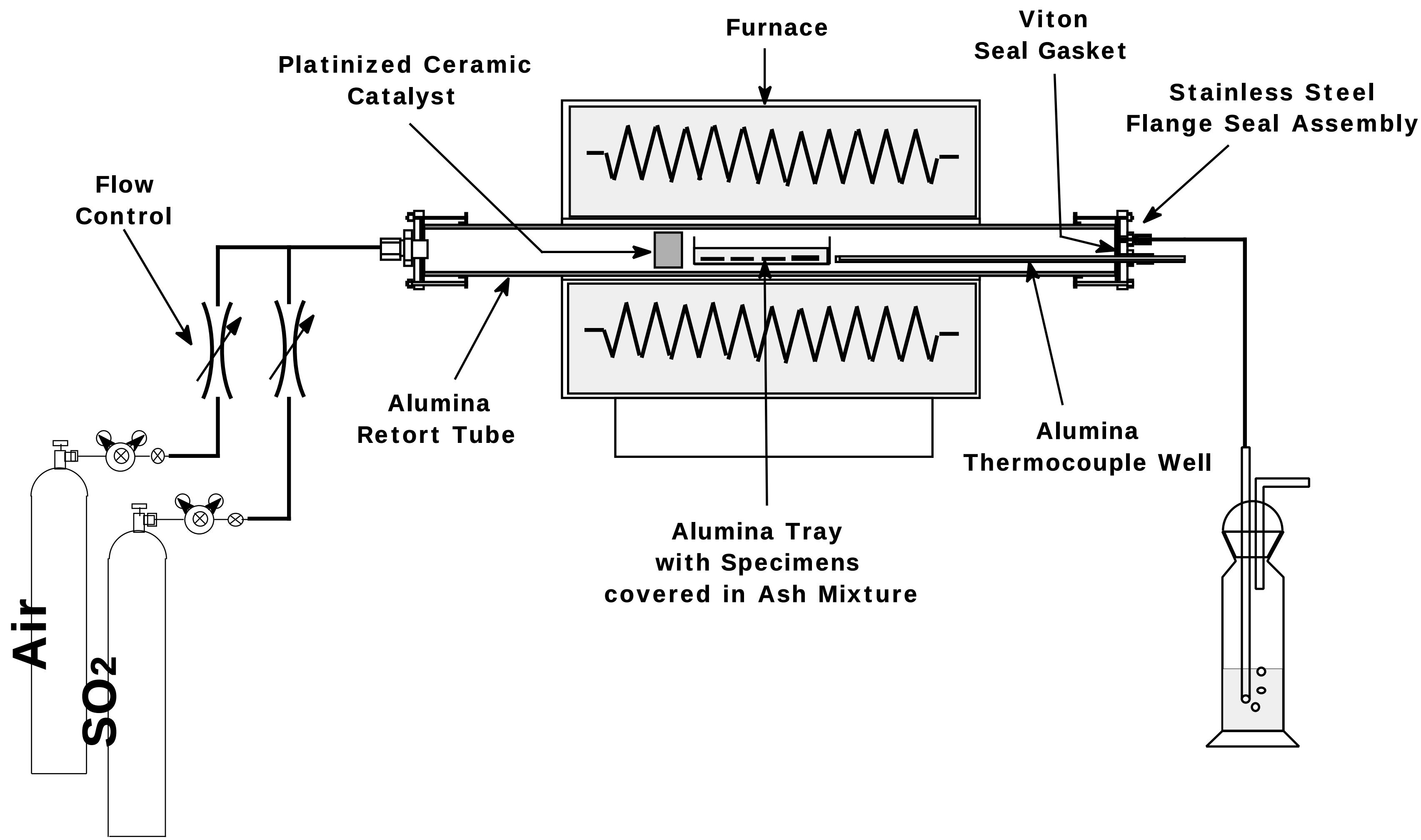
- **Solid-solution/precipitation hardening alloys**
  800HT, 310SS, 617, 671, 625, X, 556, 253MA, 214, 188

- **Oxide-dispersion-strengthened alloy**
  MA 956

- **Intermetallic alloy**
  FAL

- **Ni-base alloys: 617, 671, 625, 214, X**
- **Fe-base alloys: 800HT, 310SS, 253MA, 556, MA956, FAL**
- **Co-base alloy: 188**

Corrosion Test Facility



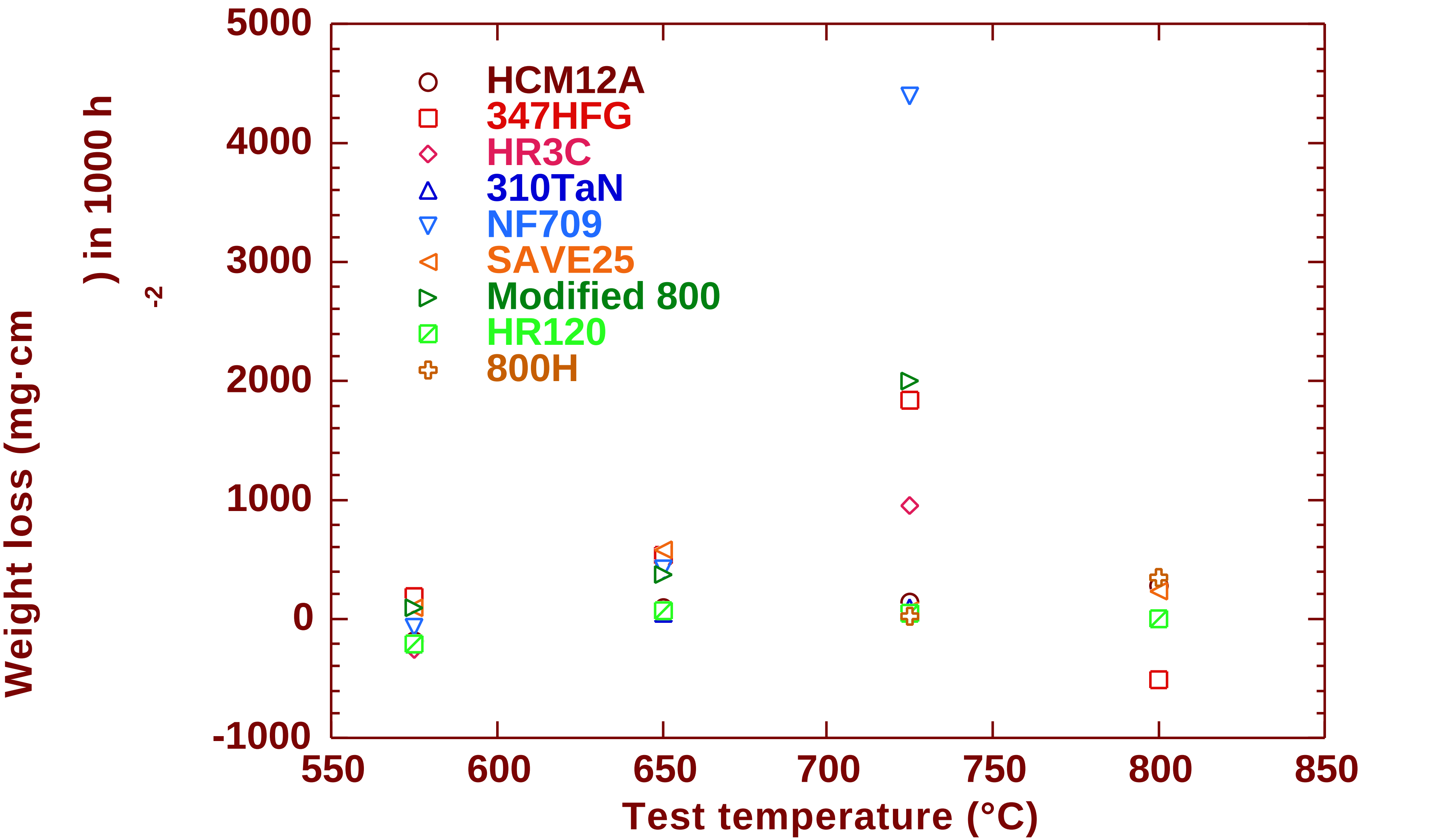
Fe-base Alloys Selected for Corrosion Tests

Material	C	Cr	Ni	Mn	Si	Mo	Fe	Other
HCM12A	0.10	12	0.3	0.5	0.3	0.4	Bal	W 2.0, V 0.2, Nb 0.05, Cu 0.9, N 0.05
Super 304H	0.10	18	9	1.0	0.3	-	Bal	Nb 0.45, Cu 3.0, N 0.09
347HFG	0.08	18	11	2.0	1.0	-	Bal	Nb + Ta = 10 x C min
HR3C	0.06	25	20	1.2	0.4	-	Bal	Nb 0.45, N 0.2
310TaN	0.05	25	20	1.0	0.2	-	Bal	Ta 1.5, N 0.2
NF709	0.07	20	25	1.0	0.6	1.5	Bal	Ti 0.6, Nb 0.2, N 0.18, B 0.004
SAVE 25	0.10	23	18	1.0	0.4	-	Bal	Nb 0.45,, W 1.5, Cu 3.0, N 0.2
Modified 800	0.10	20	30	1.5	0.2	1.5	Bal	Ti 0.25, Nb 0.25, V 0.05, N 0.03, B 0.004
HR120	0.05	25	37	0.7	0.6	2.5	Bal	Co 3, W 2.5, N 0.2, Cu 0.18, B 0.004, Al 0.1, Nb 0.7
671 clad/800H								
671	0.05	48	Bal	0.02	0.2	-	0.2	Ti 0.4
800	0.05	21	32	0.5	0.2	-	Bal	Ti 0.4, Al 0.4

Ni-base Alloys Selected for Corrosion Tests

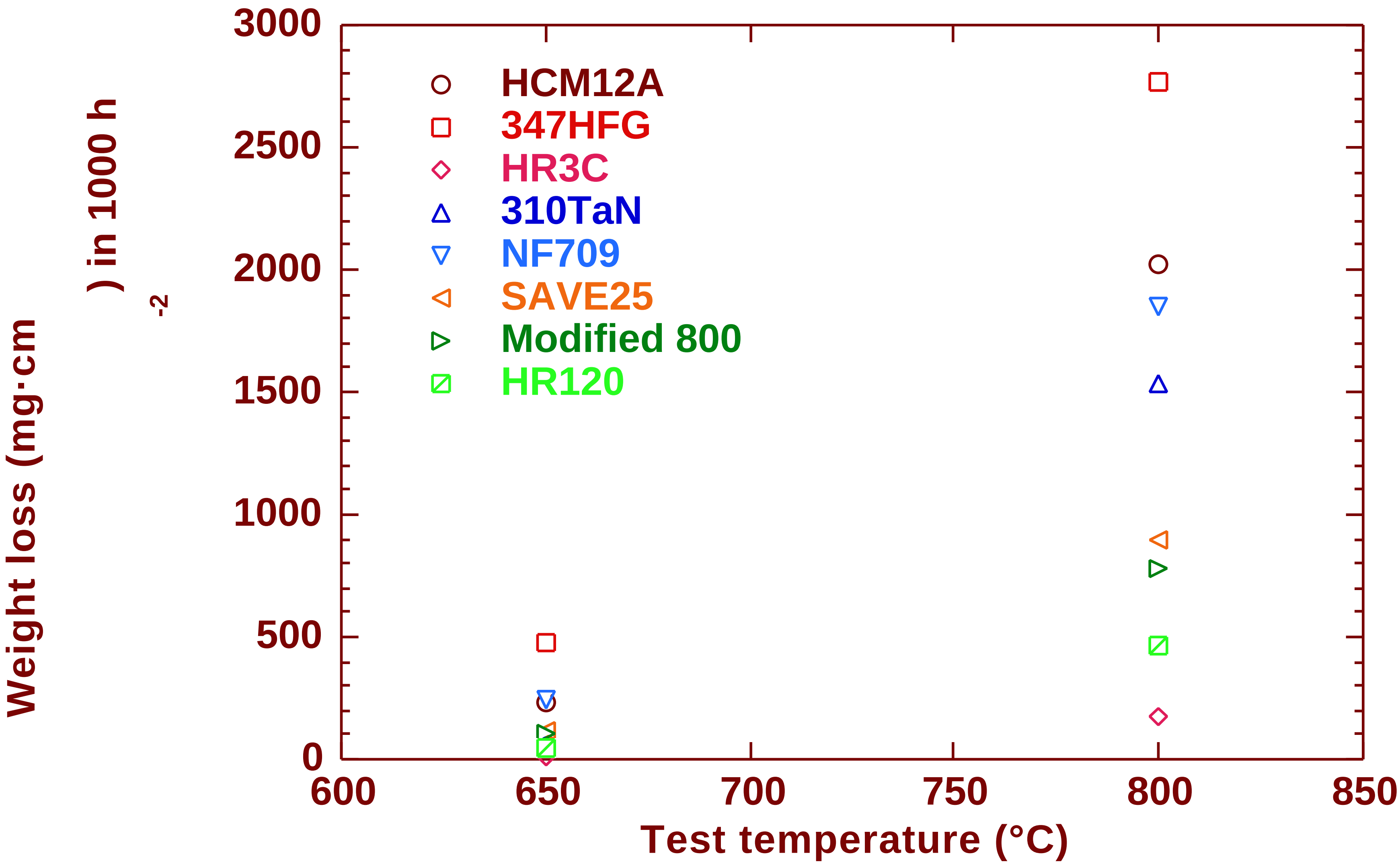
Alloy	Cr	Ni	Si	Mo	Al	Fe	Other
600	15.4	Bal	0.1	-	-	9.7	-
601	21.9	Bal	0.2	0.1	1.4	14.5	Ti 0.3, Nb 0.1
690	27.2	Bal	0.1	0.1	0.2	10.2	Ti 0.3
617	21.6	53.6	0.1	9.5	1.2	0.9	Co 12.5, Ti 0.3
625	21.5	Bal	0.3	9.0	0.2	2.5	Nb 3.7, Ti 0.2
602CA	25.1	Bal	0.1	-	2.3	9.3	Ti 0.13, Zr 0.19, Y 0.09
214	15.9	Bal	0.1	0.5	3.7	2.5	Zr 0.01, Y 0.006
230	21.7	Bal	0.4	1.4	0.3	1.2	W 14, La 0.015
45TM	27.4	46.4	2.7	-	-	26.7	RE 0.07
HR 160	28.0	Bal	2.8	0.1	0.2	4.0	Co 30.0
693	28.9	Bal	0.04	0.13	3.3	5.9	Ti 0.4, Nb 0.7, Zr 0.03

Corrosion Loss in Coal Ash + Alkali Sulfate



Presented in 2002 conference

Corrosion Loss in Coal Ash + Alkali Sulfate + NaCl



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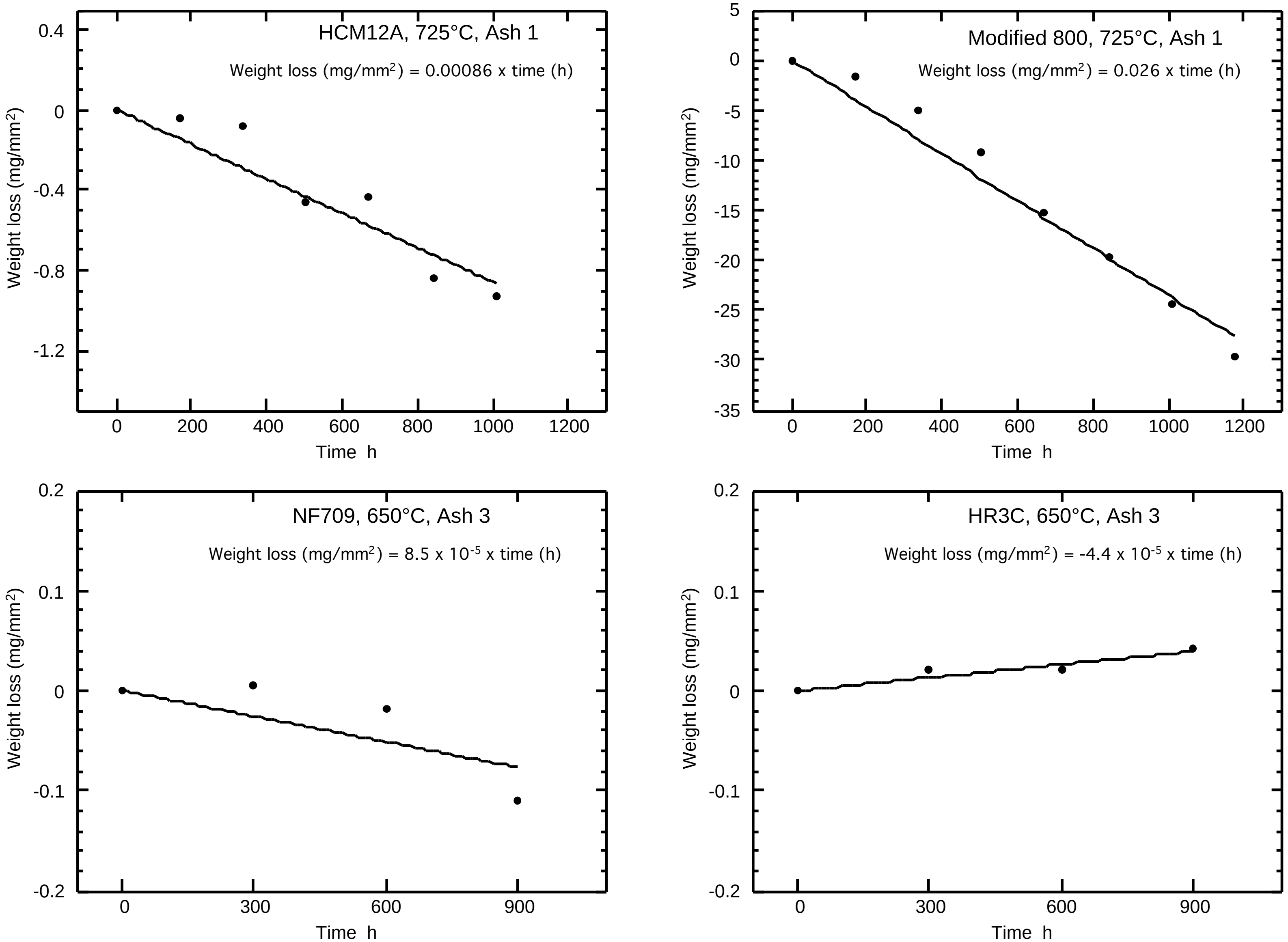
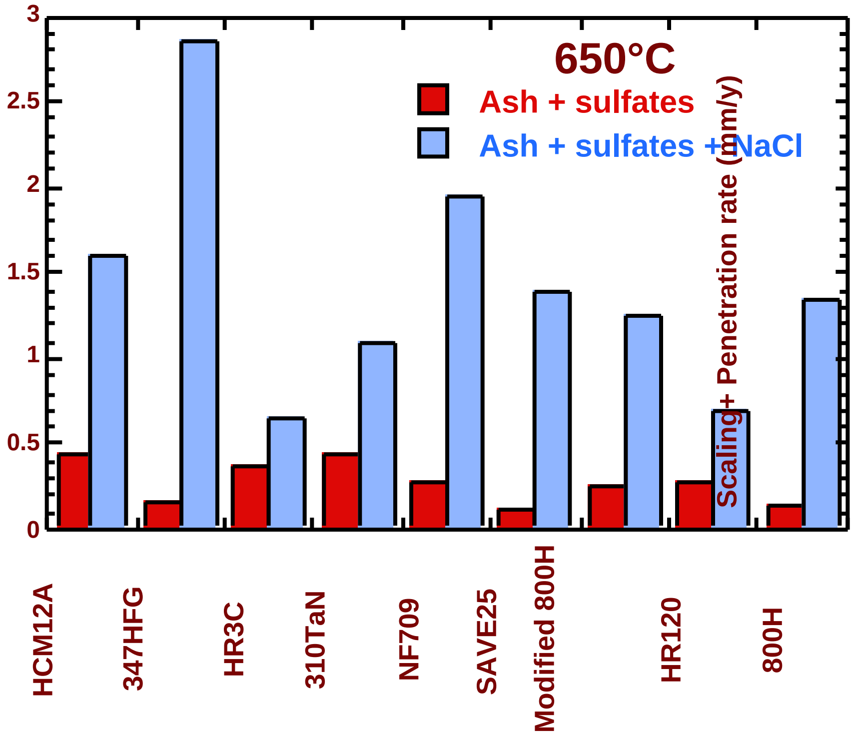
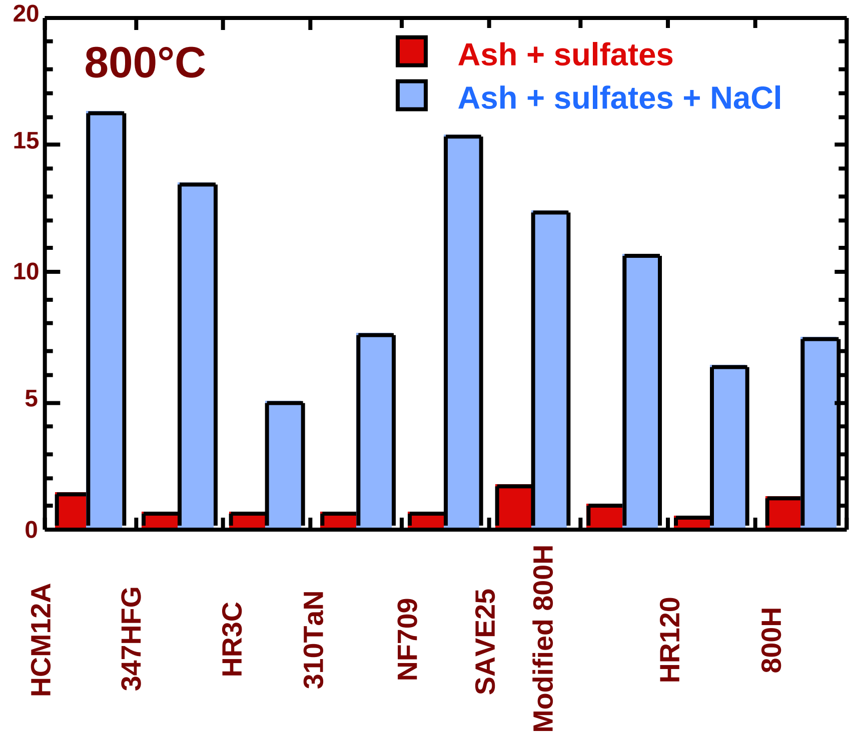
Examples of weight loss data



Effect of NaCl on Corrosion





5%NaCl
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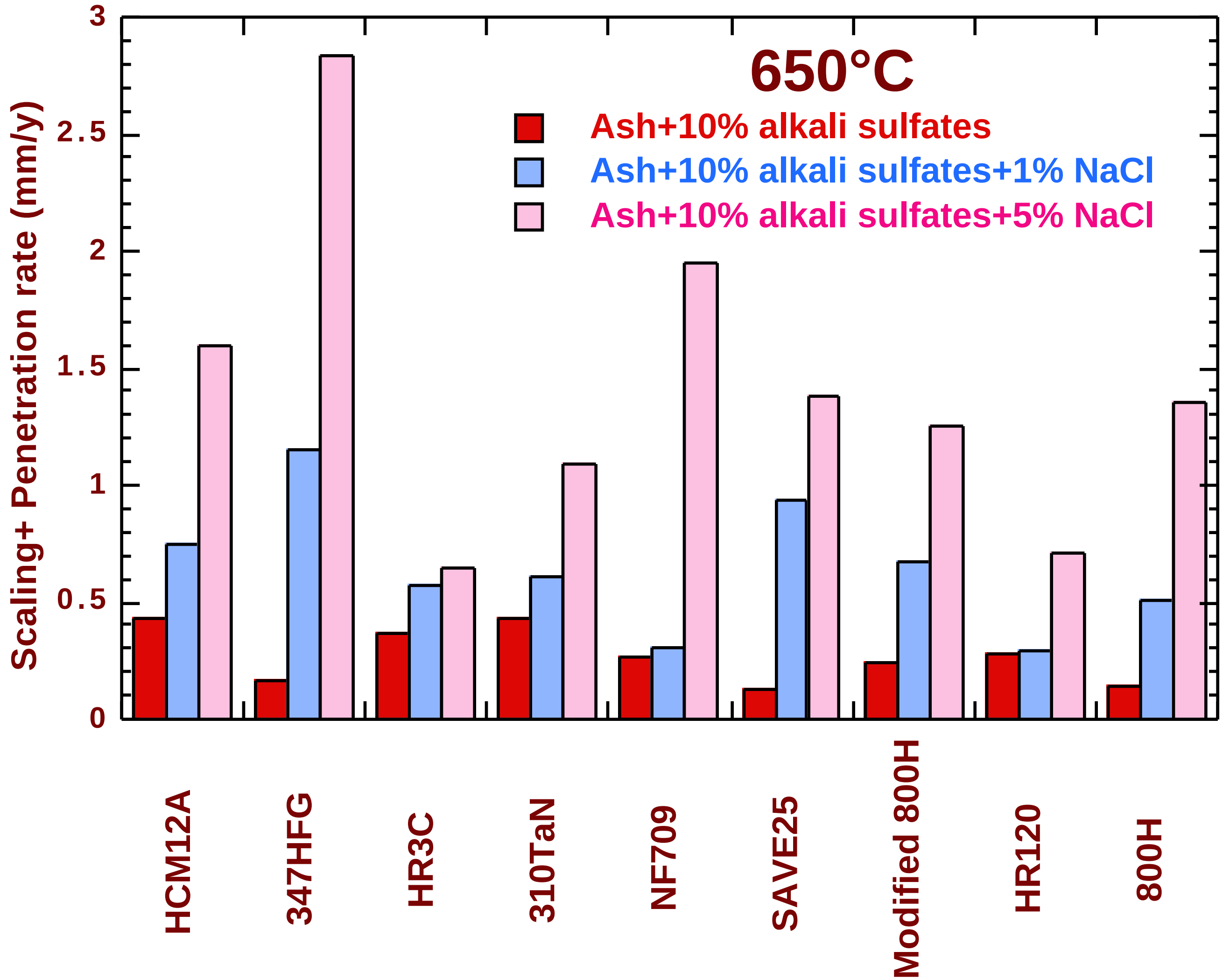
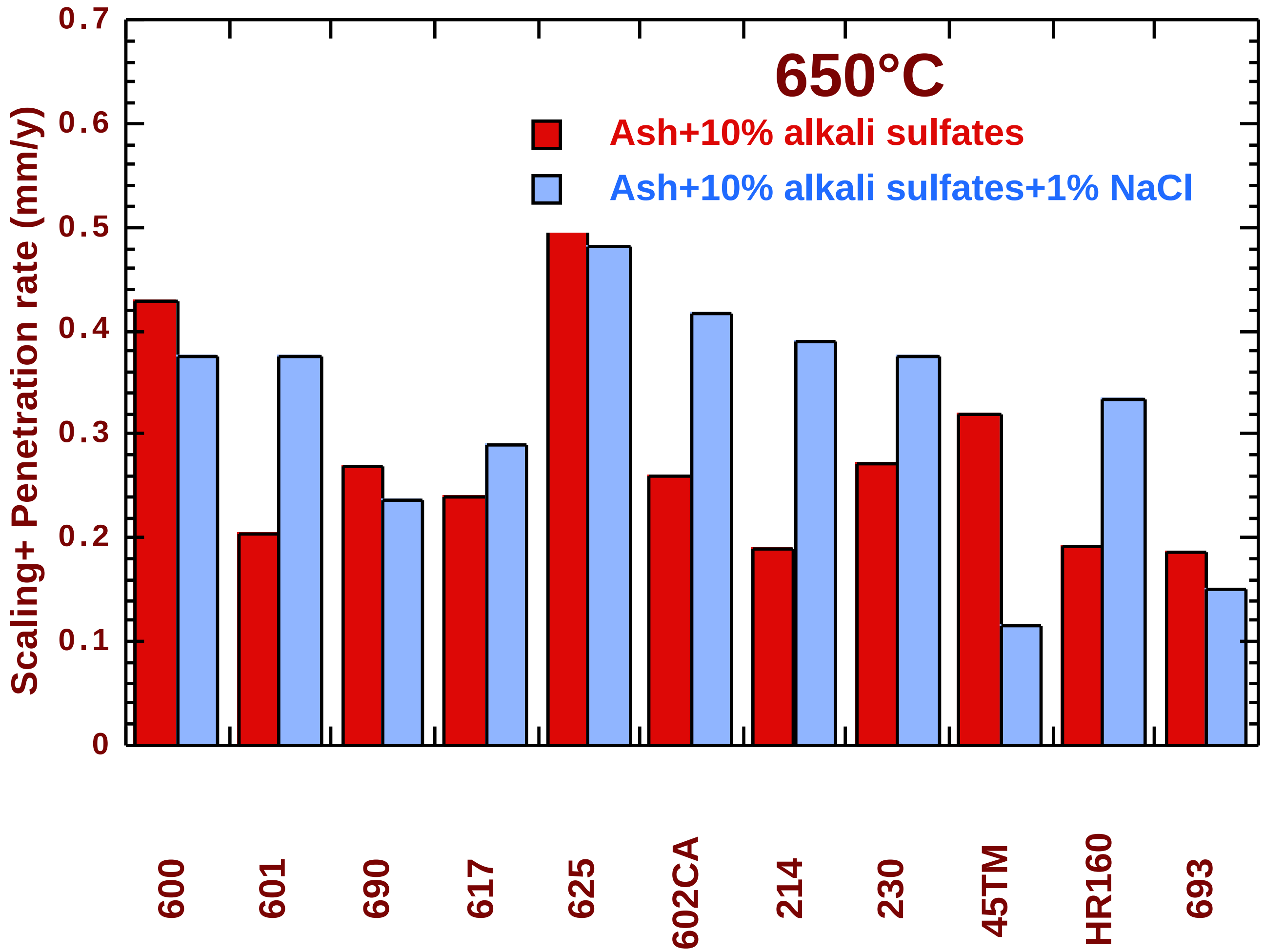
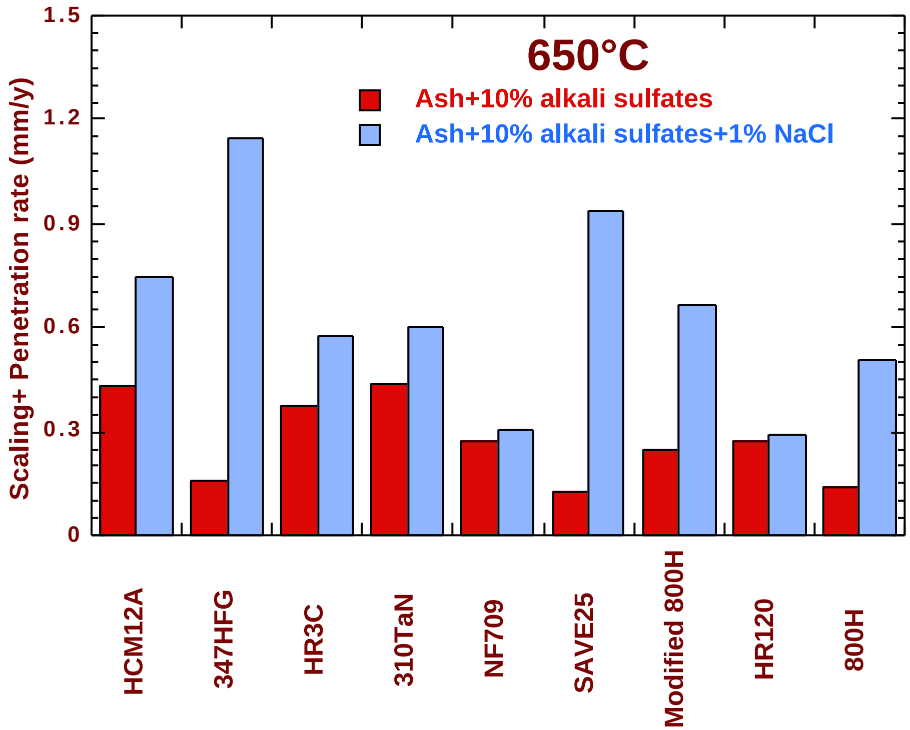
Effect of Deposit Chemistry on Corrosion of Fe-base Alloys

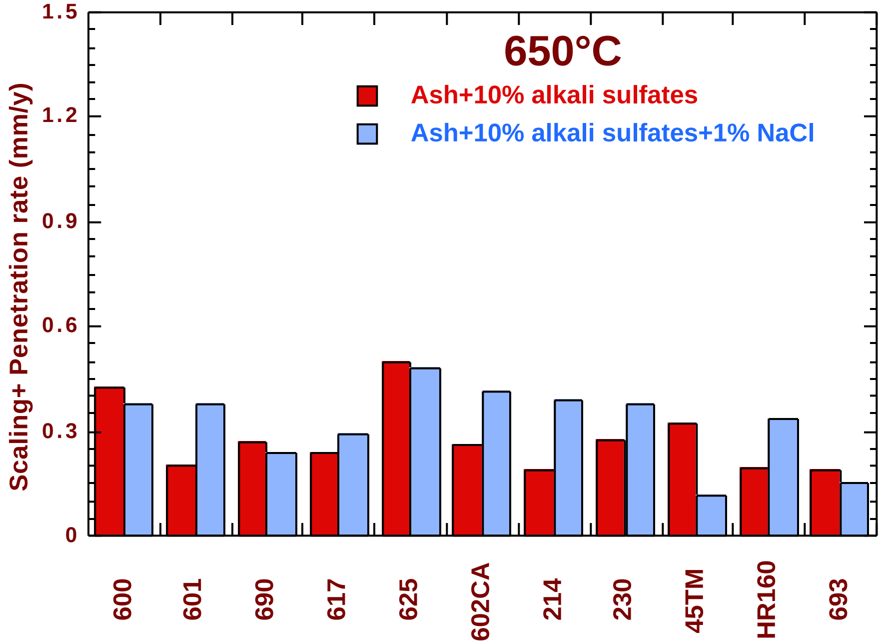


Effect of Deposit Chemistry on Corrosion of Ni-base Alloys

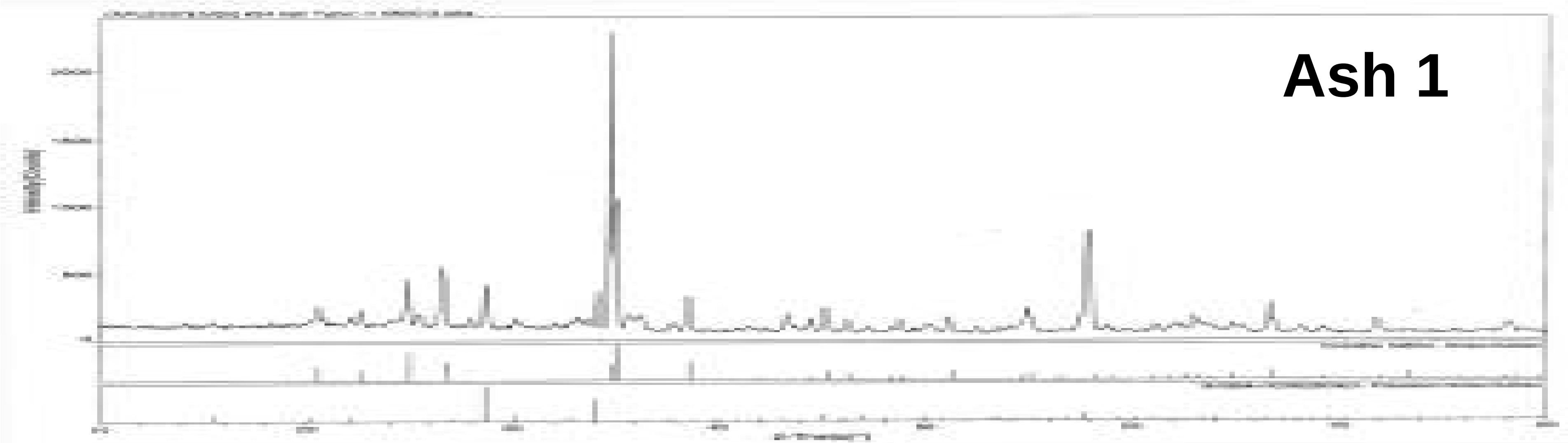


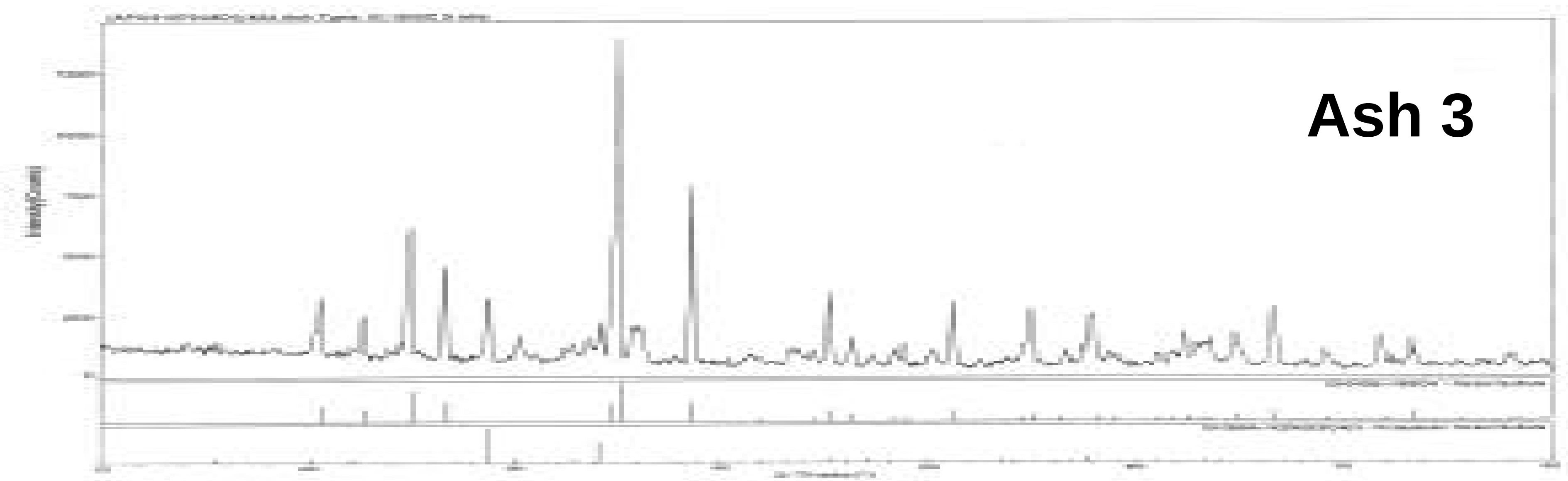
Comparison of Corrosion Rates for Fe- and Ni-base Alloys

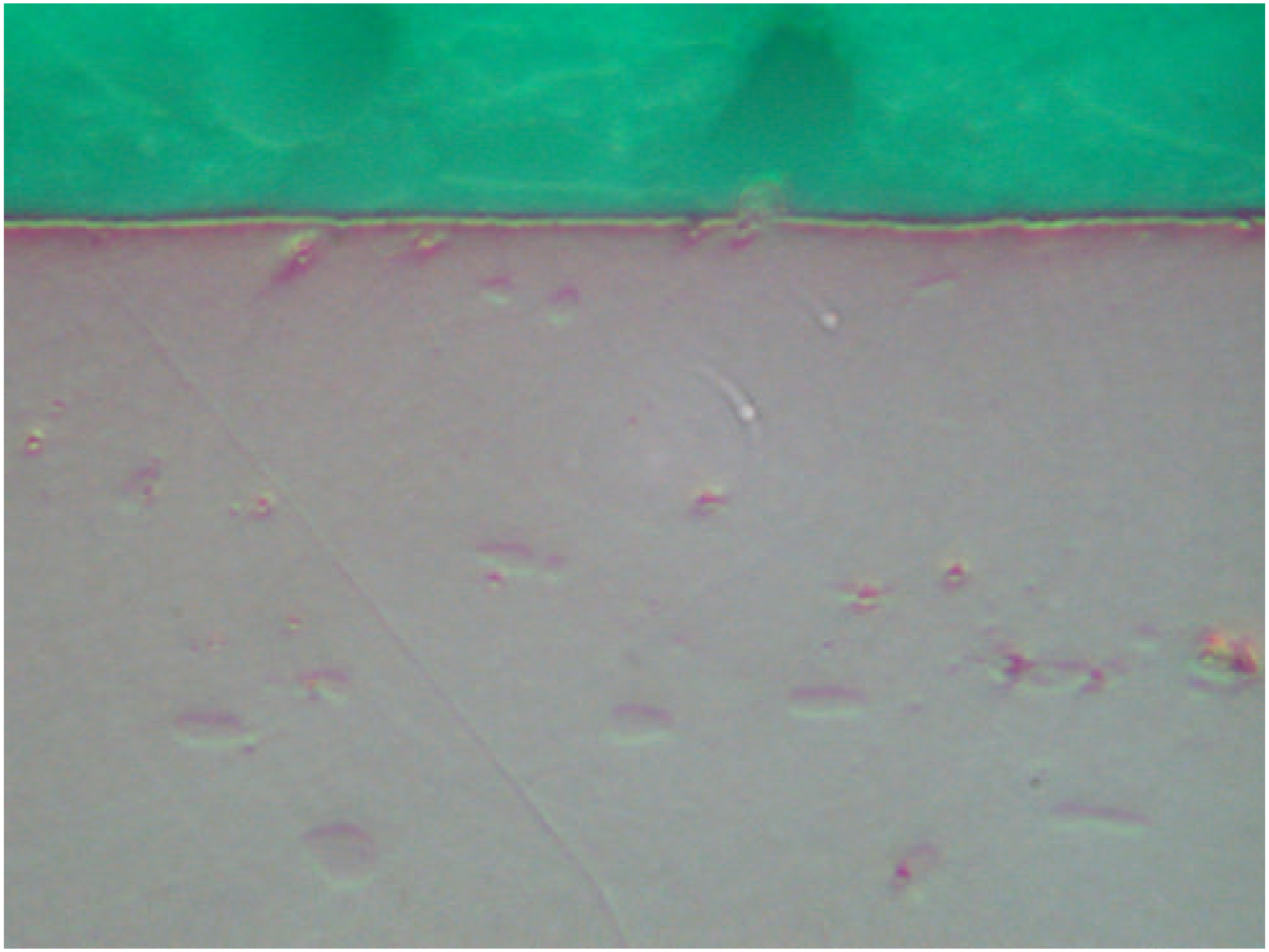




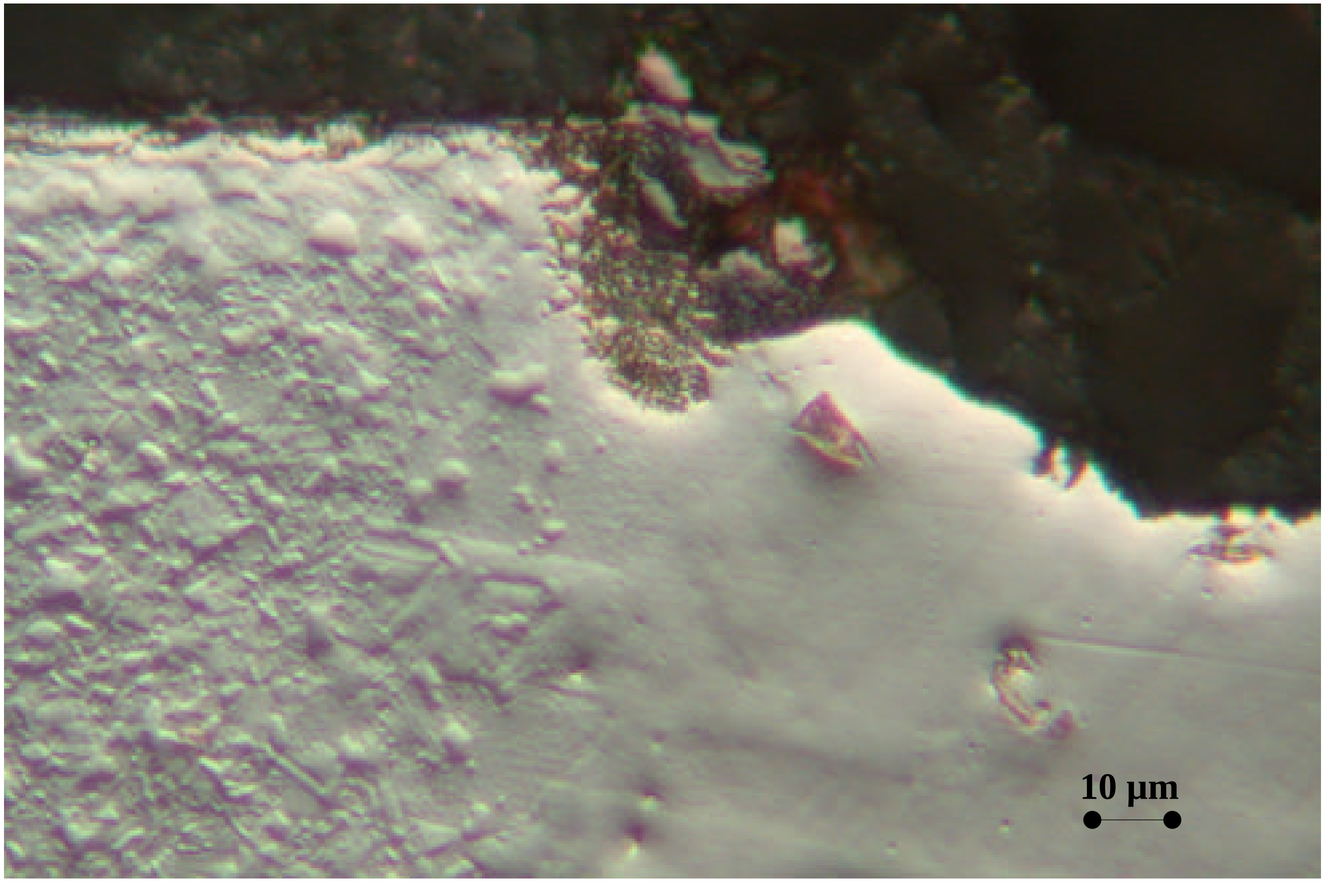
X-ray Diffraction Data







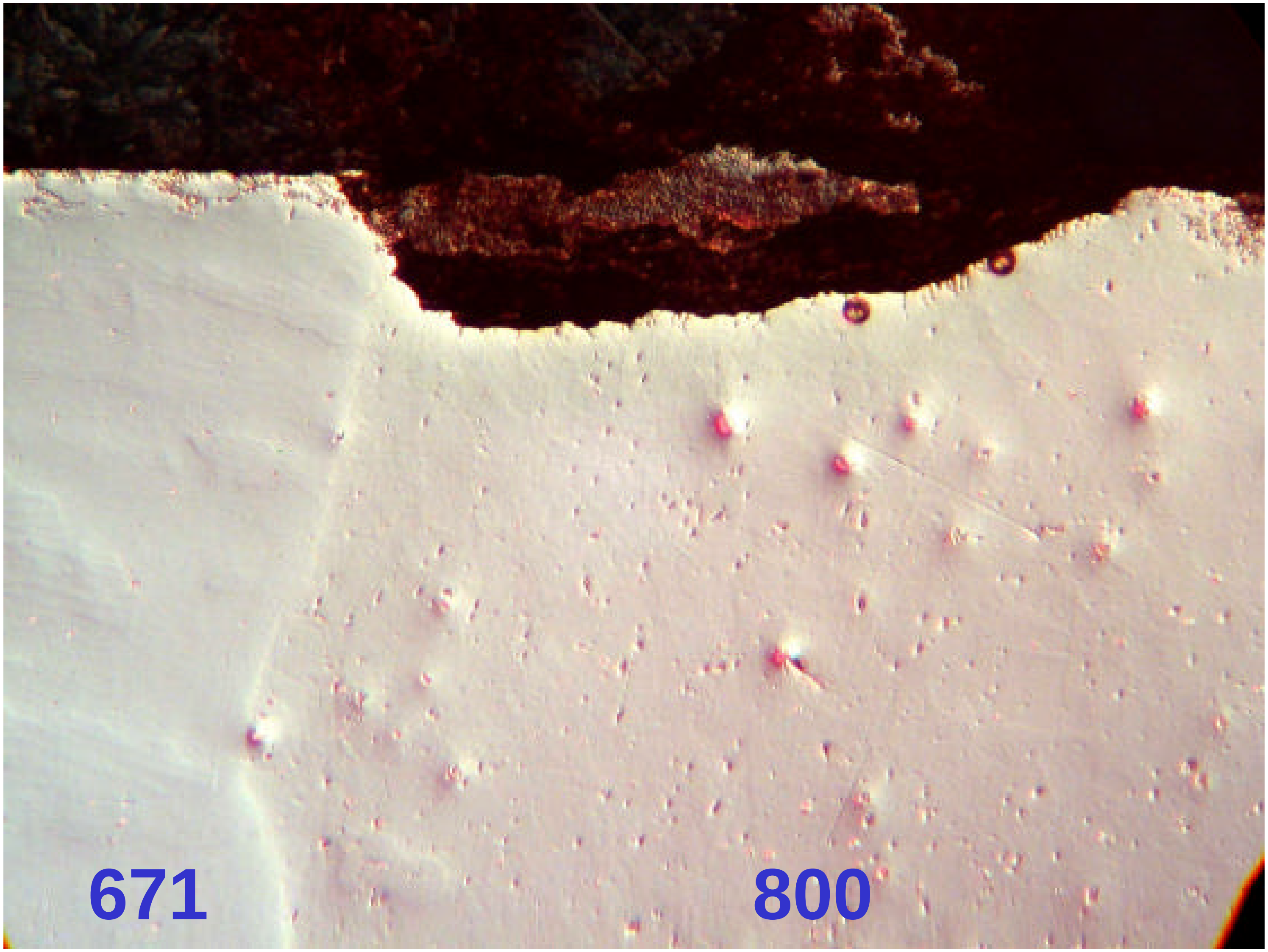
Cross section of a typical specimen before exposure



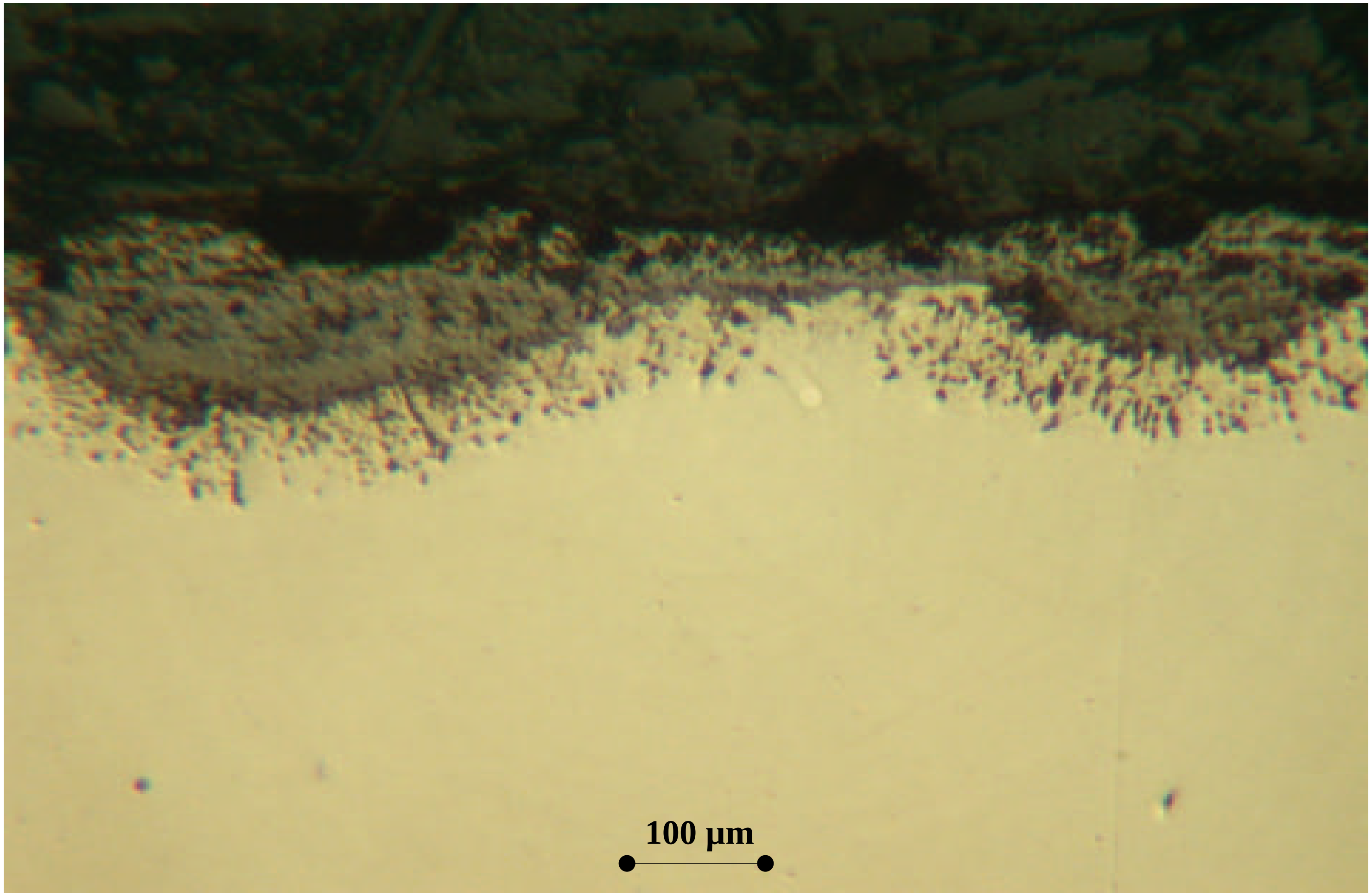
671 800

668 h exposure at 650°C in ash + sulfates

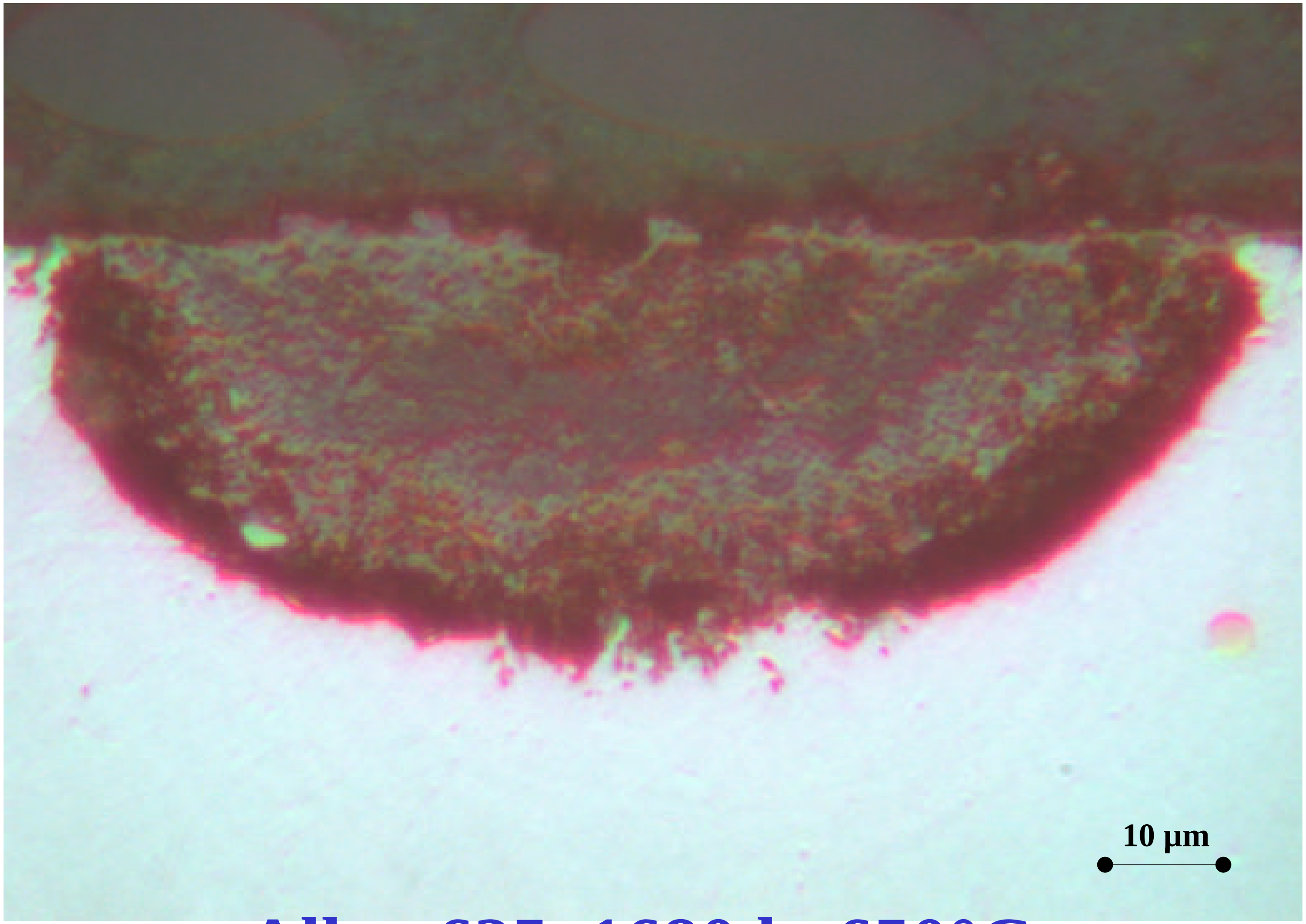
Presented in 2002 Conference



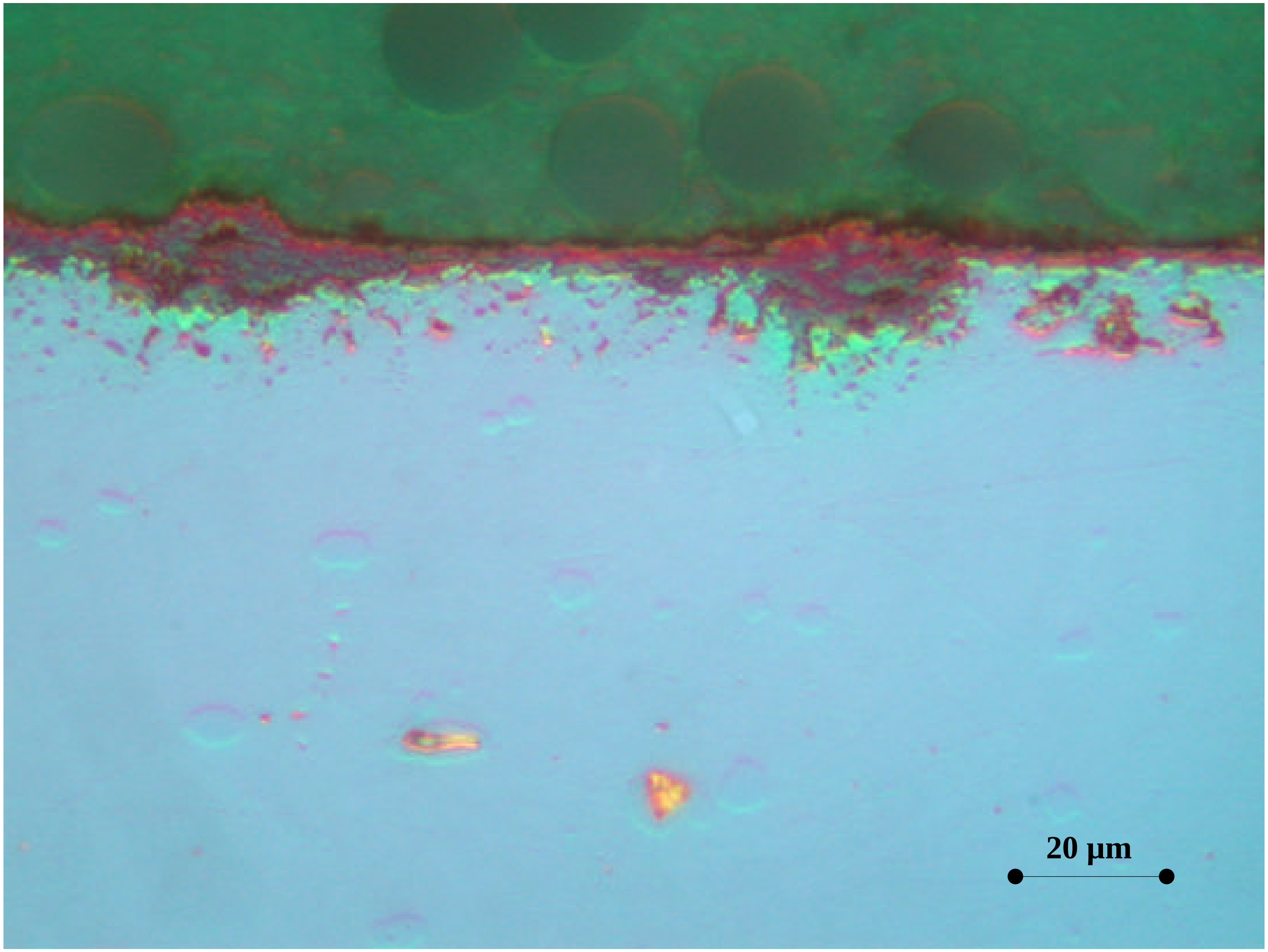
900 h at 650°C in ash + sulfates+1%NaCl



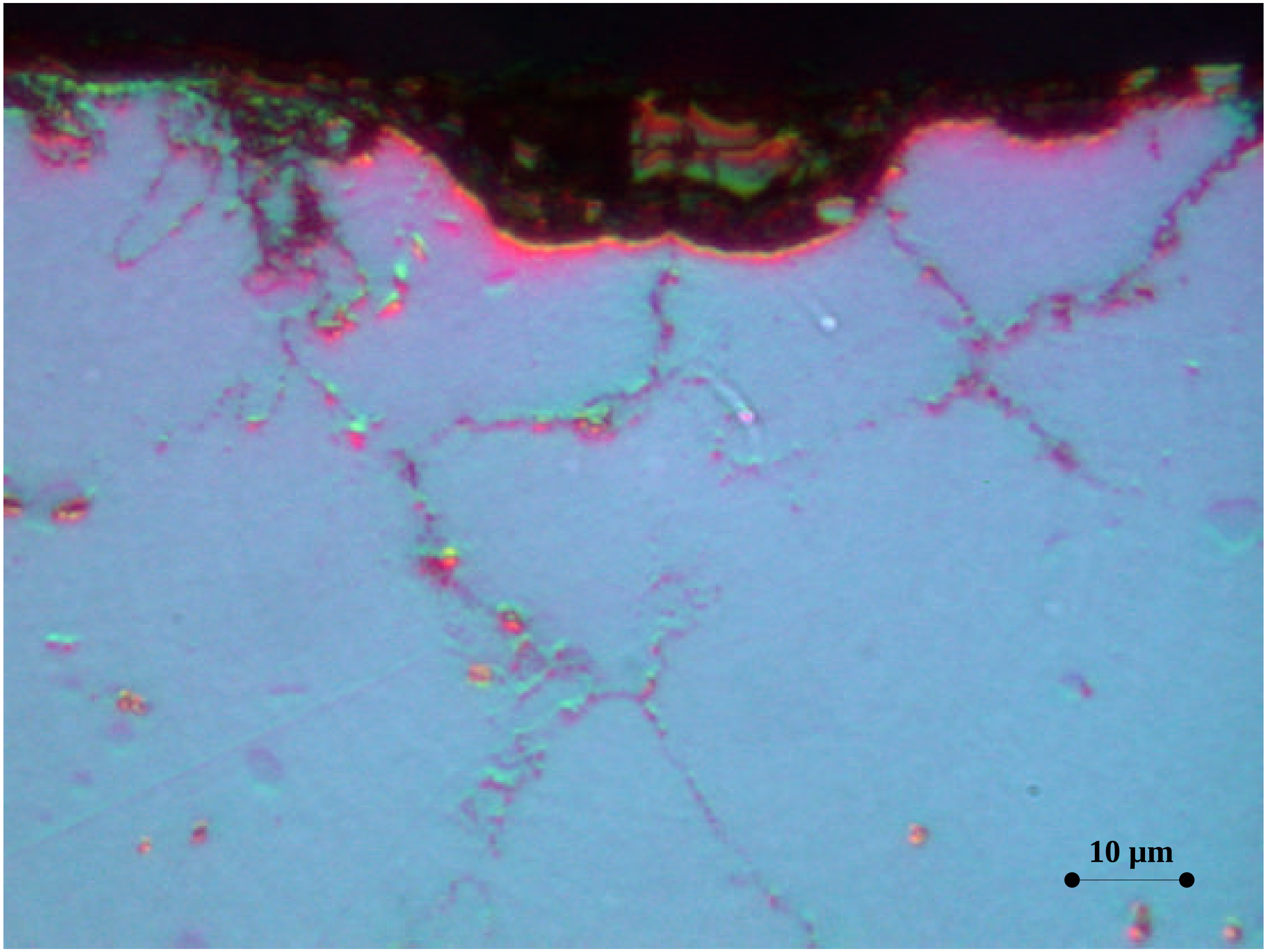
Alloy MA956, 900 h, 650°C
Ash + sulfates+ 1% NaCl



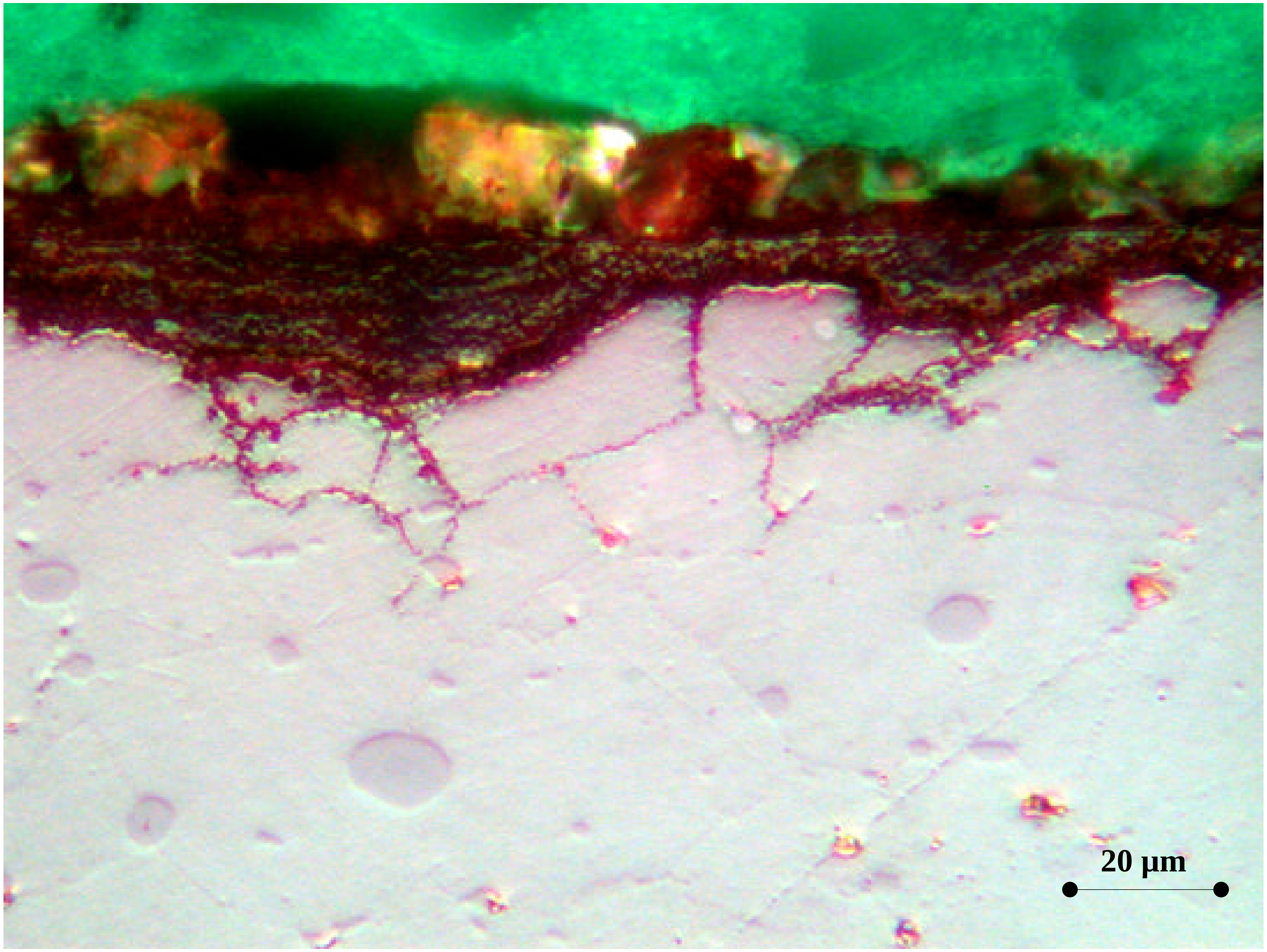
Alloy 625, 1680 h, 650°C
Ash + sulfates



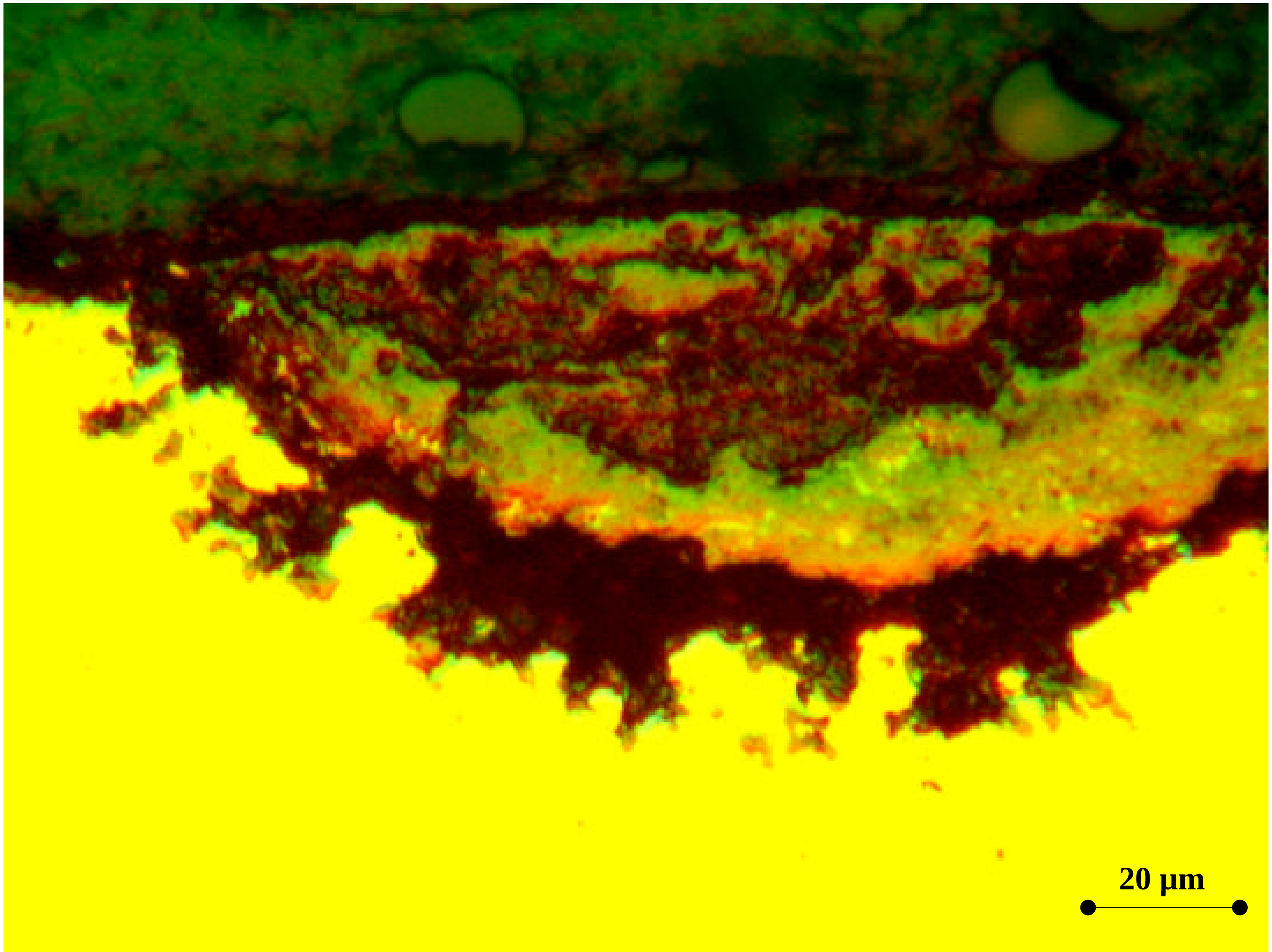
Alloy 602CA, 1680 h, 650°C
Ash + sulfates



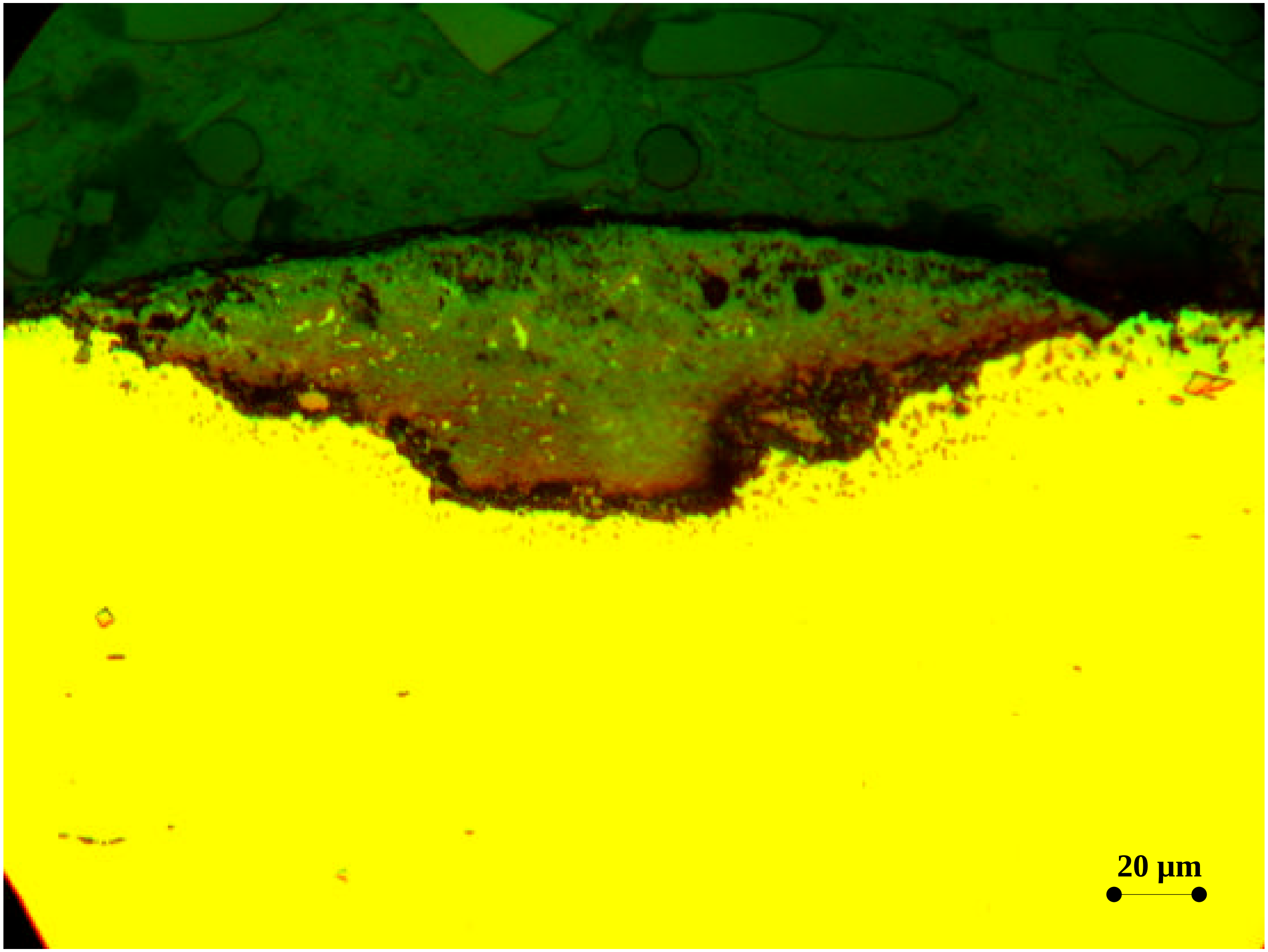
Alloy 230, 1680 h, 650°C
Ash + sulfates + 1% NaCl



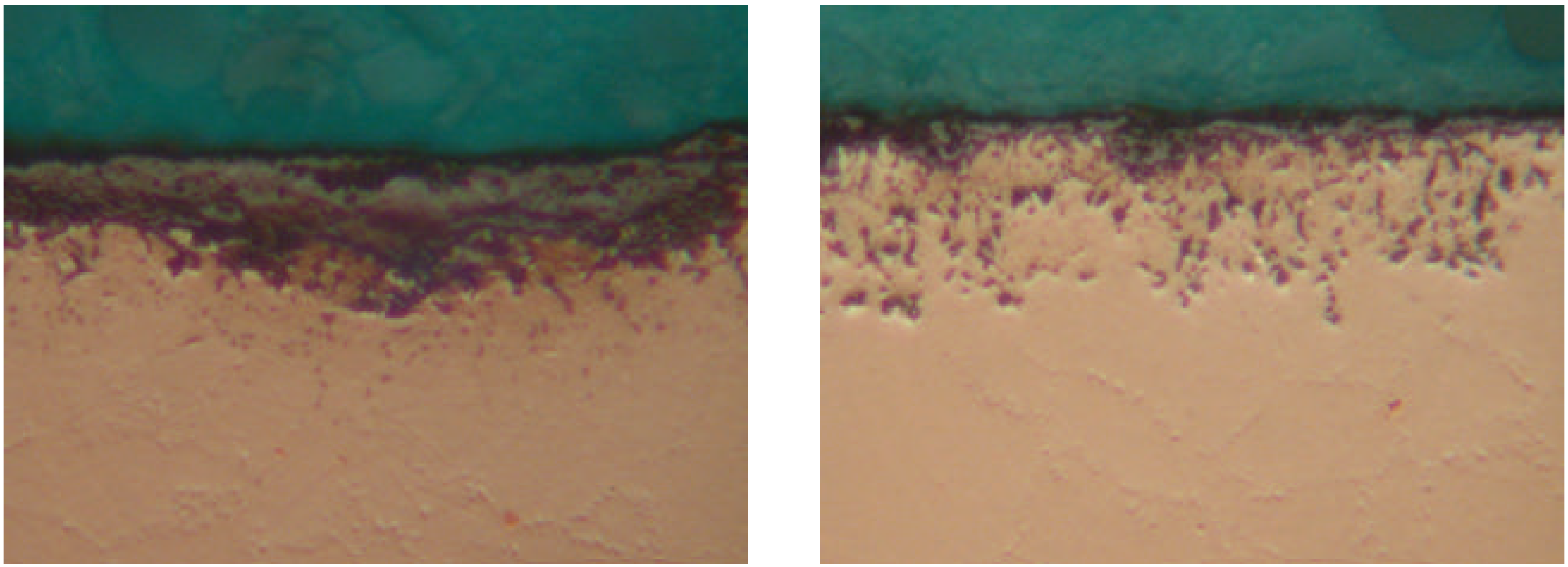
Alloy 230, 1680 h, 650°C
Ash + sulfates



Alloy 45TM, 1680 h, 650°C
Ash + sulfates

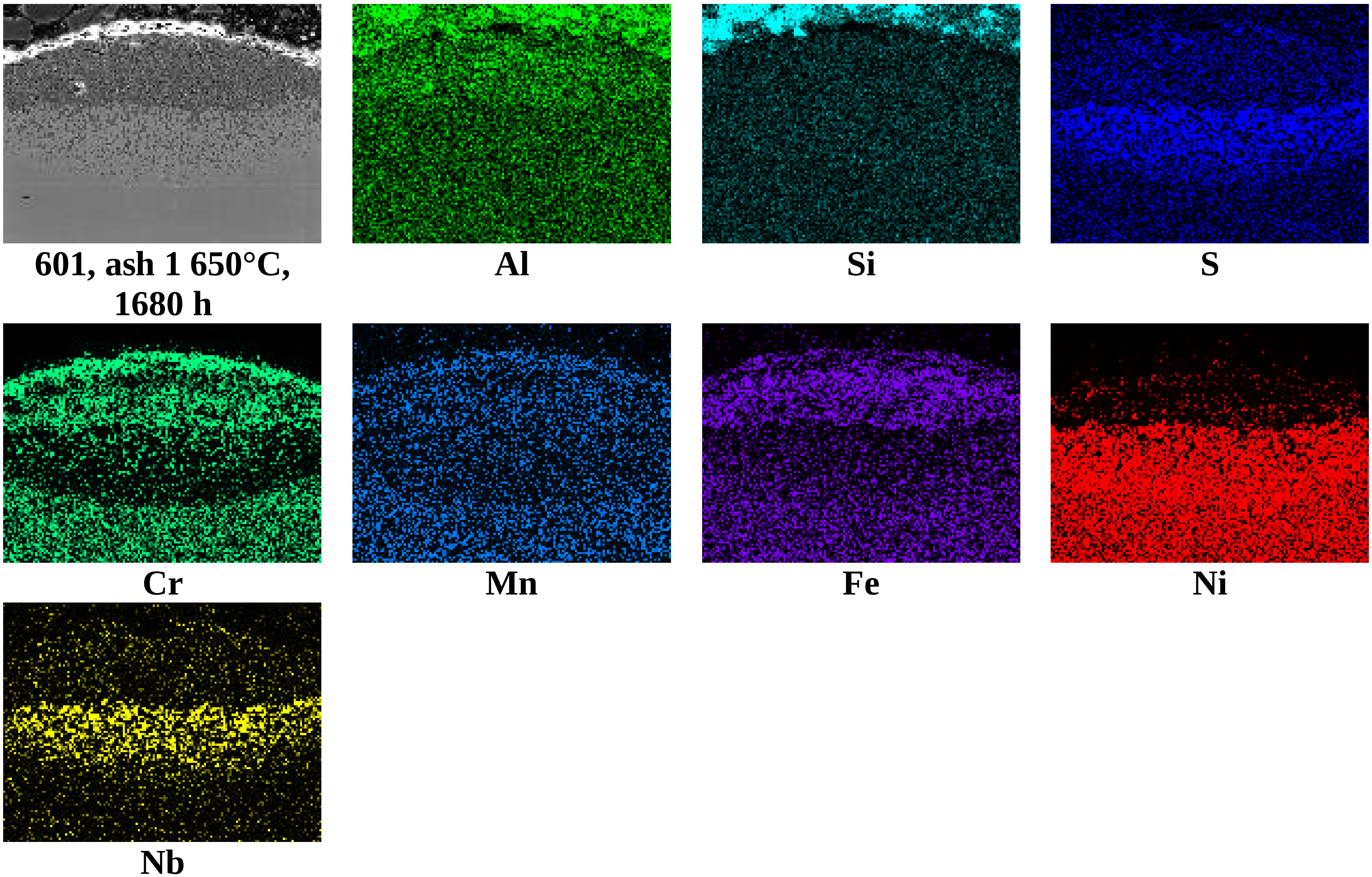


Alloy 45TM, 1680 h, 650°C
Ash + sulfates + 1% NaCl

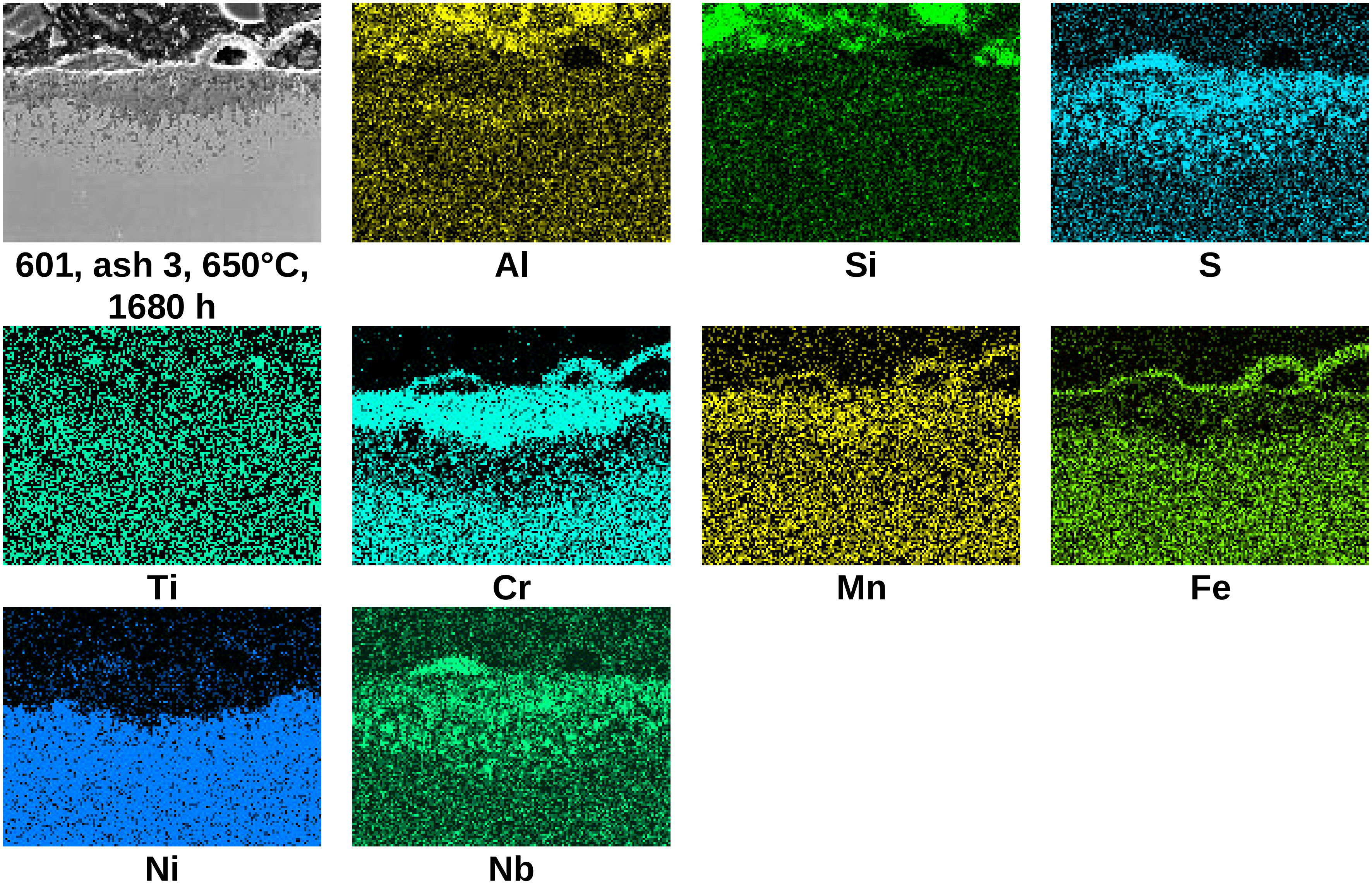


ash + sulfates | 10 µm | ash + sulfates + 1% NaCl

Alloy 693, 1680 h, 650°C

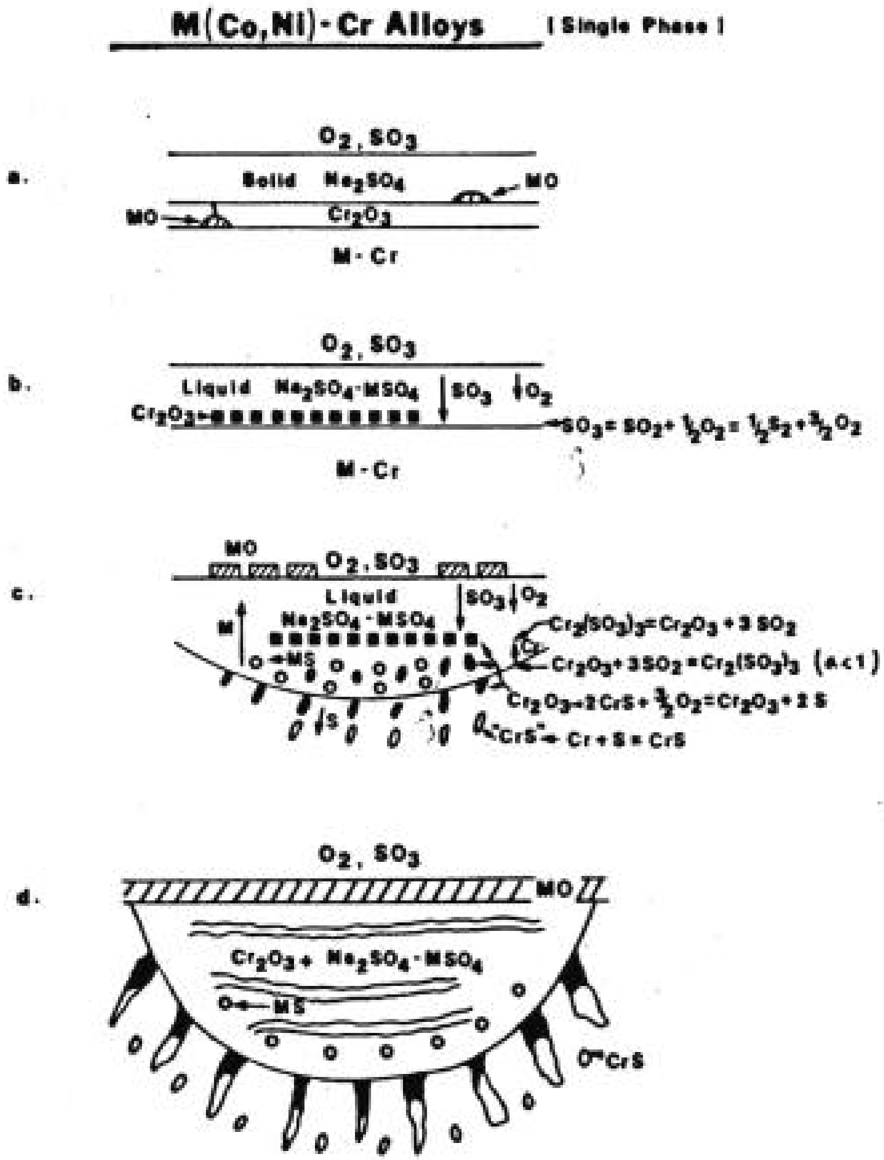


Deposit: Ash + sulfates

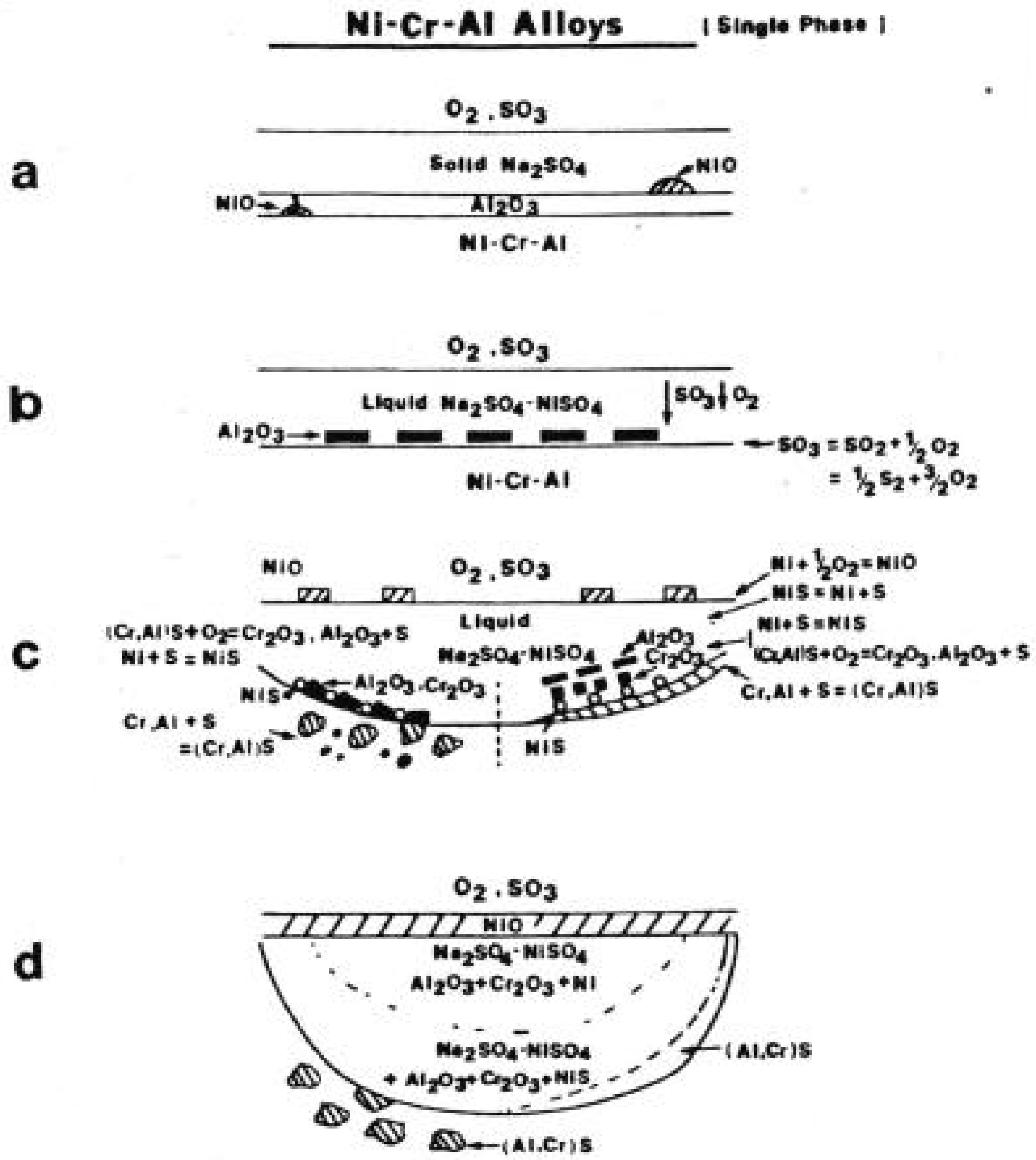


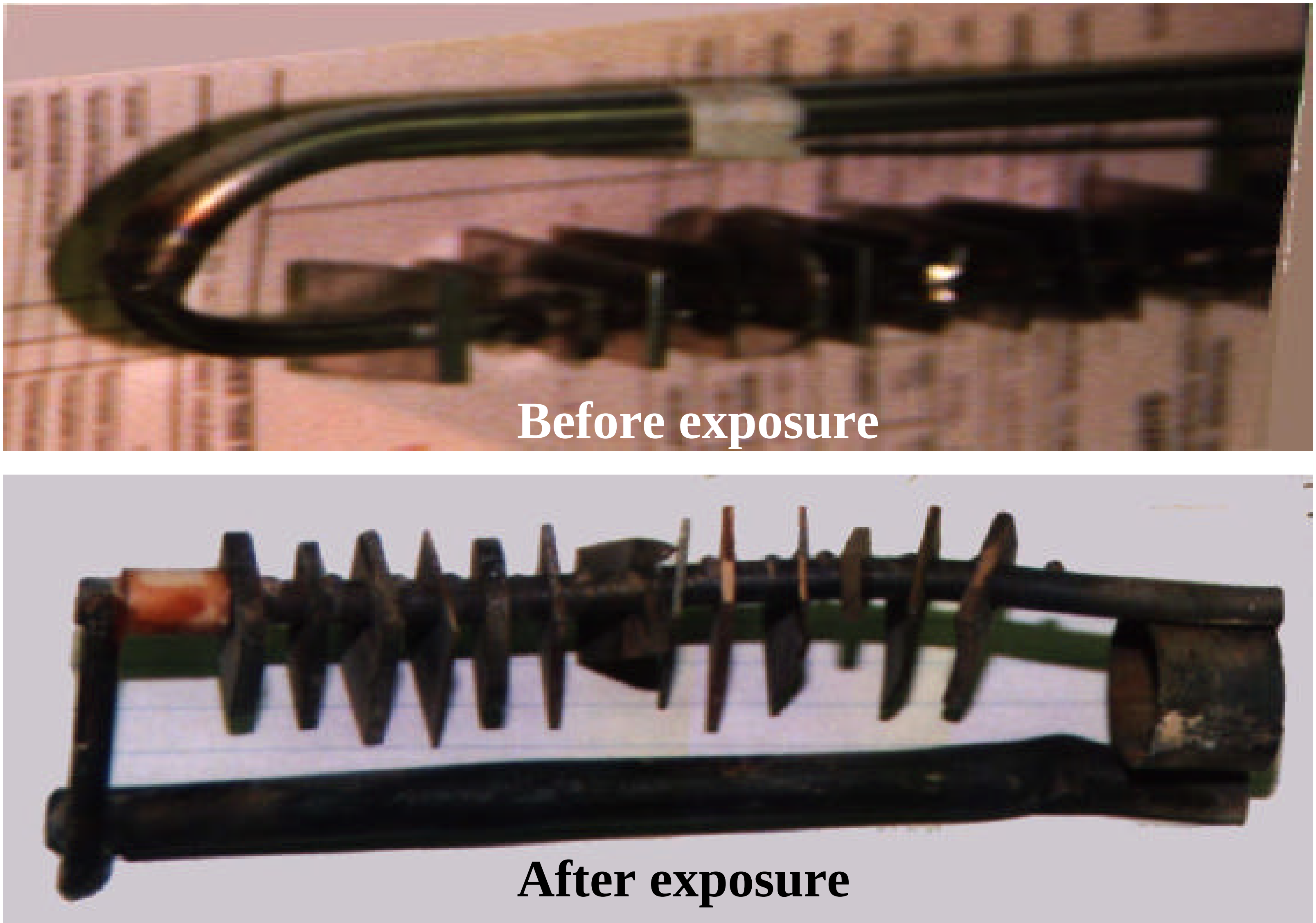
Deposit: Ash + sulfate+ 1% NaCl

Hot Corrosion of Ni-Cr Alloys



Hot Corrosion of Ni-Cr-Al Alloys





1500-1600°F (≈ 815-870°C)

Summary

- Fireside corrosion is a major issue in selection of materials for advanced steam cycles
- We have conducted studies at ANL to evaluate the corrosion performance of several Fe- and Ni-base alloys
- The laboratory tests simulated the combustion atmosphere and three deposit chemistries which included ash constituents, alkali sulfates, and two levels of NaCl
- Corrosion rates exhibited a bell shaped curve (for Fe base alloys) with peak rates around 725°C, and the rate itself is dependent on the alloy chemistry
- Several Fe-base alloys showed acceptable rates in the sulfate containing coal-ash environment; but, NaCl in the deposit led to catastrophic corrosion at 650 and 800°C

Summary (continued)

- Ni-base alloys, tested for 1680 h at 650°C, showed a substantial local attack in the form of pits and associated sulfidation of the alloy. This form of attack is well established and is known as "low temperature hot corrosion" or Type II hot corrosion (in gas turbine terminology)

- Need to establish the maximum levels for alkali sulfates and alkali chlorides in combustion environment (and their relationship to coal feedstock) for acceptable corrosion

- Additional tests are in progress with Ni-base alloys at ANL and in NETL combustor to evaluate their corrosion performance

- The combination of adequate creep strength and fireside and steamside corrosion resistance is still a challenge in materials development for advanced steam cycles