OXIDATION OF HIGH-TEMPERATURE AEROSPACE MATERIALS

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Introductory remarks

High temperature oxidation is one of the most disadvantageous consequences of chemical reactions between materials and their surrounding environment.

Methods of preventing high temperature oxidation:

- coatings
- cooling systems
- gas modification

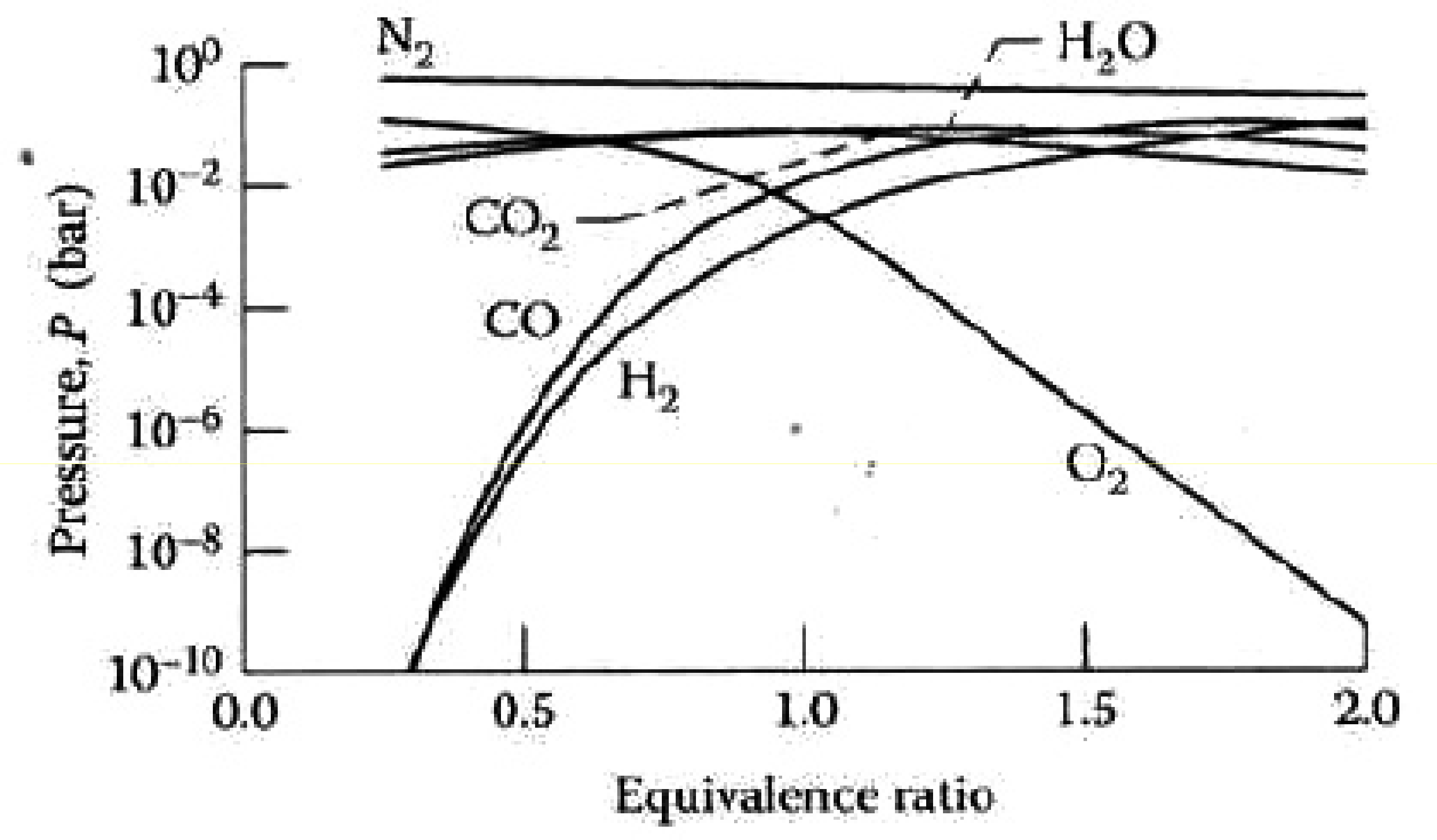
Oxidation of high temperature materials in the aeronautics and space technology field:

- hot stages of aircraft engines
- rocket engines
- re-entry surfaces on spacecrafts

Working conditions of aircraft turbine engines

- aircraft turbine engines typically burn a high purity hydrocarbon fuel
- flame temperature: 1000-2400K
- total pressure in gas turbine: 10 bar or more
- reaction products: CO_2 + H_2O (10%), H_2, CO, sulphur and nitrogen oxides, deposits of condensed phase salts

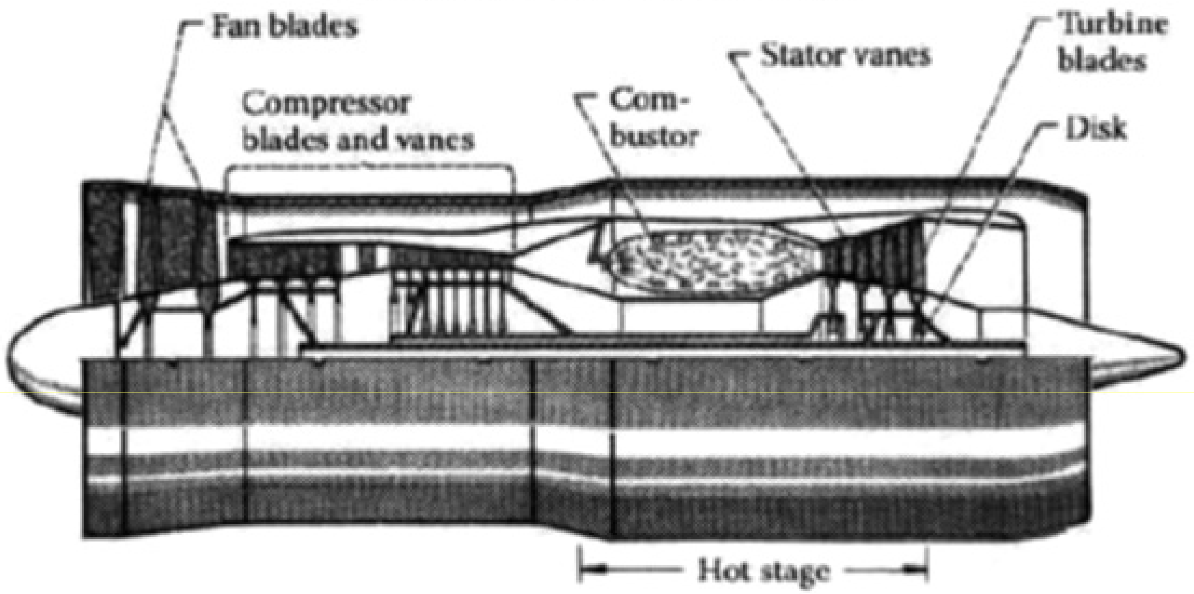
Calculated equilibrium pressures of combustion gas products as a function of equivalence ratio



An equivalence ratio, equal to 1, is defined as the stoichiometric fuel-to-air ratio, lower than 1 denotes lean fuel, and higher than 1 denotes rich fuel.

Gas turbine engine with major high temperature corrosion/degradation issues listed for each stage

Schematic diagram of turbofan engine

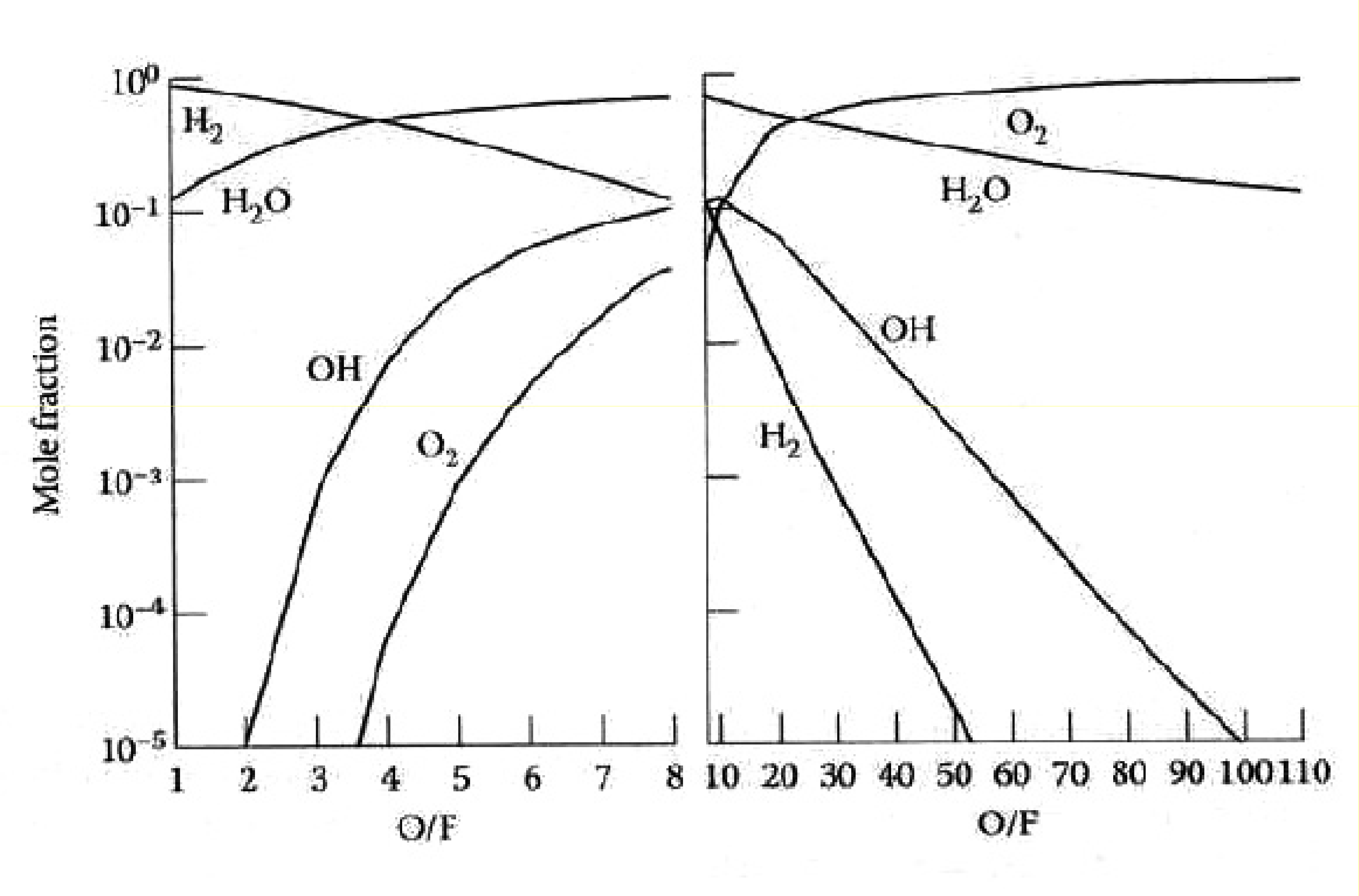


Component	Typical operating conditions			Critical problems
	Temperature (°C)	Stress (MPa)	Life (hr)	
Blades	900 – 1050	140 – 210	5000	Creep strength, stability, oxidation, hot corrosion, and thermal fatigue
Vanes	950 – 1100	35 – 70	5000	Thermal fatigue, oxidation, and hotcorrosion
Disks	400 – 650	420 – 1050	15,000	Low cycle fatigue hot corrosion
Combustors	850 – 1100	20 – 35	4000	Thermal fatigue oxidation

Working conditions of rocket engines

- variety of rocket fuels: RP-1 (kerosene), liquid oxygen (LOX)/liquid hydrogen, various solid fuels
- LOX/H_2 – the most common fuel, used on the U.S. Space Shuttle, Atlas Centaur and Saturn Rockets
- flame temperature: 1300-3700K
- reaction products: H_2 , H_2O, OH, O_2

Rocket combustion gas composition as a function of oxidizer to fuel ratio

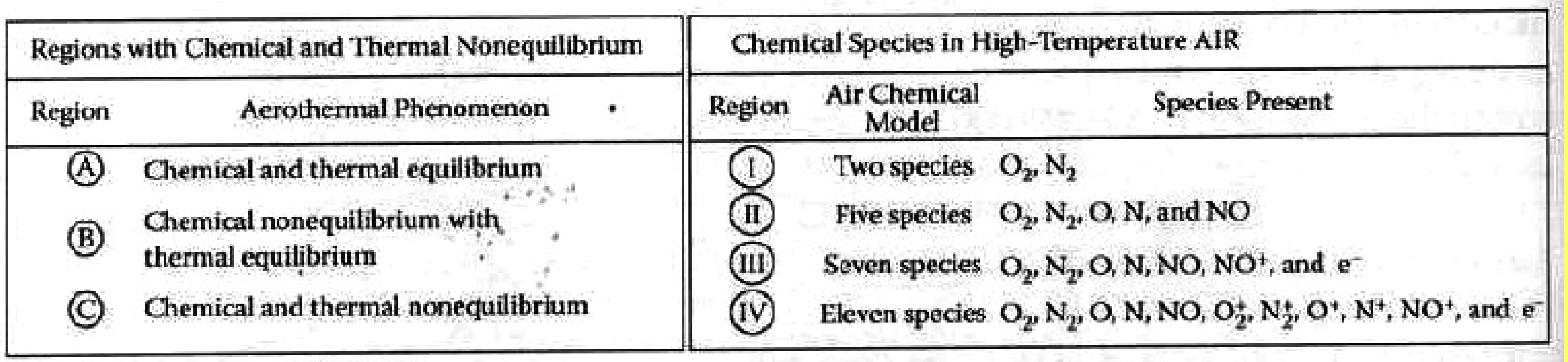


Typically, LOX/H_2 runs in a regime with excess H_2 and water vapor.

Working conditions of re-entry surfaces

- low total gas pressure
- temperature > 2300K, depends on re-entry trajectory
- very short exposure time (minutes)
- presence of highly reactive atomic oxygen and nitrogen

Exemplary trajectories and the resultant atmospheres of dissociated oxygen and nitrogen

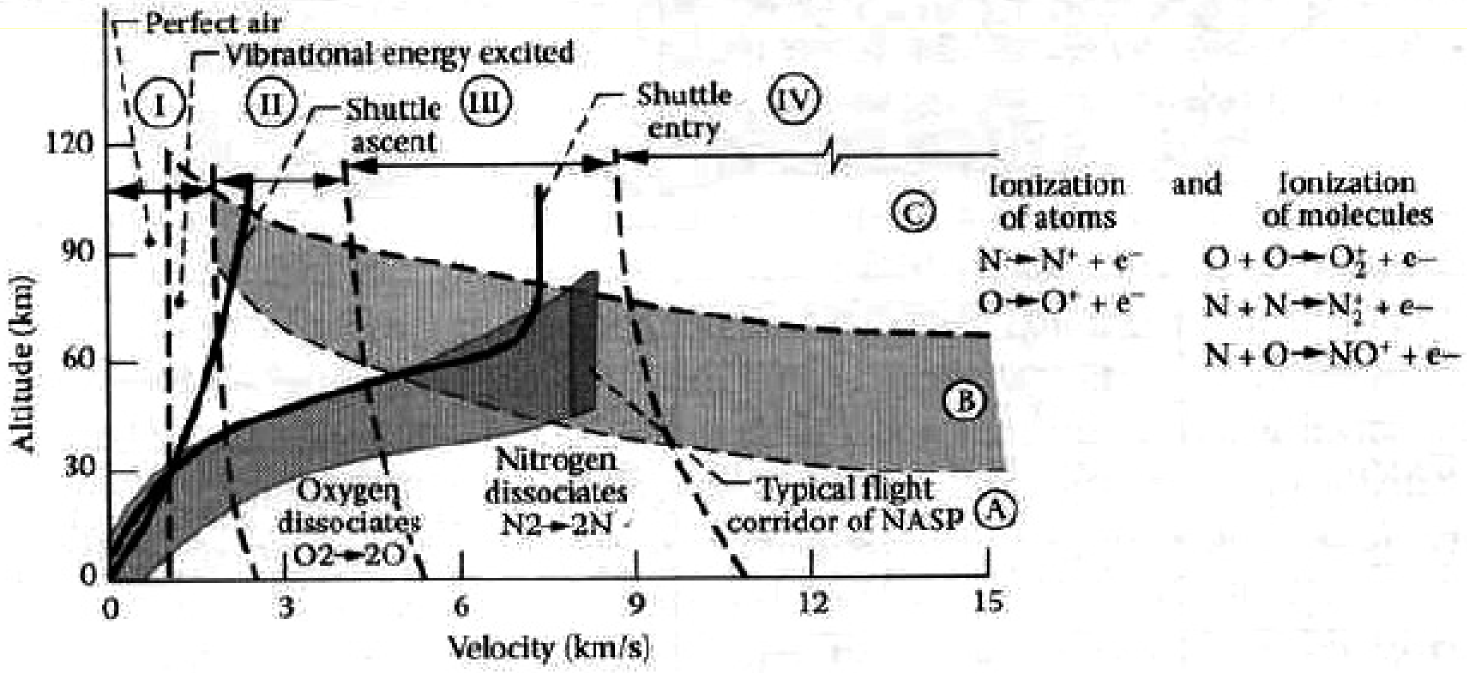


Regions with Chemical and Thermal Nonequilibrium

Region	Aerothermal Phenomenon
Ⓐ	Chemical and thermal equilibrium
Ⓑ	Chemical nonequilibrium with thermal equilibrium
Ⓒ	Chemical and thermal nonequilibrium

Chemical Species in High-Temperature AIR

Region	Air Chemical Model	Species Present
(I)	Two species	O_2, N_2
(II)	Five species	O_2, N_2, O, N, and NO
(III)	Seven species	O_2, N_2, O, N, NO, NO^+, and e^-
(IV)	Eleven species	O_2, N_2, O, N, NO, O_2^+, N_2^+, O^+, N^+, NO^+, and e^-

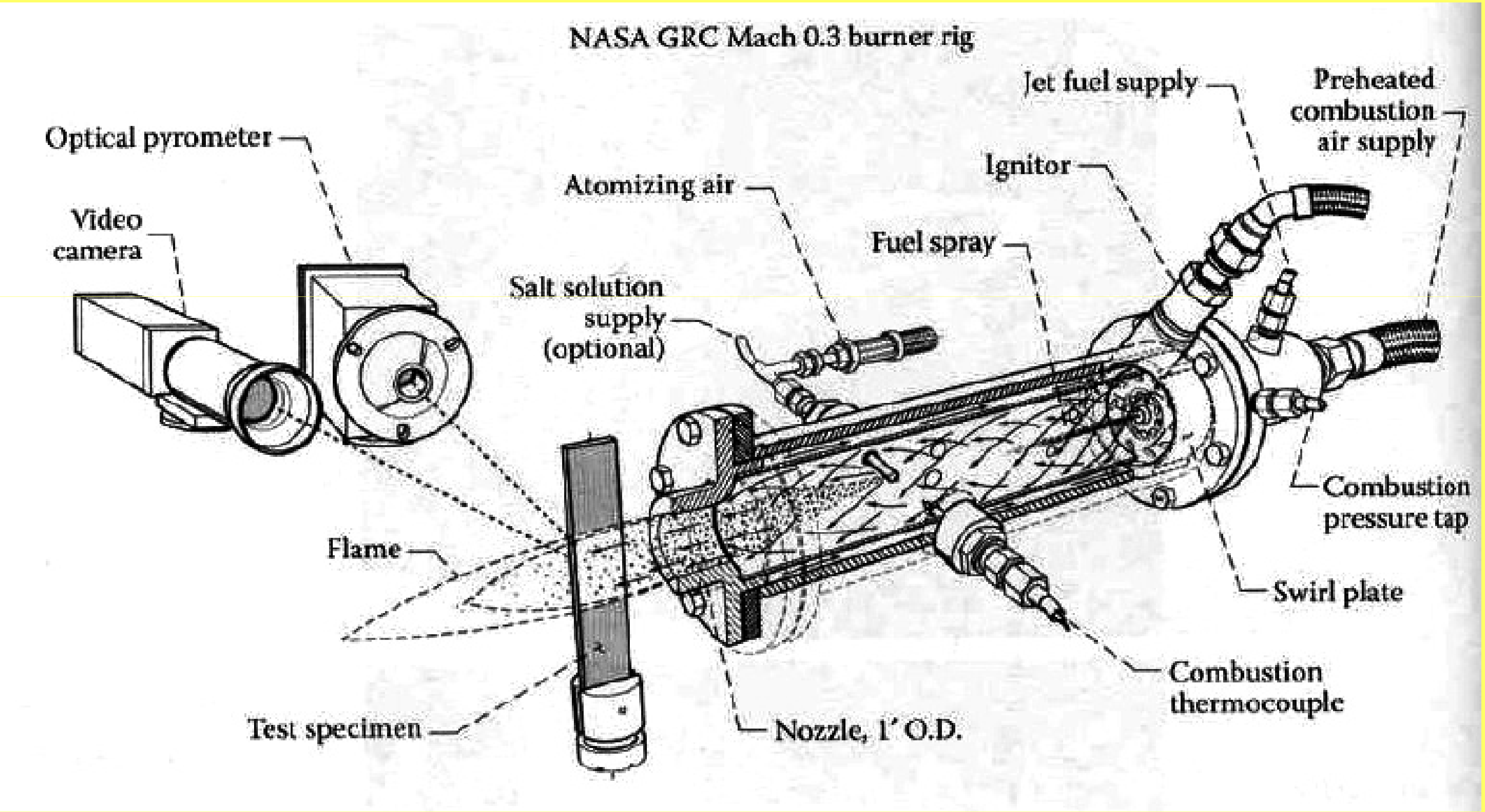


Hypersonic vehicles: the Space Shuttle Orbiter and the proposed Hyper X with sharp edges and more maneuverability

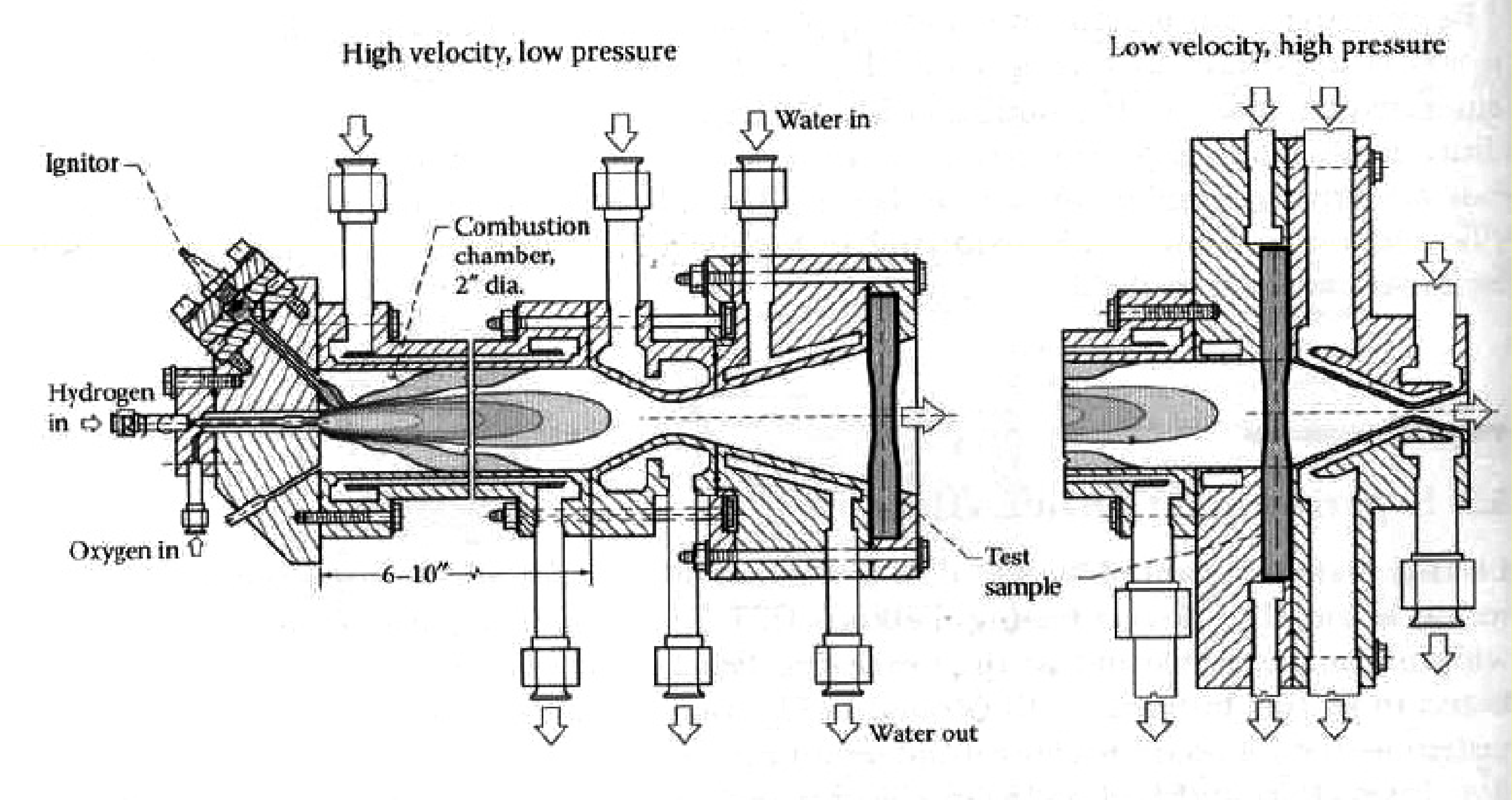
Hypersonic vehicles: the Space Shuttle Orbiter and the proposed Hyper X with sharp edges and more maneuverability

The shape of re-entry surface is important in determining temperature. Large radii edges, such as those found on the U.S. Space shuttle, do not reach temperatures as high as those for sharp edges. Now, there is interest in developing sharp-edged re-entry vehicles due to their higher maneuverability. These new vehicles will make it necessary to develop materials capable of operating at higher temperatures.

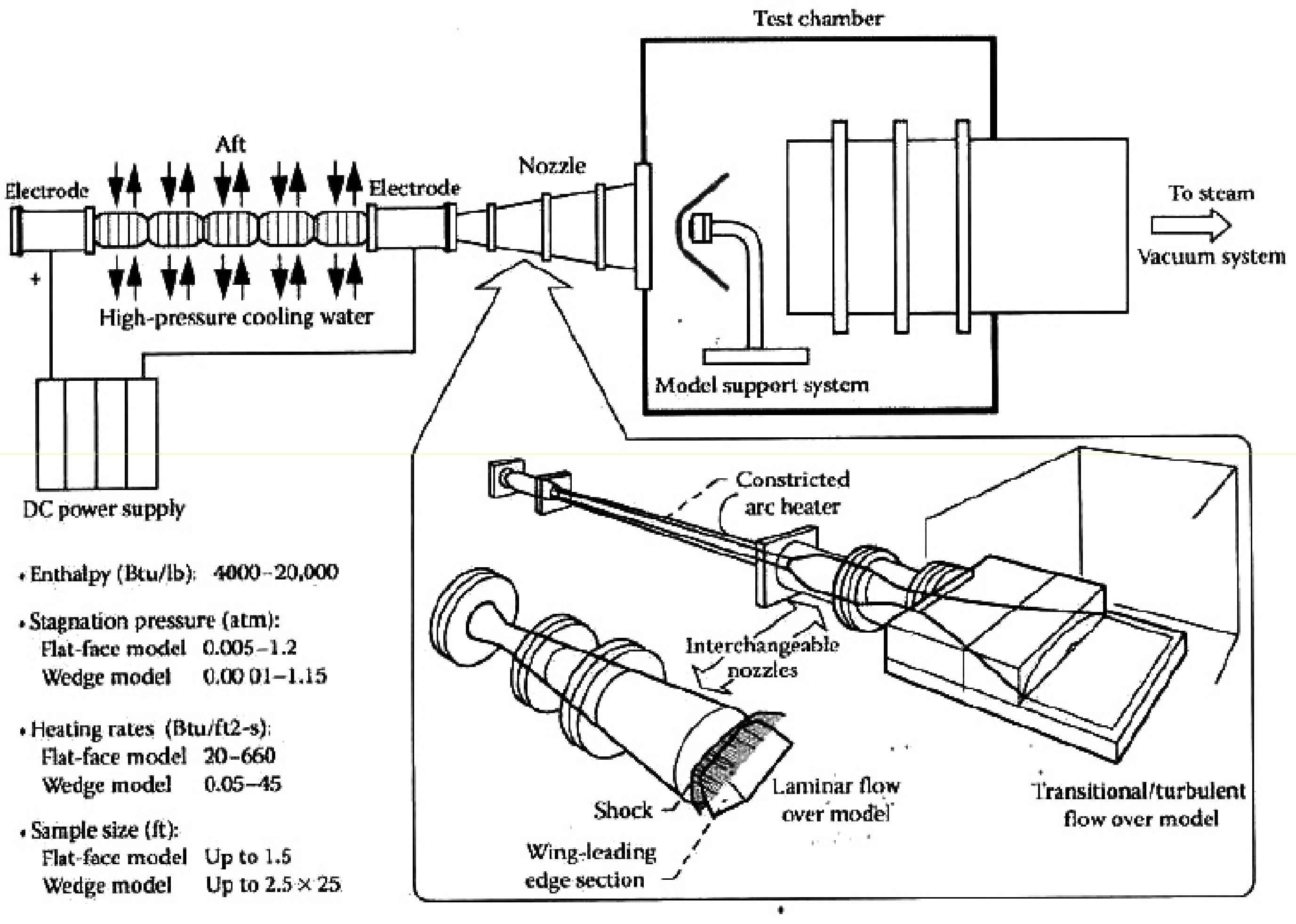
Apparatus (jet fuel burner) used to test materials for aircraft gas turbines



Apparatus for testing materials for rocket engines



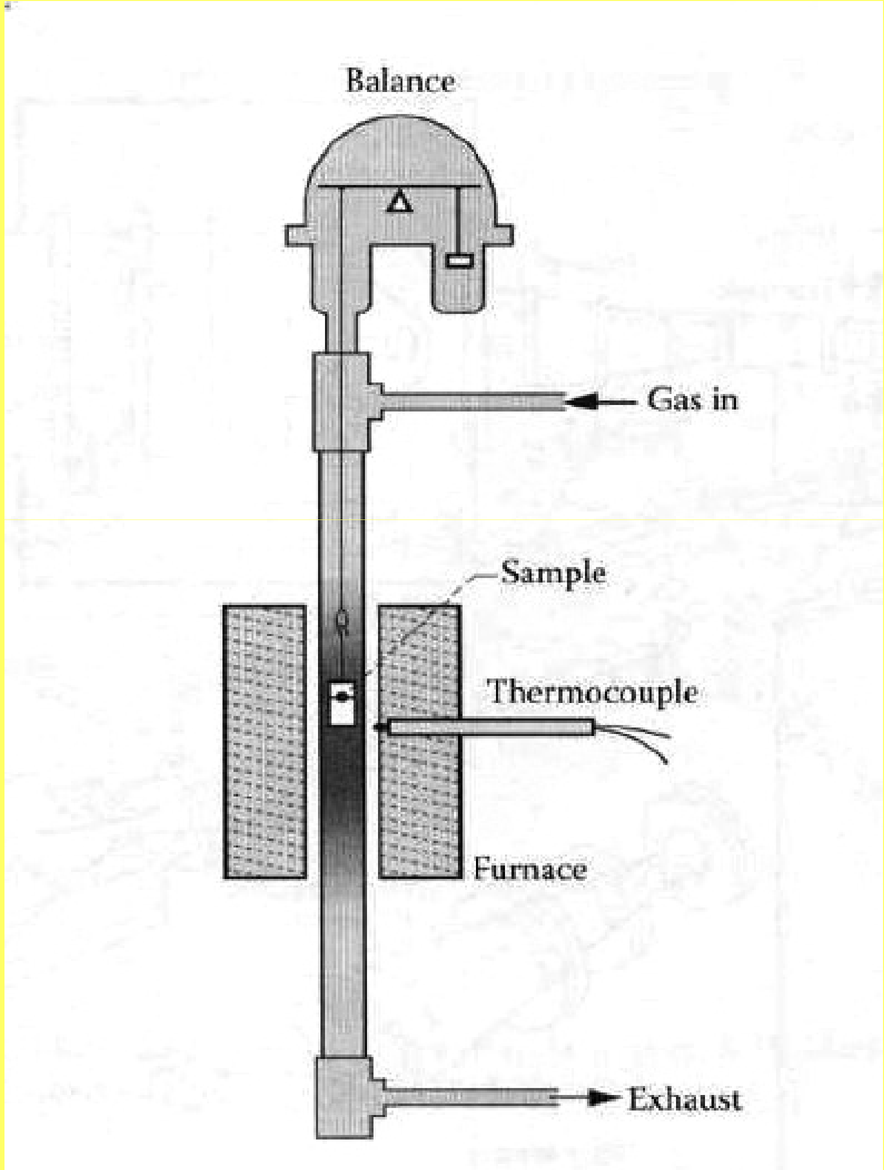
Apparatus (arc-jet) used to simulate re-entry environments



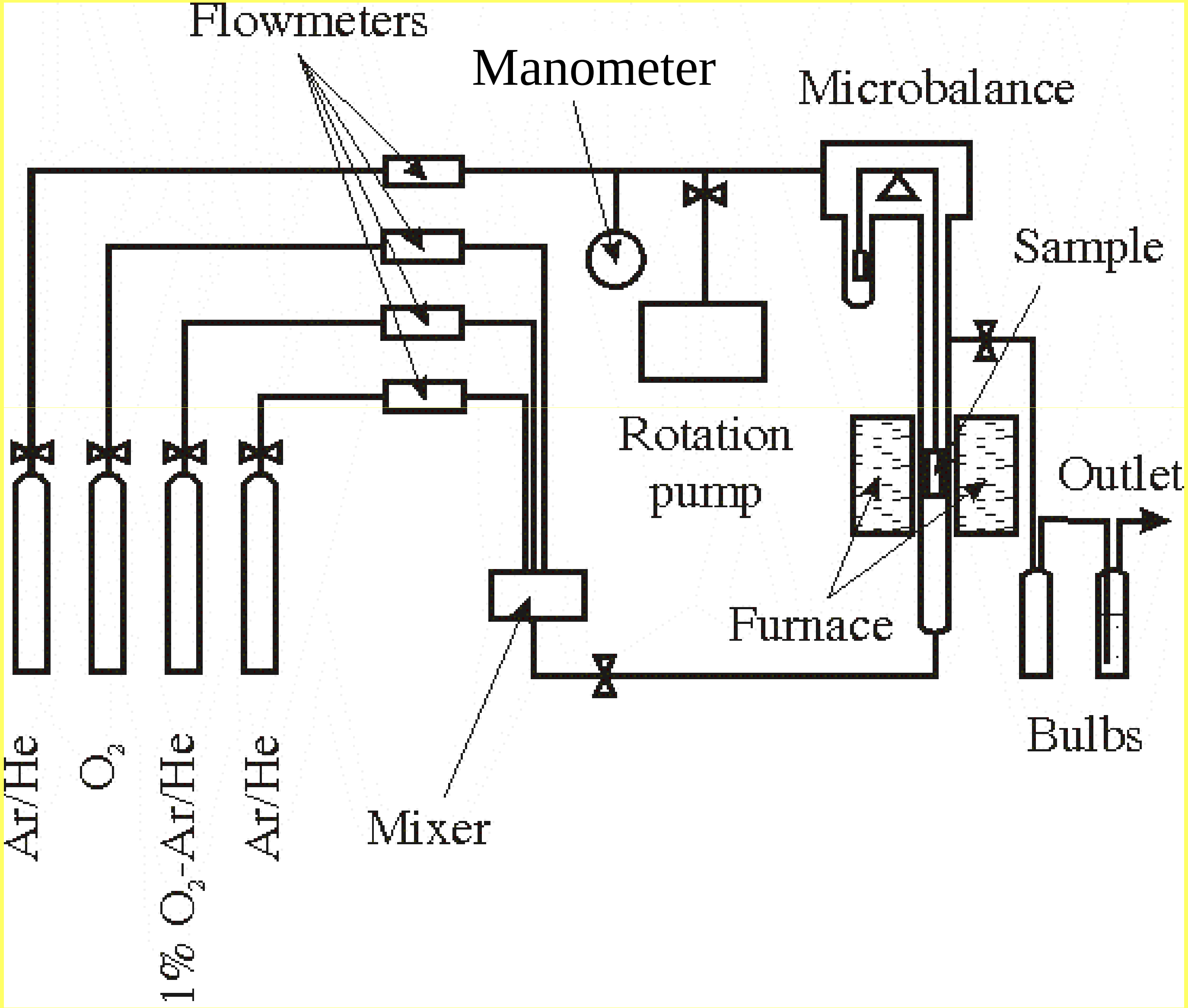
- Enthalpy (Btu/lb): 4000–20,000
- Stagnation pressure (atm):
  - Flat-face model 0.005–1.2
  - Wedge model 0.00 01–1.15
- Heating rates (Btu/ft2-s):
  - Flat-face model 20–660
  - Wedge model 0.05–45
- Sample size (ft):
  - Flat-face model Up to 1.5
  - Wedge model Up to 2.5 × 25

Re-entry environments are best simulated with an arc-jet, which provides a high velocity of atoms from dissociated O_2 and N_2. Dissociation occurs in a series of electrodes.

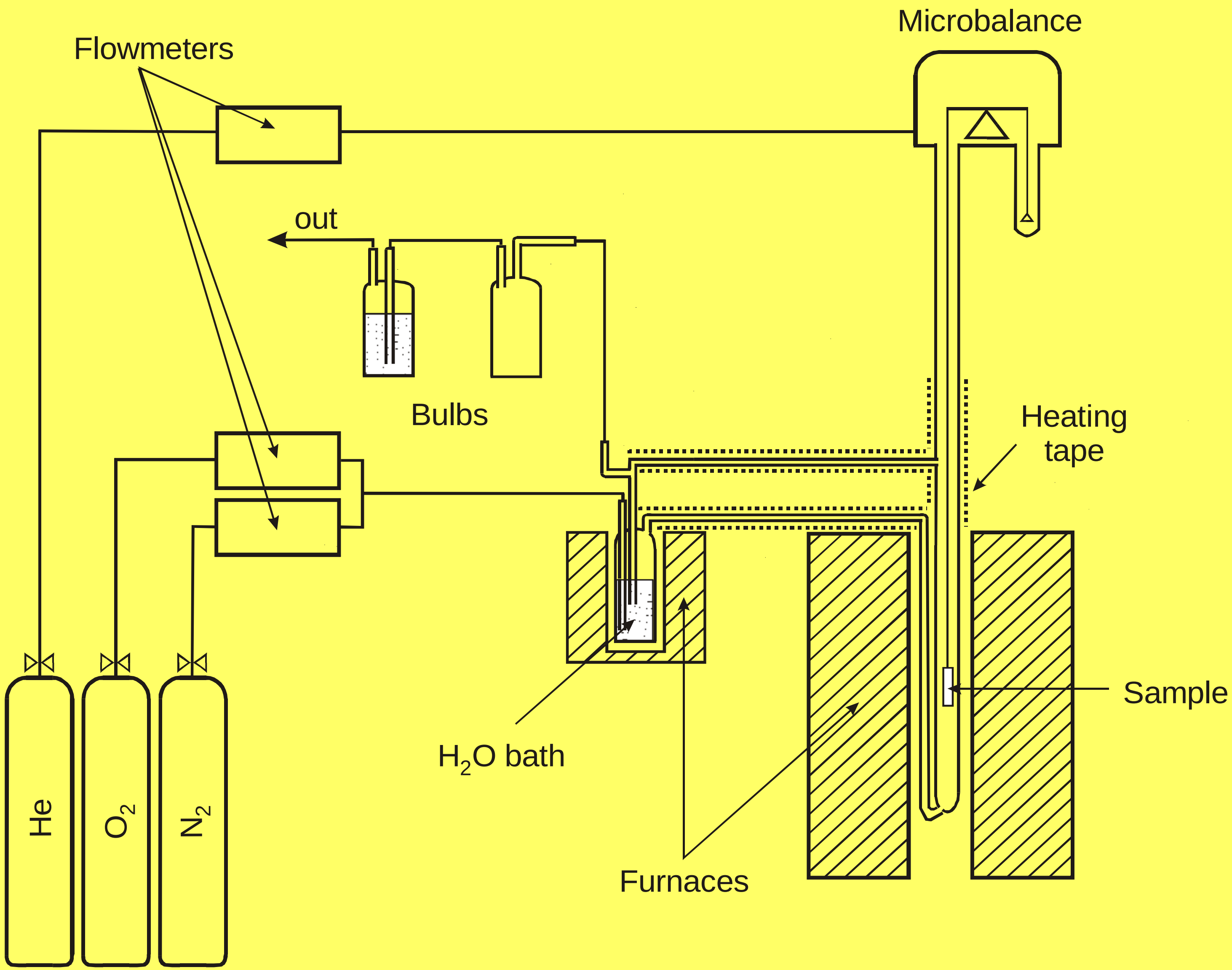
Microthermogravimetry in corrosion studies



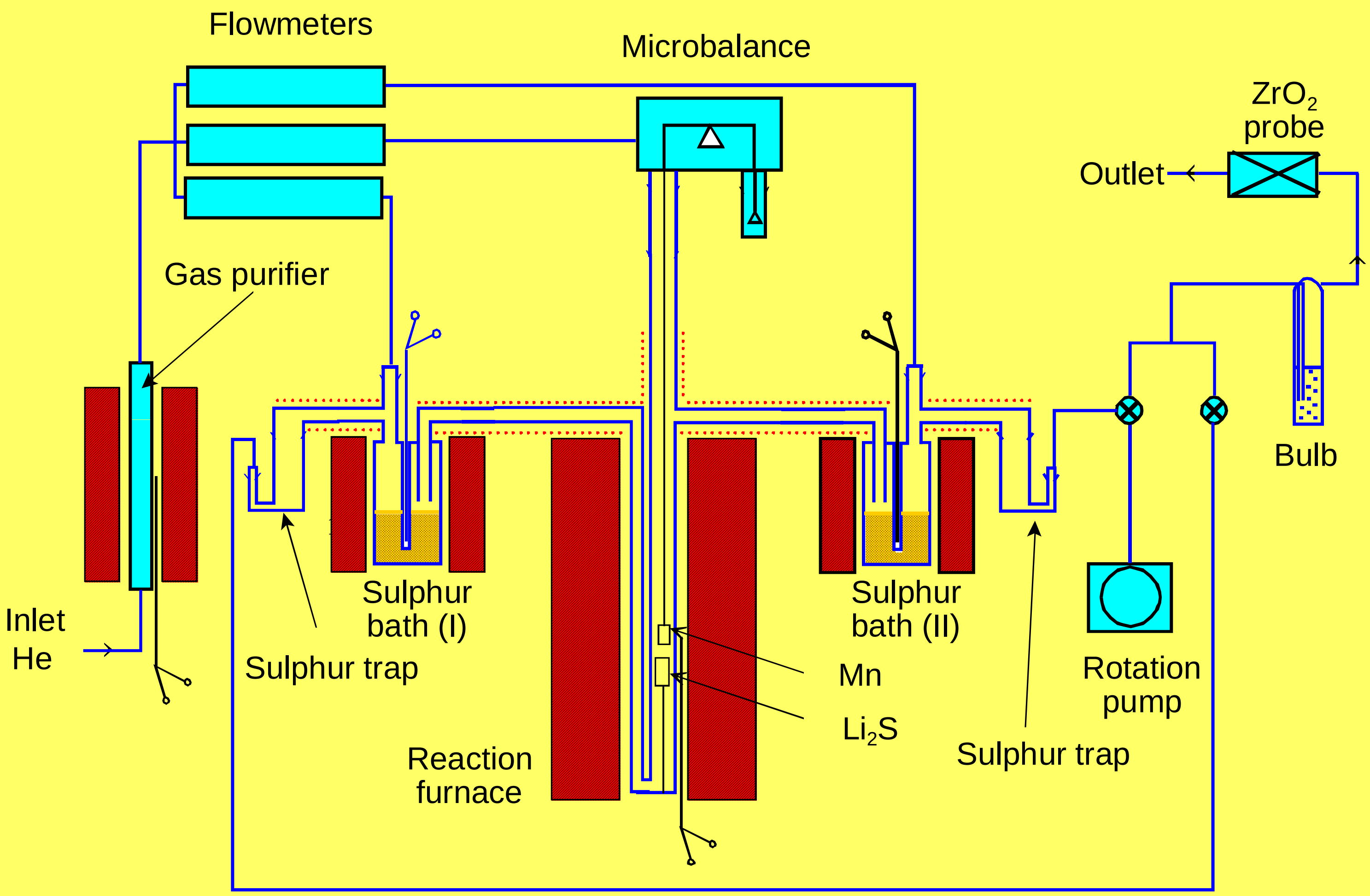
Microthermogravimetry in corrosion studies



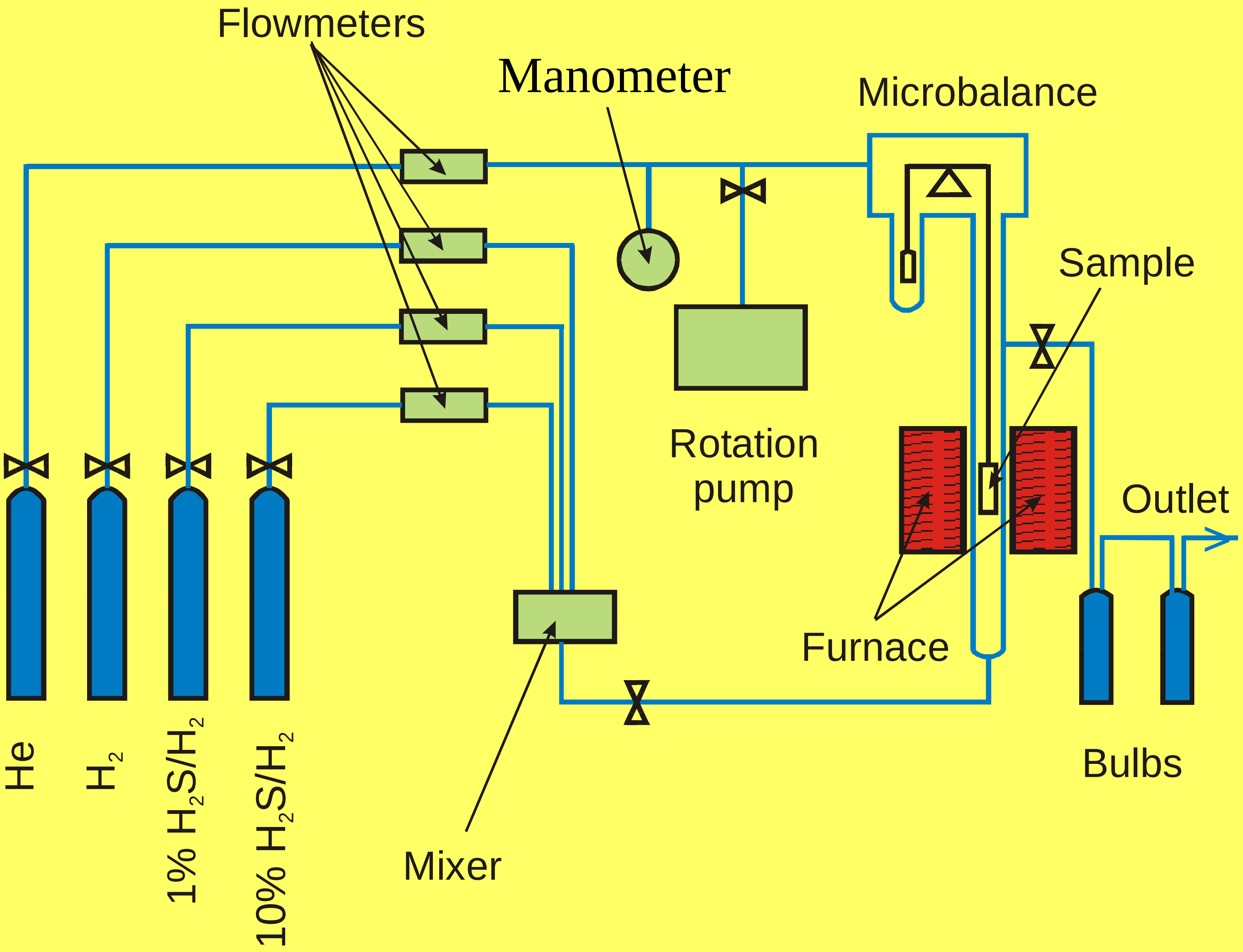
Microthermogravimetry in corrosion studies



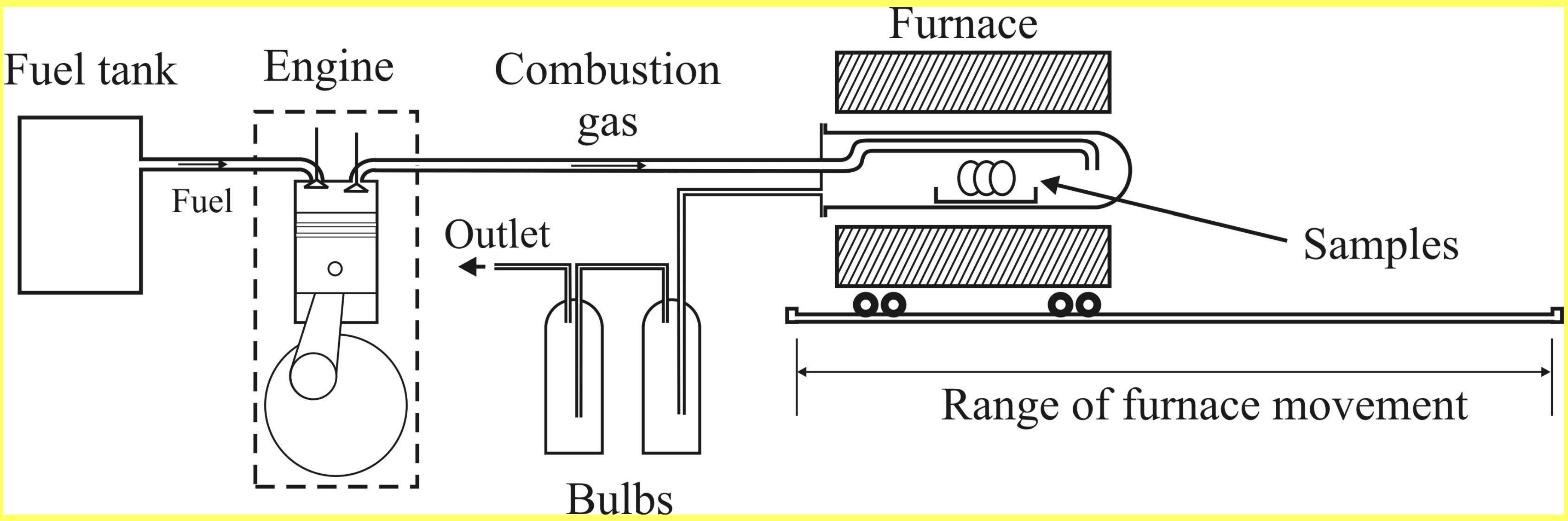
Microthermogravimetry in corrosion studies



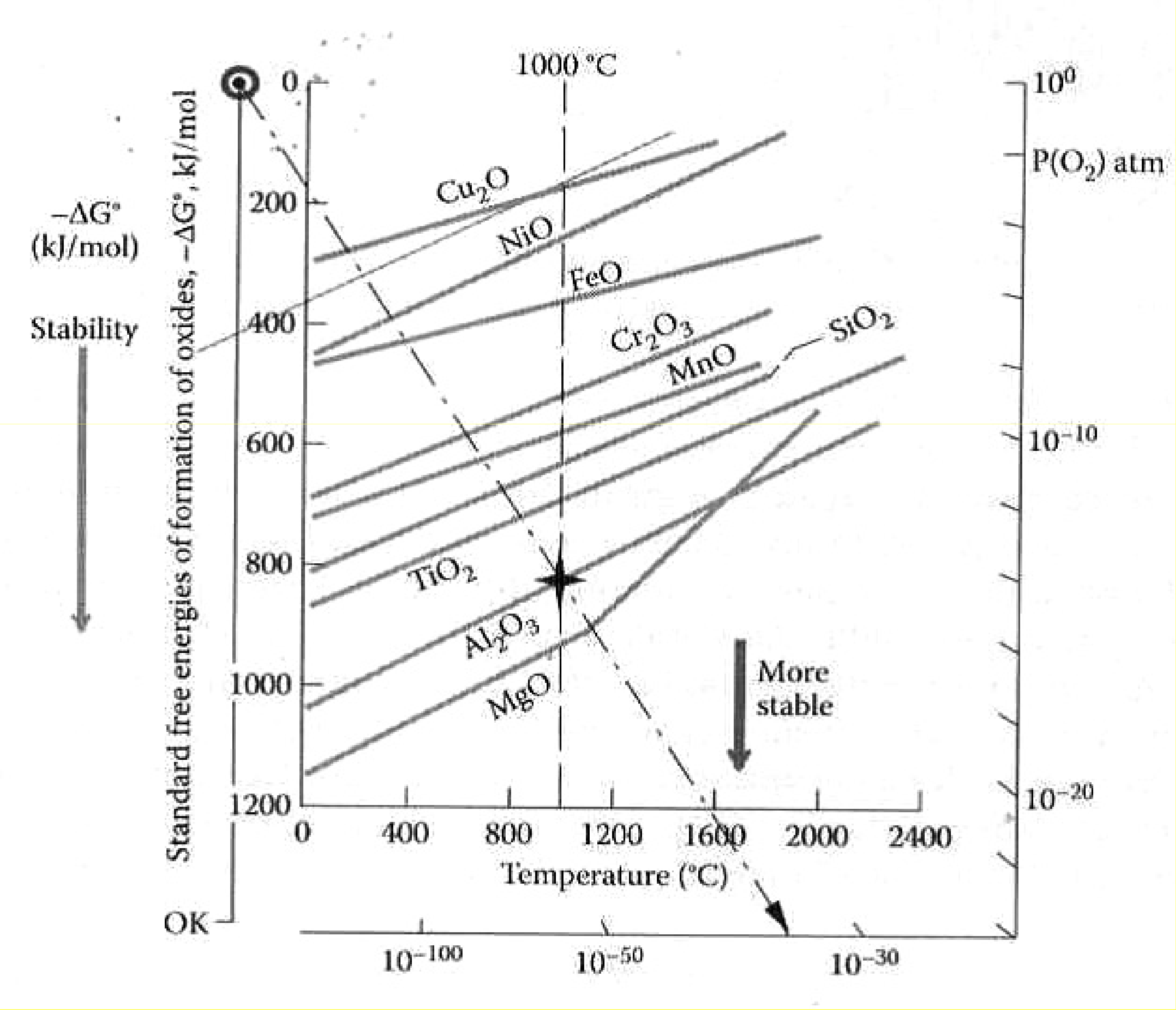
Microthermogravimetry in corrosion studies



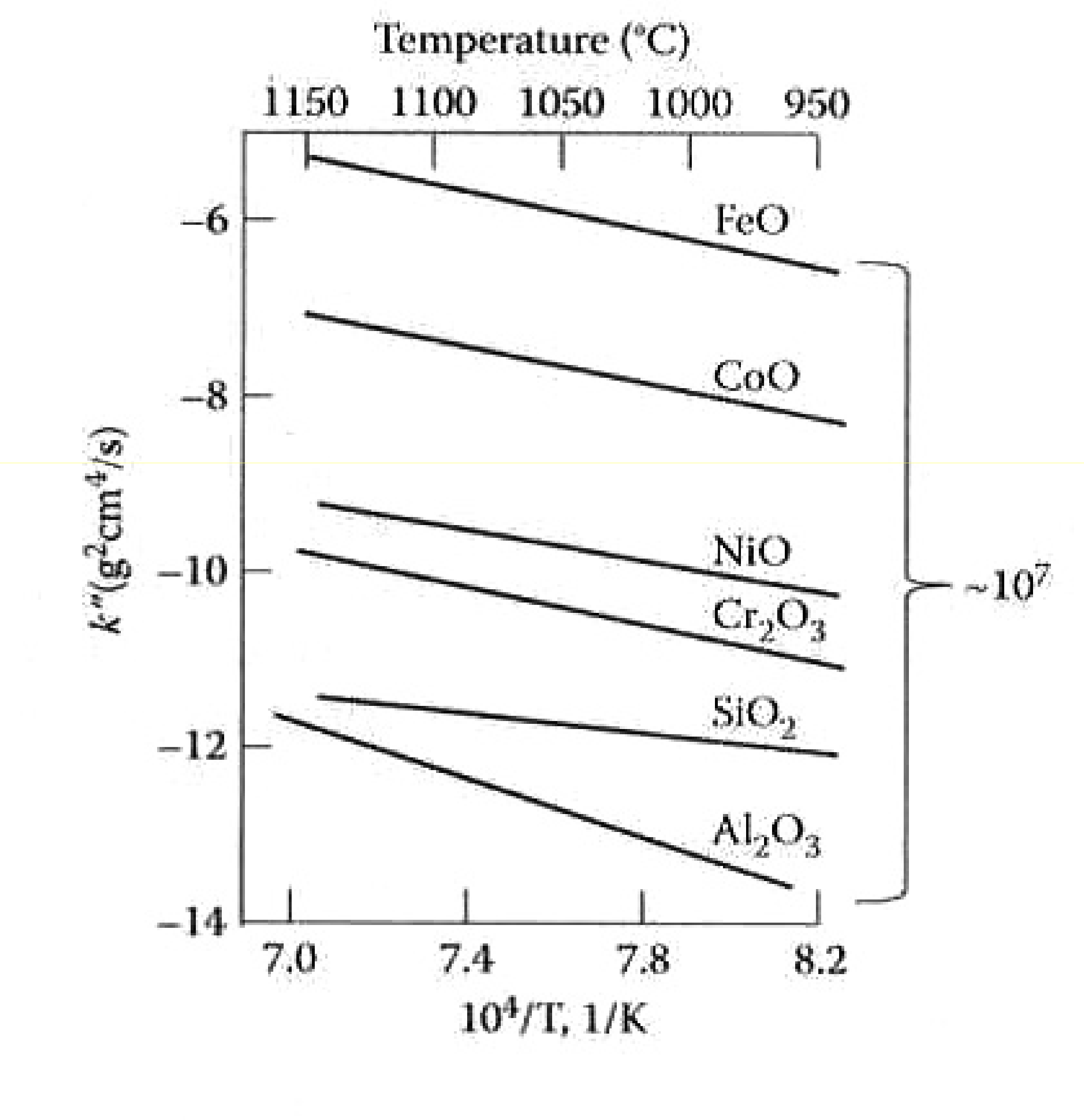
Apparatus for corrosion studies under thermal shock conditions



Oxidation – thermodynamic aspects

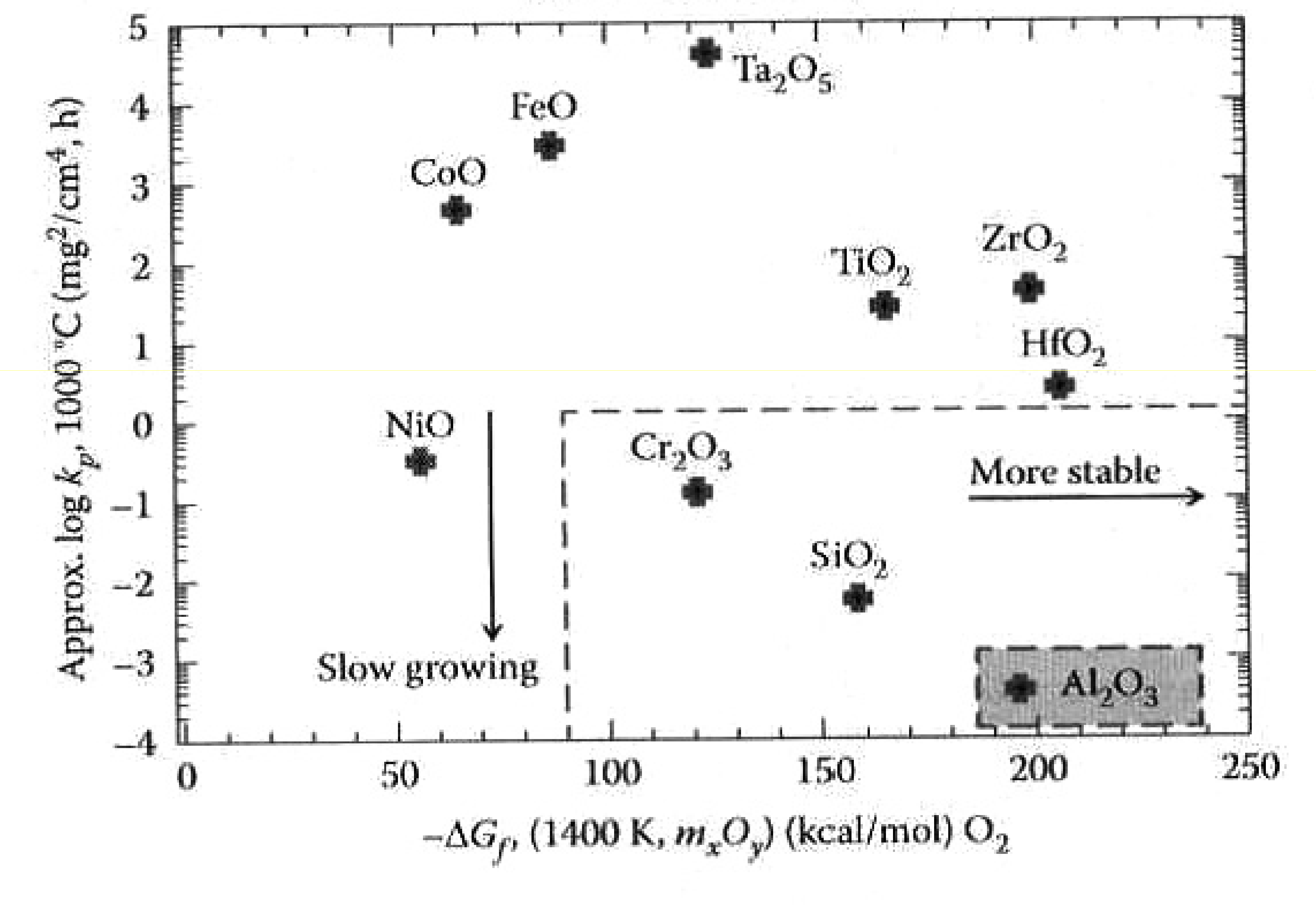


Oxidation – kinetic aspects

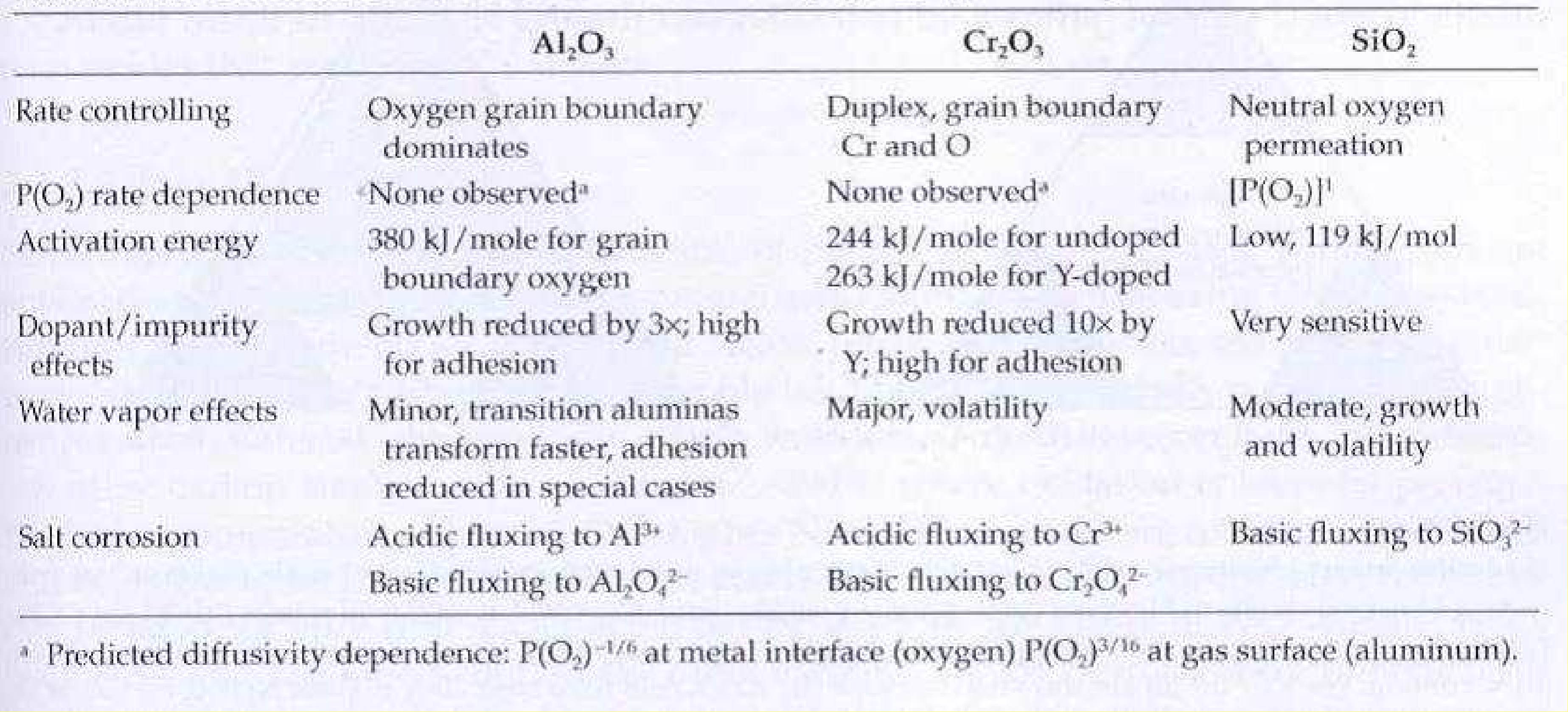


$$\left(\frac{\Delta m}{S}\right)^2 = k_p \cdot t + C$$

Thermokinetic mapping of oxide scales, illustrating growth and stability of oxides



Properties of highly protective scales



	Al_2O_3	Cr_2O_3	SiO_2
Rate controlling	Oxygen grain boundary dominates	Duplex, grain boundary Cr and O	Neutral oxygen permeation
$P(O_2)$ rate dependence	None observed[a]	None observed[a]	$[P(O_2)]^1$
Activation energy	380 kJ/mole for grain boundary oxygen	244 kJ/mole for undoped 263 kJ/mole for Y-doped	Low, 119 kJ/mol
Dopant/impurity effects	Growth reduced by 3×; high for adhesion	Growth reduced 10× by Y; high for adhesion	Very sensitive
Water vapor effects	Minor, transition aluminas transform faster, adhesion reduced in special cases	Major, volatility	Moderate, growth and volatility
Salt corrosion	Acidic fluxing to Al^{3+} Basic fluxing to $Al_2O_4^{2-}$	Acidic fluxing to Cr^{3+} Basic fluxing to $Cr_2O_4^{2-}$	Basic fluxing to SiO_3^{2-}

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[a] Predicted diffusivity dependence: $P(O_2)^{-1/6}$ at metal interface (oxygen) $P(O_2)^{3/16}$ at gas surface (aluminum).

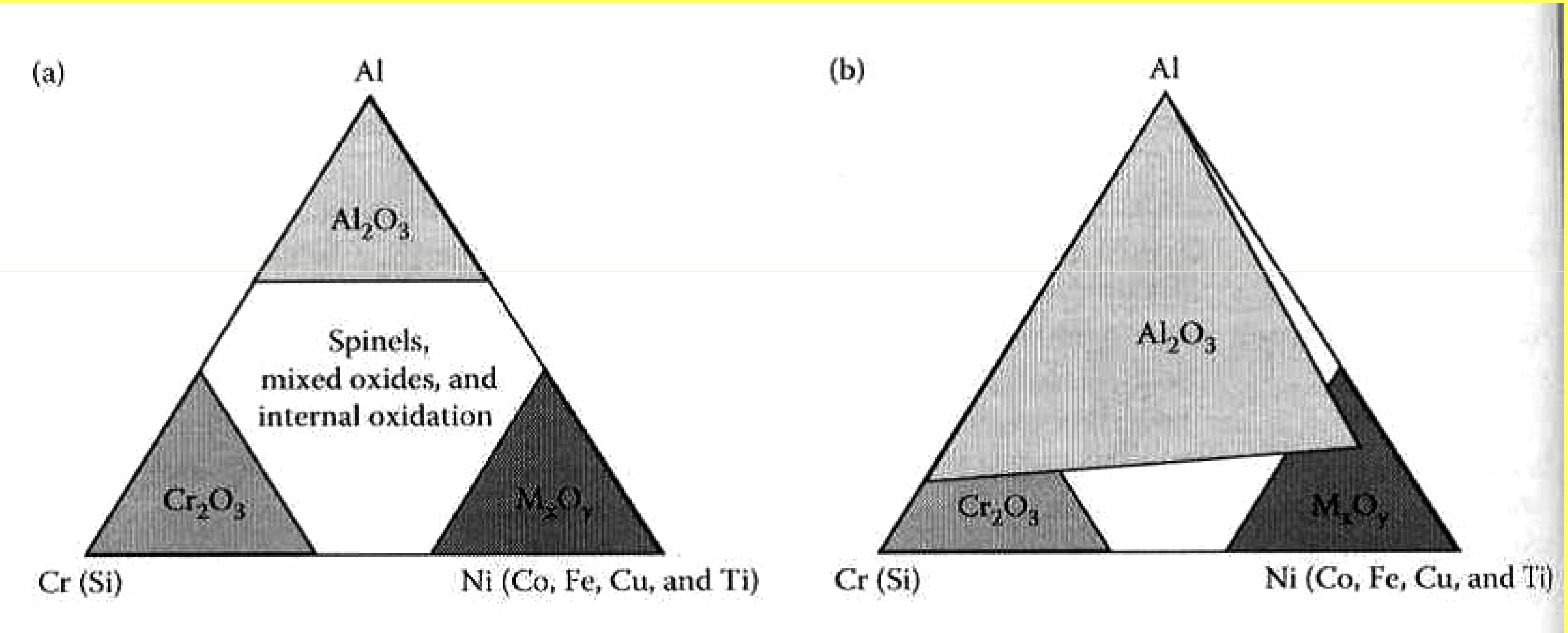
Oxidation of alloys – potential difficulties

Alloys are composed of base elements (Ni, Co, Fe, Ti, Cu, …) alloyed with additional elements (Al, Si, Cr). Base elements oxidize rapidly, while alloying additions form highly protective oxides.

Milestones:

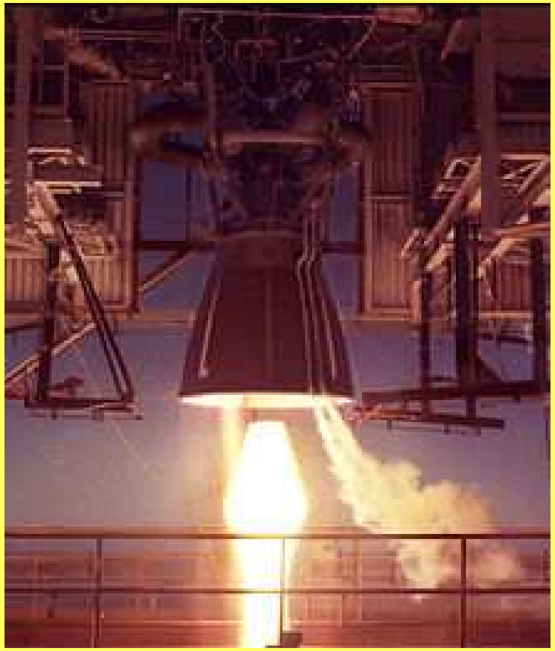
- Oxidation resistance of an alloy strongly depends on the content of alloying additions and consequently internal, transient or external oxidation can be observed.
- The concentration of a single additional element cannot be increased to the appropriate level, because that would lower the mechanical properties of alloy (Ni-25Al, Fe-40Al, Ti-75Al, Ni-25Cr, Fe-25Cr, Ni-5Si, Fe-5Si, Ti-67Si).
- A beneficial effect of a secondary oxygen getter is observed.

Oxidation of alloys
– beneficial effect of a secondary oxygen getter



Copper alloys

Melting point of Cu = 1083 ^{o}C
NARloy-Z (Cu-3Ag-0.1Zr, wt.%) was used in Space Shuttles as the material for the main engine exhaust nozzle.
Thermal load of the hydrogen-oxygen rocket exhaust = 3000^{o}C
Cooling system with -250^{o}C liquid hydrogen was used.
Reason: high thermal conductivity of Cu alloys.
Cyclic oxidation of NARloy-Z alloy results in formation and reduction of an oxide scale (Cu_2O, CuO)



Cu-Cr-Al alloys:

- 17 wt.% Cr addition reduces the oxidation rate, but a continuous layer of the Cr_2O_3 is not formed
- 5 wt.% Al addition enables the formation of highly protective Al_2O_3 oxide.

Iron alloys (steels)

Steels represent the most widespread use of metals:

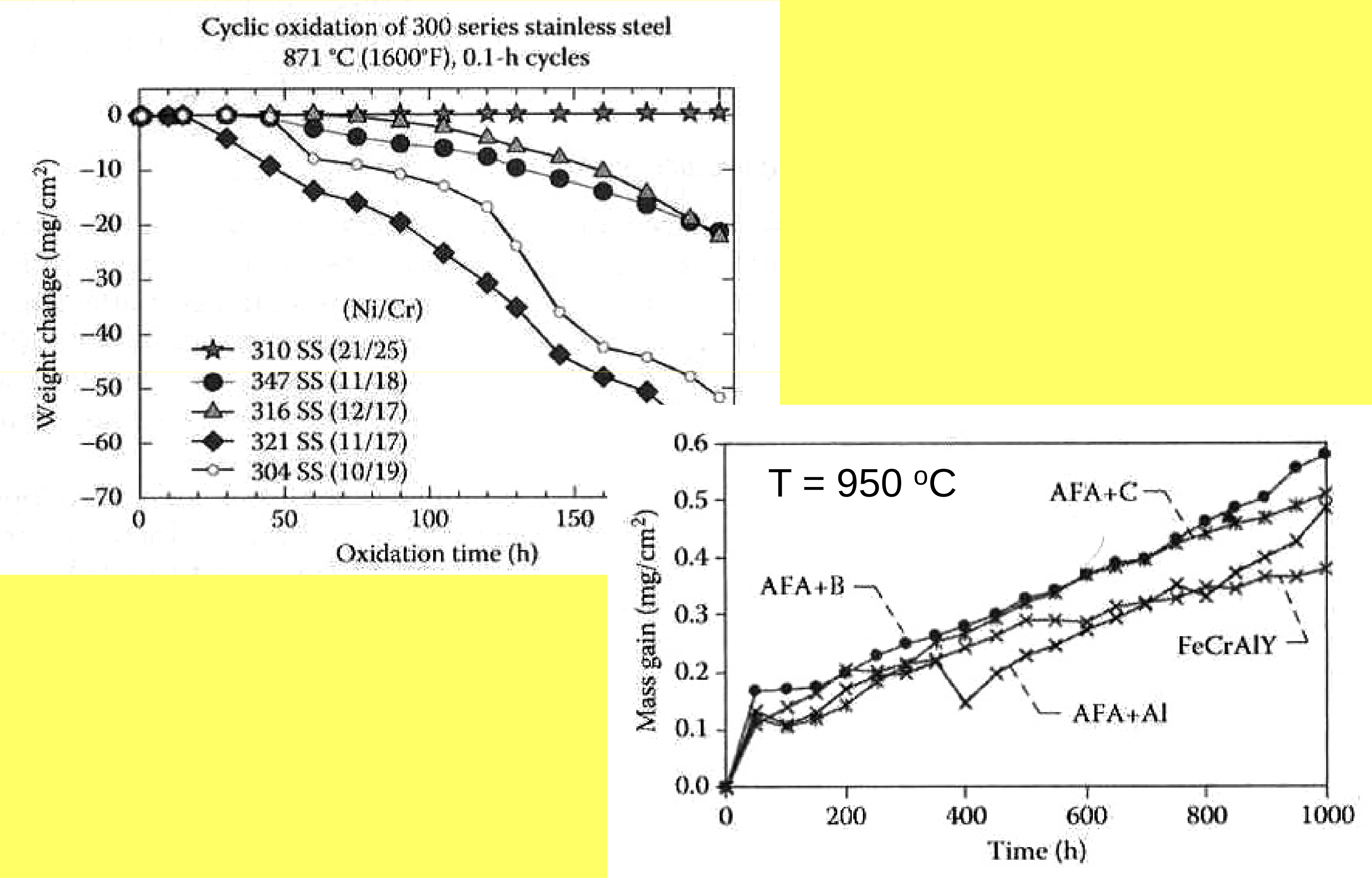
- application (up to 500 ^oC): boiler vessels, steam tubes, gas scrubbers, exhaust pipes, turbine shafts, early turbine compressor blades.
- inexpensive low alloy carbon steels can be used below 400 ^oC
- stainless steels with higher Ni and Cr contents are used up to 650 ^oC
- oxide phases in scales: FeO, Fe_3O_4, Fe_2O_3, $(Cr,Mn,Fe)_2O_3$ sesquioxides, $Fe(Fe,Mn,Cr)_2O_4$ spinels, Cr_2O_3

Considerable progress has been made recently in developing alumina forming austenitic (AFA) alloys with good high temperature strength and oxidation resistance.

Alloying elements responsible for strength: Nb, C, B

Alloying elements responsible for oxidation resistance: Al, Cr, Si, Hf, Y

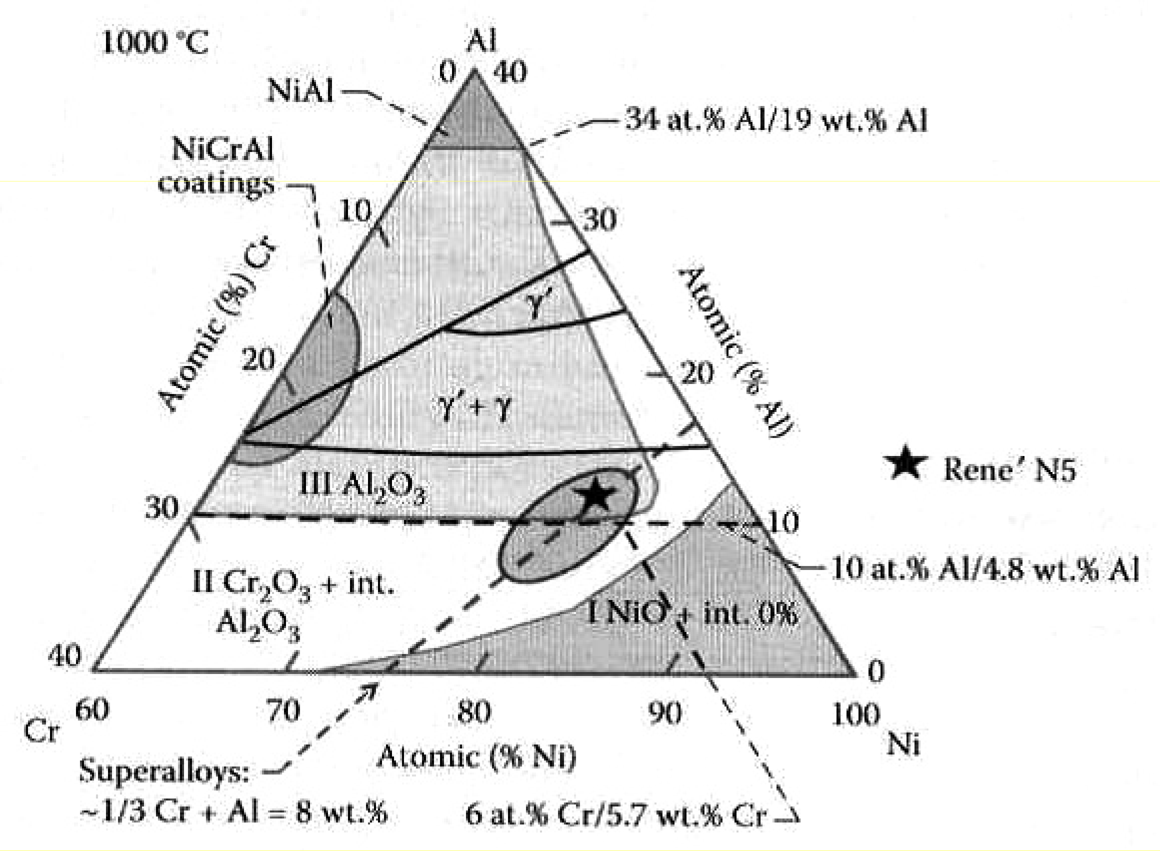
Iron alloys (steels)



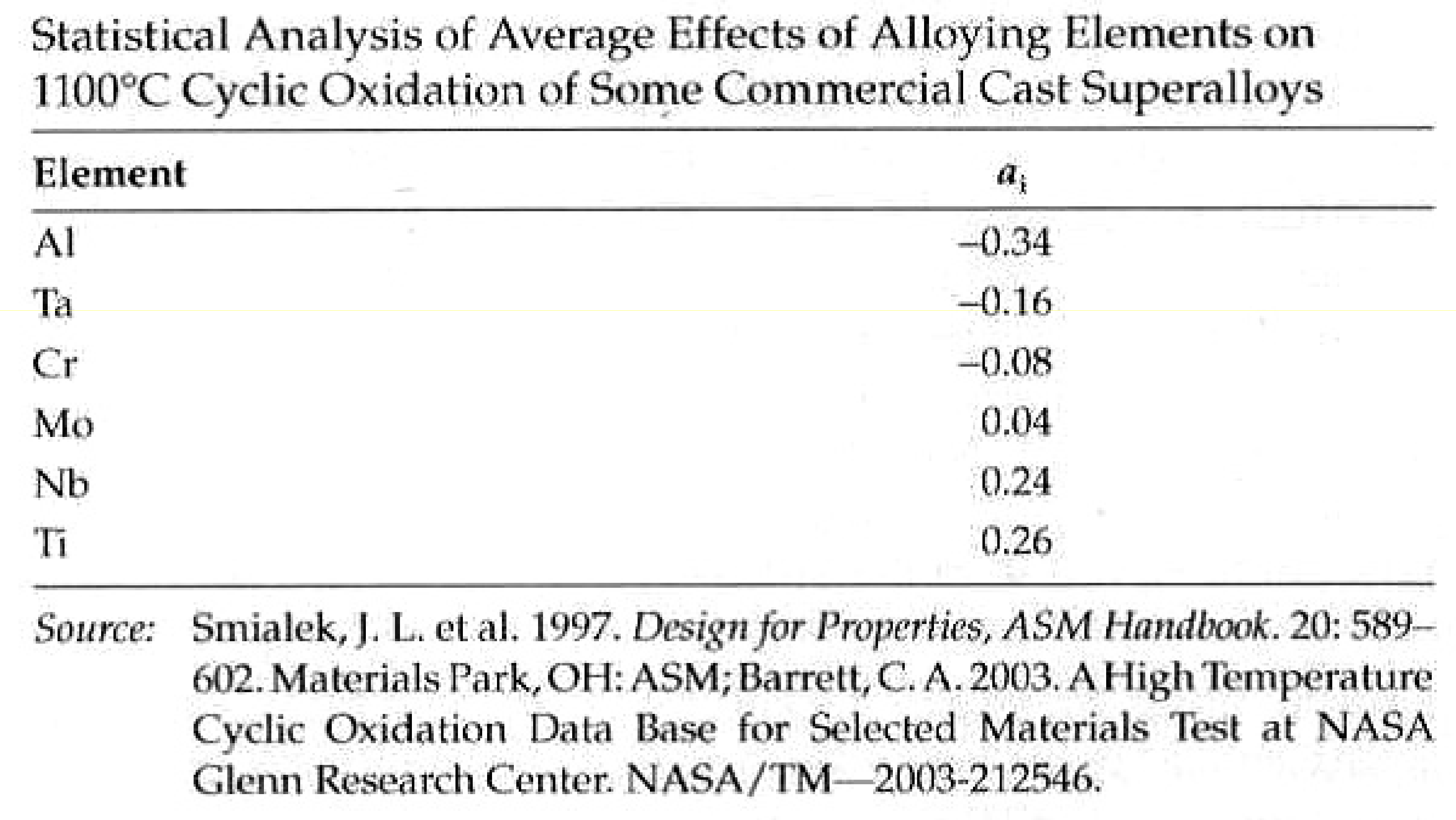
$T = 950\ ^{o}C$

High temperature nickel based alloys

Ni based alloys can contain refractory elements (Nb, Mo, Ta, W), γ'-Ni_3Al for strengthening, and Cr as well as Al to increase oxidation resistance.



High temperature nickel based alloys

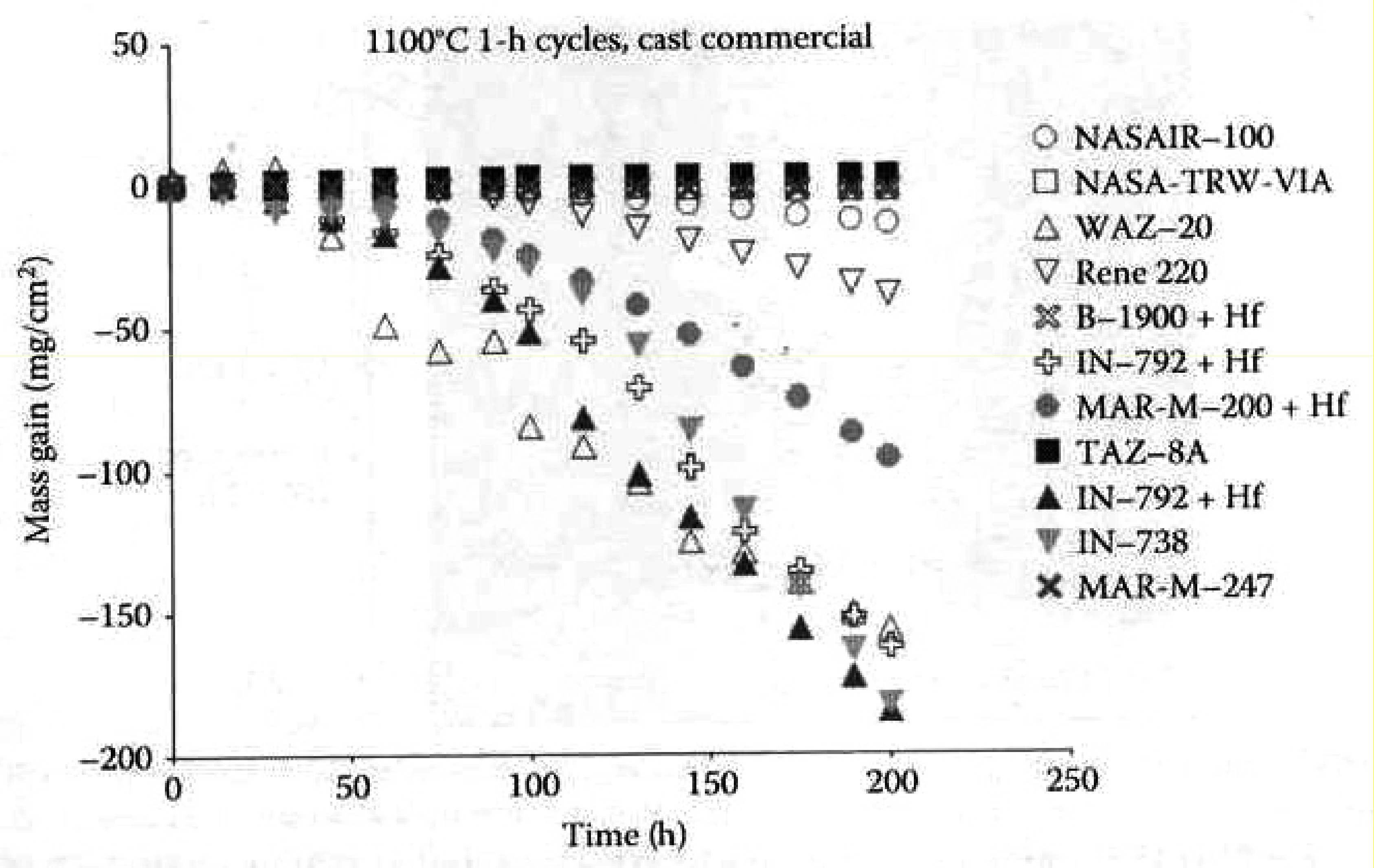


Statistical Analysis of Average Effects of Alloying Elements on 1100°C Cyclic Oxidation of Some Commercial Cast Superalloys

Element	a_i
Al	–0.34
Ta	–0.16
Cr	–0.08
Mo	0.04
Nb	0.24
Ti	0.26

Source: Smialek, J. L. et al. 1997. *Design for Properties, ASM Handbook*. 20: 589–602. Materials Park, OH: ASM; Barrett, C. A. 2003. A High Temperature Cyclic Oxidation Data Base for Selected Materials Test at NASA Glenn Research Center. NASA/TM—2003-212546.

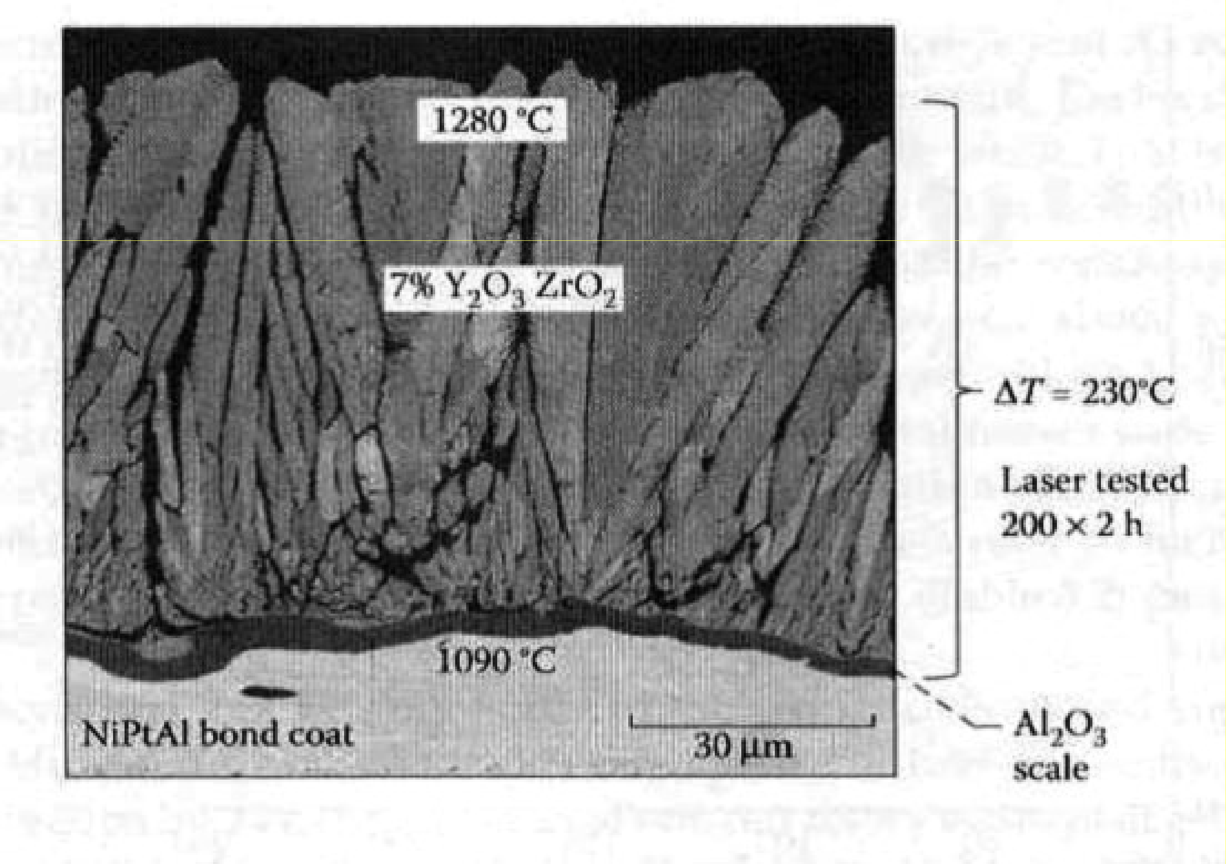
High temperature nickel based alloys



Coatings for superalloys

Strategies:

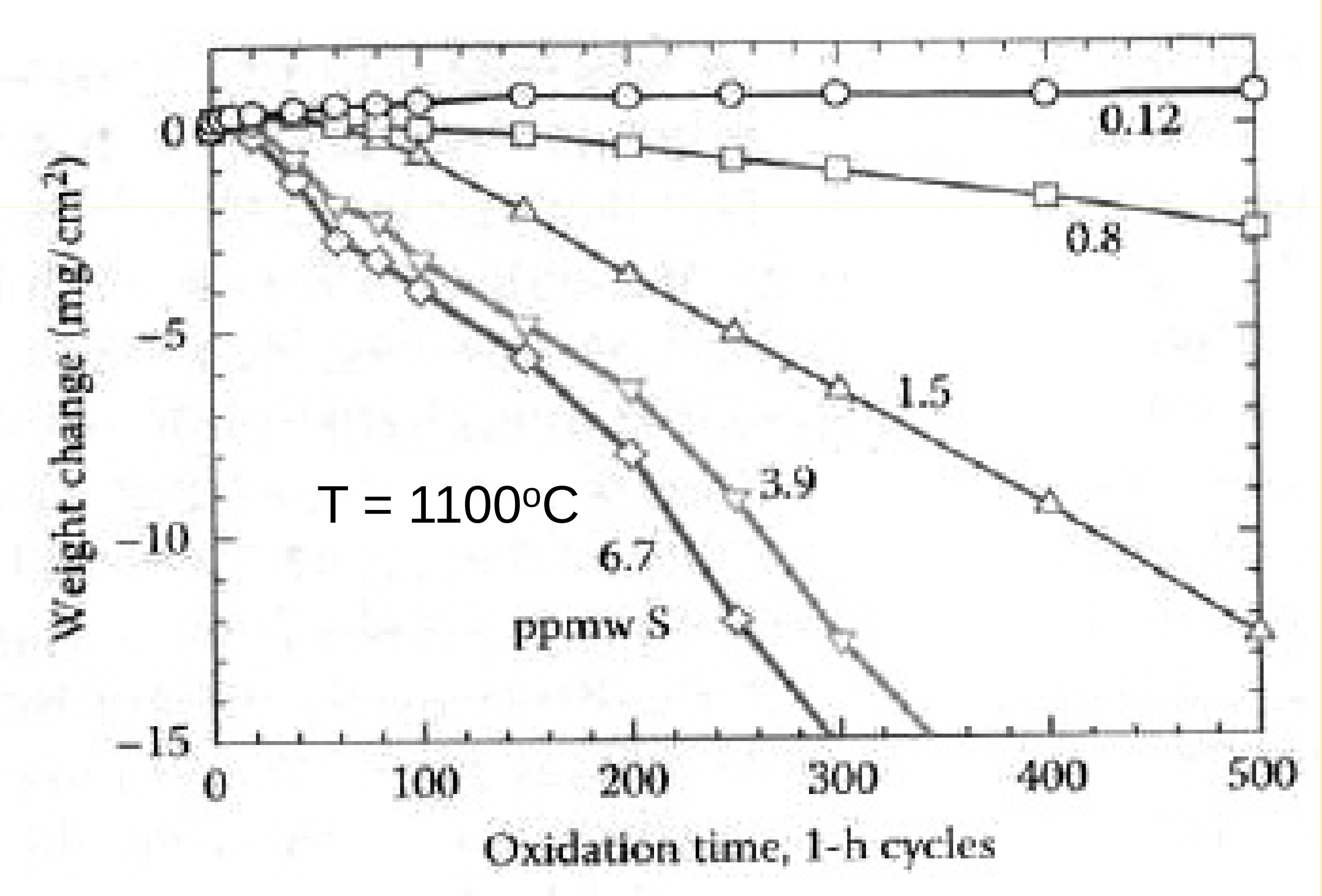
- NiAl-based diffusion aluminide coatings
- NiCrAl-based overlay coatings



Microstructure of PVD YSZ coating after cyclic oxidation

Alumina scale adhesion

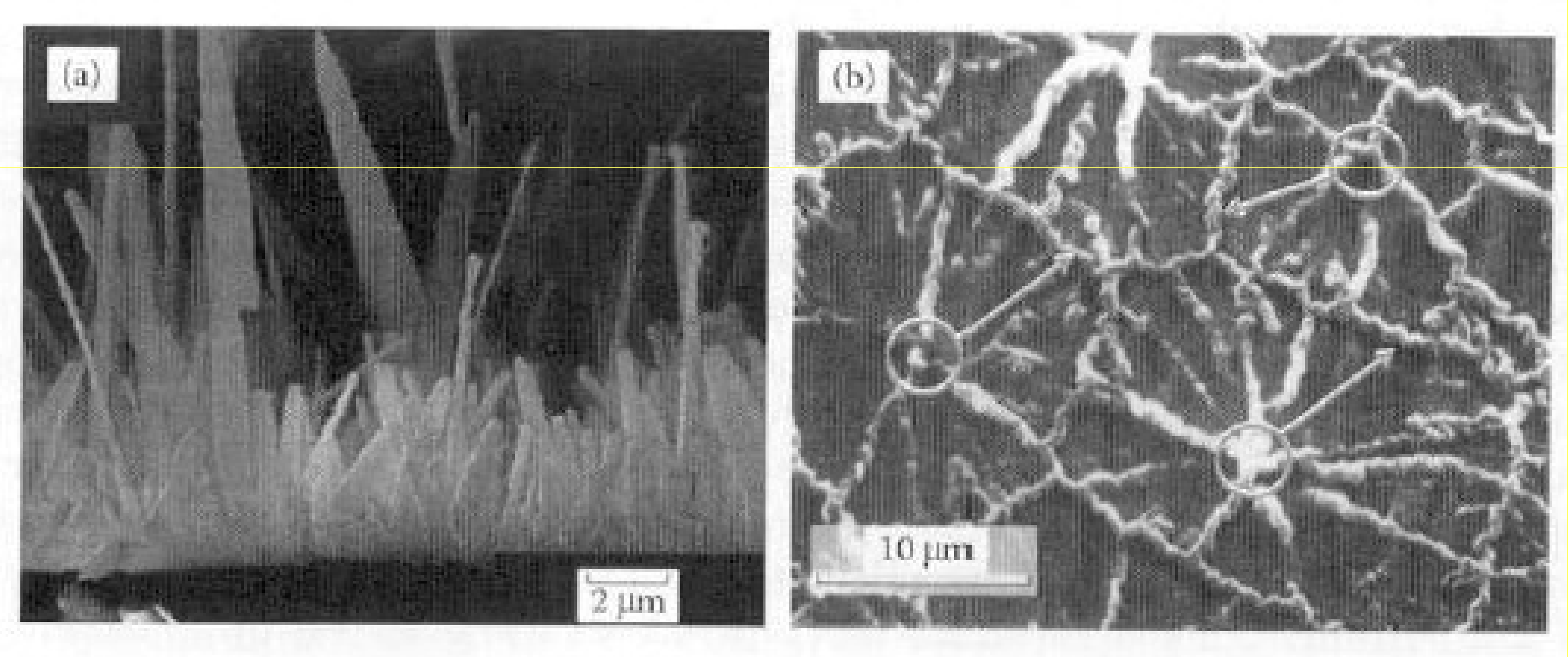
Strategy:
addition of oxygen-active elements (Y, La, Ce, Zr, Hf, …), which are also sulphur-active enables inhibition of powerful sulphur segregation to the alloy-scale interface and thereby its weakening.



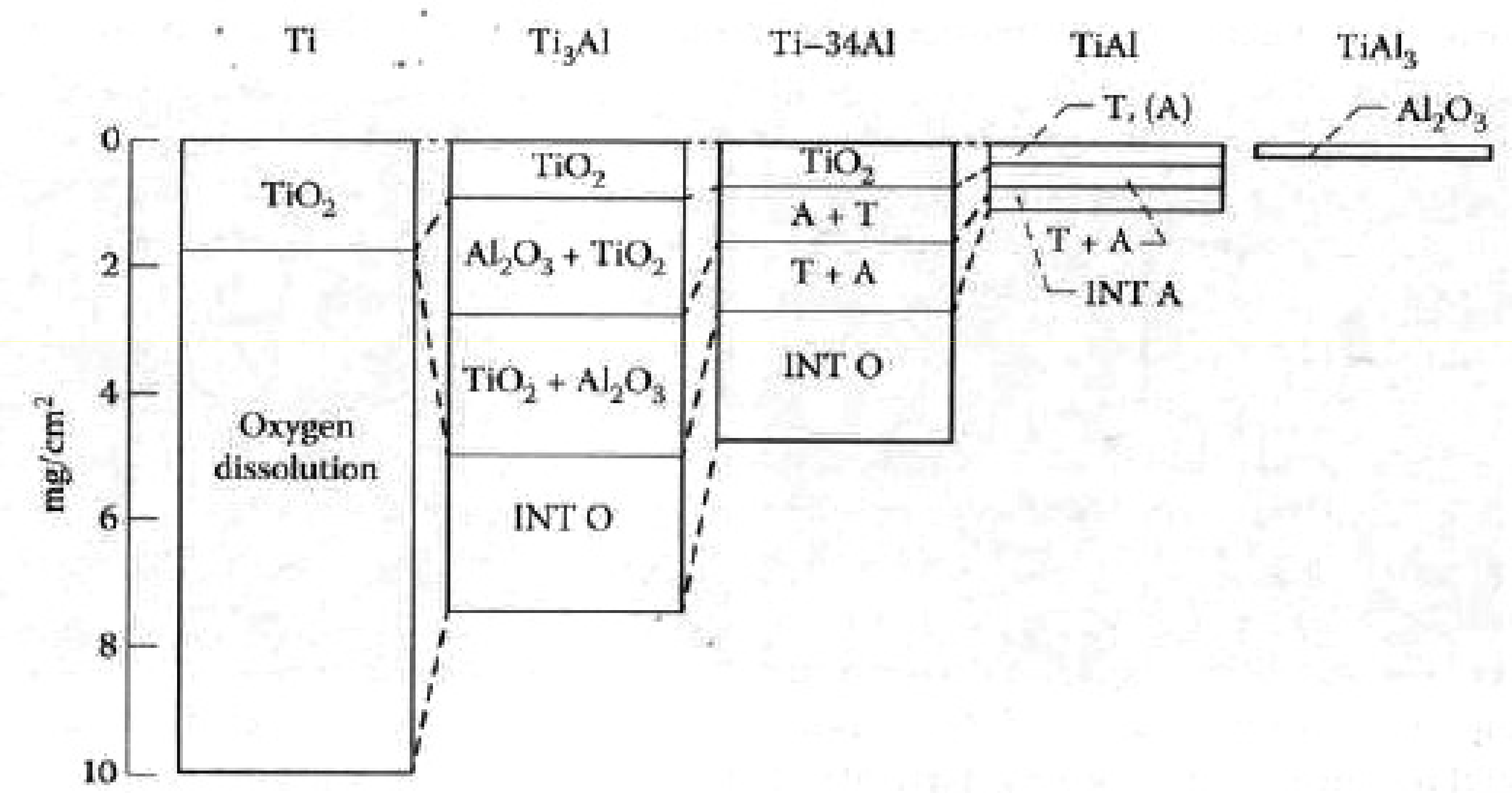
Transition alumina scales

Above ~900 ^oC transition θ-Al_2O_3 after a period of time transforms to the stable α-Al_2O_3 with a notable reduction in growth kinetics.

θ-Al_2O_3 α-Al_2O_3

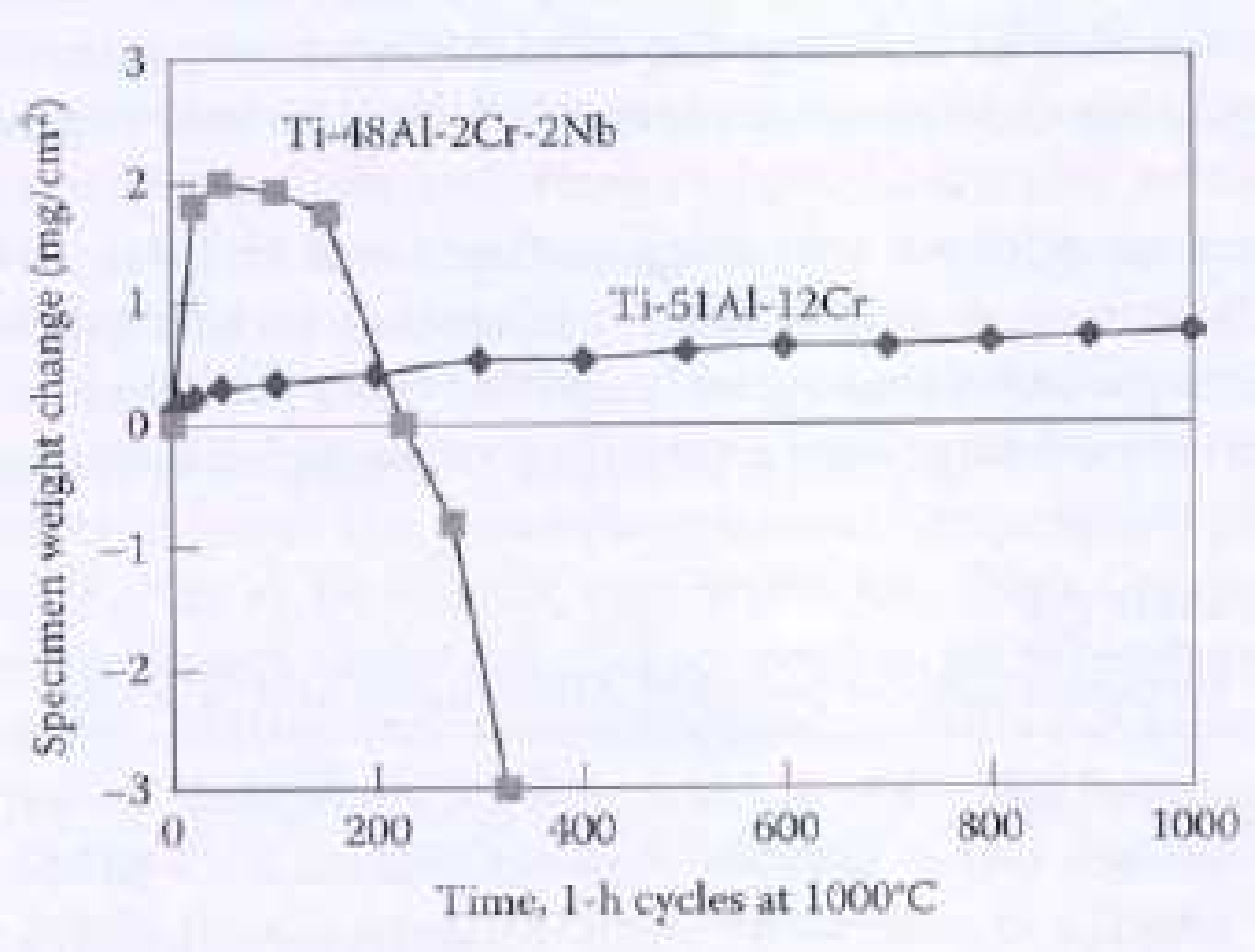


Schematic cross-sections of scales formed on a binary Ti-Al system during oxidation at 850 °C for 100 h



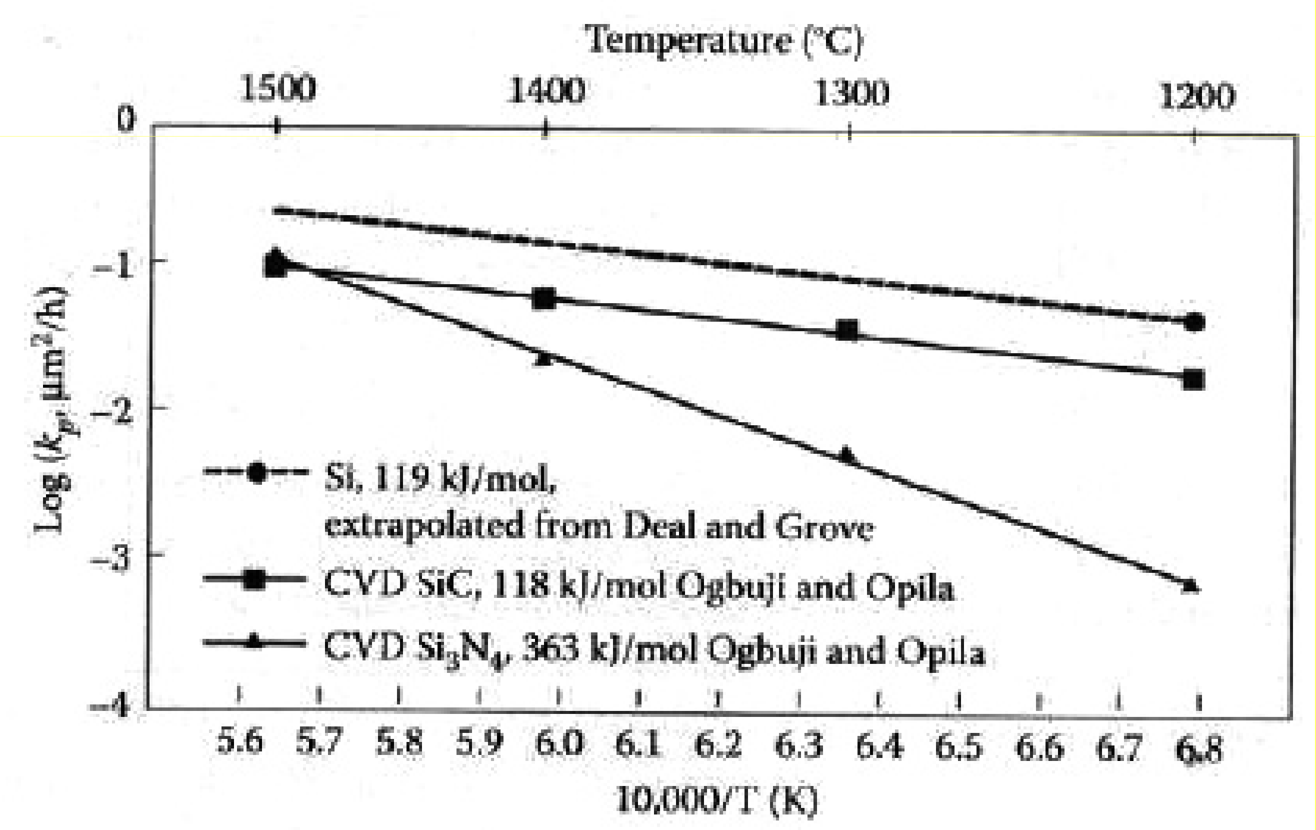
Conclusion: $TiAl_3$ has good oxidation resistance but is extremely brittle

Oxidation resistance of Ti-Al-Cr



Silicon-based ceramics (SiC, Si_3N_4, SiC-composites)

These materials show great promise as hot stage components in turbine engines and chemical process plants, as well as re-entry shields due to their corrosion resistance and ability to retain strength at high temperatures. A protective SiO_2 scale passively forms on the surface at high temperatures. Silica grows according to the linear-parabolic oxidation rate law.



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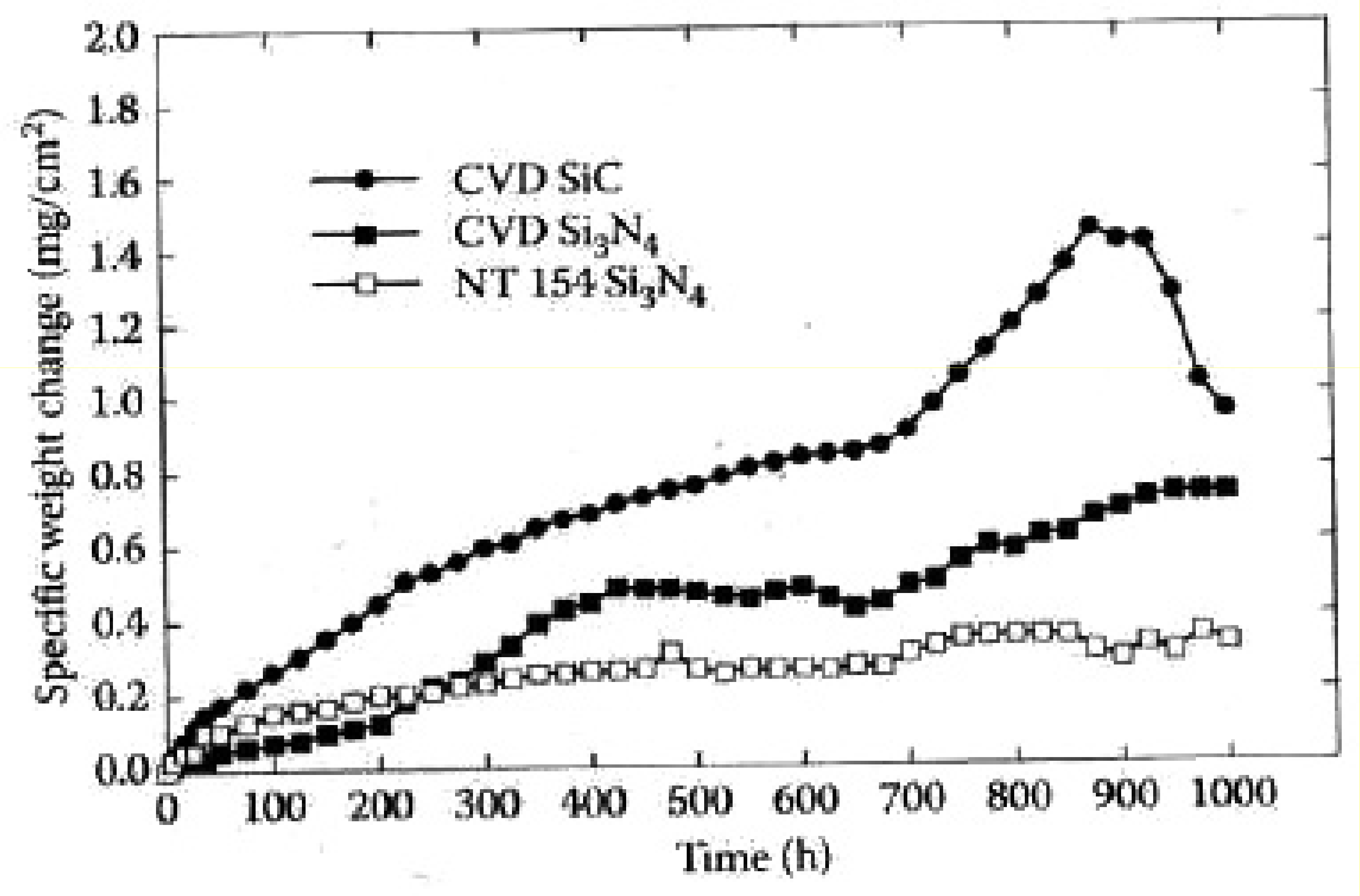
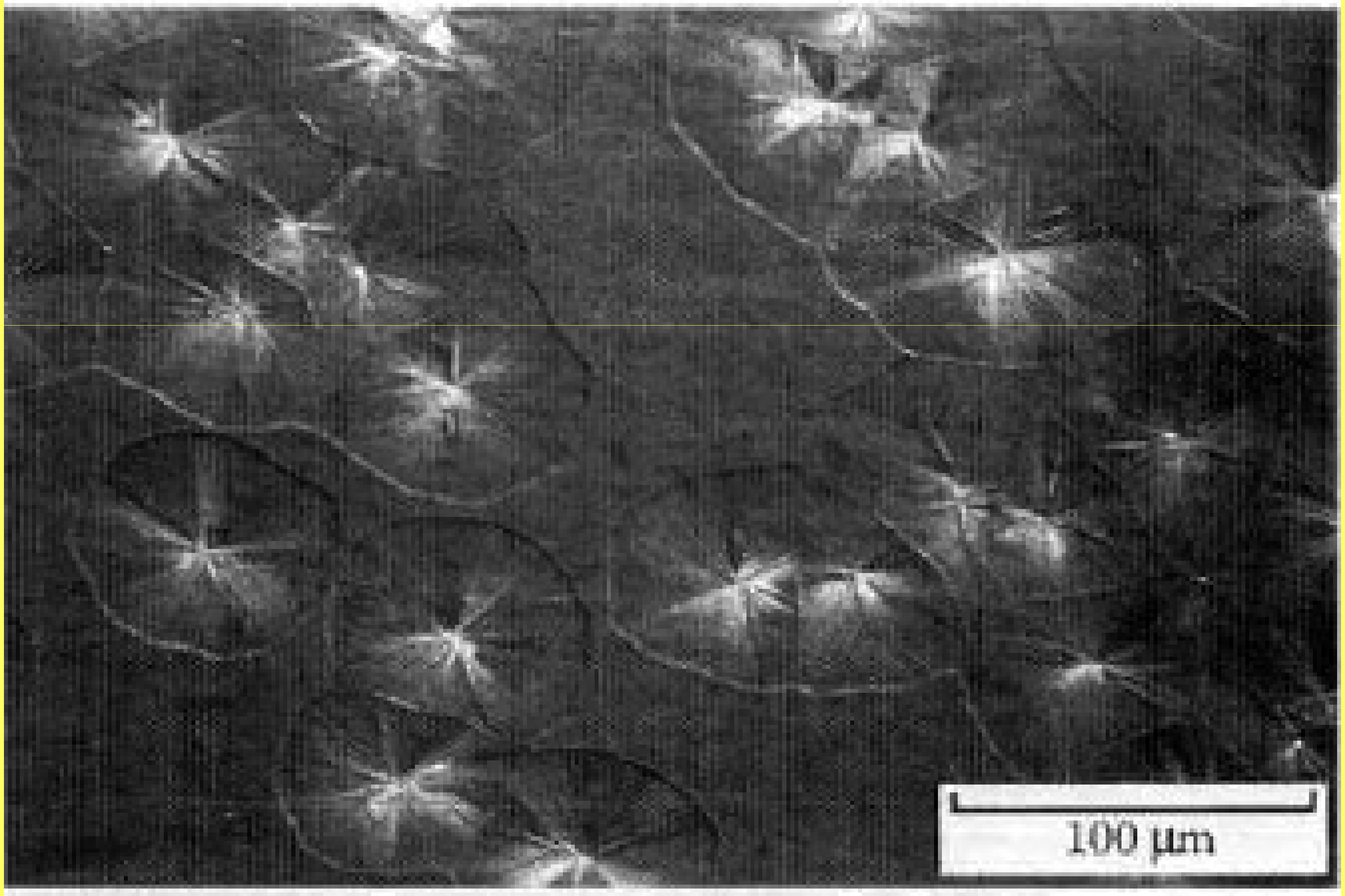
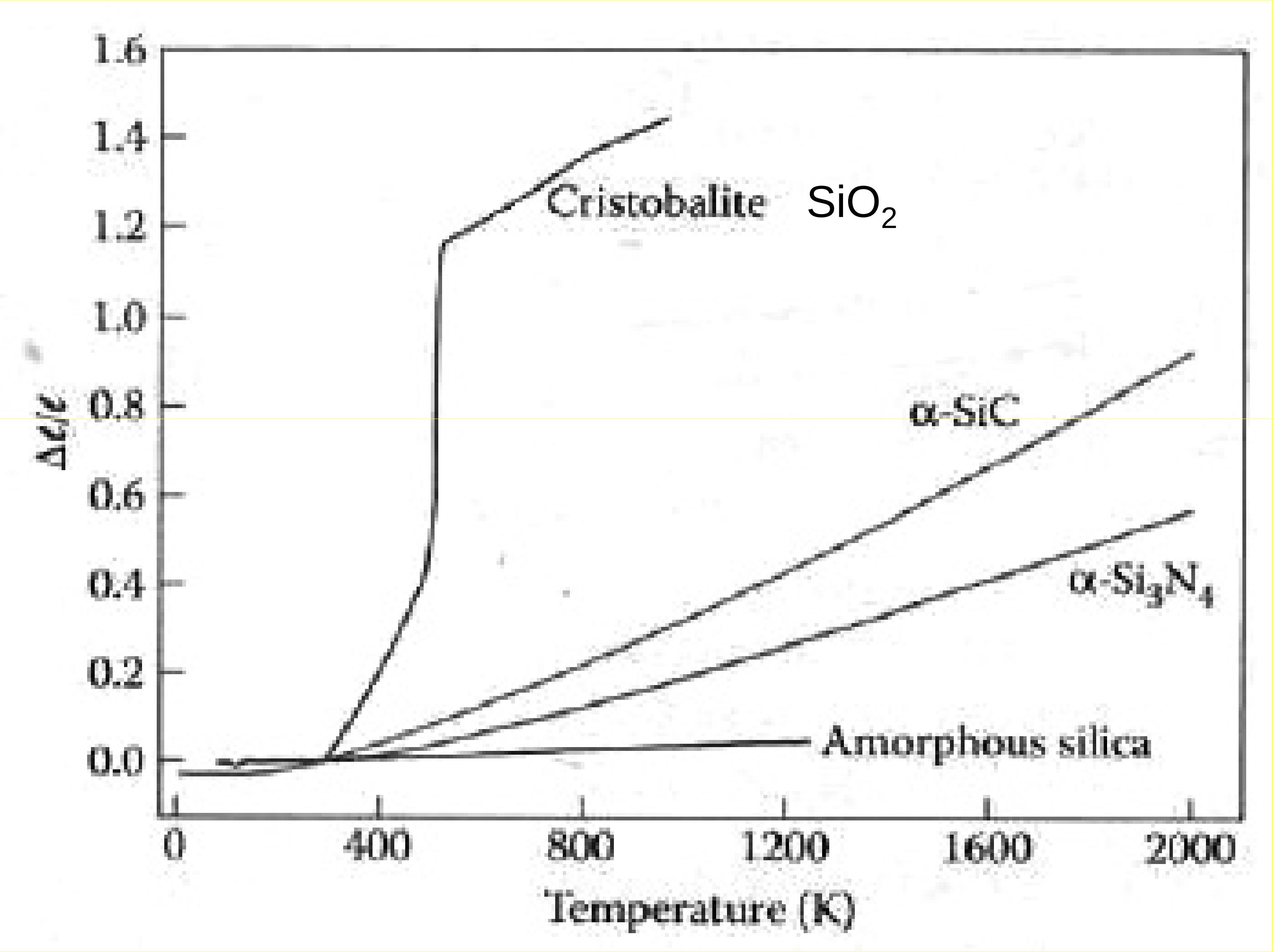


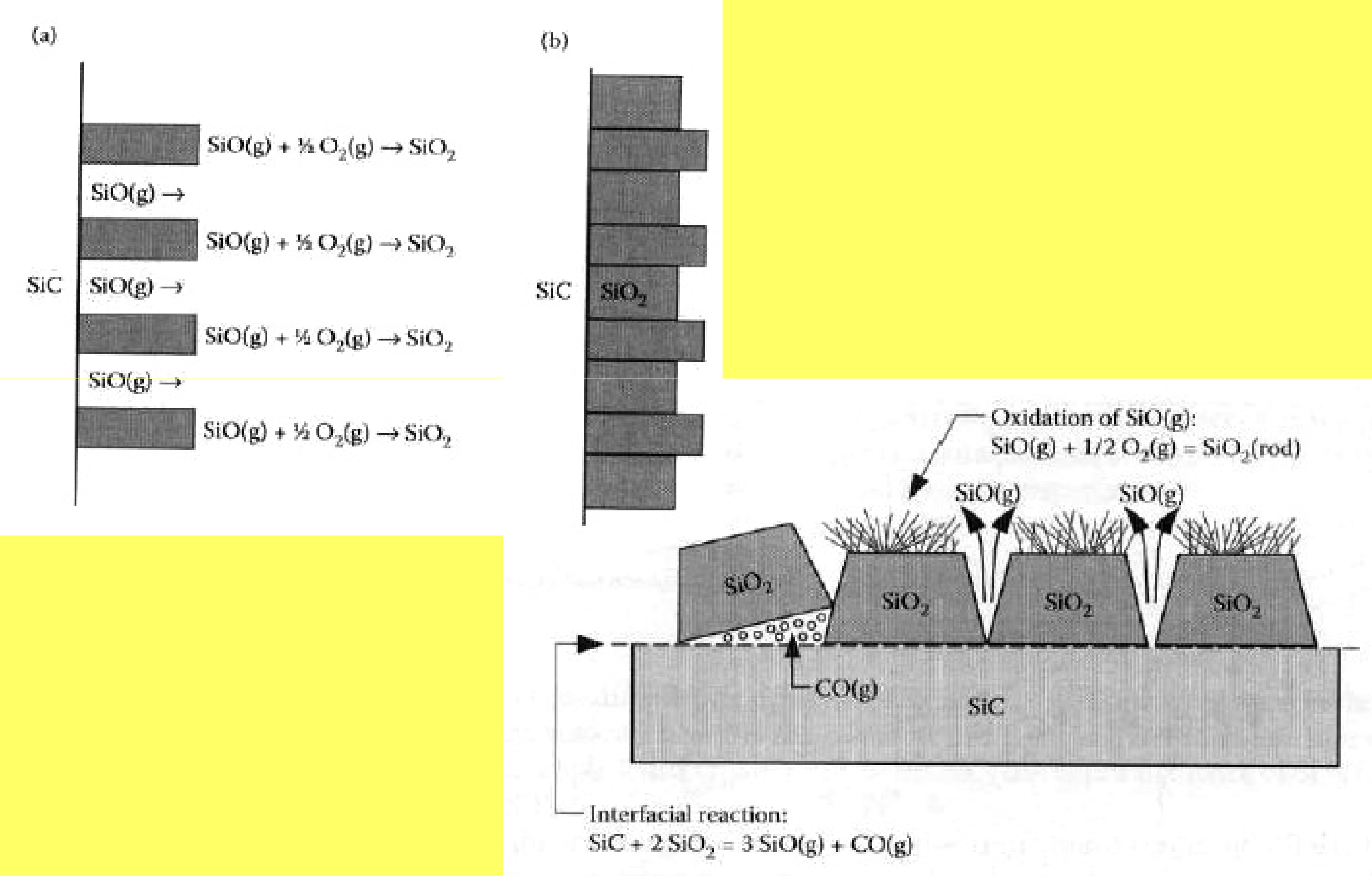
Formation of spherulitic silica scales that compress during cooling, which leads to buckling and spallation



Silicon-based ceramics (SiC, Si_3N_4, SiC-composites)



Mechanism of SiC oxidation

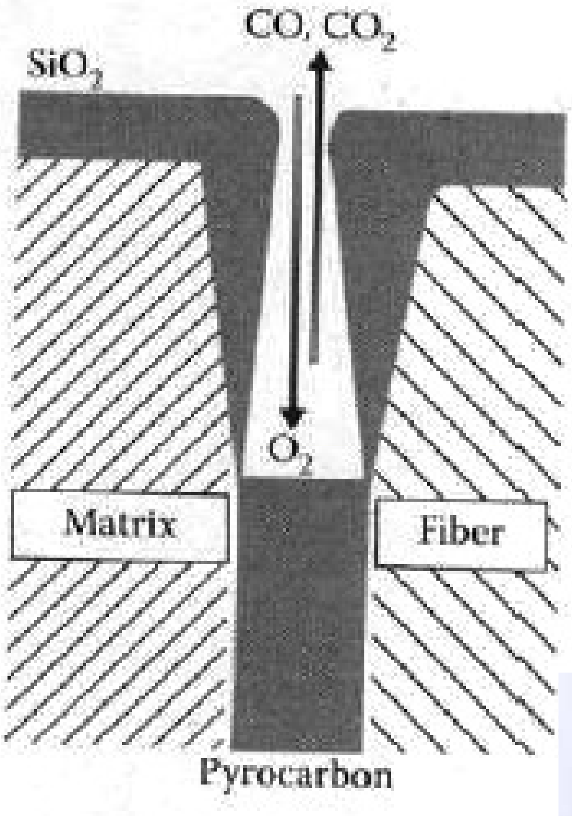


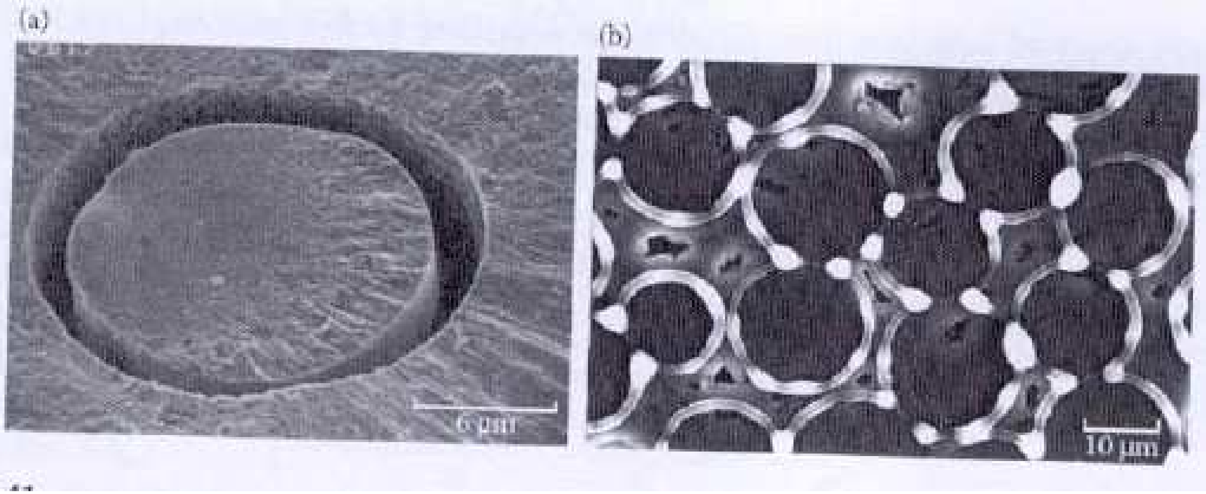
SiC based composites

The major problem that limits the use of monolithic ceramics in structural applications is the low fracture toughness of these materials. Thus, ceramic matrix composites are given special attention. Most research has focused on continuous fiber-reinforced SiC matrices to achieve high toughness. The fiber is either carbon or SiC with a C or BN coating.

The oxidation rate of such composites below 400 ^oC is very low, but up to about 1100 ^oC degradation of the carbon fibers or carbon fiber coating can create serous problems. Above 1100 ^oC, a film of silica will grow on the SiC and protect the composite against degradation.

SiC based composites

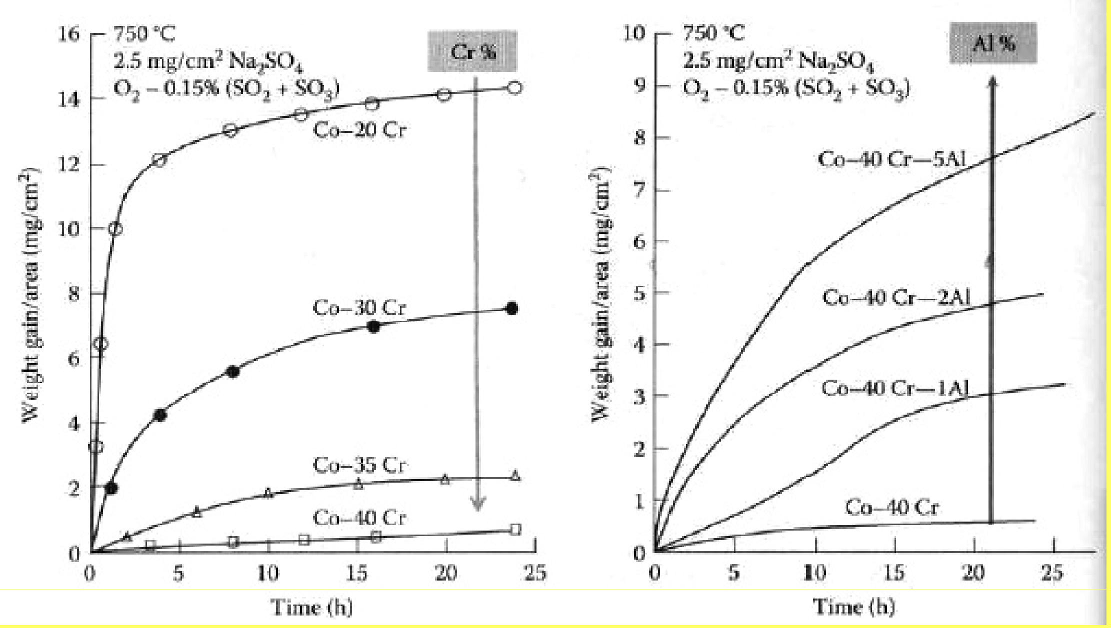


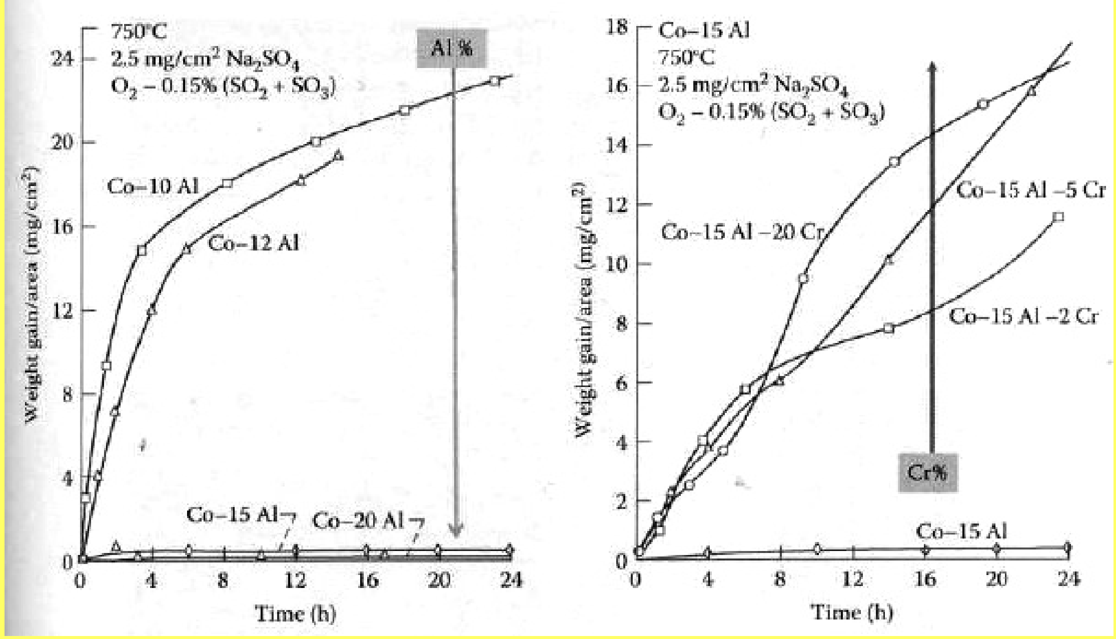


Hot corrosion of alloys

This is the most aggressive way metals, alloys and ceramics can degrade, especially when they operate at very high temperatures. Hot corrosion is induced by a film deposit of salt at elevated temperatures. The fused alkali sulfates are deposited on hot substrates via oxidation of heavy metal contaminants, such as vanadium in the fuel. Rapid degradation occurs due to the lack of a solid layer on the substrate. Components that are affected by a hot corrosion attack include gas turbines, industrial plants and jet engines.

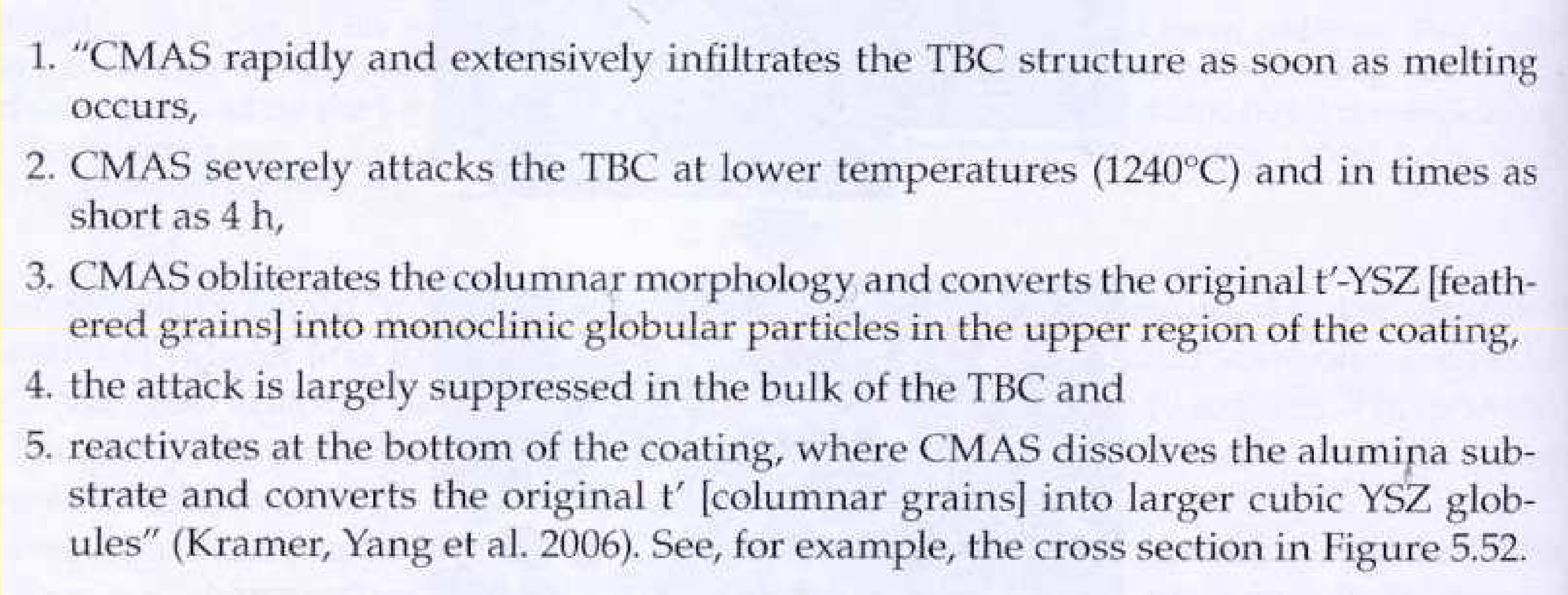
Hot corrosion of alloys





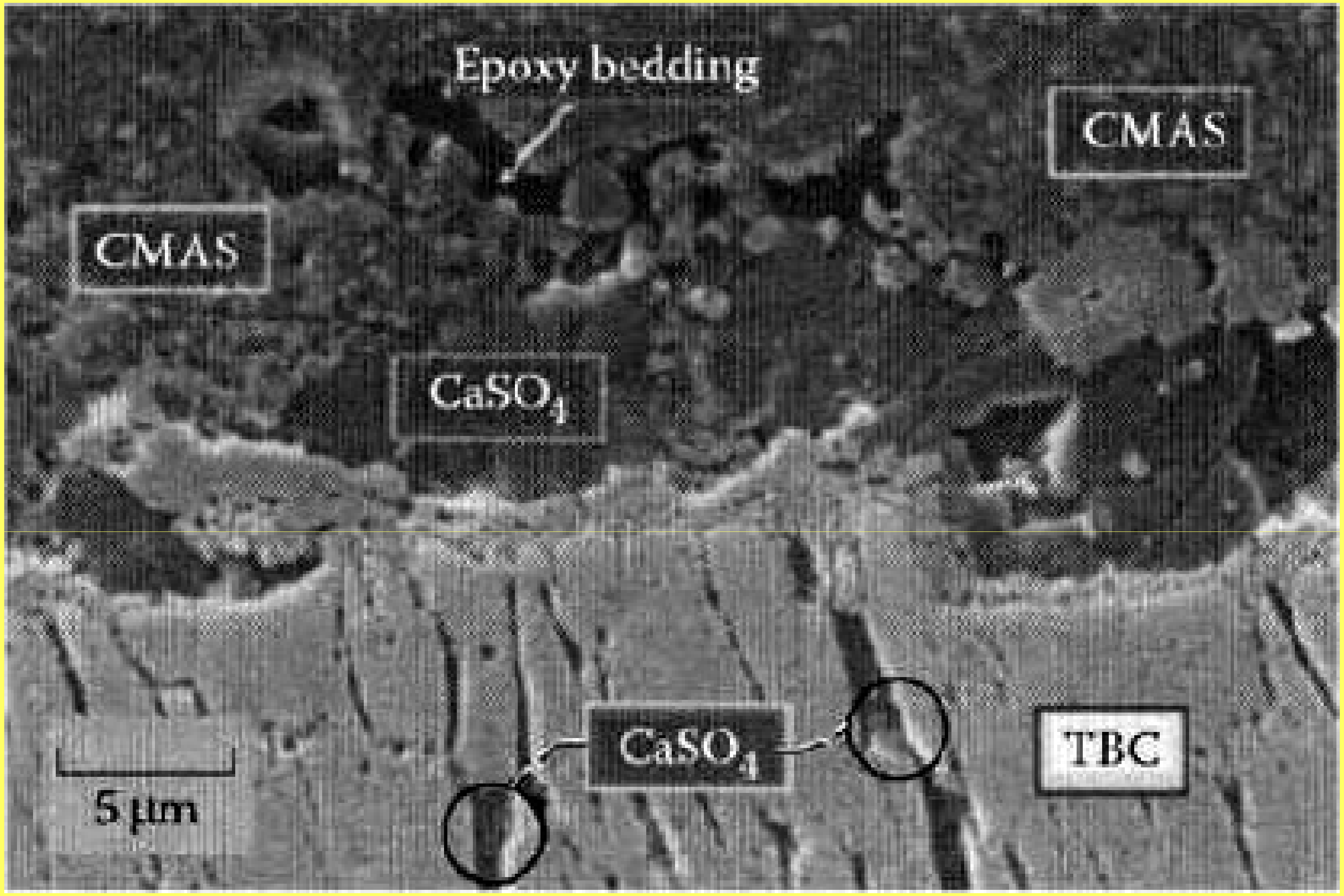
Corrosion in CMAS and volcanic ash

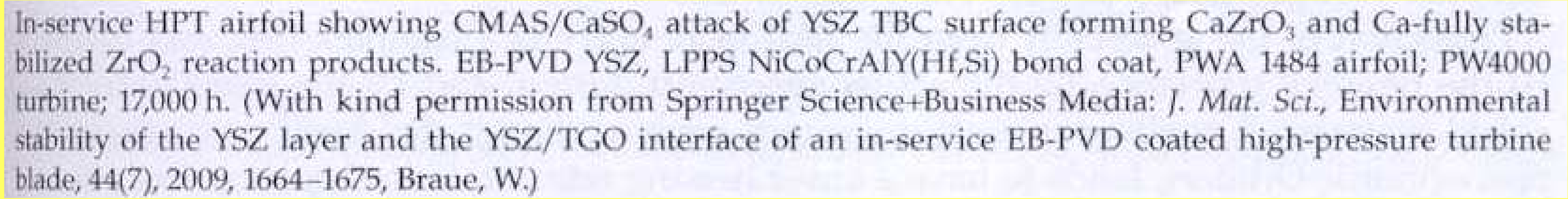
CMAS – calcium-magnesium-aluminosilicate dust



1. "CMAS rapidly and extensively infiltrates the TBC structure as soon as melting occurs,
2. CMAS severely attacks the TBC at lower temperatures (1240°C) and in times as short as 4 h,
3. CMAS obliterates the columnar morphology and converts the original t′-YSZ [feathered grains] into monoclinic globular particles in the upper region of the coating,
4. the attack is largely suppressed in the bulk of the TBC and
5. reactivates at the bottom of the coating, where CMAS dissolves the alumina substrate and converts the original t′ [columnar grains] into larger cubic YSZ globules" (Kramer, Yang et al. 2006). See, for example, the cross section in Figure 5.52.

Corrosion in CMAS and volcanic ash




In-service HPT airfoil showing CMAS/CaSO$_4$ attack of YSZ TBC surface forming CaZrO$_3$ and Ca-fully stabilized ZrO$_2$ reaction products. EB-PVD YSZ, LPPS NiCoCrAlY(Hf,Si) bond coat, PWA 1484 airfoil; PW4000 turbine; 17,000 h. (With kind permission from Springer Science+Business Media: *J. Mat. Sci.*, Environmental stability of the YSZ layer and the YSZ/TGO interface of an in-service EB-PVD coated high-pressure turbine blade, 44(7), 2009, 1664–1675, Braue, W.)

Re-entry materials

A spacecraft travels through space at tremendous speeds and experiences significant deceleration upon re-entering the earth's atmosphere. A shock wave develops around the craft that results in a highly complex atmosphere. This involves significant heating and an atmosphere containing molecules partially or fully dissociated by the shock into atoms and charged species.

Protection of the spacecraft from the heat of re-entry is a complex task and involves:

- the re-entry trajectory (heating rate and heating time)
- the actual spacecraft design
- the selection of heat shield materials

Categories of heat shield materials

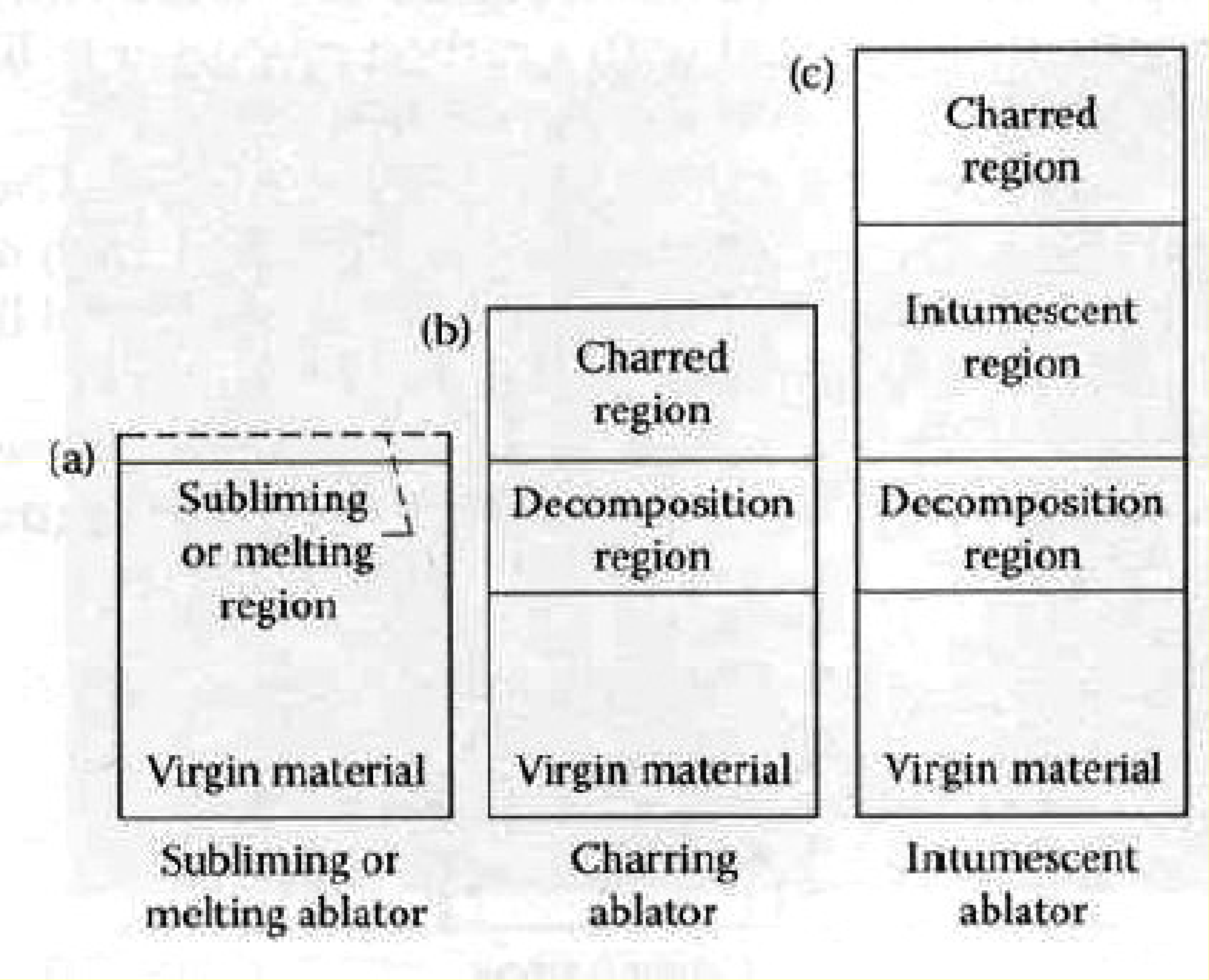
1. Ablative materials
2. Reusable materials

Ablative materials

Ablative materials – dissipate heat by losing or transforming their surface materials. Key parameters are the heat of ablation, which is the heat absorbed per unit weight, and thermal conductivity.

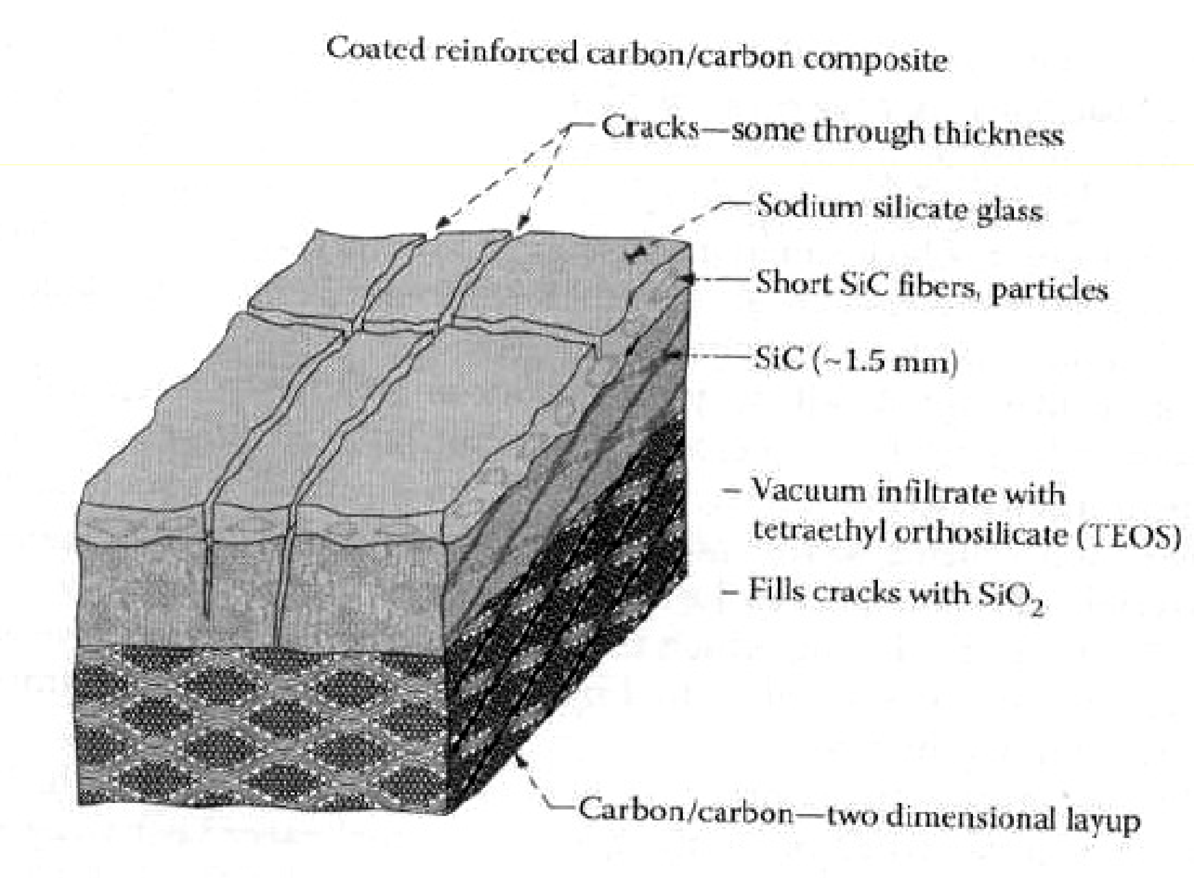
- Subliming ablators involve endothermic heat of vaporization. In addition, the generated gases carry heat away from and thicken the boundary layer around the vehicle surface. Examples: Teflon, graphite, carbon/carbon composites.
- Melting ablators involve the heat of ablation that goes into forming a liquid film on the surface. Examples: nylon, quartz.
- Charring ablators involve an endothermic reaction. Examples: carbon-phenolic materials, mixtures of epoxy resin, cork and even wood.
- Intumescent ablators undergo volume expansion and swell to form an extra layer, which leads to a decrease in thermal conductivity.

Ablative materials



Reusable materials

The Space shuttle Orbiter was the most well-known application of reusable reentry heat shields. The outer skin of the Orbiter is composed of various insulation components, including thermal tiles, thermal blankets and reinforced carbon/carbon (RCC) on the hottest parts. Tiles are highly porous and constructed of high-temperature fibers based on silica and aluminosilicate.



Schematic of RCC

THE END