

COATINGS TO CONTROL HIGH TEMPERATURE OXIDATION OF METALS

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Outline

Introduction

High temperature components

Materials and requirements

Degradation

Oxidation

Coatings and coating techniques

Thermal barrier coatings

Rare earth elements and their role

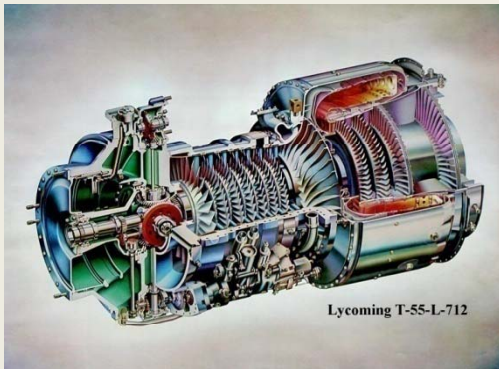
Nanostructured coatings

Challenges

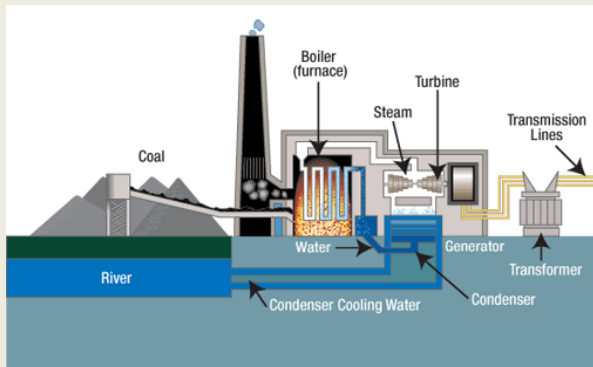


Degradation of materials at high temperatures - concern in many industries

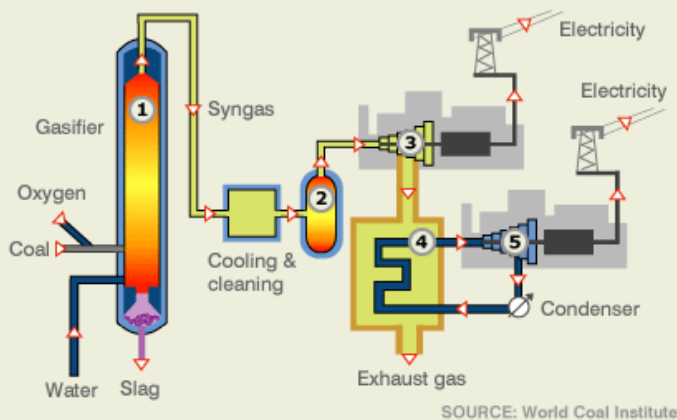
- power generation
 - refinery and petrochemicals
- chemical processing
 - metallurgical processing
- paper and pulp
 - Automotive
- Aerospace
 - defense etc.



aircraft turbine engines



Steam turbines



Coal gasification

High temperatures

Increased temperature gradients

High pressures

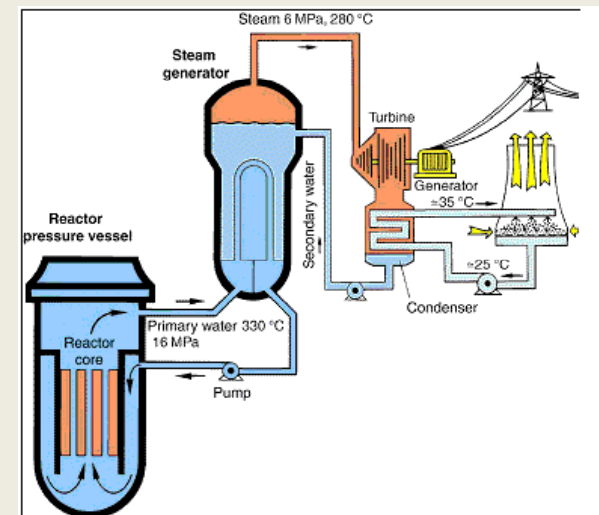
Large stresses

Oxidizing and corrosive atmospheres

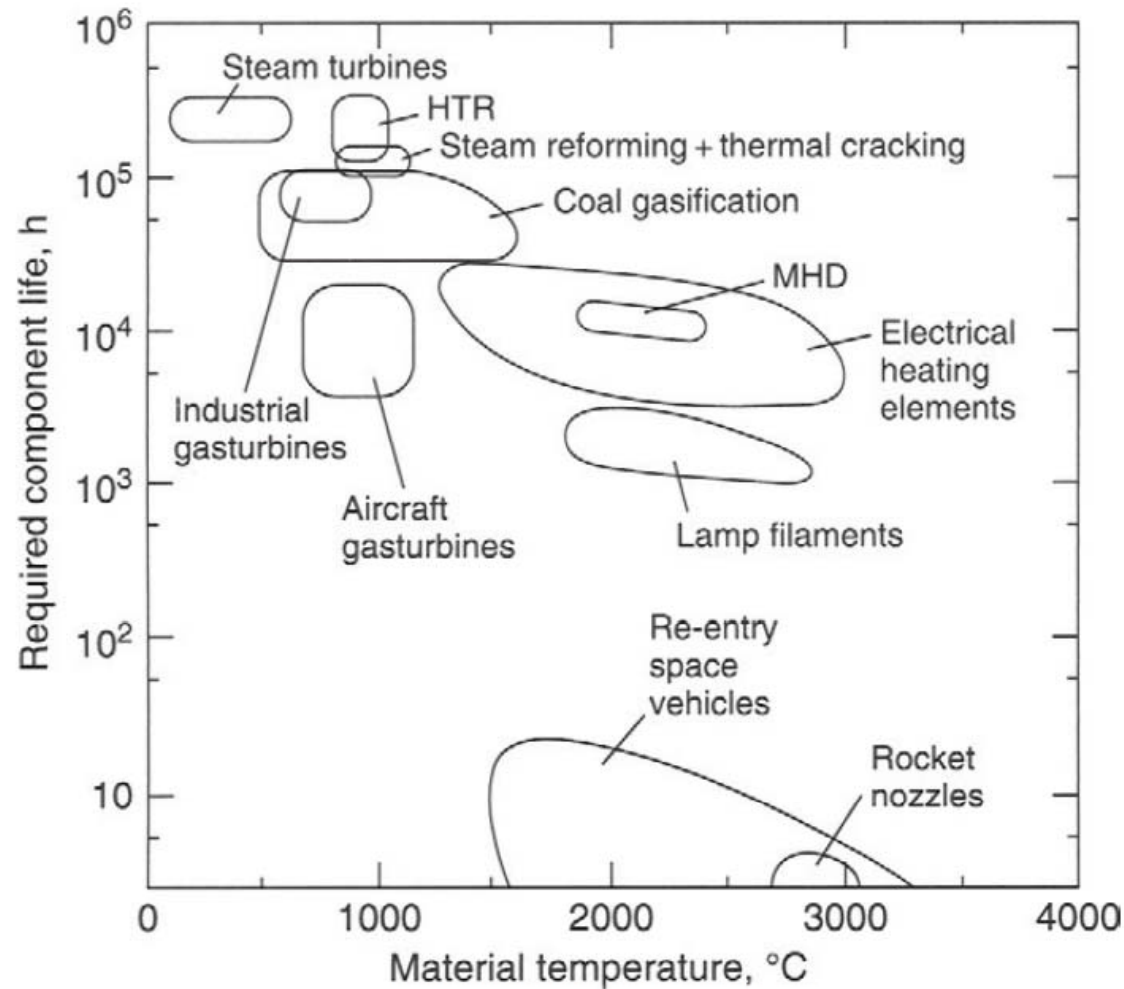
Particulates – erosion and impact damage



Petroleum refining



Nuclear power generation



High-temperature processes with component temperatures and required lives

(M.F.Stroosnijder, R. Mevrel, M.J.bennett, *Materials at High temperatures*, 1994, 12(1), 53.)



Degradation - oxidation.

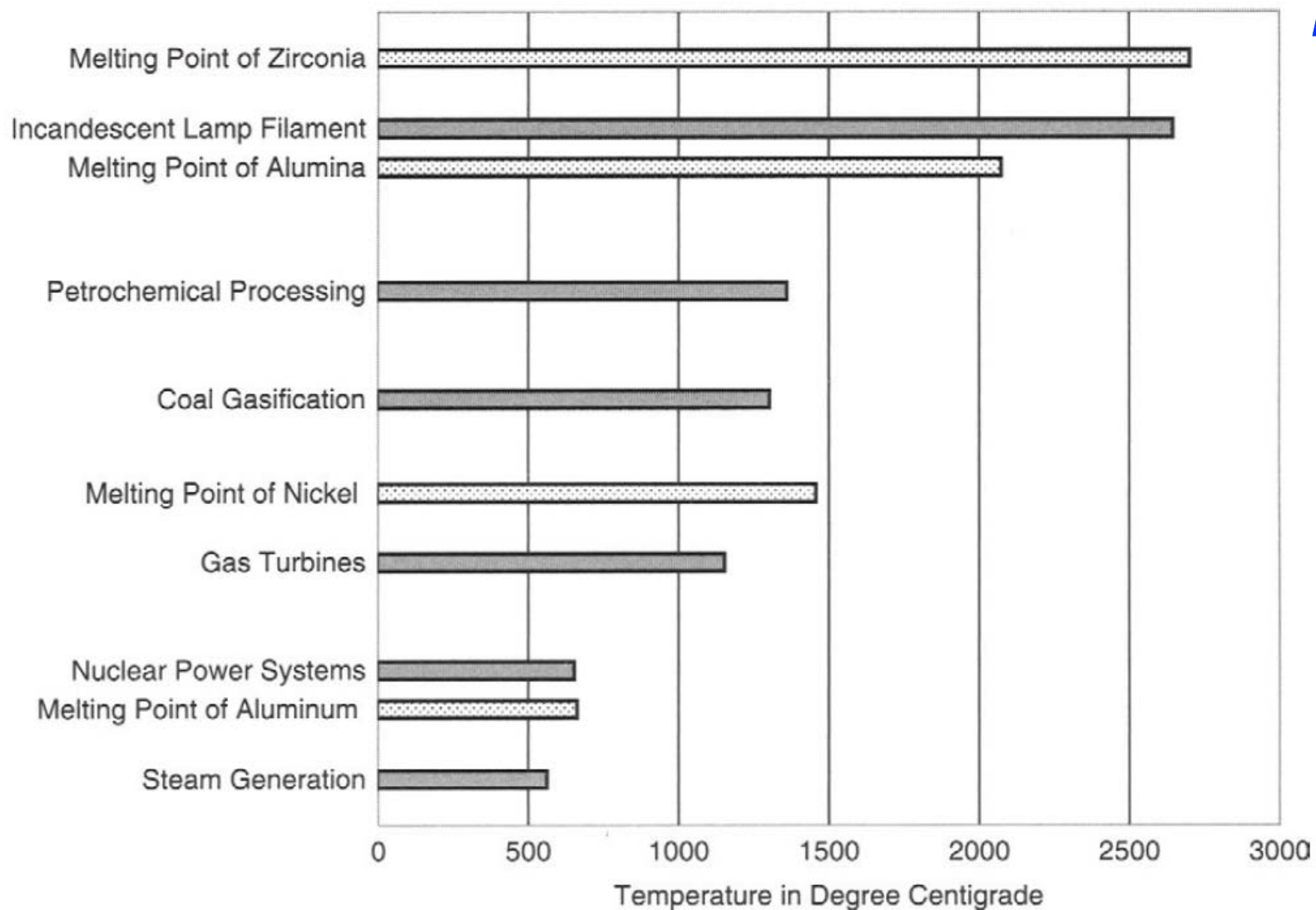
Also

- solid particle erosion,
- phase transformation,
- hot corrosion,
- spallation of surface oxide,
- volatilization etc.

Therefore materials exposed to H.T. industrial atmospheres should:

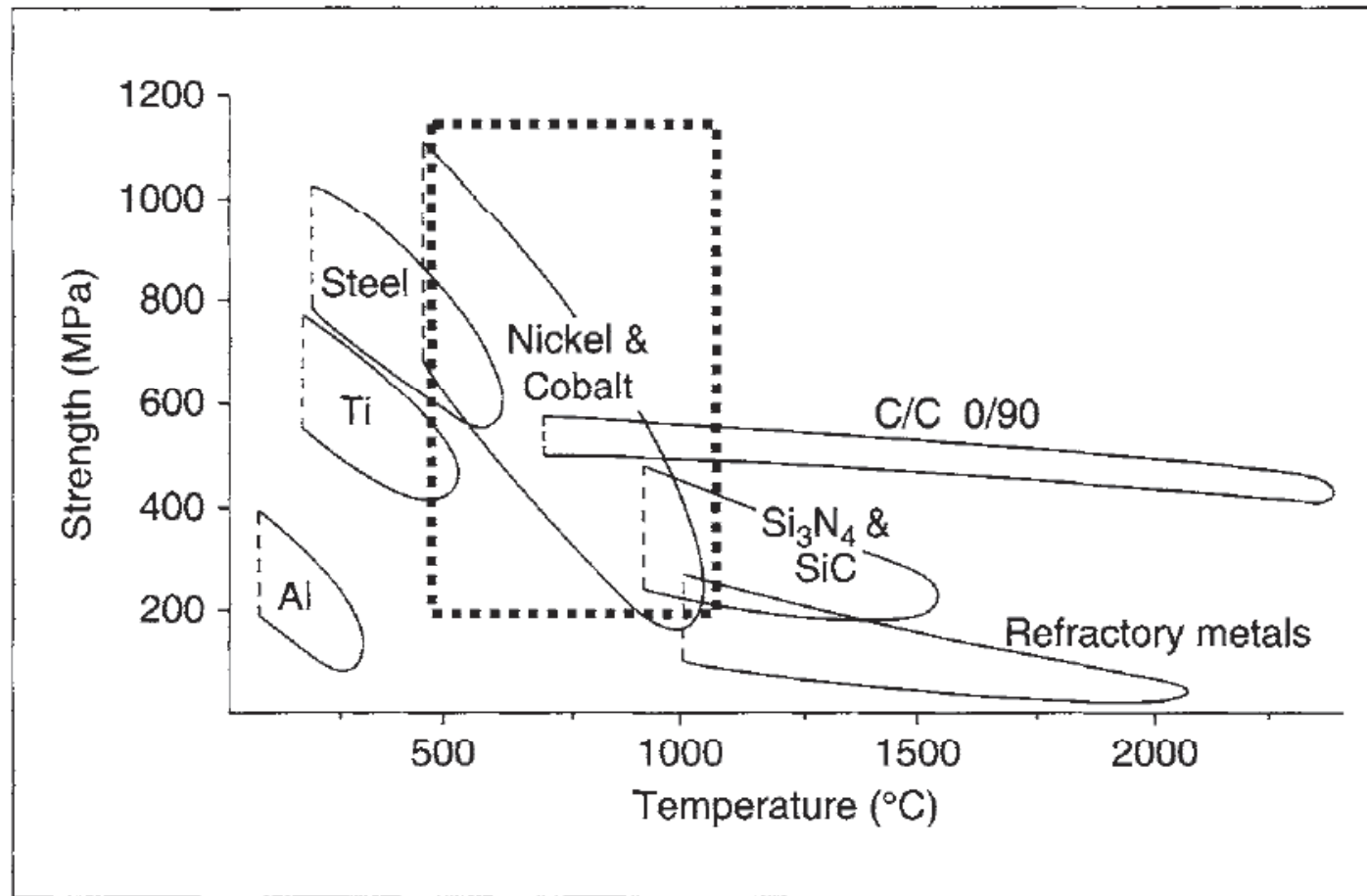
Resist attack by environment and resist deformation.

Frequently, possible to choose material with a suitable properties.



Typical temperatures for some industrial processes

(Sudhangshu Bose, High Temperature Coatings, Butterworth Heinemann , 2007)



Temperature capabilities of classes of materials

(G.W.Meetham, Materials and Design, 1988, 9(5), 247)



However, as the mechanical load and chemical severity increase, the scope to choose a material becomes limited.

Resolve this problem by designing the material where:

Surface optimized to resist attack by the environment.

•Bulk optimized to bear mechanical load.



H.T. materials: usually iron, nickel or cobalt based alloys.

Oxides formed on these metals are not sufficiently protective above 550°C.

Hence alloyed with Cr, Al and sometimes Si, to establish more protective oxide scales of chromia, alumina or silica respectively.



Another option to protect metallic components at high temperatures

COATINGS

Oxidation resistant coatings are - metallic, ceramic or composites

These coatings should:

- (a) be resistant to further extensive oxidation, if metallic;**
- (b) not undergo phase transformation;**
- (c) form a spallation resistant oxide;**
- (d) have a reduced coefficient of thermal expansion (CTE) mismatch with the substrate at the desired operating temperature;**
- (a) not compromise the coating/substrate integrity caused by inter-diffusion or solid state reactions.**

Coating Functions and Coating Materials Characteristics



Functions

Materials Characteristics

Reduction in surface temperature

Low thermal conduction Low radiative heat transfer High emittance

Reduction in rate of oxidation

Thermodynamically stable oxide formers with slow growth rates

Reduction in rate of hot corrosion

Chemically stable and impervious oxide scale

Resistance to particulate erosion

Hard, dense material

Increased abradability (sacrificial wear)

Rub tolerance via plastic deformation (densification)

Energy transformation via fracture (material loss)

Increased abrasiveness

Inclusion of hard particles to induce cutting of seal



There are mainly two types of coating processes:

(a) diffusion

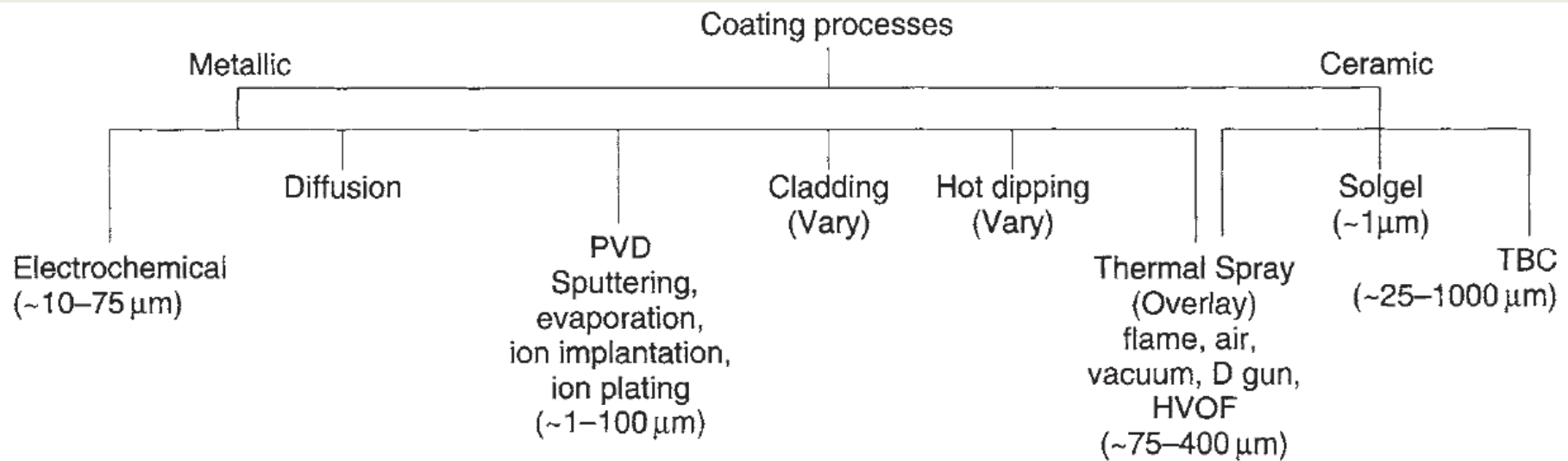
(a) overlay.

Diffusion coating - alter composition of the surface of an alloy by diffusion.

Enrich surfaces in Cr, Al or Si, and thereby aid formation of chromia, alumina or silica layers.

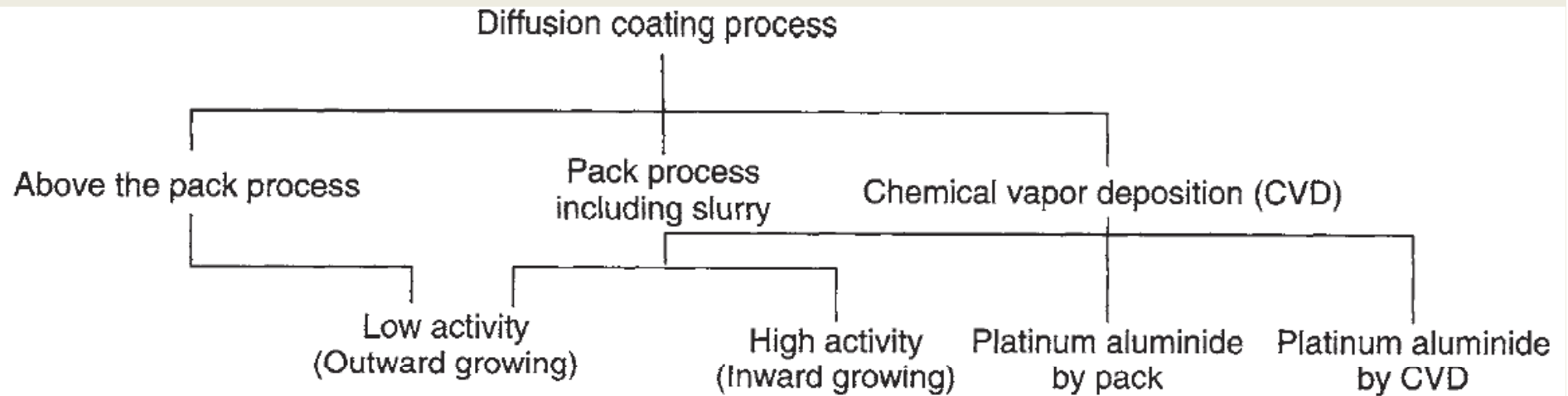
Formation and modification of the oxide that grows naturally on alloys or metallic coatings is also considered as a diffusion process in which oxygen is the active external element.

Overlay coatings - produced by the deposition of a corrosion resistant alloy, composite or a ceramic.



Some common coating processes

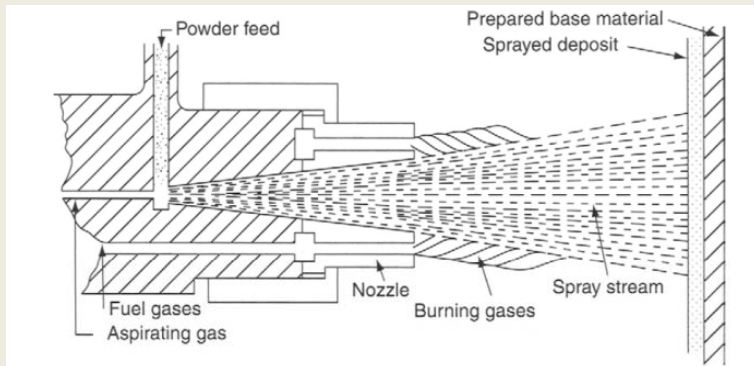
(Sudhangshu Bose, High Temperature Coatings, Butterworth Heinemann , 2007)



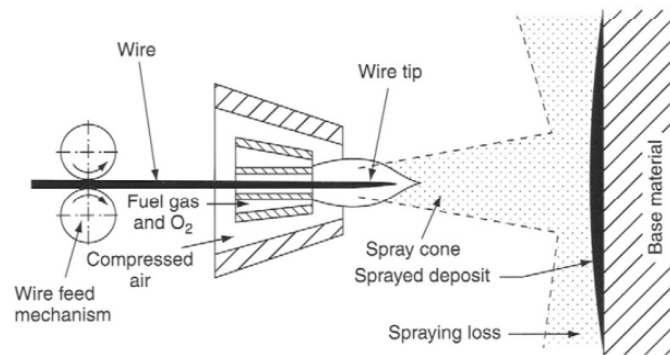
Various diffusion coating processes

(Sudhangshu Bose, High Temperature Coatings, Butterworth Heinemann , 2007)

Thermal spraying

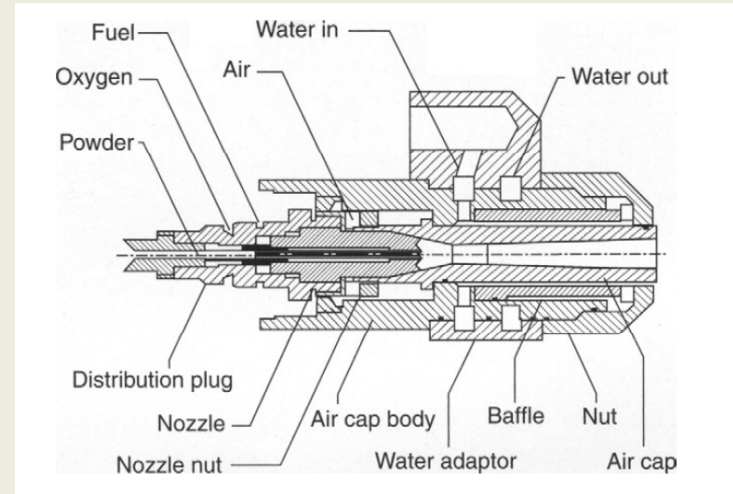


(a)

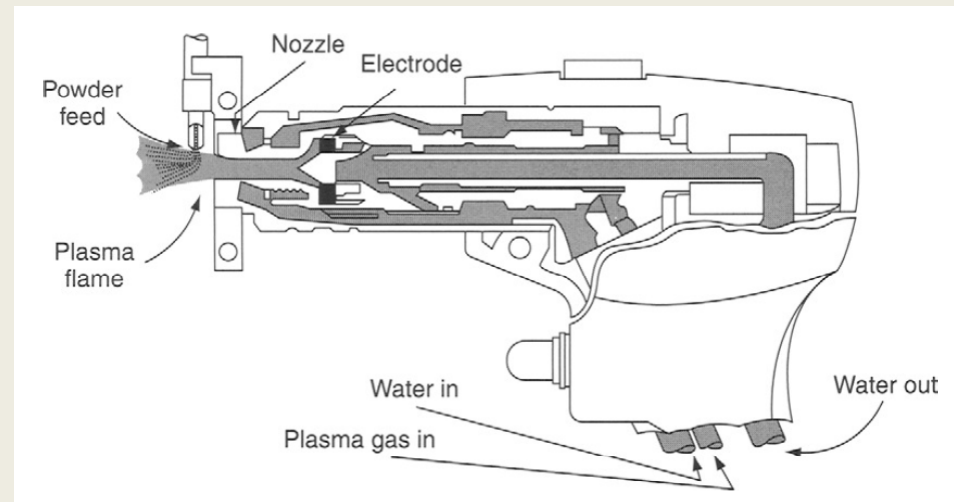


(b)

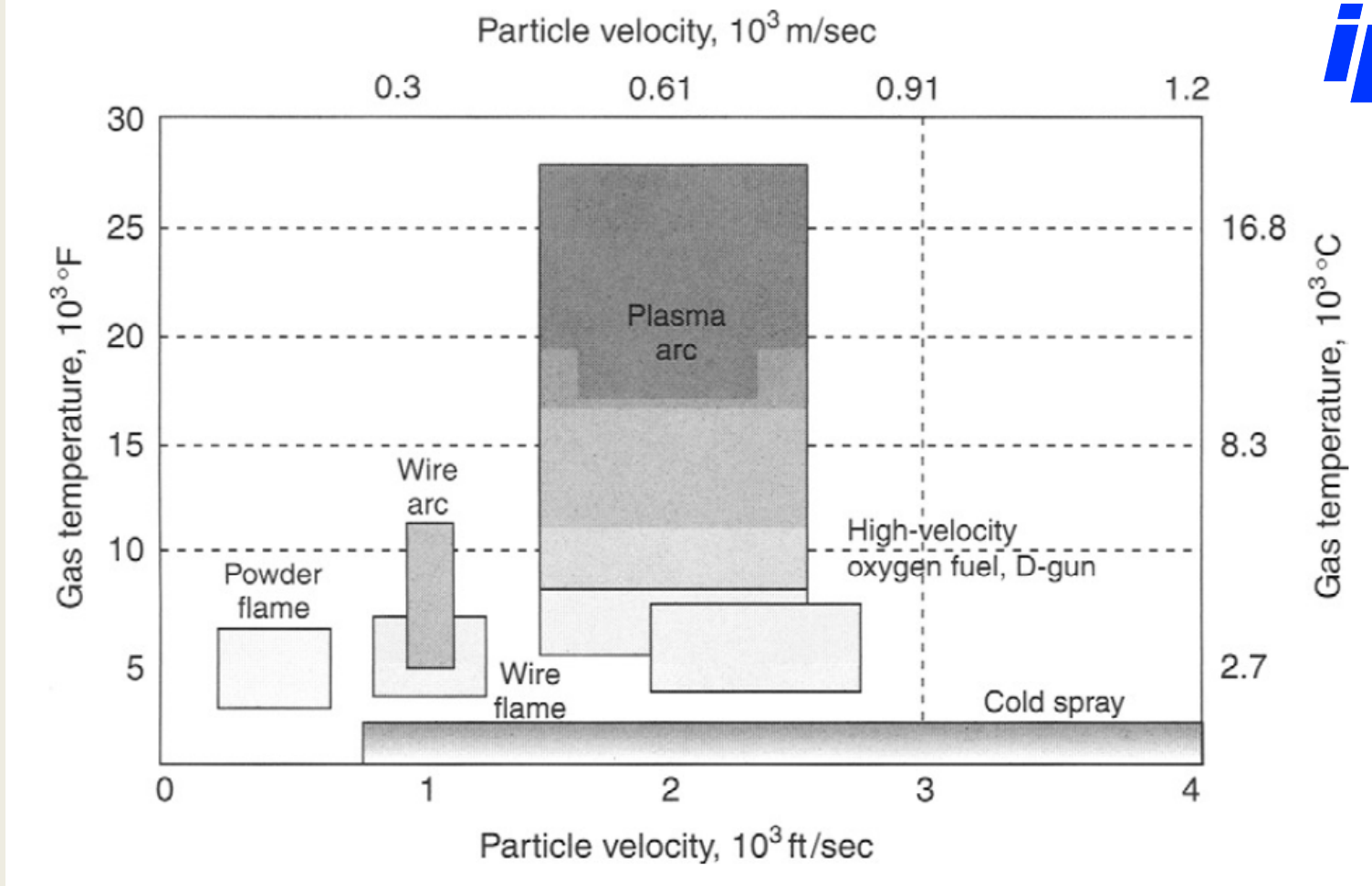
**Principles of flame spray process
(a) powder feed; (b) wire feed**



Nozzle of an HVOF gun



Internal features of a Metco Plasma gun



Gas temperature-particle velocity regimes for various thermal spray processes and the cold spray process

(Anatolii Papyrin, Adv. Mater.Proc., 2001, 159(9), 49.)

PVD Processes

Ion beam processes

Sputtering

Planar diode

Triode

Magnetron

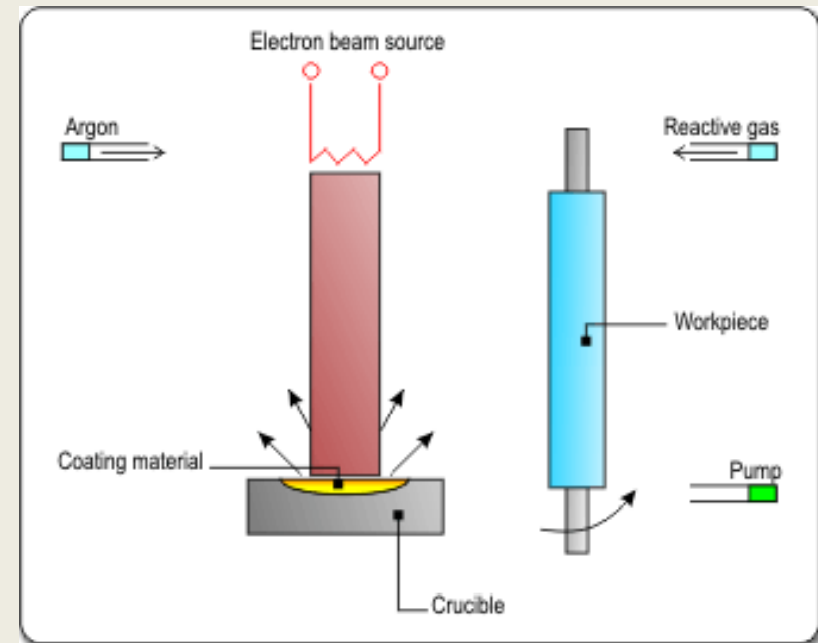
Radio frequency

Ion implantation

Ion plating

Evaporation

Electron beam physical vapor deposition



Summary of the Benefits and Limitations of the Atomistic and Particulate Deposition Methods *(Nicholls, 2000)*



Processing

Features	Evaporation	Sputtering Deposition	CVD	Electrodeposition	Thermal Spraying
Mechanism to produce depositing species	Thermal energy	Momentum transfer	Chemical reaction	Solution	Flames or plasmas
Deposition rate	Moderate (up to 750,000 Å/min.)	Low	Moderate	Low to high	Very high
Deposition species	Atoms	Atoms/ions	Atms/ions	Ions	Droplets
Complex shapes	Poor line of sight	Good but nonuniform	Good	Good	Poor resolution
Deposits in small, blind holes	Poor	Poor	Limited	Limited	Very limited
Metal/alloy deposition	Yes	Yes	Yes	Yes	Yes
Refractory compounds and ceramics	Yes	Yes	Yes	Limited	Yes
Energy of deposit-species	Low	Can be high	Can be high	Can be high	Can be high
Growth interface perturbation	Not normally	Yes	Yes	No	No
Substrate heating	Yes, normally	Not generally	Yes	No	Not normally

Requirements for metallic coatings

Successful environmental performance of metallic coatings rely on formation of thin oxide scales on the coating surface that limits access of oxygen and corroding salts.

For these scales to provide extended protection a number of requirements have to be satisfied.

Oxidation/corrosion resistance

- **Thermodynamically stable, protective scale of uniform thickness**
- **Slow growth rate of protective surface scale**
- **Adherent surface scale**
- **High concentration of scale former**



Stability

- No undesired phase changes within the coating**
- Low diffusion rate across interface at use temperature**
- Adequate compositional stability across interface**
- Minimized brittle phase formation**

Adhesion

- Good adherence of coating to substrate**
- Matched coating/substrate properties to reduce thermal stress**
- Minimized growth stresses (process parameters related)**
- Optimized surface condition (rough or smooth)**

Structural properties

- Can withstand service related creep, fatigue and impact loading of surface without failure of function.**

Elemental constituents of metallic coatings, their functions and effects



Elemental Constituent	Beneficial Aspects	Detrimental Aspects
Ni	Major constituent of substrate alloy. Provides strength.	Prone to destructive interaction with sulfur.
Co	Major constituent of substrate alloy. Provides microstructural stability and strength.	Prone to destructive interaction with sulfur.
Al	Constituent of substrate alloy. Major contributor to providing strength. Contributes to oxidation resistance.	Large concentration lowers melting point.
Cr	Constituent of substrate alloy. Contributes to oxidation resistance to 1500°F (816°C). Reduces Al requirement for formation of alumina scale. Imparts resistance to hot corrosion.	Lowers creep strength.
Ta	Enhances hot corrosion and oxidation resistance. Improves strength.	
Si	Enhances oxidation and type II hot corrosion resistance.	Large concentration leads to formation of brittle phases.
Hf, Y, Y ₂ O ₃ , oxides of other reactive elements	Improves adherence of alumina and chromia scales.	Large amounts are detrimental.
Pt	Improves oxidation and hot corrosion resistance.	

(Nicholls, 2000)



Oxidation resistance of coatings

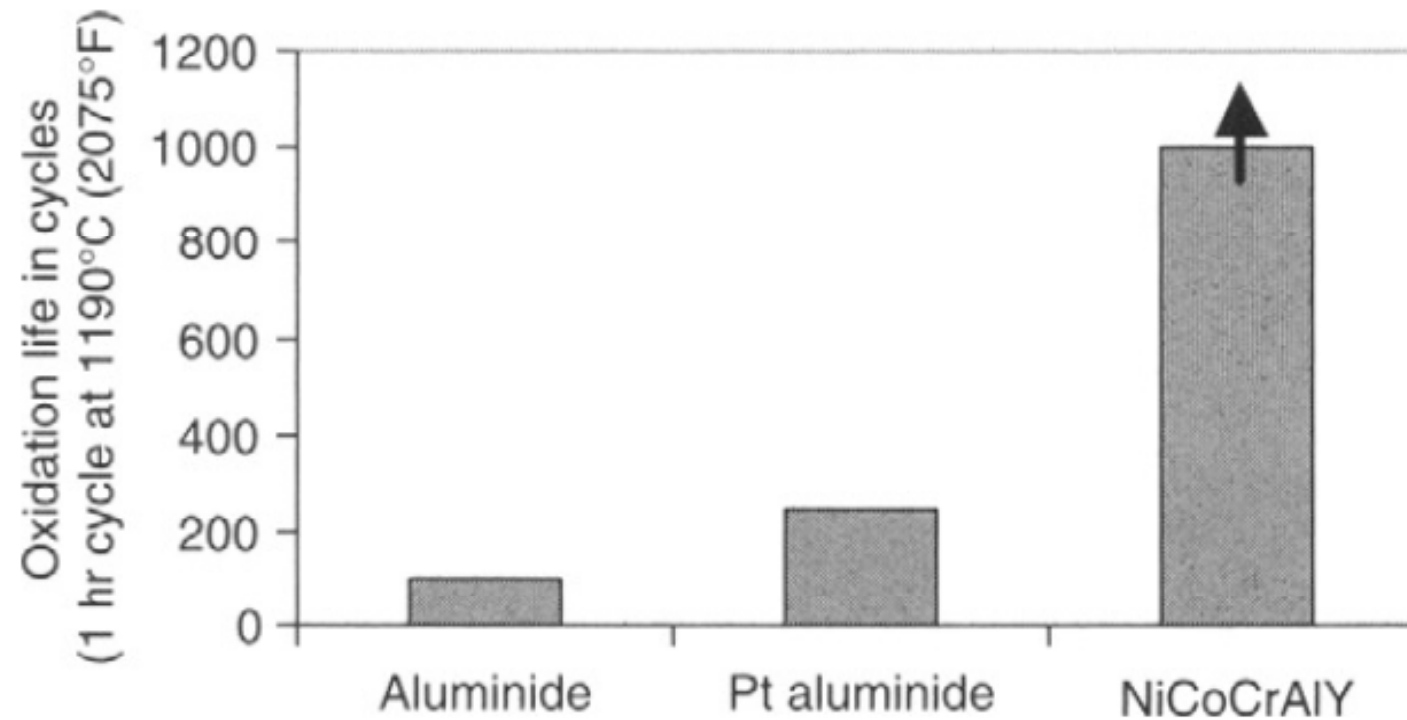
The mechanism of oxidation of coatings used in high-temperature applications is in many ways similar to that of the high temperature alloys

The key differences lie in the aluminium content, the phase distribution, the presence of reactive elements, and the effect of interdiffusion with the substrate.

Ideal scales:

- **Non-volatile**
- **Stoichiometric, to maintain low ionic transport**
- **Stress free at operating temperature to reduce scale failure**
- **Adherent - resistant to spallation**
- **Pores, cracks and other defect-free - to prevent short circuit transport of reactants**

In practice, almost impossible to form such ideal scales.



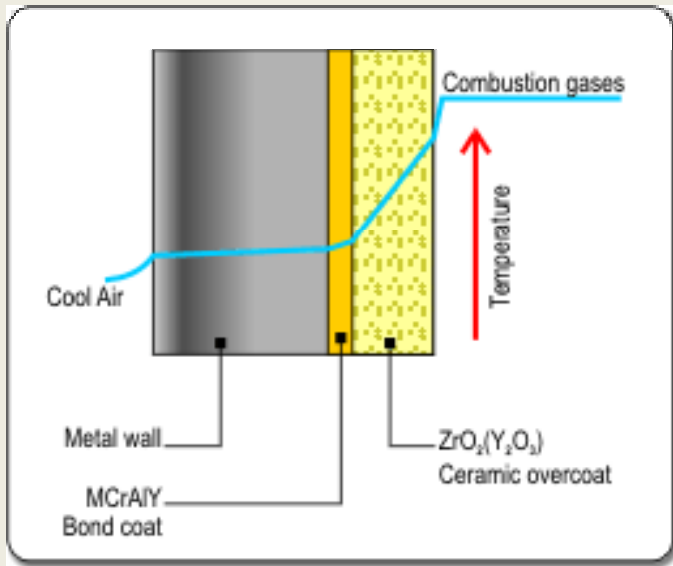
Comparison of oxidation resistance of coatings in cyclic thermal exposure of 1 Mach gas velocity in air at 1190 °C



Coatings represented by MCrAlX (M being Ni, Fe, Co and X for reactive elements) when deposited by some of the overlay processes such as LPPS or HVOF exhibit good oxidation resistance due to the presence of adequate levels of Al, Cr and the excellent oxide scale adherence afforded by the reactive elements.

***Overlay coatings* as opposed to diffusion coatings, provide more independence from the substrate alloy, but also more flexibility in design as compositions can be modified depending on the degradation mechanisms expected to prevail.**

Thermal barrier coatings (TBCs)



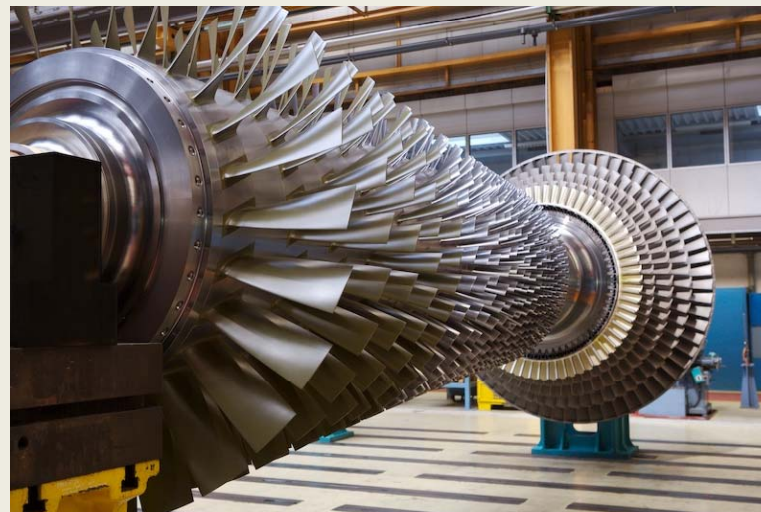
Reduce component temperatures and increase life.

A combination of multiple layers.

Top layer - thermal insulation - ceramic - typically ZrO_2 . (125 -1000 μm)

Bond coat - MCrAlY, (50 -125 μm)

Thermally grown oxide (TGO), predominantly alumina. (0.5 – 10 μm)



TBC coated
gas turbine rotor
for operation at
1400 °C

Hot corrosion and erosion



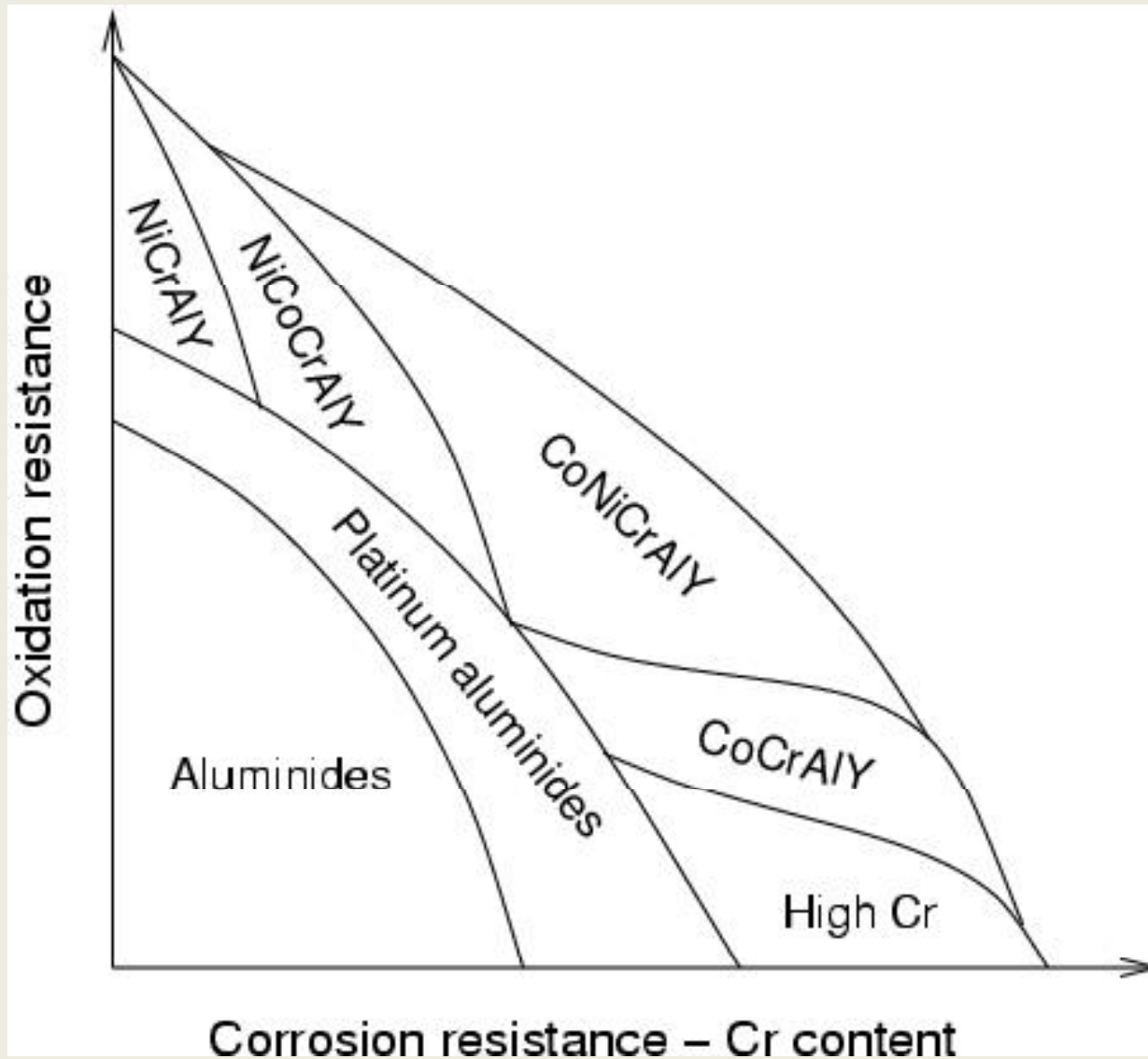
In industrial processes, materials are exposed not only to oxygen but also to other environmental constituents:

- Gasses - CO_2 and SO_2
- Fused or molten salts like alkali and alkaline earth sulphates, chlorides,
- Solid particles in the form of sand and fly ashes. The solid particles may melt during their transit through the system or remain in particulate form.

Interaction of these environmental constituents with the materials of construction results in corrosion and erosion.

Hot corrosion is that induced by fused salts in an oxidizing gas at elevated temperatures.

Erosion involves mechanical impact and associated material loss. This may also accelerate environmental interactions by removing protective oxide scales.



Optimum coating composition in relation to oxidation and hot-corrosion resistance
(M. Schütze, Corrosion and Environmental Degradation Vol. II, Wiley-VCH, 2000.)

The Reactive Element Effect



Over 60 years - addition of small quantities of cerium to a Cr containing heater alloy melt - had significant effect on lifetime of alloy

Termed 'Rare earth effect' and patented.

Now elements other than rare earths (REs) also give the same effect

Now effect termed 'Reactive element effect'.



THE RARE EARTHS

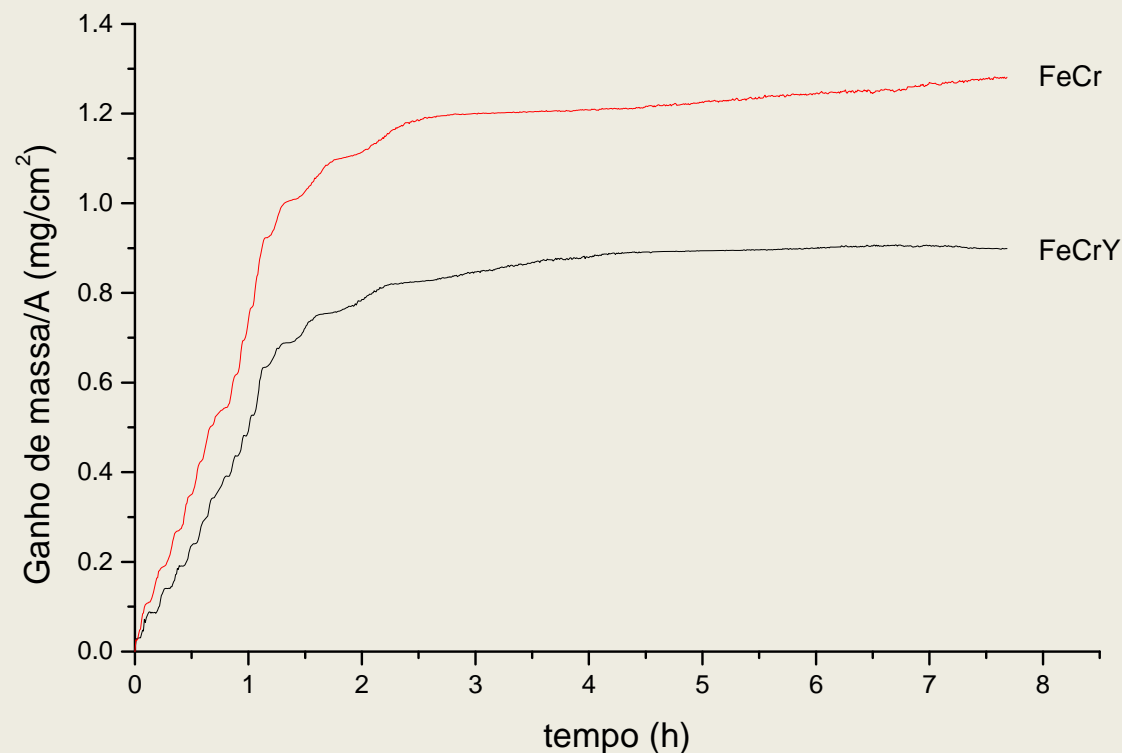
**A group of 17 elements comprising the 15 lanthanides,
scandium, and yttrium**

Periodic Table of Elements



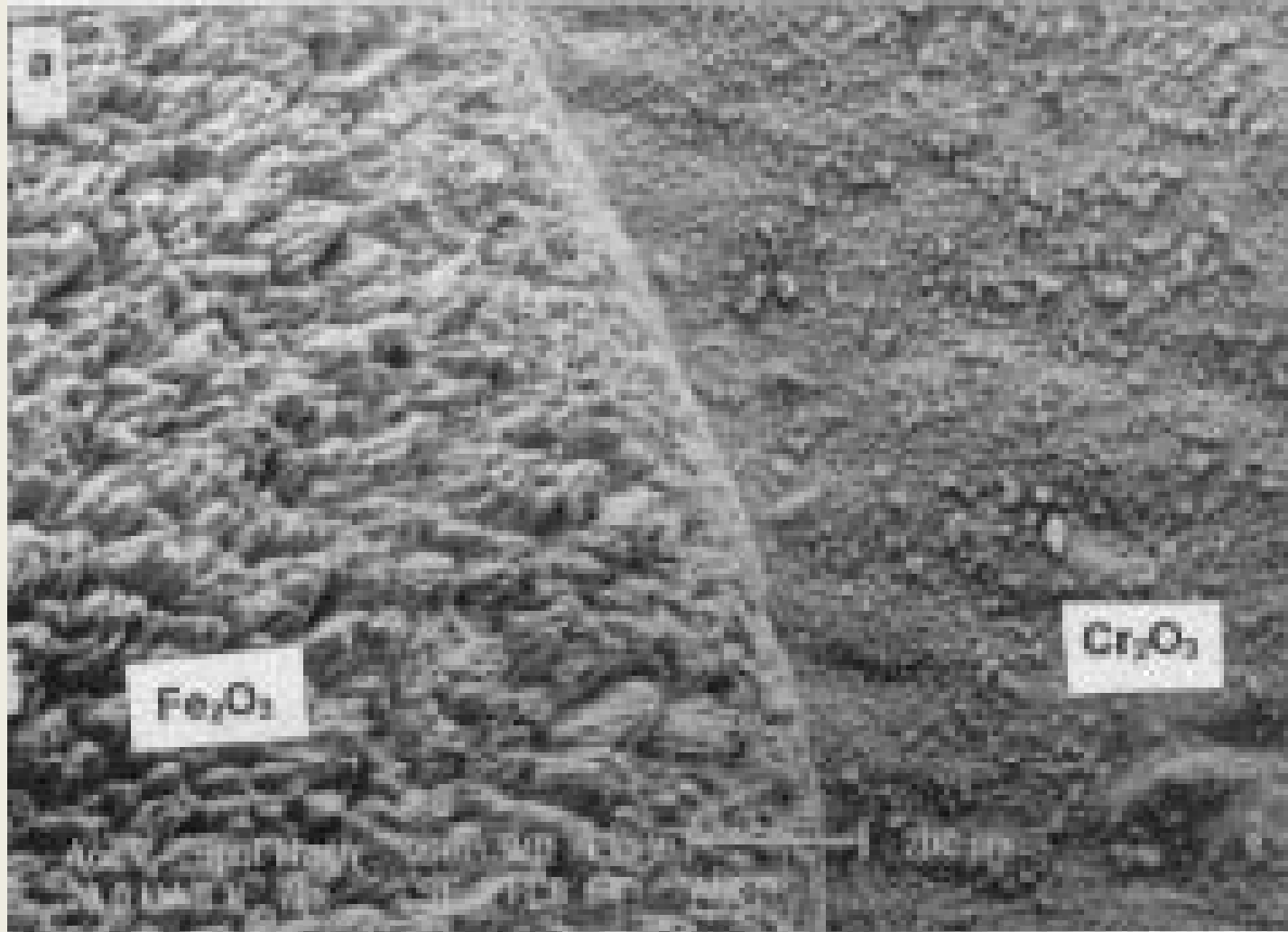
Jump start: select an element from the periodic table.

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	1 H																	2 He	
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

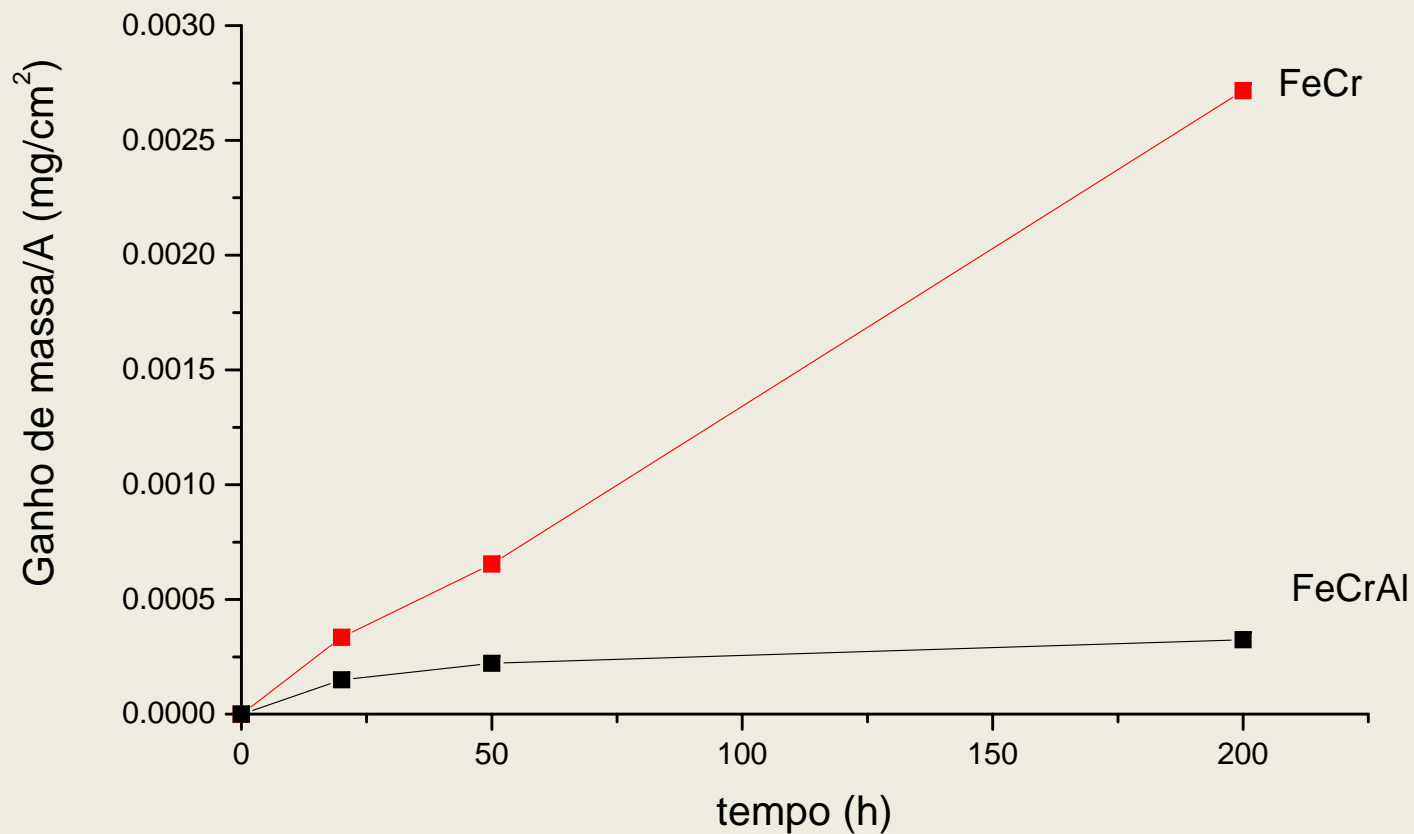


Oxidation curves of FeCr and FeCrY at 1000°C

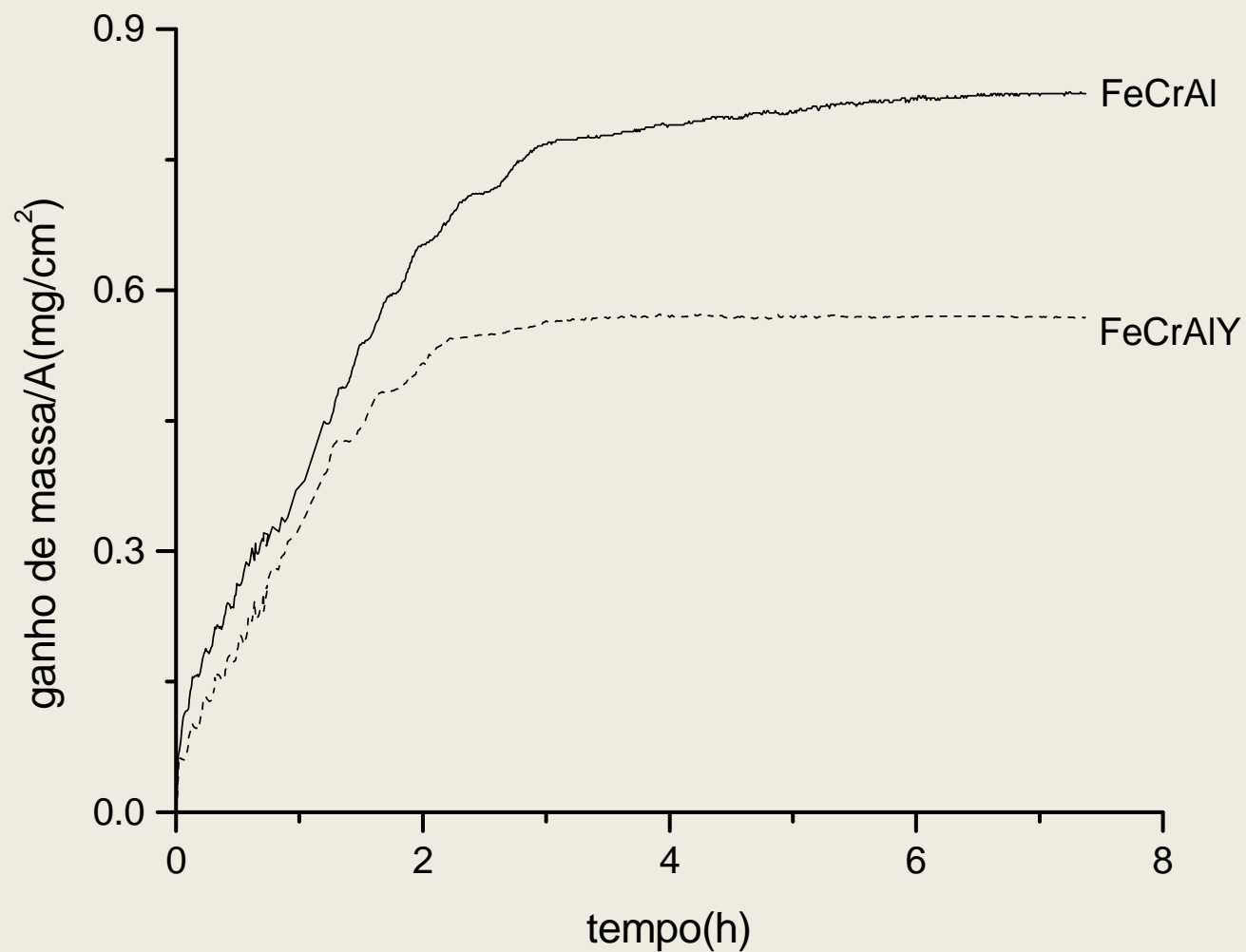
In the transient stages of oxidation - metastable oxides of base metals are present. RE effects on scale growth is not evident.



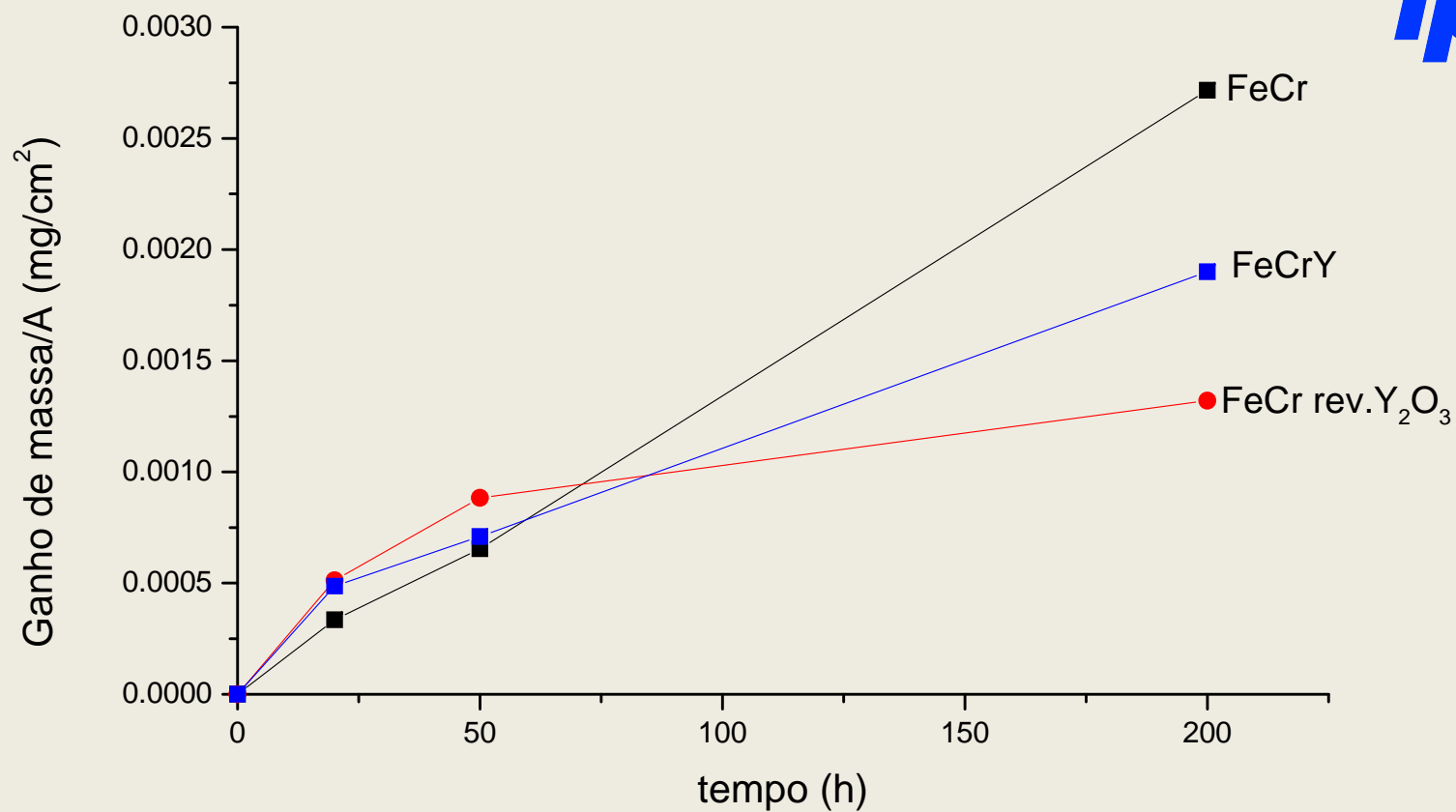
Surface of Fe-20Cr oxidized for 20 hours at 1000° C.



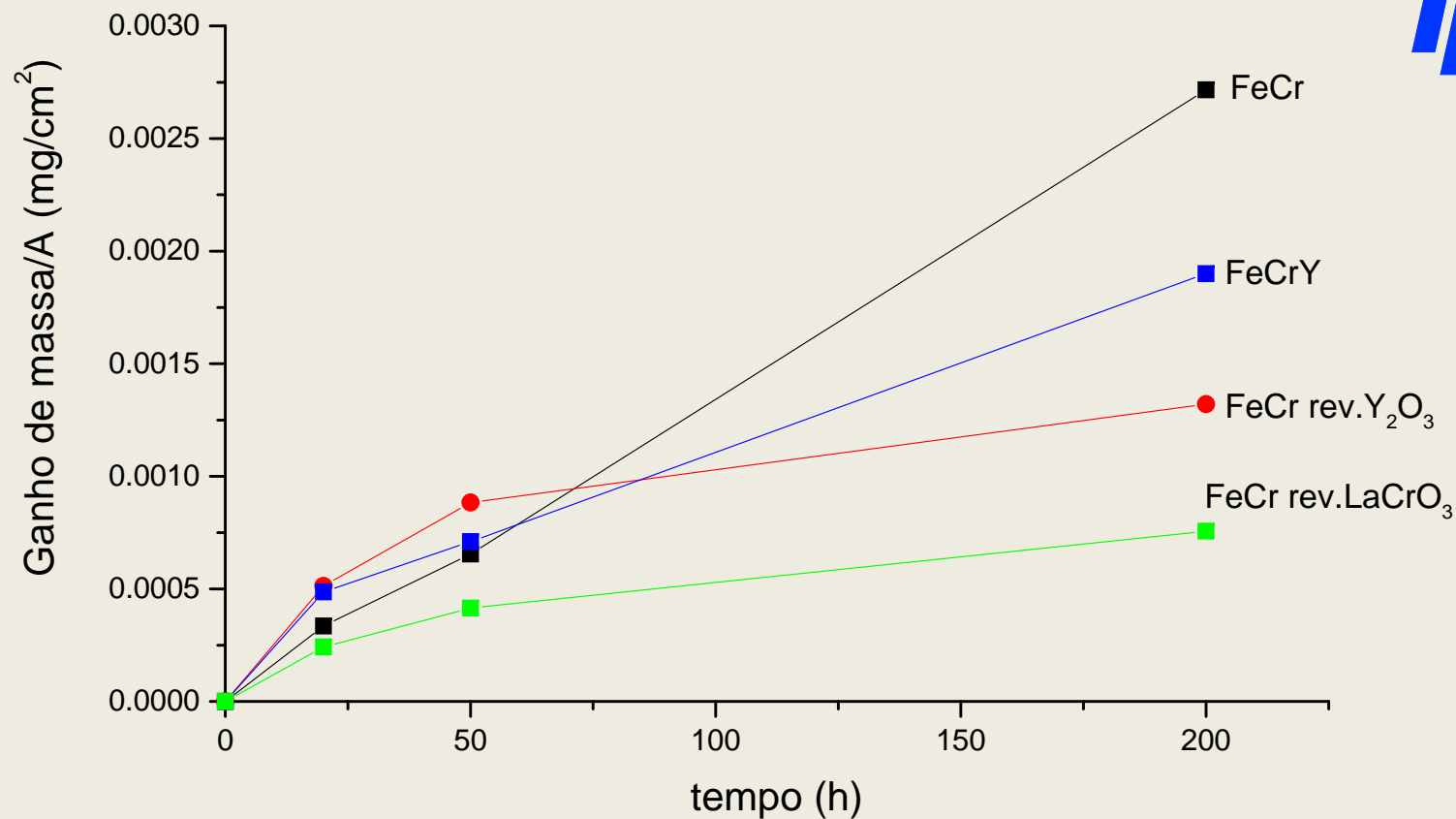
Isothermal oxidation curves at 1000°C of FeCr and FeCrAl



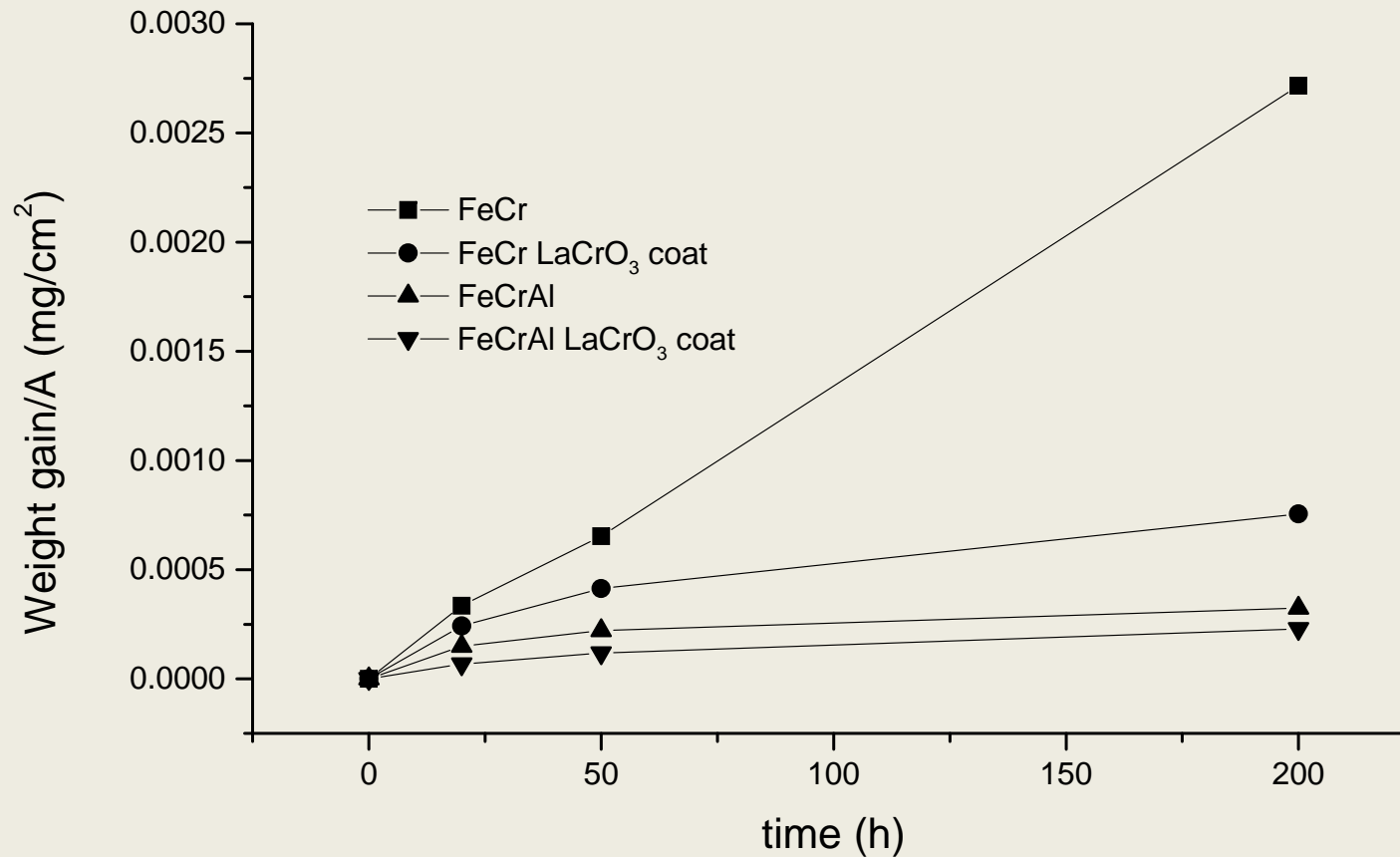
Isothermal oxidation curves at 1000°C of FeCrAl and FeCrAlY



Isothermal oxidation curves of FeCr, FeCrY and Y₂O₃ coated FeCr at 1000° C



Isothermal oxidation curves at 1000°C of FeCr, FeCrY, Y₂O₃ coated FeCr and LaCrO₃ coated FeCr.

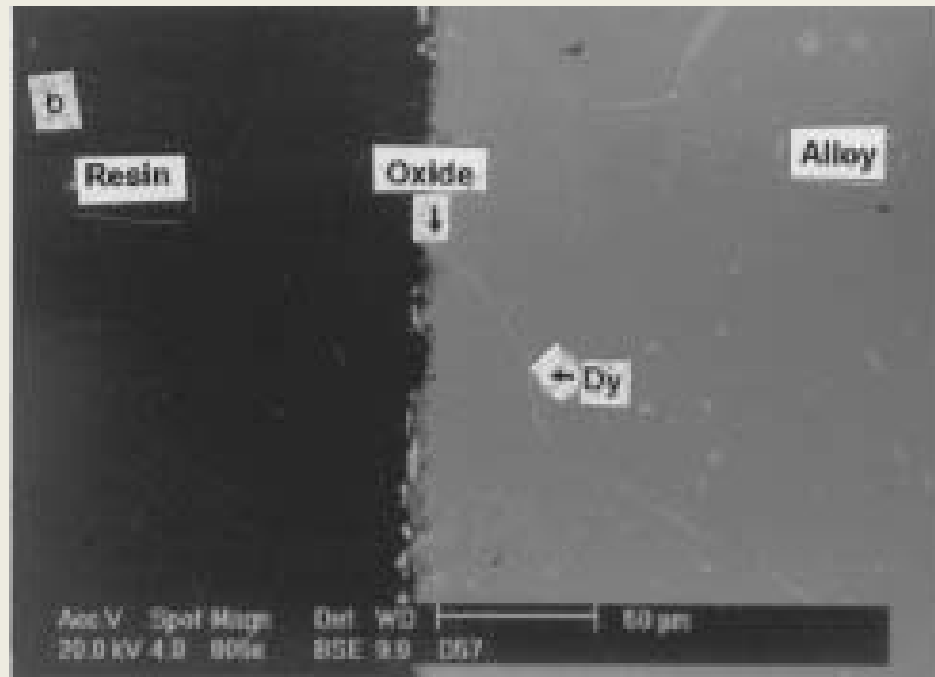


Oxidation curves of Fe-20Cr and Fe-20Cr-4Al with and without LaCrO₃ coating.

(M.F.Pillis and L.V.Ramanathan, *Mat. Res.* 7, 3, 279, 2007.)

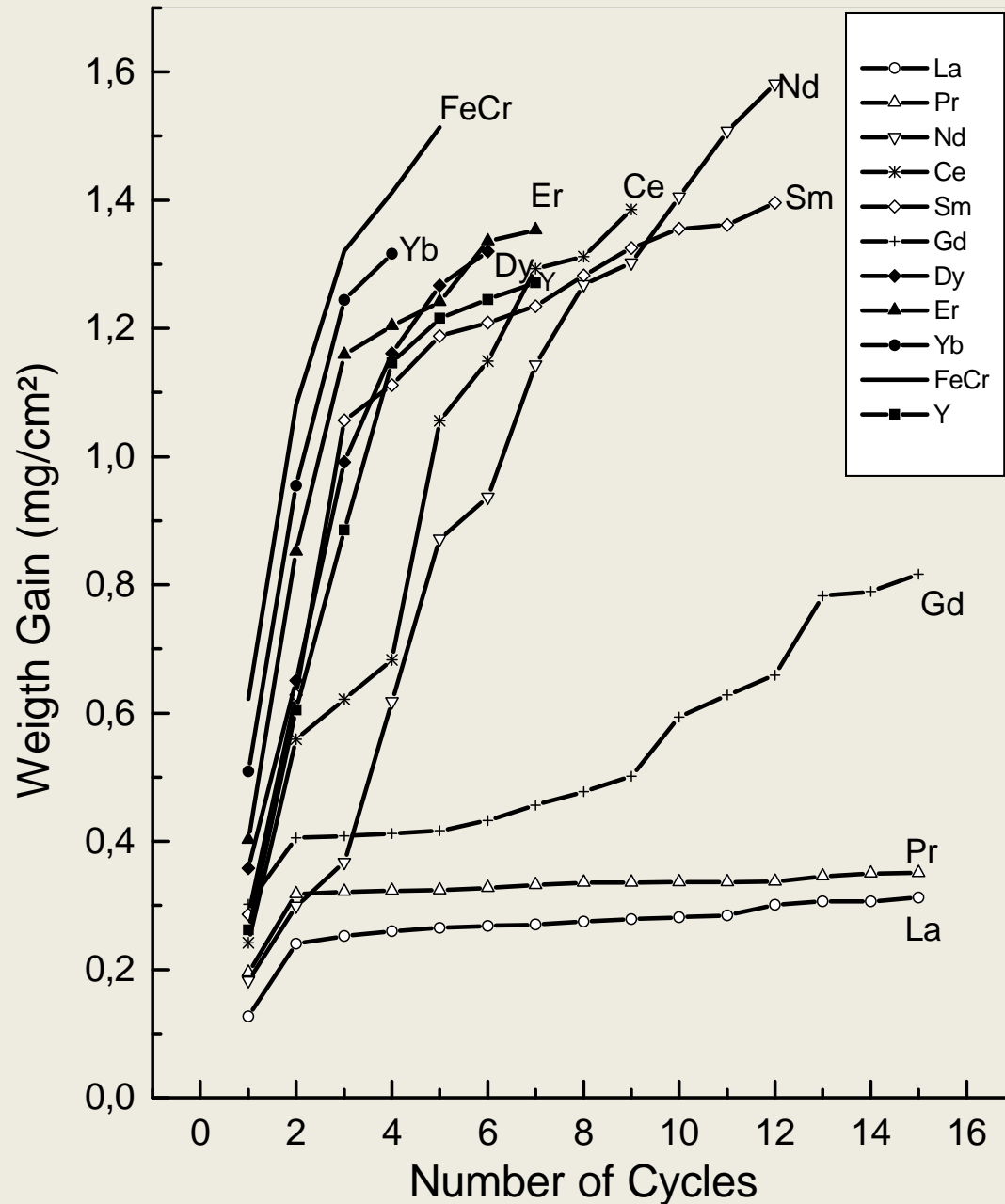
Parabolic rate constants (K_p) of the alloys oxidized at 1000°C

Alloy	K_p ($\text{g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$)
FeCr	1.31×10^{-11}
FeCrY	3.60×10^{-12}
FeCrAl	6.33×10^{-12}
FeCrAlY	6.24×10^{-13}



SE micrograph of cross-section of Fe-20Cr-0.5Dy oxidized at 1000°C for 40 hours

(S.M.C.Fernandes and L.V.Ramanathan, Surface Engineering, 16, 4, 327, 2000.)

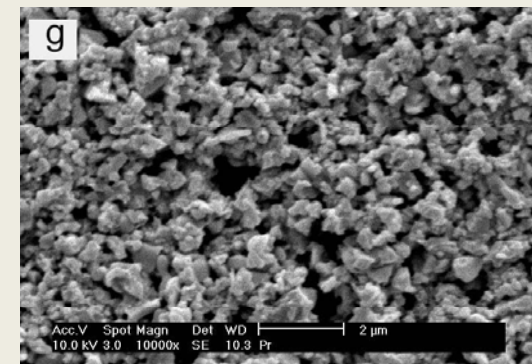
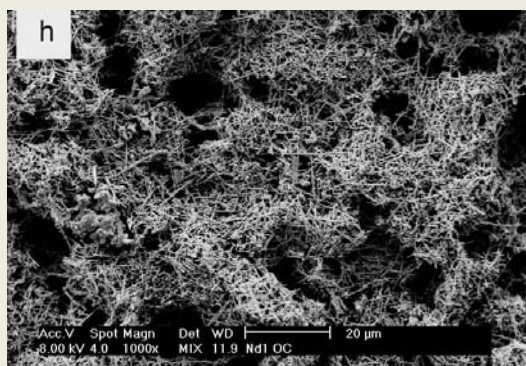
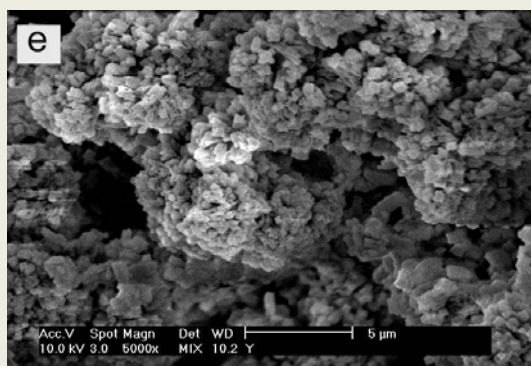
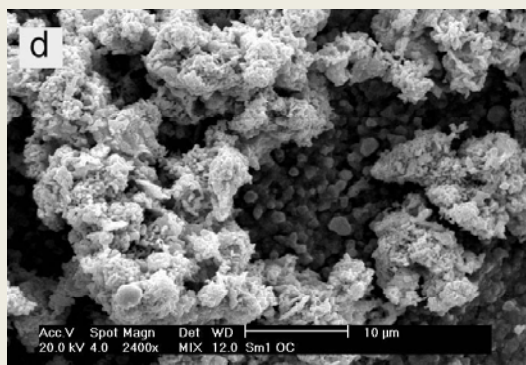
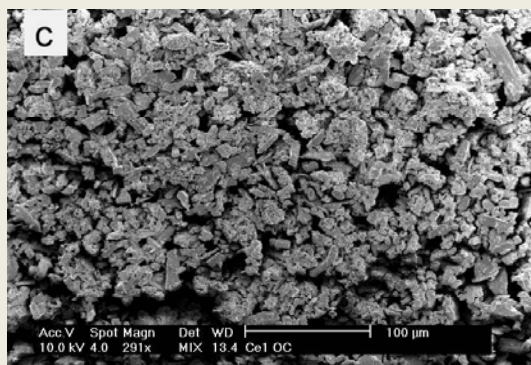
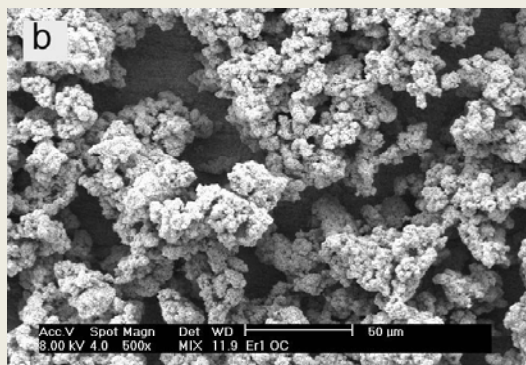
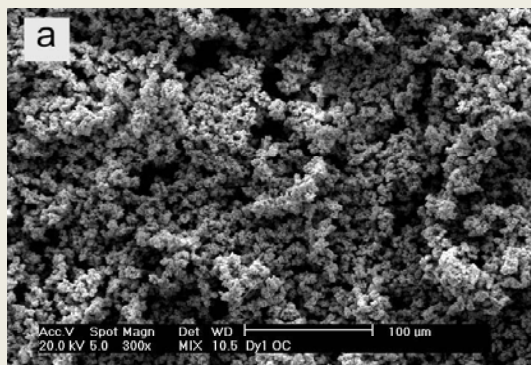


Cyclic oxidation behavior of RE oxide coated Fe-20Cr alloy. Each cycle 1000 °C – RT

(L.V.Ramanathan, M.F.Pillis, S.M.C.Fernandes, J. Mat. Sci., 43,2, 530, 2008)

Rare earth element	Number of cycles	R_{RE}/R_{Cr} ratio
Lanthanum	15	1.64
Cerium	9	1.60
Praseodymium	15	1.57
Neodymium	12	1.54
Samarium	12	1.50
Gadolinium	15	1.46
Dysprosium	6	1.42
Yttrium	7	1.39
Erbium	7	1.37
Ytterbium	4	1.34

Total number of cycles withstood by Fe₂₀Cr specimens coated with oxides of different rare earths and the ratios of the rare earth ion radius to the radius of chromium ion.



SE micrographs of different RE oxide gels. (a) Dy, (b) Er, (c) Ce, (d) Sm, (e) Y, (f) La and (g) Pr.

(S.M.C.Fernandes and L.V.Ramanathan, Mat. Res., 9,2,199,2006)



Main morphological feature of the rare earth oxides

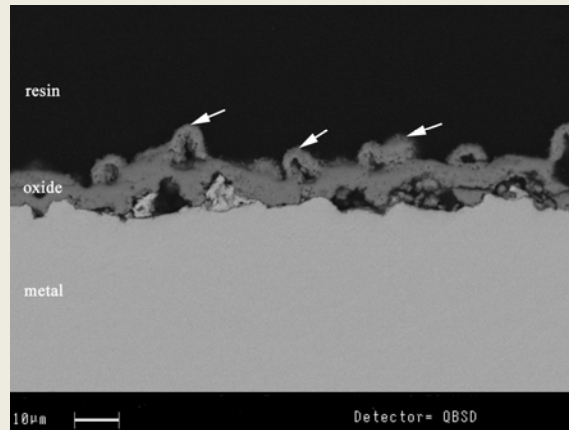
Rare earth oxide	Main morphological feature
Lanthanum	Cuboids
Cerium	Large cubes and rods
Praseodymium	Needle like
Neodymium	Fine needles, acicular
Samarium	Clusters
Gadolinium	Interlocking clusters
Dysprosium	Tiny clusters
Yttrium	Platelets
Erbium	Open clusters
Ytterbium	Clusters and disperse platelets



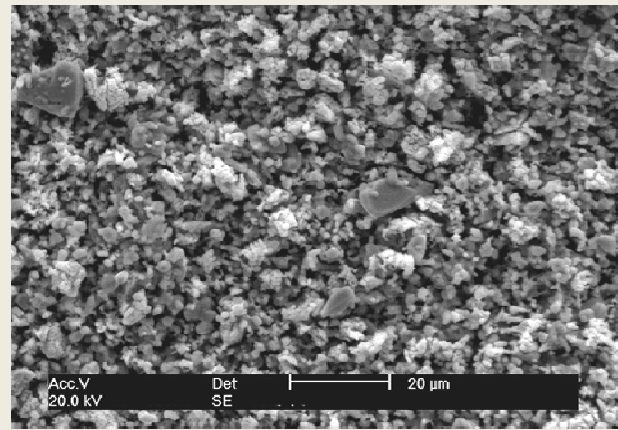
The cyclic oxidation behavior of RE oxide coated Fe-Cr and FeCrAl alloys depends on

- **the radius of the rare earth ion,**
- **the shape/size of the crystallite and**
- **the coverage.**

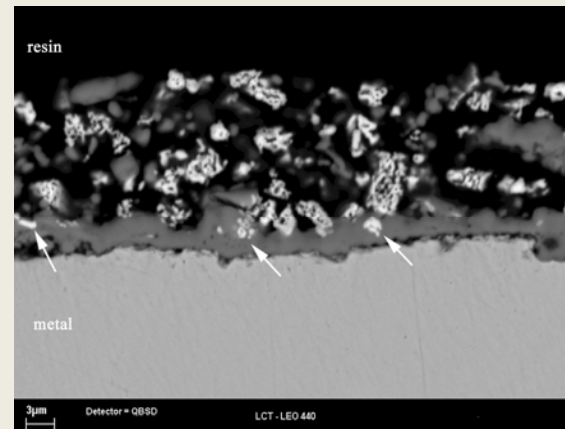
Coverage in turn depends on the size and shape of the RE oxide crystallite.



a



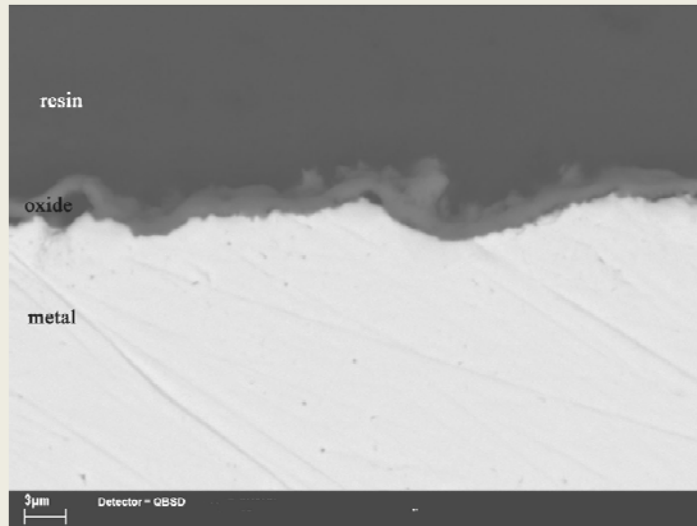
b



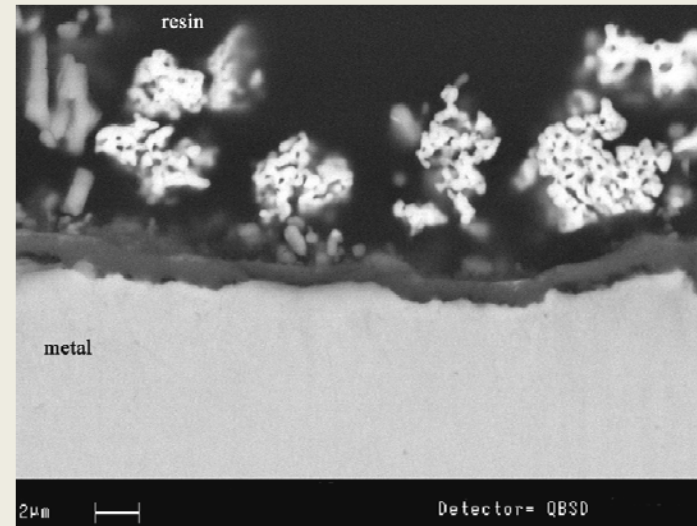
c

(a) Cross section of Fe-20Cr after 200h of oxidation at 1000°C; (b) Surface of LaCrO₃ coated Fe-20Cr after 200h of oxidation at 1000°C; (c) cross section of (b).

(M.F.Pillis and L.V.Ramanathan, Mat. Res. 7, 3, 279, 2007.)



a

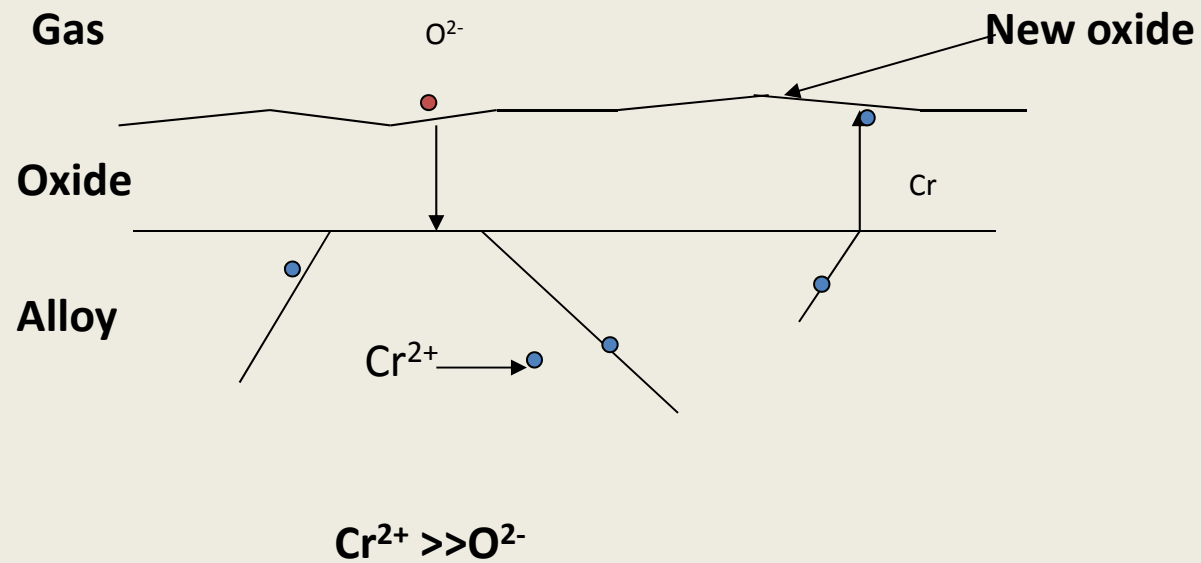


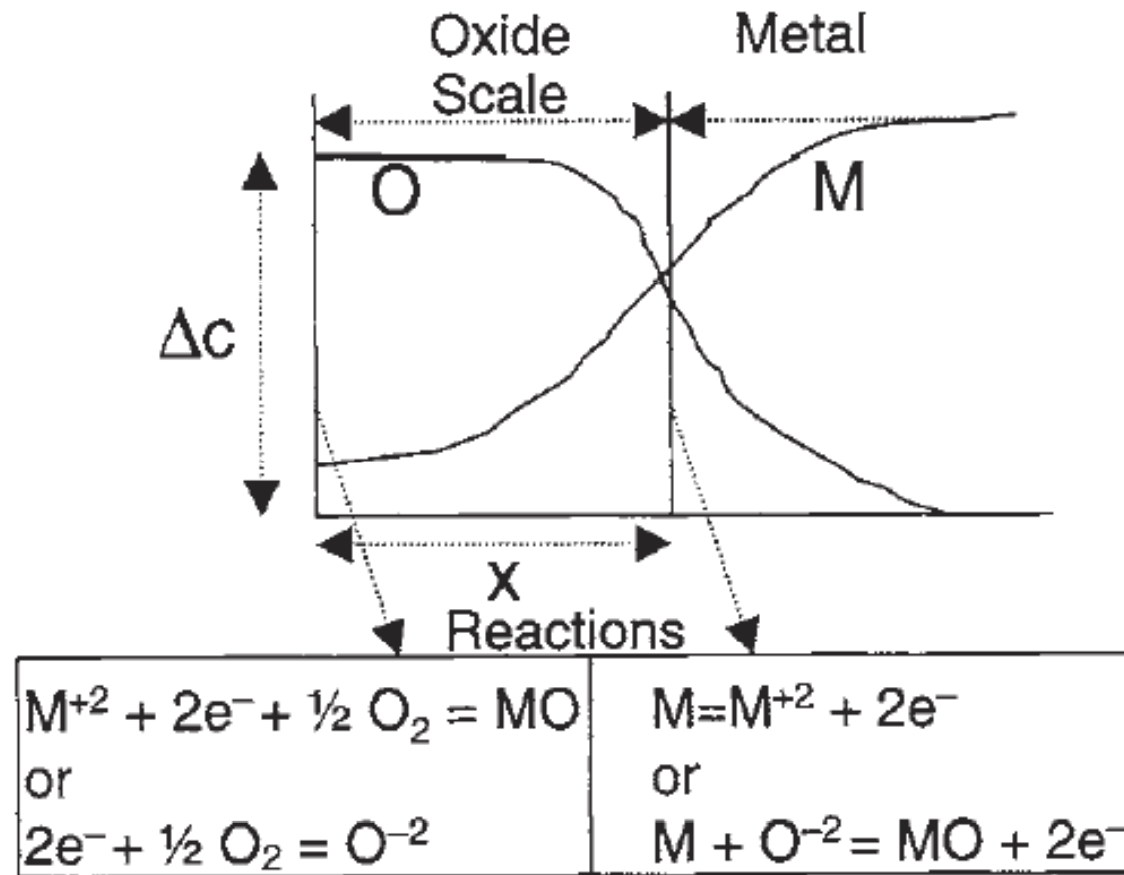
b

Cross section Fe-20Cr-4Al oxidized for 200 h at 1000°C. (a) uncoated; (b) LaCrO₃ coated.

(M.F.Pillis and L.V.Ramanathan, Mat. Res. 7, 3, 279, 2007.)

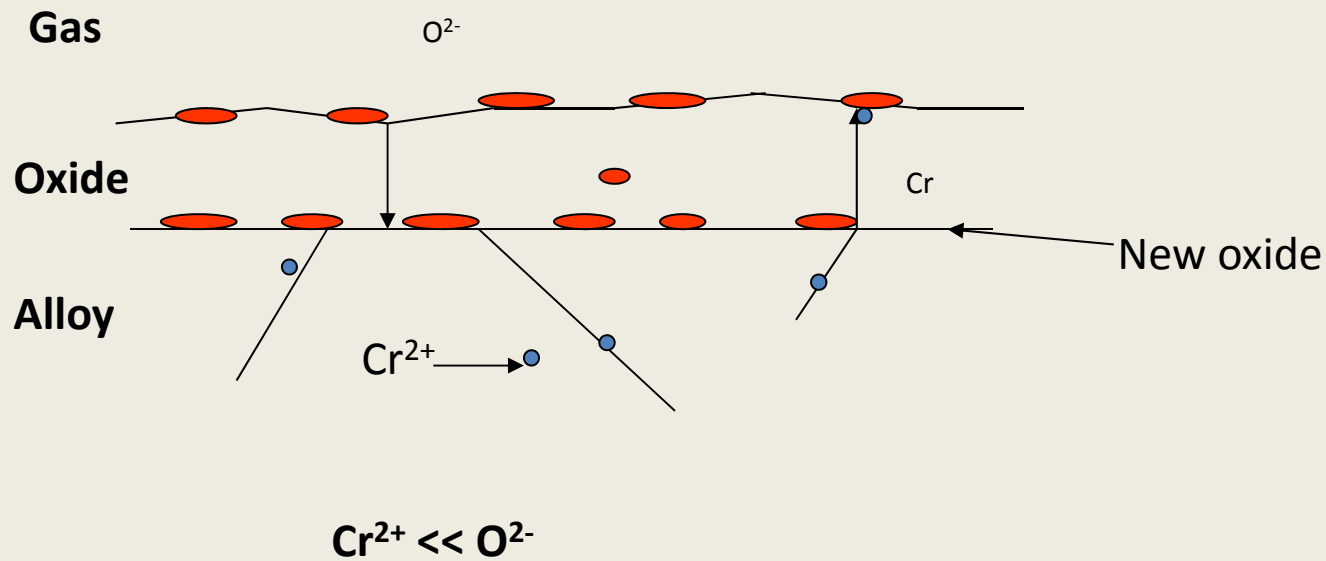
Scale formation on Fe-Cr alloy

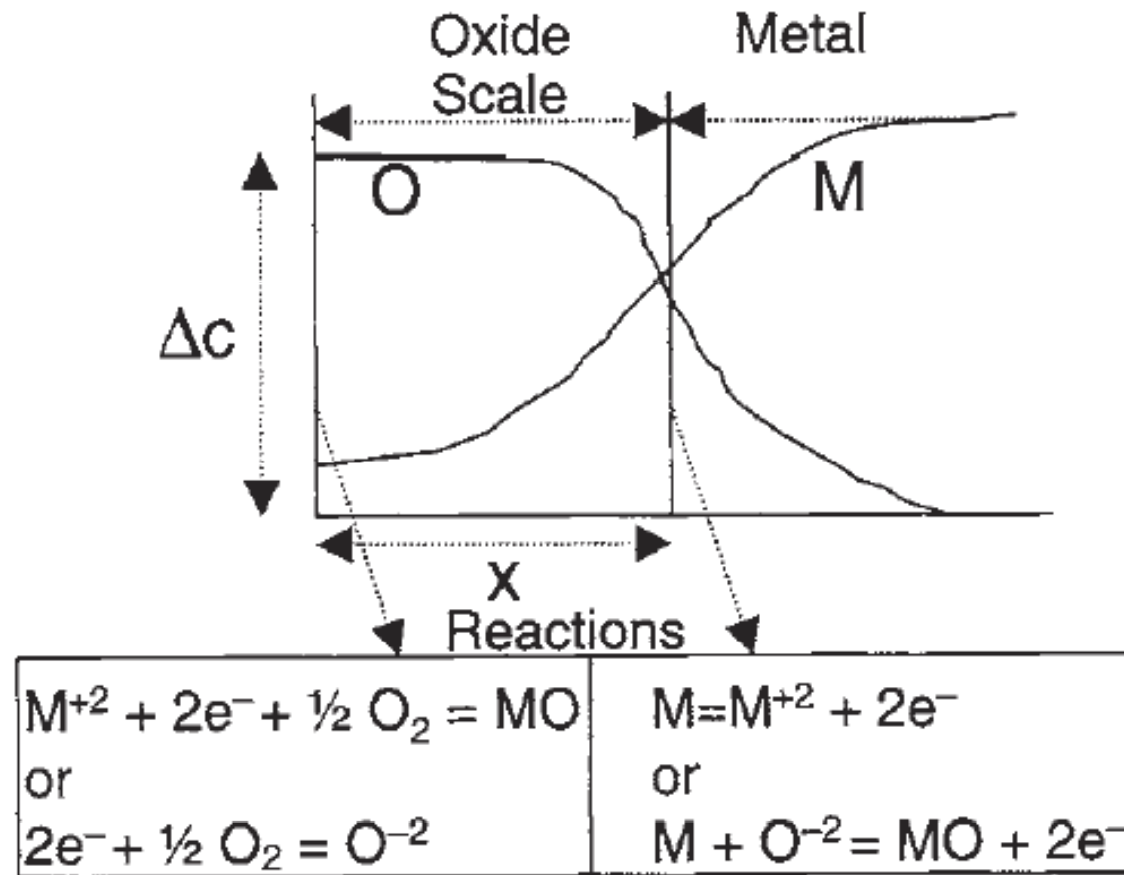




Diffusion profile for oxide scale growth

Scale formation on RE oxide coated Fe-Cr alloy





Diffusion profile for oxide scale growth



Overall, in chromia scales RE additions:

Increase oxidation resistance: i.e.

- (a) reduces scale growth rate (for steady state growth) by a factor of up to 10 or more;**
- (b) improves scale adhesion, fewer voids at alloy/scale interface**
- (c) reduces the chromium content necessary in the alloy to form a continuous chromia scale, from 20-35% to 10-13%Cr;**
- (d) changes the scale growth mechanism;**
- (e) reduces scale thickness and grain size;**
- (f) improves selective oxidation.**

Mechanism



The dynamic segregation model proposed to account for these beneficial effects.

Reactive elements present in the alloy diffuse into the scale due to the oxygen potential gradient which extends from the gas interface into the substrate.

The RE diffuses through the oxide to the gas interface.

En-route to the gas interface the RE ions first segregates to the metal-scale interface.

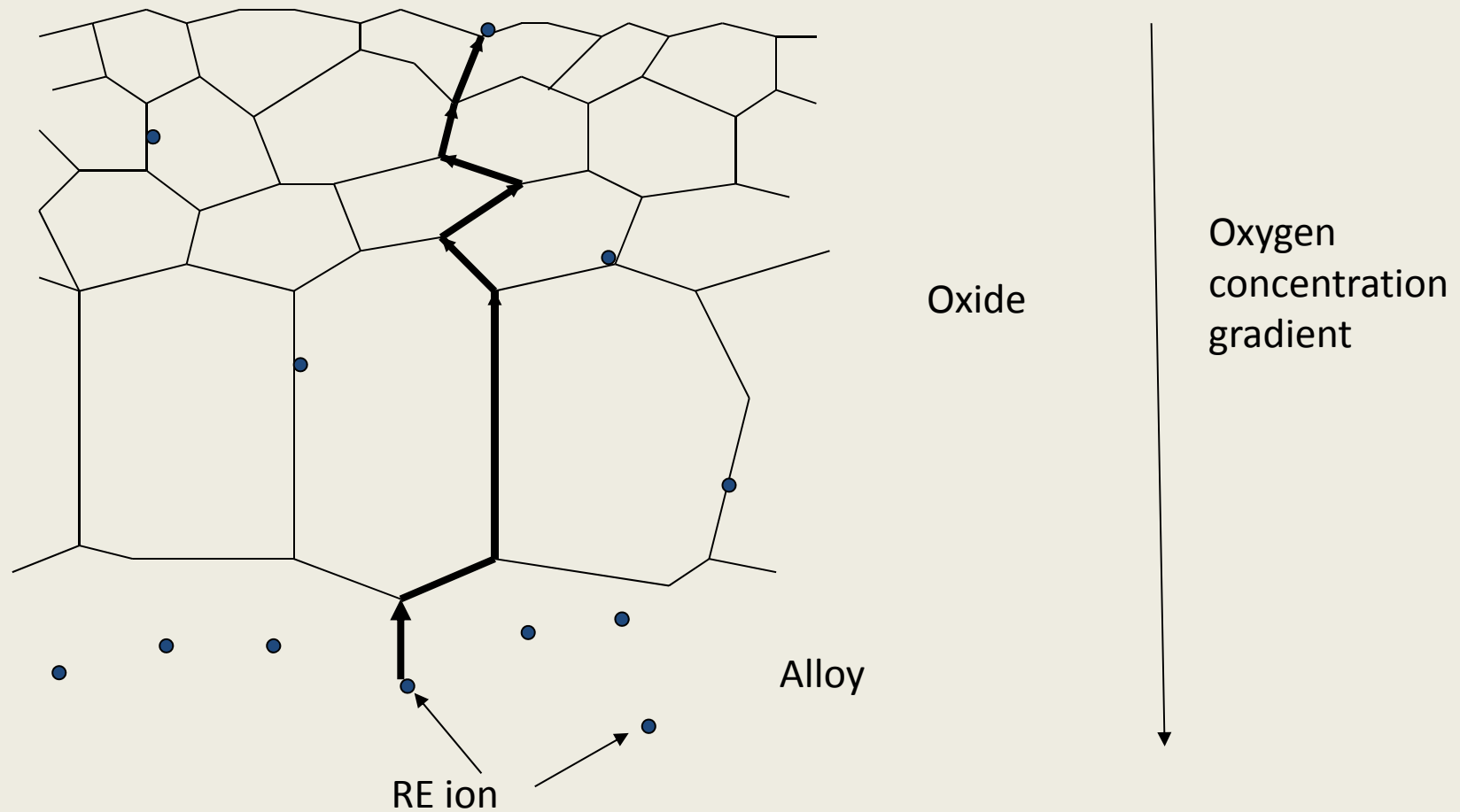
At this point, the outward diffusing RE ions then follow the fastest path to the gas interface - the scale grain boundaries.

The large RE ions diffuse more slowly than Cr or Al and thus inhibit the normal outward short-circuit transport of cations along the scale grain boundaries.

Larger the RE ion slower is its outward diffusion.

The new rate-limiting step is the inward transport of O ions along the scale grain boundaries.

The mechanism



RE ions diffuse out along scale grain boundaries.

(L.V.Ramanathan, M.F.Pillis, S.M.C.Fernandes, J. Mat. Sci., 43,2, 530, 2008)

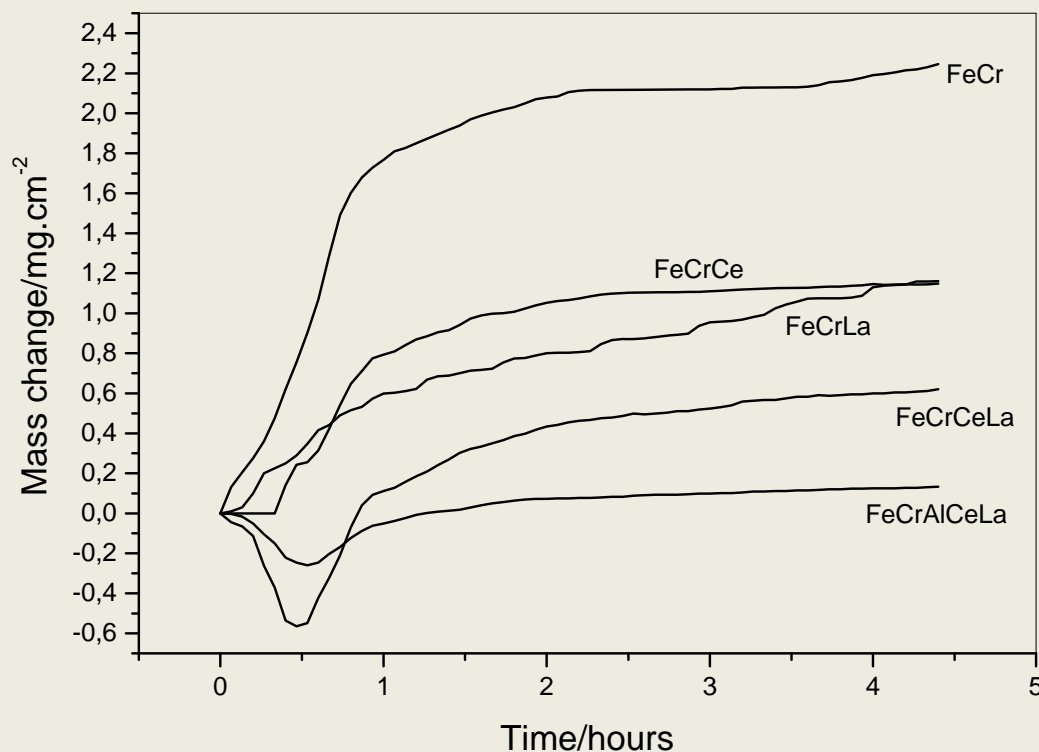


Since cation to anion transport ratio is higher in alpha-chromia, inhibiting cation transport has a much greater effect on parabolic rate constant of chromia formation than on alpha-alumina.

As observed,

in chromia, the reduction is typically 10-100x while for alumina, the reduction is only approximately 2-4x.

Optimization of rare earth additions



Isothermal oxidation curves of uncoated, CeO₂ coated, La₂O₃ coated and CeO₂ + La₂O₃ coated Fe₂₀Cr as well as CeO₂ + La₂O₃ coated Fe₂₀Cr₅Al at 1000 °C.

(S.M.C.Fernandes, O.V.Correa and L.V.Ramanathan, J. Thermal Analysis and Calorimetry, 106, 541, 2011.)

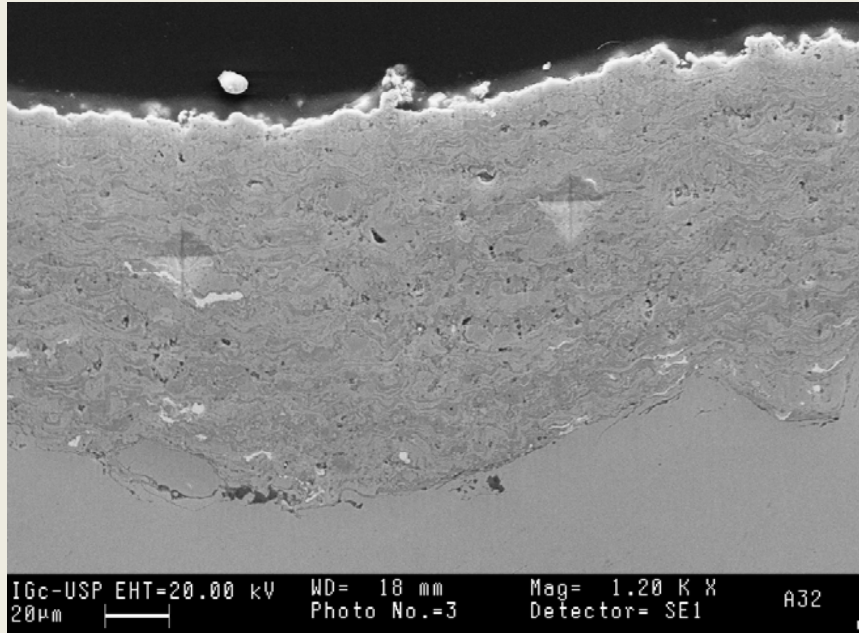


Nanostructured coatings

Chromium carbide and tungsten carbide

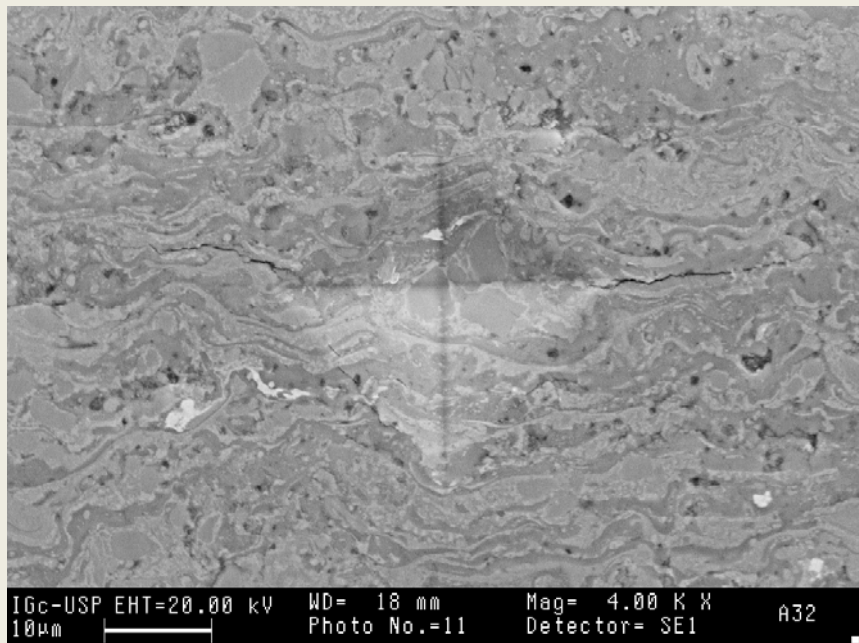
Cr_3C_2 -Ni20Cr coatings used to protect components against oxidation and wear.

Nanostructured Cr_3C_2 -NiCr coatings prepared by HVOF.



(a) Nanostructured coating layer - uniform;

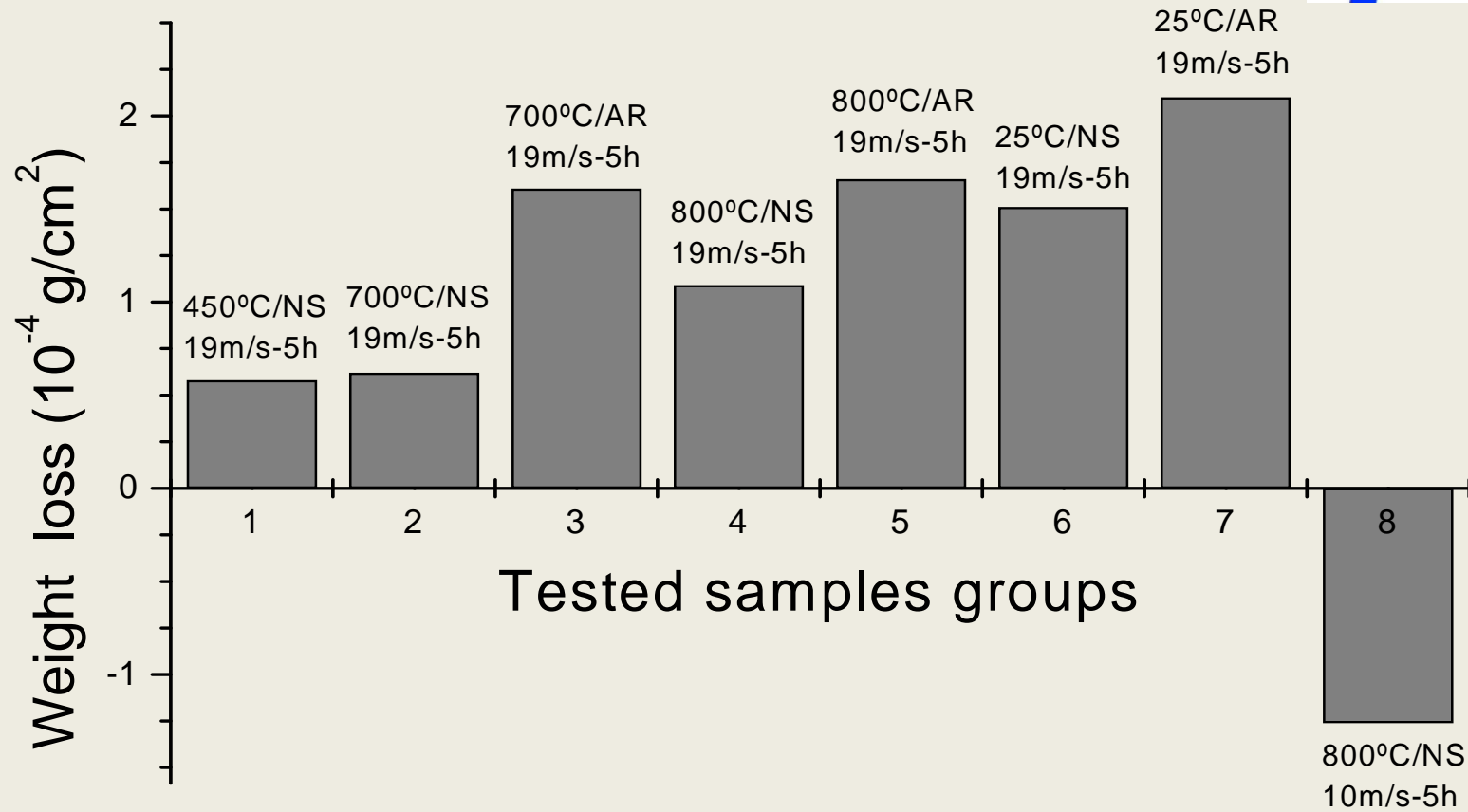
(b) same coating showing cracks emanating from the indent.





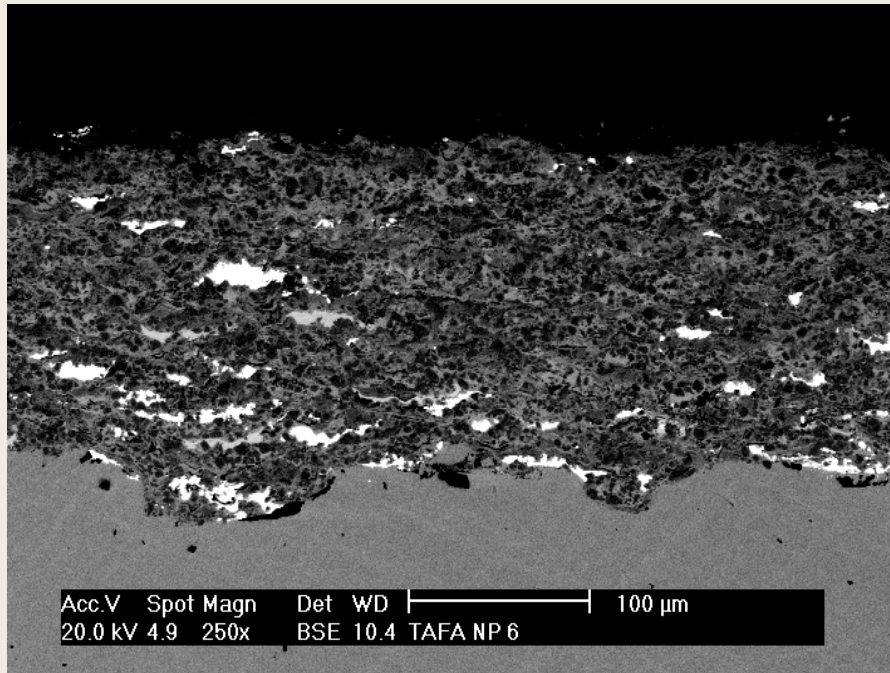
**Vickers hardness, Young modulus and fracture toughness of
Cr₃C₂-Ni20Cr coatings**

Condition	HV (GPa)	E (GPa)	K_{IC} (MPa m^{1/2})
Conventional	7.97	172.29	1.77
Nanostructured as-sprayed	10.37	223.40	2.23
Nanostructured oxidized	10.79	232.35	2.41

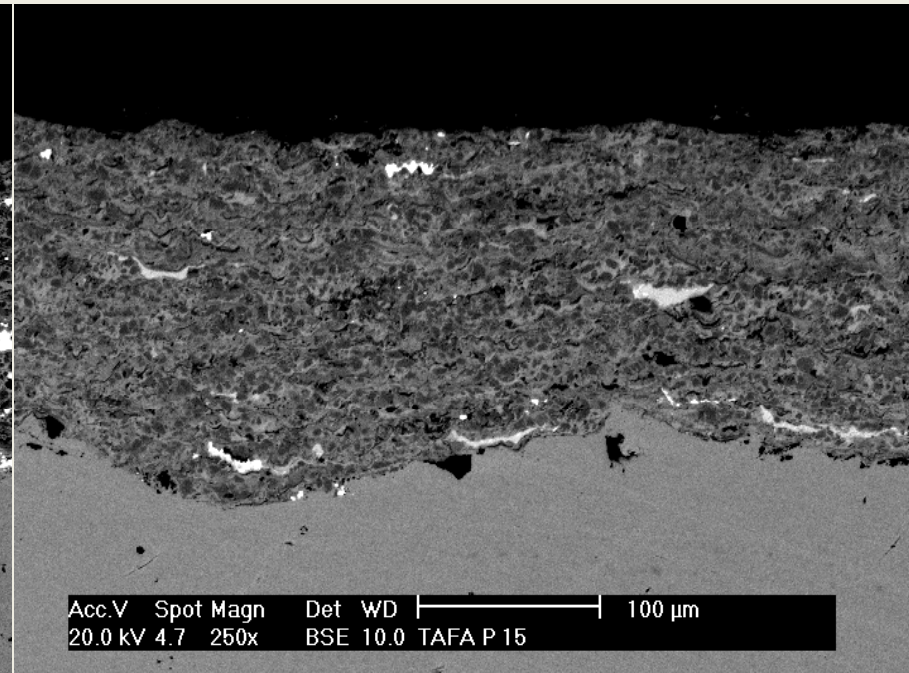


Erosion-oxidation resistance of $\text{Cr}_3\text{C}_2\text{-Ni20Cr}$ coatings

Chromium carbide coatings



As-received powder

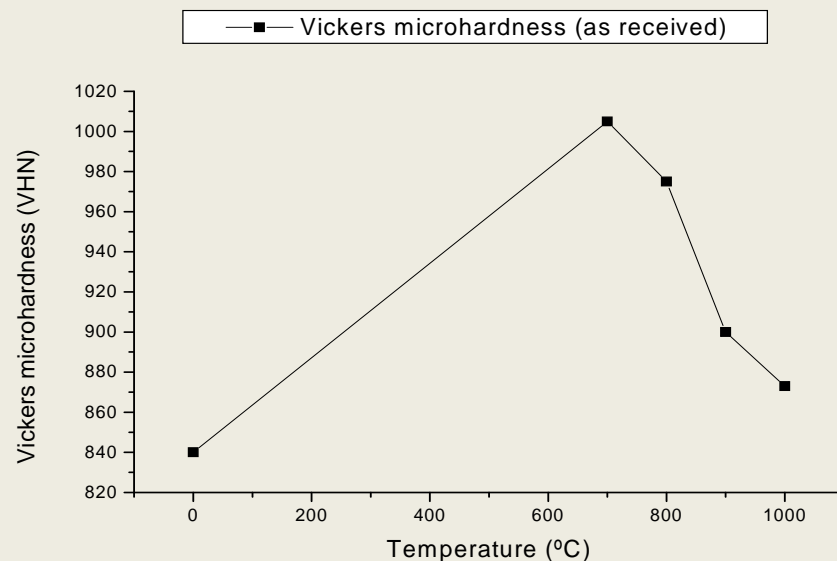


Nanocrystalline powder

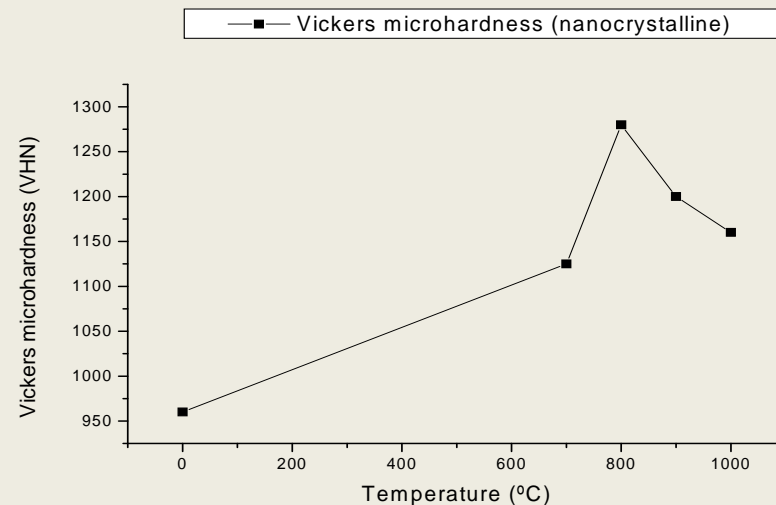
(C.A.Cunha, N.B.de Lima, J.R.Martinelli, A.H.de A.Bressiani, A.Padial and L.V.Ramanathan, Materials Research, 11, 2, 137, 2008.)



The thermal stability of $\text{Cr}_3\text{C}_2\text{-20(Ni20Cr)}$ coatings determined in terms of hardness variation as a function of heat treatment temperature.



AS RECEIVED



NANOSTRUCTURED

(A.Padial, C.A.Cunha, O.V.Correa, N.B.de Lima and L.V.Ramanathan, *Mat. Sci.Forum*, 660-661, 379, 2010.)



Challenges and needs

- **Develop a consistent approach through thermochemical modeling** to achieve and use data for coatings corroding in diverse conditions and by different mechanisms;
- Create a database to manage data on corrosion of metals, alloys and coatings in complex HT gases;
- Create an information system that can be applied to coating failure on equipment, coating material evaluation and eventually select cost effective coatings and coating techniques;
- **Develop guidelines to optimize coating design and process economics;**
- **Expand mechanical property data of various coating systems** to model coating mechanical stability and eventually predict in-service behavior.

(L.V.Ramanathan, Editorial - Surface Engineering, 23, 4, 2007)



Challenges and needs (contd)

- **Develop predictive degradation models for coatings under cyclic oxidation conditions in many other environments.**
- Consider economy in preparing coatings as a challenge.
- Develop new techniques to apply well established coatings that form alumina or chromia.
- **Reduce deposition temperatures** - substrate less likely to be degraded; lower residual stresses between dissimilar substrates and the coat materials.
- **Exploit use of nano-structured and functionally graded coatings** for HT oxidation resistance.
- Create a data base by obtaining long term corrosion rates in pilot plant or commercial size plants.



- **Challenges and needs (contd)**
- Acquire and/or expand in-depth knowledge of the physical and chemical properties of coatings to drastically reduce time required to develop new coatings. Properties include crystalline orientation, chemical composition, stress levels, interface integrity, impurity content etc. A variety of new techniques are available to determine these parameters.
- **Consider inclusion of other rare earth elements** (besides Y) to control chromia/alumina growth.
- The mechanical failure of scales has still not been adequately modeled. This is essential to eventually predict long term stability of oxide layers.



Challenges and needs (contd)

Thermal Barrier Coating

Modelling of coating reliability.

Modelling of life-prediction of TBC.

Study TBC - bond coat interface hydrogen embrittlement that leads to delayed spallation in moist environments.

Further development of more reliable TBCs that do not crumble under stresses produced by CTE mismatch between the coating layers.

Address the problem of oxidation of the substrate under an applied coating of alumina after extended exposure to elevated temperatures.

Develop non-destructive evaluation techniques to monitor the status and remaining life of the TBCs.



Existing know-how about coatings

Although extensive

Still needs to be expanded



Acknowledge the contributions of many of my colleagues and students over the years. Their data and many more from our publications were used in this presentation



I am grateful for the financial support from CNPq and FAPESP, to carry out many projects on this topic and to present the results at many conferences, including this meeting.



Thank you