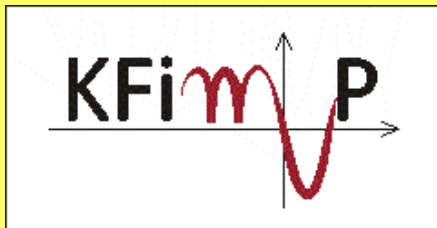


DESIGN STRATEGIES FOR NEW OXIDATION-RESISTANT HIGH TEMPERATURE ALLOYS

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Introductory remarks

There is always a need for new oxidation-resistant high temperature alloys because of the continuous push for higher service temperatures and longer component lifetimes. While there is always the possibility of a revolutionary alloy development, the periodic table is finite and the more realistic near-term prospects for improved alloys focus on Fe- and Ni-base compositions which develop protective external oxides or scales of Al_2O_3 , Cr_2O_3 or SiO_2 .

Chromia-forming alloys – alloy development

The most widely used high temperature alloys are Fe- or Ni-base alloys that form protective chromia-scales during exposure. Because of the long history of research in this class of materials, the possibility of developing new alloys is somewhat limited.

A general concept in developing oxidation resistant alloys is to increase the concentration of the protective scale forming element, i.e. Cr. However, higher Cr contents often lead to problems with phase stability (e.g. formation of brittle Cr-rich phase) or decrease in creep strength.

For coating applications, Cr contents can go as high as 53% with remainder Ni.

Chromia-forming alloys – alloy development

One area where there is considerable current interest in chromia-forming alloys is for metallic interconnectors for solid oxide fuel cells. For this application, a key figure of merit is the electrical conductivity of the external scale. This criterion excludes alumina and silica scales which are too insulating.

Chromia-forming alloys – materials for interconnectors

A commercial ferritic Fe-24Cr-0.4Mn-0.07Ti-0.004La (22APU alloy) has been developed for fuel cells.

The Cr content is likely restricted to 24% because of concern about embrittlement by sigma phase formation. However, the most critical design issue is the selection of the minor alloying additions of Mn, Ti and La:

- La is a typical reactive element addition, which reduces the scale growth rate and improve scale adhesion. The addition of La has slightly negative effect on scale electrical conductivity.
- Ti and Mn synergistically act to increase the scale conductivity more than Mn additions alone. Another role of Mn addition is to form a (Mn,Cr)-rich outer layer decreasing the volatility of Cr containing compounds that poison the fuel cell performance.

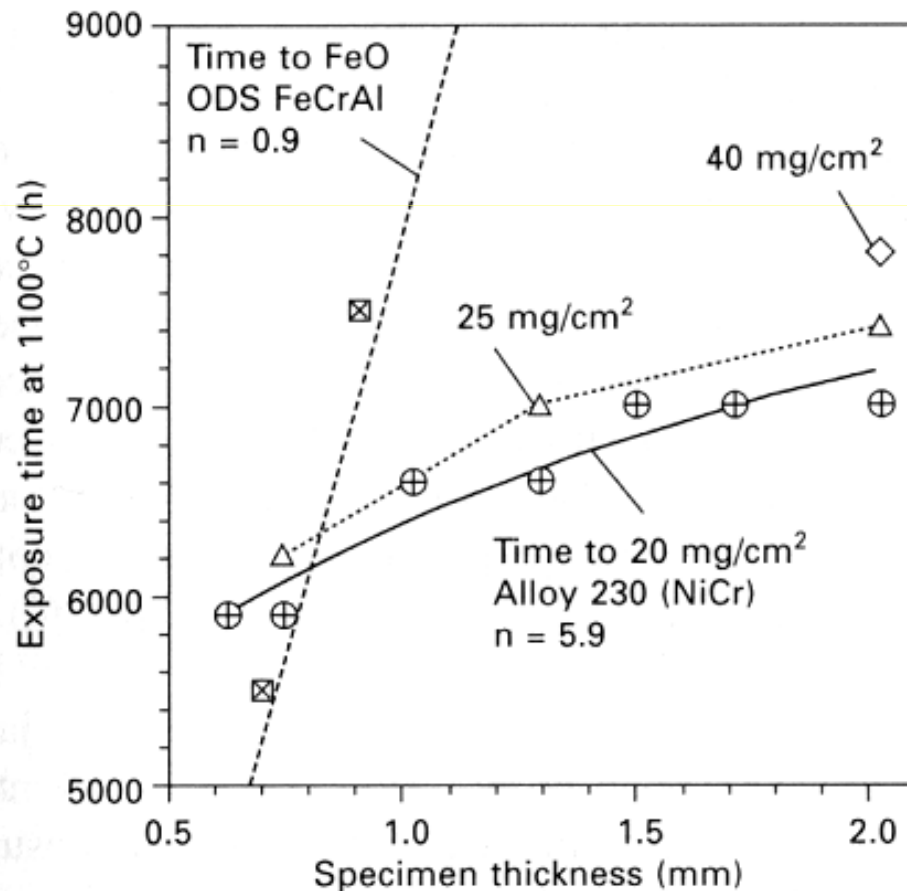
Life-time of 22APU alloy with 0.3 mm in thickness for 800 °C equals about 100 000 h.

Chromia-forming alloys – materials for interconnectors

Another issue for interconnectors is matching the coefficient of thermal expansion (CTE) of the other fuel cell components. This subject was addressed for Fe-Cr-W and Fe-Cr-Mo alloys. The lowest CTE was observed for Fe-20Cr-3W. However alloy cost with 20%Cr and 3%W may be prohibitive.

Problems with chromia-forming alloys

It is difficult to use chromia-forming alloys for future applications under higher temperatures ($> 1000\text{ }^{\circ}\text{C}$) and longer lifetimes ($\sim 40\text{ kh}$). Among many commercial alloys without Al addition, the alloy 230 (Ni-27Cr-4W + La) has the slowest oxidation rate in air.



$T = 1100\text{ }^{\circ}\text{C}$
1 cycle = 100 h

Conclusions:

- Alloy 230 will not make the 40 kh lifetime goal.
- ODS FeCrAl lifetime of the 40 kh can be reach by $\sim 4\text{ mm}$ thick elements.

Problems with chromia-forming alloys

Explanation of results presented in the previous slide.

Different behavior of both alloys results from rapid diffusion of Al in ferritic alloy and slower diffusion of Cr in the austenitic Ni-base alloy, what creates Cr depletion gradient, disabling formation of protective chromia scale. Faster diffusion of Cr in ferritic (Fe-Cr) alloys appears to eliminate this problem at 800-900 °C and likely results in longer lifetimes, but these alloys have not been investigated at 1100 °C.)

Problems with chromia-forming alloys

In addition to the temperature limitation, chromia-forming alloys suffer problems at lower temperatures due to the presence of water vapor in the environment, which accelerates corrosion rate. Prior to accelerated attack significant Cr depletion occurs in the alloy. It is believed that this effect is a result of evaporation of $\text{CrO}_2(\text{OH})_2$.

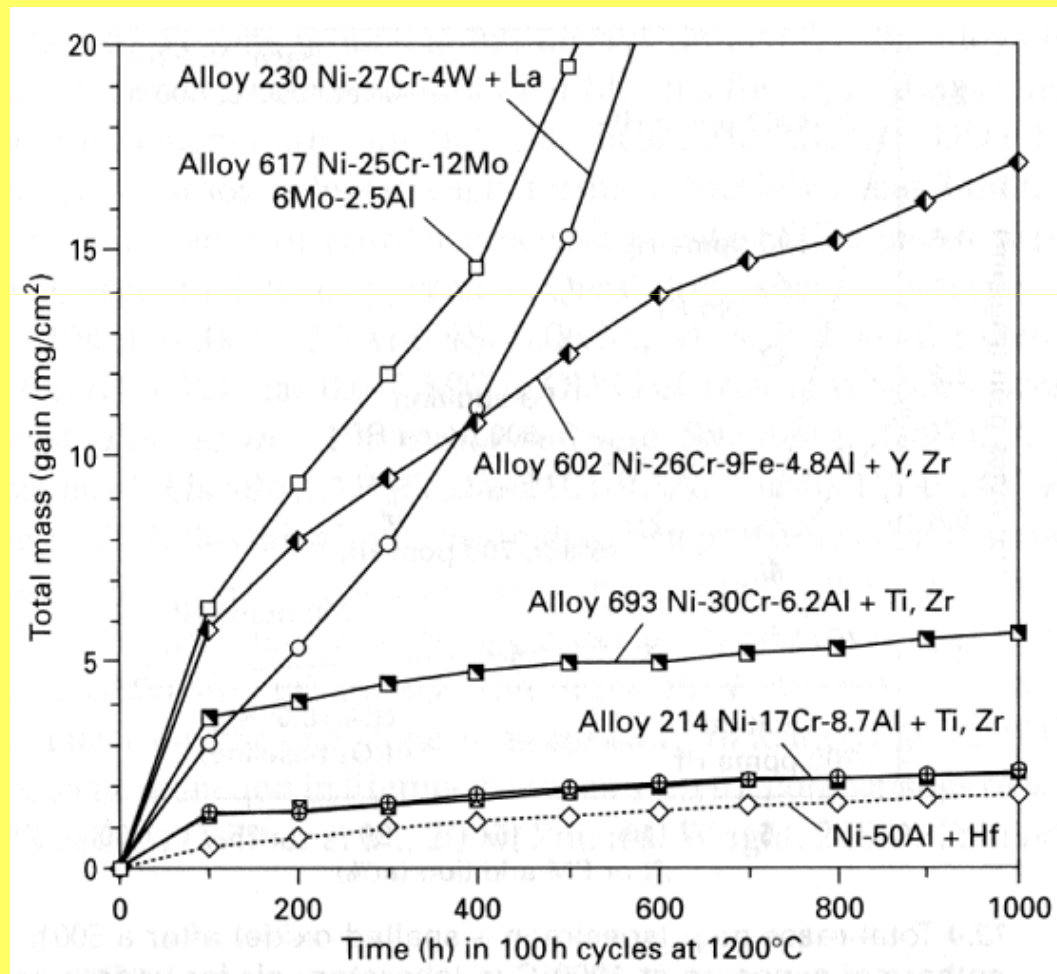
Alloy	Starting (at%)				
	Cr	Mn	650°C	700°C	800°C
Alloy 709 (lab)	21.6	1.0	-1.7 ± 1.1 at% 92 ± 5%	-2.4 ± 0.9 at% 89 ± 4%	-10.5 ± 0.4 at%* 51 ± 2%
Alloy 120 (lab)	26.4	0.7	-1.6 ± 0.3% 94 ± 1%	-2.4 ± 0.5% 91 ± 2%	
Alloy 120 (comm)	26.4	0.7		-2.1 ± 1.1% 92 ± 4%	-12.4 ± 0.3 at% 53 ± 1%
Fe-22Cr-20Ni + Mn (lab)	22.2	3.8	-2.0 ± 0.2% 91 ± 1%	-3.3 ± 0.2% 85 ± 1%	
Alloy 625 (lab)	26.0	0.04	-1.6 ± 1.0% 94 ± 4%	-2.9 ± 0.5% 89 ± 2%	-6.0 ± 1.0 at%* 77 ± 4%

*After only 6 kh.

Residual Cr remaining and amount consumed (at%) for various 100 μm thick foils oxidized in humid air for 10 kh.

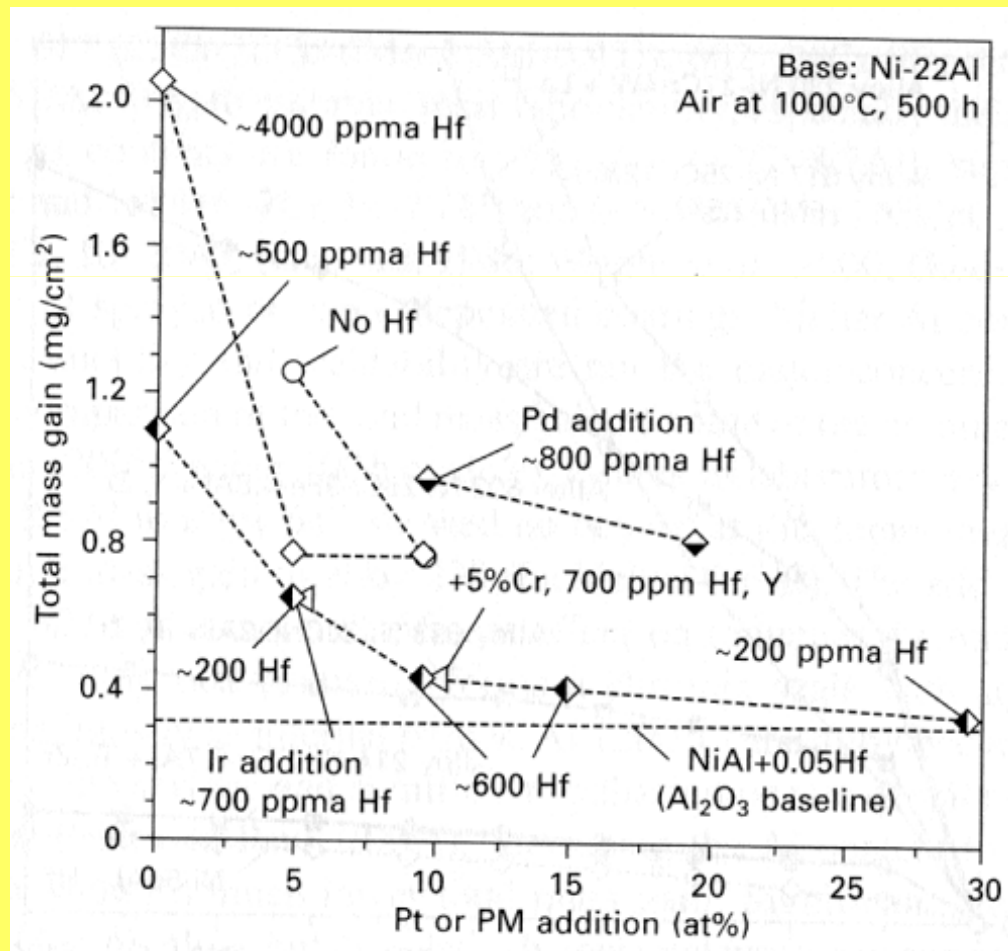
Alumina-forming alloys: Ni-base alloys

Small amounts of Al (2-3 %) are added to NiCr alloys to maintain their fabricability, especially their weldability. Higher Al contents (> 5%) are used for growth stimulation of highly protective Al_2O_3 scale.



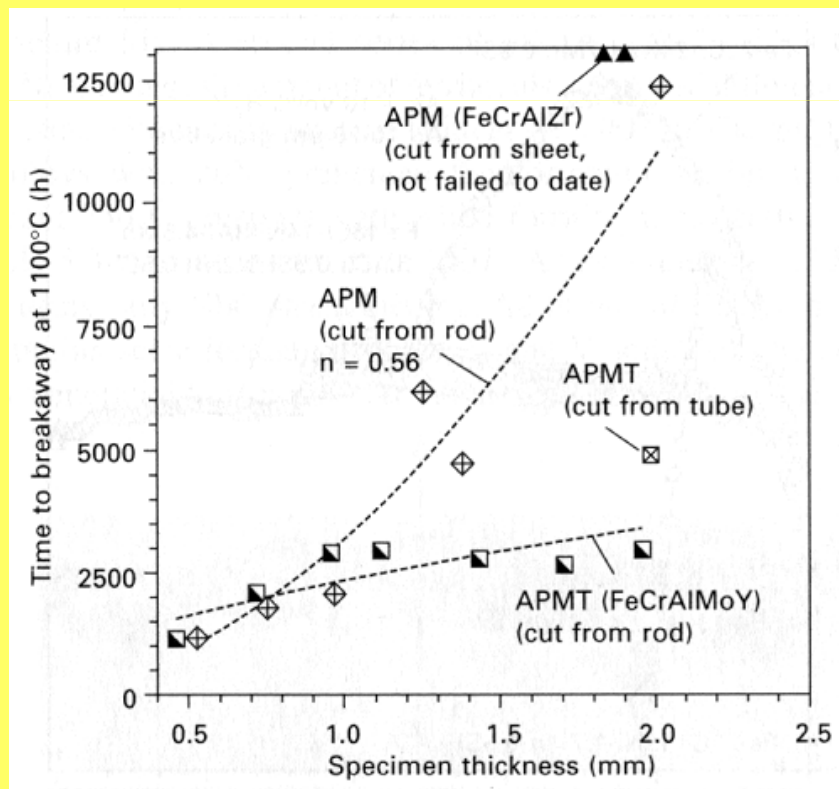
Alumina-forming Ni-base alloys – the effect of a platinum group metal (PGM)

The addition of a PGM such as Pt, Ir, Pd, etc. reduces the transient formation of Ni-rich oxide and makes the alloy a primary alumina-former.



Alumina-forming alloys: Fe-base alloys

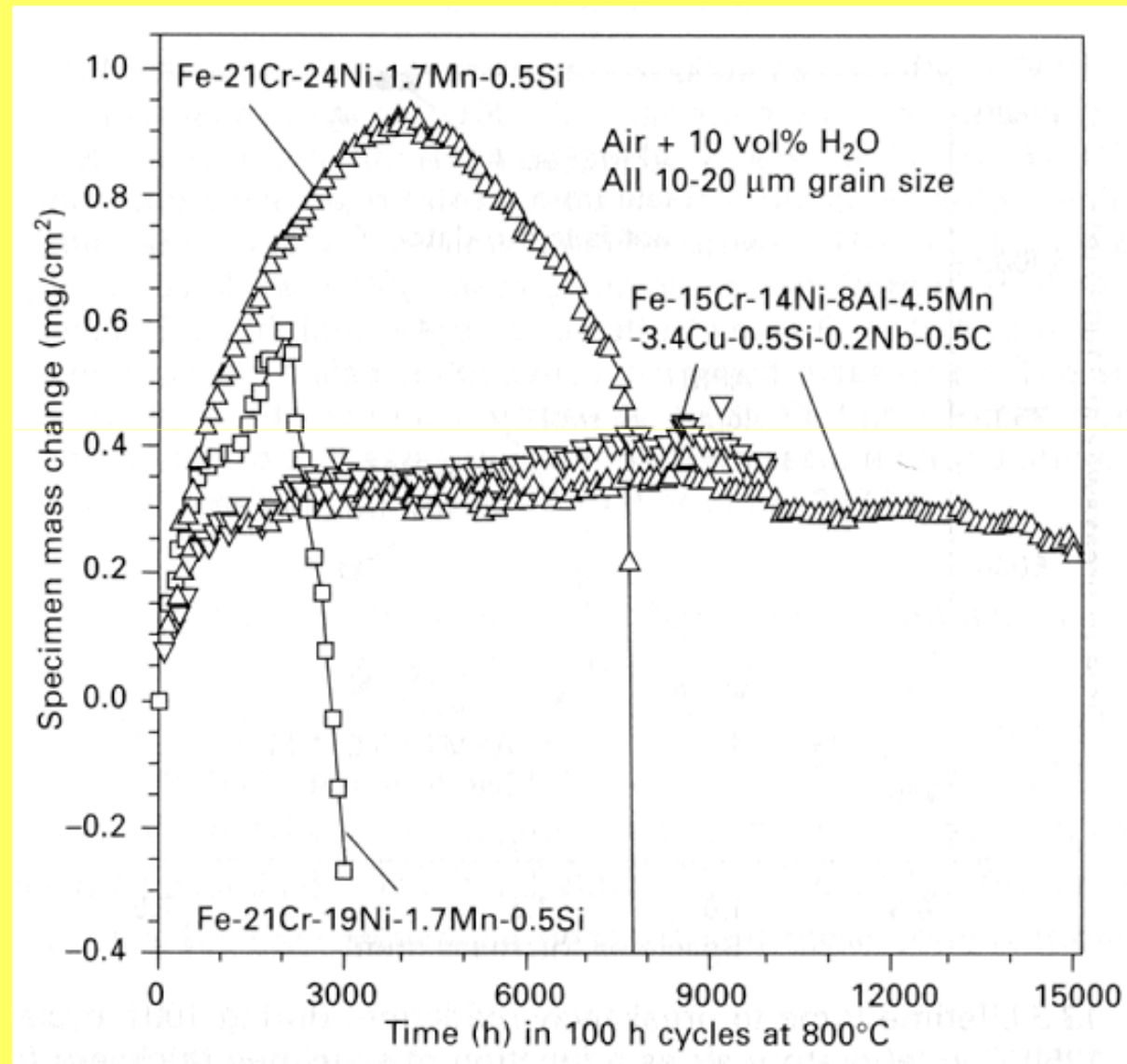
Properties of FeCrAl alloys are studied for over 40 years, due to their high oxidation resistance. Intermetallics (Fe_3Al , FeAl) can also form highly protective Al_2O_3 scale, but they exhibit scale spallation due to their high CTE, which limit their lifetime. Application of ferritic alloys is also limited by their poor creep strength. On the other hand, ODS FeCrAl alloys constitute some solution of this difficult situation.



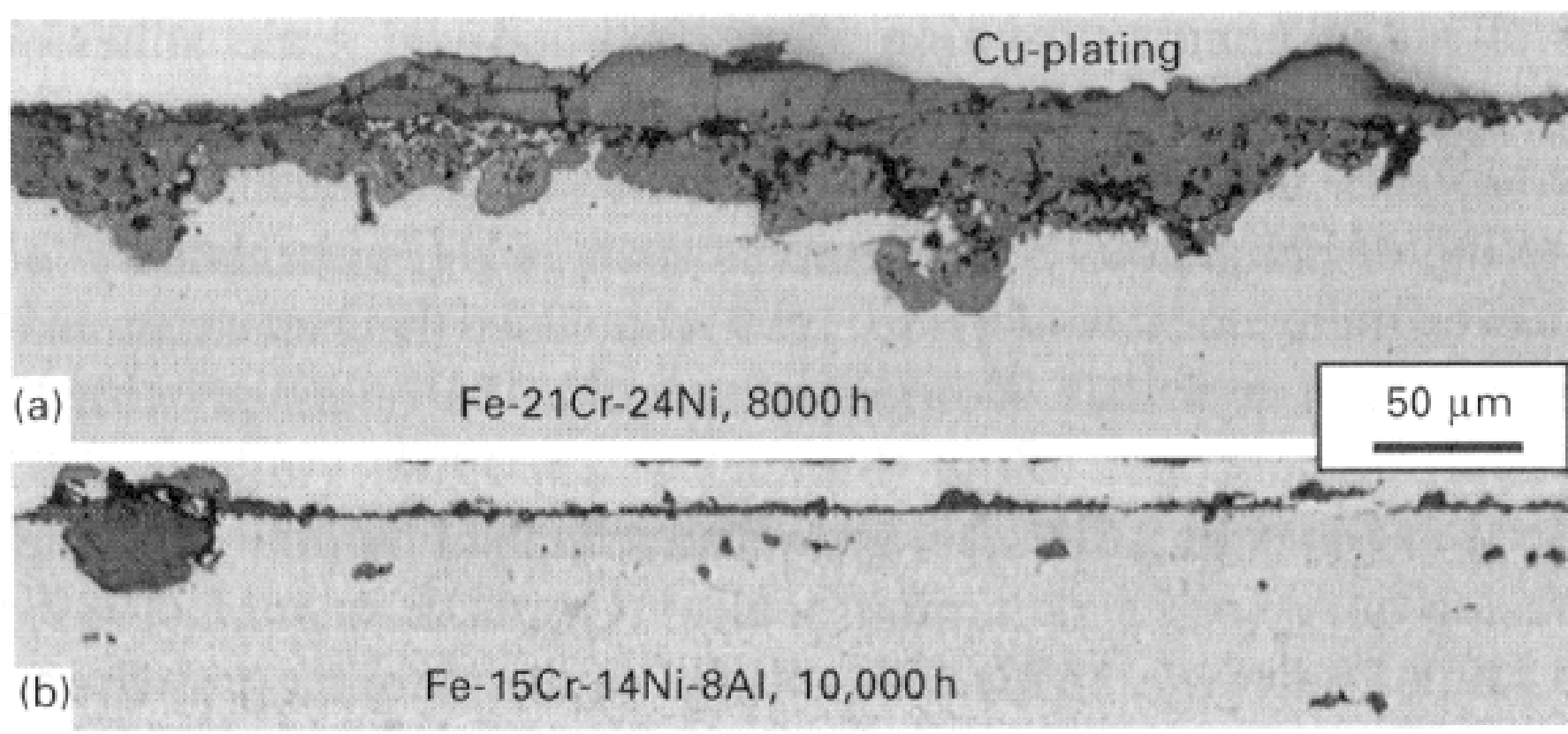
$T = 1250\text{ }^{\circ}\text{C}$
1 cycle = 100 h

$n=0.5$ for parabolic kinetics

Oxidation behavior of FeCrNi and FeCrNiAl alloys under thermal shock conditions



Morphology of scales formed on FeCrNi and FeCrNiAl alloys under thermal shock conditions



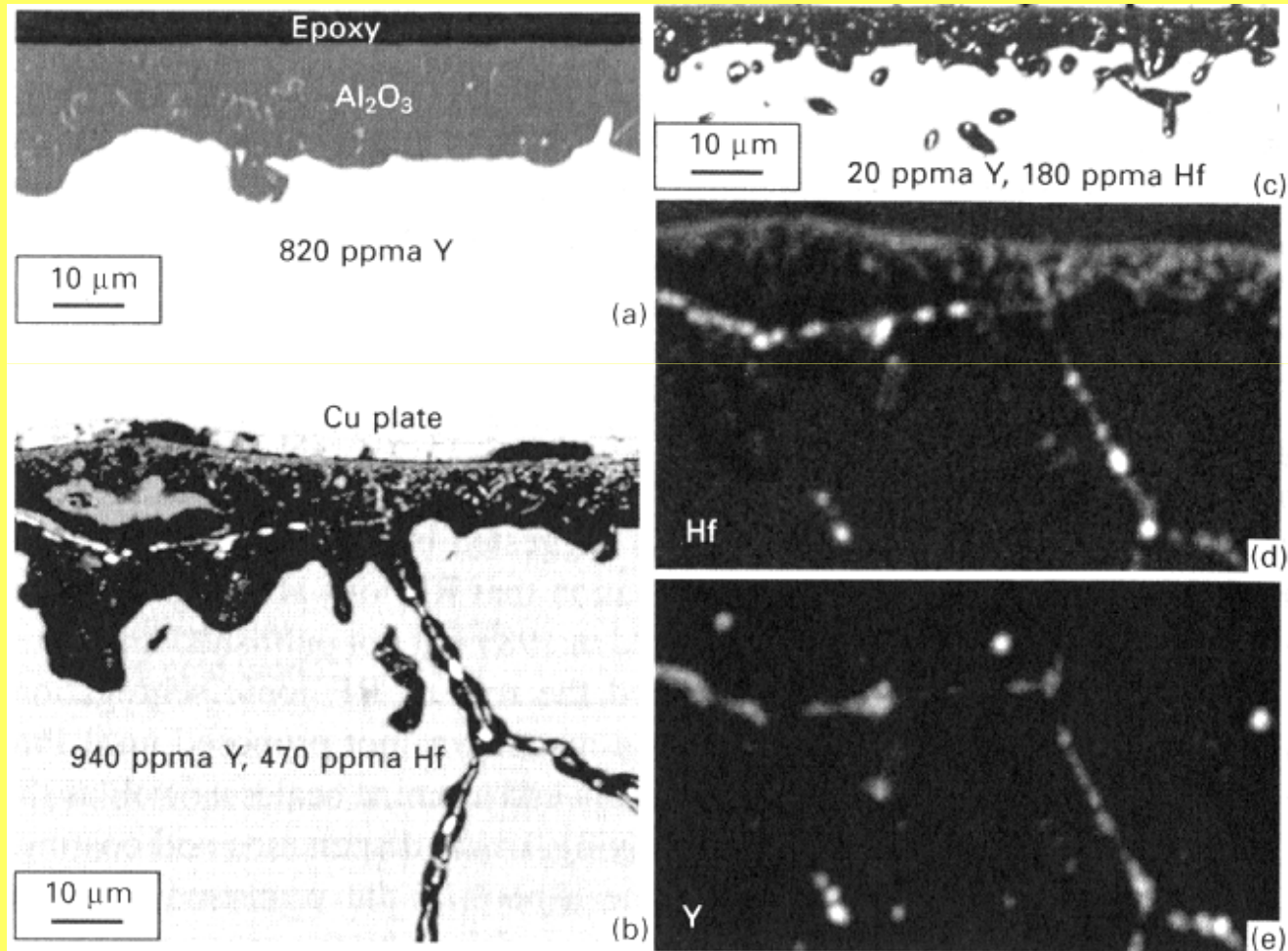
Reactive element (RE) optimization

One opportunity for the development of new high temperature materials is to maintain the base composition but consider strategies for optimizing the minor element additions, particularly RE additions. The most significant RE effect in alumina-forming alloys is improved scale adhesion, which dramatically increases the oxidation-limited alloy lifetime. The improved adhesion has been attributed to the gettering of indigenous S by elements such as Y.

Additional RE effects include:

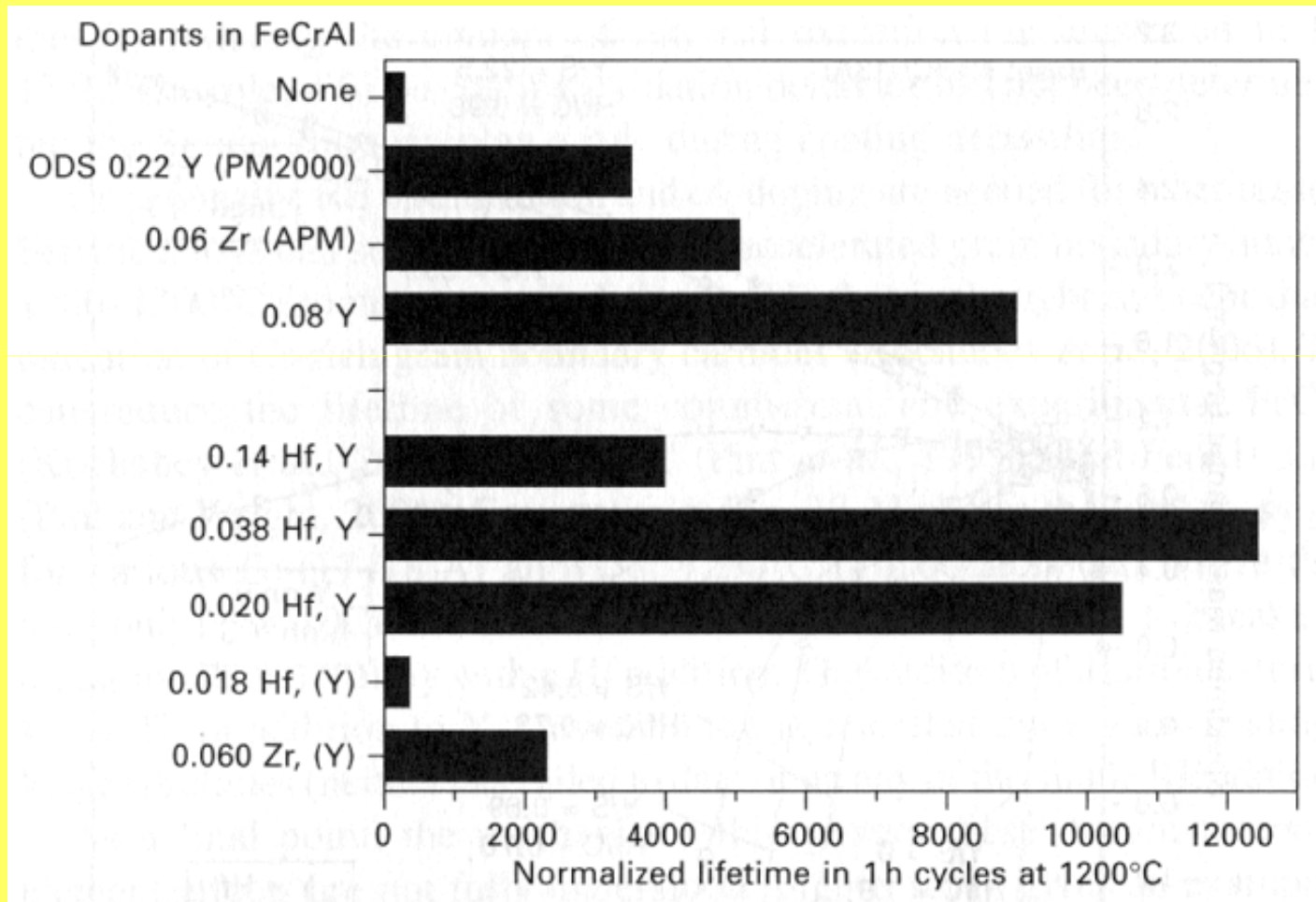
- changing the scale growth mechanism by inhibiting the outward diffusion of Al (or Cr in chromia scales)
- change in the alumina growth mechanism leads to a reduction by ~2-10 times in the parabolic growth rate constant
- change in the in the scale grain structure to a more columnar structure with smaller grains

EPMA back-scattered electron images of the scale formed after 2000 h at 1100°C on FeCrAl-0.082Y (a), FeCrAl-0.094Y-0.047Hf (b) and FeCrAl-0.002Y-0.018Hf (c)



d) and e) show X-ray maps from the upper portion of b)

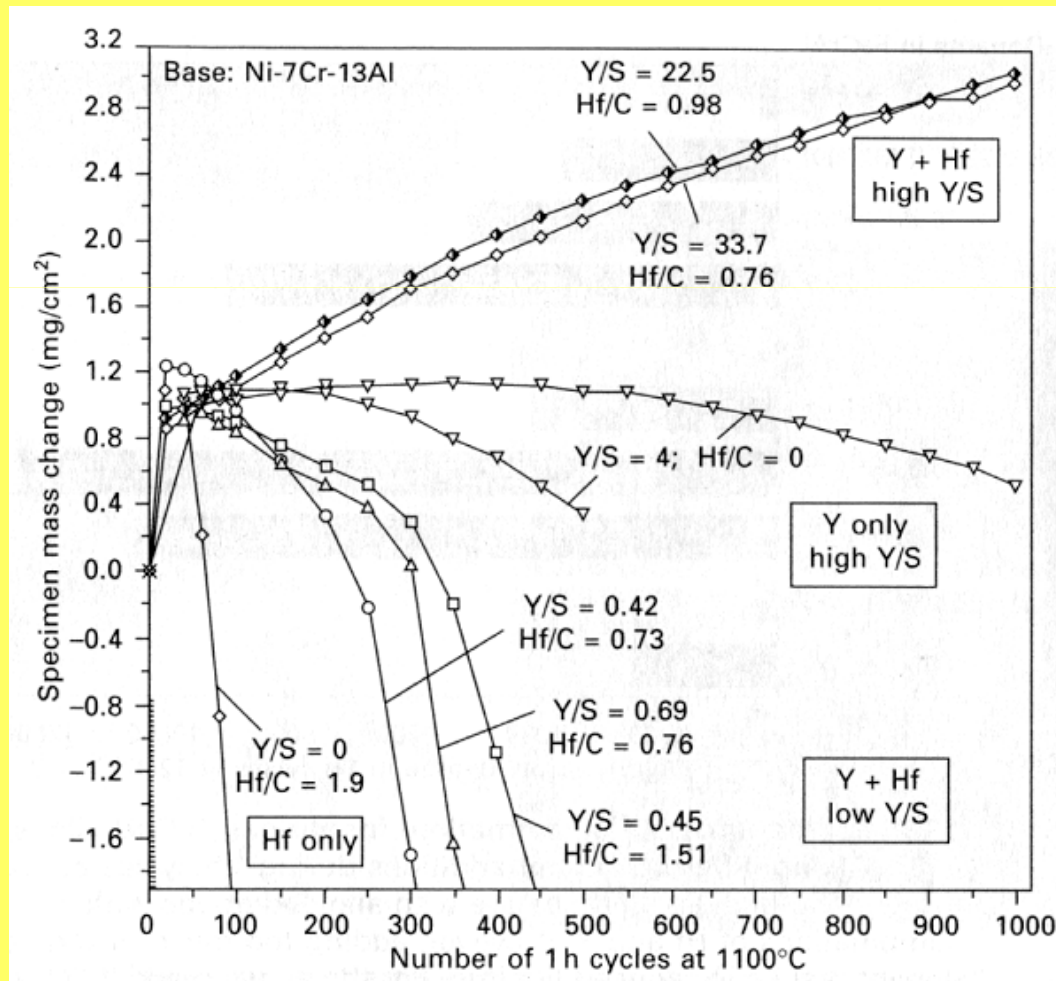
Lifetime (time to FeO formation) for various FeCrAl alloys with ~10% Al and different additions during 1 h cycles at 1200°C in dry O₂



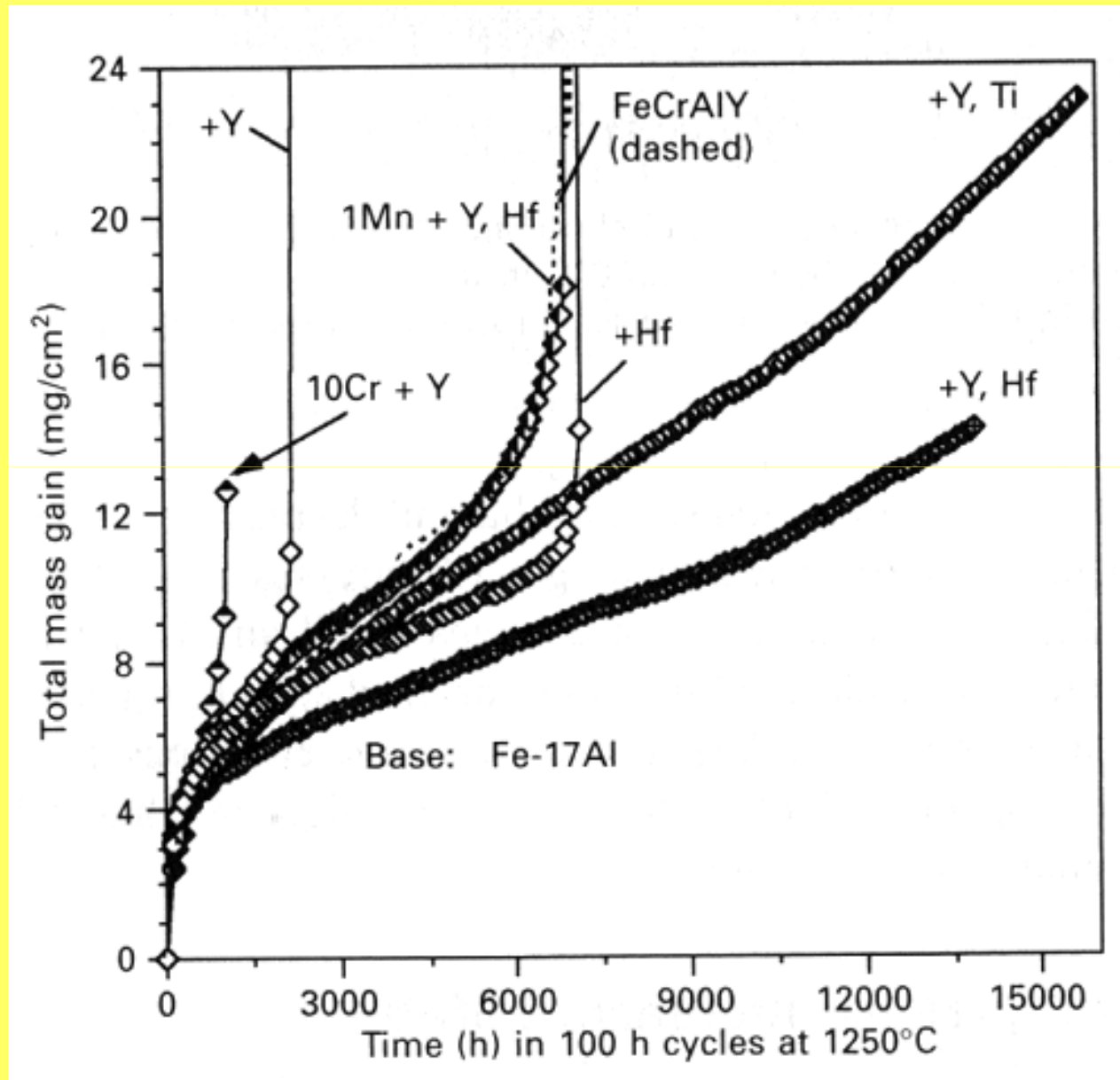
(Y) denotes that Y was not detected in the casting

Reactive element (RE) optimization

It has been observed that effective dopant levels are related to the dopant-interstitial element ratios, particularly Y/S and Hf/C or Zr/C, with ratios greater than unity being more effective.



Reactive element (RE) optimization



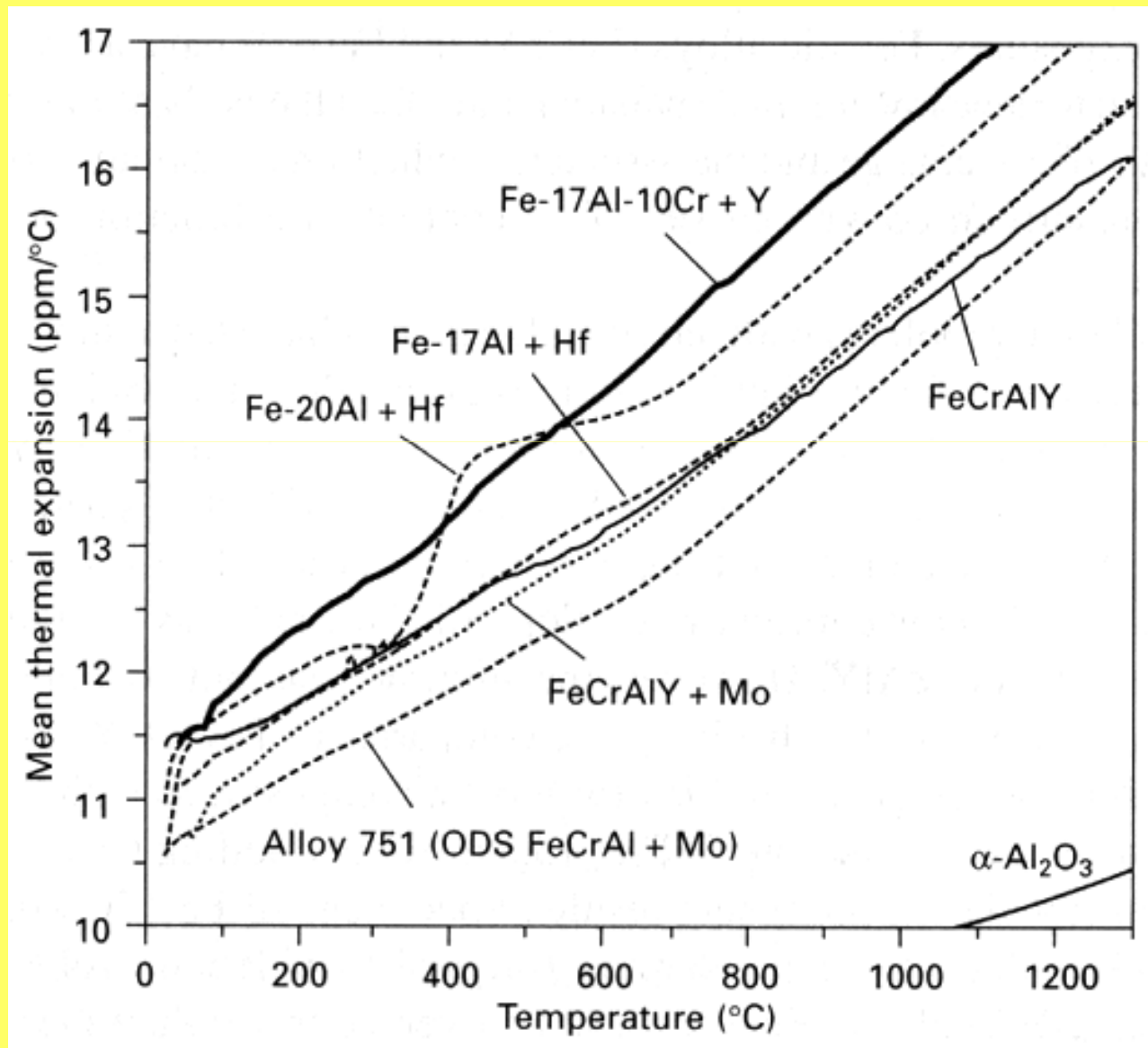
Strategies for increasing lifetime

In addition to developing alloys with higher temperature capabilities or for specific environments, another goal is to develop an alloy with a longer lifetime under the same conditions. For example, an alloy that could extend the heat exchanger lifetime from 40 kh to 60 or 80 kh could reduce the long-term operating costs.

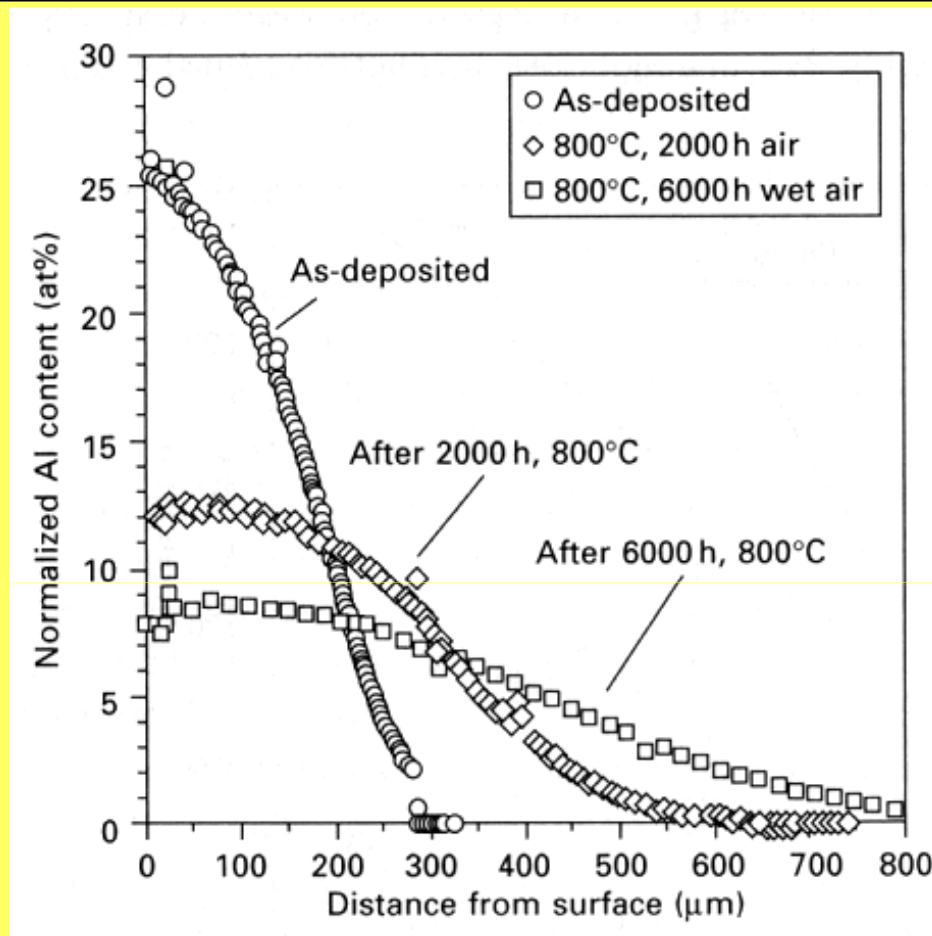
$$(C_0 - C_b)\rho d = A k t_b^n$$

where: C_0 and C_b denote initial and critical (when alloy cannot form protective alumina layer) Al content, ρ and d denote density and thickness of alloy substrate, A is a constant, k is a rate constant, t_b is the oxidation-limited lifetime, $n = 0.5$ for parabolic kinetics and $n = 1$ for linear kinetics.

Strategies for increasing lifetime



„Fantasy” high temperature materials and future trends



- Alloys containing Al and refractory metals (Nb, Mo, W)
- Non-metallic alumina formers, such as Ti_2AlC
- Mo-Si-B alloys
- ODS alloys (oxide dispersion strengthened)
- Low-cost Fe-base compositions

THE END