Karlsruher Institut für Technologie

Institut für Angewandte Materialien

High temperature steam oxidation of potential cladding materials - FeCrAl alloy and Ti_2AlC MAX phase

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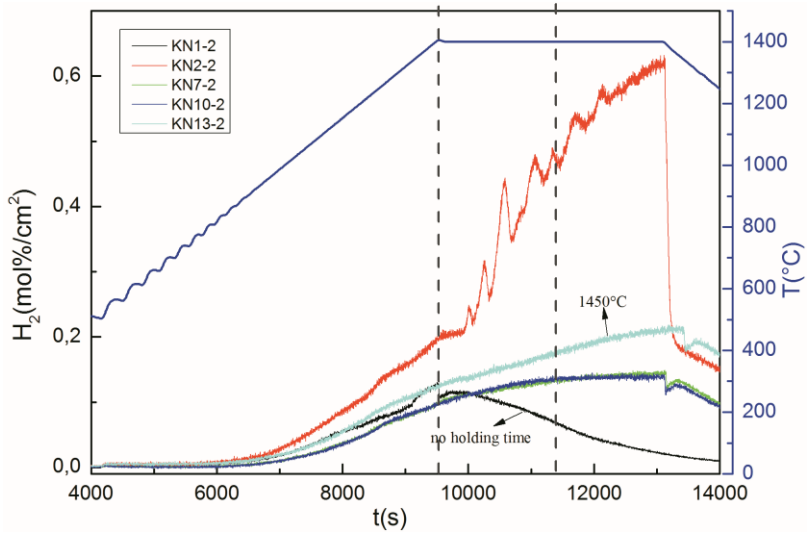
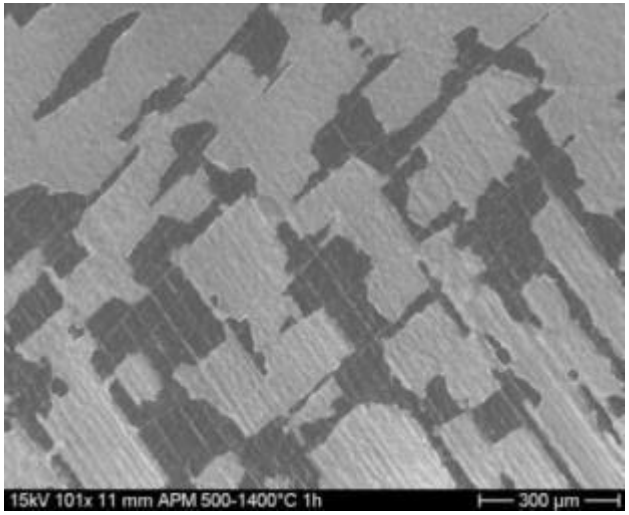
Institute for Applied Materials IAM-AWP & Program NUSAFE





Advantages and shortcomings

FeCrAl alloys

- **Excellent formability**
- **Excellent mechanical properties**
- **Excellent high temperature oxidation resistance**

- ➢ **Irradiation induced α' embrittlement**
- ➢ **High neutron absorption cross section**

Kanthal/Sandvik, Sweden.

Ti_2AlC MAX phase

- **Refractory, light weight, readily machinable**
- **Super oxidation and corrosion resistance**
- **Excellent damage tolerance and thermal shock resistance**
- **Radiation tolerance**

- ➢ **Complex preparation process**
- ➢ **Low fracture toughness**

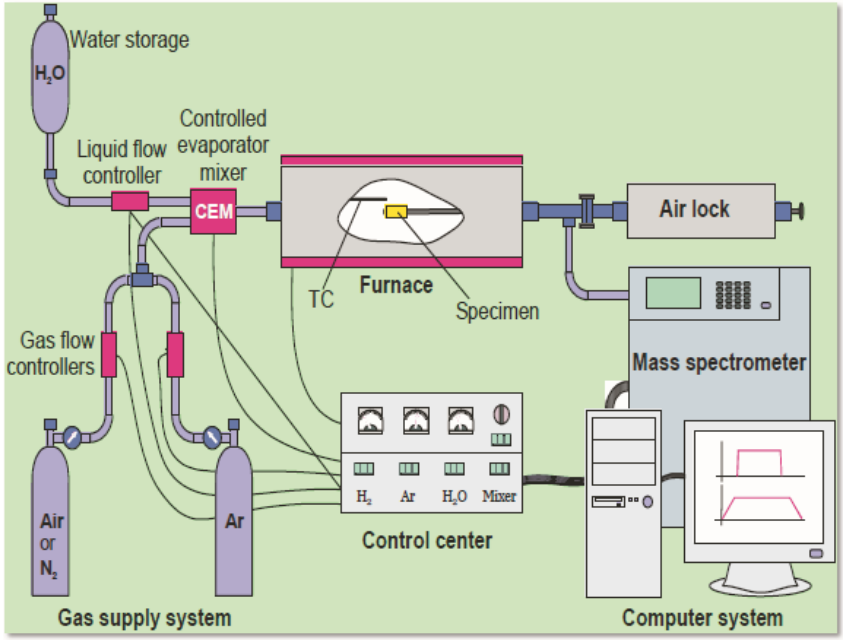
Kanthal/Sandvik, Sweden.

Experiment

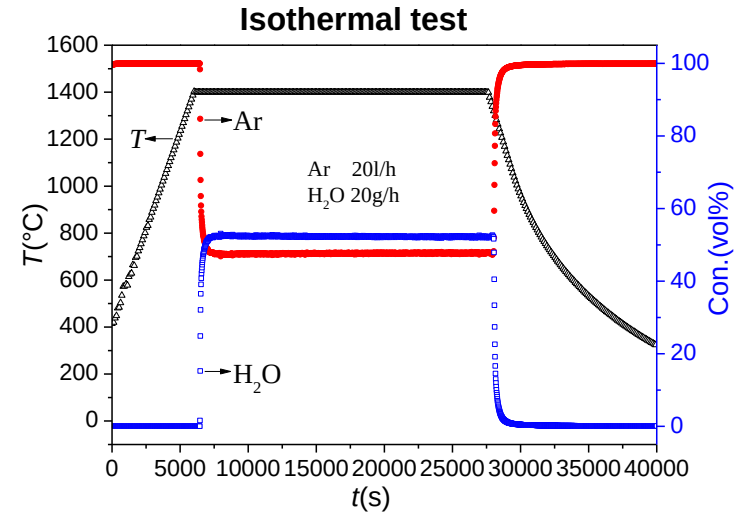
Specimens

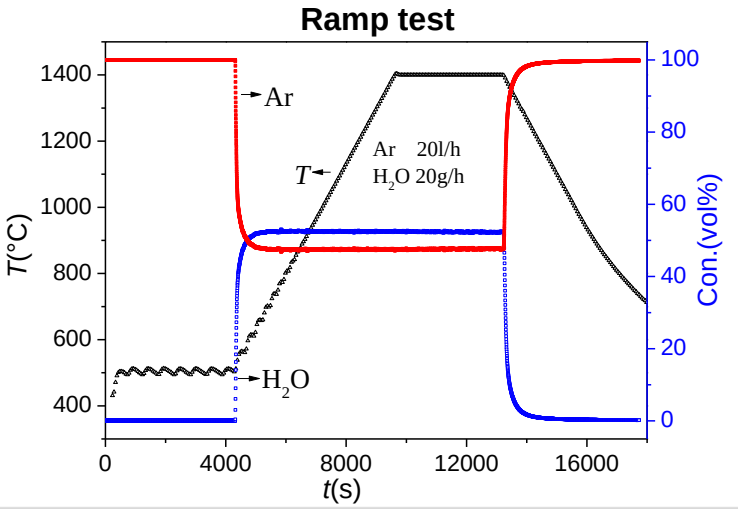
- Kanthal-APM and D, *tube*, *Kanthal/Sandvik, Sweden*
- FeCrAl(RE) model alloys, *plate*, *arc melting*
- Ti_2AlC MAX phase, *plate*, *Kanthal/Sandvik, Sweden*

BOX Facility



Typical heating and gas flow rate





Oxidation of Kanthal-APM and D in 1300-1500°C steam

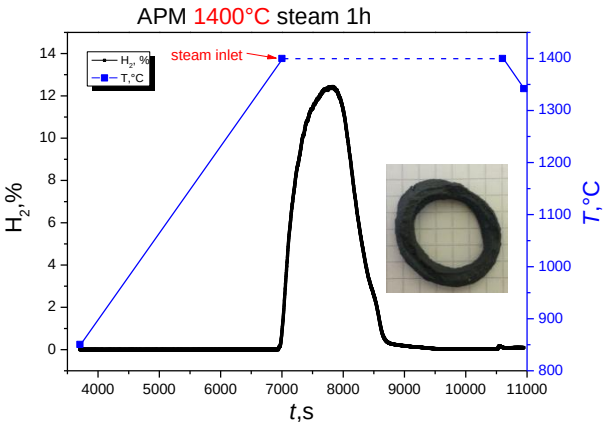
➢ Oxidation behavior

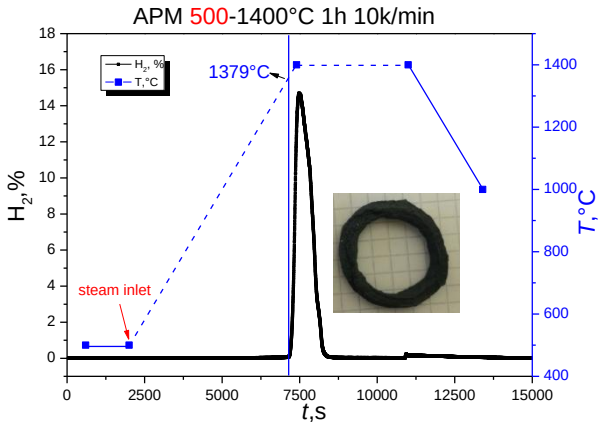
	Conditions		APM Al 5.8	D Al 4.8
Isothermal test	10K/min to 1500°C, 1h		Melt, protective oxide scale formed	Melt, protective oxide scale formed
	10K/min to 1400°C, 1h/15min		Completely oxidized	Completely oxidized
	10K/min to 1300°C, 1h		Protective oxide scale formed, 0.329mg/cm²	Protective oxide scale formed, 0.636mg/cm²
Ramp test	10K/min from 500 to 1400°C, 10min		Completely oxidized	Completely oxidized
	5K/min from 500 to 1500°C		Melt, protective oxide scale formed, 1.21mg/cm²	Melt, protective oxide scale formed, 1.80 mg/cm²
	5K/min from 500 to 1400°C	1h	1.09, 1.02, 0.94 mg/cm²	1.49 mg/cm²
		4h	1.32 mg/cm²	1.90 mg/cm²
		7h	1.85 mg/cm²	2.72 mg/cm²
		10h	2.24 mg/cm²	3.35 mg/cm²
	10K/min to 1200°C 1h, then 10K/min to 1400°C 1h		1.06 mg/cm²	1.49 mg/cm²

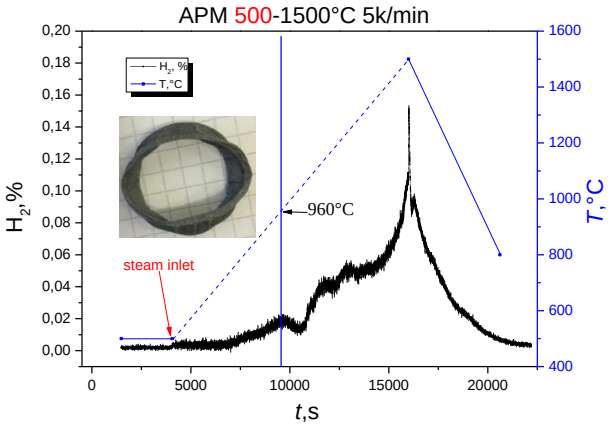
Element(wt%)	Kanthal-APM	Kanthal-D
Cr	21-24	21-24
Al	5.8	4.8
Mn	0.5	0.4
Si	0.7	0.7
C	<0.08	<0.08
Fe	Bal.	Bal.

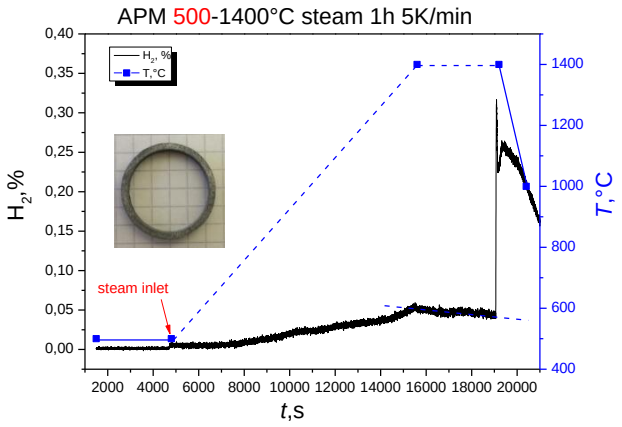
Oxidation of Kanthal-APM and D in 1300-1500°C steam

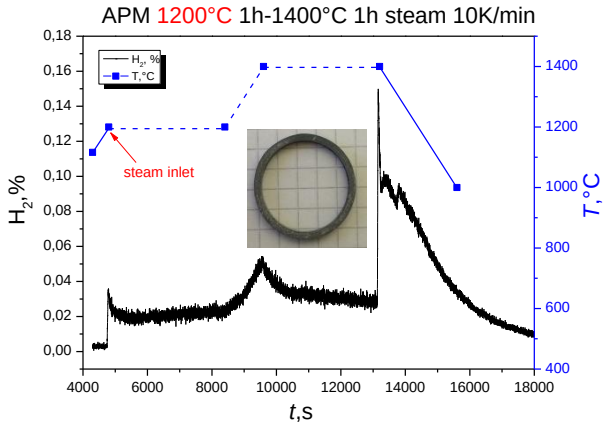
➢ Hydrogen release











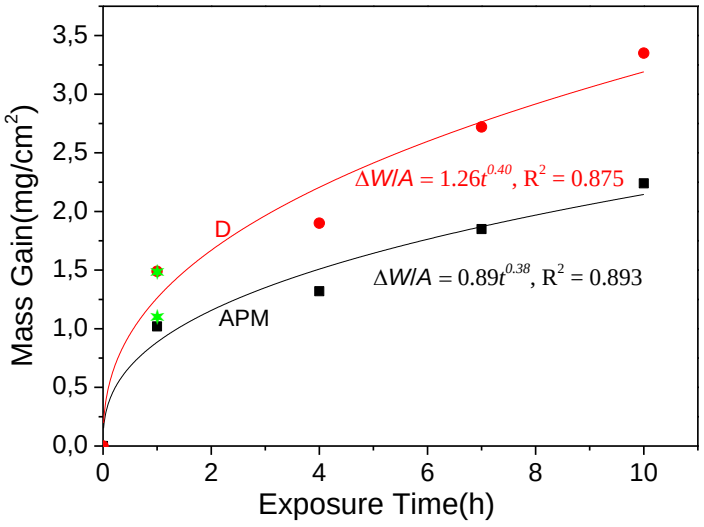
The maximum tolerance temperature represents the temperature that the alloy shows rapid and complete oxidation.

- Both APM and D were rapidly and fully oxidized in isothermal test at 1400°C or ramp test to 1400°C with heating rate 10 K/min.
- The maximum tolerance temperature of APM and D in steam with heating rate 10 K/min was 1379°C and 1374°C, respectively.
- Protective scale formed when pre-oxidized with heating rate 5 K/min from 500°C or isothermal oxidation at 1200°C for 1 hour in steam, which can provide protection up to 1500°C.

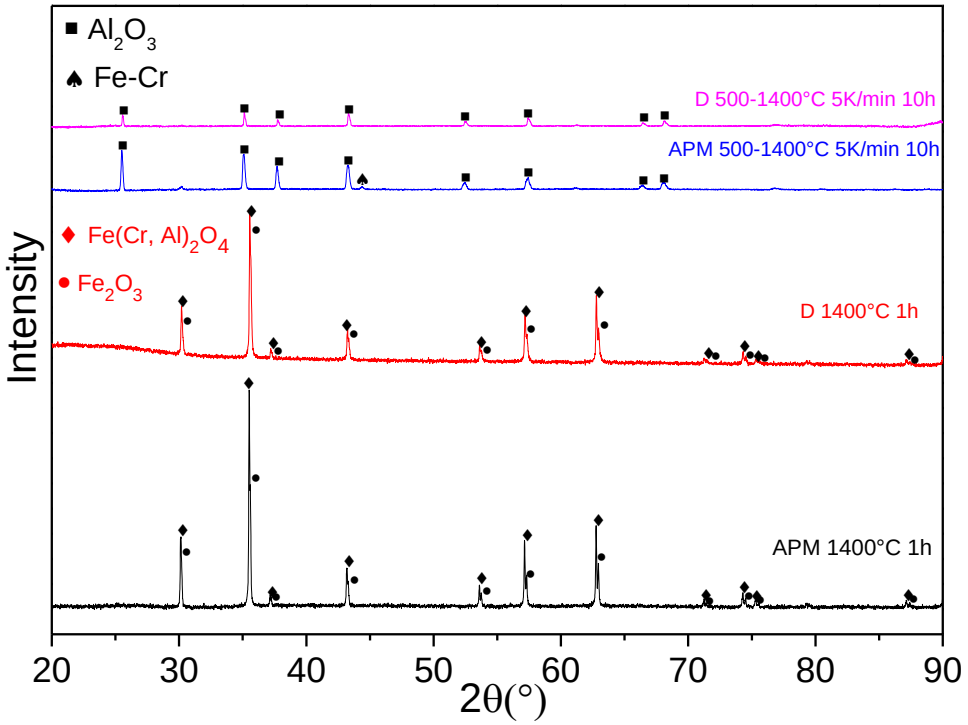
Oxidation of Kanthal-APM and D in 1300-1500°C steam

➢ Mass gain

Mass gain of ramp test of Kanthal-APM and D at 5 K/min with different holding time at 1400°C



➢ XRD



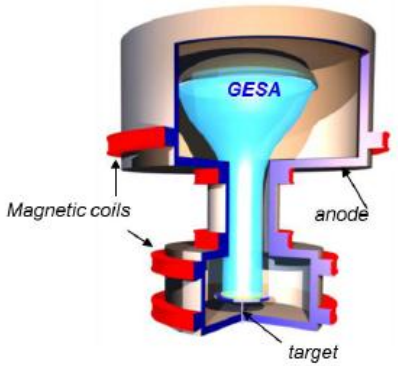
★ represented sample heated in pure Argon to 1200°C, then transfer the atmosphere to Ar and steam, hold 1h, then 10 K/min to 1400°C and hold 1h.

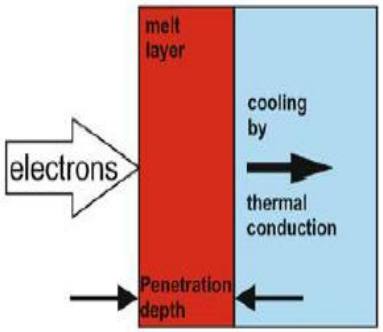
Oxidation of FeCrAl(RE) model alloy in steam

➢ Specimens

No.	Composition(wt%)
K16	Fe16Cr8Al
K17	Fe12Cr8Al
KN1	Fe16Cr8Al0.5Zr
KN2	Fe16Cr6Al0.5Zr
KN7	Fe16Cr8Al0.25Zr0.25Hf
KN10	Fe16Cr8Al0.5Mo
KN13	Fe16Cr8Al0.5Y

One side of KN specimens were treated by GESA.





- Penetration depth of electrons: 10 - 100 µm
- 3 -20 J/cm^2 are necessary for melting
- Rapid cooling by thermal conduction into underlaying materials (10^7 -10^9 K/s)
- efficient energy coupling

Oxidation of FeCrAl(RE) model alloy in steam

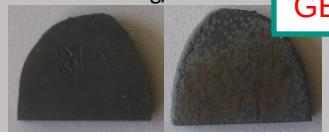
➢ Ramp test

Different morphologies were observed after oxidation for fresh side and GESA modified side.

Low aluminum content cannot provide protection at high heating rates.

The adhesion of the scales were significant improved with addition of active elements, expect for molybdenum.

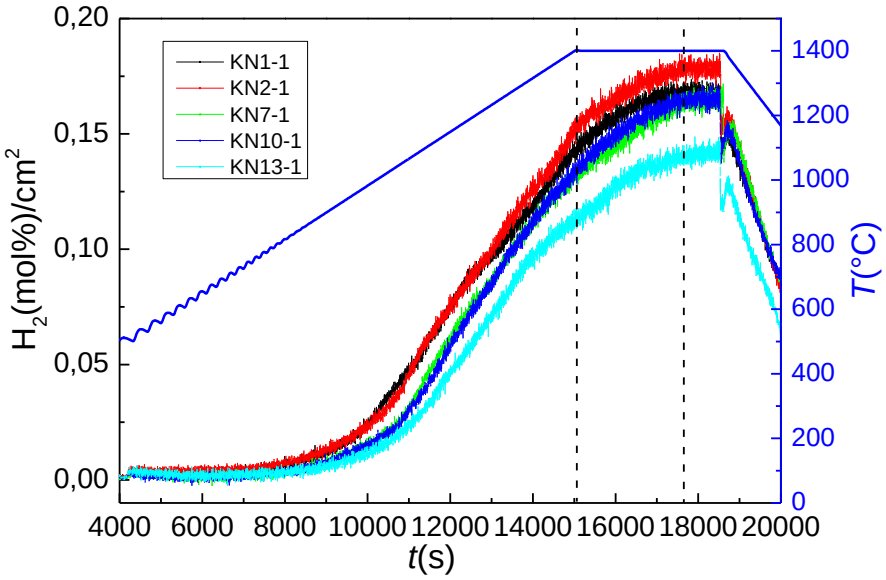
Yttrium provided optimal steam oxidation resistance improvement, comparing to other elements.

Alloys(wt%)	5K/min from 500°C to 1400°C, hold 1h at 1400°C	10K/min from 500°C to 1400°C, hold 1h at 1400°C
KN1-Fe16Cr8Al0.5Zr	4.49 mg/cm^2 GESA 	1.71 mg/cm^2(not hold) 
KN2-Fe16Cr6Al0.5Zr	4.97 mg/cm^2 	Some parts completely oxidized, Some parts remained protective 
KN7-Fe16Cr8Al0.25Zr0.25Hf	1.91 mg/cm^2 	2.43 mg/cm^2 
KN10-Fe16Cr8Al0.5Mo	1.09 mg/cm^2 Scales spalled off observed 	1.05 mg/cm^2 Scales spalled off observed 
KN13-Fe16Cr8Al0.5Y	1.09 mg/cm^2 	1.10 mg/cm^2(1450°C) 

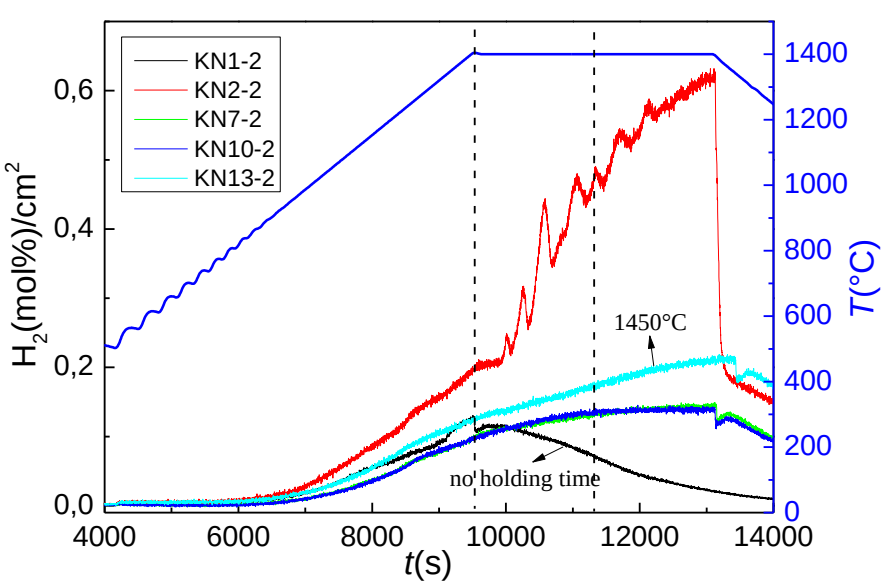
Oxidation of FeCrAl(RE) model alloy in steam

➢ Hydrogen release

5 K/min



10 K/min

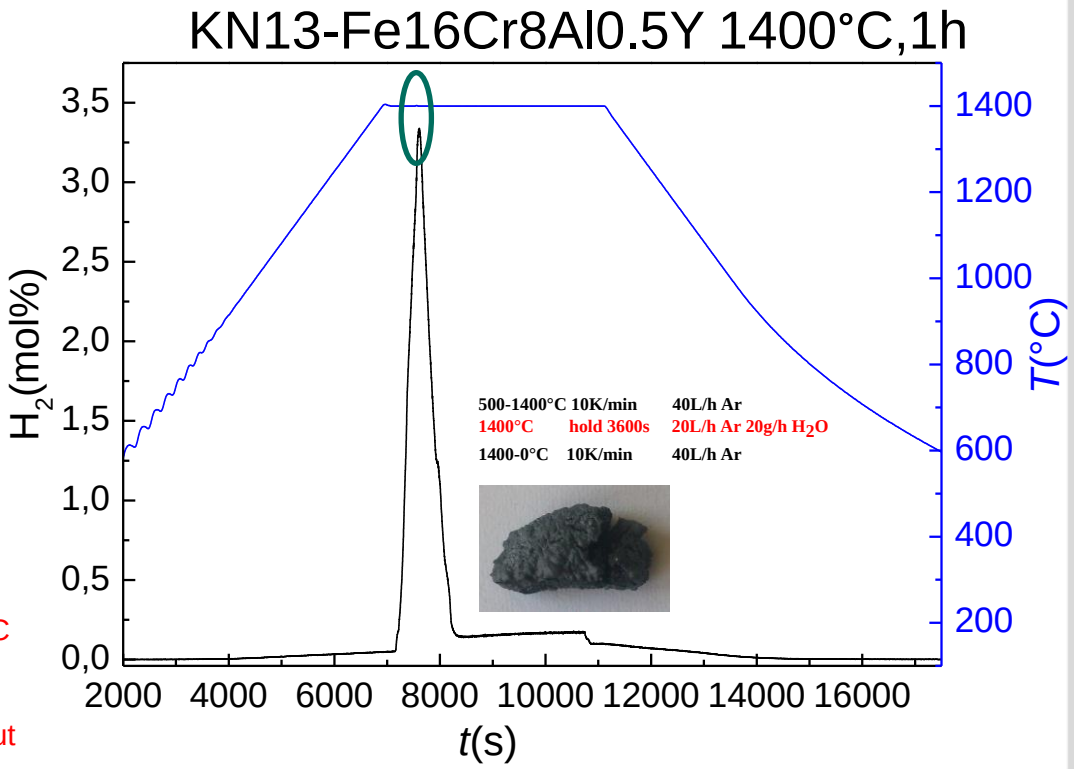


Hydrogen release rates still increase gradually before becoming steady when temperature reaches 1400°C, suggesting that it needs some time to form a continuous protective scale.

Oxidation of FeCrAl(RE) model alloy in steam

➢ Isothermal test

No.	Temp., Tim.	Result
K16-Fe16Cr8Al	1500°C,15min	Melt, remain protective
K17-Fe12Cr8Al	1400°C,15min	Failed
KN13-Fe16Cr8Al0.5Y	1400°C,1h	Failed

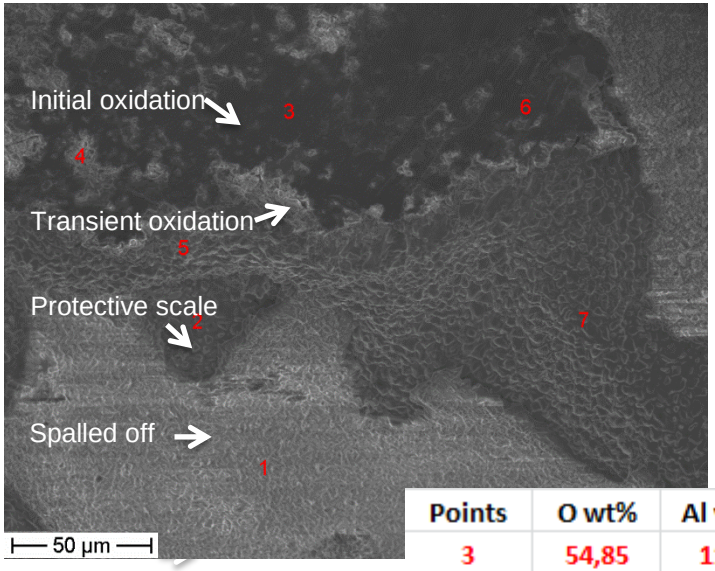


- KN13-Fe16Cr8Al0.5Y can provide protection up to 1450°C when heated in steam with heating rate of 10 K/min form 500°C.
- Catastrophic oxidation of KN13 occurred at 1400°C without pre-oxidation, i.e. heating to desired temperature in high purity Ar, meanwhile, large amount of heat was released through reaction of steam with FeCrAl alloy because of the furnace temperature increasing by more than 1K.

Oxidation of FeCrAl(RE) model alloy in steam

➢ Surface SEM

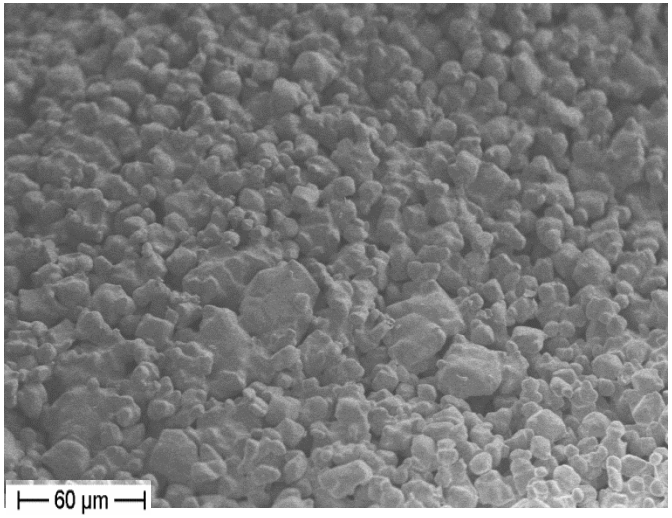
K16_Fe16Cr8Al_1500°C steam 15min



Melt and protective

Points	O wt%	Al wt%	Cr wt%	Fe wt%
3	54,85	11,7	2,88	30,57
6	7,93	9,39	15,22	67,46
4	26,12	44,28	11,13	18,47
2	39,58	46,11	4,19	10,12
5	35,84	46,25	4,99	12,92
7	30,36	46,57	7,78	15,29
1	41,53	41,32	3,22	13,93

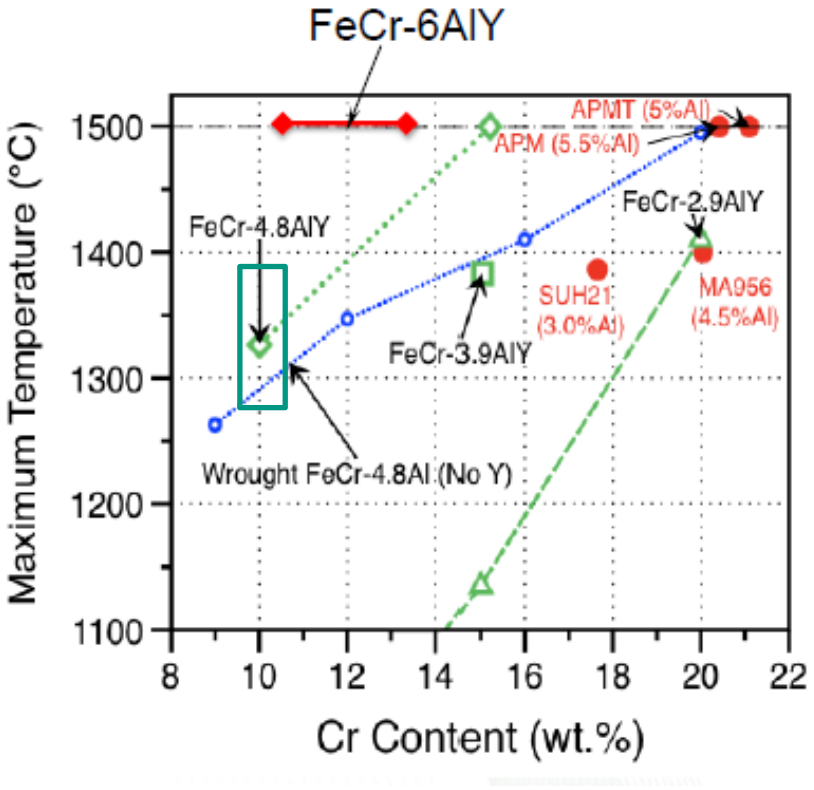
K17_Fe12Cr8Al_1400°C steam 15min



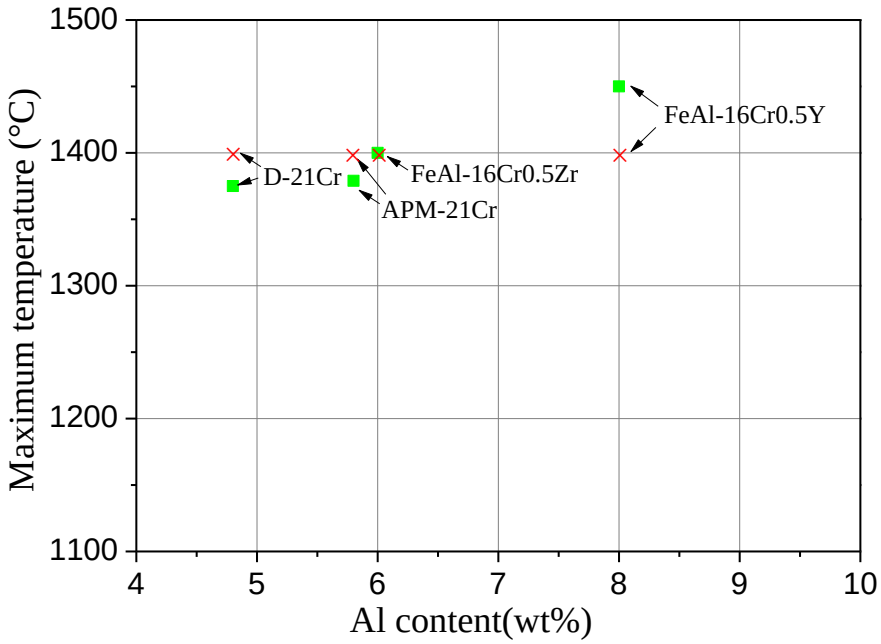
Rapidly and completely oxidized

Oxidation of FeCrAl(RE) model alloy in steam

➢ Max Application Temperature



Starting at 600°C, 5 K/min
100% steam, 1 atm



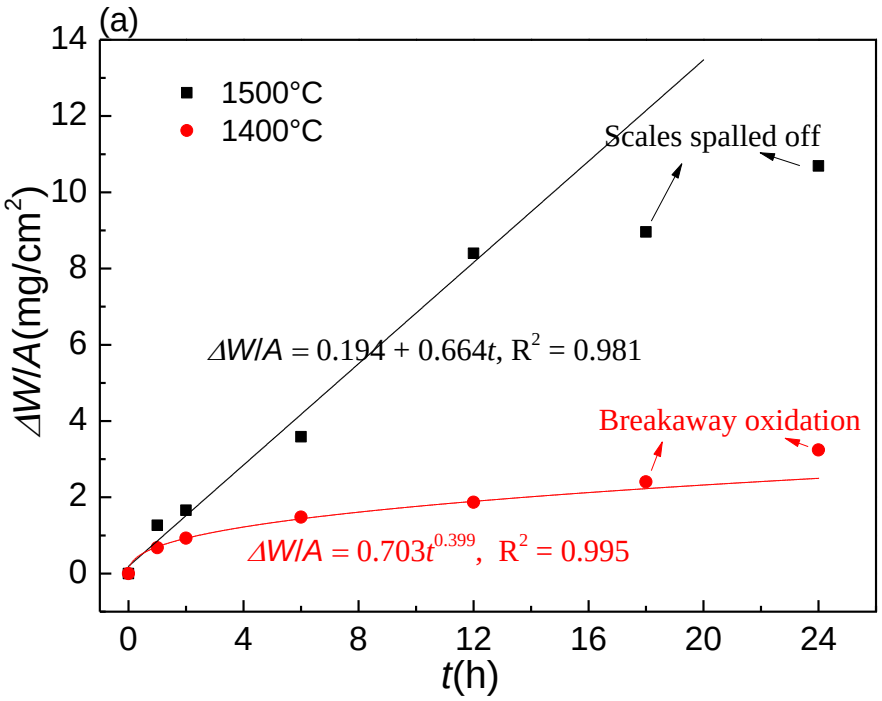
■ Starting at 500°C, Ar-52%H_2O, 1 atm, 10 K/min

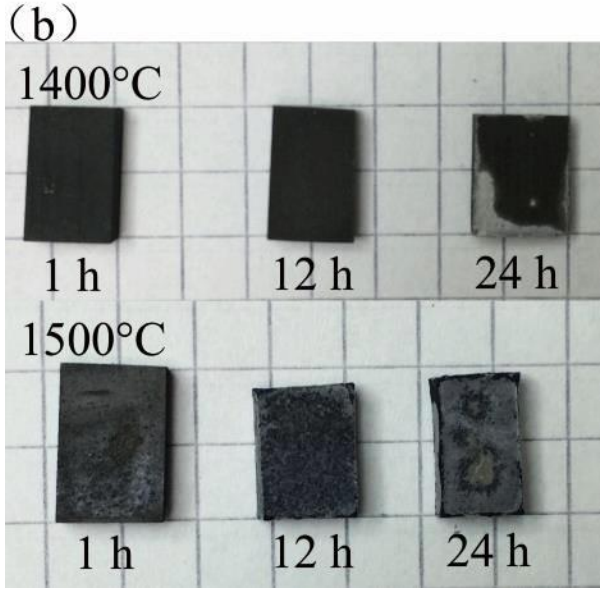
× All failure at 1400°C without pre-oxidation

 [1]B. Pint et al., Mater. High Temp. 32 (2015) 28.

Oxidation of Ti_2AlC in high temperature steam

- **1400°C and 1500°C**

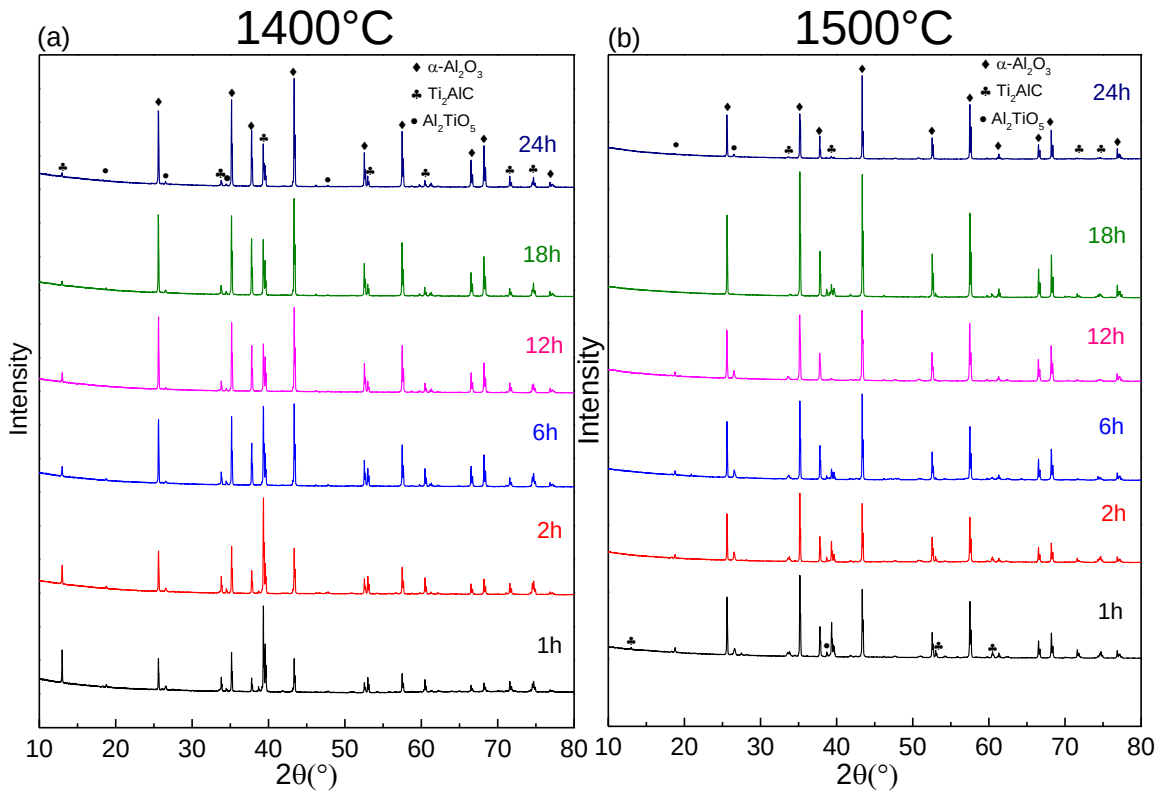




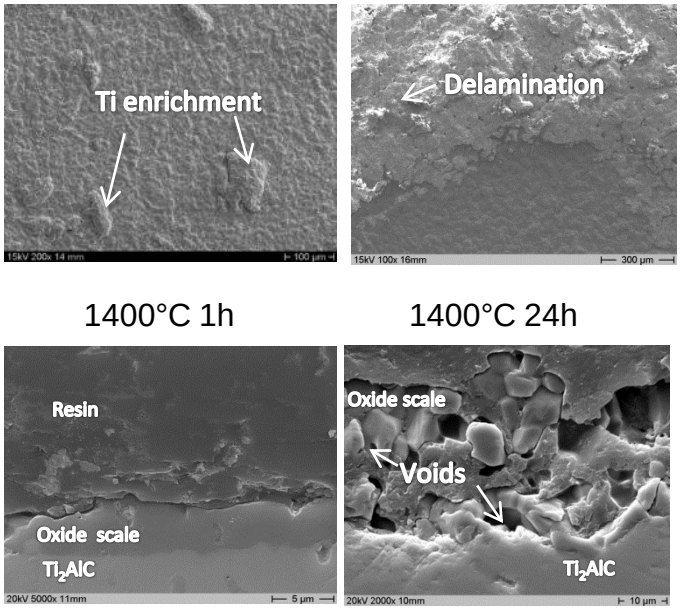
The oxidation kinetics followed a sub-parabolic law at the early stage of oxidation at 1400°C, then transferred to a linear law beyond 18 hours and obeyed a linear law at 1500°C.

Oxidation of Ti_2AlC in high temperature steam

➢ XRD



➢ SEM

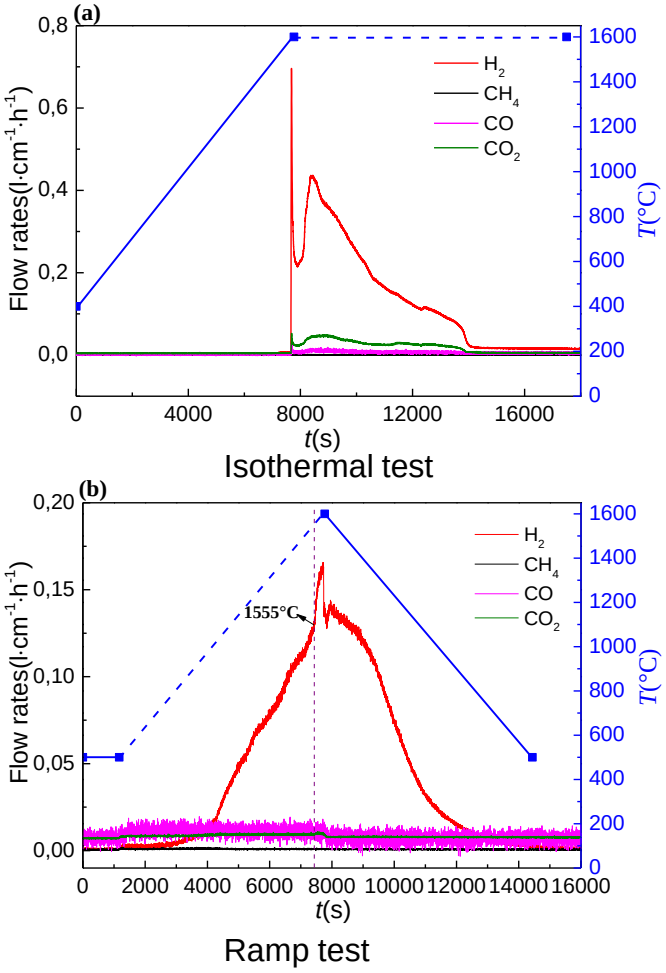


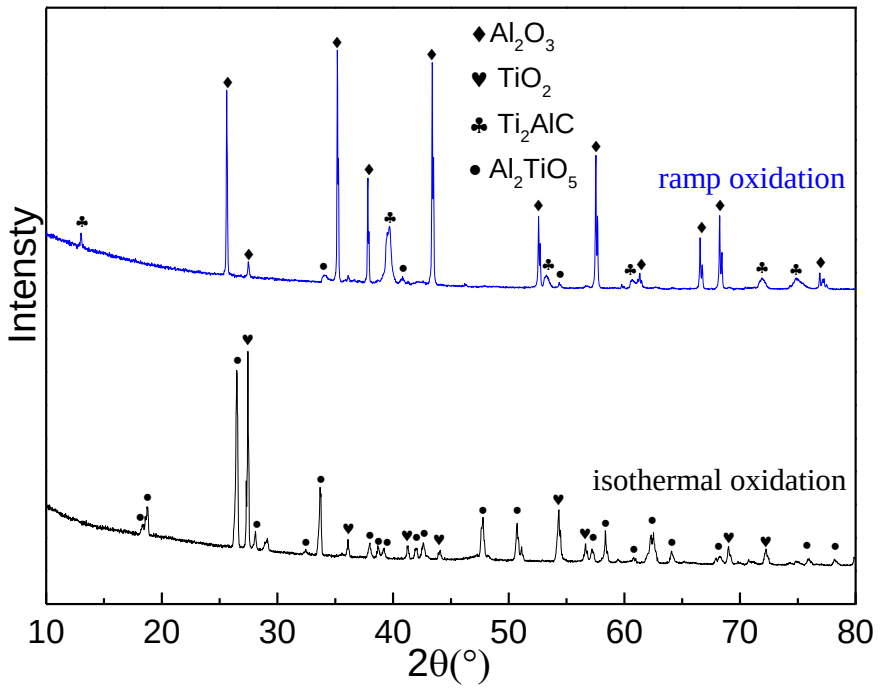
The oxide scale consisted of a inner continuous coarse α-Al_2O_3 scale and a outer discontinuous Al_2TiO_5-containing isolated islands.

Oxidation of Ti_2AlC in high temperature steam

➢ Max Application Temperature

1600°C 10K/min

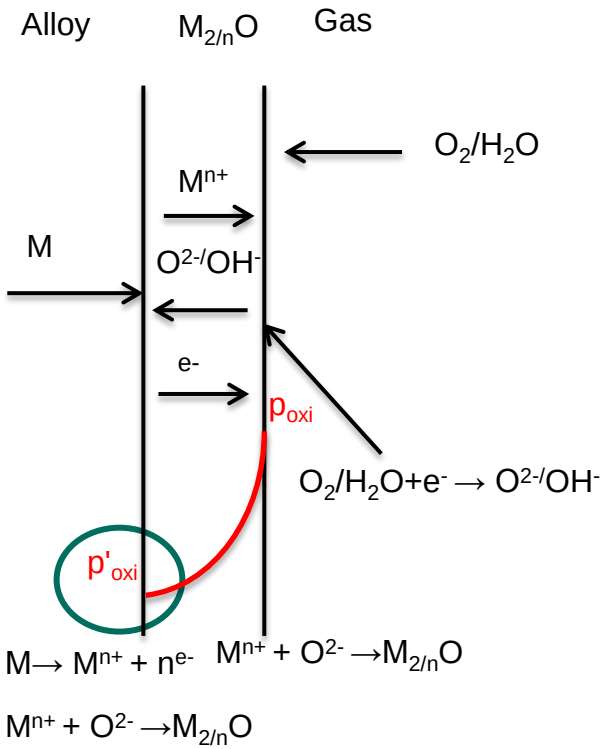


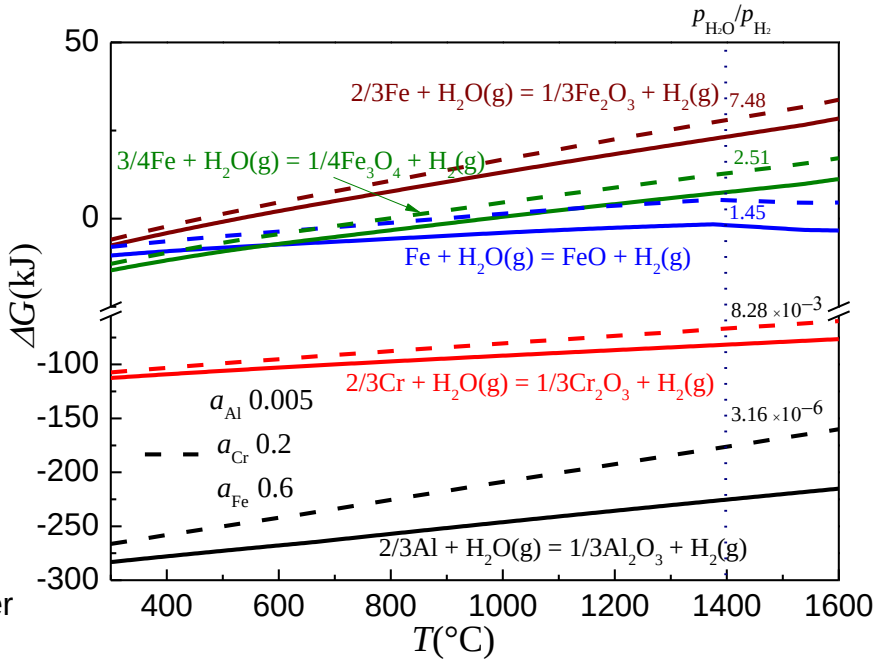


$$Ti_2AlC + 15/2H_2O = 3/2TiO_2 + 1/2Al_2TiO_5 + CO_2 + 15/2H_2$$

Enthalpy of this reaction at 1600°C : c.a. -943.53kJ/mol.

Failure mechanism analysis





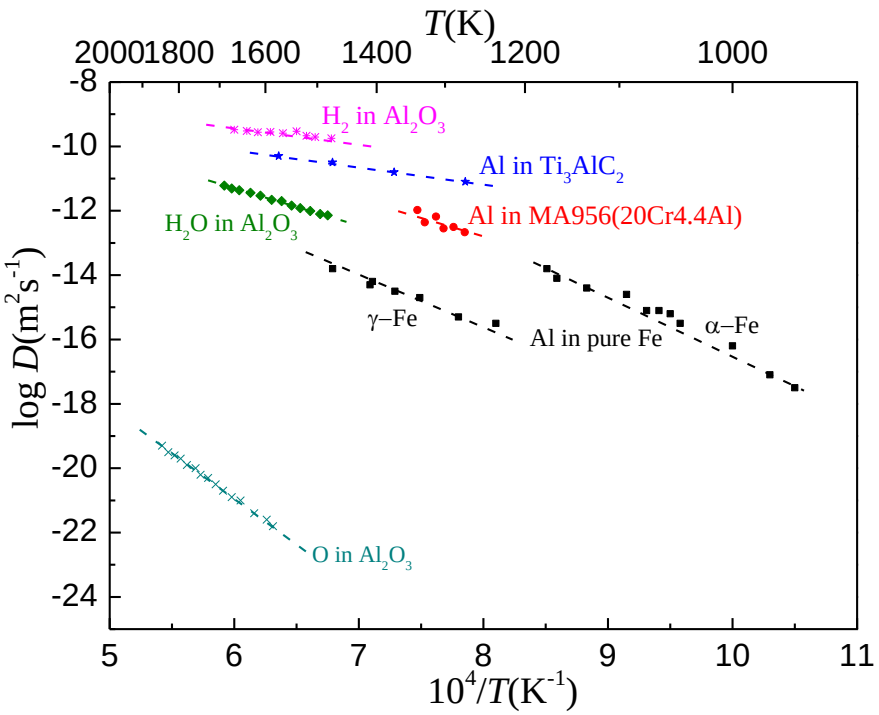
(1) Delivery of oxidant to the scale/gas interface via mass transfer
(2) Incorporation of oxidant into the oxide scale
(3) Delivery of reacting metal from the alloy to the alloy/scale interface
(4) Incorporation of metal into the oxide scale
(5) Transport of metal and/ or oxidant through the scale

The Gibbs free energy change and the minimum ratio of pH_2O/pH_2 to form corresponding oxides at 1400°C

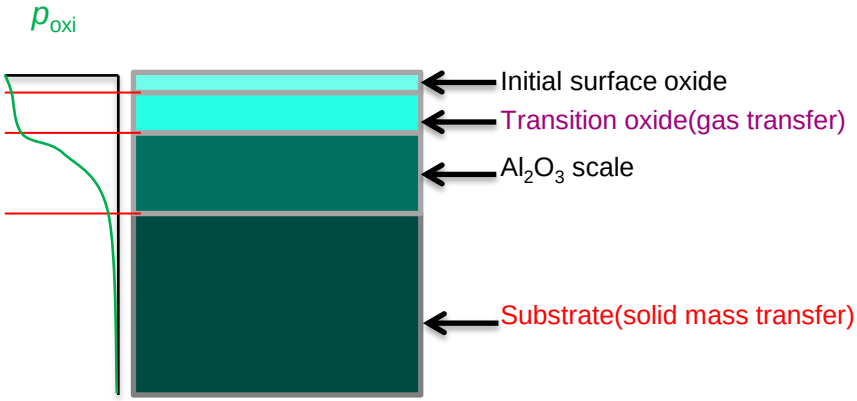
Controlling-steps: gas phase mass transfer, solid-state mass transfer, diffusion in oxide scale

[1] J. Young, High Temperature Oxidation and Corrosion of Metals, Elsevier, 2008.
[2] Thermo-Calc-4.0
[3] HSC 8

Failure mechanism analysis



Diffusion coefficients of different species



Influence factors

- Oxidant gas transfer rate
- Aluminum diffusion rate
- Thick oxide scale by pre-oxidation
- Aluminum content
- Transient oxidation

FeCrAl alloys

- Increasing Al + Cr content
- Reactive element
- Pre-oxidation

[1]R.H. Doremus, J. Appl. Phys. 100 (2006).
[2]B. Lesage, L. Maréchal, a. M. Huntz, R. Molins, Defect Diffus. Forum 194-199 (2001) 1707.
[3]X.H. Wang, F.Z. Li, J.X. Chen, Y.C. Zhou, Corros. Sci. 58 (2012) 95.
[4]G. Neumann, C. Tuijn, Self-Diffusion and Impurity Diffusion in Pure Metals: Handbook of Experimental Data, Elsevier, 2011.

Conclusion and future work

- The catastrophic oxidation phenomenon, i.e. rapid and complete consumption of FeCrAl alloys was observed when isothermal oxidized or ramp heated with fast heating rates (10 K/min) to high temperature in steam.

- An α-Al_2O_3 protective scale formed on the surface of FeCrAl alloys by pre-oxidation with slow ramp heating rate (5 K/min) or at lower temperature (1200°C) in steam, which can provide protective effect to the melting temperature.

- Ti_2AlC MAX phase possesses super steam oxidation resistance, and the max application temperature in steam reaches up to 1555°C.

- The maximum tolerance temperatures of these two alumina-forming materials in steam are signifcantly influenced by the aluminum content, aluminum diffusion rates in the bulk materials, transition oxide scale at the early stage of oxidation and probably reactive element.

- ❖ Define the critical Al and Cr content of FeCrAl alloys for providing protection to 1400°C with 10 K/min heating rate in steam and investigate the influence of reactive element and GESA treatment.

- ❖ Application of Ti_2AlC coating on Zry-4.

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Thank you for your attention !