



Kinetics of High Temperature Oxidation and of Chromia Volatilization for Chromium Carbides-containing Alloys

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INTRODUCTION

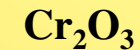
Resistance of superalloys against several constraints (mechanical deformation, corrosion by molten salts or glasses, oxidation...)



external stoichiometric oxide layer

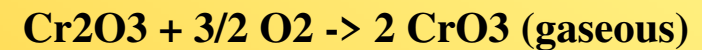


efficient against oxidation



**efficient against oxidation
and corrosion**

**Superalloys strenghtened
with carbides are often
chromia-forming**



**Problem of chromia volatilization
when $T > 1000^\circ\text{C}$: the real damage
supported by the material can be
minimized**

**Necessity to precise both oxidation
and chromia volatilization rates for
 $T > 1000^\circ\text{C}$**

How to take chromia volatilization into account in a <mass gain versus time> file?

A first method: $m = \sqrt{2 \cdot K_p \cdot t^2} \longrightarrow m = \sqrt{2 \cdot K_p \cdot t^2} - K_v \cdot t$

Another method:

$$dm = \frac{K_p}{m} \cdot dt$$

$$dm = \frac{K_p}{m} \cdot dt - K_v \cdot dt \longrightarrow m \cdot \frac{dm}{dt} = K_p - K_v \cdot m$$

Plot of $m \cdot \frac{dm}{dt}$ versus $-m \longrightarrow$ straight line

slope $\rightarrow K_v$

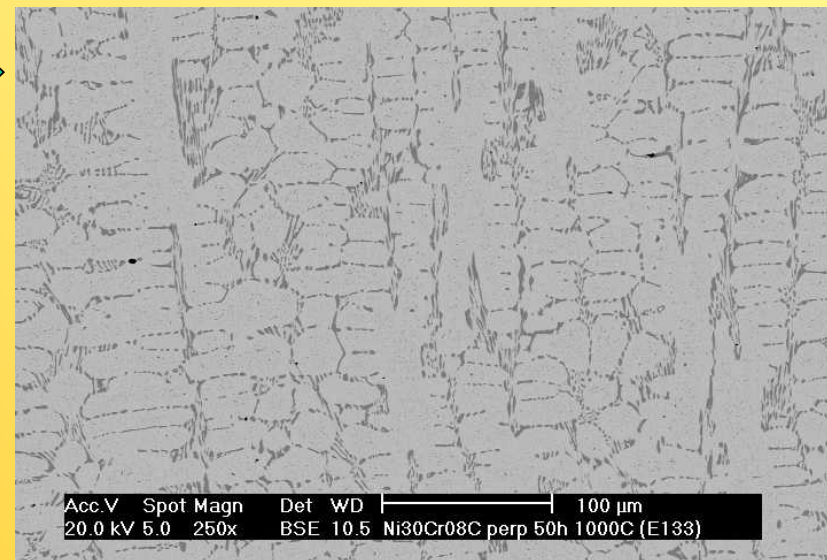
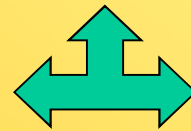
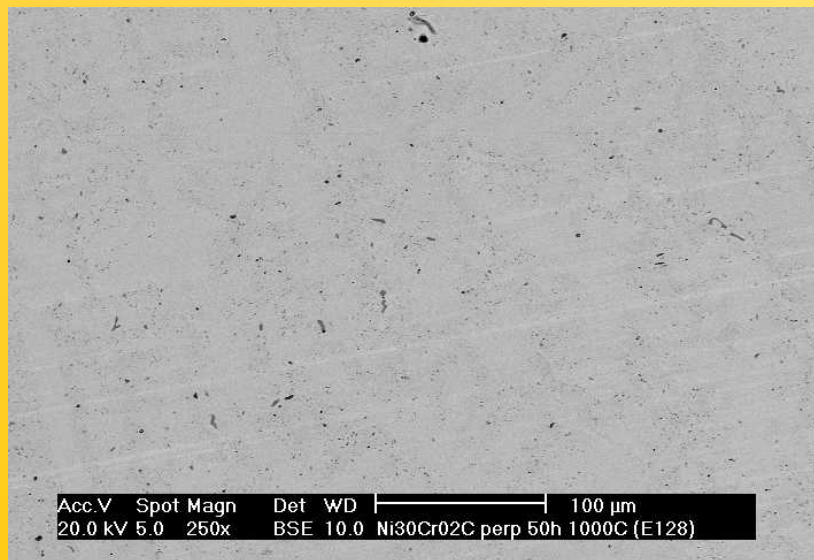
ordinate at $m=0 \rightarrow K_p$

The studied alloys

T4

Weight %	Co	Ni	Cr	C
Ni30Cr0.8C	/	69.2	30	0.8
Ni30Cr0.2C	/	69.8	30	0.2

- Two alloys synthesized by foundry (HF furnace)
- Influence of the interdendritic carbide density



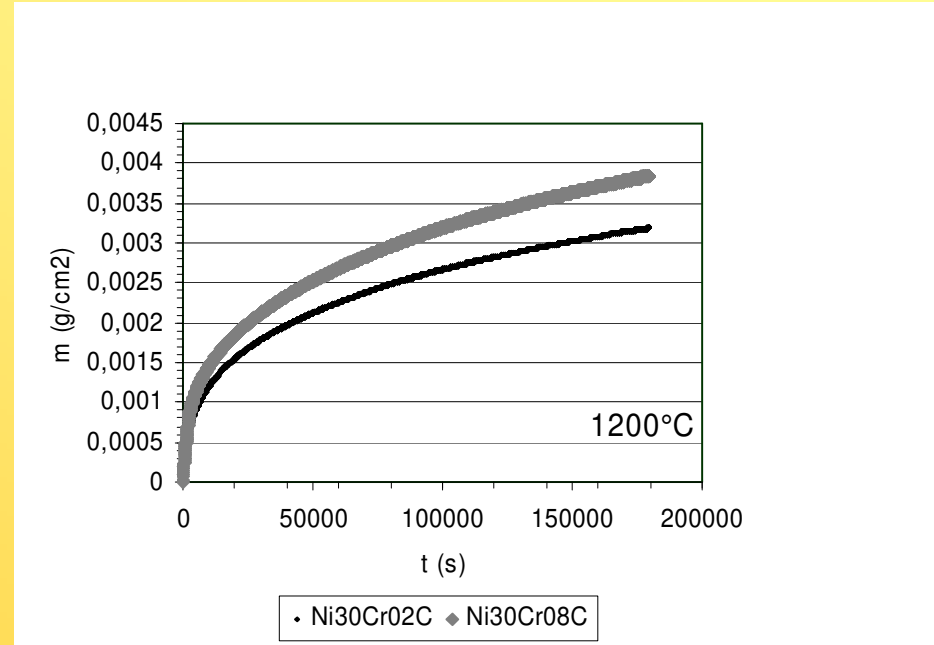
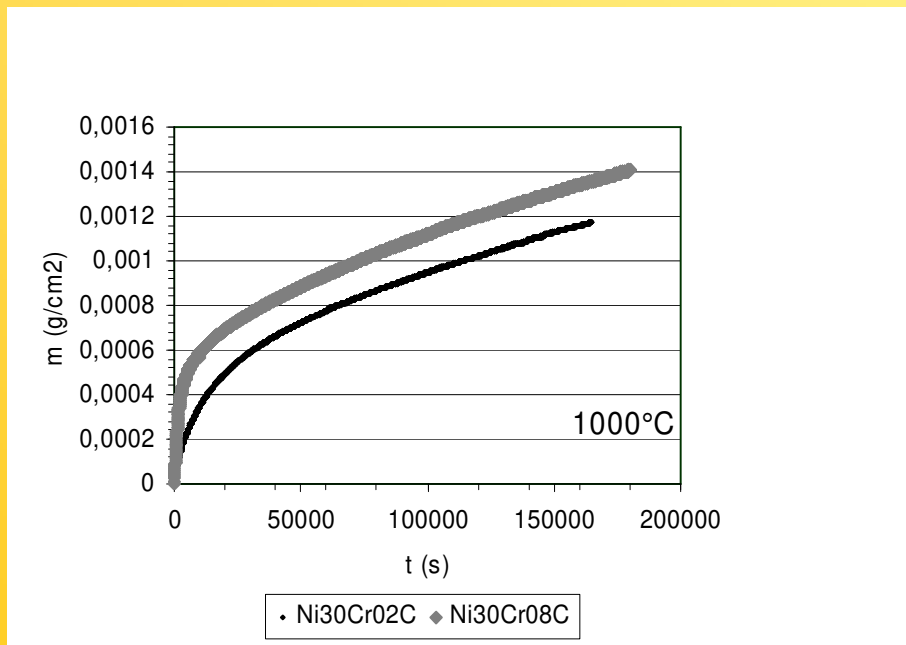
Thermogravimetry runs

T5

All tests were performed
for 50 hours at

1200°C
1100°C
1000°C

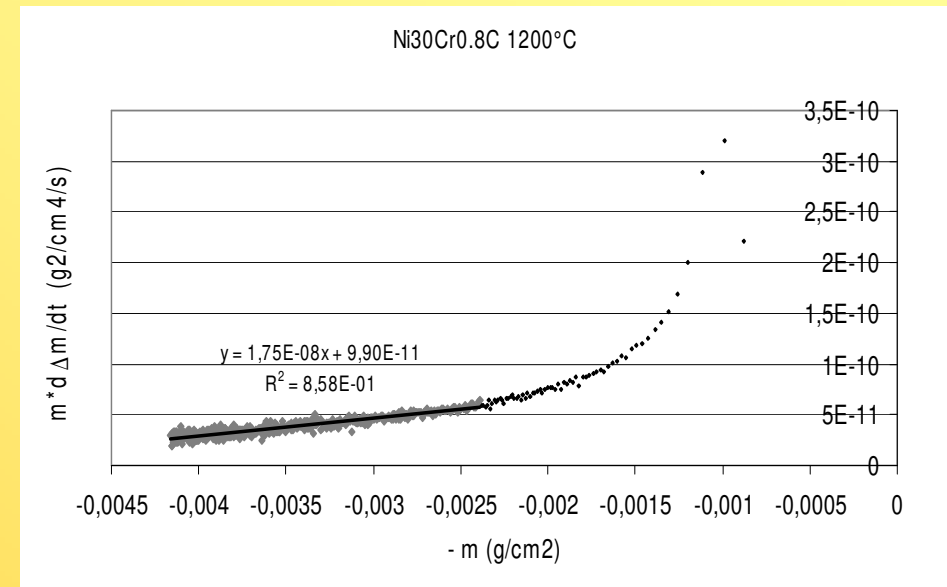
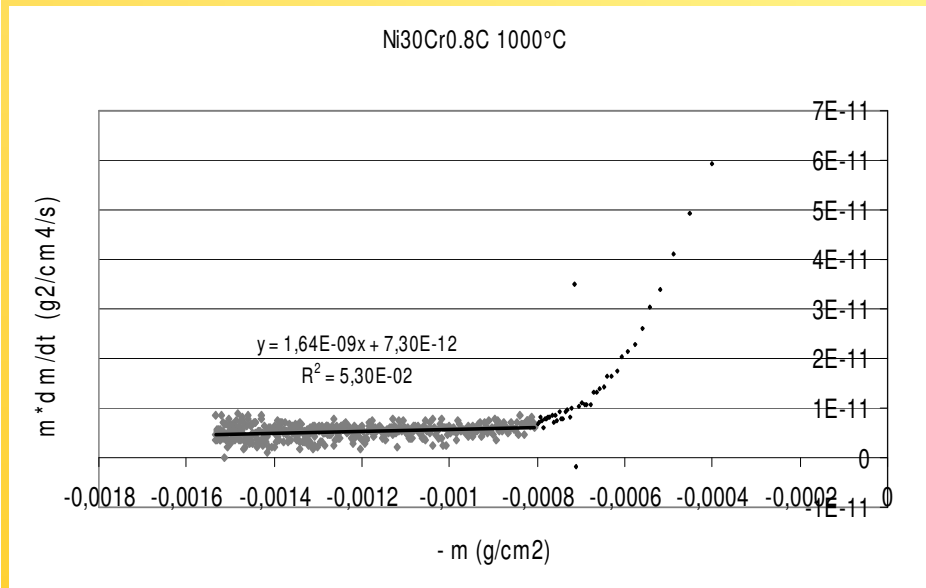
in a dry
synthetic air



→ Parabolic curves with a high speed linear part

→ Higher mass gains for Ni₃₀Cr_{0.8}C than for Ni₃₀Cr_{0.2}C

→ Plot of $m \cdot \frac{dm}{dt}$ versus $-m$:

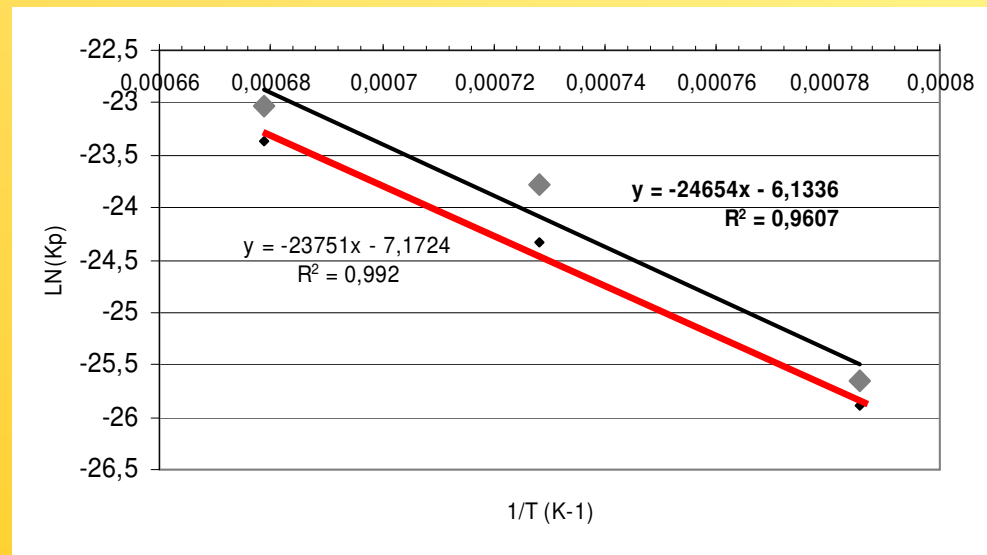


- First jump corresponding to a non-parabolic oxidation state
- Existence of a straight line (linear dependence on $-m$), possibility to simultaneously extract K_p and K_v
- Dispersion of the measures when the oxidation rate is slow (low T, end of test)

Values obtained for Kp

T7

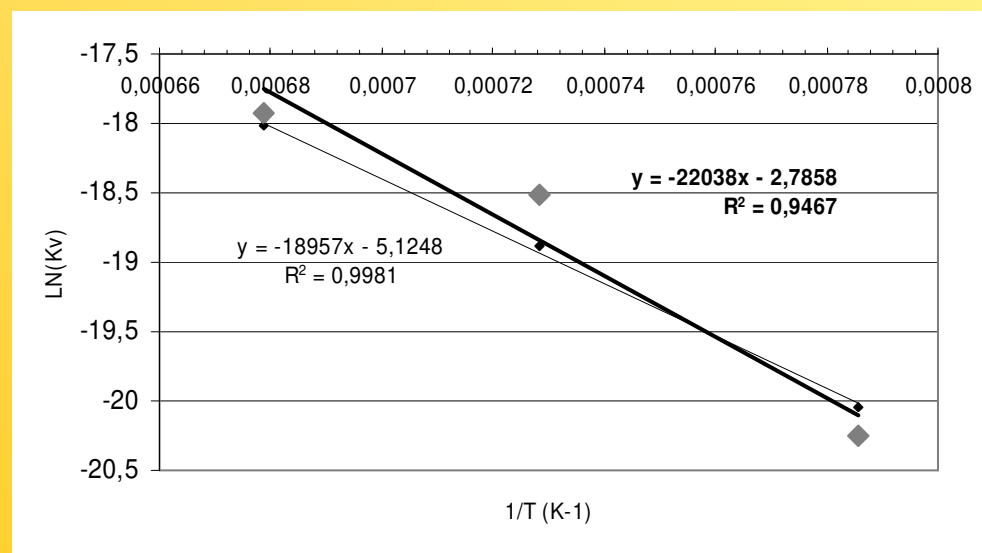
Kp ($10^{-12} \text{ g.cm}^{-2}.\text{s}^{-1}$)	1000°C	1100°C	1200°C	Kp A.E. ($\text{kJ} \cdot \text{mol}^{-1}$)
Ni30Cr0.8C	7.3	47	99	205
Ni30Cr0.2C	5.7	27	71	197



Values obtained for Kv

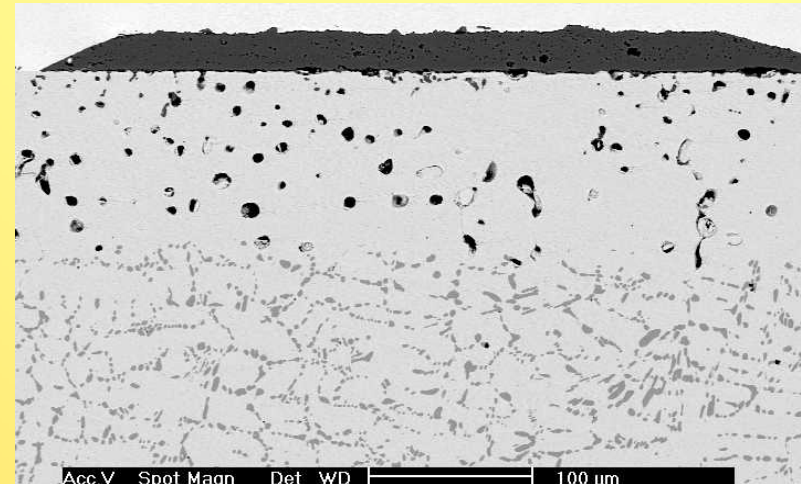
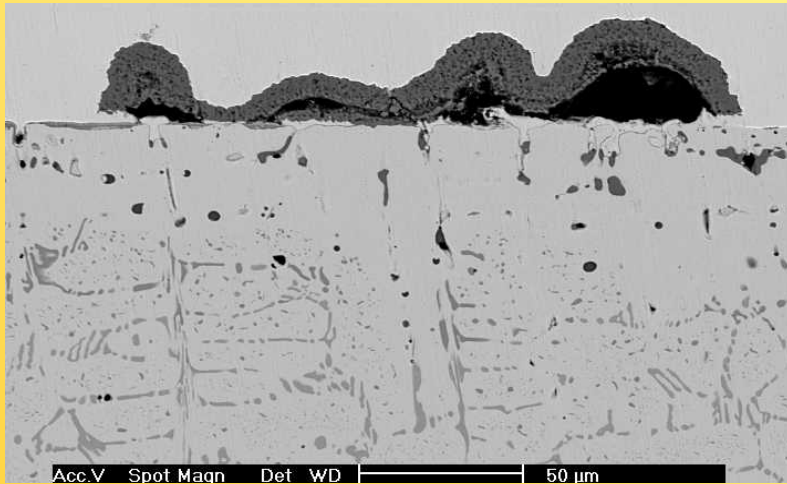
T8

K_v ($10^{-10} \text{ g.cm}^{-2}.\text{s}^{-1}$)	1000°C	1100°C	1200°C	K_v A.E. ($\text{kJ} \cdot \text{mol}^{-1}$)
Ni30Cr0.8C	16	91	165	183
Ni30Cr0.2C	20	63	149	158



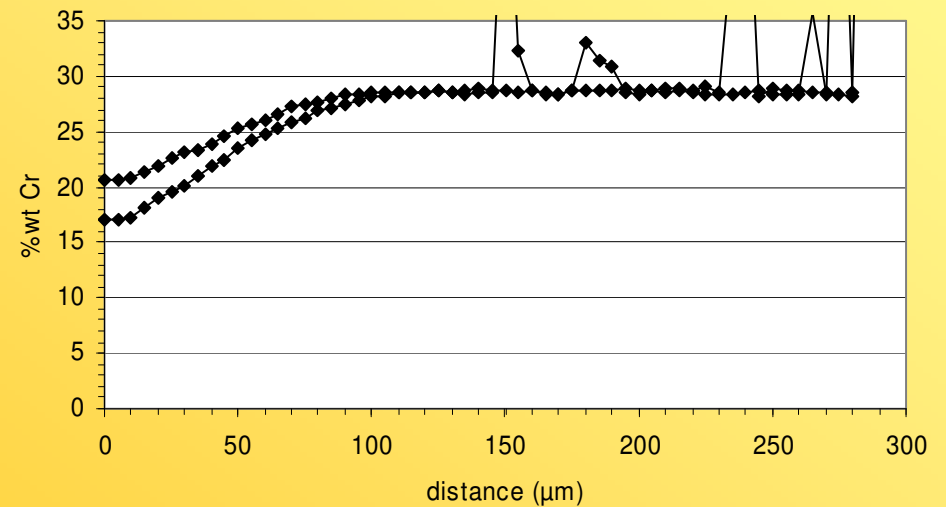
Surface states examinations

T9



Ni₃₀Cr_{0.8}C alloy after oxidation at 1000 (left) and 1200°C (right)

- Chromia scale
- Carbide free zone
- Chromium depletion in the sample matrix



Verification of the model

- Mass balance on chromium
- Comparison between the experimental curves and the mathematical results
- Comparison with previous data

Comparison between Kv constants and metallography

$$m^1_{Cr} + m^2_{Cr} = \rho \cdot \Delta e \cdot \sum_1^N [\%_w^{mat \infty} (Cr) - \%_w^{mat i} (Cr)] + \rho \cdot d_{cfz} \cdot \%_w^{all \infty} (Cr_7C_3) \cdot \%_w^{Cr_7C_3} (Cr)$$

to compare to

$$m^3_{Cr} + m^4_{Cr} = \rho_{Cr_2O_3} \cdot \left(\frac{2 \cdot M_{Cr}}{M_{Cr_2O_3}}\right) \cdot e_{Cr_2O_3} + \frac{2 \cdot M_{Cr}}{M_{Cr_2O_3}} \cdot K_V \cdot \Delta t$$

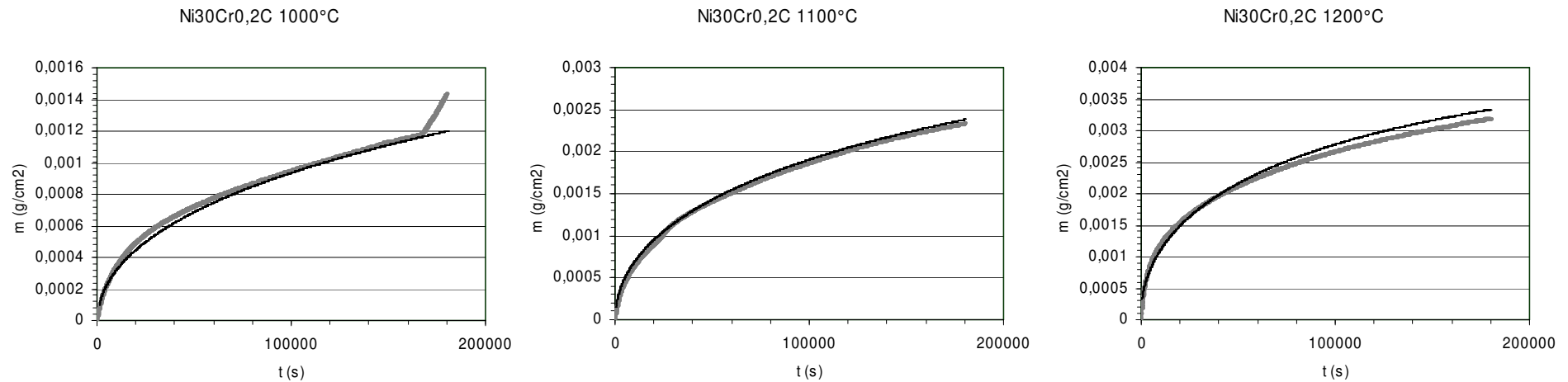
Ni30Cr0.2C mg/cm ²	Cr that left the alloy				Cr that was oxidized	
	m^1_{Cr}	m^2_{Cr}	$m^1_{Cr} + m^2_{Cr}$	m^3_{Cr}	m^4_{Cr}	$m^3_{Cr} + m^4_{Cr}$
1200°C	37.48	2.60	10.08	8.94	1.84	10.78
1100°C	5.10	1.30	6.40	4.07	0.78	4.85
1000°C	2.01	0.28	2.29	1.31	0.24	1.55
Ni30Cr0.8C mg/cm ²	Cr that left the alloy				Cr that was oxidized	
	m^1_{Cr}	m^2_{Cr}	$m^1_{Cr} + m^2_{Cr}$	m^3_{Cr}	m^4_{Cr}	$m^3_{Cr} + m^4_{Cr}$
1200°C	9.02	0.29	10.10	9.47	2.03	11.45
1100°C	6.48	3.72	5.09	1.12	1.12	6.21
1000°C	2.07	1.71	3.78	3.08	0.20	3.28

Chromia volatilization when $T > 1000^\circ C$
 $Cr_2O_3 + 3/2 O_2 \rightarrow 2 CrO_3$ (gaseous)

Chromium depletion at the alloy surface
 Chromium oxide scale

Good correspondence for most cases

(worst results obtained for Ni30Cr0.8C at high temperature)



→ Elementary mass gain step:

$$(dm)_{n+1} = \frac{K_p}{m_n} \cdot dt - K_v \cdot dt$$

→ Good fit between the experimental mass gain curves and the curves calculated from the determined K_p and K_v values

Comparison between Kv constants and previous results

T12

Kv (10^{-10} g.cm ⁻² .s ⁻¹)	1100°C	1200°C
Hagel	37*	124*
Stearns <i>et al</i>	83	280
This study: Ni30Cr0.8C Ni30Cr0.2C	91 63	165 149

* : calculated from the $K_v = 0.214 \cdot \exp(-204\text{kJ}\cdot\text{mol}^{-1} / R\cdot T)$ formula

→ Good agreement between literature data and these results

→ Oxidation of superalloys:

- Oxidation of Ni30CrxC alloys follows a parabolic law;
- Oxidation rate depends on carbon content: K_p and K_v increase with %wtC

→ New mathematical model to determine K_p and K_v :

* Drawing $m \cdot \frac{dm}{dt}$ versus $-m$ allows to determine directly both K_p and K_v

* K_p and K_v values were verified twice. They describe the real HT phenomenon.

Refer to : P. Berthod, Oxidation of Metals, Vol. 64 (3/5), oct 2005, 235-252