# Surface Films Formed on Ni-Cr-Fe Alloys including Alloy 600 and Alloy 690

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# Acknowledgements

**Electric Power Research Institute,**
**Palo Alto, CA**

Dr. Peter Andresen, GE Global Research Center for assistance with design of high pressure/high temperature Ti- water loop.

Dr. Christopher Kumai, UC Berkeley, for design of Ti autoclave and Raman spectrometer.

# Overview

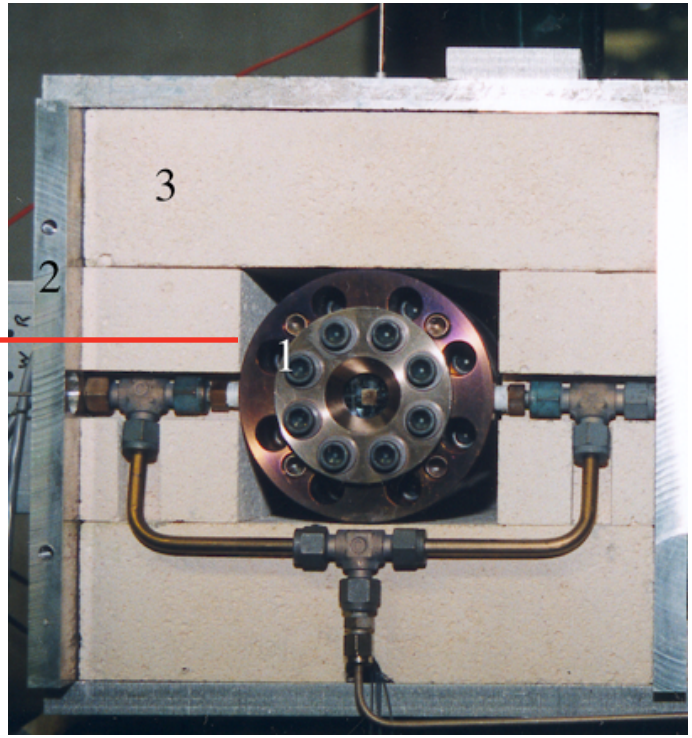
**SERS**

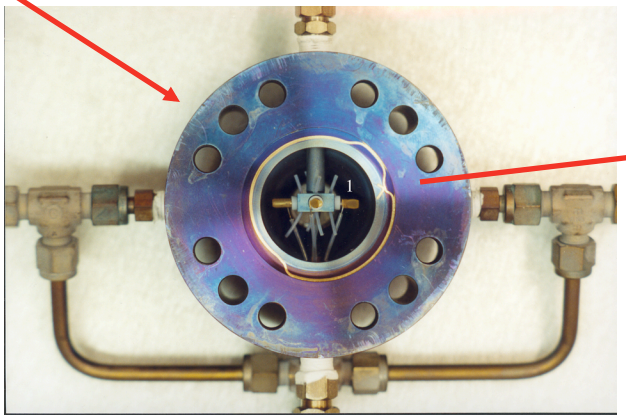
- Alloy 600
  - Ni, Cr, Ni-5Cr-8Fe, Ni-10Cr-8Fe
- Alloy 690

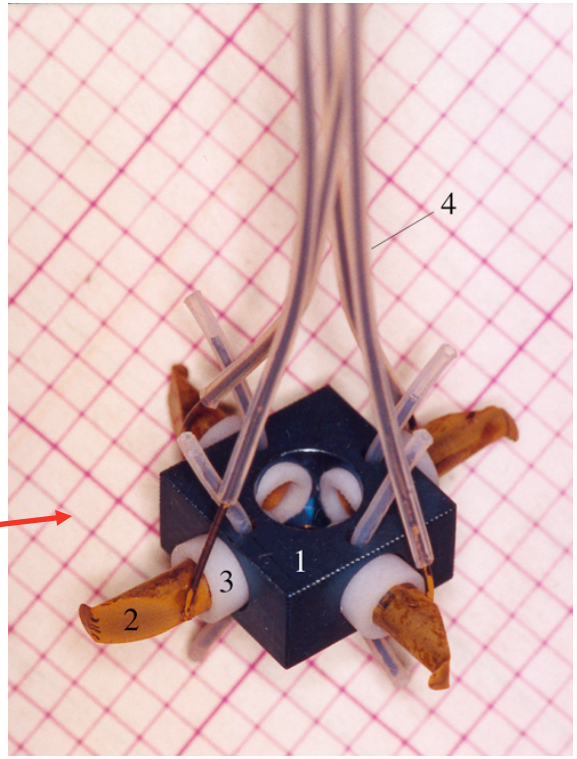
**Diffusion Path Analyses**

- Introduction
- Alloy 600
  - Mild Cr-depletion
  - Strong Cr-depletion
- Alloy 690

# Samples in titanium autoclave with sapphire window

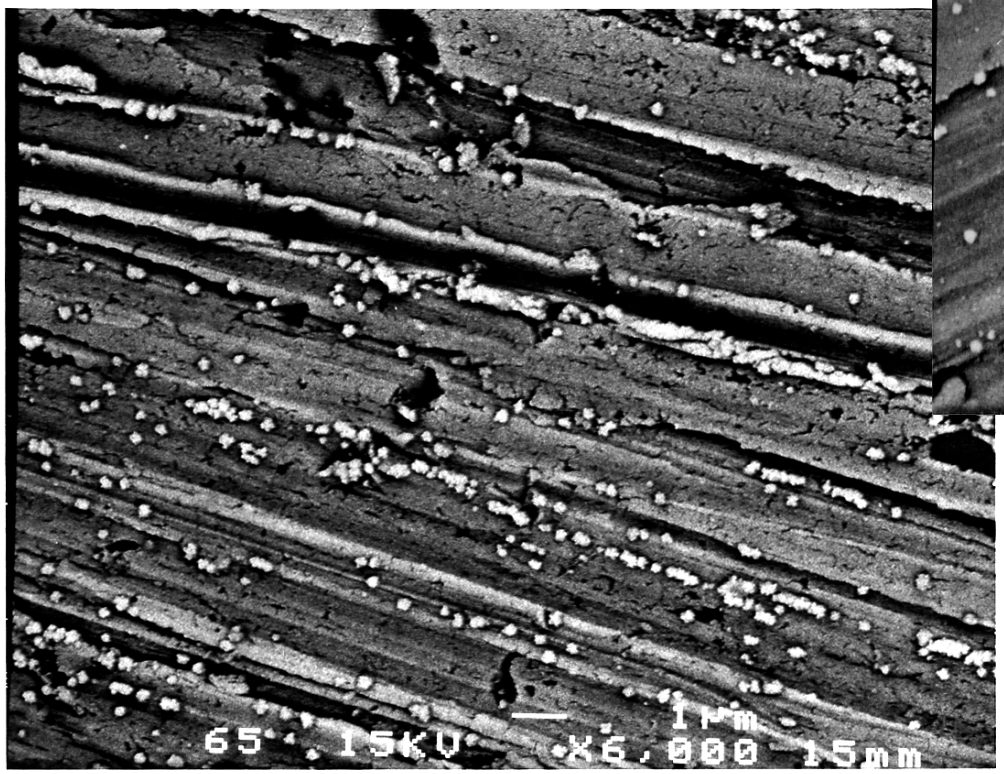


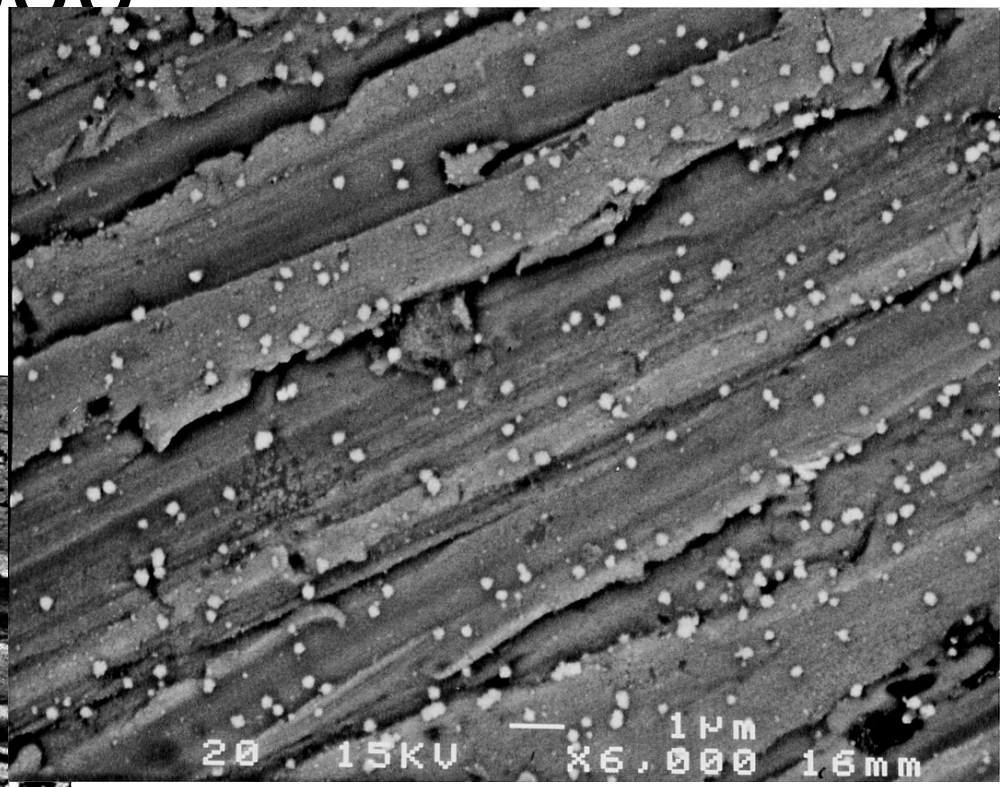



# Gold particles for SERS on Alloy 600

-500mV




-600mV

## Test Procedure

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Identify passive film of Alloy 600 and Alloy 690 (Ni, Cr, Ni-5Cr-8Fe, Ni-10Cr-8Fe)

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Cool to 22°C and measure SERS.

Remove sample from autoclave, expose to air and measure SERS.

**Alloy 600**: heated to 300°C, polarized from -900 mV to -460 mV vs SHEs

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1200 ppm B + 0.2 ppm Li
Sat'd with $N_2$-4%$H_{2(g)}$

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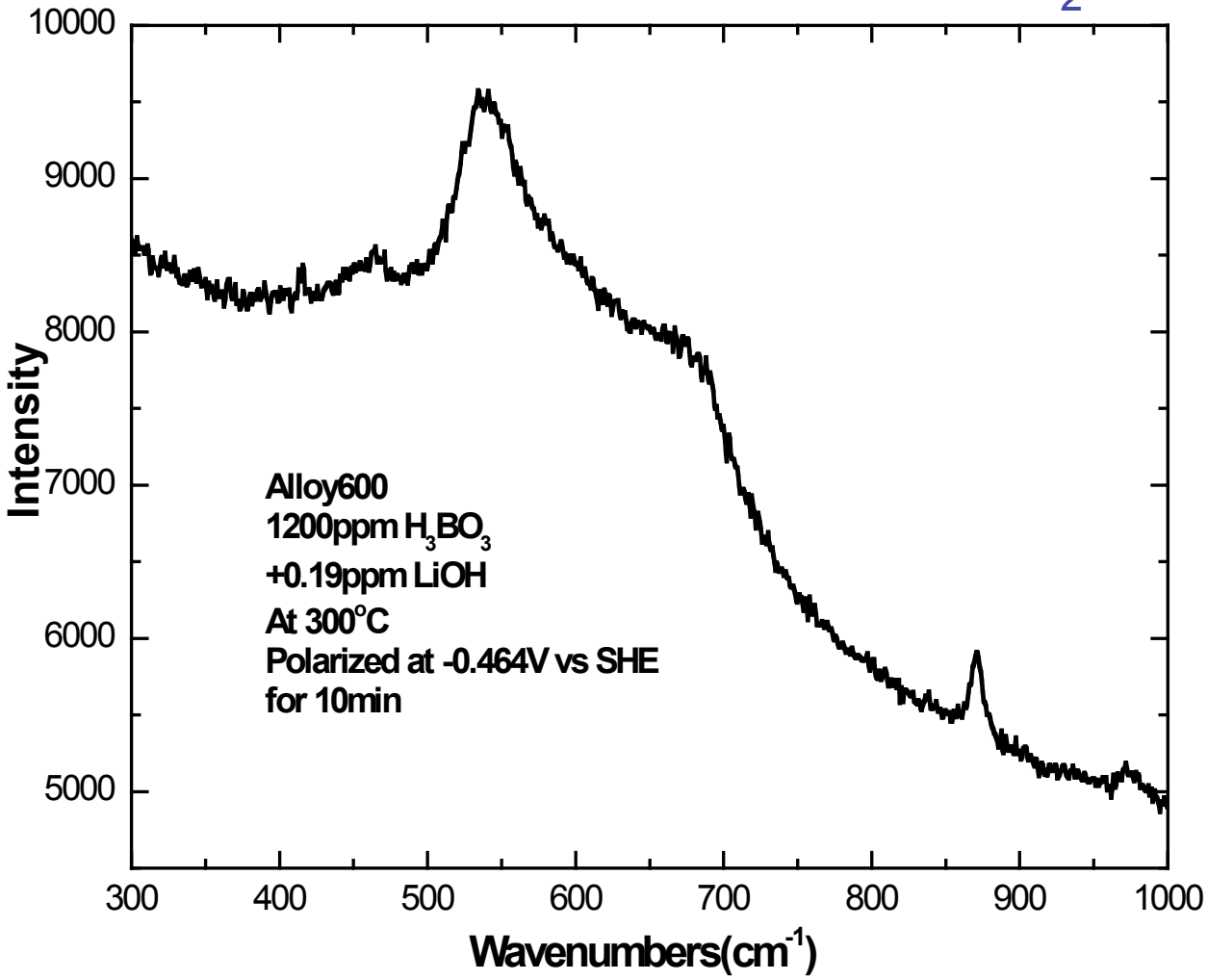


)

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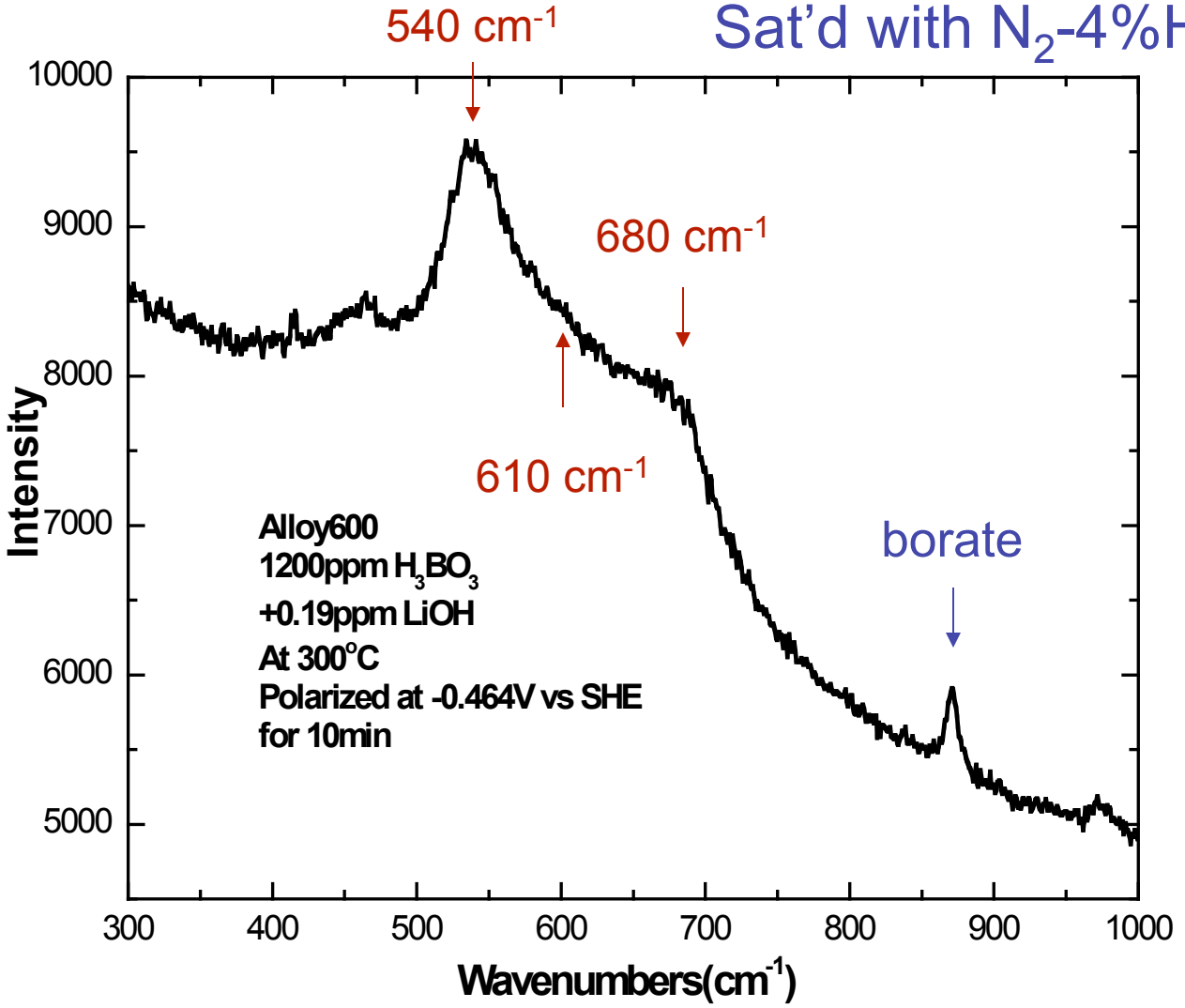
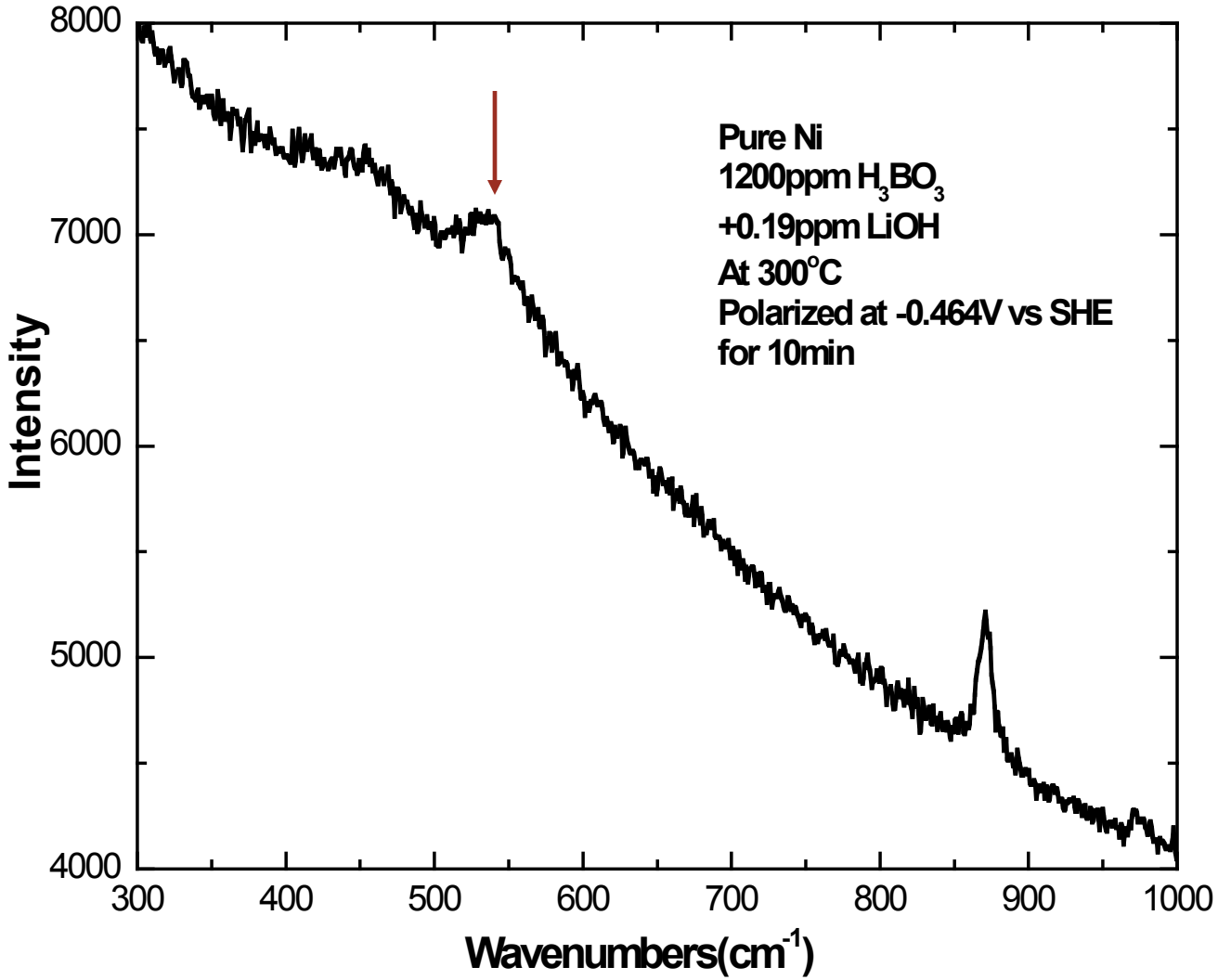



Identify Passive Film (540, 610, 680 $cm^{-1}$)

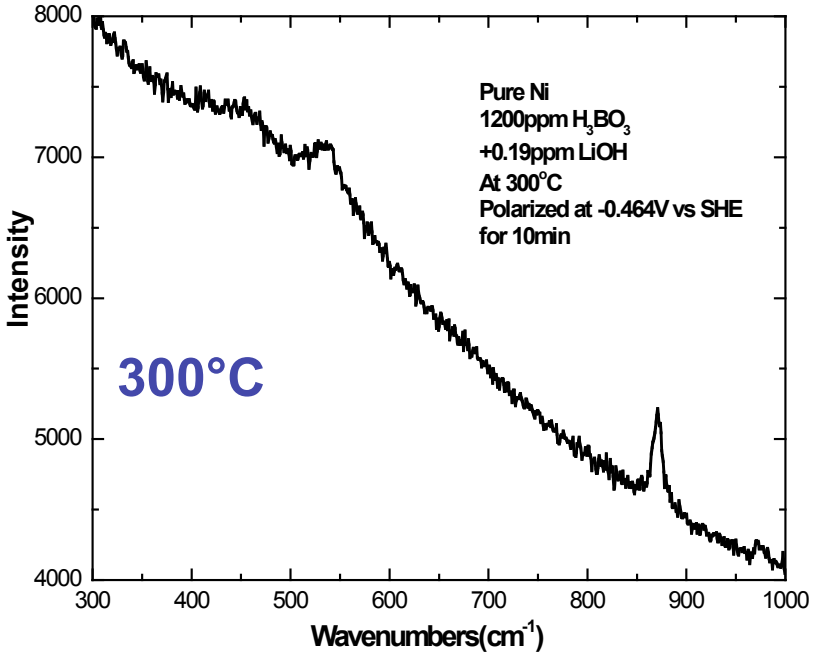
# Nickel 300°C

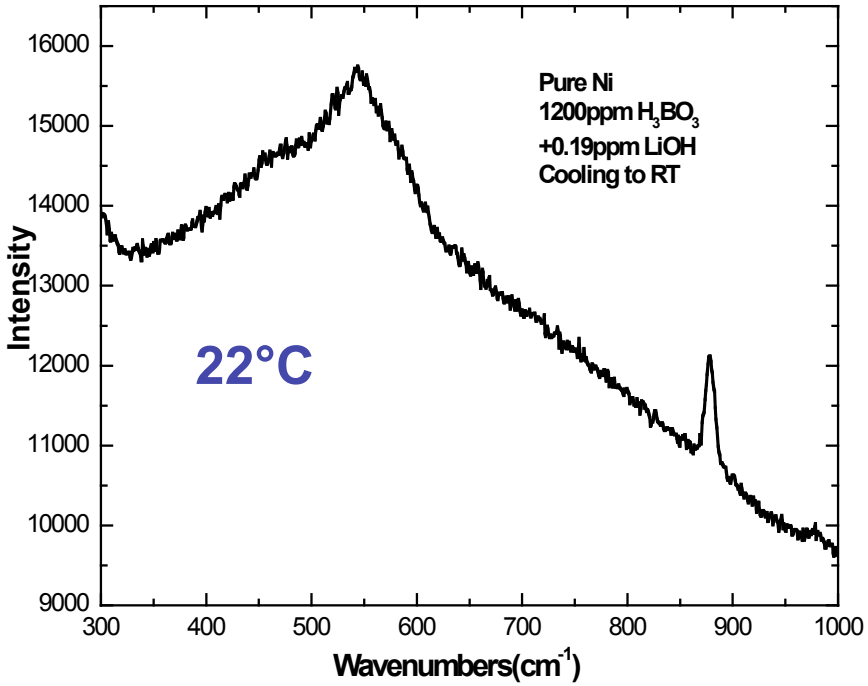
**540 $cm^{-1}$ = NiO**



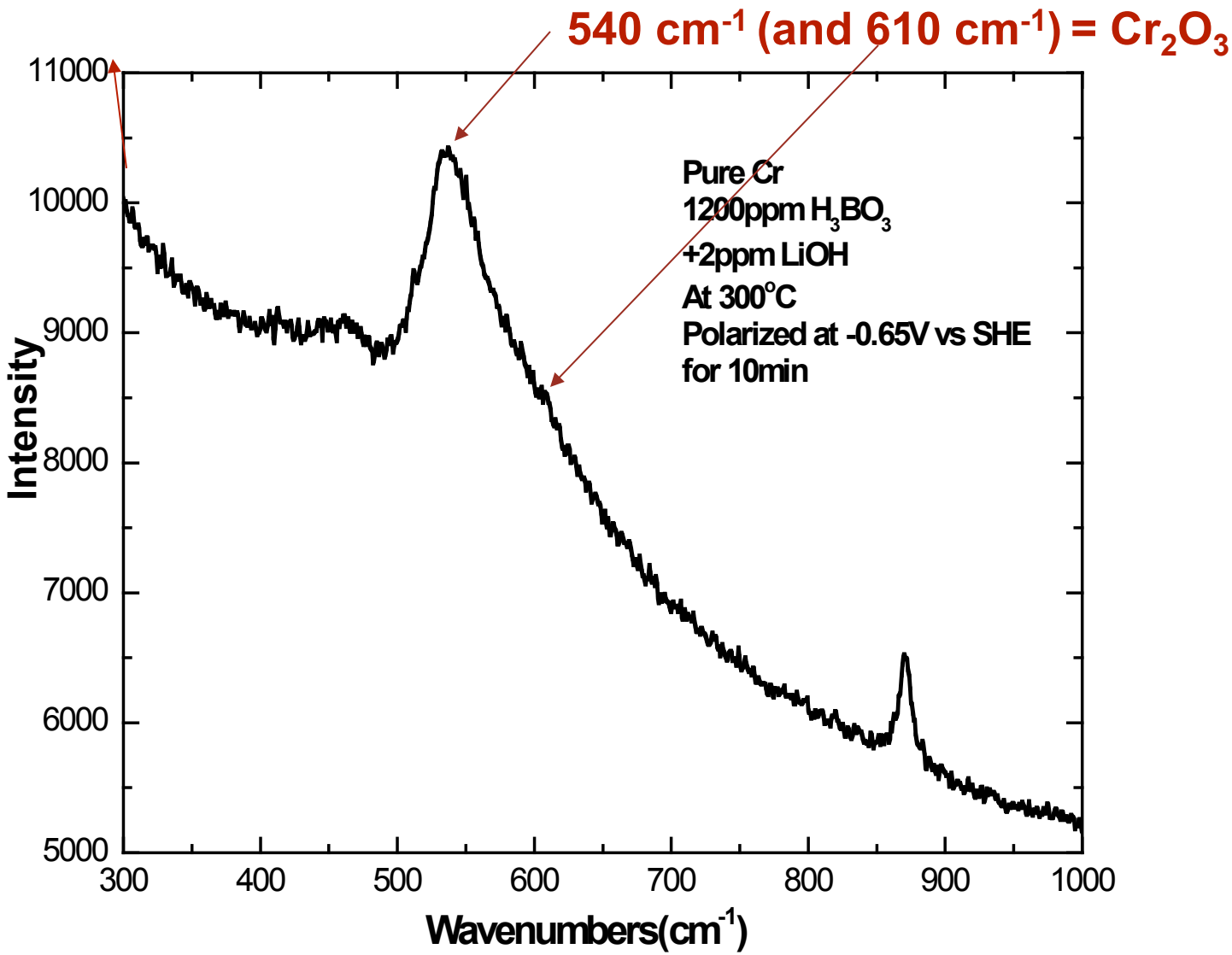
# Ni

**540 $cm^{-1}$ = NiO**



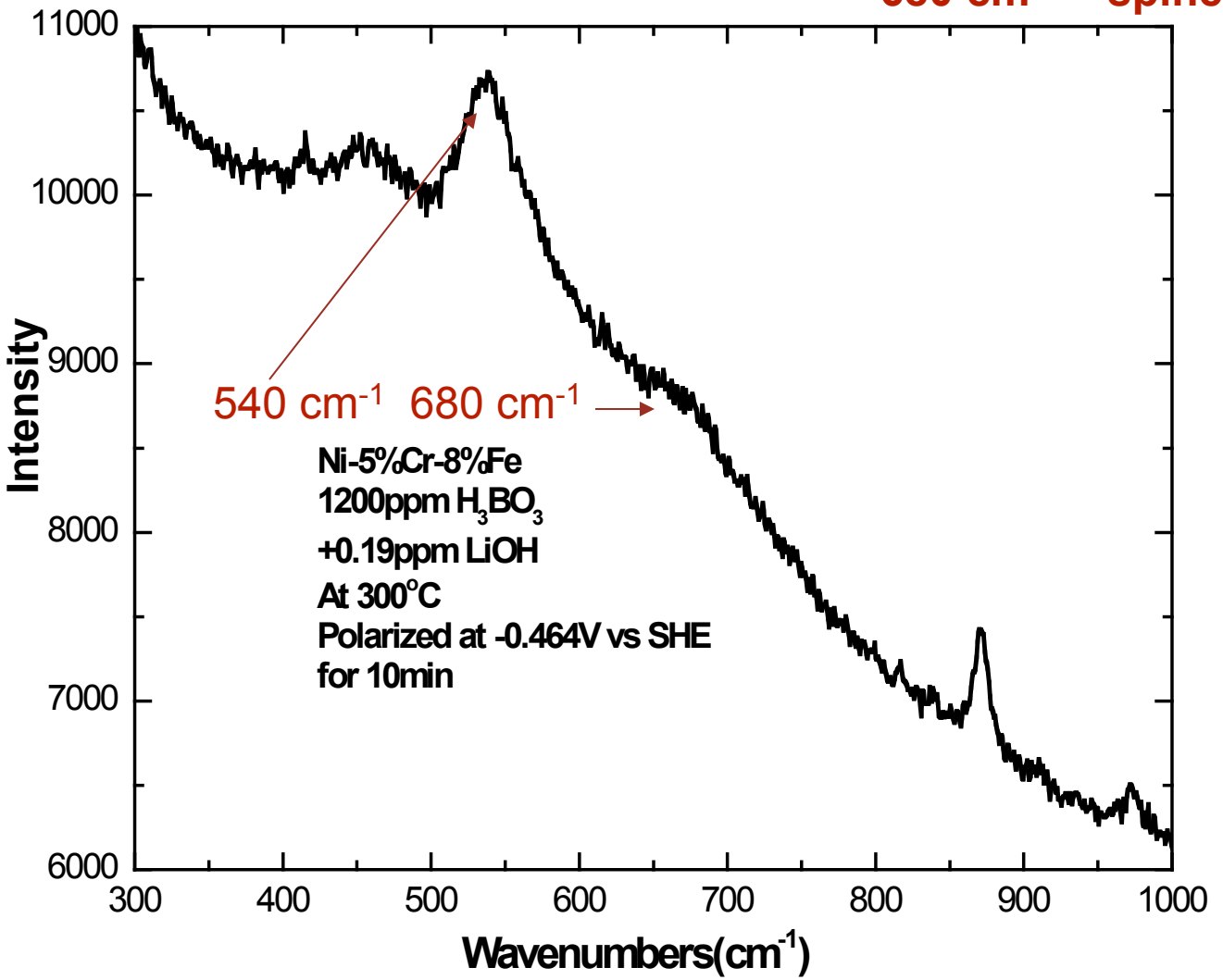
# Cr - 300°C


540 cm-1 (and 610 cm-1) = Cr2O3
Pure Cr
1200ppm H3BO3
+2ppm LiOH
At 300°C
Polarized at -0.65V vs SHE
for 10min
Intensity
11000
10000
9000
8000
7000
6000
5000
300
400
500
600
700
800
900
1000
Wavenumbers(cm-1)

# Ni-5Cr-8Fe

**540 $cm^{-1}$ = $Cr_2O_3$**

**680 $cm^{-1}$ = spinel $NiCr_2O_4$ (?)**

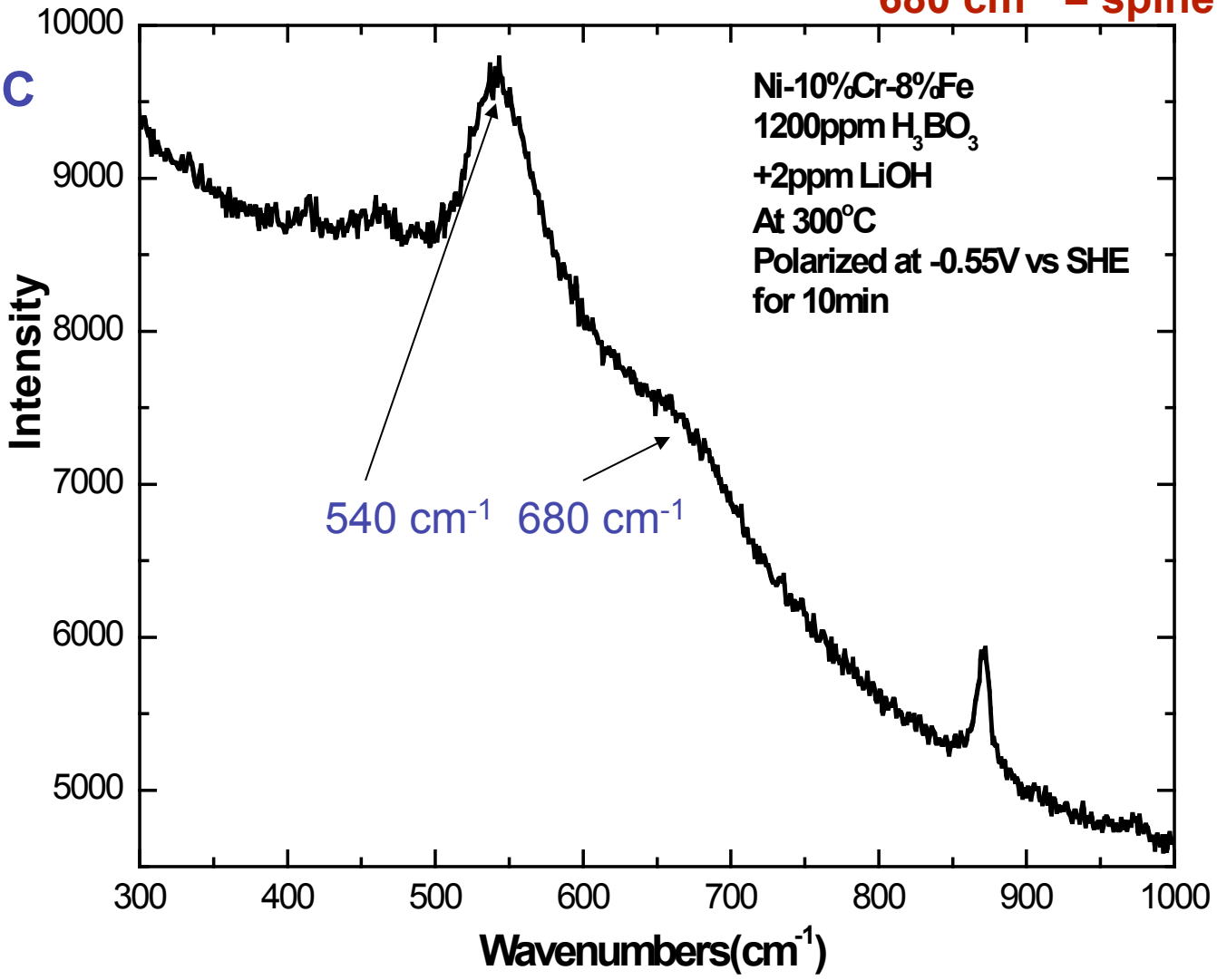


# Ni-10Cr-8Fe

**540 $cm^{-1}$ = $Cr_2O_3$**

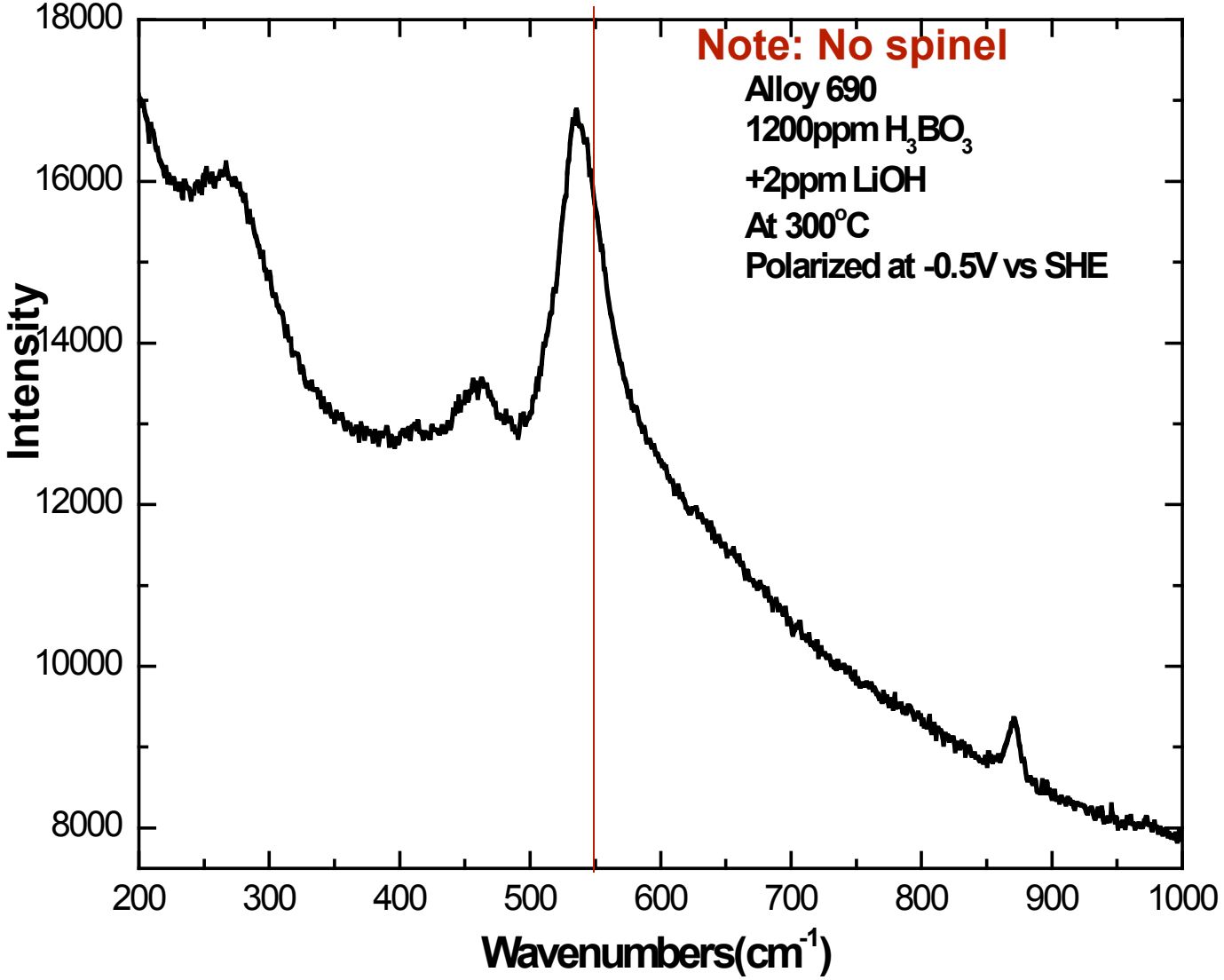
**680 $cm^{-1}$ = spinel $NiCr_2O_4$ (?)**

**300°C**



## Alloy 690 300°C

**540 $cm^{-1}$ and 610 $cm^{-1}$ = $Cr_2O_3$**



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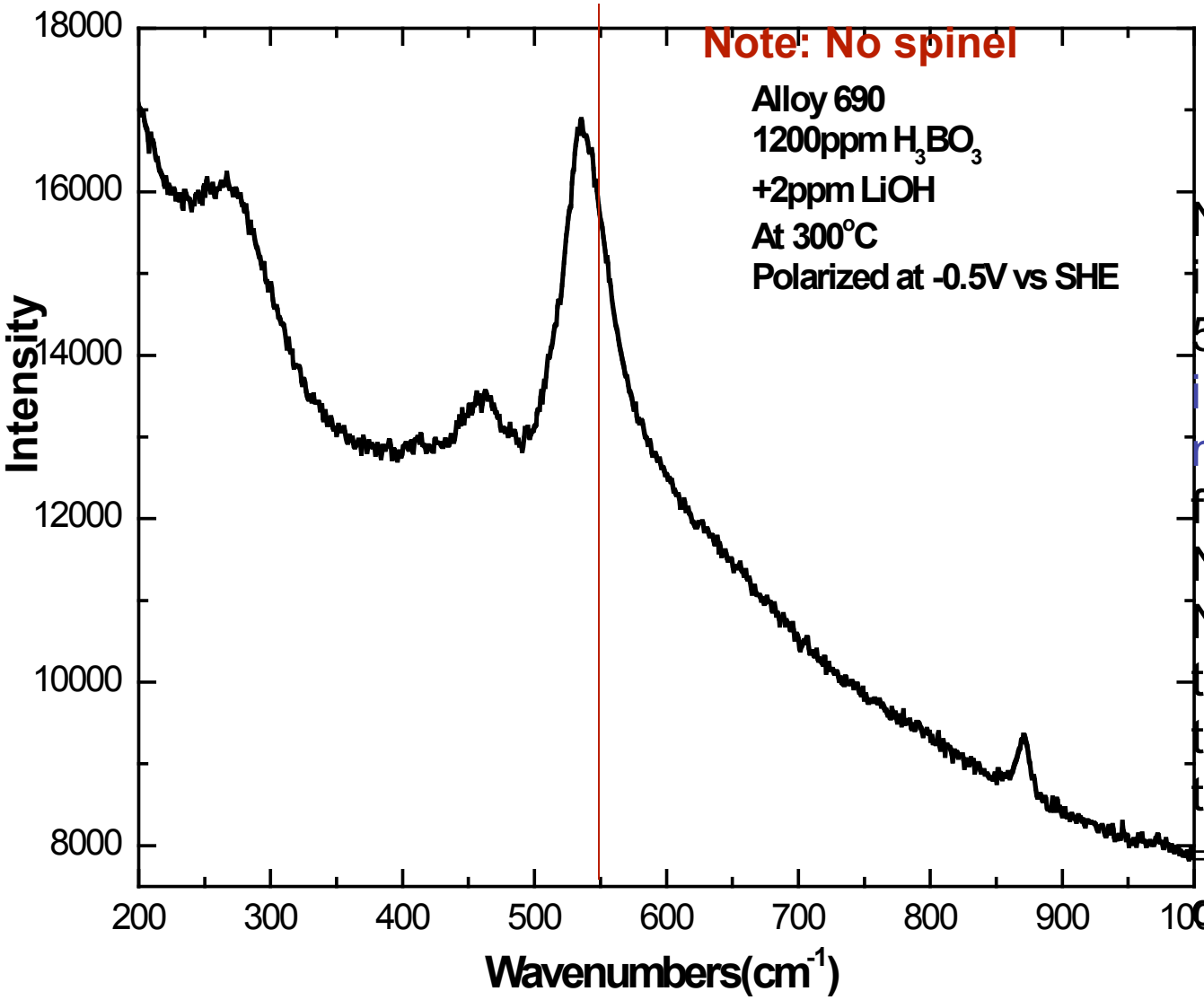



NB:The intensity of the 540 $cm^{-1}$ peak increases monotonically from Ni, to Ni-5Cr-8Fe, to Ni-10Cr-8Fe, to Alloy 600, to Alloy 690, to Cr.

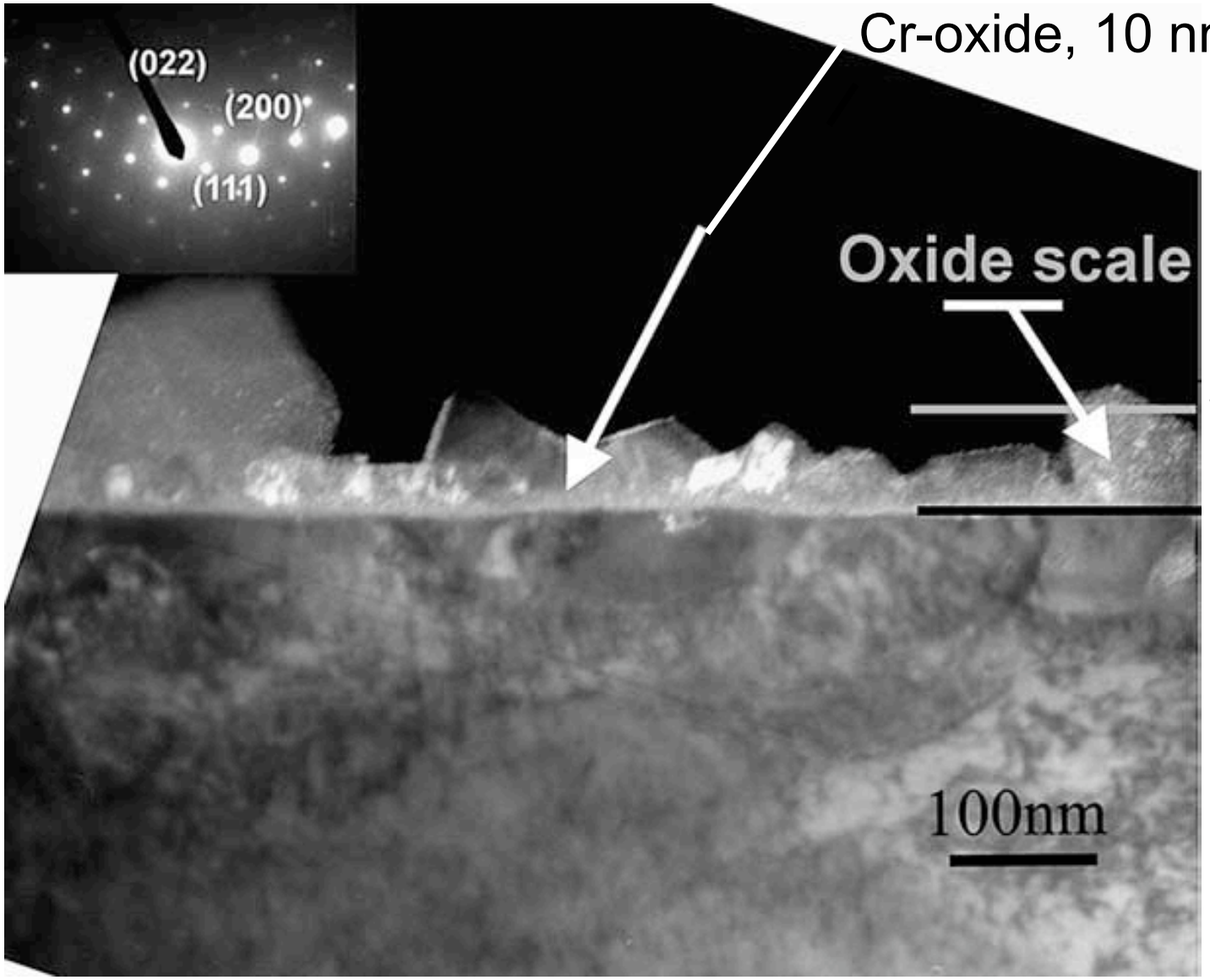
$\Rightarrow$540 $cm^{-1}$ is due to $Cr_2O_3$

## Summary

Alloy 600's passive film at 300° and 320°C= $Cr_2O_3$ + $NiCr_2O_4$

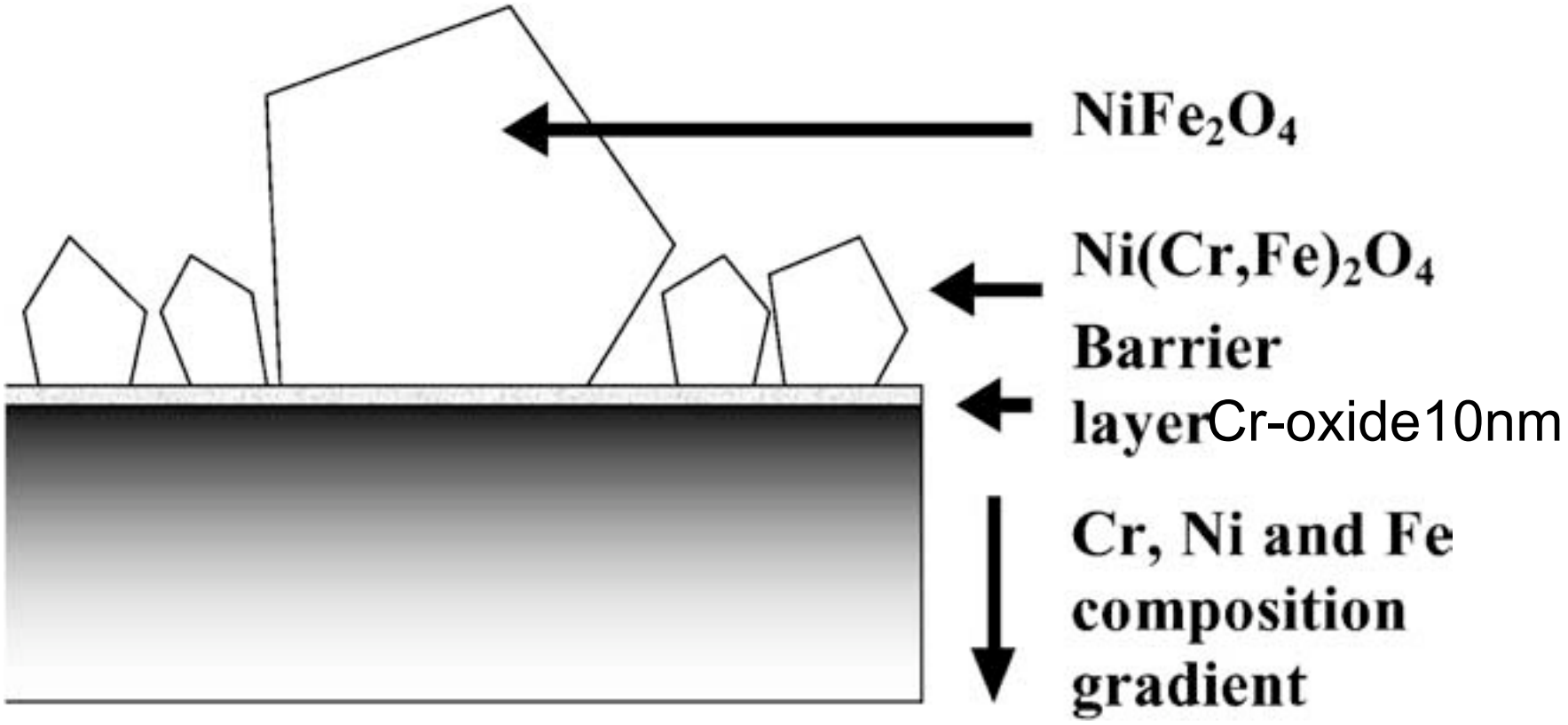
## Comparison to Other Researchers:

Alloy 600 PWRpw 360°C/300h




J. Panter et al., JNuclMaterials 348 (2006) 213-221

Comparison to Other Researchers:

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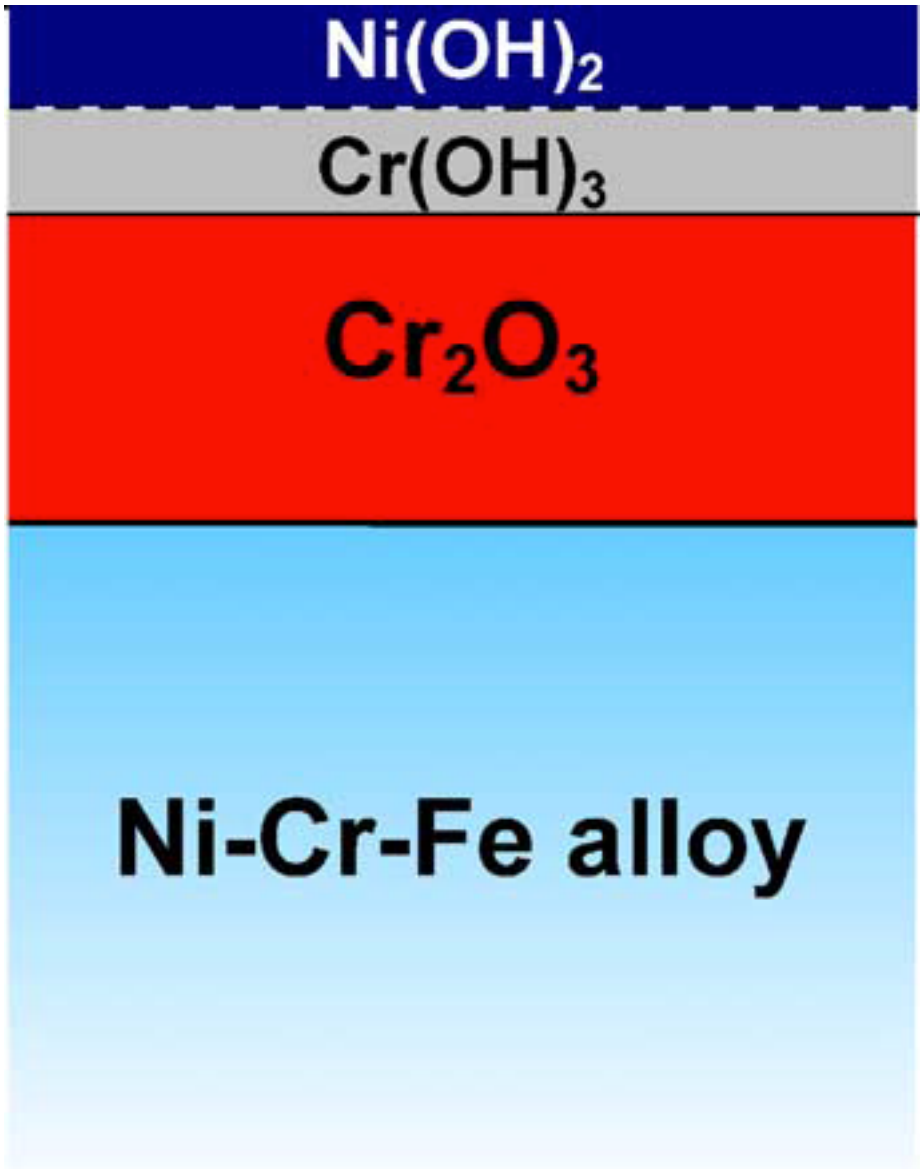


A. Machet [a,b], A. Galtayries [a,1], S. Zanna [a], L. Klein [a], V. Maurice [a], P. Jolivet [b], M. Foucault [c], P. Combrade[c], P. Scott [b], P. Marcus [a,*]

Electrochimica Acta 49 (2004) 3957–3964

# Comparison to Other Researchers: High Temperature Water

Alloy 600 High purity water 392°C = $NiFe_2O_4$
543°C = $NiFe_2O_4$, **CrOOH** and **$Cr_2O_3$** (RS)
J.e.Maslar et al., JECS, 156 C103 (2009).

Alloy 600 in $H_2$sat'd water (pH=10) at 285°C
**10 nm $Cr_2O_3$**
N.S. McIntyre, JECS 750 (1979)

Alloy 600 350°C 30cc/Kg $H_2$ **$Cr_2O_3$**/CrOOH/$NiCr_2O_4$/NiO
1 cc/Kg $H_2$ **$Cr_2O_3$**/CrOOH/NiO
Ji Hyun Kim and Il Soon Hwang, 11th Internat Conf on Envir Degrad

Alloy 625 (22Cr 8Mo 4Fe) and Alloy 718 (18Cr 3Mo 18Fe)
In SCW at 600°C: **$(Cr,Fe)_2O_3$**/spinel/NiO
X.Ren et al., Corrosion, 63, 603 (2007)

# Comparison to Results of Other Researchers: Gaseous Oxidation

Ni-10Cr air oxidation **inner layer of $Cr_2O_3$** (continuous at T>900°C)
Outer layer of NiO
D.L. Douglas, Corros. Sci., 8, 665 (1968).

Ni-16Cr-9Fe and Ni-17Cr-7Fe
0.4-4min thin (1nm) **inner layer of $Cr_2O_3$** and outer layer of $Cr(OH)_3$ + $Ni(OH)_2$
4.8 min $Cr_2O_3$ increases and CrOOH decreases.

**$Cr_2O_3$** on Ni-20Cr in flowing $10^{-4}$Pa of $O_2$ at 550°C
J.F. Schmitt et al. Oxidation of Metals, 44, 429 (1995).

# Comparison to Other Researchers: Aqueous 25°C

Alloy 600 passivated at -200 mV and 0 mV/2h vs SCE in 0.5M NaCl **(RT)**
AES => **2 nm thick inner layer of $Cr_2O_3$**, a middle layer of iron oxide and an outer layer of NiO
Cr depletion in the alloy beneath the passive film

G. Lorang,' N. Jallerat,' K. Vu Quang' and J.-P. Langeron,
SURFACE AND INTERFACE ANALYSIS, VOL. 16, 325-330 (1990)'

Ni21Cr8Fe, Ni17Cr10Fe in 0.05M $H_2SO_4$ at **RT**
**Inner layer of 96%$Cr_2O_3$**+4%$Fe_2O_3$ (6.5Å)
Outer layer of $Cr(OH)_3$ (4.5Å) ESCA
P.Marcus and J.M. Grimhal CorroSci, 33, 805 (1992)

## Summary

Alloy 600's passive film at 300° and 320°C= $Cr_2O_3$ + $NiCr_2O_4$

Ni-5Cr-8Fe and Ni-10Cr-8Fe passive film = $Cr_2O_3$ + $NiCr_2O_4$

Alloy 690's passive film = $Cr_2O_3$

Alloy 690's film is fundamentally different than the films formed on Alloy 600, Ni-5Cr-8Fe and Ni-10Cr-8Fe.

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**Diffusion Path Analyses**

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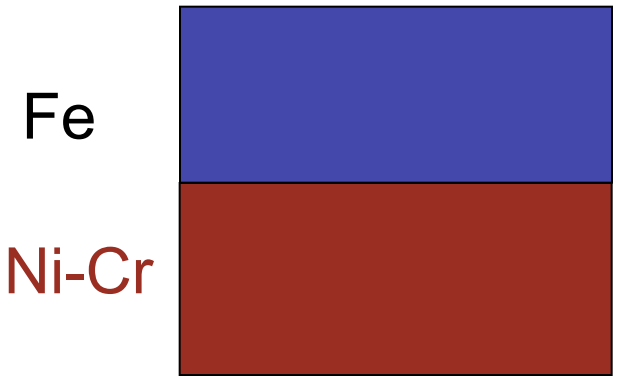
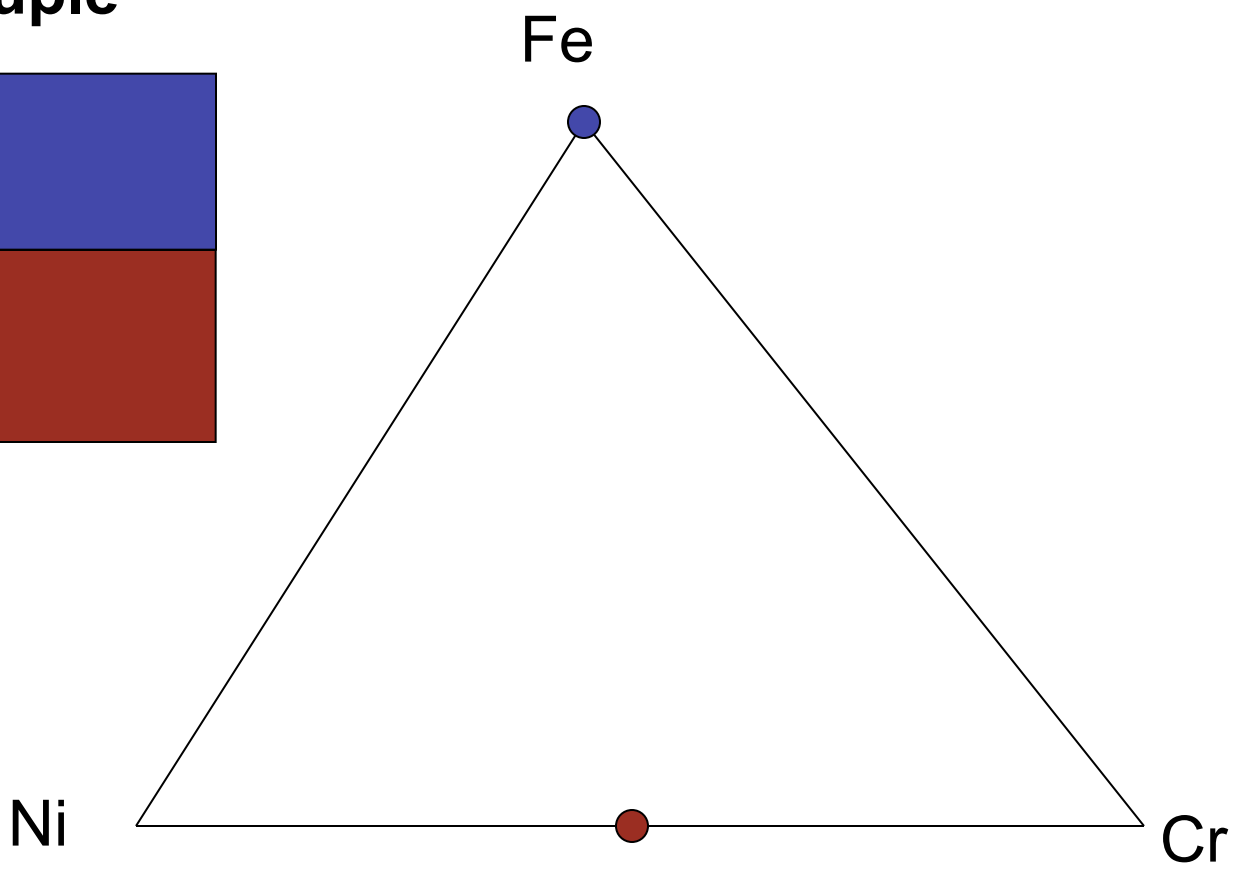
# Diffusion Path Analyses - Rhines

**Diffusion Couple**

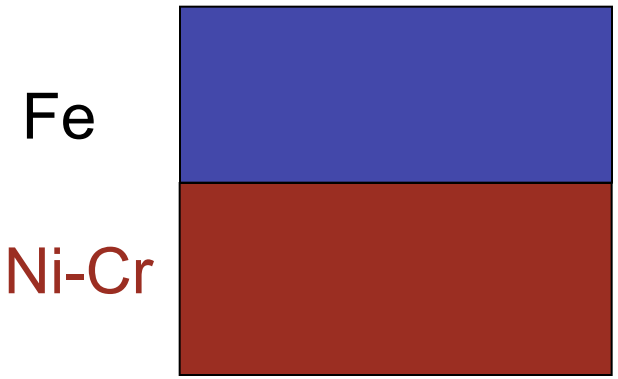


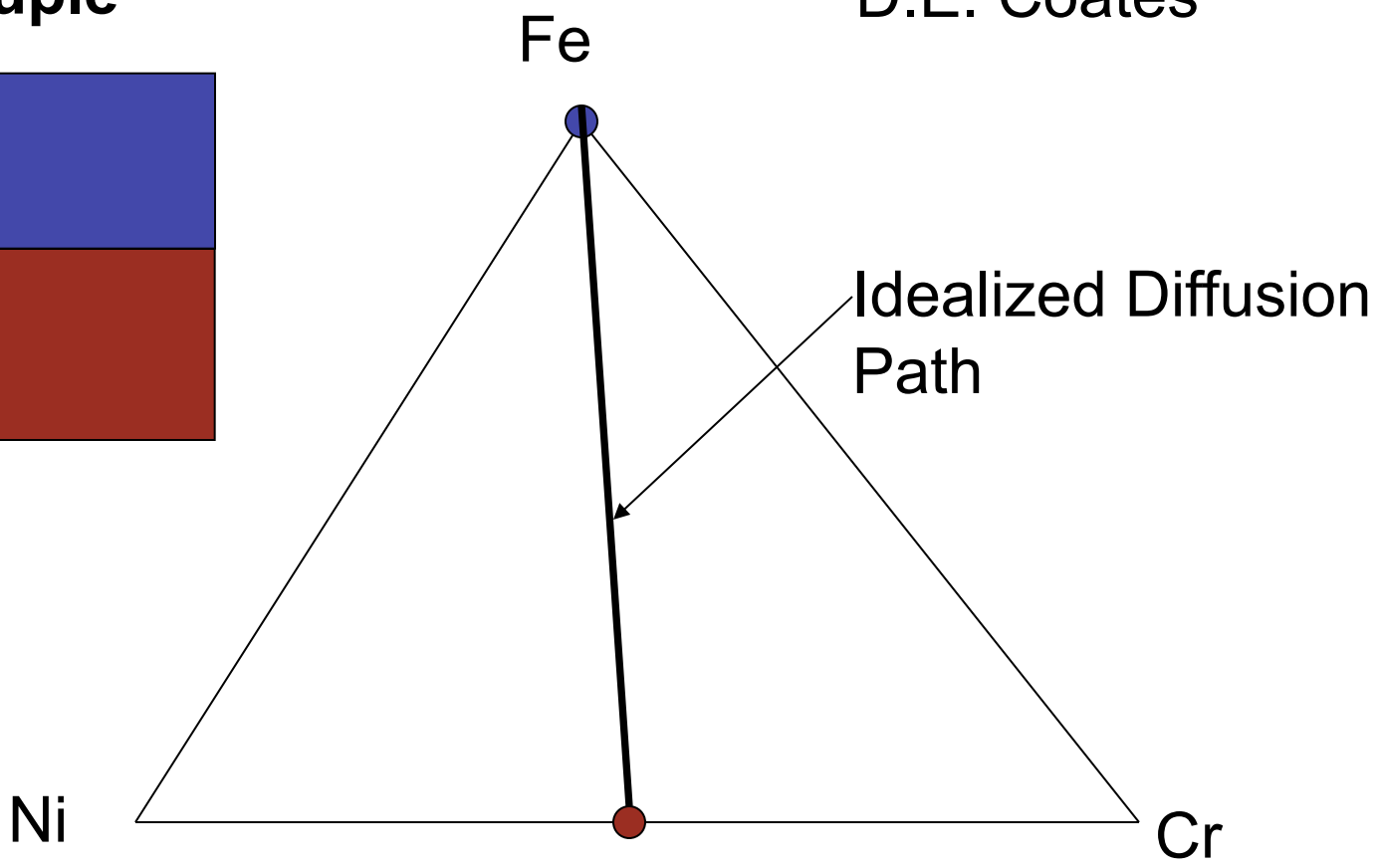



# Diffusion Path Analyses - Rhines (~1940)

J.S.Kirkaldy
D.E. Coates

**Diffusion Couple**



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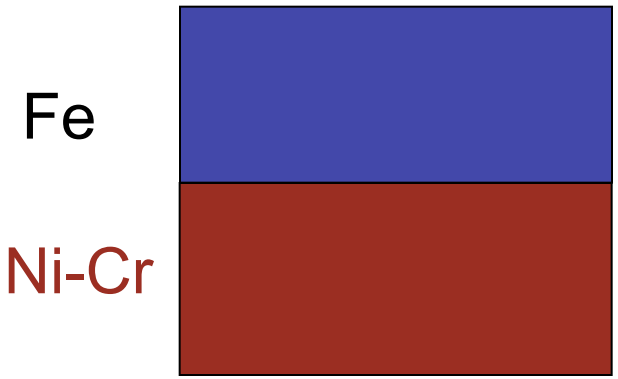
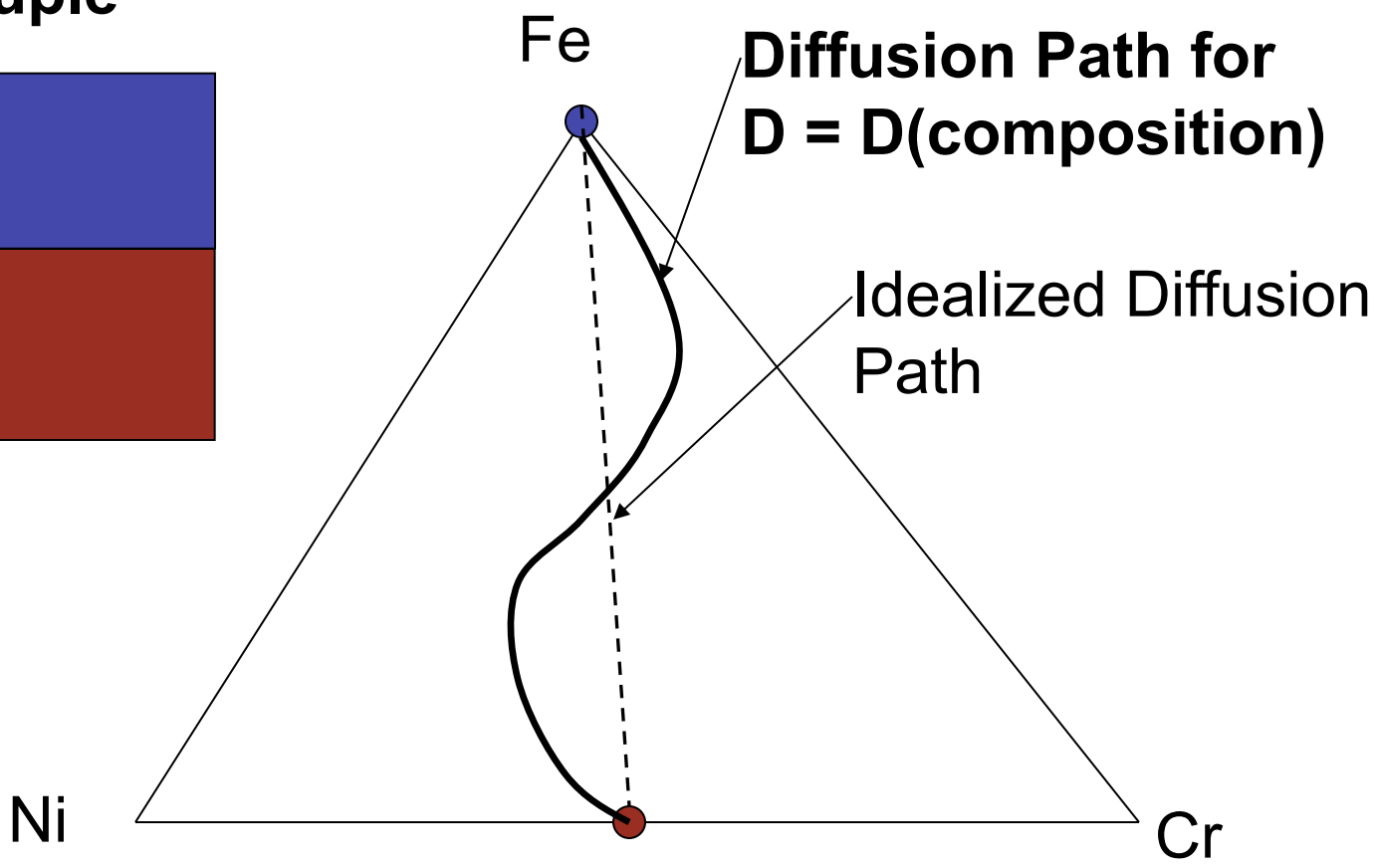
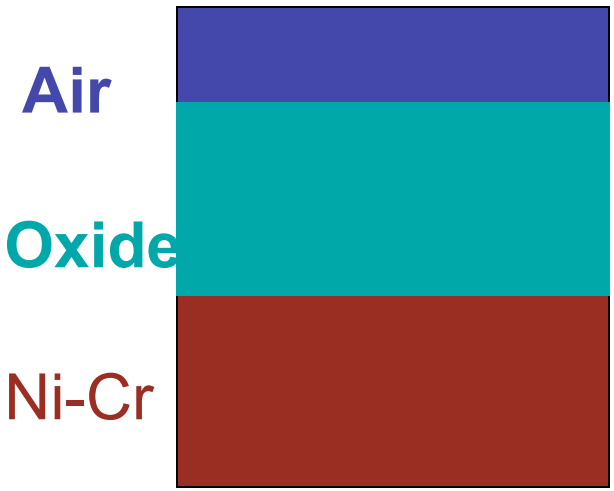


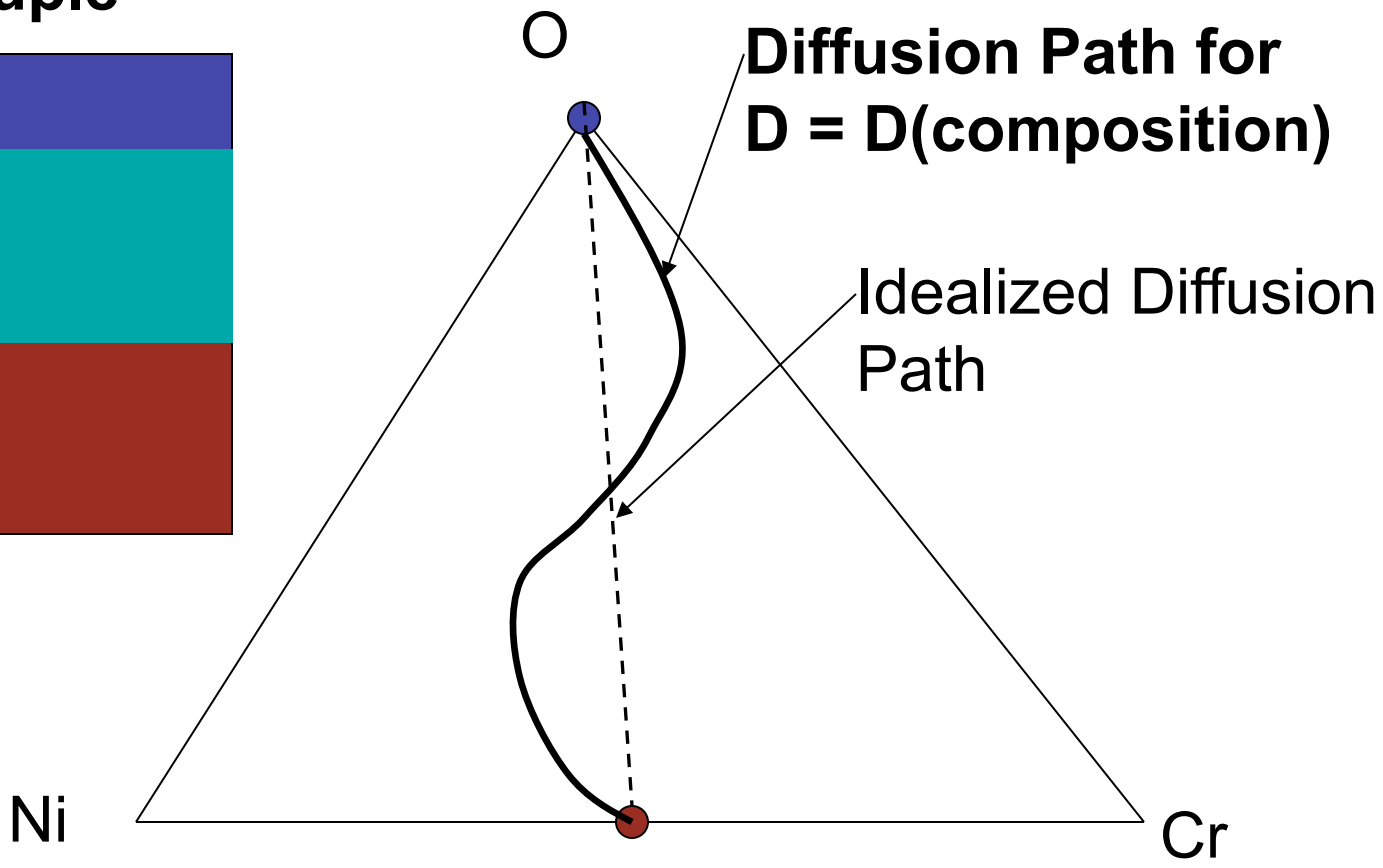



# Diffusion Path Analyses of Oxide Film Growth

**Assumptions:** Transport through the film is RDS
=> interfacial reactions are in equilibrium

**Diffusion Couple**



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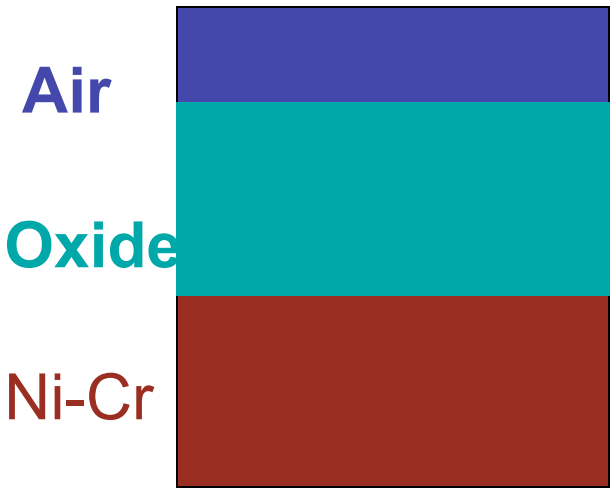


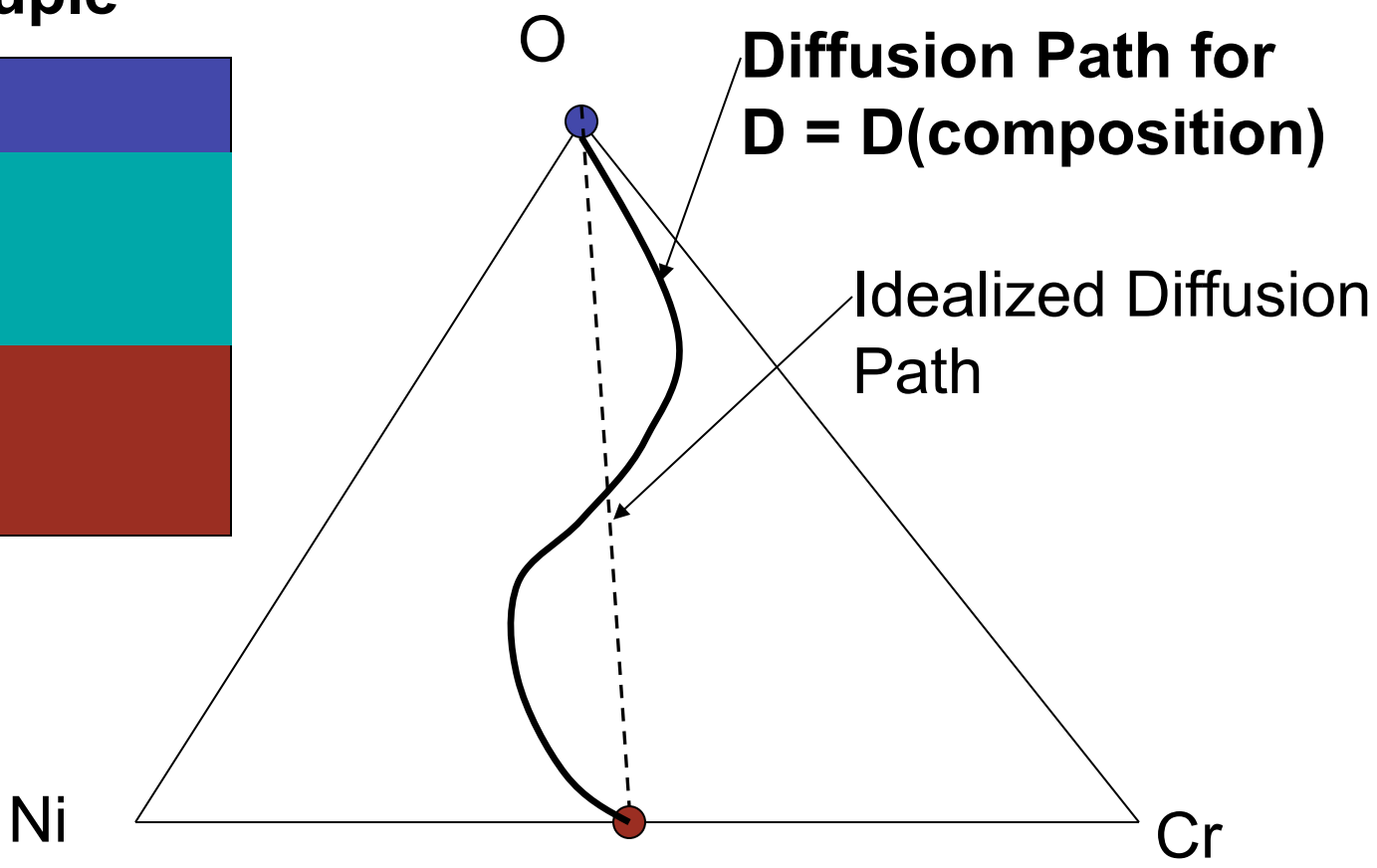


Thus, the complete microstructure of the surface is predicted from knowledge of (1) the ternary Ni-Cr-O phase diagram, and (2) the diffusivities of Ni, Cr, and O in each of the phases present in the phase diagram.

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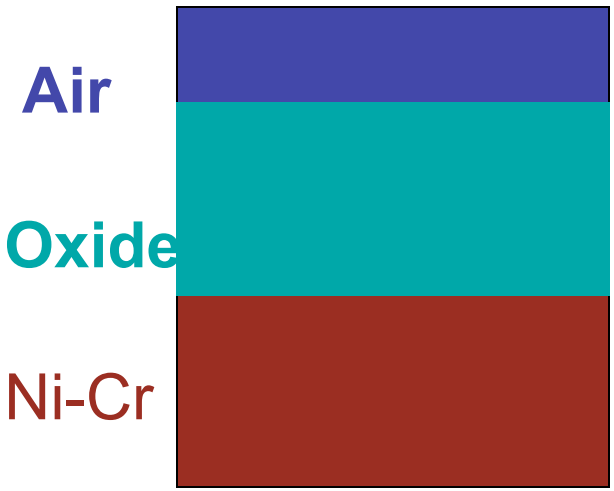


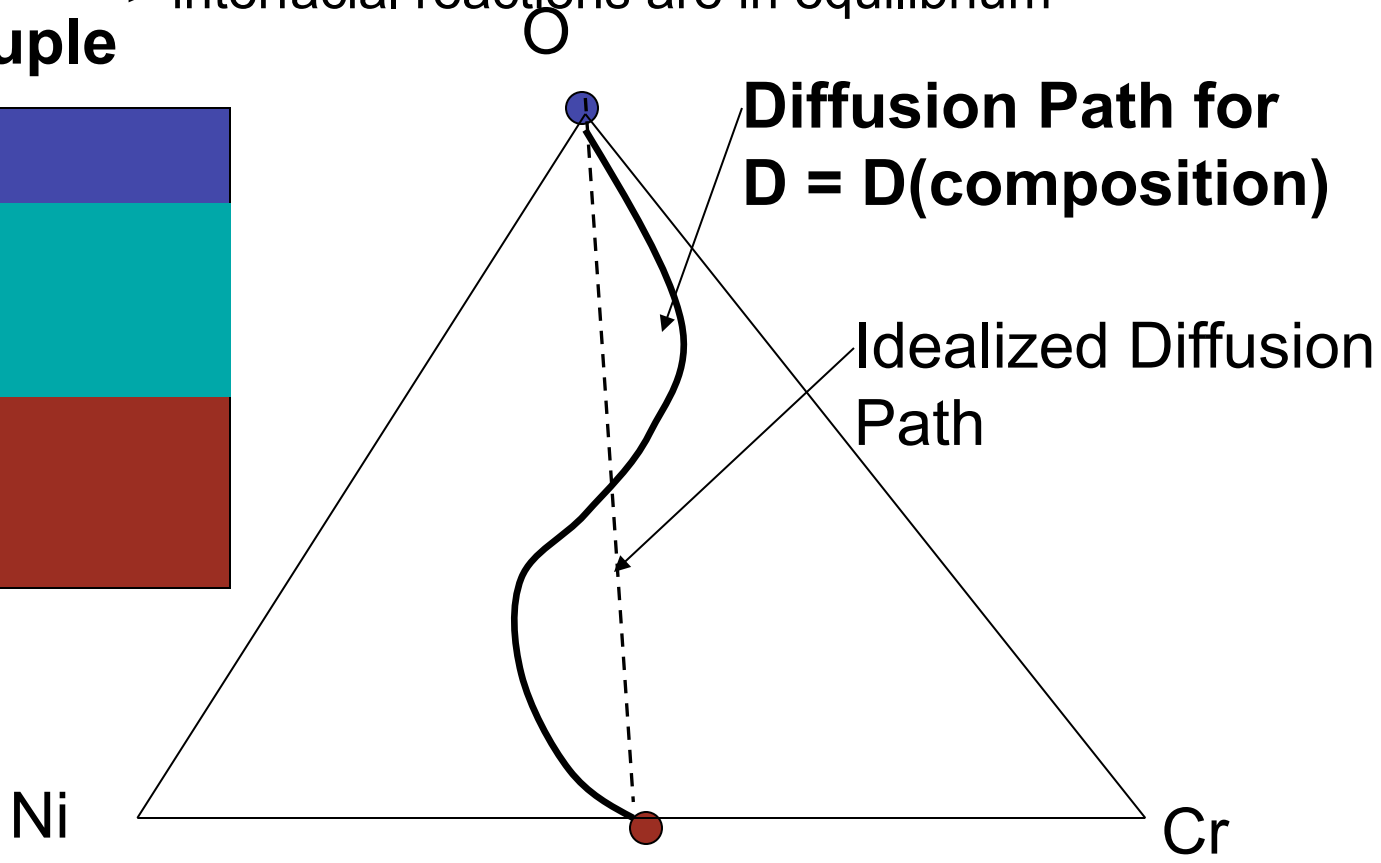


For Alloys 600 and 690 in water at 320°C, we don't know the phase diagram or the diffusivities. However, important information about the film is obtained by measuring the species present in the film and plotting the results on an assumed phase diagram.

# Overview

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# Hypothesized Ni-Cr-Water Ternary Phase Diagram* at 300°C

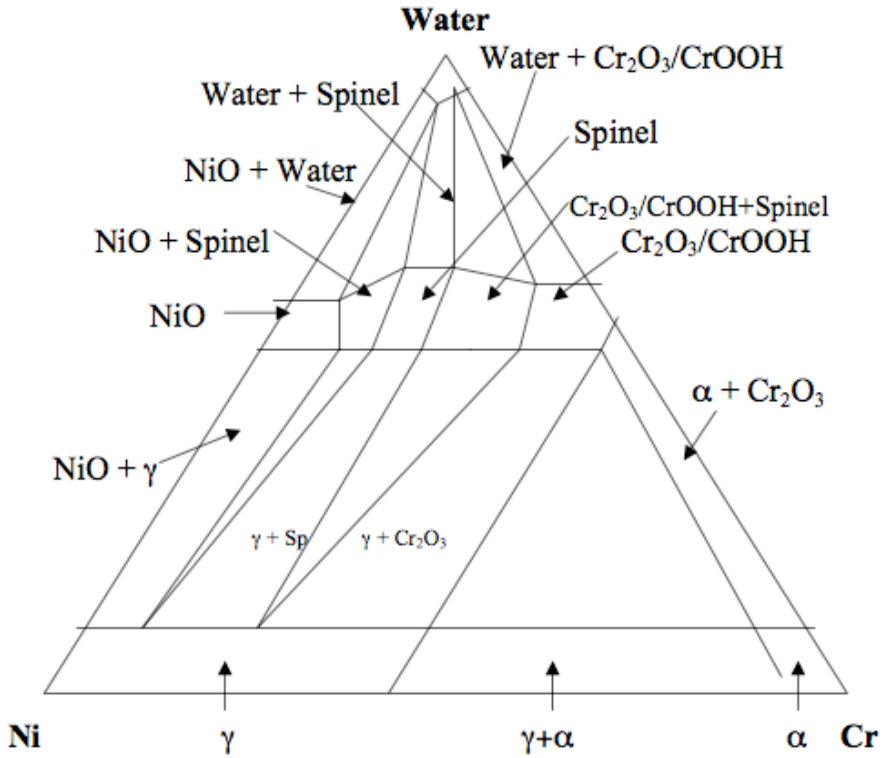
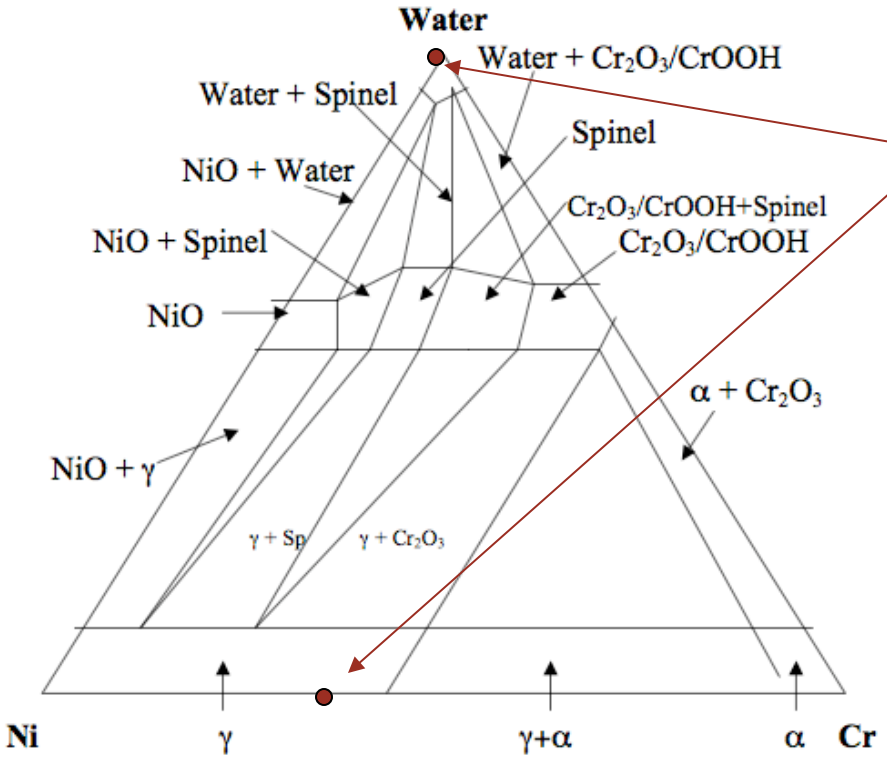



Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

NB - diagram is significantly distorted

* Based on Ni-Cr-O at 1000°C, Croll and Wallwork

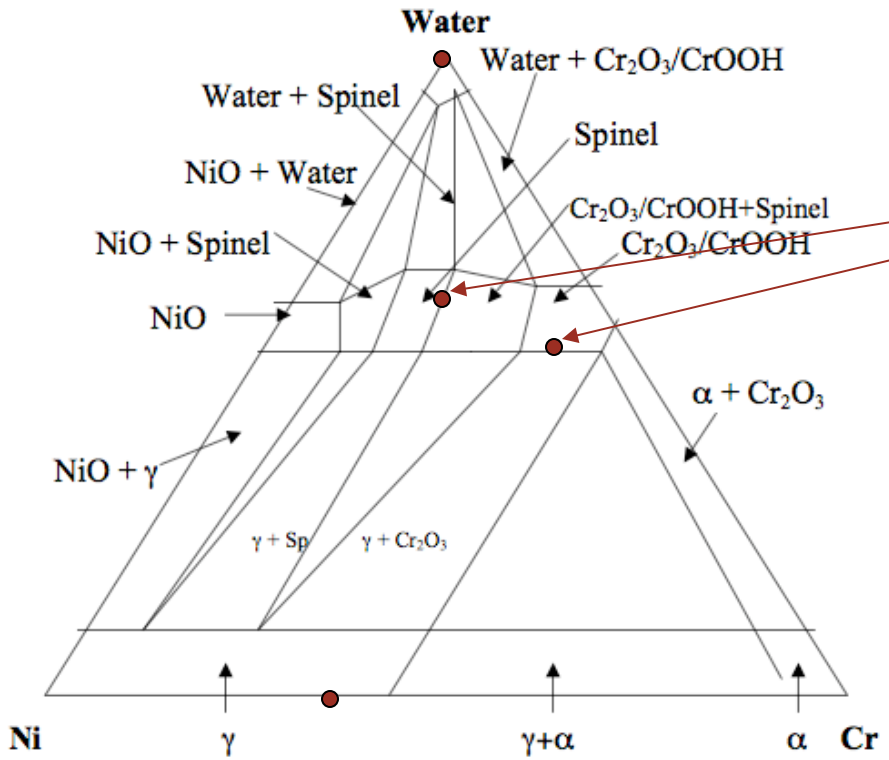
# Ni-Cr-Water Ternary Phase Diagram




End Points Of Diffusion Couple: Alloy 600 - Water

Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

# Ni-Cr-Water Ternary Phase Diagram




SERS of Alloy 600

Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

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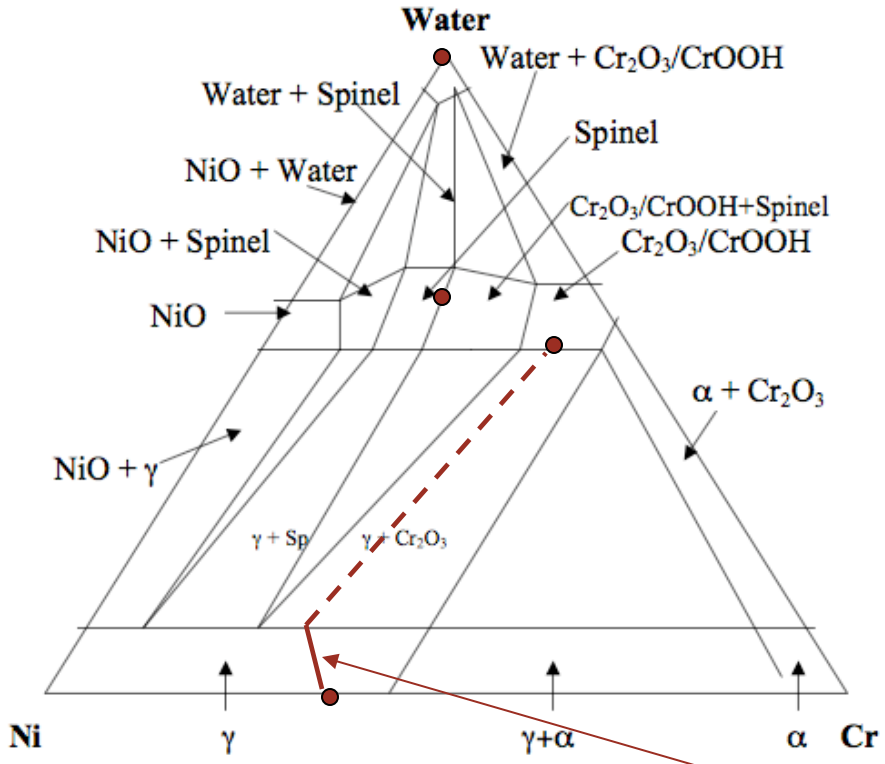
# Ni-Cr-Water Ternary Phase Diagram

## Construction of Diffusion Path

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"Mild" Cr-depletion of Alloy 600 contacting oxide

# Ni-Cr-Water Ternary Phase Diagram

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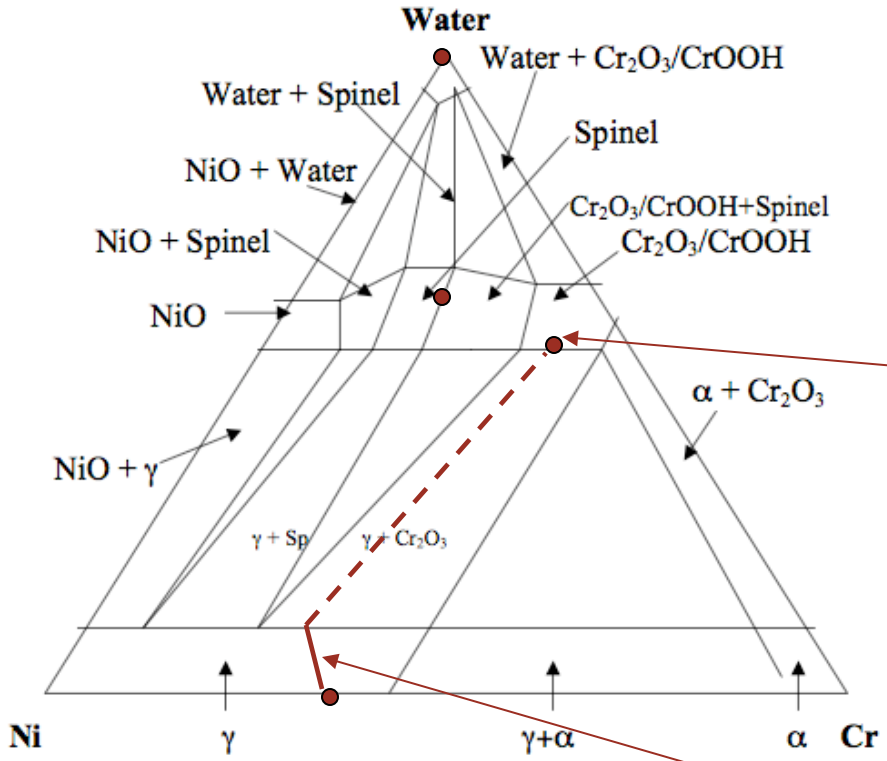


Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

Inner layer of $Cr_2O_3$

"Mild" Cr-depletion of Alloy 600 contacting oxide

# Ni-Cr-Water Ternary Phase Diagram

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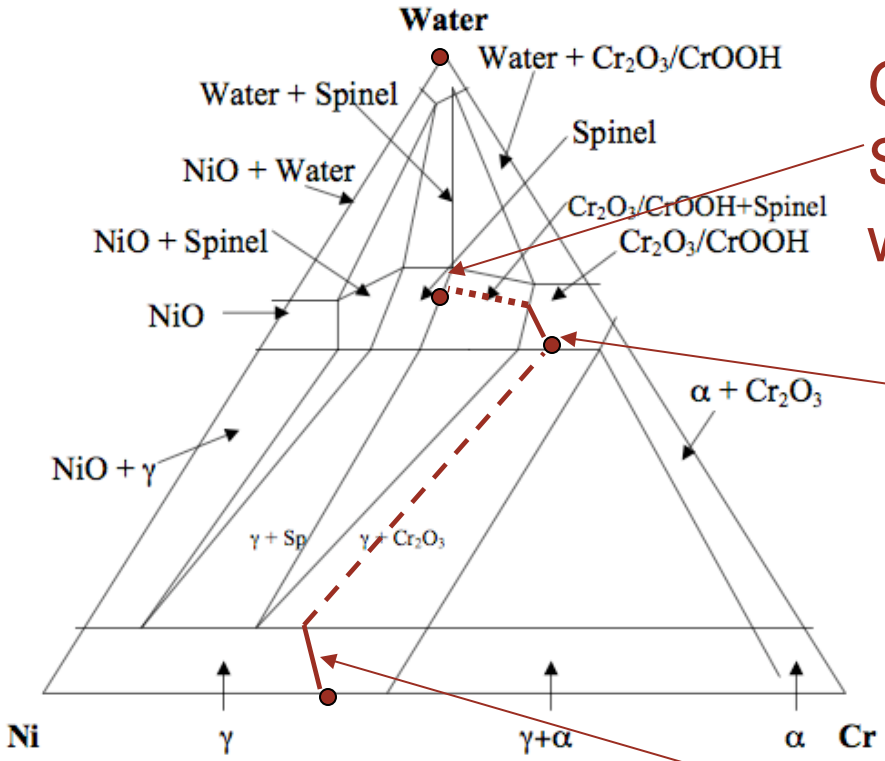



Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

Outer layer of Spinel in contact with $Cr_2O_3$

Inner layer of $Cr_2O_3$

"Mild" Cr-depletion of Alloy 600 beneath oxide

# Ni-Cr-Water Ternary Phase Diagram

## Construction of Diffusion Path

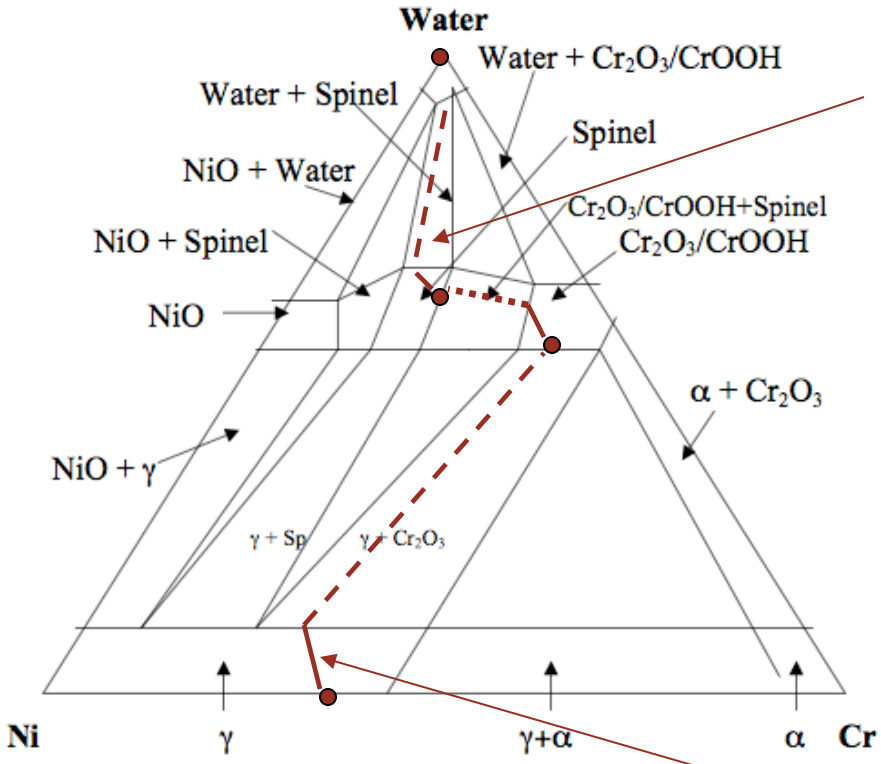



Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

Spinel is outermost layer

"Mild" Cr-depletion of Alloy 600 beneath oxide

# Ni-Cr-Water Ternary Phase Diagram

## Construction of Diffusion Path

Outermost layer of NiO

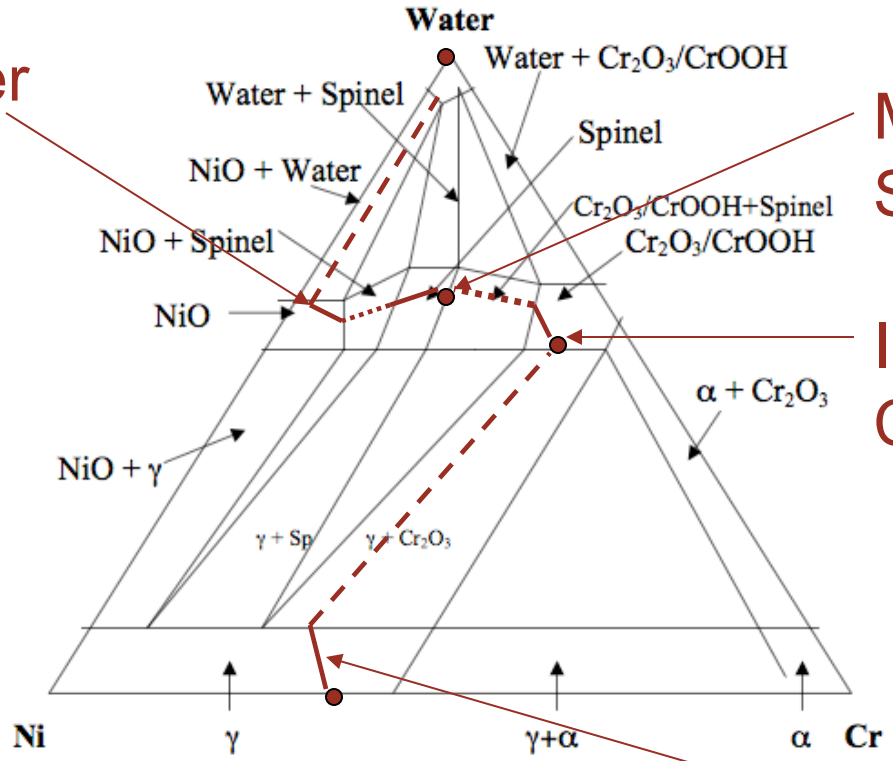



Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

Middle layer of Spinel

Inner layer of $Cr_2O_3$

"Mild" Cr-depletion of Alloy 600 beneath oxide

# Overview

**SERS**

- Alloy 600
  - Ni, Cr, Ni-5Cr-8Fe, Ni-10Cr-8Fe
- Alloy 690

**Diffusion Path Analyses**

- Introduction
- **Alloy 600**
  - Mild Cr-depletion
  - **Strong Cr-depletion**
- Alloy 690

# Ni-Cr-Water Ternary Phase Diagram

## Construction of Diffusion Path for "Severe" Cr-depletion of Alloy 600

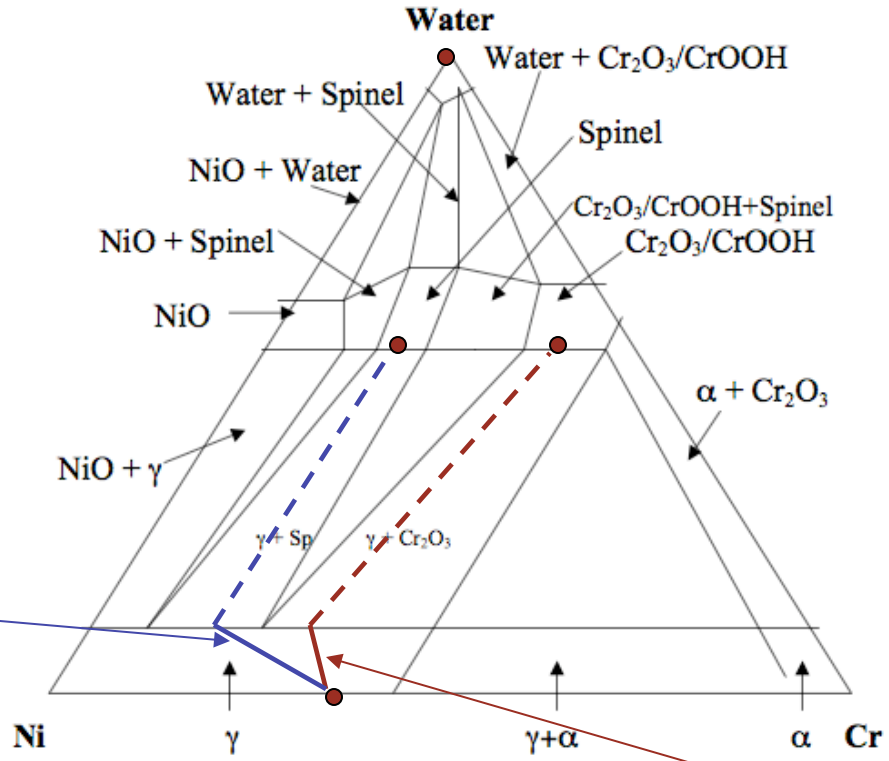



Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

"Severe" Cr-depletion Of Alloy 600 Beneath oxide

"Mild" Cr-depletion of Alloy 600 beneath oxide

# Ni-Cr-Water Ternary Phase Diagram

## Construction of Diffusion Path for "Severe" Cr-depletion of Alloy 600

"Severe" Cr-depletion Of Alloy 600 Beneath oxide

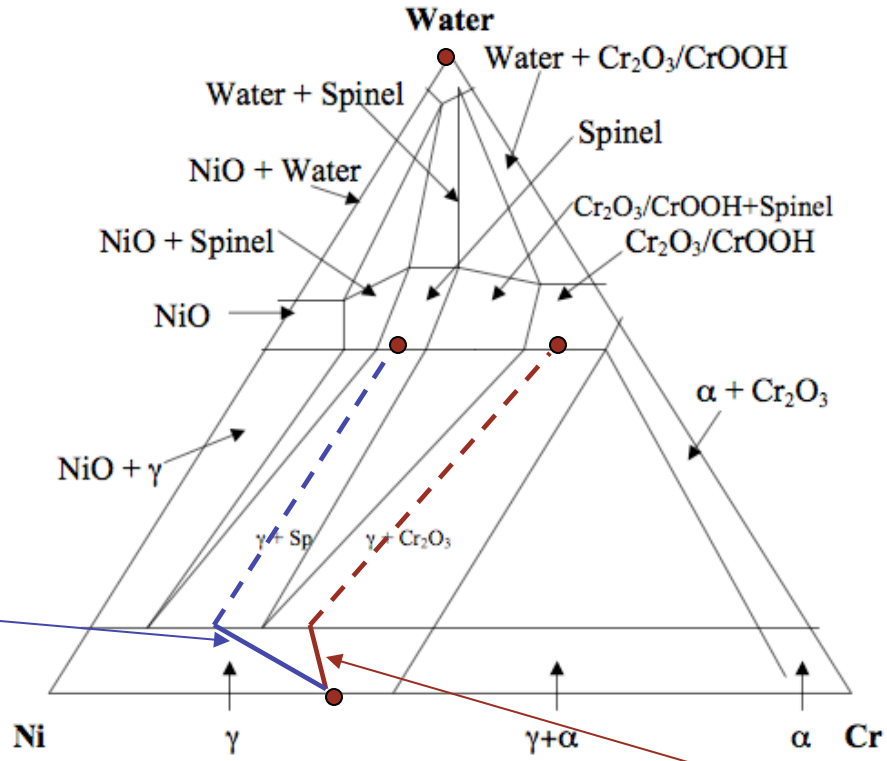



Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

"Mild" Cr-depletion of Alloy 600 beneath oxide

Evidence of spinel as the inner layer of Alloy 600's film: Ziemniak and Hanson, (Corr. Sci.,48, p498 (2006)): inner layer of $NiCr_2O_4$ and outer layer of $NiFe_2O_4$.
=> Diffusion path exits the $NiCr_2O_4$ phase and crosses the two phase $NiCr_2O_4$+ $NiFe_2O_4$

# Ni-Cr-Water Ternary Phase Diagram

## Construction of Diffusion Path for "Severe" Cr-depletion of Alloy 600

Inner layer of Spinel

"Severe" Cr-depletion of Alloy 600 Beneath oxide

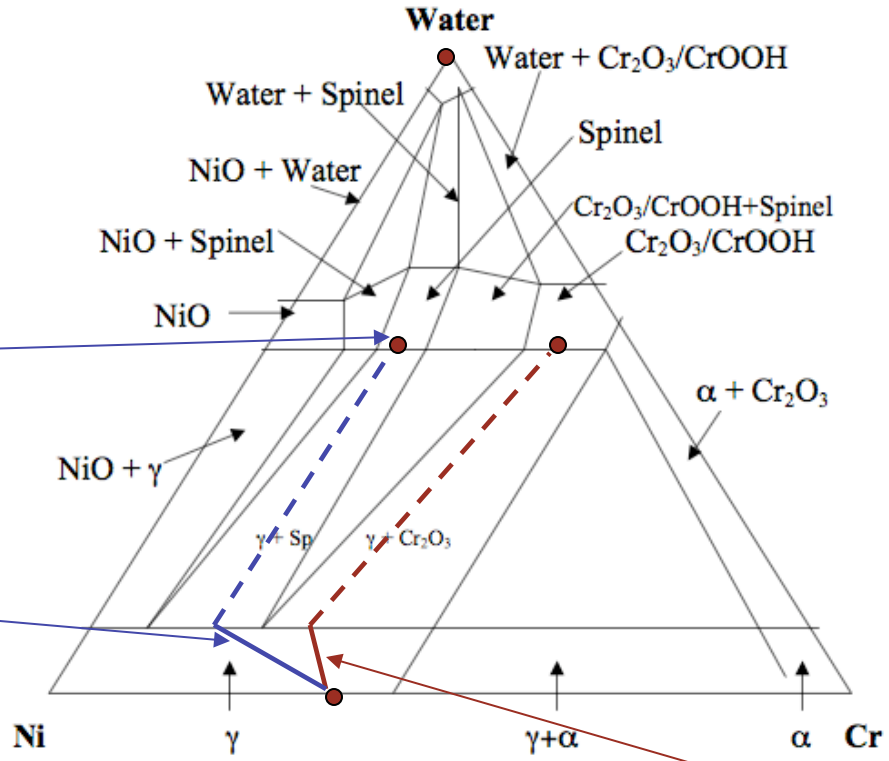



Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

"Mild" Cr-depletion of Alloy 600 beneath oxide

# Ni-Cr-Water Ternary Phase Diagram

## Construction of Diffusion Path for "Severe" Cr-depletion of Alloy 600

Inner layer of Spinel

"Severe" Cr-depletion of Alloy 600 Beneath oxide

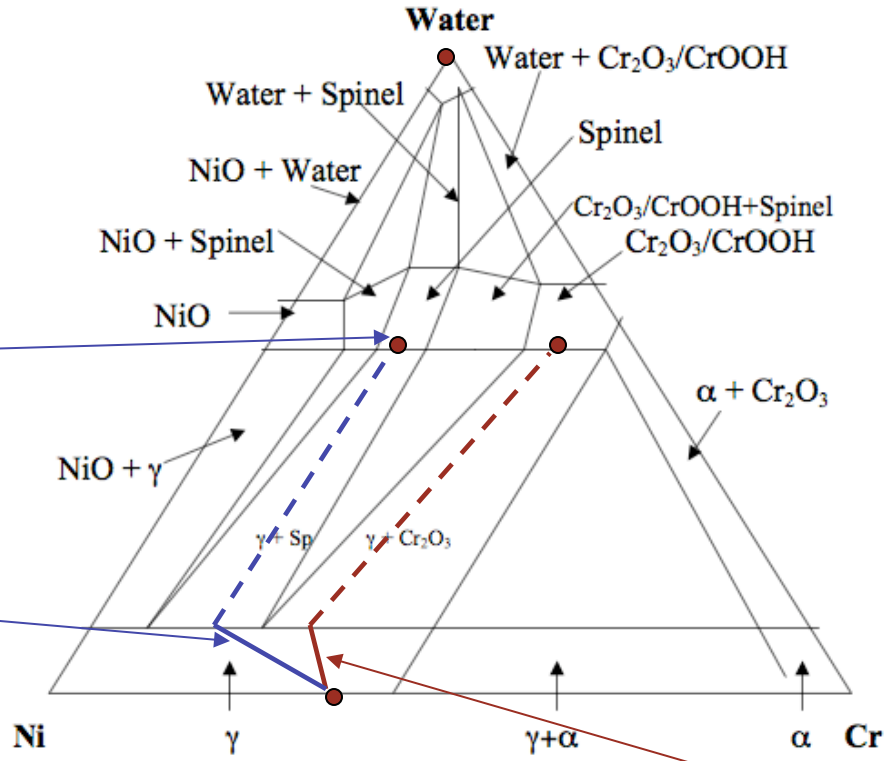



Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

"Mild" Cr-depletion of Alloy 600 beneath oxide

Evidence of spinel as the inner layer of Alloy 600's film: Ziemniak and Hanson, (Corr. Sci.,48, p498 (2006)): inner layer of $NiCr_2O_4$ and outer layer of $NiFe_2O_4$.
=> Diffusion path exits the $NiCr_2O_4$ phase and crosses the two phase $NiCr_2O_4$+ $NiFe_2O_4$

# Ni-Cr-Water Ternary Phase Diagram

## Construction of Diffusion Path for "Severe" Cr-depletion of Ni-16Cr

Outer layer of NiO

Inner layer of Spinel

"Severe" Cr-depletion of Alloy 600 Beneath oxide

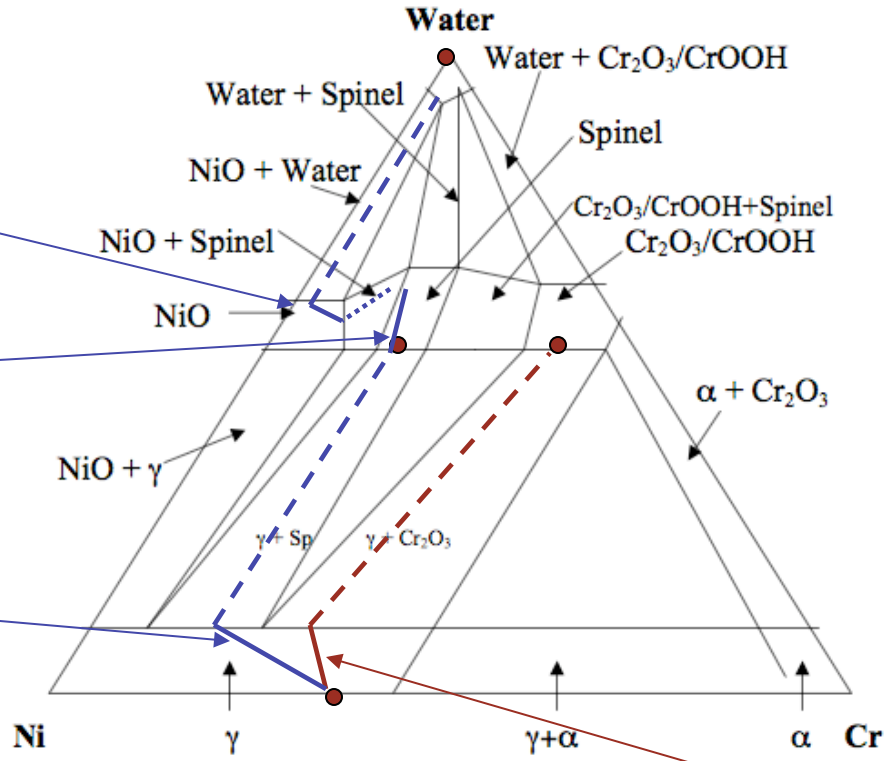



Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

"Mild" Cr-depletion of Alloy 600 beneath oxide

Results suggest that conditions that cause severe Cr depletion of Ni-16Cr (≈ Alloy 600?) will produce an inner layer of spinel and an outer layer of NiO

# Ni-Cr-Water Ternary Phase Diagram

## Diffusion Paths of Alloy 600, Ni-10Cr-8Fe, Ni-5Cr-8Fe

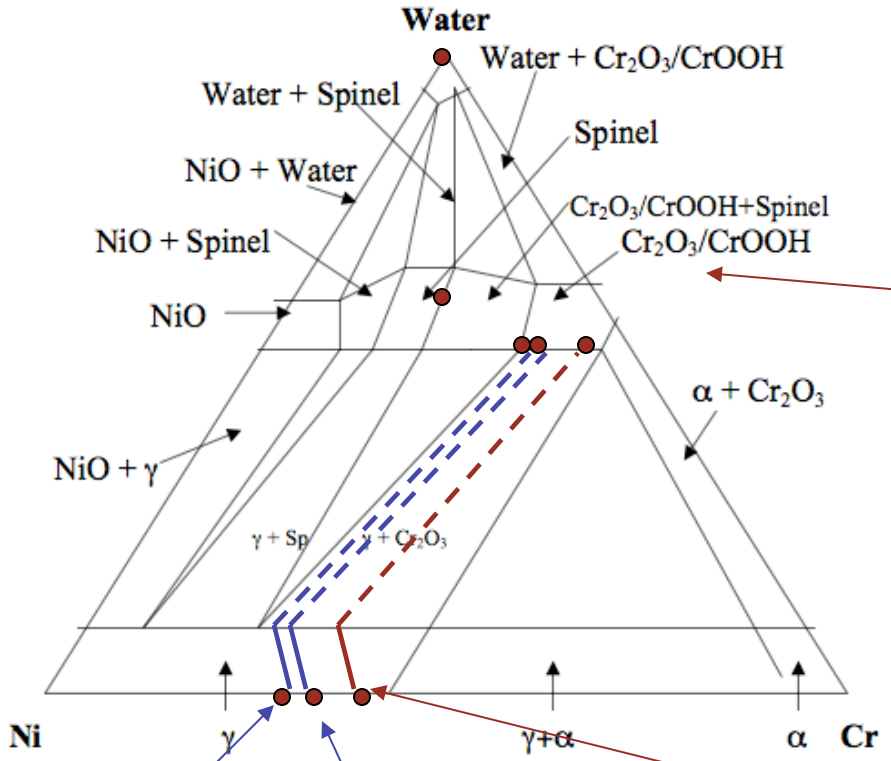



Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

Inner layer of $Cr_2O_3$

Alloy 600

Ni-5Cr-8Fe

Ni-10Cr-8Fe

# Ni-Cr-Water Ternary Phase Diagram

## Diffusion Paths of Alloy 600, Ni-10Cr-8Fe, Ni-5Cr-8Fe

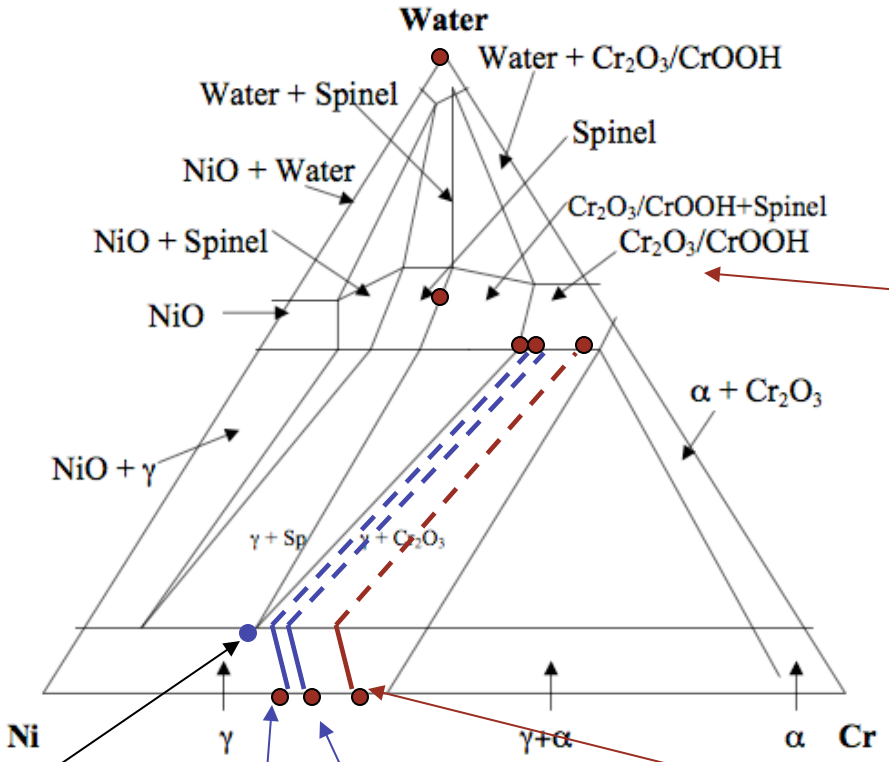



Figure 1. Hypothetical ternary Ni-Cr-Water phase diagram at 300°C.

Inner layer of $Cr_2O_3$

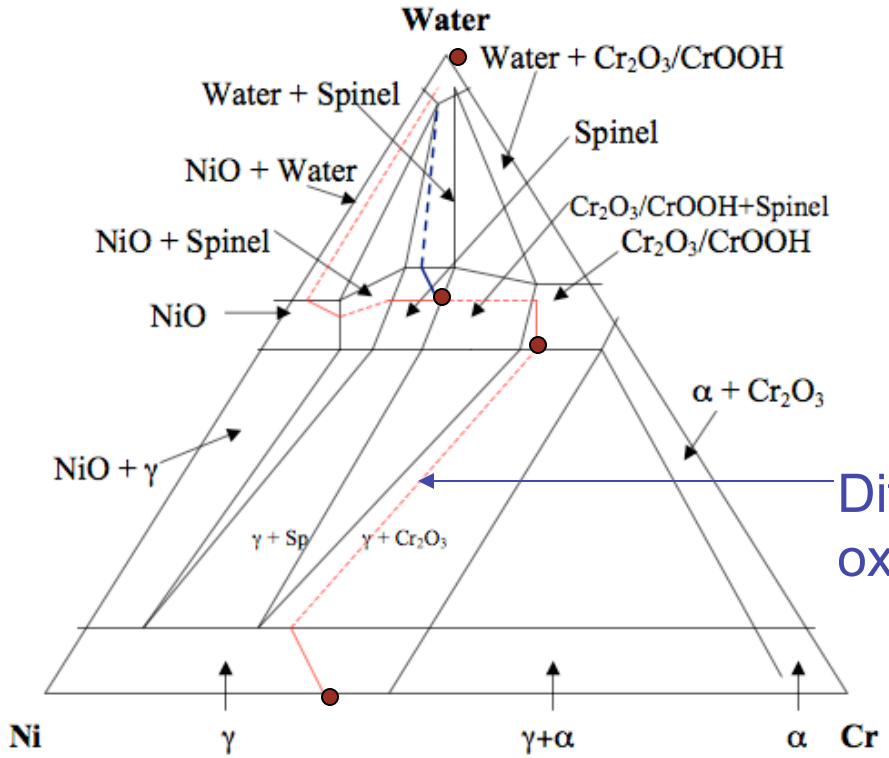
Alloy 600

Ni-5Cr-8Fe  Ni-10Cr-8Fe

Similar films of Alloy 600, Ni-10Cr-8Fe, and Ni-5Cr-8Fe indicate low value of $[Cr]_\gamma$ in equilibrium with spinel:i.e., $[Cr]_\gamma < 5\%$;

$[Cr]_\gamma \approx 10\%$ at 1000°C (Croll and Wallwork, 1969)

Before comparing the films of Alloy 600 and Alloy 690, we reiterate the Alloy 600's Oxidative Diffusion Path




End points of diffusion couple and SERS data

Diffusion path during oxidation of Alloy 600

Figure 39. Two diffusion paths (DP) of Alloy 600 sketched on a hypothetical ternary Ni-Cr-Water phase diagram at 300°C. The DPs are based on SERS measurements. Note that the ternary phase diagram is distorted. For example, the sizes of the single phase regions of NiO and $Cr_2O_3$ are relatively large, and the oxygen concentrations of NiO, spinel, and $Cr_2O_3$ are indicated as being equal. The two-colored Red + Blue path represents DP#1 in which the film formed on Alloy 600 consists of an inner layer of $Cr_2O_3$ and an outer layer of $NiCr_2O_4$. The single colored Red path represents DP#2 in which Alloy 600's film consists of an inner layer of $Cr_2O_3$, and intermediate layer of $NiCr_2O_4$, and an outer layer of NiO. The dashed lines are the portions of the DP that pass

# Point of Detail of Alloy 600's Oxide Diffusion Path

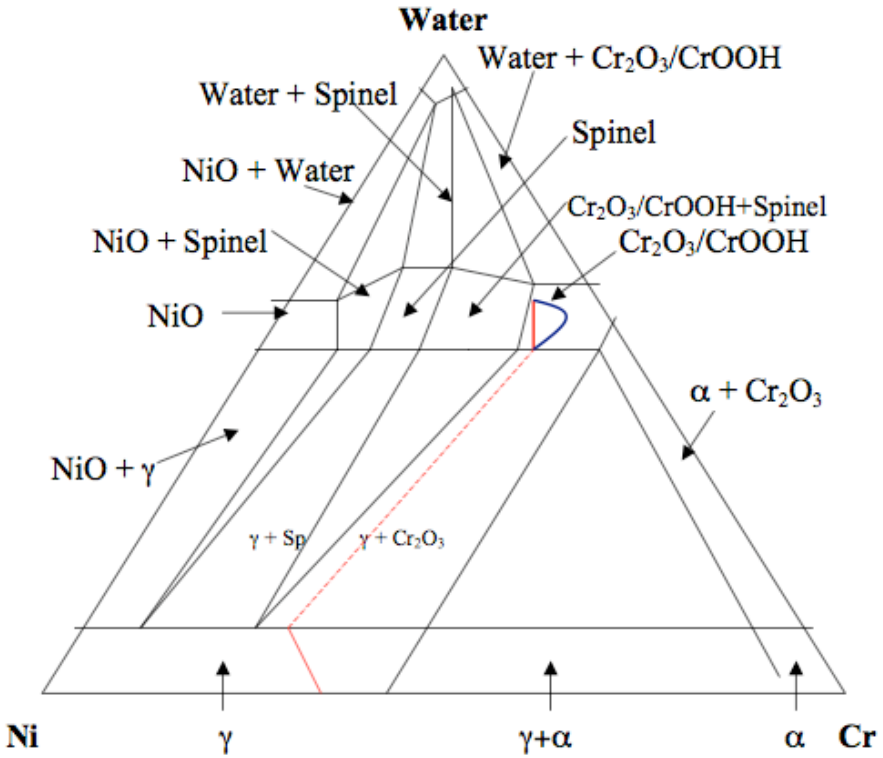



Figure 40. Two diffusion paths (DP) of Alloy 600 through the $Cr_2O_3$ region. The red colored path through the $Cr_2O_3$ phase field indicates the ratio of cation transport to anion transport is extremely small. The nearly horizontal portion of the blue colored path indicates the ratio of cation tansport to anion transport is very high.

# Overview

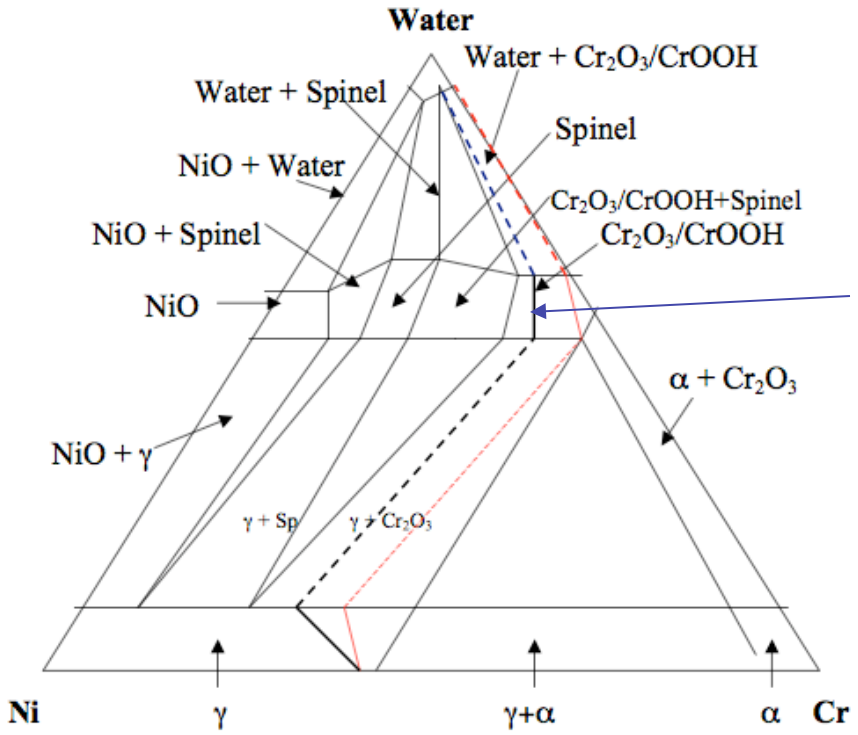
**SERS**

- Alloy 600
  - Ni, Cr, Ni-5Cr-8Fe, Ni-10Cr-8Fe
- Alloy 690

**Diffusion Path Analyses**

- Introduction
- Alloy 600
  - Mild Cr-depletion
  - Strong Cr-depletion
- **Alloy 690**

# Construction of Diffusion Paths of Alloy 690 at 300°C and 320°C

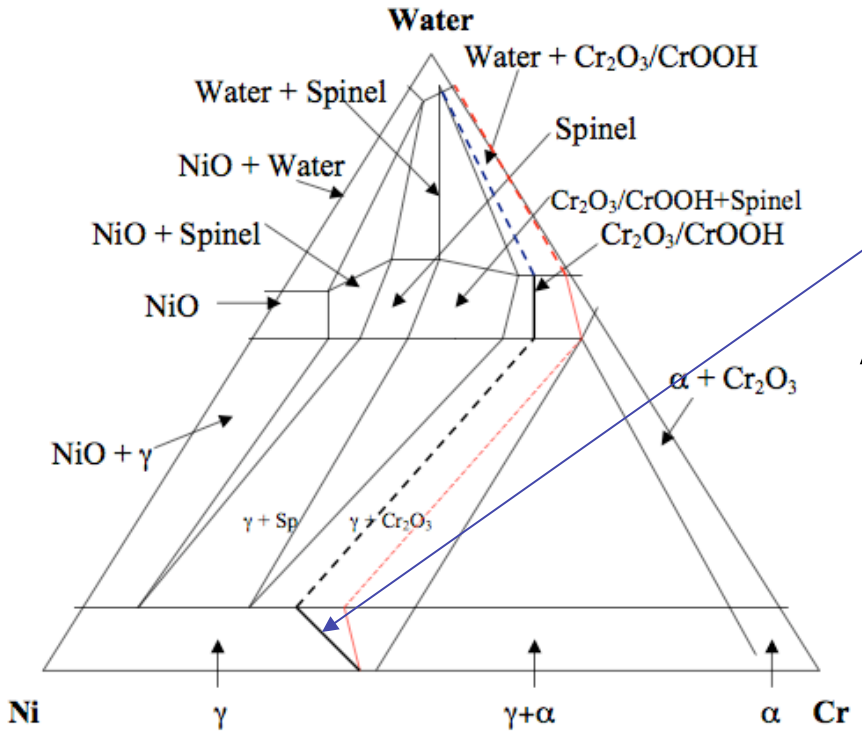



⇒Large [O⁼] gradient in $Cr_2O_3$ of Alloy 690

Figure 41. Two diffusion paths (DP) of Alloy 690. The DP at 300°C is colored red. The DP at 320°C is colored blue.

At 300°C, DPA => Alloy 690's film is a consequence of (1) the alloy's high [Cr], and (2) the growth of $Cr_2O_3$ is controlled by $O^{=}$ diffusion.

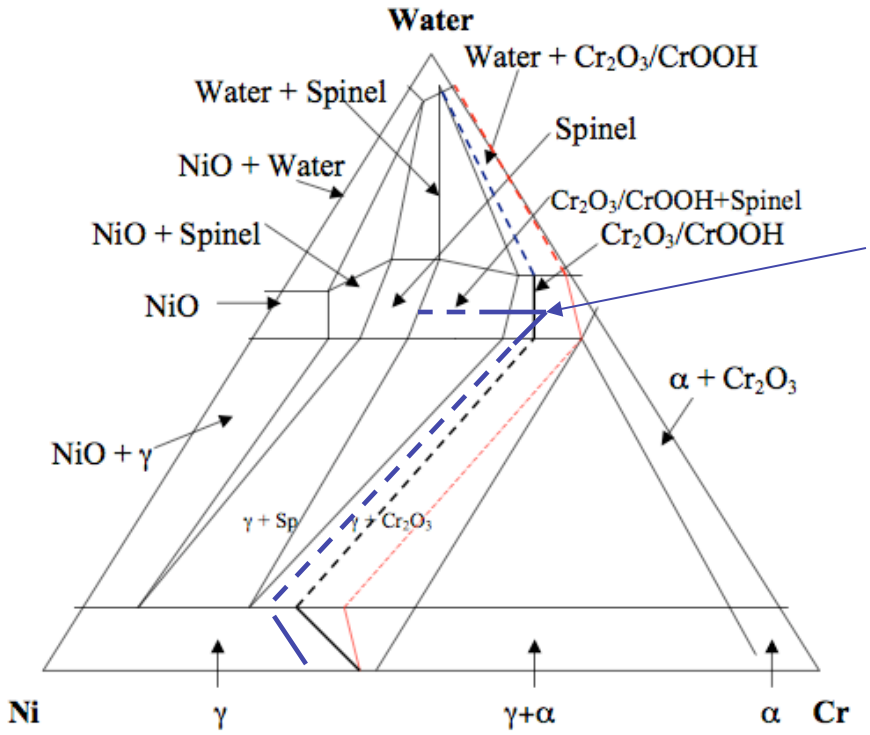
# Construction of Diffusion Paths of Alloy 690 at 300°C and 320°C




More severe Cr depletion of Alloy 690 at 320°C results in mixed cation $M_2O_3$

Figure 41. Two diffusion paths (DP) of Alloy 690. The DP at 300°C is colored red. The DP at 320°C is colored blue.

# Comparison of Diffusion Paths of Alloy 690 and Alloy 600




Approximately no [$O^=$] gradient in $Cr_2O_3$ of Alloy 600

Figure 41. Two diffusion paths (DP) of Alloy 690. The DP at 300°C is colored red. The DP at 320°C is colored blue.

At 300°C, DPA => Alloy 690's film is a consequence of (1) the alloy's high [Cr], and (2) the growth of $Cr_2O_3$ is controlled by $O^=$ diffusion.

# Summary

Ni-5Cr-8Fe, Ni-10Cr-8Fe, Alloy 600 have films of $Cr_2O_3$

+ Spinel ($NiCr_2O_4$?)

Alloy 690's Film = $Cr_2O_3$

Diffusion Path Analyses

# Value of Empirical Diffusion Path Analyses

In general, DPA helps explain the observed films' microstructures

In the particular case of Alloys 600 and 690, DPA indicates fundamental differences in the films of Alloy 600 and Alloy 690

e.g. $Cr_2O_3$ (A690) vs $Cr_2O_3$ + spinel (A600)

Cation gradient in $Cr_2O_3$ of A600 vs Oxygen ion gradient in $Cr_2O_3$ of A690.

# Future Work

High resolution compositional analyses throughout the thickness of the films of Alloy 600 and Alloy 690

TEAM at NCEM, LBNL

Transmission Electron Aberration-Corrected Microscopy

Map results onto the ternary Ni-Cr-Water phase diagram and the quarternary Ni-Cr-Fe-Water phase diagram