# The Role of Deformation in the Oxidation Behavior of Binary Nickel-Chromium Alloys

ENGINEERING HONORS PROGRAM
UNIVERSITY OF MICHIGAN

Aaron Cooke (Honors Capstone), Prof. Emmanuelle Marquis

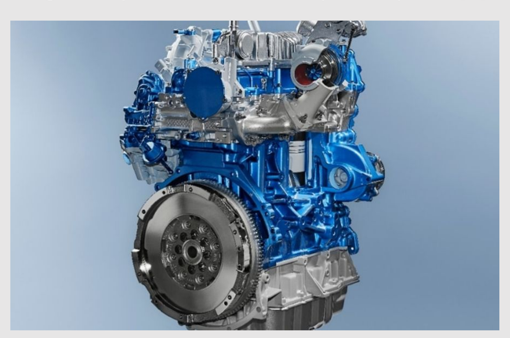
## Motivation

Chromium containing nickel-based alloys are often used in high temperature, high load applications due to their oxidation resistance as chromia formers and their retention of mechanical properties at elevated temperatures [1]. In the nickel-chromium system, formation of chromia ($Cr_2O_3$) is dependent on a variety of factors including the chromium content, the oxidation temperature, and the deformation due to processing and resulting microstructure of the material. Different deformation inducing processing techniques have been used in industry to reduce oxidation, but the mechanisms are not well understood [2].

Applications
- Jet engine turbines
- Power plant turbines
- Automotive applications

Waspaloy gas turbine engine [3]

High temperature rotor for power plant [4]



Ford EcoBlue diesel engine [5]

Pros of Ni based alloys
- Strength at high temperatures
- Creep and stress rupture resistant
- Can be oxidation resistant
  - Composition dependent

***What is the effect of deformation on the oxidation behavior of NiCr alloys?***

## Methods

1. Arc melt to produce buttons of atomic composition $Ni_{70}Cr_{30}$.
2. Homogenize for 24 hours at 1200°C in argon.
3. Cut and prepared as one of three conditions:
   a. **Electropolished (EP)** with 10% perchloric acid in methanol (deformation-free).
   b. **Surface deformed (SD)** by grinding with 240 grit SiC grinding paper.
   c. **Bulk deformed (BD)** by cold-rolling to a 50% reduction.
4. Oxidize in a furnace at 600°C for 50 hours or 900°C for 10 minutes or in a thermogravimetric analyzer at 900°C for 100 hours.
5. Characterize with scanning electron microscopy and focused ion beam.

Arc melt Ni-30at%Cr → Induce Deformation → Prepare Sample → Oxidize in air → Characterize SEM/FIB/TGA

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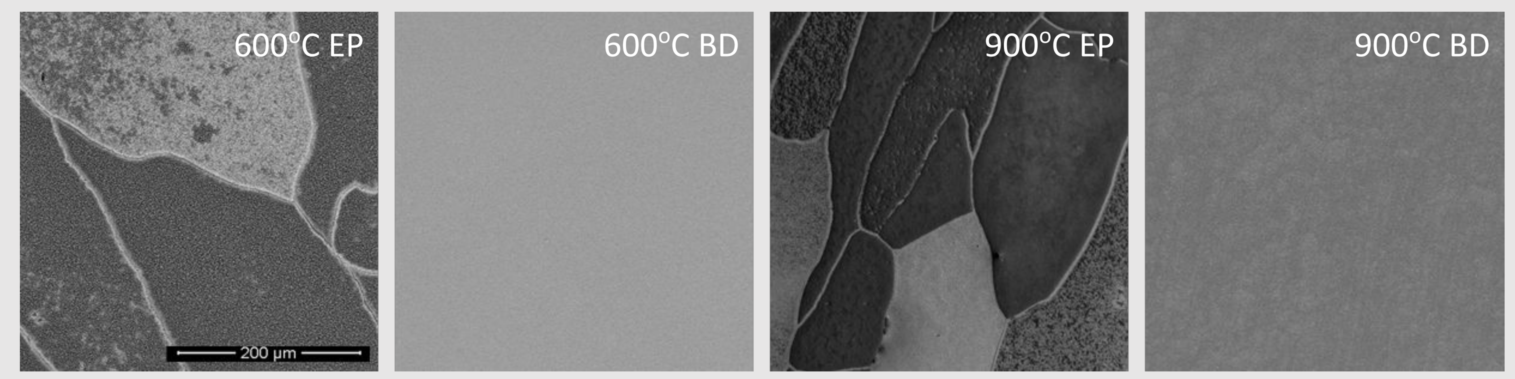
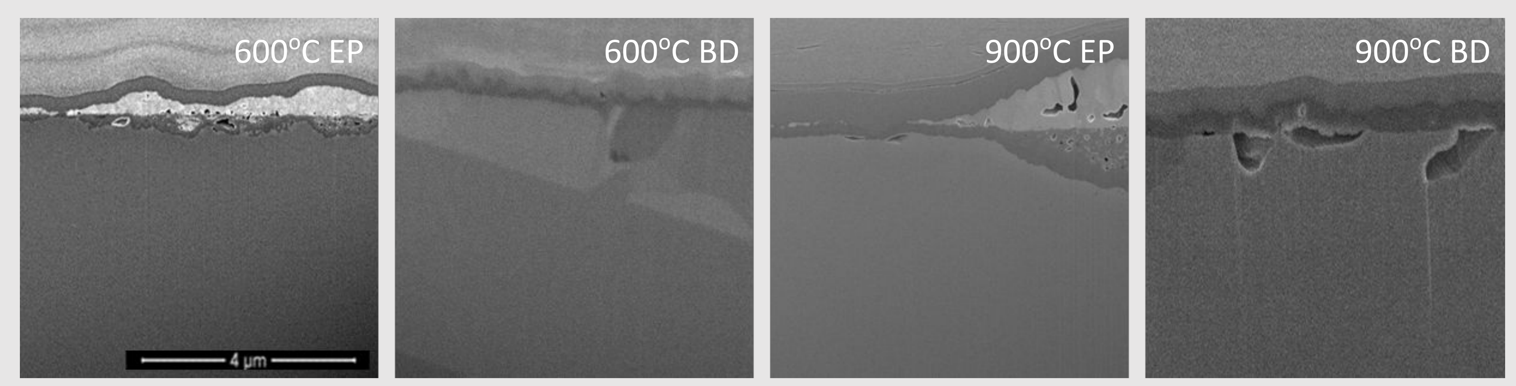
## Effect of Deformation

For 600°C and 900°C, the bulk deformation produced grain sizes in the metal of 2.9 and 4.3 microns respectively after oxidation while the deformation-free electropolished baseline had grain sizes of 309.3 and 254.2 microns. In addition, the electropolished showed variable oxide microstructure.

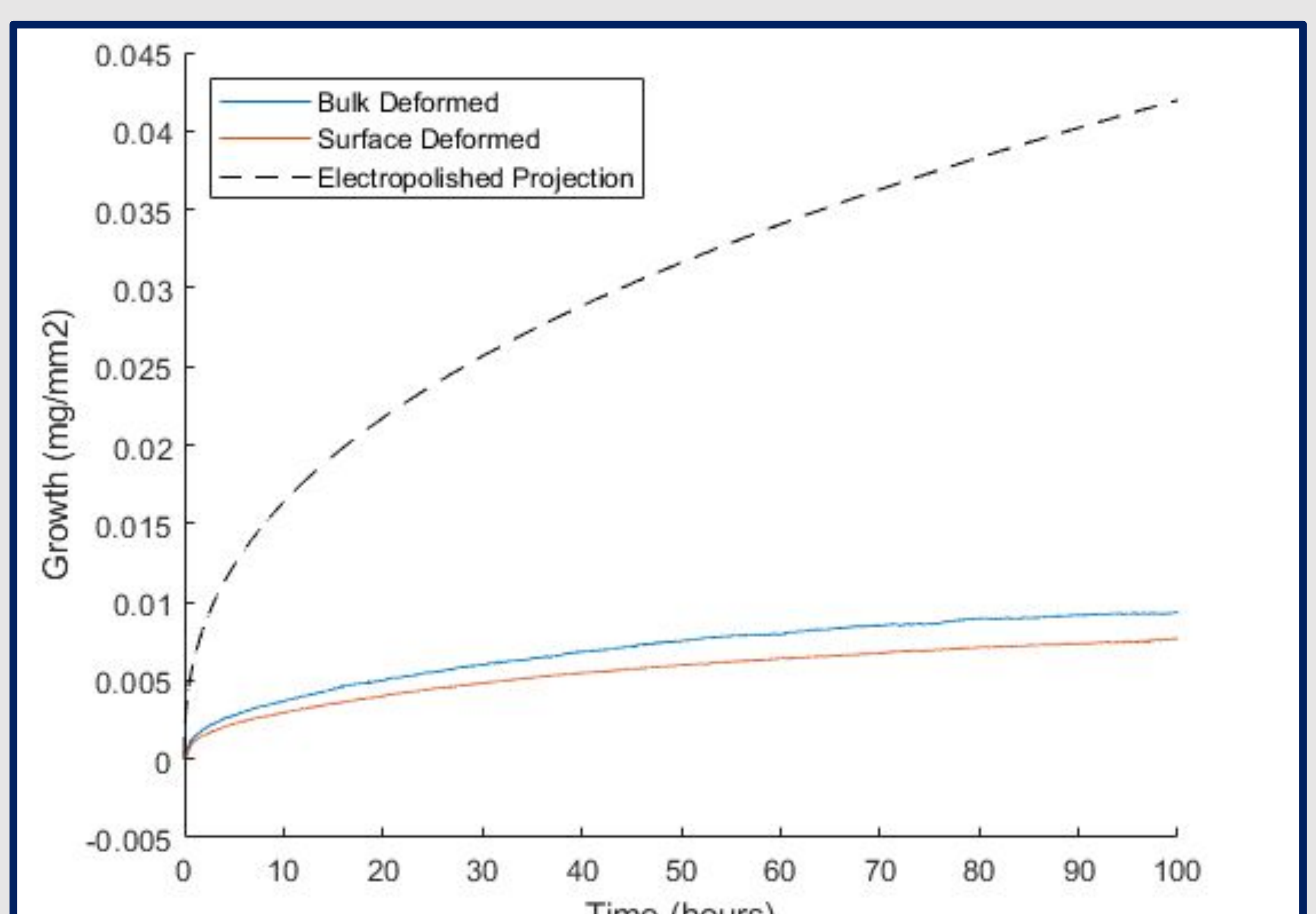



Further investigation shows that the electropolished condition formed two different oxides ($Cr_2O_3$ and NiO) that had different structures across various grains. On average, the electropolished samples had thicknesses of 585 and 1736 nm at 600°C and 900°C while the bulk deformation yielded thicknesses of 229 and 390 nm.



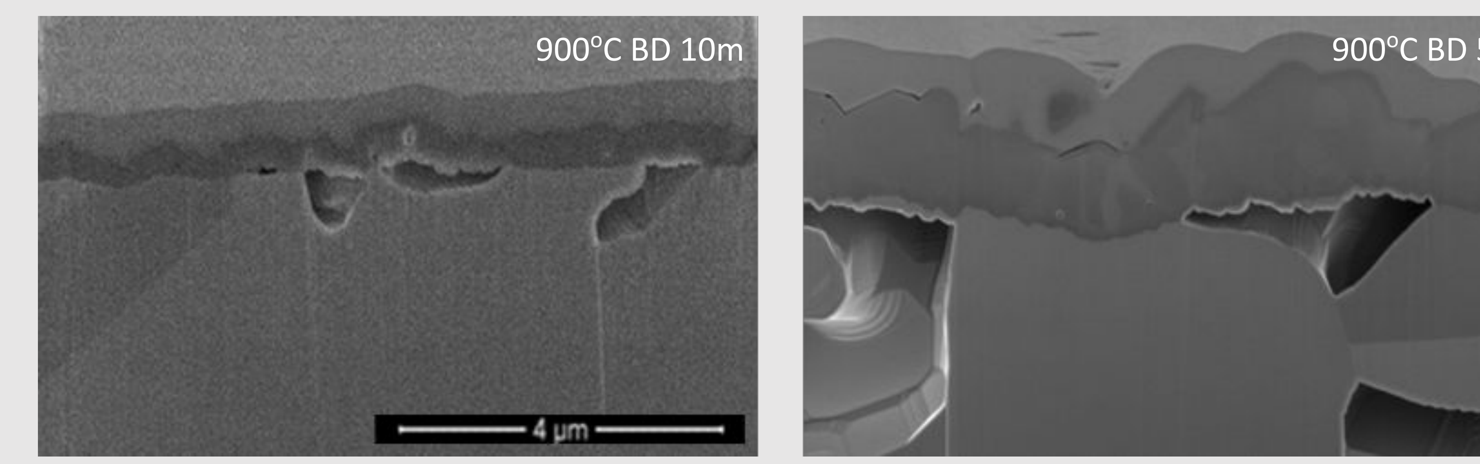

These smaller grains provided short circuit chromium diffusion pathways which led to a thinner oxide scale and increased oxidation resistance. A previous study on surface deformed alloys showed that this effect is most likely due to diffusion-induced grain boundary migration (DIGM) [1].

Thermogravimetric analysis (TGA) was used to gain a more global understanding of the oxide development. Oxidation of this alloy follows the parabolic rate law, so the oxidation behavior of the electropolished sample can be projected using the measured oxide thickness. The data show that bulk and surface deformation have similar oxide growth kinetics while the electropolished has oxide mass gain approximately an order of magnitude higher.




## Pore Formation

The bulk deformed samples exhibited formation of sub-surface pores during oxidation at 900°C while the electropolished condition and 600°C conditions did not. These pores formed primarily under the scale and on grain boundaries up to a consistent depth which is in agreement with prior studies [6]. The typical pore formation depth is related to the depth of chromium depletion due to diffusion to the surface and additional experimentation for longer times at 900°C showed deeper pores which helped to corroborate this. Pores can serve as stress concentration sites which can mechanically weaken the specimen and lead to early failure [7].




## Grain Orientation Dependence

The electropolished samples exhibited different oxide structures across various grains. It is believed that this is evidence of grain orientation dependent oxidation. Anisotropy in diffusion and oxidation has been studied before in HCP alloys [8], but very little research has been done to show that anisotropy and grain orientation dependence is a major factor in FCC alloys like $Ni_{70}Cr_{30}$. Preliminary investigations were done to determine which grain orientations preferentially oxidize to specific oxide scales ($Cr_2O_3$ or $Cr_2O_3$ and NiO duplex scale); however, more work is needed before drawing significant conclusions.

## Outlook

1. The $Ni_{70}Cr_{30}$ alloy exhibits heightened oxidation resistance from deformation at both low (600°C) and intermediate (900°C) temperatures.
2. Bulk and surface deformation exhibit very similar abilities to reduce the oxidation of NiCr alloys. Industry can reliably use cheaper surface treatments like grinding and shot peening instead of more expensive bulk treatments to achieve oxidation resistance.
3. Oxidation rate is not the only aspect of the material affected by deformation and operation temperature as both pore formation and grain boundary dependence show some connection with these factors.

## References

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[8] Chen et al., *Materials Letters*, v. 286, 2021.