Evolution of an Alloy 690 Surface During Oxidation in a Simulated PWSCC Environment

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Introduction

- Alloy 690 contains 30% Cr, which, according to the classical theory of oxidation [1], is well above the transition from internal to external oxidation.
- Recently, Persaud et al. [2] reported a surprising case of internal Cr oxidation in Alloy 690 exposed to hydrogenated steam at 480 °C, an environment considered to simulate and accelerate primary water exposure and potential stress corrosion cracking in a PWR or CANDU system. Intragranular internal oxidation of Cr was accompanied by formation of nodules of metallic Ni on the alloy surface. A strip of material adjacent to each grain boundary formed a green external oxide and was free of large nodules; the large width of this zone (microns) offers a challenge to theories of internal-external oxidation transitions.
- The purpose of this study is to investigate time resolved formation of Ni nodules and changes in the relatively nodule-free grain boundary area.

Experimental Methods

1. Sample preparation

- Coupons for oxidation experiments, 10x10 mm, were cut from 2 mm thick rolled sheet of alloy A690 supplied by Rolled Alloys.
- Coupons were solution annealed for 1 h at 1200 °C in Ar/2.5% H_2 gas mixture followed by water quenching.
- Slight surface oxidation and sub-surface Cr depletion were removed with abrasive paper. Subsequently, coupons were polished down to 0.05 μm alumina.
- Absence of sub-surface Cr depletion was confirmed by cross-sectional EDX analysis.

2. Reactor exposure

Coupons were exposed to a steam/hydrogen mixture at atmospheric pressure and 480 °C in a tube reactor located at Western University. The partial pressure of oxygen was kept below the dissociation pressure of NiO.

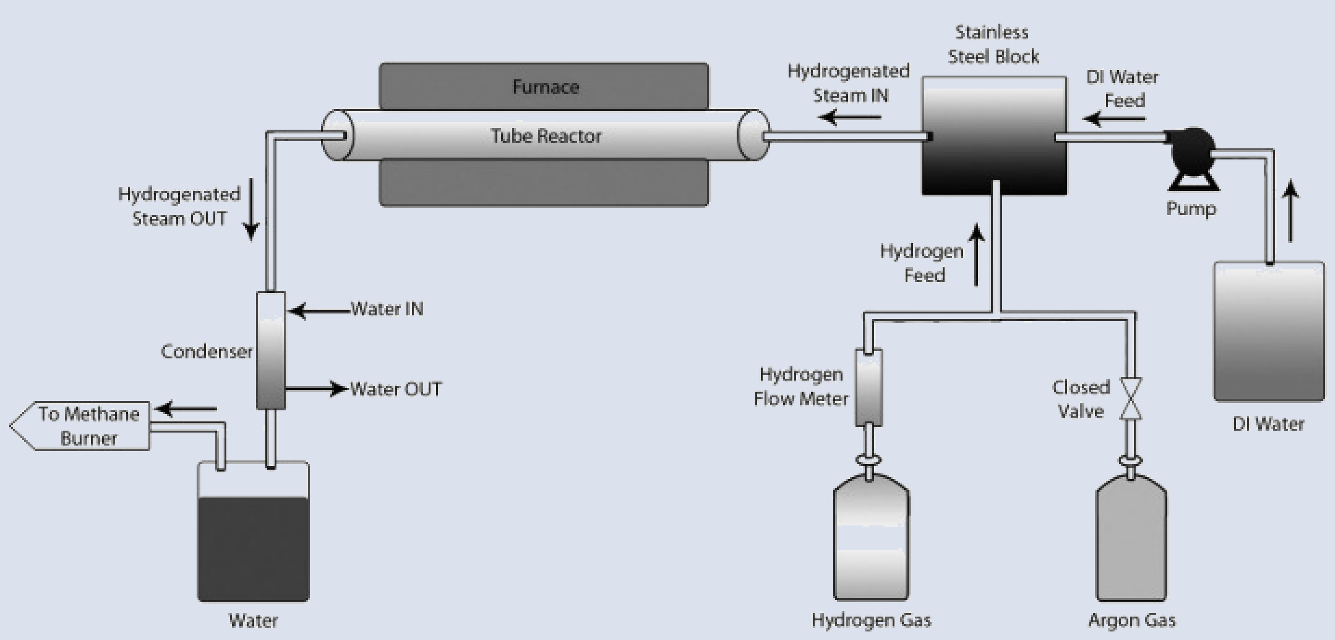
$$Ni_{(s)} + \frac{1}{2}O_2 \rightleftharpoons NiO$$

$P_{O_{2,eqm}} = 3.14 \times 10^{-24}$ bar

$P_{O_2} = 9.15 \times 10^{-26}$ bar

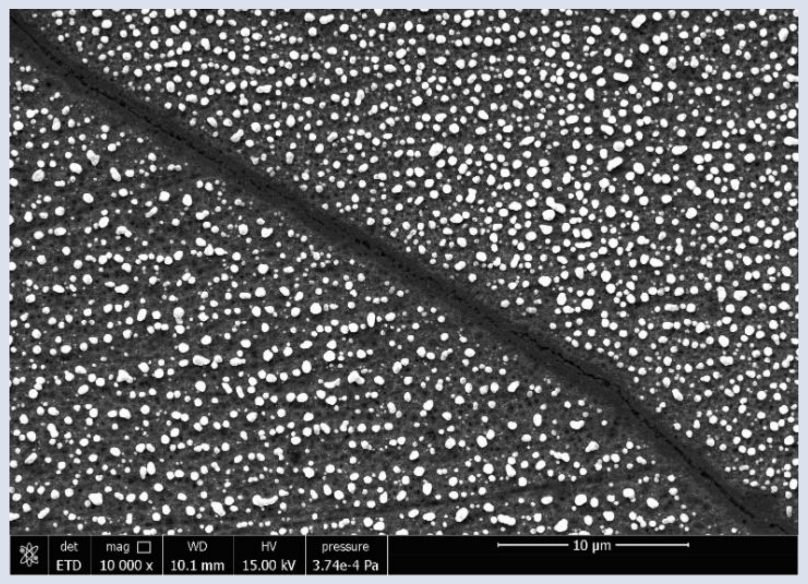
One of the coupons was exposed 5 times for a total of 100 h with interruptions after 1 h, 3 h, 10 h and 30 h of cumulative exposure. Between the consecutive exposures, the coupon surface was imaged with SEM and analyzed with EDX. Indentations were used to locate the same area each time.

Tube reactor for oxidizing specimens in a hydrogen-steam environment [2]

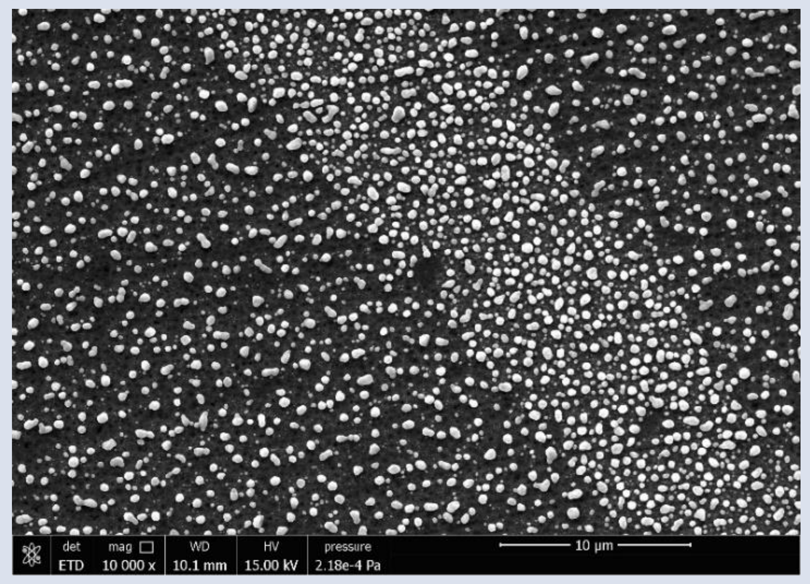


Results

SEM micrographs of the surface exposed for 10 h



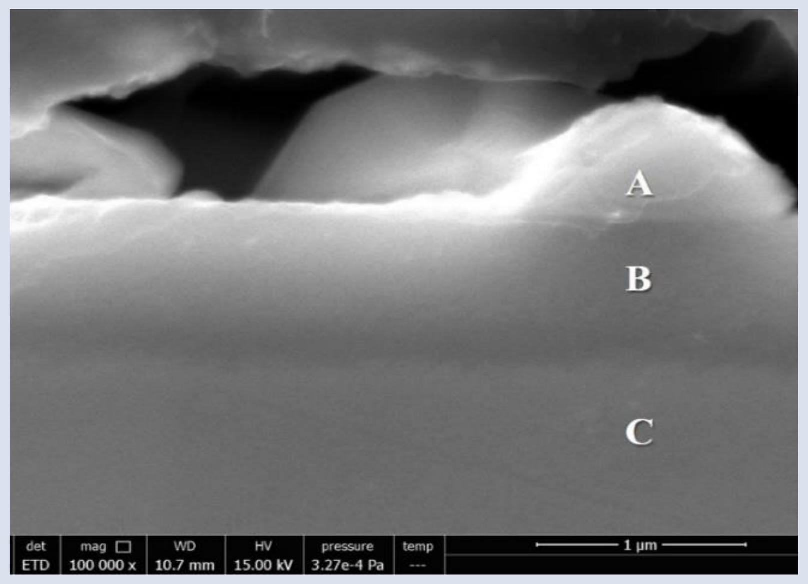
High angle grain boundary



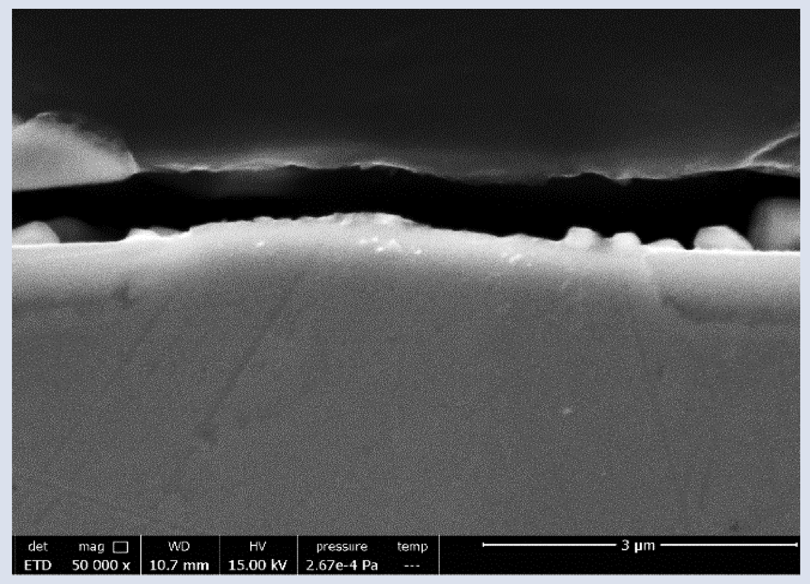
Twins separated by a ∑3 twin boundary

Interiors of grains intersecting the surface are covered with nodules of metallic Ni [2]. The coverage is uniform within each grain, but the size and arrangement of nodules varies between differently oriented grains. A nodule-free zone, roughly 2 μm wide, formed along high-angle grain boundaries (GBs). Twin boundaries do not show a significant nodule-free zone.

Cross section after 120 h exposure



A. Ni nodule
B. Internal Oxidation Zone (IOZ)
C. Bulk alloy



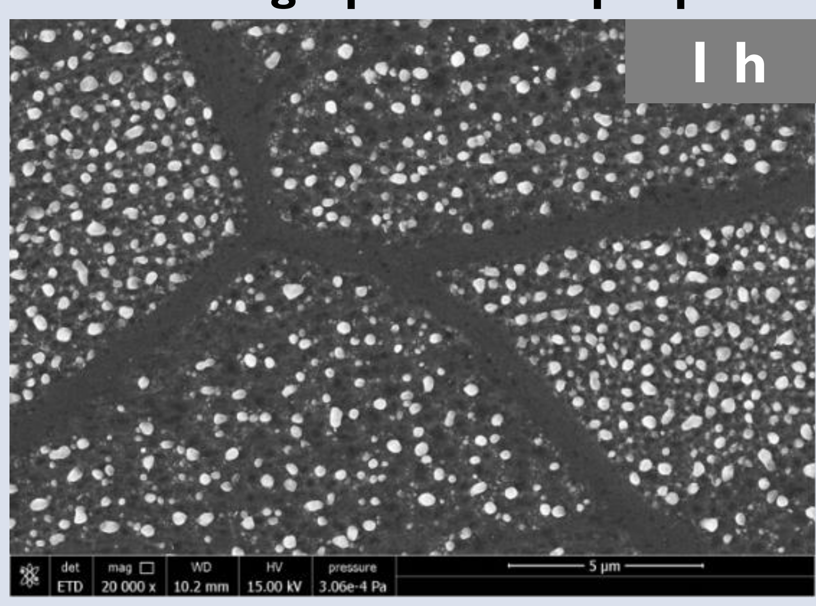
The IOZ is discontinuous in the vicinity of grain boundaries

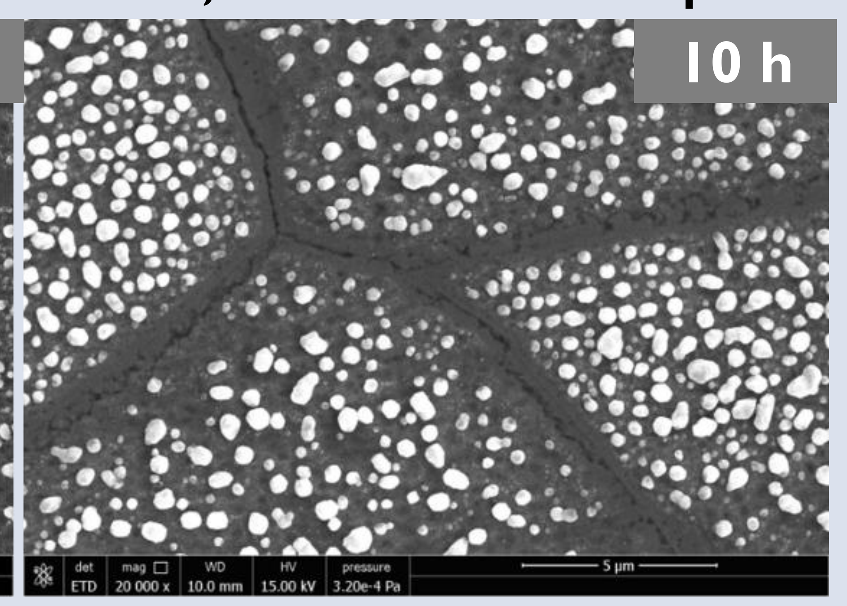
Elemental analysis (atomic percent):

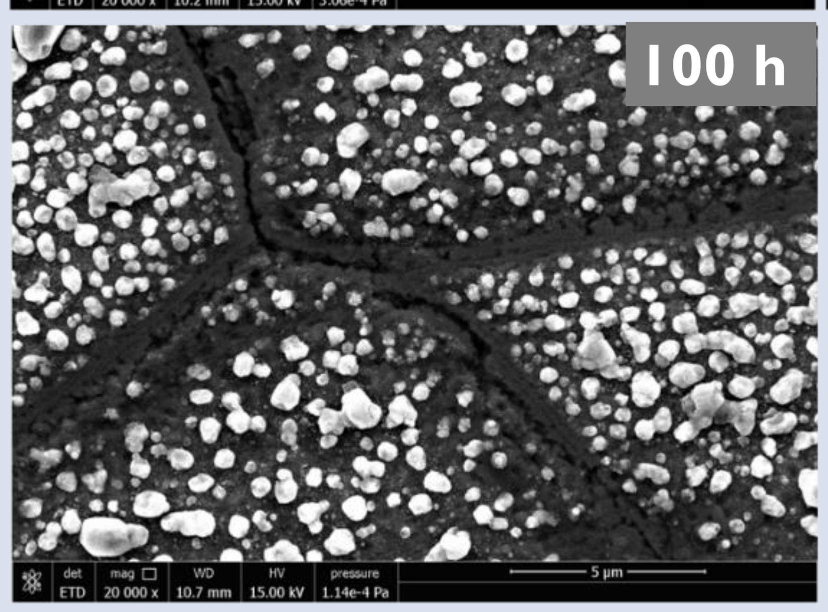
	Ni	Cr	Fe
B	38	48	14
C	58	32	10

Roughly half of the Ni was pushed out from the IOZ to the surface. This may be in line with the molar volume difference between Cr oxide and the alloy, but the detailed evaluation of this has not been done. A similar phenomenon was observed in a number of studies on alloys such as Cu-Pd and Cu-Pt alloys [3] and In-Ag alloys [4].

SEM micrographs of a triple point after 1 h, 10 h and 100 h of exposure

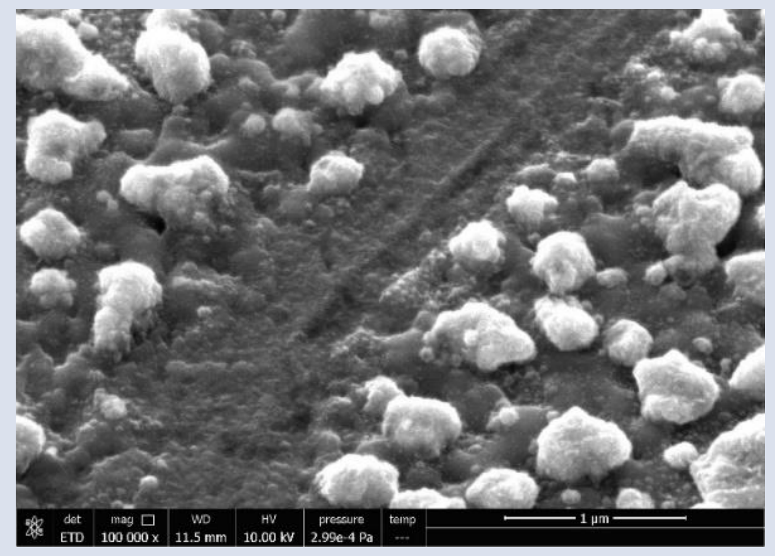






The surface coverage of nodules increases with exposure time mostly through growth of the existing nodules rather than nucleation of new ones. In some cases, adjacent nodules experience enough growth to impinge on one another and consolidate into one non-spherical nodule. Nodules close to the GB area grow less than the nodules in grain interiors and, in many places, stop growing altogether

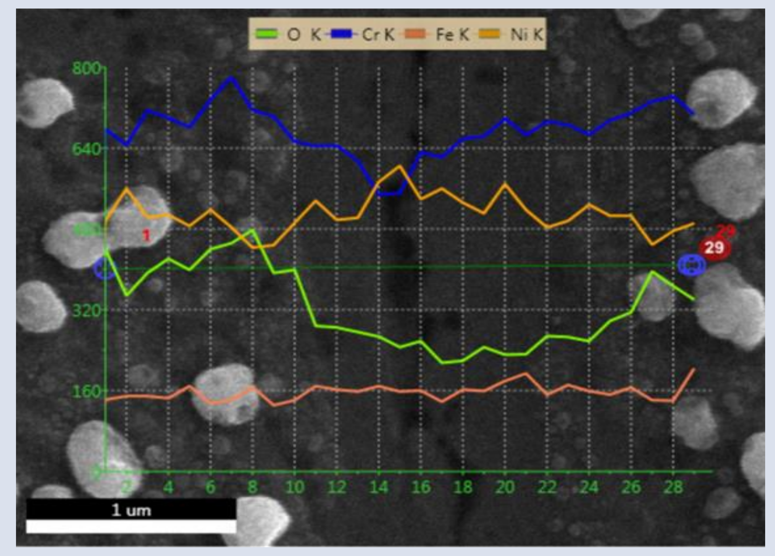
SEM micrograph of the grain boundary zone after 100 h of exposure



The relatively nodule-free zone along GBs undergoes changes as the exposure time increases. The initially smooth GB zone develops topographic contrast with increased exposure time.

Such observations may explain the unexplained large width of the "externally oxidized" zone – there is always some internal oxidation initially, but it ceases close to the GB.

Elemental profiles across a grain boundary



The nodule-free GB region shows enrichment in Ni and depletion in Cr and O. While most of the Ni diffuses towards the sample surface to form external nodules, Ni also diffuses towards GBs to relieve stress.

The oxygen profile reflects the difference in thickness of the oxide at the nodule-free zone and adjacent grain interior. Even though the oxide covering the nodule-free zone is an external one, it is less than 50 nm thick, while the IOZ is more than 500 μm thick.

Conclusions

The 690 Ni based alloy oxidizes internally under simulated PWR conditions despite its Cr content of 30 %. To release compressive stresses associated with internal formation of Cr_2O_3, Ni diffuses towards the surface, where it forms external nodules, and towards grain boundaries. Surface nodules form within the first hour of exposure. With increase of the exposure time, the nodules grow in size, except near grain boundaries, while their areal density remains practically constant.

Acknowledgements

- NSERC – Natural Sciences and Engineering Research Council
- UNENE – University Network of Excellence in Nuclear Engineering

References

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[4] Guruswamy, S., S. M. Park, J. P. Hirth, and R. A. Rapp. "Internal oxidation of Ag-In alloys: stress relief and the influence of imposed strain." Oxidation of Metals 26, no. 1 (1986): 77-100.

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