Analysis of Unexpected Pitting Corrosion in Corrosion Resistant Ni Based Superalloy

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A Ni-Cr-Mo-based, corrosion resistant superalloy produced by Haynes International occasionally fails an intergranular pitting corrosion test, but the conditions for failure are currently unknown. By analyzing the measured alloy composition using a random forest model with a set of 20% test and 80% training data, we were able to correctly predict passing or failing of the test dataset 79% of the time. Using the model, we found that limiting the composition of two key trace elements below certain thresholds reduced the rate of failure from 23% to 3%. Further analysis is required to determine the mode of failure.

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HAYNES International

Project Background

Haynes International is a leading producer of Ni-Cr-Mo based corrosion resistant superalloys. One particular alloy occasionally fails a test for pitting corrosion. Each of the processing steps shown in Figure 1 has many parameters that could lead to potential corrosion failures, making this a complex problem.

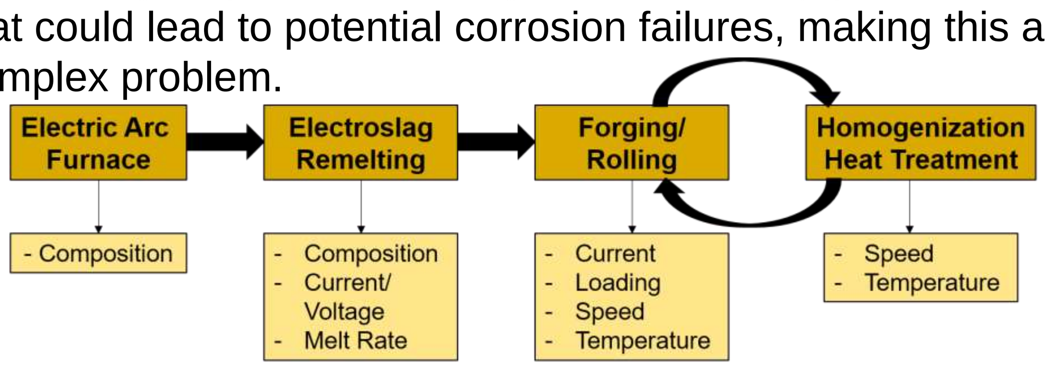


Figure 1: Production flow chart and processing parameters

The alloy is tested for intergranular pitting corrosion via method B of the ASTM G28 standard. After the sample is boiled in a sulfuric acid base mixture for 24 hours, a corrosion rate is calculated using the equation below.

$$Corrosion\ Rate = \frac{(K \times W)}{(A \times T \times D)}$$

Unit Constant; Mass loss (g); Surface Area (cm^2); Time ($hours$); Density ($\frac{g}{cm^3}$)

The alloy protects itself from corrosion by forming a passive layer as shown in Figure 2. This layer is made up of corrosion products. The Cr_2O_3 rich inner layer prevents nucleation of pits and the Mo rich outer layer assists in repassification [1].

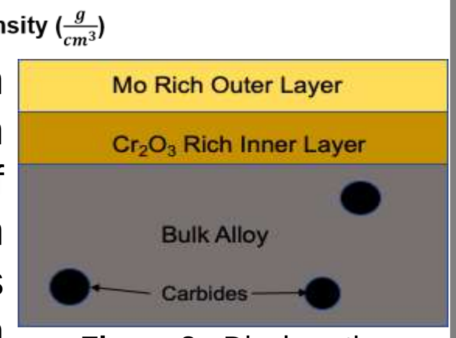
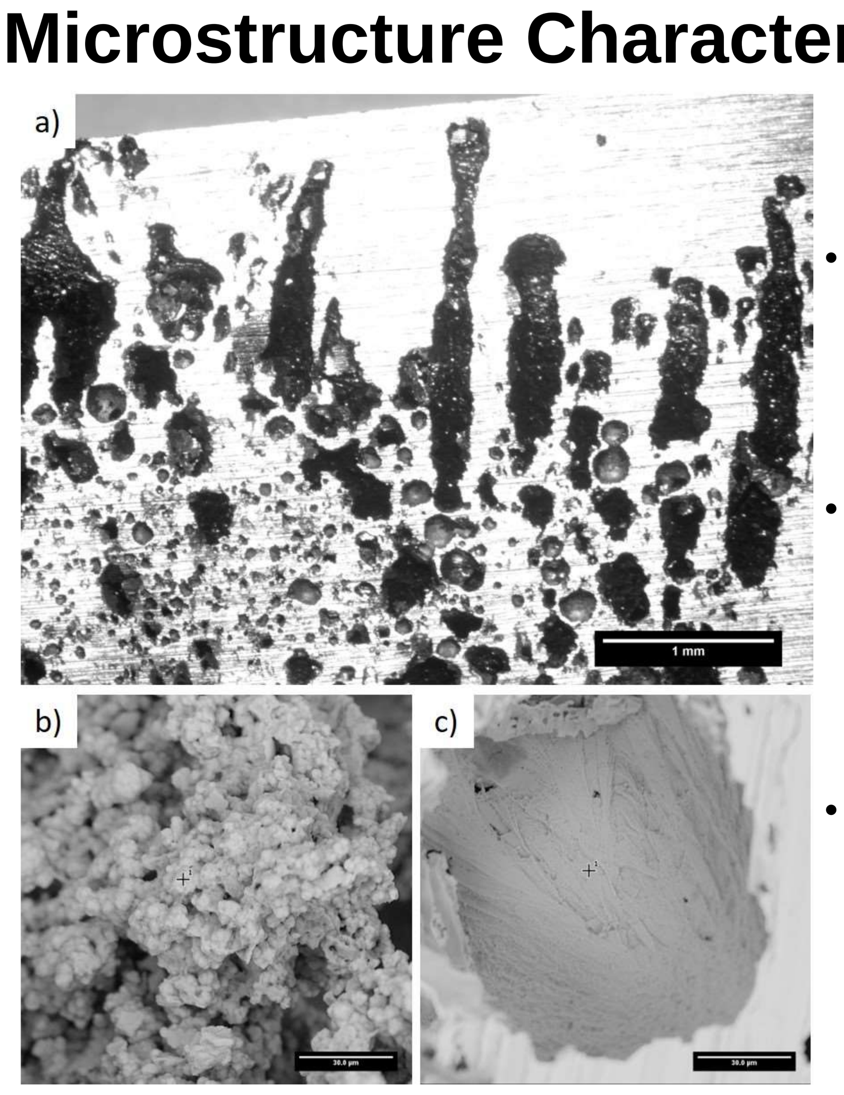


Figure 2: Displays the passivating layers

Microstructure Characterization



- Tested samples showed 2 types of pits.
- Columnar pits were comprised of mostly oxygen.
- Equiaxed pits consistent with nominal composition.

Figure 3: a) Macroscopic view, b) Scanning electron microscope (SEM) of columnar pit and c) SEM of equiaxed pit of corroded samples.

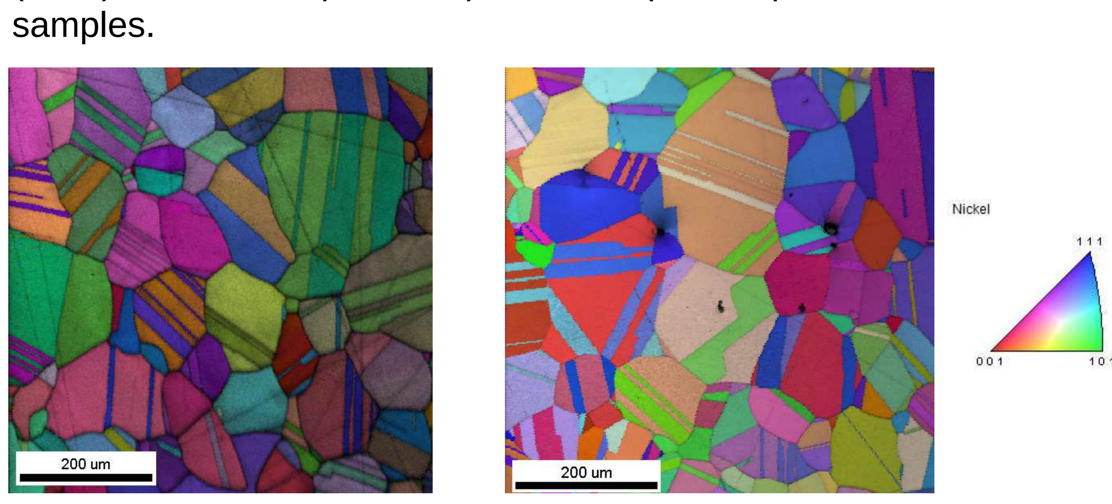


Figure 4: Displays an inverse pole images of the passing (left) and failing sample (right), demonstrating the grain orientation from EBSD scans.

- Stereology found G 4 and G 4.5 for passing and failing specimens, respectively.
- Passing grain sizes typically range from G 2 to G 5.5 suggesting grain size is not responsible for corrosion failures observed.
- Energy dispersive X-ray spectroscopy (EDS) did not show any macro or micro segregation.

Random Forest Model

A random forest model was created to predict if any given composition would pass or fail the corrosion test. A random forest is made up of multiple decision trees like the one in Figure 5.

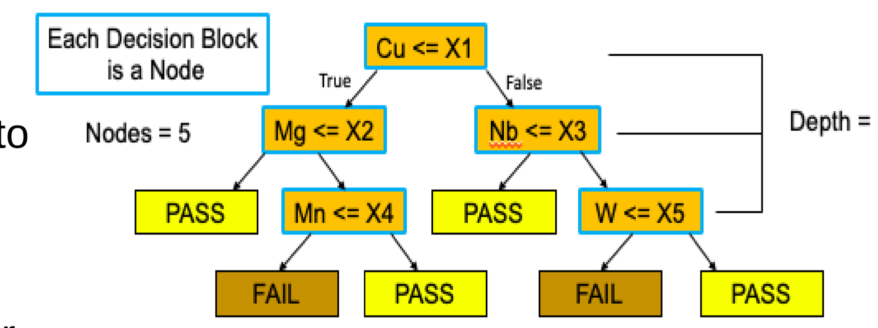


Figure 5: An example of a labeled decision tree used in a random forest

\# Passing Trees > # Failing Trees
Prediction = Pass

\# Failing Trees > # Passing Trees
Prediction = Fail

Table 1: Displays the optimized parameters used in the random forest model

Parameter	Value
# of Decision Trees	114
Total Inputs	14
Inputs per Decision Tree	7-8
Maximum Depth / Tree	None
Average Depth / Tree	4
Maximum Nodes / Tree	None
Average Nodes / Tree	21
Training Data Set	80%
Testing Data Set	20%

- The random forest was optimized to maximize the performance and prevent overfitting.
- Overfitting occurs when the model performs well on the training data and poorly on test data

The model is evaluated using a receiver operating characteristic (ROC) curve and a confusion matrix as shown in Figure 6. ROC values range from 0-1 with one being perfect and a random prediction having a value of .5

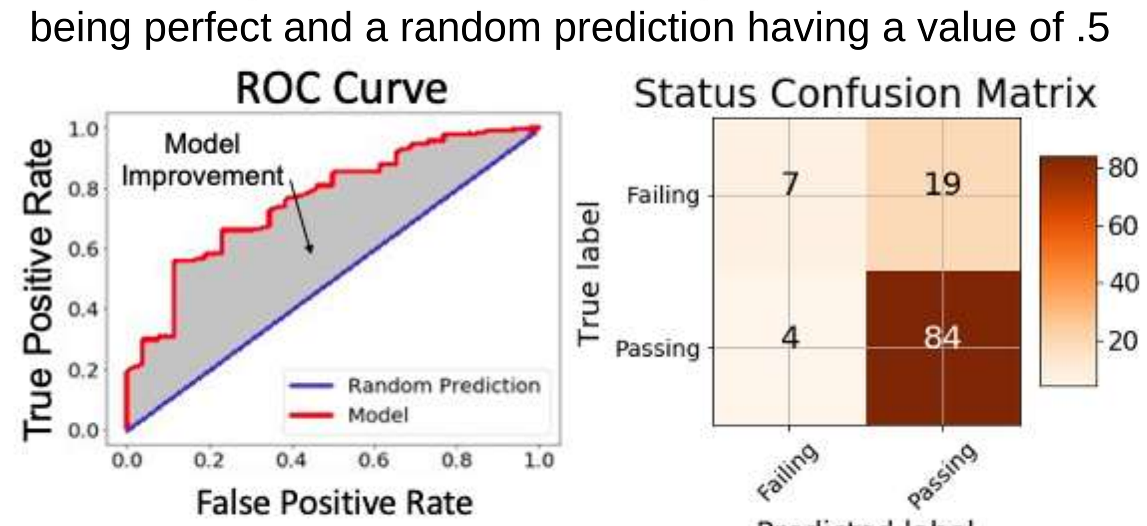


Figure 6: Displays a ROC curve with a value of .79 on the left and a confusion matrix on the right.

Each input into a random forest impacts the output by a different amount. The top five contributors to this prediction are displayed in Table 2.

Table 2: Displays the feature importance for the top five input variables.

feature	importance
Cu	0.465239
W	0.150657
Cb	0.080475
Mg	0.078317
Fe	0.053168

- A model was constructed which included grain size as an input parameter
- The feature importance of grain size was ninth with a value of.0387
- It was determined that grain size is not a significant contributor to this model
- Grain size was omitted in order to use a larger dataset

Trace Element Effect

Table 3: Displays the effect of limiting two specific trace elements (criterion 1 and 2) to below certain weight percent on the failing rate.

	Samples Meeting Criteria	Failing Samples	Passing Samples	% Total Failing Samples	Failure Rate
No Criteria	567	129	438	100.00	22.75
Criterion 1	275	17	258	13.18	6.18
Criterion 2	282	53	229	41.09	18.79
Criterion 1 and 2	164	5	159	3.88	3.05

EBSD

Electron Backscatter Diffraction Analysis (EBSD) is a tool for quantitative microstructural analysis that yields more data than traditional SEM image analysis, such as accurate grain size and orientation. Any significant differences in these would give insight on processing differences that could leave the alloy more susceptible to intergranular pitting corrosion.

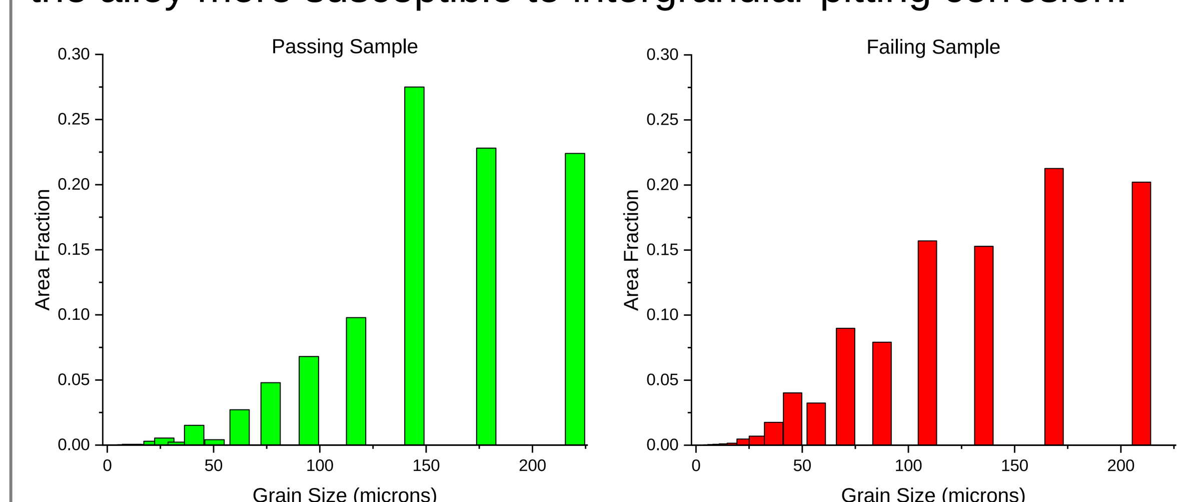


Figure 7: Bar charts showing the distribution of grain size measured by EBSD in the passing (left) and failing (right) samples. The average grain sizes are 76.3 ± 63.1 μm and 61.7 ± 51.9 μm, respectively.

There was no significant difference in grain size, and the two samples shared a common orientation distribution in the scans performed. However the scans were only over a small portion of the samples, and a larger scan could reveal greater differences.

Potentiodynamic Sweep

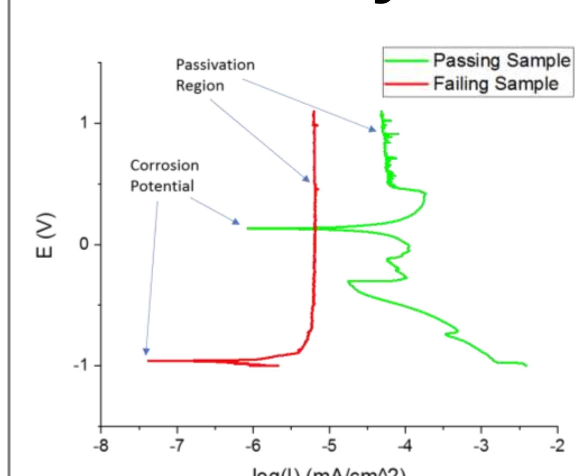


Figure 8: Shows the tested current density curve as a function of changing potential.

Corrosion Rate:
- Passing Sample: 24.039 mil/yr
- Failing Sample: 2.635 mil/yr

- Corrosion test used to find corrosion potential and rate
- Force a controlled potential and measuring the resulting current
- Shows corrosion potential, passive region and breakaway potential
- Used to estimate the spontaneity of passivation and evaluation of corrosion in a sample

More testing is needed to identify a defined difference between the corrosion potential and region of passivation of the passing and failing samples and identify other important aspects of corrosion in the samples.

Recommendations

The team recommends limiting the two key trace elements below the threshold found by the random forest model to reduce the failure rate from 23% to 3%. A full implementation of the model could be used to better predict the status of a heat of the alloy.

Conclusions and Future Work

Table 4: Summary of results

Variable	Conclusion
Composition	Has effect
Grain Size	Found no effect
Micro-/macro-segregation	Found no effect
Processing	No conclusive evidence

To determine the mode of failure, future work would include:
- Further potential sweep tests
- Larger area scans and analysis using EBSD
- A deeper analysis of the processing parameters

References

1. Wong, F. (2009). The effect of alloy composition on the localized corrosion behavior of Ni-Cr-Mo alloys (dissertation).