Characterization and Comparison of Carbide Evolution in Intermediate Nickel Alloys - II

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Exhaust valves in Caterpillar's engines are made of nickel-based alloys due to their strength in high temperature and highly corrosive environments. Inconel 751 (INCO 751) is a high-nickel alloy, while VAT-36 is a cost-effective intermediate nickel alloy, which potentially demonstrates similar high performance to INCO 751 in extreme environments. This project investigates the mechanical and microstructural changes of both materials after aging at high temperatures to simulate service life in an engine with the purpose of evaluating the behavior of the alloys in this environment and extrapolating this out to predict what will happen at a long service life of 10,000+ hours.

This work is sponsored by Caterpillar Inc., Lafayette, IN

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Background & Objectives

Background

Inconel 751 and VAT-36 are commonly used in diesel exhaust valves due to their high strength and high corrosion resistance at high temperatures. The diesel engine is an extreme environment, typically operating at around 730-760ºC with temperatures reaching as high as 900ºC during service.

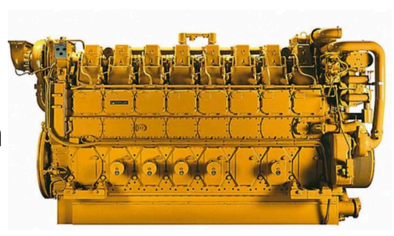

Figure 1: Example Caterpillar diesel engine

After long-term, high-temperature use, these materials develop intergranular carbides and the γ' phase coarsens, which impact material properties including yield strength, hardness, and grain size [1, 2].

Objectives

To enhance the research from the 2023-24 Senior Design project an additional alloy will be investigated, and hardness of VAT-36 and Inconel 751 alloys will be connected to their corresponding microstructures throughout the high temperature aging process, which aims to simulate the working environment in a diesel engine.

Understanding changes in microstructure and mechanical properties of exhaust valves throughout aging will enable Caterpillar to better utilize their alloys by improving knowledge of the mechanical limits of the cost-effective intermediate nickel alloy, VAT-36, and the more expensive alloy, INCO 751.

Alloy Composition

Table 1: Elemental composition of VAT-36 and INCO 751 [3]

	Fe	Ni	Cr	Nb	Al	Ti	Mn	Si	C
VAT-36	Bal.	36.00	19.00	2.00	1.95	1.20	0.30	0.20	0.05
INCO 751	Bal.	73.90	15.50	0.95	1.20	2.30	1.00	0.25	0.10

Experimental Procedure

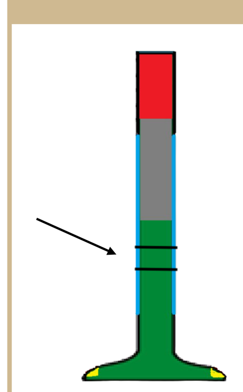

Figure 2: Sample cutting method from the valve stem.

Sample Preparation

- 14 VAT-36 and 14 Inconel 751 cylindrical samples were cut from the valve stem shown in Figure 2.
- One sample of each material was set aside to be used as the control, as fabricated sample.

Heat Treatment

- Samples were placed in an oxygen environment furnace at 800ºC for an aging time of up to 672 hours.
- An additional 2 INCO 751 samples with previous engine aging of 400 hours were placed in the furnace for an additional 672 hours.
- Every 4 days, 2 samples of each material were removed from the furnace and cooled by air for 10 minutes before being quenched in room temperature water.

Figure 3: Prepared samples in furnace.

Etching

- INCO 751 samples were etched with Marbles Reagent for 10 seconds, and VAT-36 samples were etched with diluted Marbles Reagent with a volume fraction of 3:1.

Scanning Electron Microscopy (SEM)/Electron Dispersive Spectroscopy (EDS)

- The NanoScience Phenom SEM was used to explore the grain boundaries, and phases. The composition of areas of interest were collected using EDS.
- Additional high resolution SEM imaging was performed using the ZEISS EVO 15 SEM.

X-ray Diffraction (XRD)

- The Bruker D8 Focus XRD was used to collect crystallographic and microstructural information about the alloys.
- Data was collected in the range of 30°-100° 2θ, with a scan speed of 5.2° per minute, and a divergence slit of 2.452. For each material, data was normalized to compare peak intensity throughout aging.

Hardness Testing

- Hardness was recorded using the LMT-247 Microhardness Tester to obtain Vickers hardness values.

Optical Microscopy

- Optical micrographs were collected using the Olympus BX41m microscope to identify grain boundaries and grain size.
- Grain sizes were measured using ImageJ particle size analysis for only INCO 751 samples due to the lack of grain boundaries appearing for VAT-36.

Results - Microstructure

X-Ray Diffraction

- Each peak in the spectra corresponds to an FCC plane, as both the γ and γ' phases are FCC structured.
- A near nonexistent lattice parameter misfit between the phases minimizes coarsening at lower temperatures, but at 800 °C, the thermal energy is too much to stop it completely [4]
- A slight increase in the peak intensity is observed in the Inconel 751, most notably in the first peak representing the (111) plane
- Changes in the VAT-36 are not as uniform – do not see any changes in intensity in certain peaks relative to others
- Peak intensity increases in first peak in Inconel 751 likely represents coarsening of the γ' phase

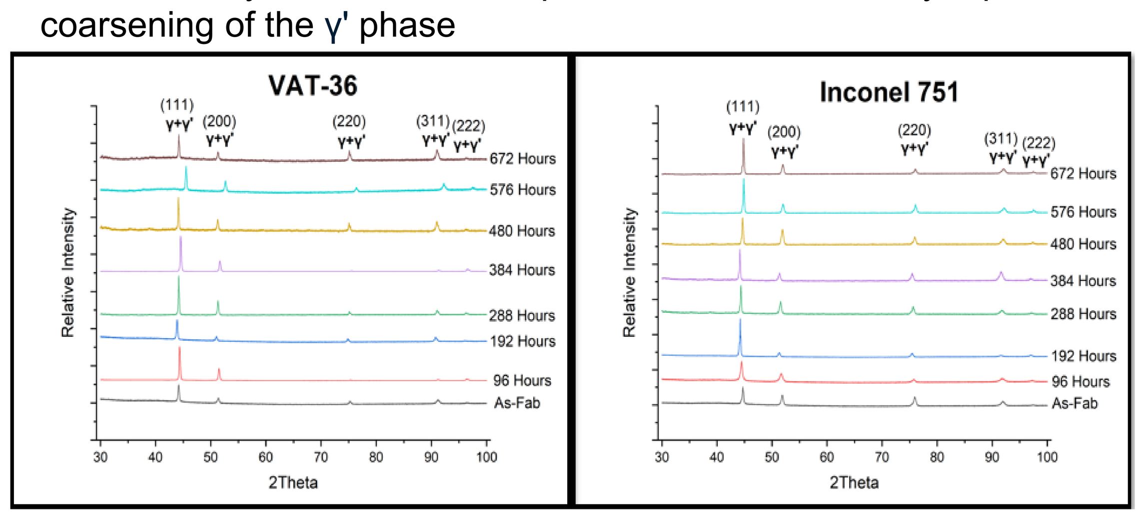

Figure 4: XRD Spectra of Alloys During Aging

Optical Microscopy Grain Size Analysis

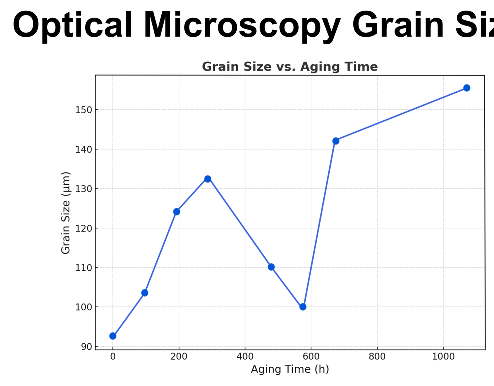

Figure 5: The effect of aging time on grain size at intervals of 96 hours at 800ºC.

- Grain size generally increased as the aging time increased as shown in Figure 5. As grain size increases, an increase in ductility and decrease in strength are expected.

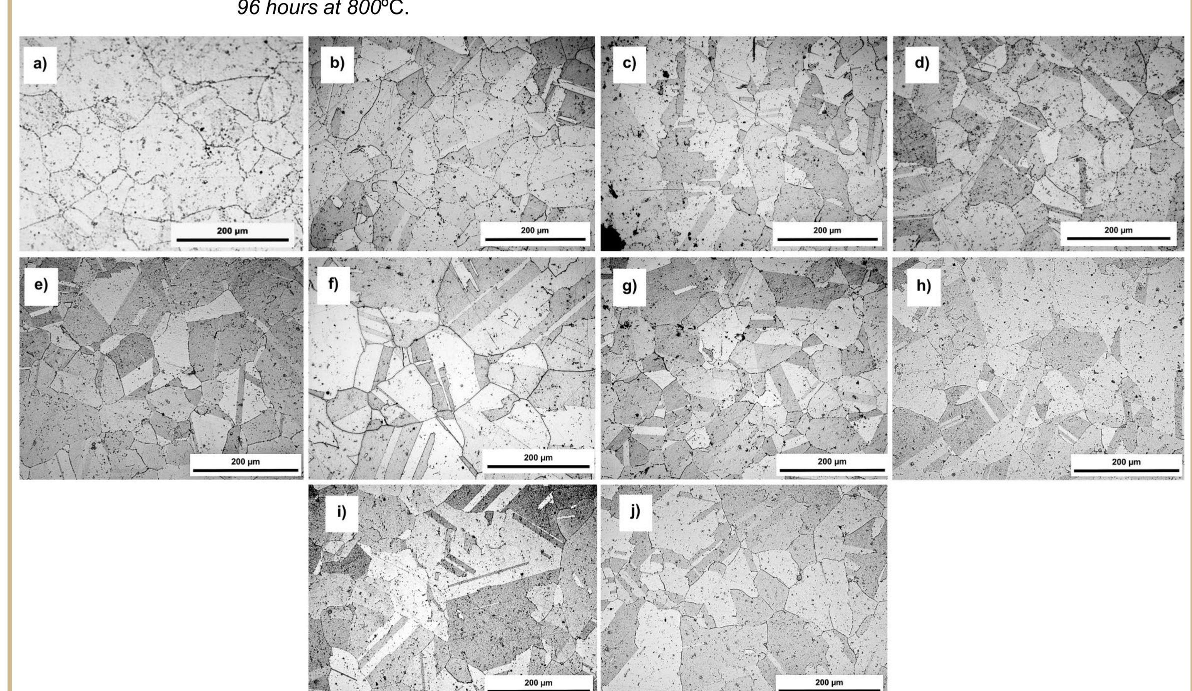

Figure 6: Optical microscopy images of INCO-751 during the aging process beginning at 0 h and ending at 1072 h. a) 0 h, b) 96 h, c) 192 h, d) 288 h, e) 384 h, f) 400 engine h, g) 480 h, h) 576 h, i) 672 h, j) 400 engine h + 672 furnace h.

Carbide Presence

- 12 spot analysis locations (investigating 6 grey and 6 black defects) were recorded for each aging time
- Figure 8 displays examples of each defect
- VAT-36 white defects are Nb rich
- INC-751 black defects are Ti rich
- Carbide concentration in defects increases with aging time
- The black defects showed large variation in Ti content within the 96-hour samples

Table 2: Element concentrations (at%) averaged from point scans (± 1 standard deviation) of carbide inclusions.

White/Grey						
Alloy	INCO-751			VAT-36		
Sample	AF	96-hr	672-hr	AF	96-hr	672-hr
Ti	10.94±6.04	12.21±9.43	16.50±8.67	3.98±2.88	20.04±6.83	18.32±1.34
Nb	12.08±7.69	13.04±10.85	17.14±10.33	20.62±4.33	51.74±16.01	52.30±5.88
C	9.45±1.83	5.38±2.57	7.27±3.24	0.89±2.19	9.74±3.28	10.89±3.15
Black						
Ti	81.25±9.23	43.55±35.59	82.45±4.68	16.33±26.92	69.61±31.37	10.20±16.50
Nb	1.04±1.43	2.51±2.78	3.96±0.85	7.27±12.01	4.52±2.39	7.72±16.20
C	1.73±2.40	2.13±3.12	0±0	0.62±0.98	1.27±1.79	13.41±13.60

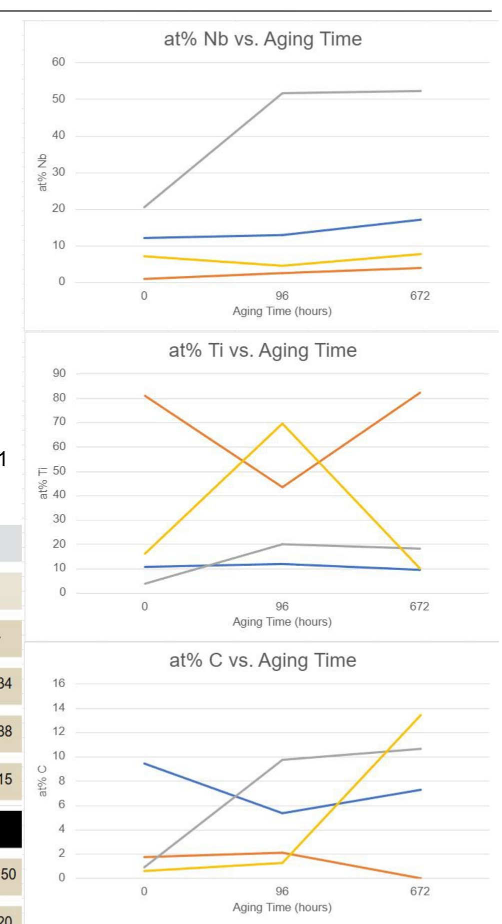

Figure 7: Relationship between at% of carbide elements and aging time for each type of defect.

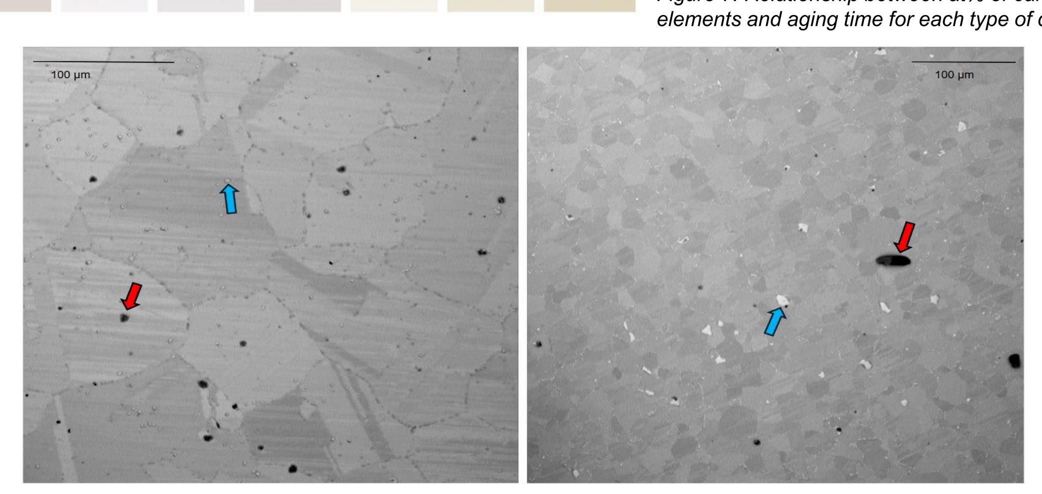

Figure 8: SEM image of INCO-751(left) and VAT-36 (right) both aged for 672 hour. Red arrows indicate defects classified as black and blue arrows indicate defects classified as white or grey.

Results - Microstructure Cont.

High-Magnification SEM

- No significant observable phase changes in either alloy
- Hypothesized γ' seen in Figure 9.f. but inconclusive in determining coarsening

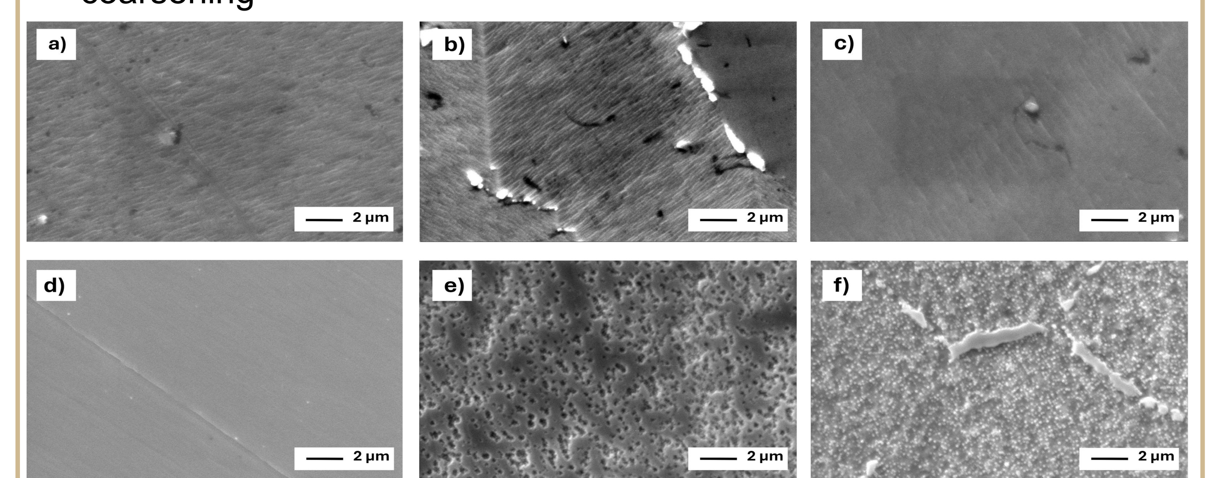

Figure 9: 40,000x magnification SEM images throughout the aging process for both alloys: a) INC-751 AF, b) INC-751 96 hr, c) INC-751 672 hr, d) VAT-36 AF, e) VAT-36 96 hr, d) VAT-36 672 hr

Results - Mechanical Behavior

Hardness

- At the maximum operating temperature, the hardness of all materials decreases but Inconel 751 retains strength better than VAT-36 samples

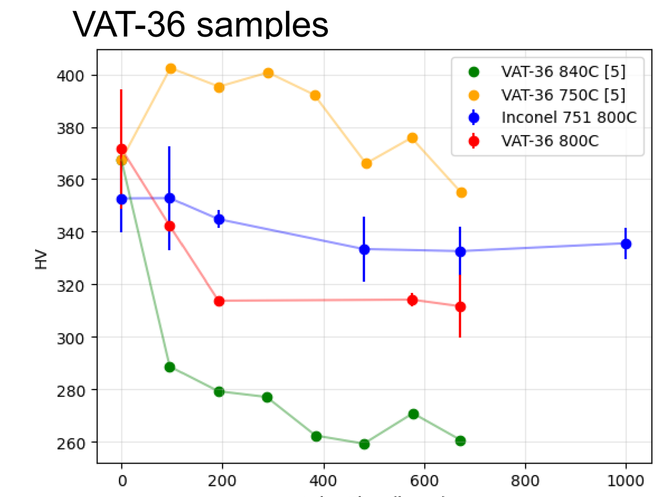

Figure 10: Vickers Hardness of Inconel 751 and VAT-36 through aging.

Inconel 751 sample shows less drastic decrease in hardness and maintains a higher plateau than VAT-36 VAT-36 at 750°C increase is a result of a phase change from Cr-rich to NbSi-rich phase as seen in Figure 7 [5].

- The γ' phase initially precipitates within the matrix, inhibiting dislocation motion and increasing hardness. [6]
- Coarsening of the γ' phase has a detrimental effect on mechanical behavior due to the loss of matrix coherency upon reaching a critical grain size. [7]

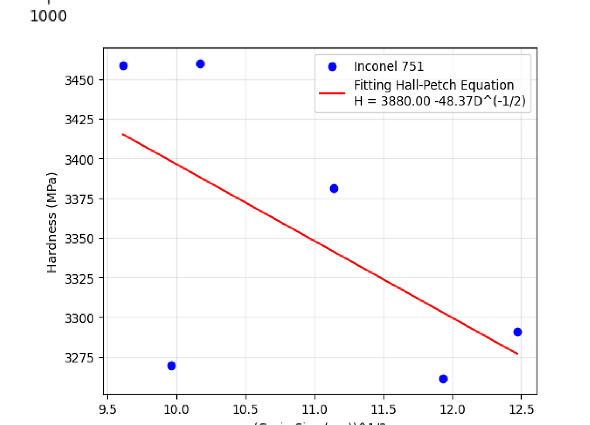

Figure 11: Grain size and hardness correlation shown by the Hall-Petch Equation. Aging times increase as grain size increases.

- At relatively low aging times (<1000 hours), the increase in grain size dominates the mechanical property development.
- Phase changes have a reduced effect on hardness at extended service times, instead controlling the infancy stage properties.

Conclusions & Future Work

Conclusion

Using XRD, some γ' coarsening was observed in Inconel 751 and VAT-36. VAT-36 and Inconel 751 both decreased in hardness over the aging span of 672 hours at 800ºC, with the Inconel generally retaining higher hardness. SEM images and grain size analysis revealed an increase in grain size for Inconel 751, and it can be inferred this is also occurring in VAT-36. EDS of carbide inclusions show a general increase in intergranular phases as aging progressed. Based on the data gathered from this short aging time, it's likely that Inconel 751 will perform better than VAT-36 over the course of a 15,000-20,000-hour service life. Its higher hardness and larger amount of γ' is likely to help the alloy retain its mechanical advantage over VAT-36.

Future Recommendations

To understand further degradation of mechanical properties, longer aging times are necessary. In service, diesel engine valves are subject to high temperatures, high pressure, and corrosion from fuel contaminants. Additional investigation into performance at high temperatures would also aid research on the engine valve materials. Specifically, the high temperature hardness and high temperature creep testing would enhance research on diesel engine valves.

References

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