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**USE OF PRECIOUS METAL-MODIFIED NICKEL-BASE
SUPERALLOYS FOR THIN GAGE APPLICATIONS
(PREPRINT)**

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14. ABSTRACT Precious metal-modified nickel-base superalloys are being investigated for use in thin gage applications, such as thermal protection systems or heat exchangers, due to their strength and inherent oxidation resistance at temperatures in excess of 1050 °C. This overview paper summarizes the Air Force Research Laboratory (AFRL) and Rolls-Royce North America interest in experimental two phase γ -Ni + γ' -Ni ₃ Al superalloys. AFRL is interested in alloys with a base composition of Ni-15Al-5Cr (atomic %) with C, B, and Zr additions for grain-boundary refinement and strengthening. The alloys currently being evaluated also have 4-5 atomic % total of platinum-group metals, in this case platinum and iridium. The feasibility of hot rolling these alloys to a final thickness of 175-250 μ m and obtaining a nearly fully recrystallized microstructure was demonstrated. However, an anomalous grain-growth behavior was also observed at the surface in the intermediate and final rolled products. Future work will include evaluating alloys with a combination of rhenium and tantalum (up to 2 atomic % total) in place of the platinum and iridium.					
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Use of Precious Metal-Modified Nickel-Base Superalloys for Thin Gage Applications

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Abstract

Precious metal-modified nickel-base superalloys are being investigated for use in thin gage applications, such as thermal protection systems or heat exchangers, due to their strength and inherent oxidation resistance at temperatures in excess of 1050°C. This overview paper summarizes the Air Force Research Laboratory (AFRL) & Rolls-Royce North America interest in experimental two phase γ -Ni + γ' -Ni₃Al superalloys. AFRL is interested in alloys with a base composition of Ni-15Al-5Cr (atomic %) with C, B, and Zr additions for grain-boundary refinement and strengthening. The alloys currently being evaluated also have 4-5 atomic % total of platinum-group metals, in this case platinum and iridium. The feasibility of hot rolling these alloys to a final thickness of 175-250 μ m and obtaining a nearly fully recrystallized microstructure was demonstrated. However, an anomalous grain-growth behavior was also observed at the surface in the intermediate and final rolled products. Future work will include evaluating alloys with a combination of rhenium and tantalum (up to 2 atomic % total) in place of the platinum and iridium.

Keywords: thermal protection systems, nickel, superalloy, thermomechanical processing

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Nickel-base superalloys having densities exceeding 8 g/cm^2 may not initially be thought of as viable materials for acreage thermal protection systems (TPS) on hypersonic or space vehicles. Indeed, as the only reusable spacecraft currently in operation, the Space Shuttle utilizes many types of non-metallic TPS materials, in both tile and blanket form. In many cases, these nonmetallic materials are the only option under extreme environments (in terms of temperature, stress, etc.) which demand properties exceeding those of metallic thermal protection systems (MTPS)¹. However, shuttle refurbishment between flights has been reported to require more than 17,000 labor hours² with a total inspection and refurbishment time exceeding 40,000 hours³. This level of maintenance is unacceptable for U.S. Air Force applications, where the turn-around time goal is hours to days rather than weeks to months. As a result, thin gage metallic sheet and foil may become an acreage option because the time for inspection can be significantly reduced, durability is improved, and replacement time is shortened because MTPS panels are mechanically attached rather than adhesively bonded. Historically, sandwich construction MTPS (outer surface-Alloy 617 nickel-base superalloy honeycomb core and face sheets; inner surface titanium alloy honeycomb core and face sheets) was evaluated (Figure 1) and was considered to be a leading candidate for a significant portion of the lower surface of the National Aeronautics and Space Administration (NASA) X-33 vehicle², a wedged-shaped subscale prototype of a reusable launch vehicle⁴ designed by Lockheed Martin.

Weight is critical in vehicle design because total vehicle weight will impact performance³. In both current and proposed systems, the TPS is parasitic and not designed to carry significant structural load regardless of material selection⁵. Because of the increase in density of MTPS, materials under consideration must be very thin, 0.17 mm-0.25 mm for a typical face sheet and 0.05mm-0.10 mm for honeycomb core. One experimental class of alloys

being evaluated for MTPS applications is platinum-group-metal (PGM)-modified nickel-base superalloys where one substitutes PGM, in this case platinum and iridium for nickel. Table 1 identifies a few of the alloys that have been evaluated at the Air Force Research Laboratory as well as a baseline platinum-modified nickel aluminide- β -NiAl(Pt) composition, e.g. Ni-50Al-15Pt used in the turbine-engine industry for airfoil coatings because of its oxidation resistance⁶⁻⁹. However, using β -NiAl(Pt) for a monolithic application is not practical because it is brittle and does not perform well across the entire service temperature range, particularly below 600°C.^{10,11} Recent results on PGM-modified Ni + Ni₃Al (γ + γ') compositions for bond coats^{8,12-13} suggest that these γ -Ni + γ' -Ni₃Al compositions may be suitable thin gage candidates due to the formation of an adherent, protective α -alumina scale which provides increased environmental resistance over a larger service temperature range.¹⁴ In addition, results reported in the late 1970's and early 1980's by Corti, et al¹⁵⁻¹⁷ concluded that platinum had the best overall performance in both oxidizing and sulfidizing environments. Figure 2 compares the oxidation resistance of β -NiAl(Pt), candidate materials, and commercial alloys. Cyclic oxidation testing was performed at Iowa State University and the detailed test procedures are described in reference **. Although there is no added benefit to environmental resistance, iridium is added to the candidate alloys because it partitions almost equally to both γ and γ' – there is a slight preference for the γ phase – and reduces the lattice mismatch.^{20,21}

Corti, et al also documented¹⁵⁻¹⁷ that platinum provided the best strength at temperatures in excess of 1000°C because it partitions to and strengthens the γ' precipitate phase.^{18,19} A high volume fraction of the precipitate phase is desirable for reasonable high temperature strength and adequate creep resistance, which are important MTPS design considerations and may allow the

use of thinner foils than is possible with conventional Ni-based superalloys. Figure 3 compares the tensile strength of commercial alloys to the PGM-modified candidates at room and elevated temperatures at comparable thicknesses.

Platinum prices fluctuate substantially²⁰ with a high in early-mid 2008 at over \$2200/troy oz and an average price for the 1st quarter of 2010 at \$1600/troy oz. Because some of the candidate compositions being evaluated at AFRL contain a Pt content of 2-3 atomic %, the material cost is not trivial. However, the inherent environmental resistance may justify this high cost if the alloy does not require additional environmental or thermal barrier coating (E/TBC) prior to service. Introduction of an E/TBC to either the face sheets or the core dramatically increases system complexity and expense. Also, these high cost alloys may not make up the entire sandwich structure, but instead used for the most demanding environmental applications. This assumes thin gage sheet and foil of a candidate alloy can be 1) produced by conventional hot working processes, 2) further manufactured into honeycomb core, and 3) subsequently joined to fabricate MTPS panels. However, processing of superalloys, let alone PGM-modified superalloys into the desired thin gages can be challenging. At present, most of the experience with PGM-modified Ni-base superalloys has been in the area of casting; relatively little has been reported on wrought processing.^{21,22} Hypersonic heat exchanger applications will not be discussed in any detail but the processing, manufacturing and joining issues identified above are a consideration for this application as well. Research results to date include evaluating the hot working characteristics of and establishing the feasibility of near-conventional processes for producing sheet and foil products of an experimental PGM-modified Ni-base superalloy composition.²³

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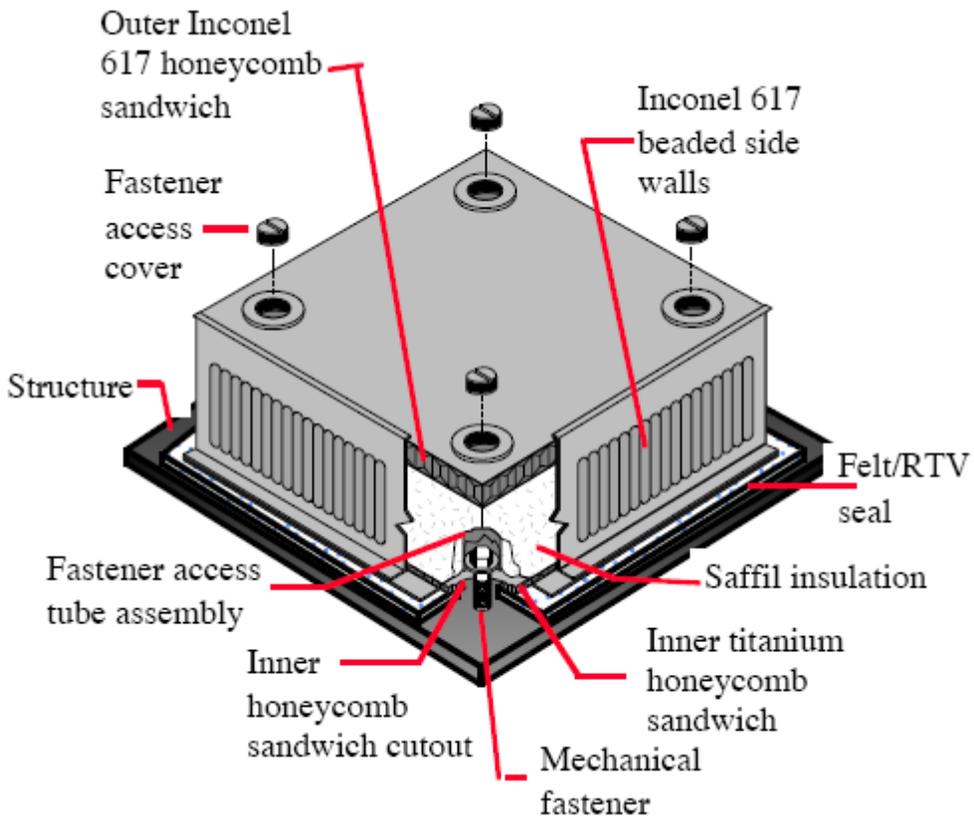


Figure 1.

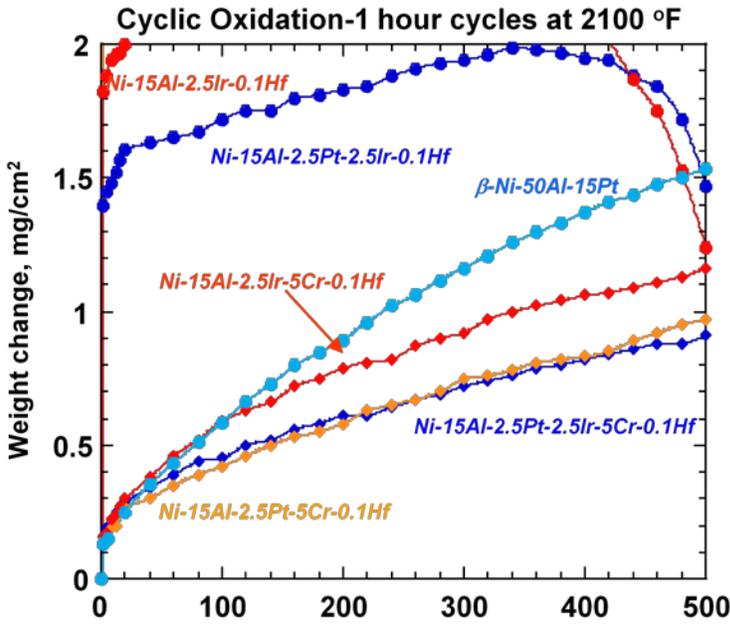


Figure 2. Oxidation performance of β -NiAl(Pt), PGM-modified Ni-base superalloys and commercial Ni-base superalloys. This is a representative figure. Candidate alloys and commercial alloys will be added to final figure.

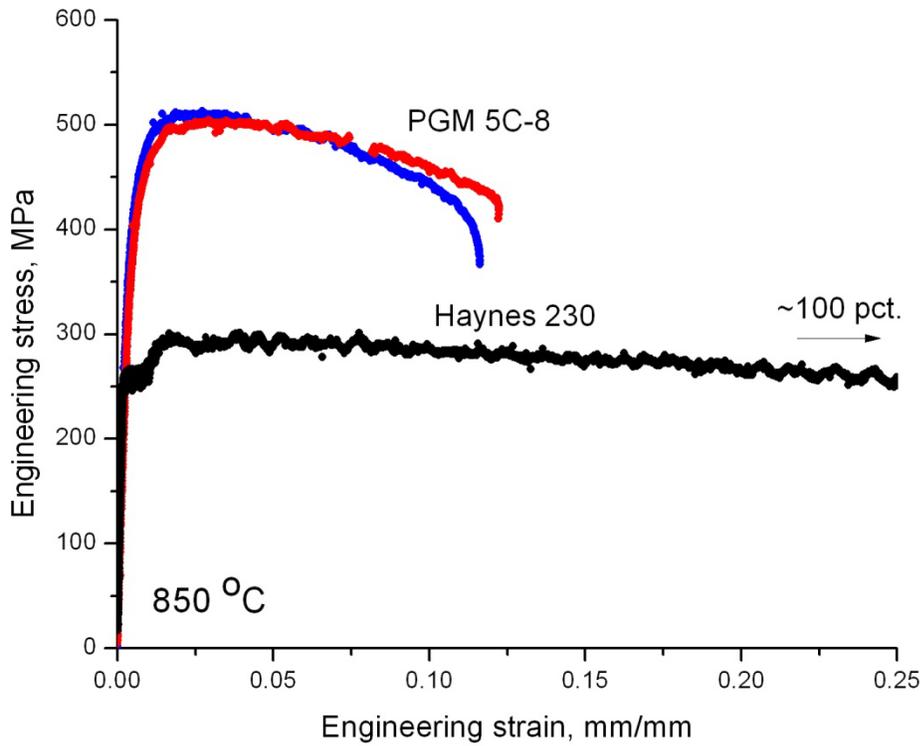


Figure 3. Tensile property comparison at 850 °C of candidate materials to commercial Ni-base superalloys. These are representative curves. Will add commercial alloys to final figure.

Table 1. Atomic Percent

Heat Number	Ni	Cr	Al	Hf	C	B	Zr	Pt	Ir
Pt-modified β	35.0		50.0					15.0	
5A	79.4	5.0	15.0	0.30	0.25	0.04	0.04		
5B	74.4	5.0	15.0	0.30	0.25	0.04	0.04	5.0	
5C	74.4	5.0	15.0	0.30	0.25	0.04	0.04	3.0	2.0
8A	75.6	5.0	15.0	0.15	0.12	0.08	0.03	2.0	2.0
10A	75.6	5.0	15.0	0.15	0.12	0.08	0.03	2.0	2.0
10B	79.6	5.0	15.0	0.15	0.12	0.08	0.03		
10C	74.4	5.0	15.0	0.30	0.25	0.04	0.04	3.0	2.0
10D	79.4	5.0	15.0	0.30	0.25	0.04	0.04		
10E	75.6	5.0	15.0	0.10	0.12	0.08	0.03	2.0	2.0