

## HIGH TEMPERATURE OXIDATION OF A MODIFIED ALLOY 625

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### Abstract

The isothermal oxidation behavior of a modified Alloy 625 was studied at 1100°C and 1200°C in flowing air. Modifications to Alloy 625 included the addition of palladium to the alloy in varying amounts. Palladium additions replaced nickel while other constituents were maintained at nominal levels. At 1100°C Pd levels were 1, 3, and 10 atomic percent. At 1200°C Pd levels were 1 and 3 atomic percent. Results show that Pd additions can reduce the oxidation rate of Alloy 625 and that the relative effect of Pd additions increases with increasing temperature. These findings are consistent with previous studies into the effect of Pd additions in other alloys. However, Pd additions will reduce the melting point of Alloy 625. It is proposed that adjustments to Cr and Pd content are necessary to maintain acceptable melting points and improve oxidation resistance.

### Introduction

Alloy 625 derives its oxidation and corrosion resistance from the additions of a considerable amount of chromium, about 24 atomic percent. As is well known, the primary protective oxide is Cr<sub>2</sub>O<sub>3</sub>. Further, the weldability of Alloy 625 is excellent due to its single-phase austenitic nature. The combination of weldability and oxidation/corrosion resistance has made Alloy 625 the clear choice for many applications.

It is generally believed that above about 1050°C that alloys that form alumina scales are more oxidation resistant than alloys that form primarily chromia. To illustrate this point the isothermal oxidation resistance of two alloys, Alloy 625 and Alloy 738, are shown for 1050°C and 1150°C in Figure 1 and Figure 2 respectively. Note that at 1050°C Alloy 625 gains less mass than Alloy 738. This is probably because the higher Cr content in Alloy 625 allows for a dense and homogenous Cr<sub>2</sub>O<sub>3</sub> layer to form. However, at 1150°C, Alloy 738 performs better. Alloy 738 contains Al and Ti that leads to an oxide scale containing these elements.

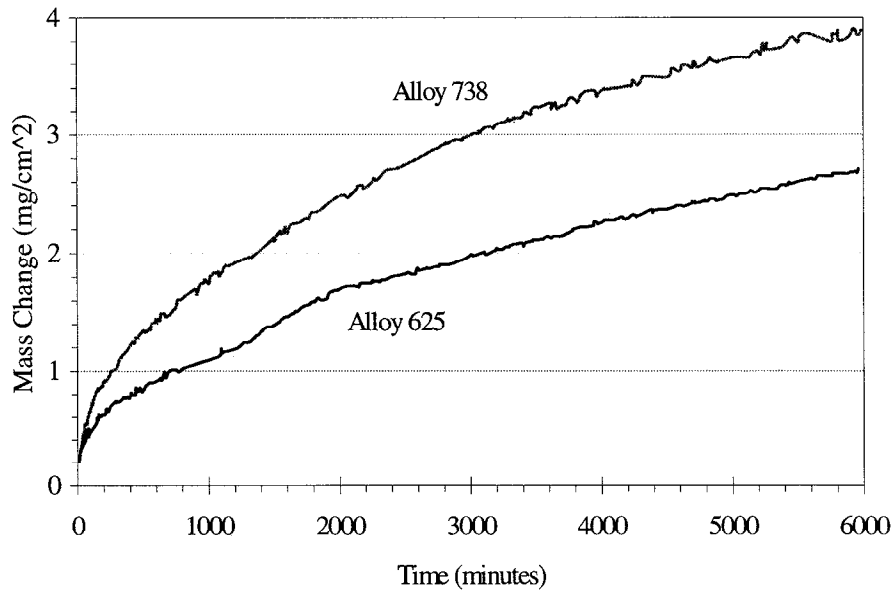


Figure 1 Isothermal Oxidation of Alloy 625 and Alloy 738 at 1050°C

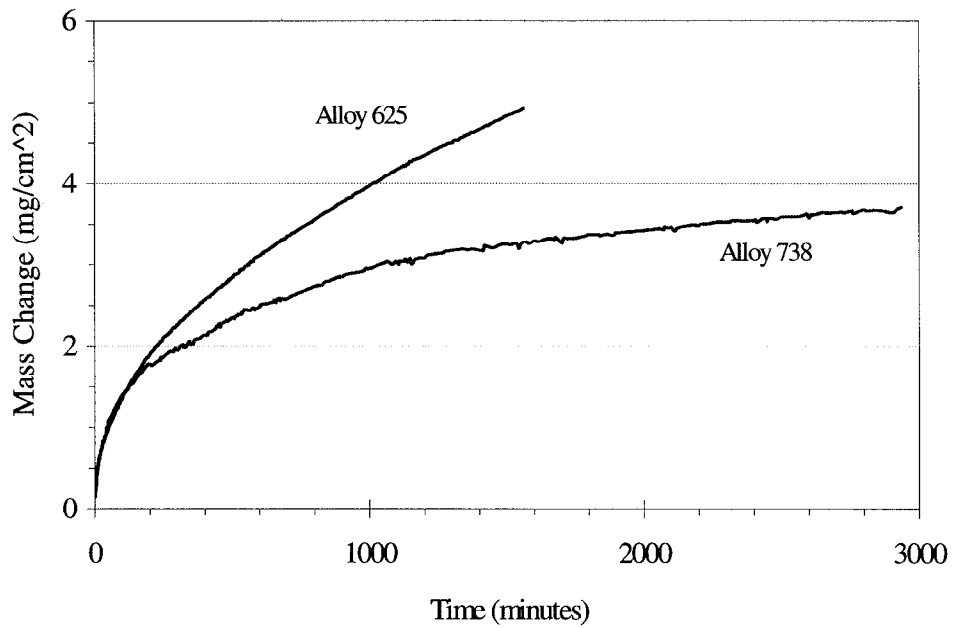


Figure 2 Isothermal Oxidation of Alloy 625 and Alloy 738 at 1150°C

These figures illustrate one of the reasons why alloys that form alumina scales are preferred at high temperatures. Another reason for using aluminum containing alloys at high temperatures is strength. Generally, aluminum is present in sufficient quantities to form Ni<sub>3</sub>Al,  $\gamma'$ , precipitates. Ni<sub>3</sub>Al precipitation represents the most important attribute of superalloys. Unfortunately, as Al content increases weldability decreases. As result most modern superalloys are generally considered very difficult to fusion weld<sup>1</sup>.

The purpose of the present study was to determine if palladium additions to Alloy 625 would decrease its high temperature oxidation rate. This would effectively increase the useful service temperature of the alloy while maintaining its excellent weldability.

#### Oxidation of Alloy 625 and Alloy 738+Pd

Kumar, et al.<sup>2</sup>, studied in detail the early stage ( $t < 150$  minutes) of oxidation in a temperature range from 600° to 1250°C and at two different oxygen partial pressures. They found that the parabolic rate constant was independent of oxygen partial pressure, indicating that cation movement through the scale to the scale-gas interface was the controlling the rate of scale growth. Thus, the point defects in the scale were not a steep function of the oxygen potential. In addition, they found that the oxide scale becomes enriched in Cr<sub>2</sub>O<sub>3</sub> as the temperature increases from 600°C. Between 800° and 1050°C the oxide scale is almost exclusively Cr<sub>2</sub>O<sub>3</sub>. However, as temperatures increased from about 1050°C the oxide scale became enriched in Nb and Ti. The presence of Nb in the oxide scale was thought to be the reason the alloys deviated from parabolic rate behavior towards slower oxidation. The investigators estimated that at 1250°C 3% by weight of the Cr<sub>2</sub>O<sub>3</sub> would be lost in 90 minutes according to the reaction observed by Tedmon<sup>3</sup>:



Although loss of Cr<sub>2</sub>O<sub>3</sub> is apparently not significant during the early stage of oxidation the effect of equation (1) may be important at longer times.

The isothermal oxidation rate of Alloy 738 and Alloy 738+5, 10, and 20 atomic percent Pd was studied at 1050°, 1150°, and 1200°C for times of approximately 100 hours by Whitney<sup>4</sup>. Alloy 738 pre-alloyed powder was mixed with palladium powder and melted using a laser beam. Because Pd was added to pre-alloyed powder the Pd additions effectively diluted the alloy in solute, most importantly Cr and Al. The addition of 20 atomic percent Pd to Alloy 738 diluted the Cr content from 17.2 atomic percent to 13.8 atomic percent and the Al content was reduced from 6.9 atomic percent to 3.3 atomic percent. In spite of the reduction in scale forming elements the oxidation rate of the Pd containing alloy was significantly reduced at 1150° and 1200°C. Figure 3 shows the results obtained at 1150°C. Oxidation of the 20% Pd sample was nearly arrested; the slight mass loss was probably due to CrO<sub>3</sub> vaporization. The 10% Pd sample also showed lower mass gain than the base Alloy 738 at times greater than about 4100 minutes (68 hours).

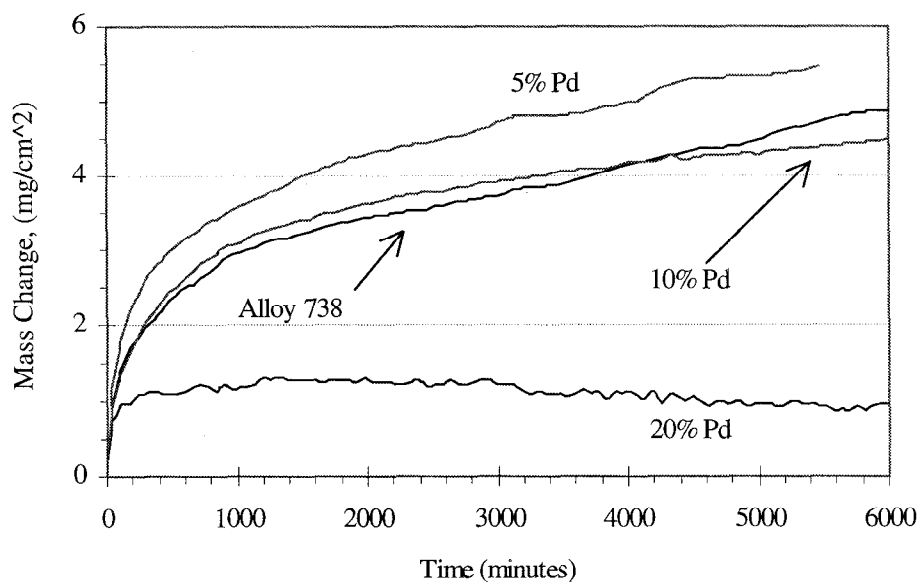


Figure 3 1150°C Isothermal Oxidation of Alloy 738 + Pd

### Experimental Procedures

Experimental material was fabricated by arc melting buttons using elemental powders as precursors. The purity of the precursor powders was 99.9% minimum. The weight fraction of each constituent was adjusted to maintain equivalent solute concentrations between samples. Essentially, nickel was replaced by palladium. Table I lists the nominal compositions of the test alloys in atomic percent.

Table I Nominal Composition of Test Alloys

Alloy Type	Atomic Percent				
	Cr	Ni	Mo	Nb	Pd
Alloy 625	24.7	68.25	5.6	1.45	0
Alloy 625 + 1%Pd	24.7	67.25	5.6	1.45	1
Alloy 625 + 3%Pd	24.7	65.27	5.6	1.45	3
Alloy 625 + 5%Pd	24.7	63.25	5.6	1.45	5
Alloy 625 + 10%Pd	24.7	58.25	5.6	1.45	10
Alloy 625 + 15%Pd	24.7	53.25	5.6	1.45	15
Alloy 625 + 20%Pd	24.7	48.25	5.6	1.45	20

After arc melting the buttons were homogenized under argon for 24 hours at 1200°C.

Melting of some samples occurred during the 1200°C homogenization heat treatments. Although a quantitative analysis was not performed the degree of sample melting was a function of palladium content. Table II lists the visual impressions of the sample melting.

Table II Qualitative Degree of Melting of Samples

Alloy Type	Degree of Melting at 1200°C (Visual Inspection)
Alloy 625	None
Alloy 625 + 1% Pd	None
Alloy 625 + 3% Pd	None
Alloy 625 + 5% Pd	Very Small
Alloy 625 + 10% Pd	Slight
Alloy 625 + 15% Pd	Moderate
Alloy 625 + 20% Pd	Nearly Complete

Preparation for oxidation testing included sectioning individual buttons using a diamond cut-off saw and polishing. Polishing consisted finishing each face of the sample to a 4000 grit SiC finish. Sample edges were finished using an air driven polishing tool with a Scotch Brite wheel. The surface area of each sample was measured by taking a photomicrograph of each sample and correlating the sample area in the photomicrograph to the actual area of the sample. The area of the samples sides was determined by estimating the sample circumference and multiplying by the sample thickness.

Oxidation testing was performed on a CAHN 1000 Thermogravimetric Balance. Mass changes were recorded automatically by a computer and written to disk. Dried air was continuously purged through the reaction tube at a rate of 60 cc/min. Post processing of the data was accomplished using standard spreadsheet software. Because of the melting observed in some of the samples, oxidation test conditions were limited to those shown in Table III.

Table III Isothermal Oxidation Test Conditions

Alloy Type	1100°C	1200°C
Alloy 625	Yes	Yes
Alloy 625 + 1%Pd	Yes	Yes
Alloy 625 + 3%Pd	Yes	Yes
Alloy 625 + 10%Pd	Yes	No

### Results

The TGA results for 1100°C are displayed in Figure 4. Palladium levels of 1 and 3% did not have a significant effect on the oxidation rate. However, the 10% palladium sample exhibited a reduction in overall oxidation rate. Figure 5 shows the TGA data plotted in parabolic space and it appears to be fairly linear. A parabolic rate constant for each alloy was calculated and is shown in Table IV. There is very little difference in  $k_p$  between Alloy 625, 1%, and 3% Pd samples. However, the  $k_p$  for the Alloy 625+10%Pd sample is about ½ that of the other three samples.

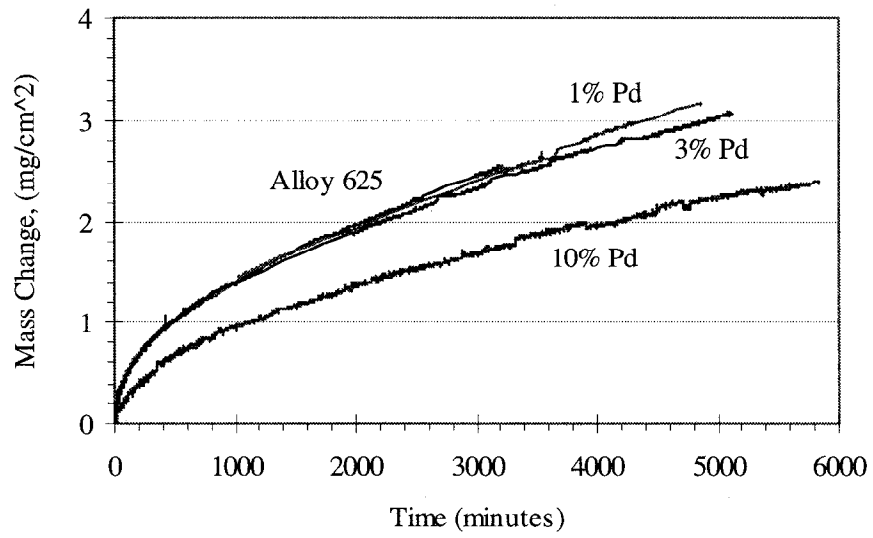


Figure 4 1100°C Isothermal Oxidation of Pd Modified Alloy 625

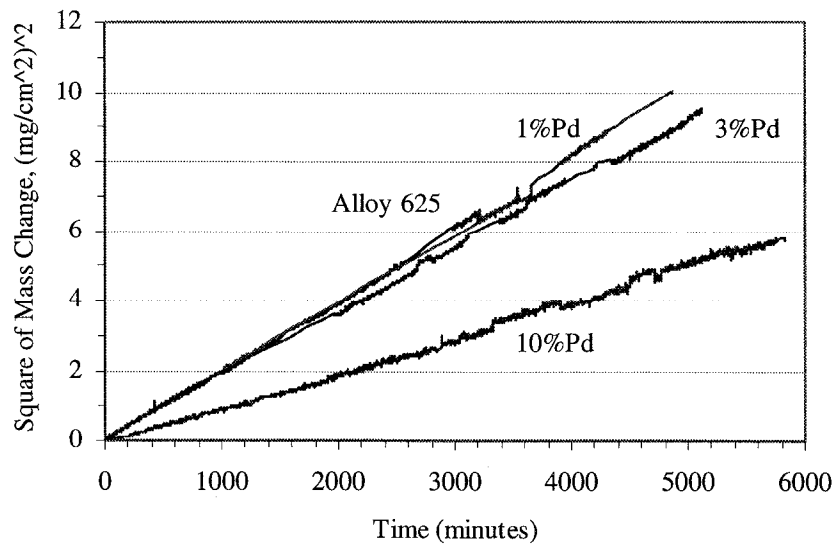


Figure 5 Square of Mass Gain Against Time for 1100°C Data

Table IV Calculated Parabolic Rate Constants for 1100°C

Alloy Type	$k_p$ ( $\text{kg}^2/\text{m}^4\text{sec}$ )
Alloy 625	$3.23 \times 10^{-9}$
Alloy 625 + 1%Pd	$3.35 \times 10^{-9}$
Alloy 625 + 3%Pd	$3.03 \times 10^{-9}$
Alloy 625 + 10%Pd	$1.67 \times 10^{-9}$

The TGA results for 1200°C are shown in Figure 6. As can be seen, the Pd additions to Alloy 625 have reduced total mass gain. The effect of small Pd additions is relatively greater at higher temperatures. The 1200°C data did not exhibit parabolic behavior and a plot in parabolic space is not presented.

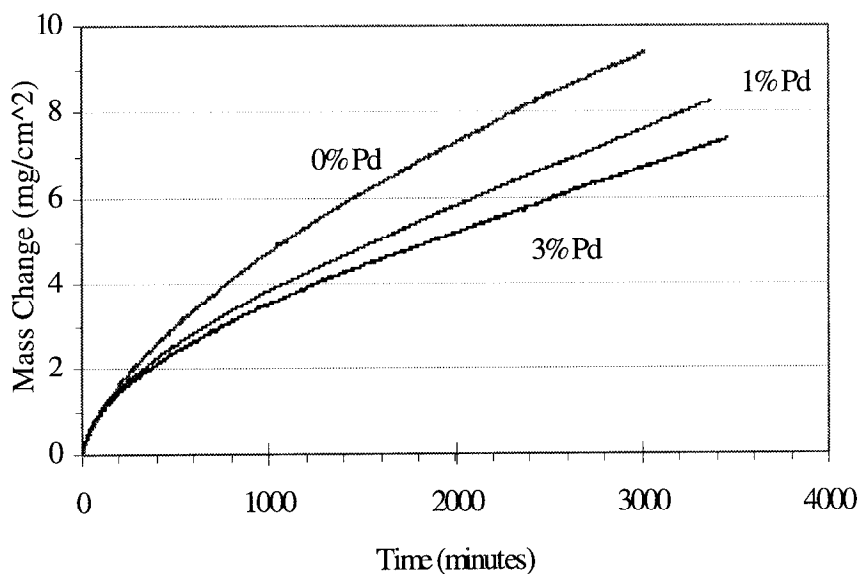


Figure 6 1200°C Isothermal Oxidation of Pd Modified Alloy 625

### Discussion

Based on the results of this and previous investigations, palladium addition are effective in reducing the oxidation rate of nickel based alloys. Significant melting of Alloy 625 + 20%Pd was observed at 1200°C while Alloy 738+20%Pd did not exhibit melting at the same temperature. A composition comparison between Alloy 625 and Alloy 738 and the same alloy with 20% Pd is shown in Table V.

Table V Comparison of Composition Between Alloy 625 and Alloy 738

Element	Alloy Composition, Atomic Percent			
	Alloy 625	Alloy 625+20%Pd	Alloy 738	Alloy 738+20%Pd
Al	0	0	6.92	5.52
B	0	0	0.06	0.05
C	0	0	-	-
Co	0	0	8.01	6.39
Cr	24.7	24.7	17.22	13.74
Mo	5.6	5.6	1.02	0.81
Nb	2.25	2.25	0.57	0.45
Ni	67.45	47.45	67.28	53.9
Pd	0	20	0	20
Ta	0	0	0.92	0.74
Ti	0	0	4.16	3.32
W	0	0	0.78	0.62
Zr	0	0	0.04	0.03

Note that Alloy 625 is approximately 92% nickel and chromium and because solute concentrations were held constant the Alloy 625 + 20%Pd is 92% nickel, chrome, and palladium. For the Alloy 625 system, it is reasonable to expect that the melting point of the alloy will be driven primarily by the relative amounts of Ni, Cr, and Pd given constant Mo and Nb atom fractions. Treating the Alloy 625 + Pd alloys as simple ternary systems the composition of the test alloys can be plotted on a ternary phase diagram shown in Figure 7<sup>5</sup>. As can be seen the addition of Cr to the ternary system significantly lowers the liquidus. One of the major differences between Alloy 625 + 20%Pd and Alloy 738 + 20%Pd is the amount of Cr in each system. In the Alloy 625 + 20%Pd system the chromium level is 24.7% while it is only 13.74% in Alloy 738 + 20%Pd.



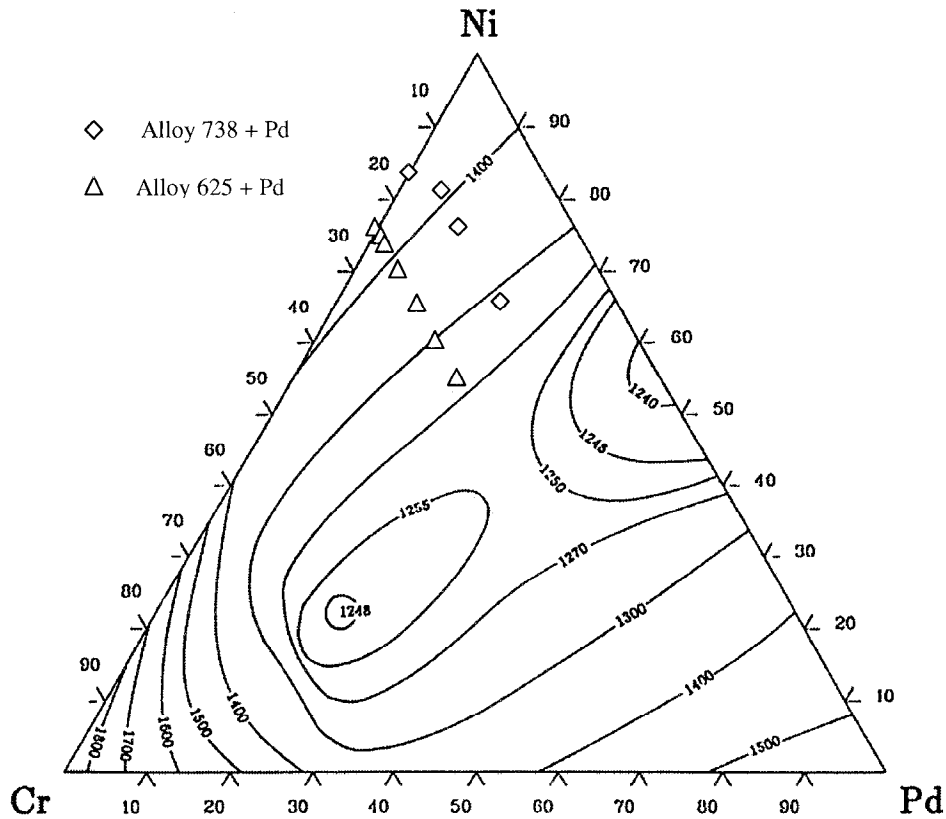


Figure 7 Liquidus Projection for Ni-Cr-Pd Ternary (atomic percent), with Pseudo-ternary Alloy 625 and 738 Plotted for Reference

The Ni+Cr+Pd level in the Alloy 738 + Pd samples are approximately 88% and as a result representing these alloys as simply Ni-Cr-Pd ternaries is risky. However, the compositions that may represent Alloy 738 + Pd are also shown in Figure 7. It can be seen that reducing Cr and Pd in the base Ni-Cr-Pd ternary will increase the melting point.

The TGA results clearly show that the effect of palladium is more pronounced at higher temperatures. This is consistent with previous studies. The mechanism in which palladium affects oxidation in nickel alloys has not been established. The effect of palladium on oxidation of other alloy systems has been investigated. Lee and Simkovich<sup>6,7</sup> studied the oxidation of Mo-W-Cr-Pd alloys and found that palladium segregates to the grain boundaries and promotes the formation of  $\text{Cr}_2\text{O}_3$  and also that Pd retards the inward diffusion of oxygen, preventing internal oxidation.

It is unlikely that Pd will significantly segregate to grain boundaries in nickel systems, due to the complete mutual solid solubility between Pd and Ni. However, Pd may affect the bulk diffusivity of solute atoms in the matrix. This may explain why the affect of Pd is more pronounced at higher temperatures, where bulk diffusivities become more important.

### Conclusions

Palladium can act to reduce the oxidation rate of nickel alloys, and the effect is larger at higher temperature. However, the addition of palladium will significantly reduce the melting point of the alloy. Therefore, the amount of Cr and Pd must be adjusted to maximize melting point and achieve low oxidation rates at all temperatures.

### Acknowledgements

The authors would like to acknowledge the support of Mr. Steven Linder of the Navy Mantech office and Mr. Gray Simpson of Cherry Point Naval Air Depot. We also would like to thank Mr. Lewis Watt, Mr. Paul Denney and Dr. J. T. Schriempf for their support. We also thank Mark Zurbuchen for arc melting the materials used in this investigation and R-F Yan for helping with sample preparation and TGA testing.

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