

THE BENEFICIAL EFFECT OF ALUMINIZATION ON THE OXIDATION RESISTANCE OF A Ni-BASE ALLOY AT HIGH TEMPERATURE¹

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Abstract

In the present work, a pack cementation process was carried out for aluminisation onto a specific Nickel-base alloy to evaluate the improvements of the oxidation resistance at high temperature. Two master alloys compositions (Al and Ni₂Al₃) were used in the presence of a halide salt activator (CrCl₃). The halide gas species equilibrium during the CVD reactions was determined with the chemistry software HSC. The coated samples were characterized by SEM and Electron Probe Micro-Analyzer (EPMA). Oxidation tests were carried out at 1050°C for 24 hours in a thermobalance so that the mass gain of the samples could be measured and compared with the uncoated alloy.

Key Words: Pack cementation; Coatings; Computational thermodynamics; Nickel-base alloys.

O BENEFÍCIO EFEITO DA ALUMINIZAÇÃO NA RESISTÊNCIA À OXIDAÇÃO DE UMA LIGA À BASE DE NÍQUEL EM ALTA TEMPERATURA

Resumo

No presente trabalho foi realizado um processo de aluminização pela técnica Pack Cementation em uma específica liga a base de níquel para avaliar as melhorias da resistência à oxidação em alta temperatura. Duas composições de liga mestre (Al e Ni₂Al₃) foram utilizadas na presença de um sal ativador (CrCl₃). Os equilíbrios entre as espécies gasosas durante as reações de CVD foram simulados com o auxílio do software HSC. As amostras revestidas foram caracterizados via MEV e análise química por micro-sonda eletrônica (EPMA). Ensaio de oxidação foram realizados em 1050°C durante 24 horas em uma termobalança de modo que o ganho de massa das amostras pode ser medido e comparado com a liga não revestida.

Palavras-chave: Pack cementation; Revestimentos; Termodinâmica computacional; Ligas a base de níquel.

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1 INTRODUCTION

Nickel-base alloys are commonly aluminized to improve the oxidation resistance at high temperatures. When an aluminized alloy is exposed to high temperatures in an oxidizing atmosphere, initially a continuous adherent Al_2O_3 scale is quickly formed on the surface of the alloy. This scale prevents the rapid oxidation of the alloy and inward diffusion of oxygen atoms into the substrate. Pack cementation is a simple technique to produce aluminide coatings on steels^[1,2,3] and superalloys,^[4,5] to improve their high-temperature oxidation and sulphidation resistance. The Pack consists of four elements: the substrate or parts to be coated, the master alloy, which consists of a mixture of one or more elements or even an alloy to be deposited on the surface of the parts (NiAl or Cr for example), an halide salt activator such as NaF or CrCl_3 , and an relatively inner filler powder, Al_2O_3 or SiO_2 .^[6] At high temperatures the halide activator reacts with the masteralloy forming the gas phase that surrounds the alloy to be coated. The mass transport, so as the coating composition, is than a function of the partial pressure of the different gas phase species (halide species). With the aid of chemistry software's (thermochemical calculations) it's possible to study the gas phase equilibrium, so as combinations of suitable masteralloys and activator salts can be indentified.^[6] So that pack cementation is an in-situ chemical vapor deposition (CVD) that can be used to deposit one or more elements over the surface of a specific alloy or device to improve its corrosion and the oxidation resistance.

2 EXPERIMENTAL PROCEDURES

The substrate alloy employed throughout the present investigation consisted of a specific nickel-base alloy with principal alloying additions of Cr, W, C, Co and Mo. All the samples had mass about 1g with a rectangular geometry and they were taken from the same alloy plate. The surface preparation of the samples consisted of grinding and rounding of the corners with 800 grid SiC paper. Then the samples were cleaned in ethanol bath with ultrasound.

Two compositions of pack were used; one using pure Al (60% in weight) and the other one using the Ni_2Al_3 alloy as masteralloy (60% in weight). The other 40% consisted of Al_2O_3 . The Ni_2Al_3 alloy was prepared by high frequency melting of their individual components in argon atmosphere. 17 mg of a halide salt activator (CrCl_3) were added to each 10 cm^3 of quartz vessel.

Before performing the experiments, the thermodynamics of the process were studied with the aid of the HSC chemistry software so as to determine the halide gas species equilibrium during the CVD reactions. Parameters such as concentration of the elements presents in the masteralloy and in the substrate, composition of the halide salt activator and the temperature of the cementation are fundamentals information for the calculation of the gas phase equilibrium, then is possible to determine the composition of the coating.

The Pack aluminisations were then conducted for times between 1 and 12 hours at 650°C , for the pure Al aluminisation, and 1050°C for the Ni_2Al_3 aluminisation. Each pack contained two samples, one for high temperature oxidation tests in thermobalance and the other one for microstructure characterization (SEM) and microprobe analysis. The condition

to all of the oxidation tests were 1050°C for 24 hours. The samples for microstructure characterization were embedded in an epoxy resin and analysed with scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

3 RESULTS AND DISCUSSION

3.1 Microstructure, Microanalysis and Calculation of the Chemical Equilibrium of Pure Al Pack Aluminisation

The cross-sectional microstructure of the pure Al pack aluminisation sample, named HN – 3, is shown on Figure 1. After 3 hours of cementation treatment at 650°C the thickness of the coating was about 30 µm and it's possible to observe three different scales. On top of the coating we have a very thin darker scale, which is the richest in aluminum. Soon after, we have another scale which is thicker and clear, due to higher concentration of heavier elements than aluminum, with respect to the top scale. These first two scales are apparently single-phase. And finally, making the interface with the substrate, we have an even thicker layer where it is possible to note the presence of a fine and homogeneous second phase. Is also possible to note the presence of inclusions of cement, which is basically Al₂O₃.

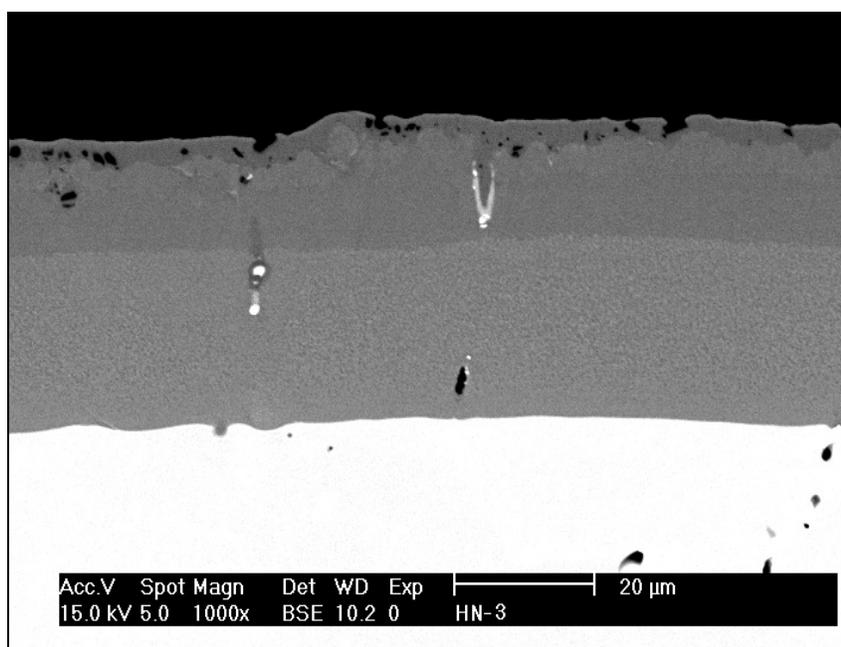


Figure 1. Cross-section of the pure Al Pack Aluminisation sample. After 3 hours of cementation at 650°C the thickness of the coating is about 30 µm.

The results of microprobe microanalysis confirm that the composition of the coating varies through its thickness (Figure 2). According to these results, the top scale has the higher concentration of aluminum. As we approach the substrate, Al concentration decreases with increasing concentration of heavier elements such as Ni, Cr, W and Fe, which come from the alloy (substrate) to the coating by solide state diffusion.

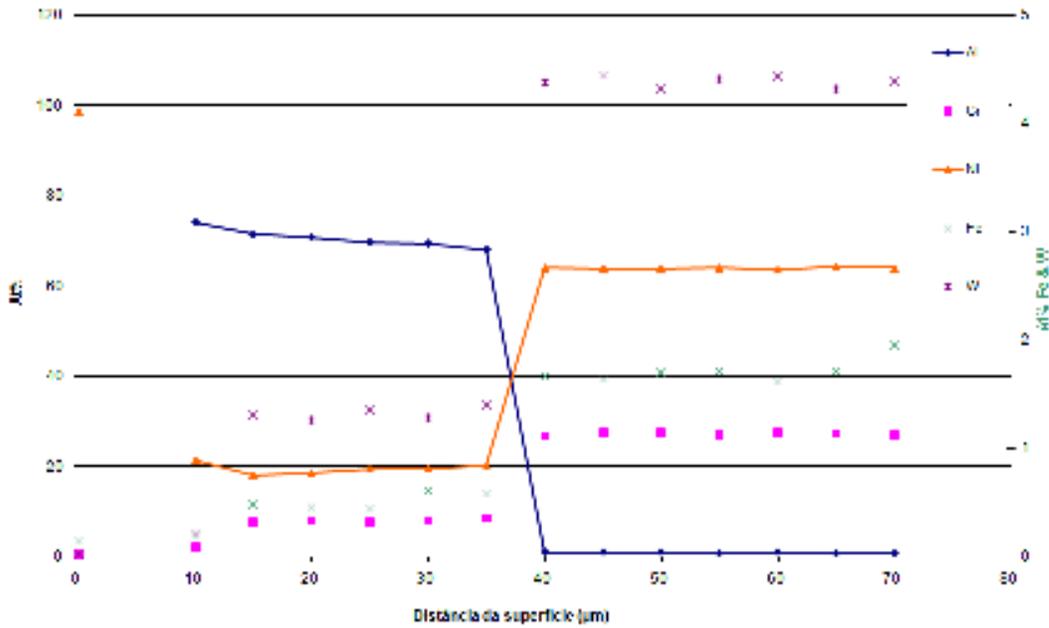


Figure 2. Graph obtained with the results of microprobe microanalysis showing the variation in chemical composition depending on the thickness of the coating for the 3 hours of pure aluminum pack aluminisation sample HN-3.

The equilibrium of the gas phase for the pure Al pack aluminisation, which was done by the HSC chemistry software, shows the variation of partial pressures of each gas species as a function of temperature. The range is 500°C and 650°C (Figure 3). The obtained results show that Ni containing gaseous compound is not present in the gas composition.

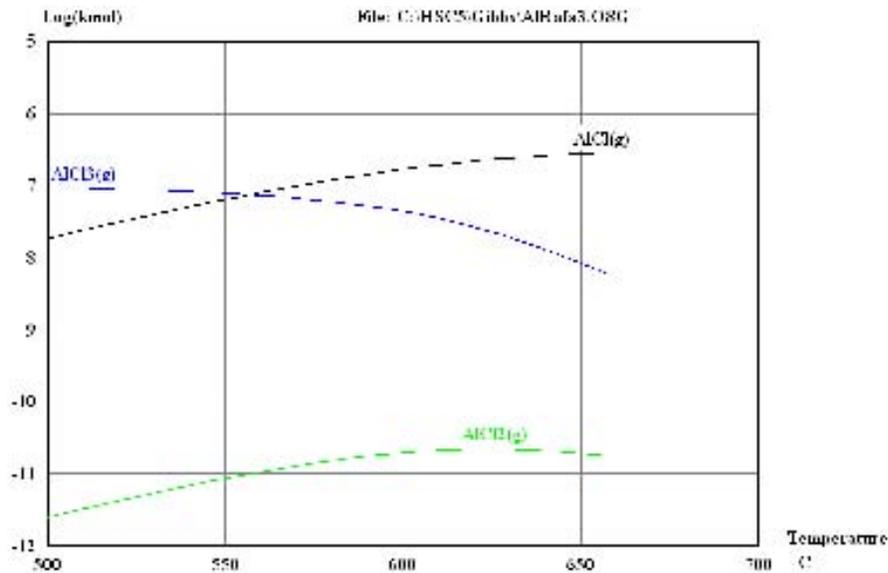


Figure 3. Result of the calculation of the chemical equilibrium of the gas phase for the pure Al masteralloy in presence of CrCl_3 halide salt activator and a nickel substrate. The presence of the AlCl_3 , AlCl and AlCl_2 indicate that it's possible to have Al deposition on the surface of the substrate, which was confirmed by the pack aluminisation experiments and microprobe chemical analysis.

3.2 Microstructure, Microanalysis and Calculation of the Chemical Equilibrium of Ni₂Al₃ Pack Aluminisation

The cross-sectional microstructure of the Ni₂Al₃ pack aluminisation sample, named HN-13, is shown on Figure 4. Before metallographic preparation, this sample had to be coated by nickel using an electrochemical process, in order to avoid tearing of the deposited coating during the stages of grinding and polishing. However, due to problems of adhesion of the nickel on the coating, one stage of the gold plating had to be included, so that finally it was possible to make a nickel electroplating. Those scales (Nickel and Gold) are shown on Figure 4, on top of the deposited coating.

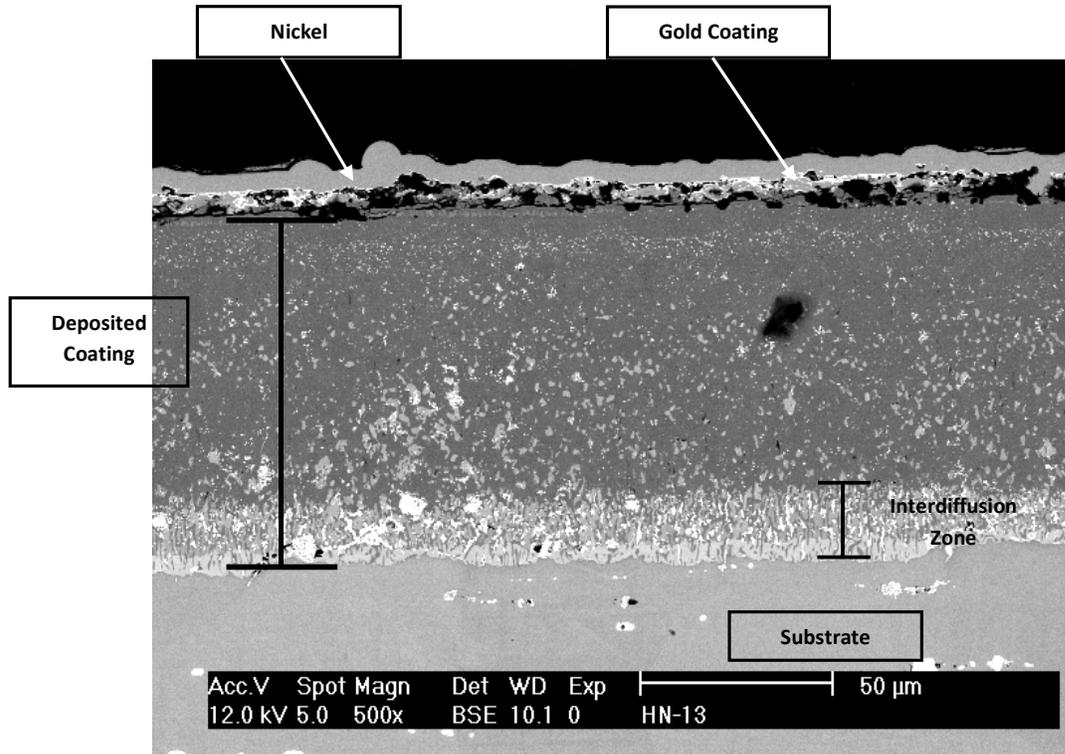


Figure 4. Cross-section of the Ni₂Al₃ Pack Aluminisation sample. After 8 hours of cementation at 1000°C the thickness of the coating is about 70 µm.

After 8 hours of cementation treatment at 1000°C the thickness of the coating was about 70 µm. Similarly to the sample HN-3, along the coating thickness is possible to note the presence of more than one phase, which is mainly a result of interaction between aluminum and nickel, present in the masteralloy and the substrate. But in this case, it is not possible to determine accurately the composition of the different scales. Making the interface with the substrate, we have a typical interdiffusion zone, where the diffusion process between the substrate and the coating is very intensive.

The results of microprobe chemical analysis show the predominant presence of nickel and aluminum along the thickness of the coating (Figure 5). At some points it's possible to observe sharp fluctuations in chemical composition. Looking carefully we might notice that these oscillations show a large drop in the amount of nickel and aluminum and at the same time, we have

a great increase in tungsten and chromium levels. These particular compositions would be probably related to carbide phase owing to the well known tungsten and chromium high affinity for carbon.

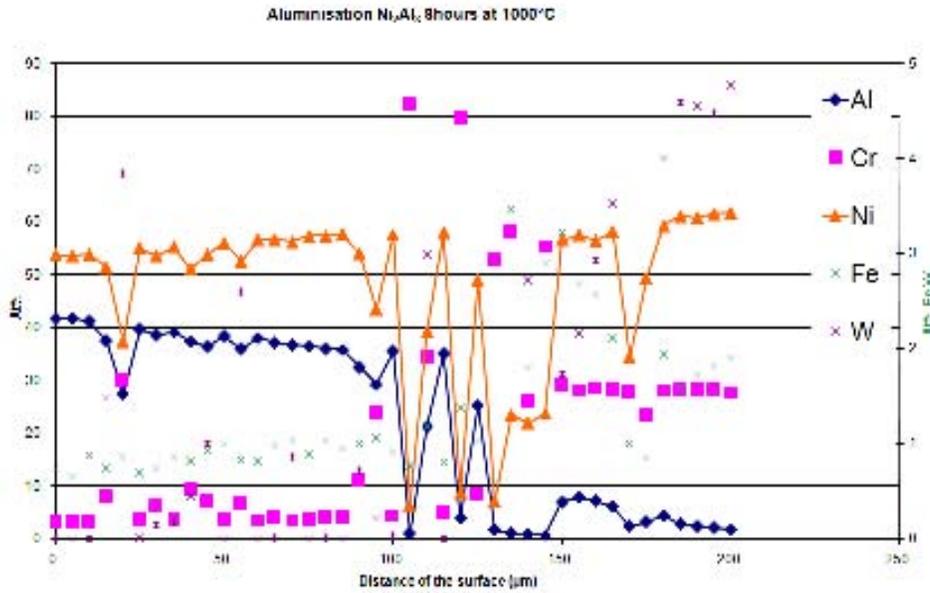


Figure 5. Graph obtained with the results of microprobe microanalysis showing the variation in chemical composition depending on the thickness of the coating for the 8 hours at 1000°C of Ni₂Al₃ pack aluminisation sample HN-13.

The result of computer simulation for the range of 700°C to 1200°C of the gas phase equilibrium shows that aluminum is the main component of the gas phases having the higher partial pressure. In this case, particularly at higher temperatures, nickel appears as component of the gas phase but with a so low partial.

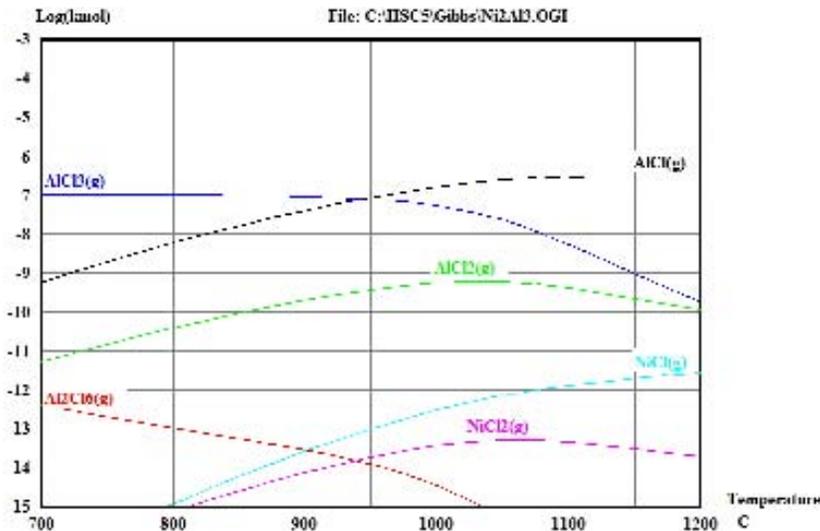


Figure 6. Result of the calculation of the chemical equilibrium of the gas phase for the Ni₂Al₃ masteralloy in presence of CrCl₃ halide salt activator and a nickel substrate. The presence of the AlCl₃, AlCl, AlCl₂, NiCl and NiCl₂ indicate that it's possible to have Al and Ni deposition on the surface of the substrate, which was confirmed by the pack aluminisation experiments and microprobe chemical analysis.

3.3 Isothermal Oxidation Tests

Samples of the uncoated alloy, pure Al and Ni₂Al₃ pack aluminizing were selected for oxidation tests, which were performed on a thermobalance (TG) of the mark SETARAM at 1050°C with artificial air (dry air) for 24 hours. During the tests, the mass gain was measured by the thermobalance. The results of the tests are illustrated on Figure 7.

The results of the oxidation tests show that the uncoated sample had a continuous mass gain during the test. This mass gain is due to oxidation of the alloy, which during this process, gain mass as oxygen reacts with the alloy elements forming oxides on its surface (Chromina and spinelle NiCr₂O₄ oxides). Differently of the uncoated sample, the mass gain of coated samples was much smaller. In fact, after a few hours, the mass gain of coated samples was very small, practically zero, which indicates a good increase in resistance to oxidation of the alloy, promoted by coating.

In each case, the Al reservoir allows the formation of the protective and adherent alumina scale.

Concerning Al coating, in parallel to the oxidation process, the NiAl₃ phase constituting the initial superficial layer undergoes a phase transformation leading notably to the formation of NiAl. During the two first hours of test, the uptake of oxygen is high probably because the oxide/coating interface is moving due to the transformation of NiAl₃ into NiAl.

In the case of Ni₂Al₃ coating, the initial stage of oxidation is characterized by a low weight gain because the NiAl stable phase at 1050°C is initially present at the upper part of the coating and therefore, an adherent and protective Al₂O₃ layer can form on a stable substrate. In both cases, one can note that after the initial transitory stage the oxidation rate is similar for both coatings. This feature seems indicating that the composition of the substrate is becoming similar.

Comparing the performance of the two different compositions of coatings it's notorious that the coating formed by the Ni₂Al₃ masteralloy had superior performance compared to the shape of the pure Al masteralloy.

Mass gain depending of time of oxidised samples at 1050°C 24h

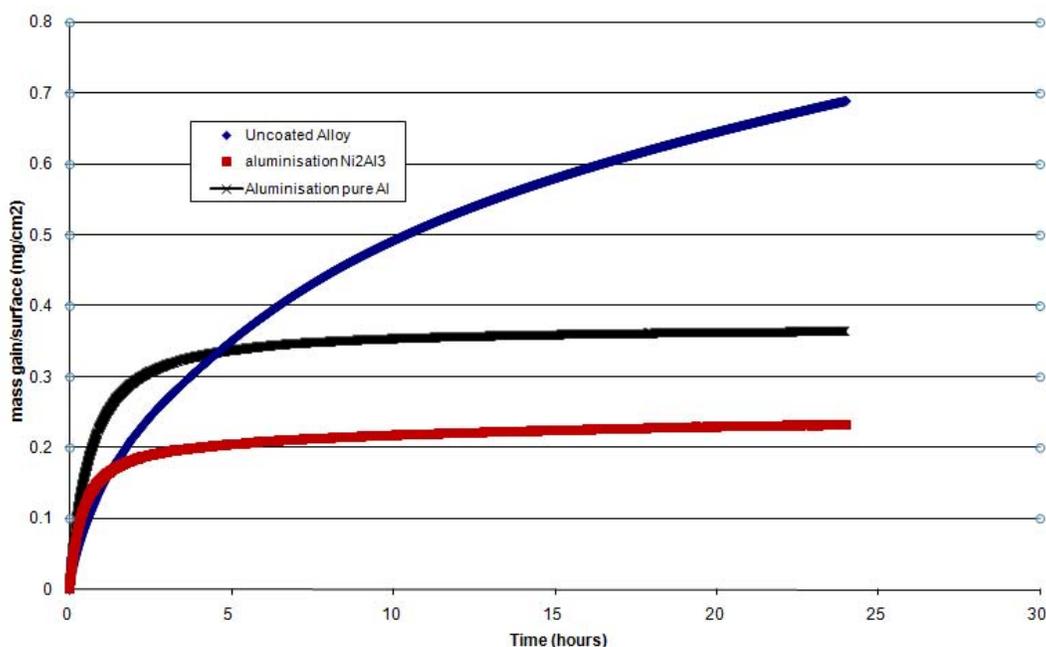


Figure 7. Resulting graph of oxidation test run 1050°C for 24 hours in thermobalance (TG). The blue line is respect to the uncoated alloy. The black line is respect to the pure Al pack aluminisation. The red line is respect to the Ni₂Al₃ pack aluminisation.

4 CONCLUSIONS

Pack Cementation process shown to be a very efficient way for the aluminisation of this specific nickel alloy. The results of the thermochemical calculations done with the chemistry software HSC shown to be in agreement with the results of the microprobe microanalysis, which means that the thermodynamics data base is reliable.

The two different compositions of masteralloys, pure Al and Ni₂Al₃, resulted in different compositions of coatings on the alloy, however both significantly increased the oxidation resistance of the alloy. Moreover, the Ni₂Al₃ pack aluminizing sample presented the best oxidation resistance performance in respect to the pure Al pack aluminizing samples, due to the lower mass gain.

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