

## LOW TEMPERATURE ALUMINIZATION EFFECT ON MONEL 400 ALLOY PRODUCED BY PACK CEMENTATION METHOD

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### Abstract

In this study, aluminum coating process was performed on Monel 400 alloy at a temperature of 600°C using the low-temperature pack cementation method for durations of 2, 4, and 6 hours. The mixture for the coating consisted of metallic Al powder as the aluminum source, Al<sub>2</sub>O<sub>3</sub> as the inert filler, and Ammonium Chloride (NH<sub>4</sub>Cl) as the activator. The formed coatings were characterized using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analyses to examine their microstructures, and phase analyses were conducted using X-Ray Diffraction Analyses (XRD). SEM analysis revealed that the coating layers were homogeneous, compact, and pore-free, demonstrating a strong bond between the coating and the matrix. The thickness of the coating layer was measured from the surface to the matrix, and it was observed to vary between 4 µm and 10 µm. It was determined that 600°C was sufficient for the accumulation of an aluminate layer and a successful coating layer was obtained. The hardness values of the alumina layer formed on the surface were measured, and an increase in hardness values was observed with increasing process duration and temperature.

**Keywords:** Monel 400 alloy, Pack cementation, Super alloy, Aluminate-based coating

## KUTU SEMENTASYON YÖNTEMİ İLE ÜRETİLEN MONEL 400 ALAŞIMININ ÜZERİNE DÜŞÜK SICAKLIK ALÜMİNYUMLAMA ETKİSİ

### Özet

Bu çalışmada, Monel400 alaşım üzerinde 600°C sıcaklıkta, 2, 4 ve 6 saatlik süreler boyunca düşük sıcaklıkta kutu sementasyon yöntemi ile alüminyum kaplama işlemi gerçekleştirilmiştir. Pota karışımı; alüminyum kaynağı olarak metalik Al tozu, inert dolgu olarak Al<sub>2</sub>O<sub>3</sub> ve aktivatör olarak Amonyum Klorür (NH<sub>4</sub>Cl) kullanılarak hazırlanmıştır. Oluşan kaplamaların mikro yapıları SEM ve EDS analizleri ile karakterize edilmiş, XRD analizi ile faz analizleri gerçekleştirilmiştir. SEM analizi, kaplama tabakalarının homojen, kompakt ve gözeneksiz olduğunu ve kaplama ile matris arasında sağlam bir yapıya olduğunu ortaya koymuştur. Kaplama tabakasının kalınlığı yüzeyden matrise doğru ölçülmüş ve değerlerin 4 µm ile 10 µm arasında değiştiği gözlenmiştir. 600°C'nin alüminid tabakasının birikmesi için yeterli olduğu ve başarılı bir kaplama tabakasının elde edildiği tespit edilmiştir. Yüzeyde oluşturulan alüminid tabakasının sertlik değerleri ölçülmüş ve artan işlem süresi ve sıcaklıkla birlikte sertlik değerlerinde artış gözlenmiştir.

**Anahtar Kelimeler:** Monel 400 alaşımı, Kutu sementasyonu, Süper alaşım, Alüminyumlama

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### 1. Introduction

Nickel-based superalloys are highly favored in various industries due to their exceptional mechanical properties, such as superior friction resistance, high temperature resilience, and impressive tensile strength. These alloys find extensive applications in demanding sectors, including aerospace, nuclear energy, marine, and automotive, where they are specifically utilized for high temperature applications [1], [2]. The inclination

towards nickel-based superalloys stems from their outstanding corrosion resistance, lightweight nature, and remarkable stability at elevated temperatures[3]–[7]. Additionally, these alloys possess notable attributes, such as low thermal conductivity, heightened chemical reactivity at high temperatures, high hardness, and low elastic modulus [8]. Monel 400 is a nickel-based superalloy that has garnered commercial acceptance due to its chemical inertness, relatively low cost, and exceptional corrosion resistance. This alloy exhibits

robust resistance to corrosion under reducing conditions while displaying diminished performance under oxidizing conditions. The International Nickel Company created the first nickel-copper alloy, known as Monel 400, which was patented in 1906. It has good qualities like high strength, high corrosion resistance, and high wear resistance. [9] Due to its light weight, high strength and ductility, non-toxicity, cost effectiveness, non-ferromagnetism, and ease of processing, aluminum can be regarded as one of the most suitable coating components among those tested by many researchers on Ni-Cu alloy [10]. Individually, the corrosive media and appropriate amounts of stress have a significant impact on the fatigue phenomena of environmental-induced corrosion for aluminum and its alloys. Notably, Monel 400 alloys showcase superior corrosion resistance in atmospheric settings compared to copper counterparts [11], [12]. Originally introduced as a sheet material in 1908, Monel 400 has found diverse applications across various sectors, including but not limited to clothing and food shelving. Its remarkable suitability for challenging environments stems from its resilience and high-quality performance across a broad temperature range [13]. Particularly, Monel 400 exhibits exceptional resistance to corrosive agents such as seawater, alkaline solutions, salt, and acidic mediums. Furthermore, it exhibits excellent formability and machinability compared to other nickel-based superalloys [11]–[13]. In addition that the application of surface hardening techniques can effectively increase the material's surface hardness, thereby imparting superior resistance to wear and scratches such as aluminizing, chromizing, siliconizing etc.. Low temperature aluminizing technique used in this study for producing aluminide type coating on the surface. This process is quite basic, process cheap, environmentally friendly and many researches have been done on the pack aluminizing process, which has attracted the attention of researchers due to some important advantages [1], [14], [15]. Pack aluminizing process has been applied to different materials under different processing conditions by many studies have been carried out on the coating layer, especially oxidation and corrosion resistance [1], [16], [17].

In this paper it is aimed to improve the surface properties of Monel 400 alloy such as a very low temperature and low duration process time.

## 2. Methodology

In this study, commercially sourced Monel 400 was chosen as the substrate material for the aluminum coating process. Monel 400 is considered one of the prominent nickel-based alloys and possesses a superior operating temperature of 540°C, surpassing that of pure nickel. The chemical composition of Monel 400 is presented in Table 1.

Table 1. Chemical composition of Monel 400 [18].

Elements	wt.Percentages
Ni%	63 min.
Cu%	28-34
Mn%	2
P%	0,024
Fe%	2.5 max.
C%	0.3 max.
Si%	0.5

The pack cementation method was applied to achieve the deposition of an aluminum coating on the surface of the Monel 400 alloy. The process involved precise weighing of an activator consisting of 10% NH<sub>4</sub>Cl, and a coating powder composed of 35% pure Al powder and 55% commercially pure Al<sub>2</sub>O<sub>3</sub> powder, in predetermined weight ratios. Following this step, powders were mixed to ensure a homogeneous blend. Subsequently, the powder mixture was placed within a steel crucible containing the Monel 400 alloy and subjected to aluminisation treatment in an open atmospheric furnace at a temperature of 600°C for varying durations of 2, 4, and 6 hours. Upon completion of the coating process, the samples were carefully cooled to ambient temperature and subsequently extracted from the furnace. The cross-sectional surfaces of the coated samples were subjected to metallographic preparation for subsequent microstructural analysis. The microstructural characterization of the samples, treated using the pack aluminisation method, was conducted using a JOEL JSM-5600 model scanning electron microscope (SEM). Rigaku X-ray diffractometer, utilizing CuK $\alpha$  radiation with a wavelength of 1.54056 Å and a 2 $\theta$  angle range of 10° to 90°, was employed to identify the phases formed on the coating surface. The hardness analysis was performed using a Leica WMHT-Mod hardness tester equipped with a Vickers diamond pyramid indenter using a load of 25 g and dwell time 15 s.

## 3. Result and Discussion

### 3.1. SEM-EDS Analyses

Based on the SEM analyses results, it is seen that a thin, homogeneous, continuous aluminide layer is formed as a result of the aluminization process applied on the Monel 400 alloy at a low temperature of 600 degrees for 2 hours. While this thin layer was about 4 microns thick, it increased due to the increase with duration time and turned into a two-layer coating. The layer exhibits homogeneity and uniformity across the entire surface area. Similarly, the Figure 1c demonstrates that the coating layer achieves a thickness of 10 $\mu$ m following a processing time of 6 hours.

The EDS analysis of a sample subjected to a 6-hour treatment at 600°C, resulting in the formation of a layer, is presented in Figure 2. The observations reveal varying stoichiometric ratios within the formed layer, indicating

changes in the composition. Additionally, a trace amount of oxygen also detected on the sample. Specifically, upon closer examination of point 2, the presence of the nickel aluminide phase is evident. Furthermore, the analysis indicates the migration of copper towards the surface. As one moves towards the matrix of the layer, a decrease in the aluminum content is observed. These findings provide valuable insights into the elemental distribution and composition of the formed layer during the 6-hour treatment.

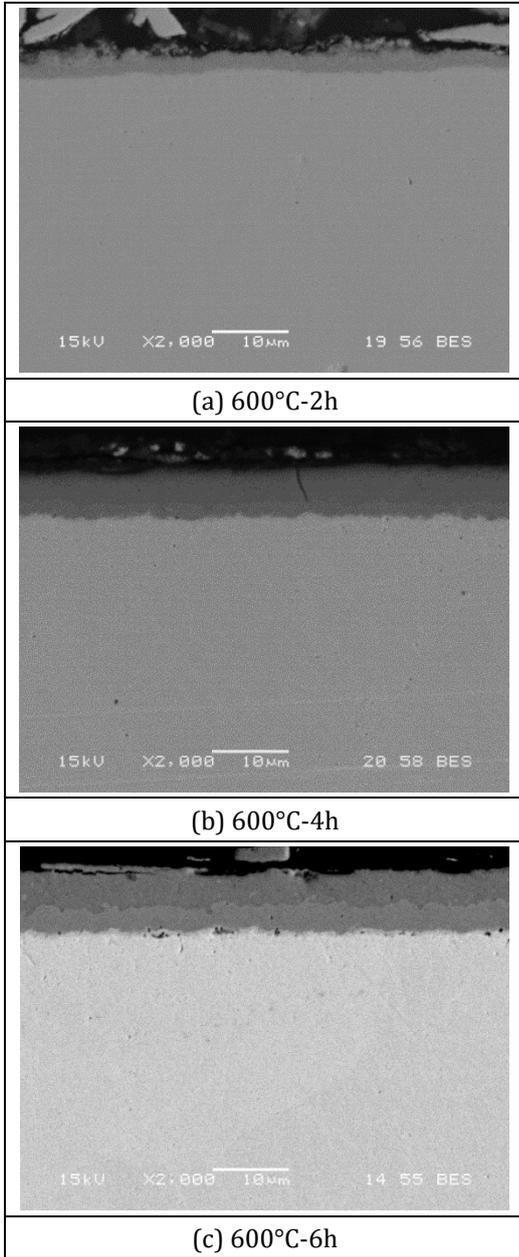
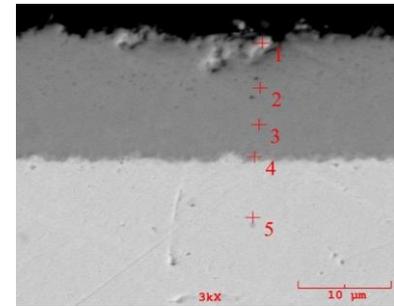


Figure 1. The SEM images of Monel 400 alloy Al coated at 600°C

The SEM-MAP analysis presented in Figure 3 provides elemental distribution of a Monel 400 alloy that applied aluminization process for a duration of 6 hours at a temperature of 600°C. The aluminum represented by this pretty purple color is densely deposited on the surface. Although a large amount of nickel has been

moved from the base material to the surface also the upward transfer of copper is clearly seen not only in the map analysis but also in the XRD analysis. The analysis reveals a minimal presence of oxygen on the surface. While forming a pack cementation coating with materials such as aluminum with high affinity for oxygen, it was inevitable to encounter oxygen at these levels in such works carried out in open atmosphere [15], [19].



	Wt.%				
Elt.	1	2	3	4	5
O	1.497	0.102	1.060	0.000	0.103
Al	66.42467	10866.93957	769	0.535	
Ni	21.96923	0.1226	18740.18074	382	
Cu	10.110	9.778	5.814	2.051	24.980

Figure 2. The SEM-EDS analyses of Monel 400 alloy, aluminum-coated for 6 hours at 600°C

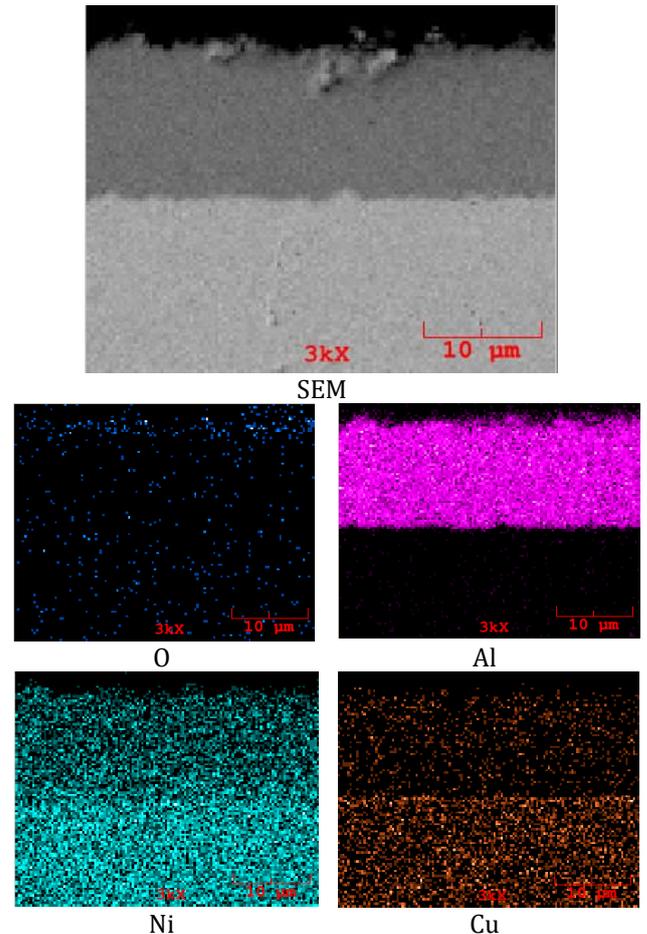


Figure 3. The SEM-MAP analyses of Monel 400 alloy, aluminum-coated for 6 hours at 600°C

### 3.2.XRD Analyses

X-ray diffraction (XRD) analysis was performed on the samples applied aluminization process for 2 and 4 hours at a temperature of 600°C in order to investigate the phase composition. The XRD analysis results indicate the presence of  $\text{Al}_3\text{Ni}_2$  and  $\text{Cu}_9\text{Al}_4$  phases in the resulting coating layer formed through the aluminization process. Figure 4 displays the XRD diffraction patterns corresponding to the materials treated with the aluminization process for 2 and 4 hours at 600°C. When it is compared to SEM-EDS analyses results the weight percentages values also corresponds to this phases presence on the surface of the alloy. The main phase  $\text{Al}_3\text{Ni}_2$  is common such this kind of nickel aluminide coatings. This Al rich Ni intermetallic is results from high rich aluminium content of pack process. And Cu rich intermetallic phase is much more obtained from thin coating layer. This result can be attributed to the counting of the substrate material due to the thin layer. Since the layer is at about 4 microns, the count was taken not only from the surface but also from the substrate, which is interpreted as the fact that the intermetallic phase with a high Cu percentage is obtained more during the

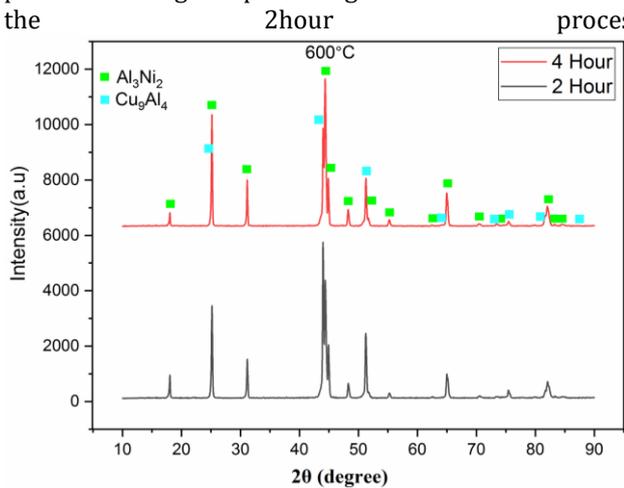


Figure 4. XRD analyses of Monel 400 alloy, aluminum-coated for 2-4 hours at 600°C

### 3.3. Hardness

The thickness of the aluminide layers resulting from the aluminum coating process on Monel 400 alloy was assessed, and the hardness measurements were conducted on multiple points within the metallographically prepared samples. The measurements were performed at incremental distances from the surface to the matrix, allowing for the evaluation of hardness variations across the aluminide layer. The hardness measurements were continued until reaching the core hardness value of the material. The hardness values exhibited changes depending on the temperature and duration of the aluminum coating process. The initial hardness of the Monel 400 alloy was measured at 230 HV. Subsequently, the obtained

aluminide layers displayed hardness values ranging from 450 to 700 HV, exhibiting an increasing trend with prolonged treatment durations. This increase in hardness can be attributed to the presence of new intermetallic phases formed and the achievement of the desired hardness on the surface[1], [14]. Figure 5 graphically illustrates the evolution of hardness values as one progresses from the surface to the matrix region.

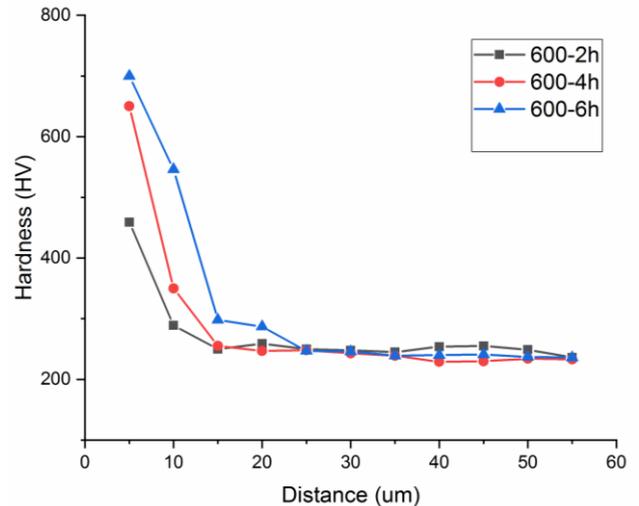


Figure 5. The hardness distribution of aluminum-coated Monel 400 alloy from surface to interior.

### 4. Conclusion

The following conclusions can be drawn from this study:

- 1) Nickel aluminide and copper aluminide layers were successfully formed on the surface of Monel 400 alloy using pack cementation method.
- 2) The obtained coating layers exhibit a highly smooth, pore-free, and continuous structure, with a distinct interface observed between the coating and substrate.
- 3) X-ray diffraction (XRD) analysis revealed that the coating layer consists of intermetallic compounds such as  $\text{Al}_3\text{Ni}_2$ ,  $\text{Cu}_9\text{Al}_4$ ,  $\text{AlNi}_3$ ,  $\text{CuAl}$ , and  $\text{NiAl}$ .
- 4) The thickness of the obtained aluminide layers ranges from 4 to 10  $\mu\text{m}$ . The thickness of the aluminide layer increases with an increase in processing time.
- 5) The hardness value of the matrix is 230 HV, whereas the hardness values of the obtained aluminide layers range from 230 to 700 HV, increasing with an increase in processing time.
- 6) The increase in the applied coating time positively affects the thickness of the coating layer. With longer processing times, the coating layer thickness increases from 4  $\mu\text{m}$  to 10  $\mu\text{m}$ .

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