Avrupa Bilim ve Teknoloji Dergisi
Özel Sayı 28, S. 1102-1106, Kasım 2021

Araştırma Makalesi

www.ejosat.com ISSN:2148-2683

European Journal of Science and Technology
Special Issue 28, pp. 1102-1106, November 2021

Research Article

Effect of Low-Temperature Aluminizing on 904L Stainless Steel

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(1st International Conference on Applied Engineering and Natural Sciences ICAENS 2021, November 1-3, 2021)

(**DOI:** 10.31590/ejosat.1012930)

ATIF/REFERENCE: Öksüzoğlu, E. & Döleker, K.M. (2021). Effect of Low-Temperature Aluminizing on 904L Stainless Steel. European Journal of Science and Technology, (28), 1102-1106.

Abstract

Intermetallic materials exhibit desirable properties for many applications. They can be produced by traditional production techniques such as casting or powder metallurgy. In addition, they can be manufactured using some coatings techniques. Pack cementation technique is a very cheap, fast and simple operation to produce an intermetallic layer. 904L super austenitic stainless steel composed of high amounts Fe, Ni and Cr. It can be used in pulp and paper processing, some acid processing plants, cooling devices or oil refinery material. Its hardness is not high, and its usage temperature is low (<400 °C). To enhance these properties, aluminizing technique can be used. In the current study, 904 L super austenitic stainless steel was used as substrate material for the pack aluminizing process. The aluminizing process was applied at 675 °C for 2 and 4 h. After the aluminizing process, an aluminide layer formed on the 904L steel. The obtained aluminide layer thickness is about 19.2 and 290 µm for 2 and 4 h aluminizing process, respectively. The Aluminide layer is composed of $FeAl_2$, Fe_2Al_5, FeAl and Al_5FeNi phases in both aluminized samples. The formation of aluminide phases provided higher hardness on the surface of 904L stainless steel compared to untreated 904L.

Keywords: Intermetallic, Aluminizing, 904L stainless steel, Aluminide phase, Pack cementation.

904L Paslanmaz Çeliğe Düşük Sıcaklık Alüminyumlamanın Etkisi

Öz

İntermetalik malzemeler birçok uygulama için arzu edilen özellikler sergilemektedirler. Döküm veya toz metalurjisi gibi geleneksel üretim teknikleri ile üretilebilirler. Ayrıca bazı kaplama teknikleri kullanılarak üretilebilirler. Kutu sementasyon tekniği, intermetalik bir tabaka oluşturmak için çok ucuz, hızlı ve basit bir işlemdir. 904L süper östenitik paslanmaz çelik yüksek miktarda Fe, Ni ve Cr' den oluşmaktadır. Kağıt hamuru ve kağıt işlemede, bazı asit işleme tesislerinde, soğutma cihazlarında veya petrol rafinerisi malzemelerinde kullanılabilmektedir. Sertliği yüksek değildir ve kullanım sıcaklığı düşüktür (<400 °C). Bu özellikleri geliştirmek için alüminyumlama tekniği kullanılabilir. Mevcut çalışmada, kutu aluminyumlama işlemi için altlık malzemesi olarak 904 L süper östenitik paslanmaz çelik kullanılmıştır. Alüminize etme işlemi 675 °C'de 2 ve 4 saat süreyle uygulanmıştır. Alüminize etme işleminden sonra 904L çeliği üzerinde bir alüminid tabakası oluşmuştur. Elde edilen alüminid tabaka kalınlığı, 2 ve 4 saatlik alüminize işlemi için sırasıyla yaklaşık 19.2 ve 290 µm'dir. Alüminid tabakası, her iki alüminyumlanmış numunede $FeAl_2$, Fe_2Al_5, FeAl ve Al_5FeNi fazlarından oluşmaktadır. Alüminid fazlarının oluşumu, 904L paslanmaz çeliğin işlem görmemiş haline kıyasla yüzeyinde daha yüksek sertlik sağlamıştır.

Anahtar Kelimeler: İntermetalik, Alüminyumlama, 904L paslanmaz çelik, Alüminid faz, Kutu alüminyumlama.

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1. Introduction

904L stainless steel has high toughness, malleable and weldability. It also exhibits high stability and corrosion resistance in service conditions. The presence of Mo, Cr and Ni provide good corrosion resistance. Ni provides stress corrosion resistance while Cr_2O_3 formation on the surface is seen through high Cr during the oxidation. Besides, Cu addition enables resistance to strong acids. 904L can be used in oil refineries, heat exchangers, condenser tubes, seawater cooling, etc. (Koppula, 2021) .

Martensite phase formation is not obtained at room temperature in 904L due to its full austenitic structure. Its strength can be only improved by cold-working process. It can be used up to 400 °C. Therefore, its both mechanical and high temperature properties are limited. However, it is very suitable for surface modifications such as carburizing, nitriding, boronizing and aluminizing (Çetin, 2021; Maistro, 2017; Jiang, 2019). These modifications can significantly enhance the surface hardness of 904L. Çetin et. al. (Çetin, 2021) boronized 904L stainless steel to increase its wear resistance. They found very complex phases, which has 2366-2396 HV. High hardness in borided 904L provided better wear resistance compared to 904L. The hardness of untreated 904L with 210 HV was significantly increased by the boronizing. In another study (Koppula, 2021), carbonitriding process provided 640-803 HV in 904L. Similarly, this enhanced the wear performance compared to the untreated 904L.

There are various aluminizing techniques such as chemical vapor deposition, physical vapor deposition, hot-dip aluminizing, or pack cementation (Priest and Zhang, 2015). Pack cementation has a low cost and simple technique compared to others. It does not contain a complex production system. There are two types as low and high temperature in the aluminizing process. Low temperature aluminizing is achieved below 700 °C (Erdogan, 2021). Therefore, substrate material does not affect temperature significantly. Activator, filler, and Al mixtures are used in the aluminizing process. Filler is used to inhibiting the aluminum sintering. The activator (NH_4CI, $AlCl_3$ or NaF) forms metal halide gas ($AlCl_3$) reacting with the substrate surface (Xiang and Datta, 2004). Diffusion of the aluminum enables the aluminide phase formation on the surface of the substrate. In this study, low tempetaure aluminizing is carried out to 904L stainless steel to increase high temperature resistance and hardness. Aluminized samples were investigated in terms of microstructure and hardness.

2. Material and Method

904L super austenitic stainless steel was used as a substrate for the low-temperature aluminizing process. It was commercially provided by Birçelik company from Turkey. Its chemical composition is shown in Table 1.

Table 1. The chemical composition of 904L steel (wt.%)

Ni	Cr	Mo	Cu	Mn	Si	C	Fe
25	20	4.3	1.5	1	0.7	0.02	Bal.

Disc-shaped substrate material has 25.4 mm diameter and 4mm thickness. All samples were prepared metallographically before the aluminizing process. Substrates were ground up to 1000 grit SiC emery paper and then ultrasonically cleaned with ethanol. 15 g powder mixture was prepared for each specimen's aluminization. 7% NH_4Cl as an activator, 38% Al, and, 55% Al_2O_3 as filler were used. These powders were mechanically mixtured for 30 minutes. Afterward, the prepared samples were immersed in pack powder mixtures into a stainless steel crucible and sealed with a lid and fire clay mortar. The prepared pack was exposed to 675 °C for 2h and 4h in an electric furnace to get an aluminide layer on the surface of 904L steel. The cooling of the samples was carried out in the open air. Afterward, the aluminized samples were taken out and cleaned for microstructure, phase and hardness examinations. Micro-vickers hardness tests were carried out with 25 g load and 15 s duration. The aluminized samples were examined using an optical microscope (OM) (Leica), Scanning Electron Microscopy (SEM) (JEOL JSM-6060, FEI Co., Japan) and X-ray diffraction (XRD) (Rigaku, CuKα, DMAX 2200, Japan) analysis. In the etching of 904L, 10 ml HCI, 10 ml H_2O and 1 ml HNO_3 were used. For SEM examinations, metallographically prepared samples were used and, the aluminide layer was examined using cross-sectional SEM images.

3. Results and Discussion

Fig. 1 shows the OM image of etched 904L. Austenitic grains and some twin boundaries can be seen in the image. These grains and twins are characteristic properties of austenitic structured steel.

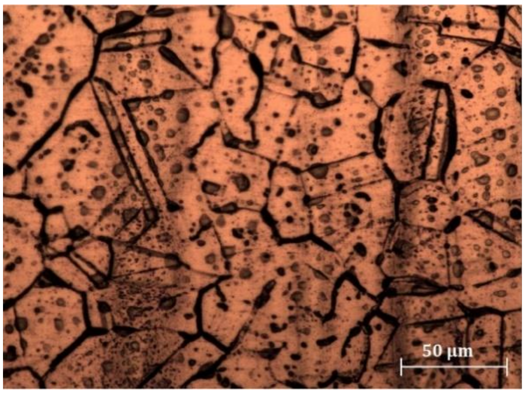

Fig. 1. OM image of etched 904L

XRD pattern of 904L is shown in Fig. 2. The obtained patterns belong to the austenite phase. The obtained three peaks show FCC structured austenite phase and, any other phase was not observed according to XRD analysis.

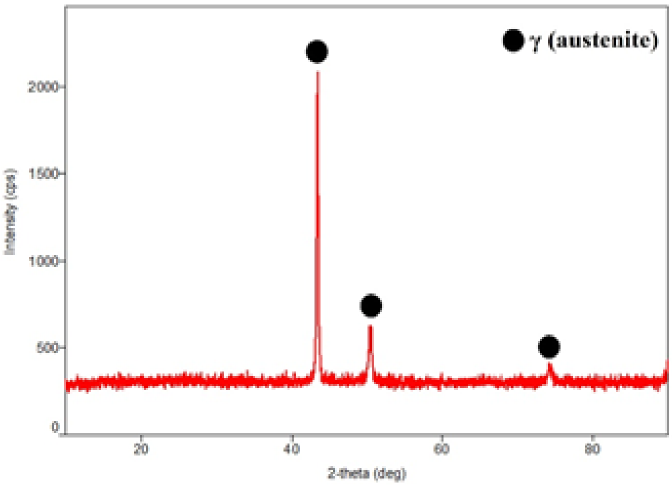

Fig. 2. XRD pattern of 904L

In Fig.3, a cross-sectional SEM image of the aluminized 904L at 675 °C for 2h is given. The formed aluminide thickness is 19.2 µm. The coating layer with dark gray color has a homogenous distribution. There is an interdiffusion zone (IDZ) with gray color between the coating layer and substrate. Its thickness is about 1µm. The formed coating layer has quite good adherence and, there is also no crack formation in the coating layer.

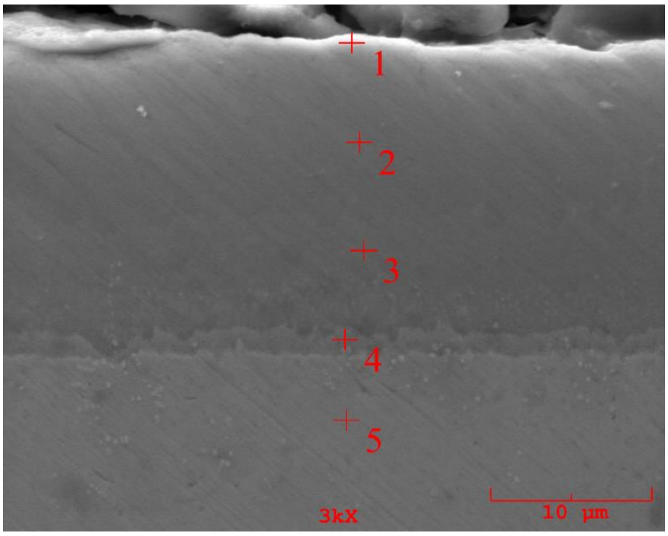

Fig. 3. SEM image of 2h aluminized 904L

EDX analysis result of Fig. 3 is given in Table 2. According to Table 2, the coating layer is dominantly composed of Al-rich phases (point 1, 2 and 3) and, the coating's composition did not almost change from top to IDZ (point 4). This shows that the coating layer has Al-rich intermetallic formations. At the interface, Al concentration slightly decreased yet, this region is also an aluminide intermetallic phase. According to elemental distribution, Fe-Al formation is more dominant than the others (Ni-Al, Cr-Al). Point 5 in Table 2 belongs to the substrate (904L).

Table 2. EDX results of 2h aluminized 904L (wt.%)

Pt.	Al	Fe	Ni	Cr	O	Mo	R.
1	59.96	12.19	8.14	6.12	4.83	-	-
2	69.91	15.58	7.04	5.64	1.82	-	-
3	65.23	18.37	8.16	7.04	1.21	-	-
4	41.40	27.61	13.94	11.82	2.42	-	2.81
5	0.61	49.5	20.68	21.52	1.87	5.82	-

Fig 4. shows the cross-sectional SEM image of aluminized 904L at 675 °C for 4h. The coating layer has 290 µm thickness and a more complex phase distribution in deeper zones compared to 2h-aluminized 904L.

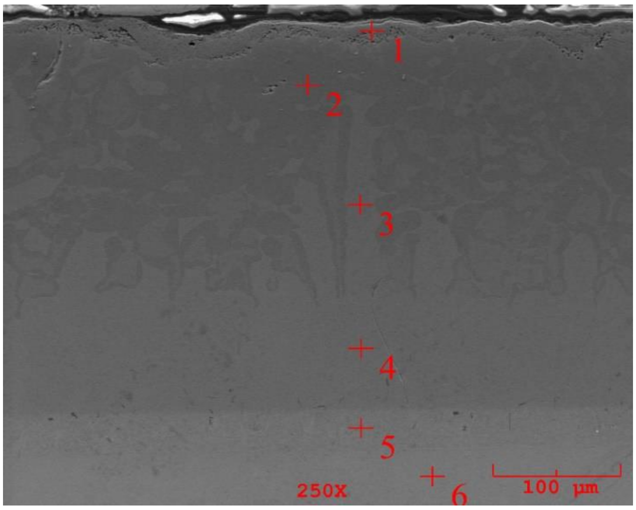

Fig. 4. SEM image of 4h aluminized 904L

In Table 3, EDX analysis results of 4h-aluminized 904L were shown. According to obtained EDX data, upper regions (1 and 2) with dark gray color are dominantly composed of Al-rich intermetallics while middle regions with gray color composed of (Fe, Ni)x-Aly intermetallics. The interface (IDZ) with light gray between the substrate and coating layer consists of Fe-Cr rich phases according to point 5 values.

Table 3. EDX results of 4h aluminized 904L (wt.%)

Pt.	Al	Fe	Ni	Cr	Si	Mo	O	R.
1	13.1	39.44	11.95	9.83	-	3.17	6.32	16
2	60.02	25.15	7.84	5.6			1.2	0.2
3	43.89	28.97	17.13	7.92	-	-	0.56	1.5
4	43.29	28.55	17.74	7.43	-	-	0.59	2.4
5	2.2	46.36	3.72	31.46	3.36	7.37	2.2	2.5
6	0.15	49.85	20.55	20.75	1.22	4.63	1.72	1.4

Fig. 5 shows the XRD patterns of aluminized samples. After both 2h and 4h aluminizing, $FeAl_2$, Fe_2Al_5, FeAl and Al_5FeNi phases were detected. Al-rich Fe-Al phases are more dominant according to XRD patterns. This is consistent with the EDX analysis of aluminized samples.

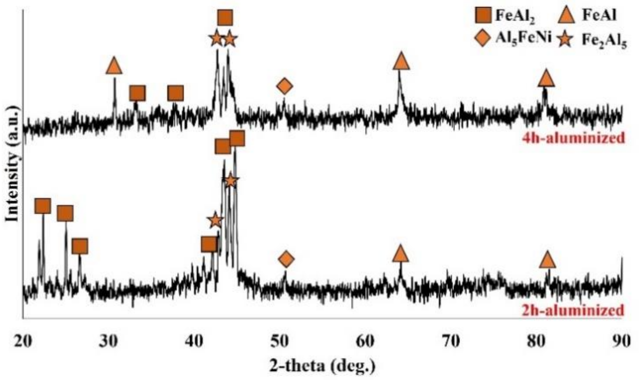

Fig. 5 XRD patterns of 2h and 4h aluminized 904L

After the hardness measurements, 2h-aluminized sample has 926 HV whereas 850 HV is obtained in 4h-aluminized 904L. There is no dramatic difference among the samples. This slight difference can be related to phase distribution of aluminides. After the aluminizing process, the hardness of 904L increased about 4-5 fold through the formation of aluminide phases.

In the formation of the aluminide layer, $AlCl_3$ gas, decomposed from the activator (NH_4Cl), reacts with the Al. This reaction enables the formation of AlCl and $AlCl_2$ gaseous. The formed gaseous diffuses to the substrate and, active Al atoms, which dissolved into substrate, form. After this reaction, Fe_2Al_5 forms and, other phases ($FeAl_3$, $FeAl_2$ and FeAl, respectively) form on the substrate's surface by the repeated reactions with Al.

There is a dramatic difference among the aluminized samples for 2h and 4h in terms of coating thickness. Increased aluminizing time significantly increased the aluminide thickness. In the aluminizing of 316L (Dong, Sun and He, 2019), the obtained thicknesses are 47 and 86 μm under 680 °C for 2 and 4h. 316L is austenitic stainless steel and its chemical composition is near to 904L stainless steel. The main difference can be related to the selected aluminizing media.

Aluminizing process provides an aluminide layer on the 904L substrate surface. The formation of the aluminide layer significantly increased the substrate's hardness. It is well known that most intermetallics have high hardness values. Some Fe-Al intermetallic hardness values are given in Table 4.

Table 4. The hardness values belonging to some Fe-Al intermetallics (Matysik, Jóźwiak and Czujko, 2015)

Compounds	Hardness (Hv)
Fe_3Al	255-357
FeAl	460-530
$FeAl_2$	918-1071
Fe_2Al_5	969-1122
$FeAl_3$	816-999

According to Table 4, different hardness values were obtained depending on Al concentration. The increase in Al content led to higher hardness values. The difference in atomic radii between Fe and Al may be shown as one of the reasons for high hardness. Besides, lattice structure goes to complex structure depending on the increased Al content (Li, 2016). This may bring about an increase in hardness values, too. According to Table 4, the obtained hardness values are consistent with the $FeAl_2$, Fe_2Al_5 and $FeAl_3$. Mirrax steel has a relatively similar composition to 904L. After the pack aluminizing, the hardness of Mirrax steel increased from 250 HV to 1000 HV value (Yener, 2021). In the current study, similar hardness increase was obtained.

The formation of aluminide phases does not only improves the hardness values of the substrate but also enhances the high-temperature oxidation resistance of the substrate. The formed aluminide phases during the oxidation form an alumina scale which is the most desired oxide at high temperatures. The oxidation resistance of Mirrax steel is improved by aluminizing process. This enhancement was provided by the formation of alumina scale on the surface during the oxidation tests (Yener, Doleker and Erdogan, 2019). The same effect can be obtained in aluminized 904L due to similar phase formations.

4. Conclusions and Recommendations

904L super austenitic stainless steel was aluminized at 675 for 2h and 4h by pack aluminizing technique. According to SEM, XRD and hardness analysis, the obtained data and recommendations were summarized below:

- The formed aluminide thickness is significantly increased by the increased aluminizing duration.
- After the aluminizing, Al-rich phases dominantly formed on the 904L surface.
- The formed phases enhanced the hardness of 904L. Similarly, these phases can contribute to an increase in high-temperature resistance of 904L.
- The effect of powder mixture, microstructural change depending on process temperature and duration can be investigated to get better aluminide layer.
- The obtained aluminide layer's phases can be observed TEM or EBSD analysis technique to see phase distribution after aluminizing process.

In future studies, wear and high temperature oxidation behaviors of aluminized 904L steel will be investigated.

Acknowledgements

This study was supported by Scientific Research Projects of Ondokuz Mayıs University (Project No: PYO.MUH.1904.21.022).

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