Scholars Journal of Engineering and Technology (SJET) **ISSN 2321-435X (Online)**
Sch. J. Eng. Tech., 2016; 4(2):107-112 **ISSN 2347-9523 (Print)**
©Scholars Academic and Scientific Publisher
(An International Publisher for Academic and Scientific Resources)
www.saspublisher.com

Research Article

Analysis of Corrosion Properties caused by Zn Fume in Ni Alloy

Min-Sook Baek[1], Man-Bok Park[1], Kyeong-Cheol Baek[2], Pub-Sung Kang[2], Ki-Bok Heo[2], Dong-Joo Yoon[1], Joon-Seop Kwak[1]
[1]Center for practical Use of Rare Materials, Sunchon National University, Suncheon 540-742, Korea
[2]SAMWOO ECO, LTD. 545-801, Korea

***Corresponding author**
Min-Sook Baek
Email: mbpark@sunchon.ac.kr

Abstract: In this study, the manufactured Ni alloy was tested on how much it had corrosion resistance against Zn fume when it was used in the hot dip galvanizing equipment in the steel plant. Two kinds of materials currently used in the equipment, SM45C(steel for mechanical structure, KS) and Inconel(typical corrosion-resistant Ni alloy), were selected as the reference groups. Two alloys of Ni-28Cr-4Mo-2Ti and Ni-20Cr-10Mo-1Ti were designed and the same heat treatment as Inconel 625 was conducted for a proper comparison. Zn fume was generated by bubbling Ar gas from molten Zn in the furnace and the samples were analyzed after 10, 20 and 30 days. According to the result of XRD and Potentiodynamic polarization test, it was confirmed that ZnO was formed on the entire metal surface, which resulted in the change of corrosion resistance on the samples. Especially the newly designed alloy out of samples showed the most excellent corrosion resistance for the high temperature in the trial for 30 days.
Keywords: corrosion, Zn fume, XRD.

INTRODUCTION

Hot dip galvanizing in the steel plant is one of the most widely used method in preventing the corrosion of steel materials including structures, steel sheets, and materials for industrial facilities. While hot dip galvanizing has the advantage of stability and economic feasibility, it has difficulty in repairing equipment and maintaining the facilities due to high-temperature oxidation caused by Zn Fume where molten zinc used in the open spaces[1].

In fact, much time, labor and cost for the replacement of equipment are being spent due to high-temperature corrosion caused by Zn fume in the environment for manufacturing the hot dip galvanized steel sheet. In order to improve these problems, in the long term, it was considered very helpful for industry and economy to change the facility into the material of corrosion resistance to high temperature and Zn fume resulting in the increase of the replacement cycle of facilities.

The melting point of nickel ally is below 1500 ℃ and some are used by the cooling technology at the higher temperature than 1500℃. However, the development of alternative alloys has been studied all over the world, which is economic and fundamentally durable for the acid resistance in ultra-high temperature and the corrosion resistance.

It is known that Inconel has a superior heat-resistant property in high temperature and is an excellent material for the facility which need heat resistance, including heat treating furnace, ultra-high-temperature electric furnace, ceramic furnace, and boiler.

This heat resistant Ni alloy by adding Mo and W is being used in in the heat exchanger, marine equipment, and nozzle in high temperature by improving the corrosion resistance rather than the heat resistant temperature[2-4].

Ni alloy (super alloy) which has been used in various fields contains high-priced materials including Ta, Nb and Re and its use has been limited in the industrial fields so far because of the price competition. To increase the price competition, new corrosion resistant Ni alloy was designed using the relatively low priced materials in this study[5-6].

The schematic diagram on high temperature corrosion by high temperature and Zn fume in the environment that hot dip galvanized steel sheet are actually manufactured is shown in Figure 1. Zn fume from molten Zn adhere to the surface of facilities, which results in the deformation and corrosion of them. In this study, the corrosion degree of each sample was analyzed in the more extreme condition than the actual condition(Ambient temperature: 100-200 ℃, Distance from the molten metal to equipment: 1m)in which Zn fume was generated by injecting Ar gas in the high-temperature furnace (500℃).

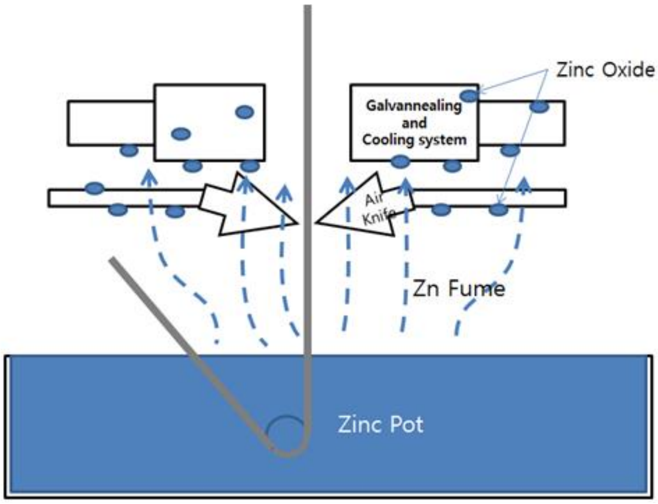

Fig. 1: Schematic diagram for hot dip galvanizing equipment

EXPERIMENTAL METHOD

Ni alloy design and its manufacture

Designed two kinds of alloys, Ni-28Cr-4Mo-2Ti (hereafter Alloy 1) and Ni-20Cr-10Mo-1Ti (hereafter Alloy2) were melted five times in order to reduce the segregation in the alloy using the Arc melting (Manufacturer: SAM_HAN VACUUM DEVELOPMENT CO.,LTD., Non-consumable electrode: Maximum φ30mm of electrode, Vacuum: 5 × 10-5 Torr, Ar gas used) in a high vacuum of argon atmosphere respectively.

Three samples of each alloy with 200g were prepared in oval-shaped rod with 200mm length, about 16.5mm width, and about 9.2mm thickness.

Hot rolling was carried out 7 times in total at 600℃ at an interval of ten minutes and samples after rolling were manufactured in long plate with 300mm length, 18mm width, and 4.7mm thickness.

Heat treatment of each alloy was based on the heat treatment method of Inconel 625 which was the standard for alloy design. The samples were maintained at 1040℃ for 1 hour and cooled down by air for solution annealing, and then they were kept at 730℃ for 8 hours and cooled down in the furnace for aging treatment.

Test of oxidation by Zn fume and evaluation

Zn fume was continuously generated by injecting Ar gas in the molten Zn of 30 kg in the alumina crucible maintaining temperature of 500℃. Distance between molten Zn and sample holder was about 40cm. The samples(Alloy1, alloy2, Inconel 625, SM45C) were placed on top of holder and they were analyzed after 1day, 10 days, 20 days, and 30 days.

Regarding the samples for corrosion test, the plates of Inconel 625 and SM45C were cut into a size of 20 × 20mm and then polished by the sand papers of 300, 600, 1200, and 2000. The heat-treated Alloy 1 and 2 after rolling were cut into a size of about 20mm then polished by the sand papers up to 2000, which was followed by the alcohol washing for analysis.

Property analysis of surface(SEM, EDS), composition and structure(XRD), and corrosion resistance (Potentiodynamic polarization) were carried out in accordance with the corrosion time and materials in the environment of high temperature and Zn fume.

RESULTS AND DISCUSSION

Figure 2 shows the surface of samples after the corrosion experiments with Zn fume by using an optical microscope (x 100).

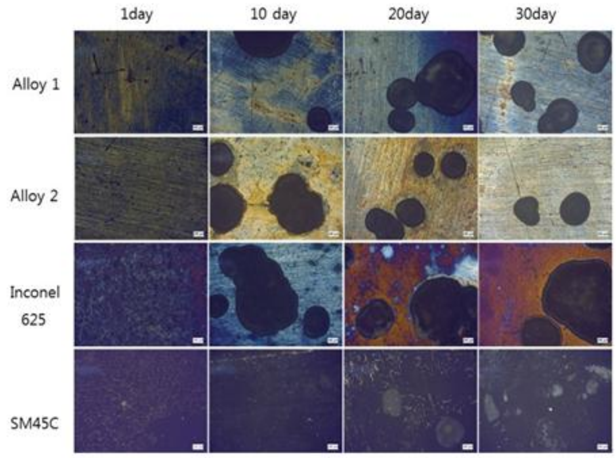

Fig. 2: Photos of optical microscope after the oxidation experiment with Zn fume

The layer considered as Zn fume was confirmed to be stacked on the surface of samples as time went on and analysis was carried out after this fume was cleaned by air compressor.

As shown in Figure 2, material assumed to be Zn oxide on the surface of the test pieces was strongly generated and its distribution and size could be confirmed to expand with time.

SM45C was confirmed to be remarkably smaller in the population and size of Zn oxide than the other Ni alloys due to thick oxide layer on the surface caused by high temperature.

In addition, compositions and shapes (x50 magnification) of material surface exposed for 30 days in the environment of high temperature of 500℃ with Zn fume using SEM and EDS mapping in order to take a closer look of oxidized surface were shown in Figure 3.

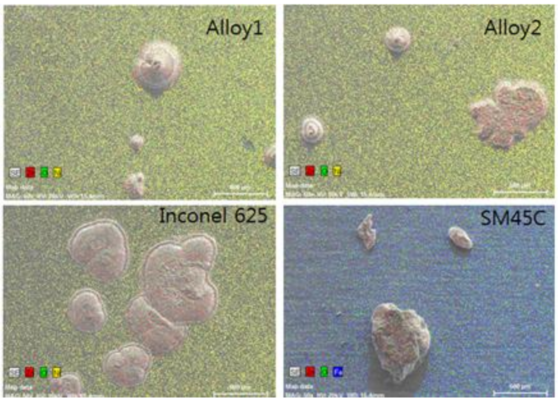

Fig. 3: Mapping (EDS) configuration of samples with Zn oxide

Red indicated Zn, green O, yellow Ni, and blue Fe. After 30 days, all substances formed on the surface of each material were determined to be ZnO of which its size was the largest(about 800μm) at Inconel 625 and the shape was the most widely spread. On the other hand, in case of SM45C, iron oxide and ZnO were confirmed to be composed of compounds with noticeable color of O generally displayed on the surface of samples, unlike Ni alloy.

Figure 4 showed the oxide phase analysis of each material. Peaks corresponding to ZnO (Space Group: P63mc) were 31°, 34°, and 36, which were confirmed at the samples after 10 days in the all the ingredients.

In Alloy1, especially ZnO Peak became significantly larger especially after 30 days, by which Zn0 was determined to rapidly be generated after 30 days. In Alloy2, the size of Peak was observed not to significantly change with time.

In case of Inconel625, ZnO Peak was well prominent in the samples after 20 days and in case of SM45C, ZnFe2O4 stood out conspicuously for the most part as the compounds of iron oxide and ZnO but ZnO Peak of 30°was confirmed to become significantly bigger in the samples after 30 days.

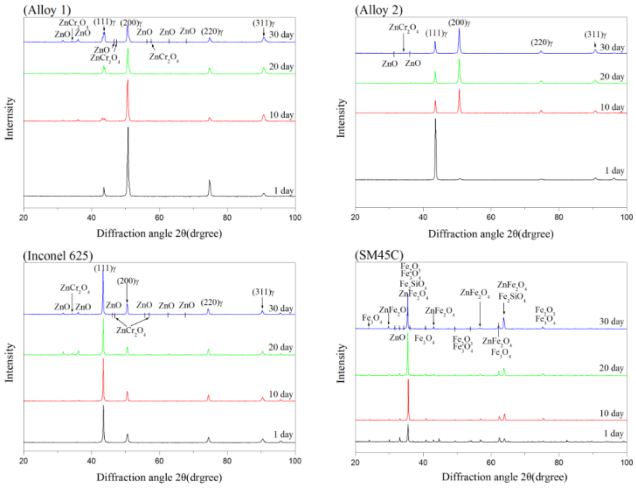

Fig. 4: X-ray peak after corrosion of each material in the environment with high temperature and Zn fume

Electrolyte solution was saline solution (0.9% NaCl) and Scan Rate (mV/s) was 10 on condition of potentiodynamic polarization analysis. Corrosion rates (mils per year) depended on the material when exposed during a given time period in the environment with high temperature and Zn fume.

Ni Alloy 1 and 2 was observed to have a superior corrosion resistance to SM45C and Inconel 625 over time of exposure. It was shown in detail in Figure 5.

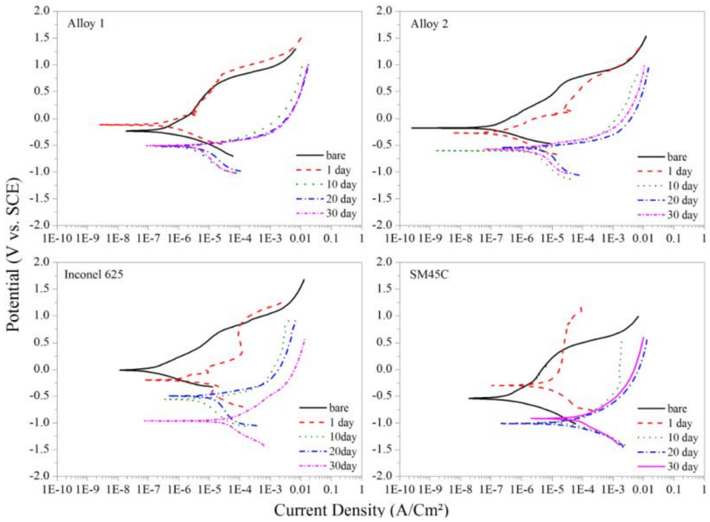

Fig. 5: Potentiodynamic polarization graph of each material

All materials increased in the value of Icorr(A) and decreased in the Ecorr(V) over time, which resulted in the increase of the corrosion rate. Considering the increased corrosion rate, SM45C was confirmed to be the highest corrosion rate.

In general, Alloy 1 and Alloy 2 with the current Icorr(A) numerical value $5.2*10^{-7}$and $2.51*10^{-7}$ which were the measure of corrosion resistance, were confirmed to have better value than Inconel625 and SM45C. Figure 6 shows the corrosion rate of each sample with time.

Ni Alloy1 and Ni Alloy2 showed very small corrosion rate compared to Inconel625 and SM45C up to 30 days. SM45C showed the highest corrosion rate. Inconel 625 showed the lower corrosion rate up to the 20 days, but its corrosion rate remarkably rose up after 30 days of exposure.

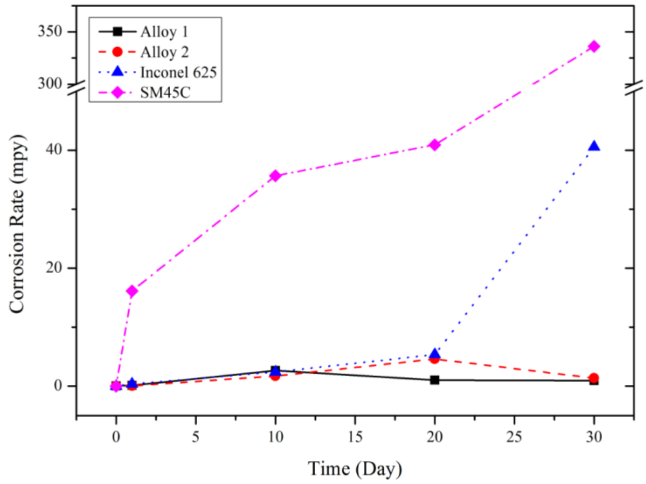

Fig. 6: Corrosion Rate(mils per year)

Decreased Icorr(A) value of Inconel 625 alloy led to the significant decrease in corrosion resistance like SM45C. On the other hand, corrosion rate of Alloy 1 and 2 were somewhat high up to 20 days but were back to a lower level up to 30 days. Therefore, Ni Alloy1 and 2 were confirmed to have the most excellent corrosion resistance in the environment with high temperature and Zn fume.

Morinaga and the like designed alloys using the two theoretical values (Md, Bo) given by calculating the energy state through DV-Xα method[7-11] and the results was given by the fractions on γ and γ‘ phase depending on the composition of each Ni ally. It was said that when the value of Md was 0.8~0.91, brittle phase didn't show up and Ti, Nb, Ta were considered the elements to form a stable γ‘phase.

According to the research results, they were ideal theoretical values. However, all the alloys designed after the prediction using these data coincided with the expected results[12-15].

All the theoretical values of alloys on Md shown in Table 1 were satisfied with the results Morinaga and the like suggested.

Table 1: Fraction criteria of γ phase by theoretical calculation

Alloy Composition (wt.%)	$\overline{Md}$
Alloy1(Ni-28Cr-4Mo-2Ti)	0.9004
Alloy2(Ni-20Cr-10Mo-1Ti)	0.9008
Inconel 625(Ni-21.5Cr-9Mo-3.6(Nb+Ta))	0.90054

Although Inconel 625 and Alloy1,2 are the same Ni alloy, they are comprised of Ni-28Cr-4Mo-2Ti(Alloy1), Ni-20Cr-10Mo-1Ti(Alloy2), and Ni-21.5Cr-9Mo-3.6(Nb+Ta)(Inconel 625) in terms of elements which contains the cheaper Ti instead of Nb and Ta. It is said that Tieven in the small amount play a role in enhancing the corrosion resistance compared with Nb and Ta.

Being divided into two groups of Ti and Nb and Ta, Ti is a transition element with 3d orbit and Nb and Ta with 4d orbit. And the main element of the alloy is Ni with 3d orbit. They have the same d orbit but there is a difference of state density between 3d-3d orbit and 3d-4d orbit when they are combined respectively[14].

In addition, it is considered that as the atom with small electronegativity, in general, is more likely[12] to donate an electron to the ambient Ni atoms, Ti with the relatively small electronegativity will have the more corrosion-resistance than Nb and Ti.

CONCLUSION

The high temperature corrosion resistance of alternative materials which were designed and manufactured was compared and analyzed, which was available for the facilities manufacturing the hot dip galvanized steel sheet in the corrosion environment with high temperature and Zn fume.

Zn oxide was strongly formed on all the materials by high temperature and Zn fume.

SM45C showed the highest corrosion rate and alloy 1 showed the most excellent corrosion resistance after being exposed in the corrosion environment with high temperature and Zn fume for a long time.

Newly added Ti was confirmed to be an element with the excellent corrosion resistance in the Ni alloy. It is considered that if oxide coating or coating was treated on Alloy 1 with excellent corrosion resistance, it will have the better corrosion resistance.

Acknowledgements

This study was supported by Korea Evaluation Institute of Industrial Technology(KEIT) through the project of Advanced Technology Center(ATC). In addition, a special thanks is given to the researchers in Regional Innovation Center(RIC)

REFERENCES

1. Moezzi A, McDonagh AM, Cortie MB; Zinc oxide particles: Synthesis, properties and applications. Chemical Engineering Journal, 2012;185:1-22.
2. Donachie MJ, Donachie SJ; Superalloys: a technical guide. ASM international, 2002.
3. Harris K, Wahl JB, Green KA; Superalloys 2004. TMS, Warrendale, PA. 2004; 45-52.
4. Davis JR; Nickel Cobalt and Their Alloys, ASM International, U.S.A., 2000; 3-6, 30, 127-137
5. Morinaga M, Kamado S; An electronic approach to the prediction of the mechanical properties of aluminium alloys. Modelling and Simulation in Materials Science and Engineering, 1993;1(2):151.
6. Morinaga N, Yukawa N; Computer aided innovation of new materials, (CAMSE'90), 1991; 803.
7. Morinaga M; Bullentin of the Society for DisreteVariational Xα, 1994; 6: 424.
8. Morinaga M, Yukawa H; Alloy design with the aid of molecular orbital method. Bulletin of Materials Science, 1997;20(6): 805-815.
9. Ellis DE, Adachi H, Averill FW; Molecular cluster theory for chemisorption of first row atoms on nickel (100) surfaces. Surface Science, 1976; 58(2):497-510.
10. Adachi H, Tsukada M, Satoko C; Discrete variational Xα cluster calculations. I. Application to metal clusters. Journal of the Physical Society of Japan, 1978; 45(3):875-883.
11. Kim YS, Ko HC, Park HS; Basic of Quantum Material science, Hanrimwon, 2000; 40-41.
12. Matsugi K, Murata Y, Morinaga M, Yukawa N; An electronic approach to alloy design and its application to Ni-based single-crystal superalloys. Materials Science and Engineering: A, 1993;172(1):101-110.
13. Zhang JS, Hu ZQ, Murata Y, Morinaga M, Yukawa N; Design and development of hot corrosion-resistant. Metallurgical transactions A, 1993; 24(11):2451-2464.
14. Moniruzzaman M, Murata Y, Morinaga M, Hashizume R, Yoshinari A, Fukui Y; Alloy design of Ni-based single crystal superalloys for the combination of strength and surface stability at elevated temperatures. ISIJ international, 2003; 43(8):1244-1252.
15. Morinaga M, Ninomiya R; An Approach to Alloy Design with the Aid of a Molecular Orbital Theory. Materials Research Society of Japan, 1993; 16: 195.
16. Ban MS, Yoo JH, Lim JS, Lee J, Kim Y, Kee C, Joung HJ; Morphology and Distribution of Motoneurons Innervating the Lateral Rectus and the Retractor Bulbi Muscles in Cat: A Retrograde Study Utilizing Horseradish Peroxidase. J Korean Ophthalmol Soc, 2000; 41(12):2765-2770.