EFFECT OF Ni AND Cr ADDITION IN P/M 316L ON MICROSTRUCTURE AND OXIDATION RESISTANCE BEHAVIOR AT 900°C

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Abstract
Stainless steel 316L, an austenitic stainless steel, is widely used as structural components in various industries because of its good strength, good corrosion and oxidation resistance at medium-high temperature. However, under more severe operating conditions, stainless steel needs higher oxidation resistance to reach longer service lifetime. Therefore, the present research had attempted to develop the new material to resist such conditions through modification of stainless steel 316L with nickel and/or chromium addition by powder metallurgy process. Nickel, chromium and nickel with chromium powders were added to 316L stainless steel powder with 1, 2, 3, 4 and 5 wt.%. After that, all mixed powders were compressed under pressure of 15 ton-force with 30-second hold duration. All compressed specimens were followed with sintering at 1300°C for 45 minutes under hydrogen atmosphere. From all results, it was found that specimens with chromium addition provide the highest oxidation resistance at 900°C tested up to 100 hours. The increasing of nickel and chromium content resulted in better oxidation resistance. The effect of pure chromium addition on oxidation behavior is similar to both nickel and chromium addition.

Keywords: 316L, Stainless steel, Powder Metallurgy, Oxidation Behavior

1. INTRODUCTION
In the present, the stainless steels play the important role in several industries such as automotive, aerospace, petrochemical even in medical equipments due to their great combination of high-temperature corrosion resistance and high-temperature strength. There are numerous engineering applications that components which operate at high temperature were made from these materials. Thus, the great oxidation resistance of stainless steel is also considered. The alternative production process, the powder metallurgy (P/M) stainless steel has been developed in recent years because P/M is found the advantages in the production of small and near-net-shaped components of complex shapes, eliminating the finishing process especially this process requires lower production cost [1]. At high-temperature application, the austenitic stainless steels were widely used more than ferritic stainless steels because of their higher elevated temperature strength. There are advantages of P/M, however, some of the restrictions are considered. The imperfect of P/M stainless, the porosity, affects their mechanical properties and reduces their corrosion resistance [2]. There are few attentions on the direct oxidation resistance at high temperature. The studies report that P/M stainless steel, compared to conventional stainless steel, the behavior does not follow the same pattern because of the presence of pores. The improvement of oxidation resistance of P/M stainless steels, in previous studies, will be included controlling of sintering parameters [3, 4], surface coating, and alloy modification through addition of elements or compounds such as molybdenum, copper silicon and yttria [5-9].

However, in this study, the AISI 316L P/M stainless steel will be modified by addition of elements such as chromium (Cr) and nickel (Ni). The effect of Cr and Ni added on microstructure and the oxidation behavior at 900°C has been investigated.
2. MATERIALS AND EXPERIMENTAL PROCEDURE

The materials used in this study were AISI 316L stainless steel powders, Cr powders, and Ni powders. Three powders were mixed together with varied amounts of Cr and Ni powders which are (1-5 wt.%)Cr added, (1-5 wt.%)Ni added, (1-5 wt.%)Ni+(1-5 wt.%)Cr added. The modified stainless steel powders were compressed into 10×30×3 mm$^3$ rectangular specimens by hydraulic compress machine under 15 ton-force pressure and 30-second hold duration. Then, all compressed specimens were followed by sintering at 1300ºC for 45 minutes in pure hydrogen atmosphere. The densities of sintered specimens were measured by water displacement method.

The oxidation test was performed at 900ºC in air for 100 hours. Microstructure was carried out using optical microscope and scanning electron microscope. The composition of the oxide layers was determined using the X-Ray diffractometer (XRD) with diffraction 2θ angle range of 20º-90º and Energy-dispersive spectroscopy (EDS).

3. RESULTS AND DISCUSSIONS

The microstructures of 316L stainless steel produced by powder metallurgy are shown in Fig.1. For the P/M 316L after sintering at 1300ºC for 45 minutes in pure hydrogen atmosphere (Fig.1a) is found that the pores are small and generally distribute in the matrix and the sintered 316L after exposure at 900ºC for 100 hours (Fig.1b) reveals the pores and some oxides forming inside the pores. Some of connected oxides between pores are also found.

![Fig.1 Optical micrograph of the AISI 316L a) after sintering at 1300ºC for 45 min. b) after exposure at 900ºC for 100 hrs.](image)

The microstructures of various modified powder stainless steels are illustrated in Fig.2. It was found that the specimens with Cr addition consist of similar size and dispersion of small pores to one of pure 316L stainless steel. The increasing of Cr content resulted in pore coarsening, as shown in Fig.2a and Fig.2b. When adding Ni powder, microstructures also consist of uniformly dispersed pores in much bigger size, which the amount and size of pores increased with Ni content, as shown in Fig.2c and Fig.2d. The addition of Ni+Cr powders resulted in the similar manner to those of Ni addition.

Fig.3 shows the densities of various modified chemical composition of stainless steel powders after sintering at 1300ºC for 45 minutes. It was found that pure 316L specimen has the highest density which was 7.35 g/cm$^3$. However, the element addition provided lower density. This was due to that element addition led to more pore formation in both size and amount. Ni+Cr addition provided the lowest density and Cr addition specimens have the highest densities comparing to those of Ni and Ni+Cr additions which all is according to optical micrographs that were shown in Fig.2a-Fig.2f.
Fig. 2 Optical micrograph of microstructures of modified 316L stainless steels after sintering at 1300°C for 45 minutes.

Fig. 3 Densities of 316L stainless steels and modified 316L stainless steels after sintering at 1300°C for 45 hours.

Fig. 4 shows the microstructures of modified stainless steel specimens after oxidation testing at temperature of 900°C for 100 hours. In all specimens, the internal pores and oxides were found in microstructures. The internal oxides could be found as fully filling in the previous small pores and occurring as oxide layers inside the coarse pores. It should be noted that Cr addition specimens consist of small internal oxides and the internal oxide layers in coarse pores were observed in Ni and Ni+Cr added specimens.

Fig. 5 shows the oxidation resistant behaviors after testing at temperature of 900°C for 100 hours of Cr, Ni and Ni+Cr added specimens. All received testing results are weight gain type, which means external oxide layers had strong binding with stainless steel substrate but very slight spallation during the oxidation testing was observed in some specimens.
From the curves of Cr added specimens in Fig.5a, it should be seen that the increasing of all curves are in parabolic type, which increased rapidly in the initial step and then constantly increased in prolonged oxidation testing time. From these results, it was found that specimens with higher Cr additions provided better oxidation resistance that 5 wt.% Cr addition gave the best oxidation resistance with total weight gain after testing at 900°C for 100 hours of 23.6 mg/cm$^2$ which was lower weight gain comparing to 31.13 mg/cm$^2$ of pure 316L specimen. However, no oxide spallation was observed in Cr added specimens.

From Fig.5b shows the increasing of the oxide weight gain of Ni added specimens that could be divided in 2 steps which first step, in the first 5 hours of testing, oxide weight gain increased very rapidly due to there were more open coarse pores of specimens. The second step, oxide weight gain increased normally and continuously with lower rate. The increasing of Ni content provided higher oxidation resistant due to the decreasing of the oxide weight gain during the test. The total oxide weight gain of 5 wt.% Ni addition could also result in better oxidation resistance than pure 316L specimen, which has weight gain of 28.91 mg/cm$^2$.

In Fig.5c, the curves of 1 wt.% and 2 wt.% Ni+Cr additions have the similar trend as those of Ni addition (see Fig.5b), which oxide weight gain increased very rapidly in the beginning of testing and then the weight gain rate decreased slowly for longer testing duration. However, when increasing the amount of Ni+Cr up to 3-5 wt.%, the oxidation behaviors would be very similar to those of specimens with Cr addition, which are in parabolic type (see Fig.5a). Furthermore, the increase of Ni+Cr content also resulted in lower weight gain, which is similar to those of specimens with Cr and Ni contents increasing. From all results, it was found that Cr addition provided the best oxidation resistance comparing to Ni and Ni+Cr additions. The specimen containing 5 wt.% Ni+Cr addition shows the lowest oxide weight gain, 27.3 mg/cm$^2$, which is also better than pure 316L specimen.

Fig.6 shows XRD pattern results of powder 316L specimens with various alloying. From the results, it was found that oxide could occur at surface and inside the specimens after oxidation testing at 900°C for 100 hours in all additions. At the surface, the oxides which were observed are Fe$_2$O$_3$, Cr$_2$O$_3$, NiFe$_2$O$_4$, NiCr$_2$O$_4$. For the oxides occurring inside the specimens, Fe$_2$O$_3$, Cr$_2$O$_3$, NiFe$_2$O$_4$ and NiCr$_2$O$_4$ were detected in microstructures of Cr, Ni, Ni+Cr additions.
Fig. 5 The oxide weight gain of the modified 316L during heating at 900ºC for 100 hours a) 1-5 wt.% Cr added, b) 1-5 wt.% Ni added and c) 1-5 wt.% Cr with 1-5 wt.% Ni added.
Fig.6 XRD patterns of modified 316L with 5 wt.% Cr, Ni and Ni+Cr additions a) at surface of the specimens b) inside the specimens.

4. CONCLUSIONS

1) Cr addition provides the highest density which the microstructure appears only small pores with uniformly distribution inside the specimens. The densities of Ni and Ni+Cr additions decrease respectively.

2) For Cr addition, the increasing of Cr content provides better oxidation resistance comparing to those of specimens with Ni and Ni+Cr additions. The kinetics of weight gain follows the parabolic type and oxide spallation was not observed. From all results, Cr addition gives the best oxidation resistance.

3) For Ni addition, the initial of testing had rapidly increasing of oxidation rate and then the rate normally and continuously decreasing with time. The oxidation resistance increase with the higher amount of Ni and some spallation was observed in specimens with low Ni content.

4) For Ni+Cr addition, 1 wt.% and 2 wt.% added give the kinetics similar to those specimens with Ni additions. The higher Ni+Cr additions, 3-5 wt.%, the kinetics would change into curves which similar to Cr added specimens. However, the increasing of Ni+Cr addition provides better oxidation resistance.

5) Oxides generated on the surface and inside pores were Fe$_2$O$_3$, Cr$_2$O$_3$, NiFe$_2$O$_4$ and NiCr$_2$O$_4$.

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LITERATURE


