Preparation of oxide powder by continuous oxidation process from recycled Fe-77Ni alloy scrap

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Abstract. The oxidation behavior of Fe-77Ni alloy scrap was studied under a 0.2 atm oxygen partial pressure at the temperature range of 400°C to 900°C. The oxidation rate was found to be increased with an increase of temperature and followed the parabolic rate law with linearly proportional to temperature. Microstructure and cross-sectional area of the oxide layer were examined by SEM, EDX, and XRD. It could be speculated that rate-limiting step was controlled by diffusion through either the spinel structure or the NiO layer, both of which were present in this alloy during oxidation at elevated temperatures. In the long run, oxide powder less than 10 μm from Fe-77Ni alloy scrap was obtained using ball-milling and sieving processes and recovery ratio approached up to 97% for 15 hours.

1. Introduction
In a field of industries, alloys containing high nickel content have been used due to their corrosion and high temperature resistance and these alloys, therefore, are adapted to sever environment in the power energy, chemical and petrochemical industries. Especially, nickel-based superalloys can be met to special requirements of high mechanical and chemical properties for strength and creep resistance as well as corrosion resistance at elevated temperatures. The aviation industries in the world are attempting to develop special structural materials that can resist high temperature to enhance the engine’s fuel efficiency [1-5]. The nickel-based alloys are, therefore, representative metal that has been widely used in the hottest parts of gas turbines both for power generation and aircraft [6, 7].

A study on the oxidation behavior of iron-nickel alloys has been conducted by many researchers for decades. Many researches have already been performed, not only at low pressure and temperatures above room temperature, but also by air or during electrochemical oxidation and plasma formation [8-12] Liu et al. focused on the research of the corrosion phenomena for a single-crystal Ni-base superalloy at 900 and 1000°C in an air and oxidation was found to be occurred in two steps. It is noted that first oxidation is controlled by NiO growth and the second by Al₂O₃ growth until Al₂O₃ layer formed beneath NiO layer [13]. Li et al. investigated the oxidation layer for NiCrAlYSi deposited by
one-step arc ion plating and this coating layer was found to be thin and more effective protection of the substrate [14]. The pure and doped nickel alloys with different Co contents in air at 1000°C was studied for oxidation behavior by Zhou et al. It was found that coating efficiency was enhanced with an increase the Co content [15].

In this study, the specimen of Fe-77Ni alloy was studied for oxidation rate by thermal gravimetric analysis (T.G.A.) on the effect of temperature and oxygen partial pressure. The cross-sectional morphologies of oxide layer were examined and characterized by scanning electron microscopy provided by energy dispersive spectrometry (SEM-EDS) and X-ray diffraction (XRD). According to kinetic data and microstructure analysis, the high-temperature oxidation mechanism was discussed. Finally, the particle size distribution was conducted to find out the range of the oxide powder and fabrication of oxide powder less than 10 μm from Fe-77Ni alloy scrap was attempted by various physical processes.

2. Materials and experimentation
Scrap plate of Fe-77Ni alloy containing 77 wt.% of Ni was purchased from TV recycling center. Samples for oxidation were machined to be a size of 1.5 cm and 2 cm. In pretreatment process, polishing machine was used to treat on the surface of the specimens and subsequently diamond ultrasonic cleaning bath with acetone was used and samples were washed again with ethanol and water, and dried under the hood.

The oxidation behavior of Fe-77Ni alloy was continuously studied under a 0.2 atm using thermogravimetric apparatus (T.G.A.) at different temperatures. The gas mixtures with oxygen and argon were going through drierites for removal of moisture before their input into the reactor tube. Also, oxygen content as an impurity in argon gas was eliminated by copper turning furnace. The gas mixture was flowing to the quartz tube from the bottom to approach reaction zone while U.H.P. argon gas was flowing through the electrobalance to minimize contamination during the experiment. The specimen of the quartz tube was suspended with a platinum wire and then heated under ultra-purity argon atmosphere. When the temperatures were reached from 400°C to 900°C, oxidizing gases was used until oxidation was completed The oxygen partial pressure was controlled by each flowmeter of argon and oxygen gases. The weight gain of the specimen during oxidation was continuously measured and recorded for up to 24 hours. The cross-sectional area of the oxidized specimens and chemical composition of each layer were examined by SEM, EDX, and XRD.

3. Results and discussion
The change in the specimen weight of Fe-77Ni alloy with time during oxidation was observed for 24 hours in temperature range of 400 °C to 900 °C with gas mixture of an oxygen partial pressure of 0.2 atm using TGA shown in Fig. 1. It was found that the weight increased as the temperature rose, and it was shown to be the highest at 900°C.

The oxidation rate for iron-nickel alloys may be represented by the parabolic rate equation that is of great importance. As per this law, the oxide grows at a continually decreasing oxidation rate, and the diffusional and integral forms of the parabolic rate equations are given as follows:

\[
dx / dt = k_p / x \\
x^2 = 2k_p t + C
\]

Where \( k_p \) indicates the parabolic rate constant and \( C \) the integration constant, plotting the variation of \( x \) with time. Parabolic oxidation at elevated temperature represents that the oxidation takes place by the diffusion of ions or electrons through the oxide scale [16]. The oxidation reaction dependence on the temperature is well described by an Arrhenius-type equation as:
\[ k_p = A e^{-\frac{\Delta E^*}{RT}} \]

Where \( \Delta E^* \) denotes apparent energy of activation, and \( A \) is the frequency factor. The value of \( \Delta E^* \) based on the Arrhenius plot related with caution in oxidation process. 16 Fig. 2 shows the plot of parabolic rate constants on the y-axis and temperature on the x-axis deduced from Arrhenius-type equation. The oxidation rate constants are almost linearly proportional to temperature, which means that the rates were proportionally increased with an increase of temperatures. The activation energy for the oxidation of Fe-77Ni at a 0.2 atm was experimentally calculated to be 17.98 kJ/mol.

The phase analysis using XRD was conducted and oxide particles were also observed by SEM after oxidation of Fe-77Ni alloy scraps at 700°C and 900°C for 24 hours in given experimental conditions. Fig. 3 shows that three oxide phases, NiO, Fe\(_2\)O\(_3\), and Ni\(_{1.43}\)Fe\(_{1.7}\)O\(_4\), were detected, and the peak patterns of the three oxides were not much different regardless of elevated temperatures from 700°C and 900°C. The irregular shape of oxide particles was observed and their size differences are ranging from ±200μm to ±10μm.

According to the previous results of XRD, the following phases might be expected: bessenite-NiO (B), spinel (S), and hematite (H). It can be seen figure 4 that various oxide phases such as hematite,
spinel, bunsenite, and complex phases are formed depending on Ni/(Ni+Fe) molar ratio and temperature, and at given experimental conditions spinel (Fe, Ni)\textsubscript{2}O\textsubscript{4} and bunsenite (Ni, Fe)O are formed in pseudo-binary phase diagram that is a good agreement with data from XRD result. It can be explained that iron ions and electrons might migrate outward through grain boundaries, microcracks, and voids and oxygen anion was also moving inward through mainly spinel and bunsenite structures. It can be explained that especially the spinel structure known as a non-stoichiometric compound of Ni\textsubscript{1.43}Fe\textsubscript{1.7}O\textsubscript{4} has voids and pores itself, and oxygen anion was therefore relatively easily moving inward.

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The microstructure of the cross-sectional area of the oxide layer at 900°C for 24 hours and its chemical composition were examined by EDX, and its result is shown in figure 5. It showed the formation of two oxide layers that could be easily verified, and cracks and voids were also easily observed between the outer and inner layers. The chemical constituent of the outside oxide layer was mainly nickel, and nickel oxide (NiO) was, therefore, primarily formed the outer layer (1). It may expected that rate-limiting step was diffusion through either the spinel structure or the NiO layer, both of which were present in this alloy during oxidation at elevated temperatures [16]. The inner oxide layer (2) was found to consist of Ni, Mn, and Fe while three oxide phases, NiO, Fe\textsubscript{2}O\textsubscript{3}, and Ni\textsubscript{1.43}Fe\textsubscript{1.7}O\textsubscript{4}, coexisted. Also, the Mo content in the inner layer was detected to about 15 wt.%, which may have been influencing the physical properties of the film. In other word, Mo content in oxide layer can be a significant factor in oxidation processes, particularly where thermal cycling is involved [17]. The substrate (3) and (4) only contained Ni and Fe as a metallic alloy, and the Mo and O were not detected.

![Figure 5](image)

**Figure 5.** Microstructure of cross-sectional area corresponding to chemical composition of each oxide layer conducted at 900°C for 24 hours.

Based on kinetic data of oxidation of Fe-77Ni alloy scrap, fabrication of oxide powder less than 10 \( \mu \text{m} \) was carried out and its overall process is shown in figure 6. The control of particle size is one of the significant factors to enhance powder properties when it comes to powder compaction, density, and sintering. Therefore, final target size of the oxide powder obtained through various processes should be less than 10 \( \mu \text{m} \) to apply it to metal injection molding (MIM) process. Scrap foils were oxidized in muffle furnace in air atmosphere at 900°C for 2 hours since oxidation rate was found to be
relatively fast at 900°C as well as initial oxidation stage up to 2 hours and cyclic oxidation was sequentially conducted every 2 hours until the foils were fully oxidized. Oxide particles obtained after oxidation process were ground using the ball-milling machine to control the particle size of the final product. Sieving process was consequently operated to obtain oxide powders less than 10 μm using various levels of sieve for characterizing the particle size distribution of the samples.

Figure 6. Overall process to manufacture oxide powder from Fe-77Ni alloy scrap.

In the ball-milling process, size control of oxide powder was conducted to obtain target size of the powder less than 10 μm shown in figure 7. It is noted that particle size was found to be reduced with an increase of milling time under a fixed RPM of 84. The particle size was dramatically reduced to about 15 μm from 3 hours to 12 hours and then its size reached to about 10 μm for another 3 hours. It was found that recovery ratio was about 70% for 3 hours at the initial phase and then it started to dramatically increase after 6 hours of ball-milling. The recovery ratio of oxide powder was finally obtained to over 95% for 15 hours, and further milling process might be no longer efficient to raise the recovery ratio.

Figure 7. Recovery ratio and size of oxide powder as a function of milling time.

Figure 8. Particle size distribution and shape of oxide powder of Fe-77Ni alloy.

The particle-size distribution (PSD) of a powder can be important in understanding its physical and chemical properties and affect in particular compaction, density, and sintering of powder. The particle-size distribution of oxide powder was analyzed using Matersizer 3000 with a capacity of particle size range of 0.01 μm to 3500 μm and its shape was examined using scanning electron microscopy (SEM) shown in Fig. 8. It shows the average particle distribution, in terms of volume, as a function of particle diameter and particle size might be estimated by the amount of volume of oxide powder. It might be expected that an average particle size is observed to be about 7 μm and the other concentration peak is shown to be approximately 3 μm, which means that the smallest size of oxide powder might be around 3 μm. In company with particle size, the shape of particles can also have a significant influence upon the performance or processing of particulate materials and SEM image of oxide powder illustrates that its shape was observed to irregular and faceted form.

4. Conclusion
The rate of oxidation for Fe-77Ni alloy scrap increased with increasing temperatures in a given oxygen partial pressure. The oxidation behavior of the specimen followed the parabolic rate law regardless of temperature and activation energies were calculated to be 17.98 kJ/mol. The oxidation mechanism may expect that rate-limiting step was diffusion through either the spinel structure or the NiO layer. Particle size distribution of the oxide powder was conducted, and an average particle size was estimated to be around 7 μm with irregular and faceted shape.

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