ANALYTICAL DATA FOR NiO REDUCTION AND Al$_3$Ni$_2$ INTERMETALLIC COMPOUND FORMATION

M. R. Parsa and M. Soltanieh

* *mansour_soltanieh@iust.ac.ir*

School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, Iran.

Abstract: *In this research, the nickel oxide was dissolved in cryolite at temperatures of 880, 940 and 1000°C. In order to reduce the nickel oxide, aluminum was added to the salt. Simultaneously the nickel oxide was reduced and Al$_3$Ni$_2$ intermetallic compound was formed. In the duration intervals of 2.5-40 minutes samples of the salt and metallic phases were taken. The variation of the nickel content in metallic and salt samples was determined by the AAS. The results indicate that increasing the temperature and duration has a positive effect on the reduction process and Al$_3$Ni$_2$ intermetallic compound formation. The nickel content in the metallic sample has its highest amount at 1000°C in 10 minutes. Furthermore, practical results of the studies of nickel content variations in metallic and salt samples confirm the data obtained from theoretical calculations.*

Keywords: *Al$_3$Ni$_2$ intermetallic compounds, Analytical data, Mass equilibrium.*

1. INTRODUCTION

Because of high melting point, thermal conductivity coefficient, low density and resistance to corrosion and oxidation Al-Ni intermetallic compounds are used in high temperature applications [1-4]. The common method of producing these compounds was melting and casting which is not so efficient due to the difference of melting points of the primary materials [5, 6].

So other methods have been used to produce these compounds, namely mechanical alloying [7, 8], combustion synthesis [9, 10], and reactive sintering [11, 12]; however, each has its particular difficulties. Another method used to produce these compounds is thermal reduction [13].

In thermal reduction method, one or more metal oxides are reduced by a metal which has a lower oxygen potential, this method is mostly used to produce metallic elements. In the thermal reduction process, calcium or aluminum is mostly used as a reductive agent; in this case, the process is called calciothermy or aluminothermy [14-17]. Due to the higher stability of aluminum in comparison to calcium, higher temperatures in aluminothermic reduction (ATR) may be used, and consequently enhance the kinetics of the reaction [18]. Besides, aluminum has a lower tendency to oxidation than calcium, so ATR can be carried out at the atmospheric pressure [13].

In previous method pure elements are merely used to produce intermetallic compounds [19], now it is claimed that by applying the method introduced in this research, intermetallic compounds can be produced of their oxides, too. In order to enhance the intermetallic formation in this method it is of great importance to lower done the activity of the products. The Al$_2$O$_3$ is one of the products of the aluminothermic process which is dissolved in the cryolite and its activity is decreased; moreover, it does not enter in the final
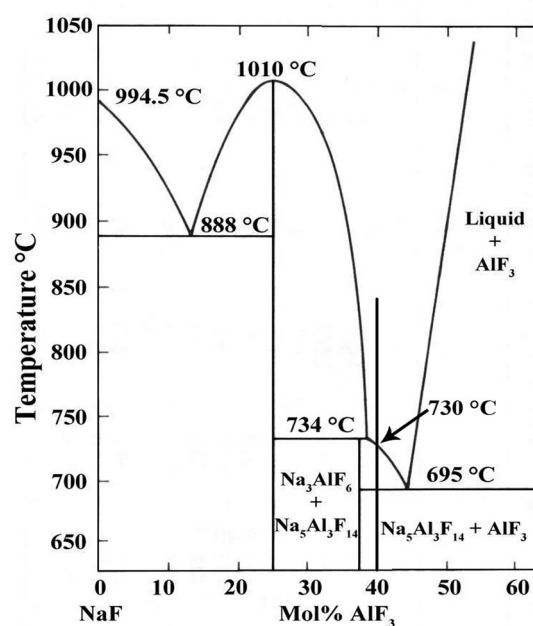

Fig. 1. NaF-AlF$_3$ binary phase diagram [21].

product [18]. According to the experimental temperatures (880, 940 and 1000 °C) it is vital to choose a salt which has a melting point below 880 C. Considering the NaF-AlF$_3$ binary diagram (Figure 1), cryolite salt (Na$_3$AlF$_6$) with molar ratio of 1.5 is most suitable for this experiment, as its liquidus temperature is about 730 °C.

2. METHODOLOGY

2. 1. Materials and Instruments

NiO (% Ni>78), Al (>99.9%), Na$_3$AlF$_6$ (>99.6%) and AlF$_3$ (>99.6%) were used in all the experiments. Graphite crucibles were used for melting treatment and a K-type thermocouple was applied to measure the melt temperature with high precision.

### 2. 2. Determining the Solubility of Nickel Oxide in Salt

To assure the solution of nickel oxide in salt with molar ratio of 1.5, according to Table 1 different amounts of salt were melted at the assigned temperature then 5 g nickel oxide was added. After stirring for 30 minutes at constant temperature, and settling for 1 hour, a sample of salt was withdrawn from the melt by sucking it up into a quartz tube immersed 5 to 7 mm into the solution. The liquid was quenched on contact with the cold upper portion of the tube. The samples were removed from the tube by cracking it, and were crushed. The nickel contents of the samples were found by dissolving crushed material in diluted nitric acid solution, and analyzing the resulting solution with an Atomic Absorption Spectrophotometer (AAS; GBC Avante Σ). Table 2 shows the obtained results, considering the results, salt #2 was used in all the tests.

Table 1. Used salts for determining the solubility of nickel oxide in cryolite with molar ratio of 1.5.

#	Na$_3$AlF$_6$ (g)	AlF$_3$ (g)	Cryolite mass (g)
1	4000	1600	5600
2	2000	800	2800
3	1000	400	1400

2. 3. Procedure

Thereafter melting the salt at the assigned temperature, 5 g nickel oxide was added to the salt. After stirring for 30 minutes at constant temperature, 3.9 g of aluminum was added to the melt. The amount of the applied aluminum was determined by the following reaction (Eq. 1):

$$6NiO+13Al \rightarrow 2Al_2O_3+3Al_3Ni_2 \qquad (1)$$
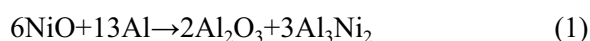
After 2.5, 5, 7.5, 10, 15 and 40 minutes of the addition of aluminum to the salt the crucible was removed of the furnace and quenched in air. The nickel content of the metal and salt samples was determined by AAS. The present phases in metal samples were also distinguished by the XRD and EDS analysis. It should also be mentioned that, the crucible content was continuously mixed during the test by a 2 mm diameter molybdenum wire.

3. RESULTS

3. 1. Solubility of Nickel Oxide in Salt

Table 2 shows the amount of solubility of nickel in molten salt at different temperatures and masses of cryolite. As it can be seen in salt #3, the

Table 2. Nickel oxide solubility in molten salt for addition of 5 g NiO.

#	Mass of the cryolite salt with molar ratio of 1.5 (g)	Concentrations of dissolved nickel in salt (wt %)		
		880 °C	940 °C	1000 °C
1	5600	0.07	0.07	0.07
2	2800	0.14	0.14	0.14
3	1400	0.15	0.17	0.23

solubility of nickel in the salt has not exceeded from 0.23 wt% at 1000 °C, which means that some of the nickel oxide was not dissolved in the salt, but for the other two masses of cryolite nickel oxide was completely dissolved in different temperatures; however, salt # 2 is more suitable due to the lower salt weight.

3. 2. Investigating theProduced Phases in the Metal Sample

The results obtained from EDS analysis show that the bright phase is Al_3Ni_2 (with 41.52 at. % Ni), the dark phase is Al_3Ni (with 26.76 at. % Ni) and the black matrix is Al (Figure 2). Also, XRD patterns were obtained from the samples acclaimed appearance of these phases. For instance, Figure 2 shows XRD pattern and SEM image that obtained from treated sample for 10 minutes at 1000 ºC.

3. 3. Nickel Content in Metallic and Salt Samples

Results obtained from metal and salt samples in different temperatures and duration intervals are showed in Tables 3 and 4, respectively. In Table 3 the third column shows the mass of metal sample after quenching and the fourth one gives the nickel weight percent of the sample measured by AAS. Moreover, the fifth column indicates the calculated nickel content of each sample; for

instance, it is calculated for the treated sample for 10 minutes at 1000 °C as following:

Having the nickel content and the reaction

**Fig. 2.** (a) SEM image and (b) XRD pattern of the treated sample at 1000 ºC for 10 min.

Table 3. Obtained data for metallic samples at different times and temperatures.

Temperature (°C)	Time (min)	Mass of the metal sample (g)	Nickel weight percent of each metal sample	Nickel content of the metal sample (g)	Consumed aluminum for reduction (g)	Theoretical aluminum content of the metal sample (g)	Measured aluminum content of the metal sample (g)	Amount of the aluminum loss (g)	Recovery of nickel in intermetallics (%)
1000	0	3.9	0.00	0.00	0.00	3.9	3.9	0.00	0.00
	2.5	4.23	16.31	0.69	0.21	3.69	3.54	0.15	17.60
	5	4.75	32.00	1.52	0.46	3.44	3.23	0.21	38.87
	7.5	5.58	49.28	2.75	0.84	3.06	2.83	0.23	69.44
	10	5.8	53.79	3.12	0.95	2.95	2.68	0.27	79.59
	15	5.77	54.07	3.12	0.95	2.95	2.65	0.30	79.59
	40	5.76	54.17	3.12	0.95	2.95	2.64	0.31	79.38
940	0	3.9	0.00	0.00	0.00	3.9	3.9	0.00	0.00
	2.5	3.98	8.29	0.33	0.10	3.80	3.65	0.15	8.41
	5	4.49	25.61	1.15	0.35	3.55	3.34	0.21	29.33
	7.5	5.08	39.96	2.03	0.62	3.28	3.05	0.23	51.91
	10	5.45	47.89	2.61	0.80	3.10	2.84	0.26	65.90
	15	5.43	48.25	2.62	0.80	3.10	2.81	0.29	66.32
	40	5.41	48.43	2.62	0.80	3.10	2.79	0.31	66.66
880	0	3.9	0.00	0.00	0.00	3.9	3.9	0.00	0.00
	2.5	3.85	3.38	0.13	0.04	3.86	3.72	0.14	3.31
	5	4.17	16.31	0.68	0.21	3.69	3.49	0.20	17.39
	7.5	4.53	27.37	1.24	0.38	3.52	3.29	0.23	31.31
	10	4.9	37.14	1.82	0.56	3.34	3.08	0.26	46.42
	15	4.88	37.50	1.83	0.56	3.34	3.05	0.29	46.44
	40	4.86	37.45	1.82	0.56	3.34	3.04	0.30	46.42

Table 4. Obtained data for salt samples at different times and temperatures.

Temperature (°C)	Time (min)	Salt mass (g)	Nickel weight percent in salt	Nickel content of the salt (g)	Mass of the nickel oxide in salt (g)
1000	0	2795.3	0.1410	3.93	5.00
	2.5	2794.4	0.1156	3.23	4.11
	5	2793.1	0.0856	2.39	3.04
	7.5	2792.2	0.0433	1.21	1.54
	10	2791.5	0.0287	0.8	1.02
	15	2789.1	0.0287	0.8	1.02
	40	2780.2	0.0291	0.81	1.03
940	0	2797.6	0.1408	3.93	5.00
	2.5	2796.5	0.1284	3.59	4.56
	5	2795.3	0.0991	2.77	3.52
	7.5	2794.4	0.0673	1.88	2.39
	10	2793.2	0.0483	1.35	1.72
	15	2791.3	0.0476	1.33	1.69
	40	2783.7	0.0471	1.31	1.67
880	0	2798.5	0.1408	3.93	5.00
	2.5	2797.3	0.1355	3.79	4.82
	5	2796.4	0.1155	3.23	4.11
	7.5	2795.7	0.0973	2.72	3.46
	10	2794.9	0.0751	2.1	2.67
	15	2793.4	0.0755	2.11	2.68
	40	2786.7	0.0754	2.1	2.67

formula (Eq. 2), the aluminum consumption for the reduction of each tests may be calculated, which are listed in the sixth column.

$$3NiO + 2Al \rightarrow Al_2O_3 + 3Ni$$
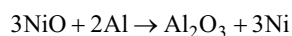
$$3.12 \times \frac{2 \times 27}{3 \times 59} = 0.95 \, g \tag{2}$$

Subtracting the amount of consumed aluminum from added aluminum to the salt (3.9 g) gives the theoretical aluminum content of the metal sample that are mentioned in the seventh column of the Table 3.

$$3.9 - 0.95 = 2.95 \, g$$

The eighth column shows the real aluminum content of the metal sample, which was determined by subtracting the nickel content of the sample from its total mass.

$$5.8 - 3.12 = 2.68 \, g$$

The difference between the theoretical and experimental aluminum content, shows the

aluminum loss.

$$2.95 - 2.68 = 0.27 \, g$$

In Table 4, the third column presents the mass of the salt sample after quenching. The fourth and fifth columns show the AAS measured nickel weight percent of the salt and the nickel content, respectively.

$$2791.5 \times \frac{0.0287}{100} = 0.8 \, g$$

Having the nickel content, the mass of the nickel oxide can be calculated. The results are presented in the sixth column.

$$0.8 \times \frac{75}{59} = 1.02 \, g$$

All the aforementioned numbers are related to the sample treated for 10 minutes in 1000°C.

4. DISCUSSION

By considering the variation of the nickel and aluminum content in metal samples, it is

illustrated that, at all three different temperatures, by increasing the experimental duration up to 10 minutes, the nickel content is increased while the aluminum amount is decreased. Since the aluminum oxide is more stable than the nickel oxide, so obviously after some duration intervals, aluminum reduces the soluble nickel oxide in the salt and alumina will form. The results showed that there were no trace of Al_2O_3 in the metallic phase [20], it could be deduced that the produced aluminum oxide had been dissolved in salt. Furthermore, it is observed that for definite test time, increasing the temperature resulted in greater nickel content; that is, higher temperature has favorable effect on reduction process. Considering the variation of the mass of the metal sample, it is appeared that by increasing the time duration from 10 to 40 minutes the sample mass is reduced, which is repeated at three temperatures, but since the nickel mass of the metal sample was constant in this duration period, it could also be related to the aluminum loss. The most important factors in aluminum loss are its solubility in cryolite and its oxidation, but since the furnace atmosphere was not controllable, the aluminum oxidation has the major contribution in the aluminum loss. According to the last column of Table 3, it can be seen that the aluminum loss is more sensitive to time rather than temperature. For example, for the duration of 10 minutes, aluminum loss is 0.27, 0.26 and 0.26 g at 1000, 940 and 880 °C, respectively, which indicates that the aluminum loss mechanism is less temperature dependent.

The fourth column of Table 3 shows the weight percent of nickel in metal samples. Now if the results are marked in the Al-Ni binary phase diagram. According to the position of these points on the diagram and by using the lever rule, the mass of the Al_3Ni_2 phase in the L-Al_3Ni_2 binary phase zone can be obtained (Table 5). For instance, in the treated sample for 10 minutes at 1000 °C, wt.% Ni which is located in the liquid-Al_3Ni_2 binary phase zone, is 53.79, and the obtained mass for this sample was 5.8 g (third column of Table 3), thus by means of the lever rule the mass of the Al_3Ni_2 phase can be calculated as follows: (Figure 3)
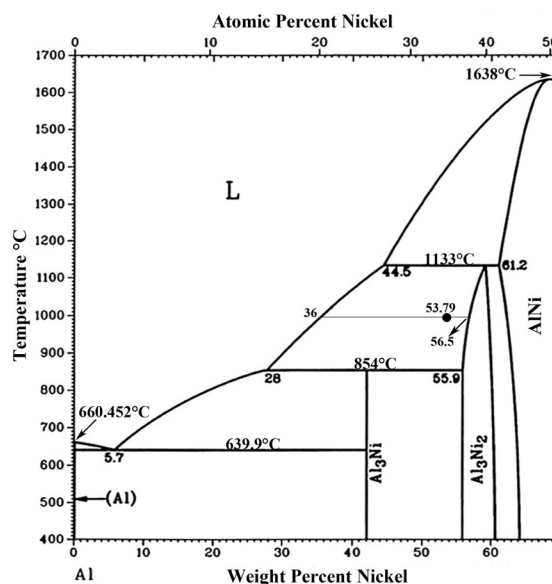

Fig. 3. A portion of the Al-Ni binary phase diagram [22].
● Sample was treated at 1000 °C for 10 min.

Table 5. Mass of the Al_3Ni_2 phase in different times and temperatures.

Temperature (°C)	Time (min)	Mass of the Al_3Ni_2 phase (g)
1000	2.5	0.00
	5	0.00
	7.5	3.62
	10	5.03
	15	5.09
	40	5.10
940	2.5	0.00
	5	0.00
	7.5	1.67
	10	3.58
	15	3.65
	40	3.67
880	2.5	0.00
	5	0.00
	7.5	0.00
	10	1.48
	15	1.53
	40	1.52

$$5.8 \times \frac{53.79 - 36}{56.5 - 36} = 5.03\,\text{g}$$

Considering Table 5, it is observed that increasing the temperature and duration has a positive effect on the formation of Al_3Ni_2.

Figure 4 shows the variation of the salt and nickel in salt masses as a function of time duration. As it is illustrated, the mass of nickel is decreased by increasing the duration up to 10 minutes, at this moment it reached its minimum value, e.g. the nickel content of the obtained salt at 1000 °C after 10 minutes was 0.8 g, while the nickel content of the metal sample was 3.12 g, the summation of the amount of nickel in salt and metal sample gives the total nickel content of the system.

$$3.12 + 0.8 = 3.92\,\text{g}$$

On the other hand, since 5 g of nickel oxide was initially added to the salt the nickel content of the system can be calculated as following:

$$5 \times \frac{59}{75} = 3.93\,\text{g}$$

It can be deduced that there is a good agreement between the theoretical and experimental results, $(3.92 \cong 3.93)$. Figure 4a indicates the reduction of the salt mass by test time. It can be associated that the reduction of the salt mass up to 10 minutes with the reduction of the nickel oxide mass in salt and salt loss, but since the mass nickel oxide was constant in the time duration of 10 to 40 minutes, reduction of the salt is only due to the salt loss. Moreover, from Figure 4a it is observed that by increasing the temperature at constant test time, the reduction of the salt mass is enhanced, so most probably the salt loss is just due to the evaporation during the process.

5. CONCLUSIONS

The finding in this work can be summarized as follows:

1. By dissolving the nickel oxide in cryolite and reducing it gradually with aluminum an Al-Ni intermetallic product can be obtained.
2. Increasing the test time and temperature has a positive effect on the reduction process treating at 1000 °C for 10 minutes and it has resulted in the greatest amount of nickel content.
3. Theoretical and experimental results are completely compatible.
4. The most important reasons for aluminum loss are its solubility in cryolite and oxidation. Also, salt evaporation during the process has the major contribution in its loss.

Fig. 4. Variation of (a) salt mass and (b) nickel in salt mass by time.

REFERENCES

1. Morsi, K., "Review: reaction synthesis processing of Ni-Al intermetallic materials."

Materials Science and Engineering A, 2001, 299, 1.

2. Stoloff, N. S., Liu, C. T. and Deevi, S. C., "Emerging applications of intermetallics." Intermetallics, 2000, 8, 1313.

3. Liu, C. T. and Kumar, K. S., "Ordered intermetallic alloys, part I. Nickel and iron aluminides." JOM, 1993, 45, 38.

4. Liu, C. T. and Stiegler, J. O., "Ductile ordered intermetallic alloys." Science, 1984, 226, 636.

5. Miura, S. and Liu, C. T., "Effects of aluminum concentration and compact thickness on reaction synthesis of Ni_3Al-NiAl alloys." Intermetallics, 1994, 2, 297.

6. Nishimura, C. and Liu, C. T., "Reaction sintering of Ni_3Al to near full density." Scripta Metallurgica et Materialia, 1992, 26, 381.

7. Koch, C. C., "Intermetallic matrix composites prepared by mechanical alloying-a review." Materials Science and Engineering A, 1998, 244, 39.

8. Dymek, S., Hwang, S. J., Dollar, M., Kallend, J. S. and Nash, P., "Microstructure and texture in hot-extruded NiAl." Scr Metall, 1992, 27, 661.

9. Dong, S., Hou, P., Cheng, H., Yang, H. and Zou, G., "Fabrication of intermetallic NiAl by self-propagating high-temperature synthesis reaction using aluminium nanopowder under high pressure." Journal of Physics Condensed Matter, 2002, 14, 11023.

10. Dyer, T. S. and Munir, Z. A., "The synthesis of nickel aluminides by multilayer self-propagating combustion." Metallurgical and Materials Transactions B, 1995, 26, 603.

11. Plazanet, L. and Nardou, F., "Reaction process during relative sintering of NiAl." Journal of Materials Science, 1998, 33, 2129.

12. Nishimura, C. and Liu, C. T., "Reactive sintering of Ni_3Al under compression." Acta Metallurgica Et Materialia, 1993, 41, 113.

13. Hosseinpouri, M., Mirmonsef, S. A. and Soltanieh, M., "Production of Al-Ti master alloy by aluminothermic reduction technique." Canadian Metallurgical Quarterly, 2007, 46, 139.

14. Abdelkader, A. M. and Daher, A., "Preparation of hafnium powder by calciothermic reduction of HfO_2 in molten chloride bath." Journal of Alloys and Compounds, 2009, 469, 571.

15. Baba, M., Ono, Y. and Suzuki, R. O., "Tantalum and niobium powder preparation from their oxides by calciothermic reduction in the molten $CaCl_2$." Journal of Physics and Chemistry of Solids, 2005, 66, 466.

16. Suzuki, R. O. and Inoue, S., "Calciothermic reduction of titanium oxide in molten $CaCl_2$." Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science, 2003, 34, 277.

17. Ramos, A. S. and Nunes, C. A., "The Effect of Excess Aluminum on the Composition and Microstructure of Nb-Al Alloys Produced by Aluminothermic Reduction of Nb_2O_5." Journal of Materials Synthesis and Processing, 1999, 7, 297.

18. Maeda, M., Yahata, T., Mitugi, K. and Ikeda, T., "Aluminothermic reduction of titanium oxide." Materials Transactions, JIM, 1993, 34, 599.

19. Li, Y., Nan, Y., Guo, W., Che, H. and Fan, Q., "Dissolution- precipitation-decomposition - crystallization mechanism of self-propagating high-temperature synthesis of Al_3Ni_2." Intermetallics, 2010, 18, 179.

20. Parsa, M. R. and Soltanieh, M., "On the formation of Al_3Ni_2 intermetallic compound by aluminothermic reduction of nickel oxide." Materials Characterization, 2011, 62, 691.

21. Grjotheim, K., Krohn, C., Malinovsky, K. and Thonstad, J., "Aluminium Electrolysis, Aluminium Verlag," 1982.

22. Baker, H. and Okamoto, H., ASM Handbook, ASM International, Materials Park, Ohio, USA, 1992.