Deoxidation of Ti-Ni alloy by the calcium and CaF_2-$MgCl_2$ flux

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ABSTRACT

The present study investigates the possibility of the direct removal of oxygen from the Ti-30Ni (wt%) alloy melt through the thermodynamic equilibrium reactions at 1623 K in the vertical tube furnace. The deoxidation efficiency of Ti-Ni alloy melt by adding different contents of metallic calcium (Ca) as a deoxidant was evaluated with the binary CaF_2-$MgCl_2$ flux.

The thermodynamic equilibrium experiments showed that the total oxygen content in the alloy decreased from about 650 ppm to 350 ppm when 3.5 wt% Ca was added to the Ti-30Ni (wt%) alloy.

Alternatively, the effect of flux composition in the CaF_2-$MgCl_2$ flux on the oxygen content was also investigated at 1623 K. Therefore, the effect of binary flux systems on the deoxidation ability was compared at 1623 K. According to the results, the flux system with 80%CaF_2-20%$MgCl_2$ exhibited the best deoxidation capability, i.e., total oxygen content in the alloy reduced from 1450 to 550 ppm.

INTRODUCTION

The escalating global energy crisis and the urgent need to address climate change have compelled the industrial sector to prioritize sustainability and responsible energy consumption (Hossain, 2024). Titanium alloy is one of the most crucial structural materials for advanced lightweight applications, especially in aerospace and automotive areas, due to its low mass density of 4.5 g/cm^3 and high strength, coupled with excellent corrosion and high-temperature creep resistance (Rabbe, 2023). However, it cannot be ignored that the cost of manufacturing titanium alloys and their low utilisation is a major limiting factor in their development. For example, machining produces titanium chips, and up to 90% of the material is lost and turned into scrap in the manufacturing step in aerospace sector. The main impurity elements are oxygen (from corrosion and oxidation during machining) and iron (from abrasion of machining tools) (Lu, 2012; Takeda, 2019). Therefore, the most urgent problem is research direction and the vital challenge for the entire Ti industry to develop a sustainable and circular economical route for Ti scraps to produce high-clean Ti alloys (Jiao, 2020).

Several researchers have discussed different methods to remove the impurity element oxygen from Ti alloys and scrap, such as powder metallurgy (Kim, 2016), electrochemical deoxidation (Chen, 2000), remelting methods (Okabe, 1992) and utilisation of hydrogen (Zhang, 2022). However, few fundamental studies have been conducted to systematically investigate the deoxidation behaviour of TiNi alloy by high-temperature thermodynamic equilibrium reactions. To address this gap in the literature, the present study investigates the effect of metallic Ca with the CaF_2-$MgCl_2$ binary flux on the equilibrium content of oxygen in Ti-30Ni (wt%) alloy at 1623 K. In addition, the effect of flux composition in the CaF_2-$MgCl_2$ flux on the oxygen content was also investigated.

EXPERIMENT

Titanium scrap produced from machining, Ca granule (99.99%, Alfa-Aesar), and Ni pellet (99.99%, Rnd-Korea) were used as raw materials. Ti scraps were pickled in 1 mol oxalic acid solution at 70 °C for 40 min, after that, the pickled Ti scraps were ultrasonically cleaned in distilled water and ethanol in sequence and then dried 12 hours at 40 °C to remove any remaining moisture. Meanwhile, reagent-grade powders of CaF_2 (>98%, Junsei-Chemical) and $MgCl_2$ (>98%, Sigma-Aldrich) were used as flux materials. The Ti-Ni master alloy was manufactured in a vacuum arc remelting (VAR) furnace under the pressure of 1.6×10^{-4} Torr.

Examination of the chemical reactions between the CaF_2-$MgCl_2$ flux and Ti-30%Ni alloy was conducted in a super Kanthal electric resistance furnace with a $MoSi_2$ heating element, as shown in FIG 1. The temperature of the furnace was controlled by a PID controller connected to an R-type reference thermocouple. The temperature was calibrated to 1623 K using another R-type thermocouple before the experiment. The Ti-Ni master alloy (10g), nickel capsule (with different Ca content), and flux powder mixture (4g) were loaded into a graphite crucible (15×12×50 mm) and placed in a graphite holder (50×40×65 mm), which were linked with a molybdenum wire. When the furnace temperature reached 1623 K, the graphite holder was then positioned in the constant hot zone of the furnace. The reaction chamber was flushed with highly purified Ar gas at a constant rate to avoid oxidation of the alloy. After 60 min of equilibration time, the samples were quickly extracted from the furnace and quenched by dipping the crucible into brine.

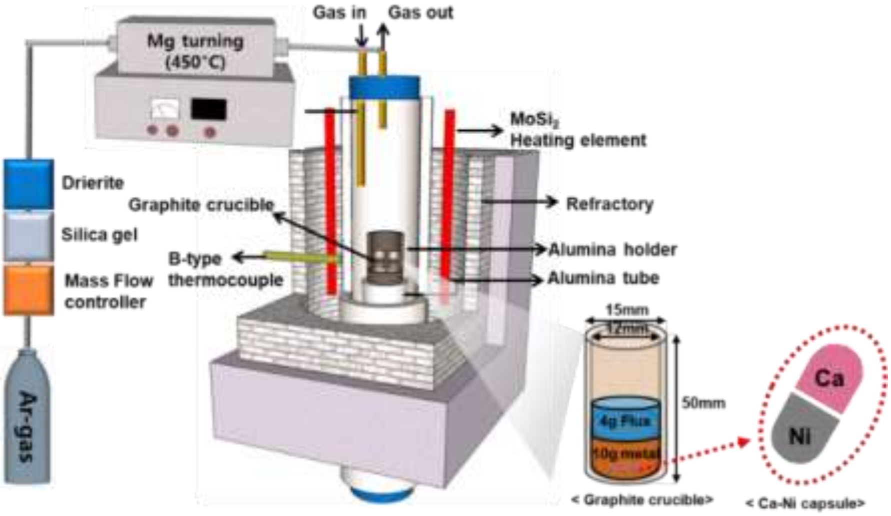

FIG 1 – Schematic diagram of the experimental apparatus.

After quenching, alloy samples were polished using a grinder to remove the surface layer, which can affect the analysis results, and then cut to a constant weight to reduce analytical error. The total oxygen and nitrogen content in the alloy samples was analysed using a combustion analyser (TC-300, LECO). The carbon content in the alloy samples was measured using a combustion analyser (CS 800, ELTRA).

RESULT AND DISCUSSION

- Oxygen removal by different remelting methods

To investigate the effect of the melting methods and halide flux on the Ti-30Ni (wt%) alloy, the changes in the total oxygen and nitrogen contents in the alloy under various melting conditions are displayed in FIG 2. According to Fig. 2, there is no significant change in the oxygen content of the alloy remelted in a graphite crucible without flux compared to the master alloy. However, the total oxygen content in the alloy reacted with the 80CaF_2-20$MgCl_2$ flux exhibits a sharply increasing tendency in FIG 2. To understand this problem, the source of oxygen contamination needs to be found. Therefore, the CaF_2 and $MgCl_2$ powder as raw materials were checked by an XRD analysis, and the result is shown in FIG 3. It was found that the $MgCl_2(H_2O)_6$ phase was confirmed in the reagent $MgCl_2$ powder.

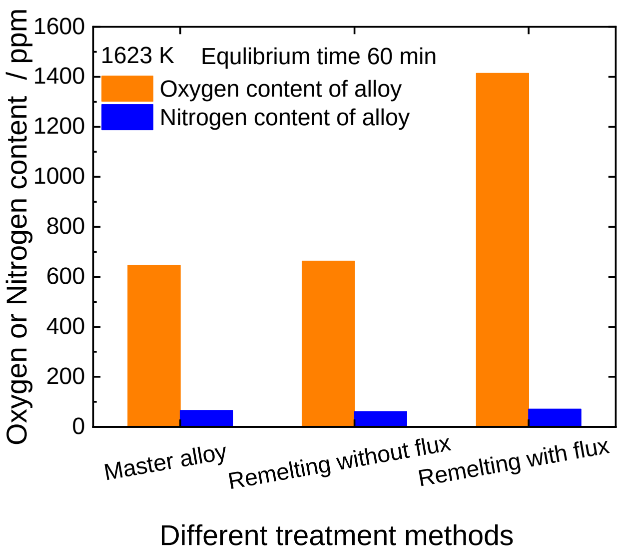

FIG 2 – Change of total oxygen and nitrogen content in Ti-30Ni alloy with different melting method.

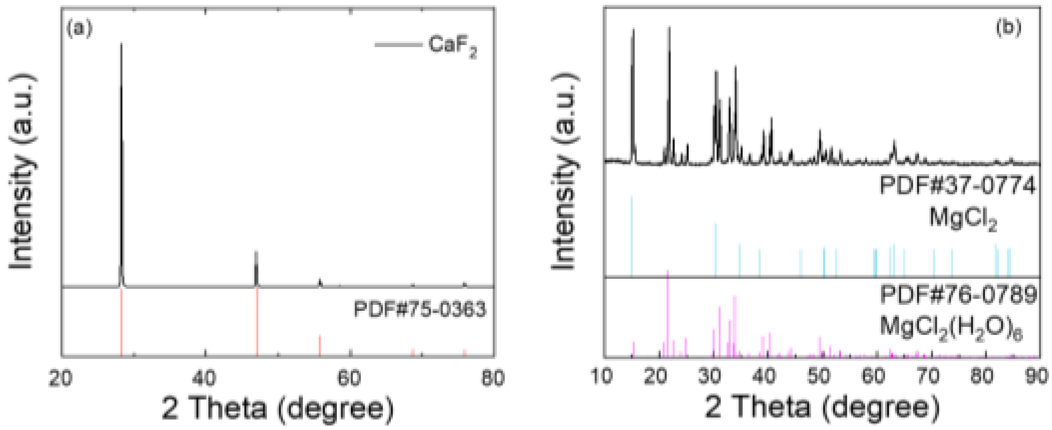

FIG 3 – XRD (scan rate of 1°/min) results of raw materials; (a) CaF_2, (b) $MgCl_2$.

Huang (2011) reported that the magnesium chloride hexahydrate, $MgCl_2(H_2O)_6$, could be decomposed to form MgO and H_2O at a temperature higher than 633 K. Therefore, it is indicated that when only adding the CaF_2-$MgCl_2$ flux, the oxygen content in the alloy sample sharply increased almost double compared with VAR and remelted sample without flux.

To investigate the deoxidation efficiency of the metallic Ca in the Ti-30Ni (wt%) alloy, the amount of Ca was increased from 0.17 wt% to 3.5 wt% in conjunction with flux system, 80CaF_2-20$MgCl_2$. Changes in the total oxygen and nitrogen content in the alloy with different Ca additions are illustrated in FIG 4. The total oxygen content of the Ti-30Ni alloy initially increases up to about 0.5 wt% Ca, followed by a dramatic decrease and reaching about 350 ppm when 3.5 wt% Ca is added. The initial increase is possibly due to the effect of the binary halide flux, which might have $MgCl_2(H_2O)_6$ compound as mentioned above. However, a significant decrease in oxygen content is found as the calcium content increases further because Ca is the most effective deoxidation agent which is enough to compensate the reoxidation due to hydrate formation at high temperature (Okabe, 1992).

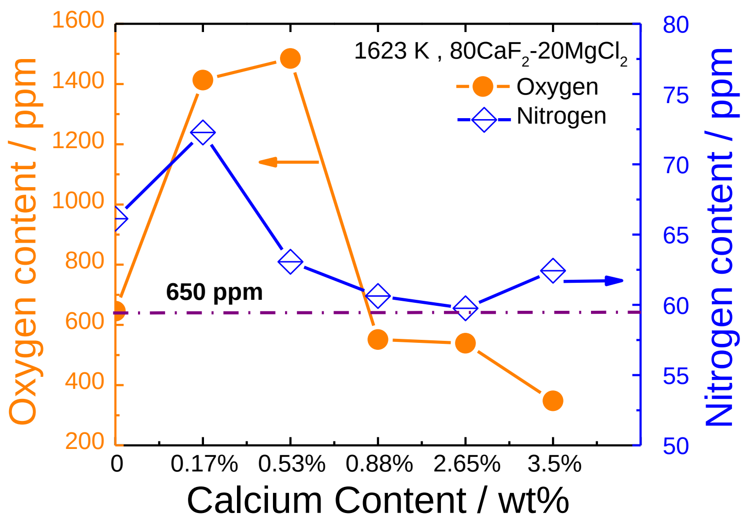

FIG 4 – Change of total O and N content in the Ti-30Ni alloy by adding metallic calcium at 1623 K.

Alternatively, the effect of different flux composition in the CaF_2-$MgCl_2$ binary flux in conjunction with about 0.9% Ca on the oxygen content in the Ti-30Ni alloy was also investigated at 1623 K and the results are shown in FIG 5. As the content of $MgCl_2$ increases from 10% to 25%, the total oxygen content of the alloy maintains nearly constant but slightly decreases to about 550 ppm even with slight fluctuation up to 20%$MgCl_2$, after which it sharply increases by adding more $MgCl_2$. The FactSage calculation shows that CaF_2 activity (a_{CaF_2}) in the CaF_2-$MgCl_2$ system sharply decreases from 1.0 to *ca*. 0.1 up to about 20% $MgCl_2$ (i.e., strong negative deviation from an ideality), after which a_{CaF_2} smoothly decreases. A sharp decrease in a_{CaF_2}

indicates the lower volatilization and the higher stability of CaF_2 in the flux, which potentially promotes the absorption capability of deoxidation product, i.e., CaO. However, when the content of $MgCl_2$ is greater than 20%, the reoxidation rate due to $MgCl_2$ would be much higher than the deoxidation rate due to combination of CaF_2 and Ca. Consequently, the flux system with 20$MgCl_2$-80CaF_2 exhibited good deoxidation efficiency in the present study.

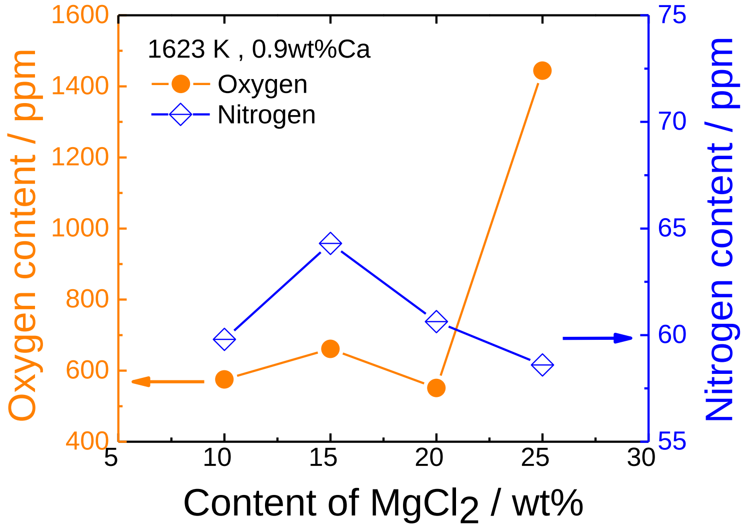

FIG 5 – Change of total oxygen and nitrogen content in the Ti-30Ni alloy with different $MgCl_2$ content in the CaF_2-$MgCl_2$ binary flux at 1623 K.

CONCLUSIONS

To establish an efficient recycling process for Ti scrap, a novel method relying on the deoxidation of Ti-Ni alloys by Ca and CaF_2-$MgCl_2$ flux was proposed. Equilibrium reactions between the Ti-30Ni (wt%) alloy and metallic Ca and CaF_2-$MgCl_2$ flux were investigated in a vertical tube furnace with a high-density graphite crucible at 1623 K. The principal findings of the present study are summarized as follows.

1. The amount of Ca added to the molten Ti-30Ni (wt%) alloy was varied from 0.17 wt% to 3.5 wt% in conjunction with the 80CaF_2-20$MgCl_2$ flux system. When 3.5 wt% Ca was added, the total oxygen content in the alloy decreased from about 1500 ppm to 350 ppm.
2. The flux system with 20$MgCl_2$-80CaF_2 in conjunction with about 0.9%Ca exhibited good deoxidation efficiency. The total oxygen content in the alloy reaches about 550 ppm at 1623 K.

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