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Al-Sc Alloy Production using Metal Ion Plasma

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Abstract
In chemical reactions using microwave irradiation, local concentration of electric and magnetic fields between particles, such as catalysts and powders, increases the reaction rate and lowers the temperature of the reduction reaction of the entire sample. The concentration of electric and magnetic fields between solid particles and plasma is believed to cause such reactions. In high-temperature reactions between individual particles, plasmas are directly involved in and accelerate chemical reactions, whose reaction temperatures reportedly become lower than the reduction reaction temperatures under normal heating. Therefore, using a cylindrical cavity in the TM_{110} mode at 2.45 GHz with a strong magnetic field, a magnesium (Mg) plasma was generated from Mg rods, and ten pellets of the Φ13×5 mm sample mixed with scandium oxide and aluminum powder were placed in an induction coil at 13.56 MHz and were reduced at 700 °C for approximately 1 h, with a conversion rate of 42%. Despite the low conversion rate, scandium oxide was successfully reduced at a low temperature by Mg plasma and induction heating without necessitating the use of additional solvents. The low conversion rate was caused by an insufficient supply of Mg, which could be resolved by increasing the reaction time. This experiment confirmed that Mg ions contribute to the lower temperature of the reduction reaction and that the generation of a Mg plasma by microwaves and the heating of the reaction zone by radiofrequency bands offer the prospect of fabricating a system larger than that obtained using microwaves alone.

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Introduction
Since Gedye first reported that chemical reactions are accelerated by microwaves in 1986, many reports have been published on organic synthesis, material synthesis, catalytic reactions, and electrochemical reactions using microwave heating [1–10]. Chemical reactions under microwave irradiation are characterized by high reaction rates, selective heating, and low reaction temperatures by operando measurements due to the local concentration of electric and magnetic fields between particles such as catalysts and powders [3–5]. In addition, microwaves can readily generate plasma owing to their ability to produce strong electric fields. Therefore, reactions between microwave plasma and catalysts are well known, such as the catalytic conversion of methane to C_2 and hydrocarbons and the use of microwave plasma-accelerated catalysis for carbon dioxide [6]. In high-temperature reduction reactions between individual particles, plasmas are directly involved in the chemical reaction, and they accelerate the reaction, which reportedly results in lower reaction temperatures than those of the reduction reaction under normal heating. The temperature of reduction of copper oxide by carbon was determined using thermogravimetric measurements. The observation of a lower reduction temperature suggests that the Ar plasma contributed to this reaction [7]. We could also reduce scandium oxide and vanadium oxide at low temperatures (below 700 °C) using a multimode applicator, using Mg as the reductant, and generated Mg plasma through microwave irradiation. In these reduction reactions, the reaction temperature was low, and the Mg ions excited by microwaves acted as reducing agents [8,9]. In these experiments, the use of a single magnetron to heat the generation of Mg ions and facilitate the reduction reaction hindered the ability to introduce substantial amounts of raw material and obtain many reaction products. This is because enlarging the multimode applicator would not be viable owing to the presence of numerous electric and magnetic field bellies and nodes.

To solve this problem, we developed a new microwave irradiation system wherein the plasma generation and reaction components could be independently controlled [10]. Specifically, in the plasma generation section, the plasma was generated using the TM_{110} and TM_{010} mode resonators, and in

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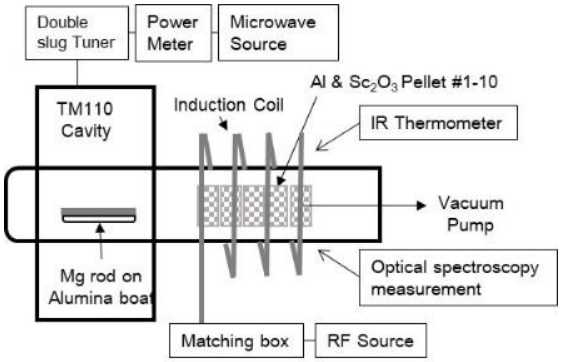
the reaction section, a TM_{110} mode resonator was used to heat the pellets. Consequently, although the plasma was generated at a low power in the TM_{010} mode, the plasma generation time was short, and the reaction was insufficient. Although plasma was generated in the TM_{110} mode for a long time, the same 2.45 GHz TM_{110} mode applicator was used in the reaction section, and therefore, the modes were the same. The resonance frequencies were close to each other and interfered with one another; hence, the reaction was inadequate. Moreover, in the plasma generator, the magnetic field mode was generated at the center of the cylinder formed by the TM_{110} mode. The presence of a conductor in the center does not change the TM_{11n} mode of the microwave cavity resonator, although the frequency may change slightly. Therefore, rods of metals such as Mg and Ca can be directly heated, and the plasma of these metals can be directly excited [11].

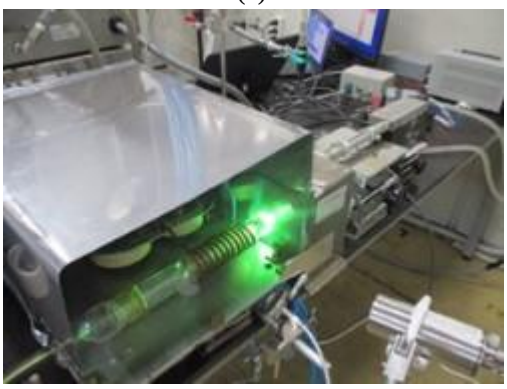
To reduce the interference between the plasma generator and reaction zone, we developed a device that used 2.45-GHz microwave heating for the plasma generator and 13.56-MHz induction heating in the radiofrequency (RF) for the reaction zone.

Experimental Methods

Ten pellets with a 13-mm diameter and 5-mm thickness were used for the reduction reaction. The pellets were mixed with scandium oxide (0.5 g, grain size 45μm) and aluminum powder (1.0 g, grain size 80μm) and pressed at 10 MPa. As shown in Fig. 1, the experimental apparatus consists of a plasma generation section with a microwave cavity resonator and a reaction section using RF induction heating. The plasma generator used a mini-circuit oscillator (ISC-2425-25+) as the microwave source and a mini-circuit high-power amplifier module (ZHL-2425-250X) to supply microwave power to a TM_{110} mode cylindrical cavity (φ110 mm) through a slug tuner. Microwave power was supplied to a TM_{110} mode cylindrical cavity (110-mm diameter) through a slug tuner. Inside the cavity, a Mg rod (4 g) of Φ8 mm and 50-mm width was placed on an alumina boat inside a double quartz tube as the Mg plasma source. Eleven turns of a Φ5-mm copper pipe, which was approximately 10 cm long, were used as the RF band induction coil section. The RF power source was from ENI Power Systems (OEM-6), and the RF power was applied through matching. A two-color radiation thermometer was used to measure the temperature of the sample of the pellets. An RF power of 110 W was applied to each pellet to confirm the performance of the RF induction heating. Although some pellets were hidden behind the coil and could not be measured, the temperature was approximately ±50 ° C in the area of ten pellets, 5 mm × 10 pellet-thick (equivalent to a length ⩽ 50 mm), as shown in Fig. 2. The



(a)



(b)

Fig. 1. Experimental apparatus for plasma generation and chemical reaction using a TM_{110} mode microwave cavity and an induction heating coil; (a) block diagram, (b) the photo with Mg plasma.

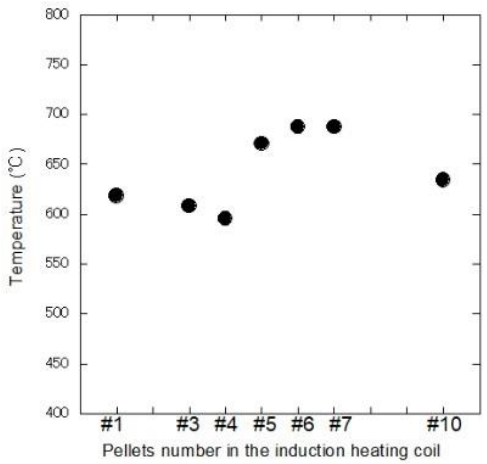


Fig. 2. Temperature distribution of #1–#10 pellets in the induction heating coil.

experimental conditions for the reduction reaction were as follows: 120 W of RF power was applied to the reaction zone to heat the pellets; meanwhile, 100 W of microwave power was applied to generate a plasma a few minutes later, which was maintained for approximately 68 min.

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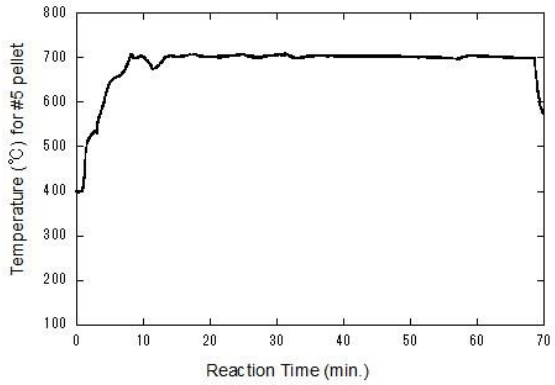

Fig. 3. Temperature for #5 pellet as a function of reaction time.

As only one pellet can be measured, the fifth pellet from the microwave cavity side was selected to obtain a representative measurement value of 10 pellets. As shown in Fig. 3, the temperature reached 700 °C 10 min after the application of RF power, and the temperature of the sample was maintained at 700° C for approximately 60 min. The state of the plasma in the reaction zone was measured via spectrometry using a HORIBA ESTECH spectrometer. The reactants were analyzed using a Rigaku X-ray diffractometer (model number), and the reference intensity ratio (RIR) method was used for quantification.

Results and discussion

Fig. 4 shows the plasma emission spectroscopy measurements of the reaction zone. The plasma-emitting species were identified using a database maintained by the National Institute of Standards and Technology (NIST). The spectroscopic data are shown at 9.5, 10, and 60 min after the reaction began. As the sample was inductively heated, a broad exothermic emission around 950 nm and an emission corresponding to Al II at 286.8 nm were observed due to Al metal evaporation from the pellets. Mg plasma luminescence (Mg I 285.1, 518.3, and 880.8 nm) was also observed until the end of the reaction; luminescence was observed in association with Sc (Sc I 485.2, 602, 655.8 nm) at 9.5 min but not after 60 min. This can be attributed to the fact that in addition to the fouling of the quartz glass, the reactive portion in the pellet moved from the surface to the interior. Thus, the reaction proceeds inward from the surface of the pellet, hindering the escape of the Sc atoms from the pellet surface.

Fig. 5 shows the results of the X-ray powder diffraction measurement of the powder of the pellets after the reactions from #1 to #10, i.e., of the product and residue.

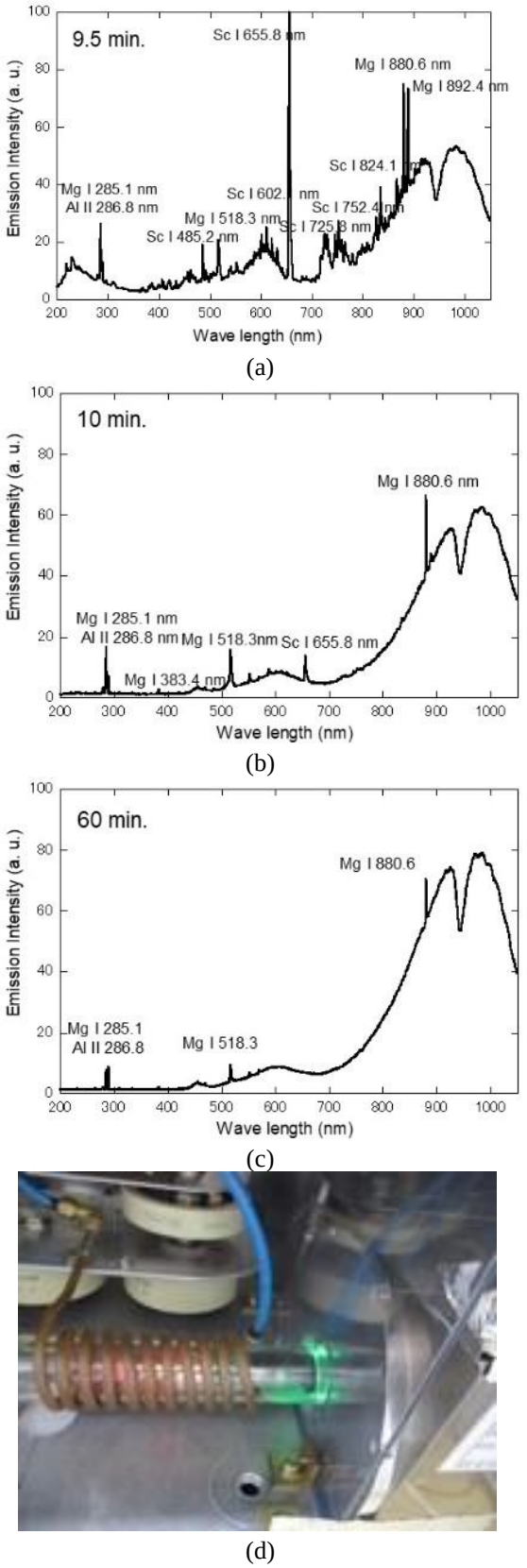

Fig. 4. Plasma emission spectroscopic measurement results near the pellet at the reaction times of (a) 9.5 min, (b) 10 min, and (c) 60 min, (d) the photo during the reduction.

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Fig. 5 shows a peak attributed to $ScAl_3$, indicating that the reduction reaction is in progress. Fig. 6 shows the composition ratios of the products obtained through RIR. Despite some variation, it ranged from 23 to 50 wt%, and no significant distribution was observed, although the Mg plasma was supplied from a location close to #1. The Mg ions, acting as the reducing agent, penetrated the pellets up to pellet #10 and contributed to the reaction. The calculated conversion ratio of Sc_2O_3 to $ScAl_3$, based on the weight ratios shown in Fig. 6, is listed in Table 1. The results of the RIR analysis for all ten pellets are presented in Table 1, wherein the average $ScAl_3$ conversion in the pellets is 42%. This shows that despite a low conversion rate, the number of pellets used was considerably more than that with the multimode applicator, and the problems caused by interference between the microwave and RF bands were reduced. In addition, the Mg ions penetrated the compressed pellets in the RF induction coil and contributed to the reaction.

The reason for this low conversion rate is discussed below. If Mg was not a plasma but the part of a thermal equilibrium reaction, then:

$$Sc_2O_3 + 3Mg \rightarrow 2Sc + 3MgO$$
$$\Delta G = 330 \text{ kJ/mol at } 660\ ^\circ C. \quad (1)\ [8]$$

However, this reaction did not occur. Therefore, Mg ions were generated in the microwave magnetic field resonance mode, and Mg ions had a large energy level of $\Delta G = 2{,}536$ kJ/mol.

$$Sc_2O_3 + 3Mg^+ \rightarrow 2Sc + 3MgO$$
$$\Delta G = -2{,}200 \text{ kJ/mol at } 660\ ^\circ C \quad (2)[8]$$

The excess energy was also used to form the intermetallic compound of Al_3Sc.

$$Sc_2O_3(s) + 6Al\ (s \text{ or } l) + 3Mg \rightarrow 2ScAl_3 + 3MgO \quad (3)$$

Therefore, the amount of Mg consumed by the plasma in the experiment could be determined from the weight measurements of the Mg rods before and after the experiment, which was approximately 0.8 g. The amount of Mg used for scandium oxide was 0.7 g, based on the results of the quantitative analysis in Fig. 6. Not all of the evaporated Mg ionized and reached the reaction zone; some adhered to the quartz tube, and insufficient Mg evaporated after 60 min, which was possibly the cause of the conversion ratio of approximately 42%. In this experiment, the reaction of 60 min was inadequate to generate sufficient Mg to achieve optimal conversion rate. Presumably, the issue of a higher amount of Mg ions owing to the application of microwaves or a higher

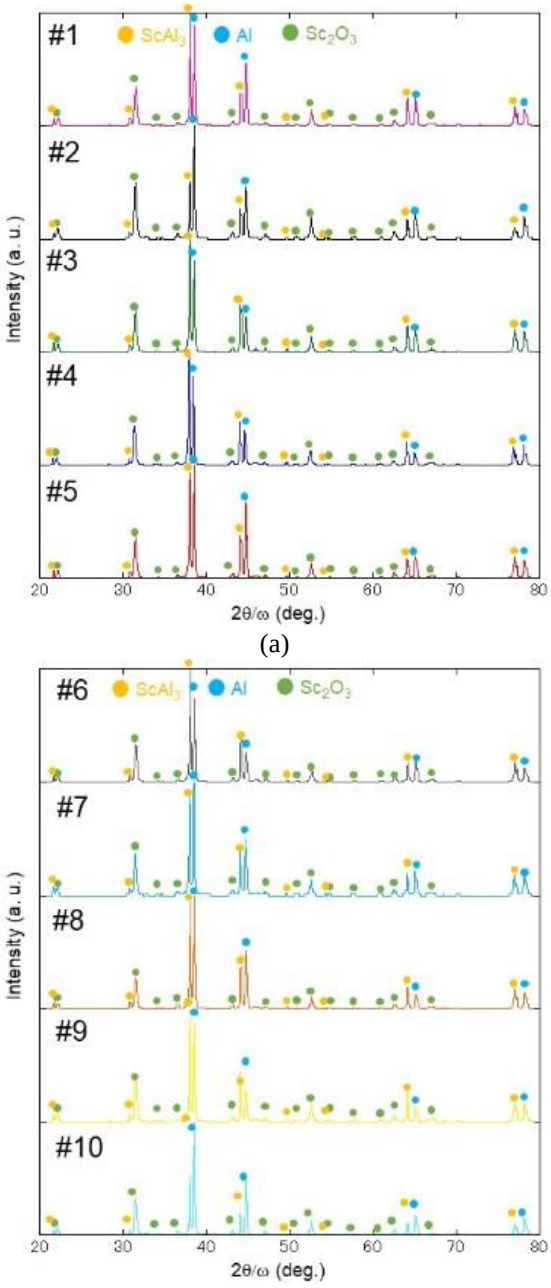

Fig. 5. X-ray powder diffraction patterns of the mixture of residues and products for the reaction: (a) #1–#5 pellets and (b) #6–#10 pellets.

reaction time can be solved by using RF induction heating. In this experiment, the combination of microwaves and RF can exceed the limit of mass production improvement through the use of microwave irradiation equipment, such as a multi-mode applicator with a magnetron.

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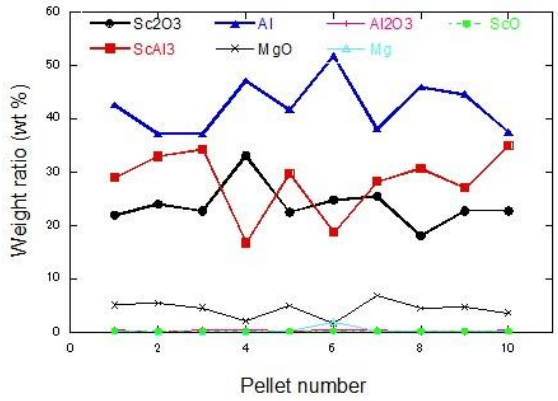

Fig. 6. Weight ratio of the residue and product mixture after reaction for each pellet

Table 1. Conversion ratio of Sc_2O_3 to $ScAl_3$.

Pellet no	Ratio $Sc_2O_3/ScAl_3$ (%)
#1	44.2
#2	45.1
#3	47.5
#4	23.3
#5	44.2
#6	31.3
#7	40.1
#8	50.4
#9	41.7
#10	48.0
Ave.	41.6

Conclusions

High-temperature reduction by microwave irradiation has previously been possible at low temperatures due to the plasma generated between solid particles. However, when microwave irradiation is used to increase productivity, a larger multimode applicator is not sufficient. In addition, there was a problem of interference when microwaves were used to heat the plasma generator and reaction zone. Therefore, we have created a completely new device in which the plasma generator is generated by a microwave resonator and the ions in the plasma are drawn into the raw material by an induction heating coil. In this device, a metallic plasma is generated and maintained directly by the microwave high magnetic field mode, and the plasma is induced to the reaction zone by induction heating, making it possible to reduce the amount of material pellets 10 times greater than conventional methods. In this experiment, it was also confirmed that Mg ions contributed to the lower temperature of the reduction reaction. The generation of Mg plasma by microwaves and the heating of the reaction zone by RF bands offered the prospect of larger equipment than that using only microwaves. The conventional method of reducing oxides of rare earth elements such as Sc involves turning them into fluorides using hydrofluoric acid at a high temperature and then reducing them using Ca metal. We have successfully shown that the proposed microwave excitation method for producing Mg ions and the reduction system comprising RF induction heating can significantly reduce energy consumption without necessitating the use of toxic substances.

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Conflicts of Interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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