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Manganese production from MnO by use of hydrogen plasma

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Abstract: Hydrogen plasma is a more potent reductant than H_2 which means that it can reduce oxides that cannot be reduced by normal gaseous H_2, an example being MnO. This work will demonstrate the formation of metallic manganese from MnO through reduction by hydrogen plasma. This opens the possibility of using hydrogen in the production of manganese, reducing our dependency on carbon-based reductants.

Keywords: Metallurgy, hydrogen, manganese, plasma.

1. Introduction

The metallurgical industry is responsible for significant CO_2 emissions. Some of these emissions can be eliminated by decarbonizing the electricity-grid, but this will not be enough since CO_2 is often an unavoidable by-product of current processes. A common example is when carbon is used as a reducing agent to remove oxygen from metal oxide ores:

$$MeO + \frac{1}{2}C \rightarrow Me + \frac{1}{2}CO_2 \tag{1}$$

In order to fully decarbonize, the metallurgical industry must also address these process-related emissions. For some systems, H_2 can replace carbon in Equation (1):

$$MeO + H_2 \rightarrow Me + H_2O \tag{2}$$

This is obviously a very attractive proposition since the reaction by-product is harmless water vapour. In the steel industry, for example, there has been considerable interest in H_2 as an enabler of sustainable steel production [1]. However, for many oxides reaction with H_2 gas is thermodynamically unfavourable. The reaction between MnO and H_2 is an example, where $\Delta G^0>0$ for $T<3000$ °C:

$$MnO + H_2 \rightarrow Mn + H_2O \tag{3}$$

In the plasma state, H_2 will be excited to species such as monoatomic hydrogen, H, rotationally/vibrationally excited hydrogen, H_2^*, and ions, H_2^+ and H^+, which are more chemically reactive [2]. As an example, the reaction between monoatomic hydrogen and manganese oxide is favourable across a range of temperatures:

$$MnO + 2H \rightarrow Mn + H_2O \tag{4}$$

If hydrogen plasma could be implemented in manganese production, this could allow for the substitution of carbon with electricity and hydrogen. Assuming both of these input factors can be produced from renewable energy, manganese production could become completely CO_2-free.

Building on the work of Filho et al. [3], our team has previously demonstrated the proof-of-concept of manganese production in hydrogen plasma [4] in an arc-melter, a set-up not designed for metal production. This work describes a continued investigation into plasma-based reduction of MnO in a specialized reactor, where the focus is on understanding the reaction mechanisms between MnO and hydrogen plasma.

2. Experimental details

Experiments were carried out in a purpose-built reactor. A simplified sketch is given in Fig. 1. The raw material was charged in a *0.15 litre* water-cooled copper crucible. Above this sits a *500 A* Plasma Systems plasma torch with a pencil shaped tungsten cathode and a copper nozzle/anode. It was operated with a non-transferred arc burning between the cathode and the nozzle creating a plasma jet. In Experiment 1, *300 A – 400 A* arc current was used, and the plasma torch was operated at *5 cm* from the crucible bottom. In Experiment 2, *300 A* arc current was used, and the torch was operated *10 cm* from the crucible bottom. The plasma power and plasma gas composition for both experiments are shown in Fig. 2.

In addition to the plasma gas through the plasma torch, 5 slpm argon flush gas was added through an observation port that enabled continuous video recording and visual observation of the experiments. Initial heating of the reactor was performed with pure argon as plasma gas before H_2 was added. Between the crucible support and the furnace mantle there is a small gap through which gas exits the reactor chamber.

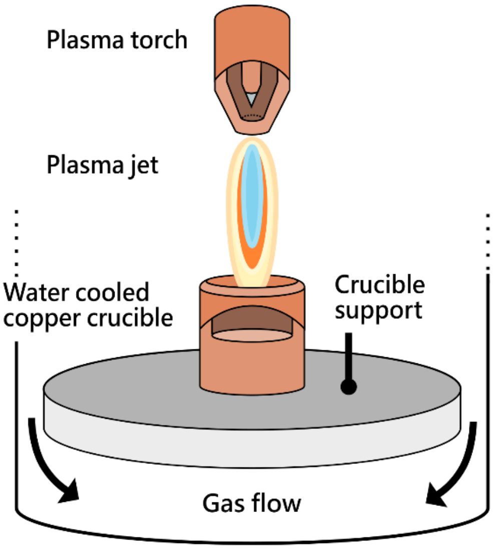
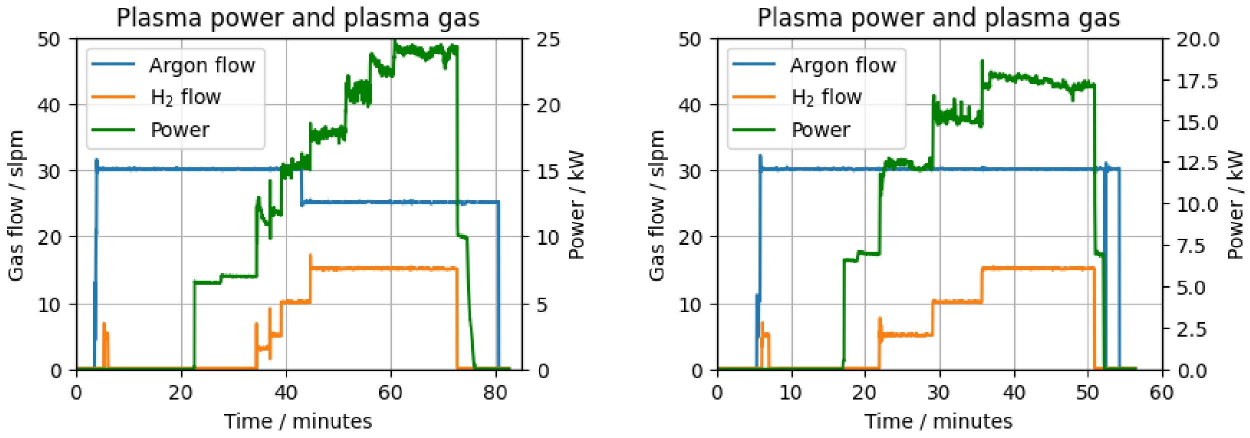


Fig. 1. Simplified sketch of the furnace set-up.



(a) Experiment 1.

(b) Experiment 2.

Fig. 2. Plasma power and plasma gas composition.

The raw material was laboratory grade MnO powder, 99% pure, metals basis (Thermo Fisher Scientific). Due to the strong jet formed by the plasma torch, the MnO powder required pre-treatment to avoid ejection from the crucible. The powder was treated in a spark plasma sintering process and pressed into solid “pucks” of *28 mm* diameter and *~1 cm* height. In Experiment 1, four pucks were distributed on the crucible bottom, while in Experiment 2, five pucks were stacked on top of each other in a “tower” configuration in the centre of the crucible. Samples were extracted from the crucible and the residue from the MnO pucks, as well as from powder gathered from the furnace interior.

The samples were analysed in an electron probe micro analyser (EPMA; JEOL; JXA-8500F) equipped with a wavelength-dispersive x-ray spectroscope. Sample preparation involved casting the entire crucible in epoxy, cutting out regions of interest, and polishing.

3. Results and discussion

General observations

The MnO did not melt under pure argon plasma gas, but upon addition of H_2 the power of the plasma increased sufficiently for liquid MnO to form. The liquid region expanded (downwards and outwards) and then remained stable, indicating that thermal equilibrium was achieved. Increasing the hydrogen content in the plasma gas would again rapidly increase the power and the liquid region.

In Experiment 1, this eventually resulted in the copper crucible becoming exposed in the crater forming between the four MnO pucks.

In Experiment 2, the MnO pucks were stacked on top of one another like a tower, and the experiment was ended when the top two pucks where almost molten through, avoiding exposure of crucible to the plasma jet. Liquid material had flowed down the edge of the tower, reminiscent of the wax from a candle.

After both experiments, substantial amounts of fine powdered condensate were found deposited on the crucible, the furnace mantle, and the plasma torch.

Chemistry and microscopic observations

Fig. 3 shows an EPMA image of a spherical, hollow, particle found in the condensate. Similar particles were found in different zones of the furnace; this particle was not unique. The main, grey, phase of this particle was confirmed by EDS to be MnO. The bright spots found inside the main phase was confirmed to be metallic manganese. This is confirmation that hydrogen has reacted with MnO to form Mn.

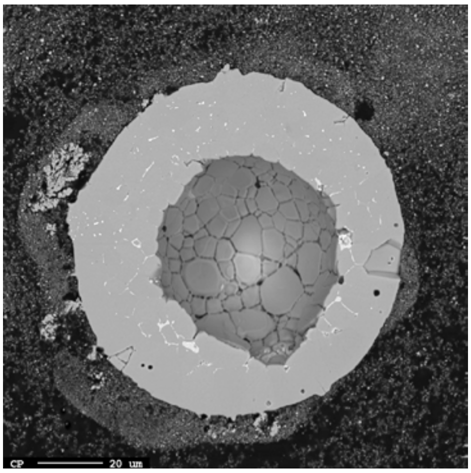


Fig. 3. EPMA image of a hollow MnO-particle gathered in the condensate. The light grey phase (within the slightly darker grey of the particle shell) is metallic manganese.

It appears that metallic Mn occurs along the grain boundaries of MnO, and in the form of droplets on the inside of the hollow particle. It is noted that no metallic Mn has been observed in the outer region of the particle. Several plausible mechanisms may contribute to the observed structure:

- When metallic Mn is removed from the conditions favourable for metal production, it has the potential to back-react with water vapour:

$$Mn + H_2O \rightarrow MnO + H_2 \quad (5)$$

- MnO solidifies before Mn during cooling (melting points *1945 °C* vs. *1246 °C*). For droplets consisting of a mixture of liquid MnO and Mn, MnO will solidify on the droplet surface whereas Mn will be displaced towards the core of the droplet, leading to Mn enrichment centrally in the solidified droplet.
- If the particle is sufficiently large, an outer layer of MnO will limit the diffusion of O, and prevent further oxidation of Mn in the droplet core.
- When the particle contracts during solidification, a void may form in its core.
- The Mn rich particle core and the outer MnO shell contract unequally during solidification and cooling. This may result in a gap forming between the core and the shell, and they may detach from each other.
- If hydrogen or water is dissolved in liquid MnO, this will outgas during cooling/solidification. If the vapour cannot escape, internal pores may form.

An optimistic interpretation of the observations is that the entire hollow centre of the particle at one time was filled with manganese. The thermal expansion of MnO was mapped by [5] and [6]. Near the melting point of MnO there is not much data, but extrapolations indicate a volume contraction of *≈10 %* between the melting point and room temperature. This would be in line with a particle which at room temperature has an outer diameter of *≈280 μm* outer diameter and *≈160 μm* pore diameter (which is approximately what is seen inf Fig. 3) having started out, at the melting point of MnO, as a particle of outer diameter *≈290 μm* and an inner pore of *≈170 μm* diameter. A liquid manganese particle filling the initial *170 μm* inner pore at MnO solidification temperature would, if one extrapolates the results of Korobeinikov et al. [7], shrink to *158 μm* before solidifying, and to *≈145 μm* after solidification and cooling.

From a purely mathematical point of view then, it is possible that a manganese sphere formed within the MnO shell; and shrunk—relatively more than the MnO—so that the resulting Mn particle is smaller than the available space within the MnO. Furthermore, the image in Fig. 3 shows manganese droplets on the inside of the MnO shell. These droplets appear quite rounded, indicating that wetting of the MnO by liquid Mn is poor. Thus, it is plausible that a shrinking Mn sphere would adhere weakly to the MnO shell. A loosely adhered Mn sphere would dislodge during sample preparation and consequently go un-detected during image analysis.

The observed structure could also be due to gas dissolution. Calculations in FactSage indicate that the solubility of H_2 in liquid MnO is about *0.12 mol-%* at *2500 °C* but only *0.04 mol-%* at the solidification temperature of MnO. For a particle similar to that in Fig. 3, the MnO in the outer shell would have the capacity to contain and degas more than enough hydrogen to fill the volume of the internal *~150 μm* pore. Hence, it is possible that the cavity was caused by gas bubble formation, not metal.

Conclusive evidence has not been seen to prove or disprove the various hypotheses regarding the formation of the void space observed within the MnO particle. It is still unclear whether the void was at one point occupied by metallic Mn or was formed by some other mechanism.

In addition to metallic manganese detected within condensate droplets as described above, manganese was also found in other samples. In fact, these samples have more and larger Mn regions.

Of particular interest were the samples from the “dripping wax” of the MnO-“tower” in Experiment 2. An example image is presented in Fig. 4. Here, for the first time, we have observed metallic manganese not completely encapsulated by manganese oxide. In other words, the metal has been exposed to the atmosphere. The location of the droplet and the fact that the plasma gas is entering from the top suggest that this droplet has avoided exposure to the H_2O rich off-gas. Thus, in effect, the droplet has been kept away from oxygen and back-reaction to MnO has been avoided. In pore channels directly below the incoming gas, any H_2O would be expected to be efficiently flushed away and/or diluted by incoming H_2. This hints at the possibility of designing a reduction process and environment where back-reaction is prevented through careful design of gas flows and/or extra addition of hydrogen.

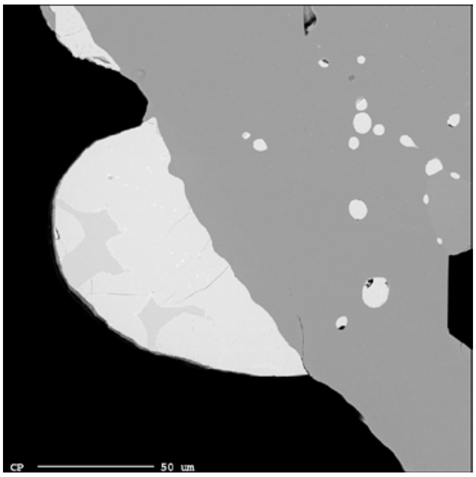


Fig. 4. EPMA image of a Mn-droplet on MnO. The two light grey phases are both metallic manganese, the variation in grey-tone is due to varying Cu content.

Surrounding oxide

Fig. 5 shows an image of a condensate sample that illustrates many of the different observed forms of MnO, including the hollow particle seen in Fig. 3. Basically, every tone of grey in Fig. 5 was confirmed with EDS to be

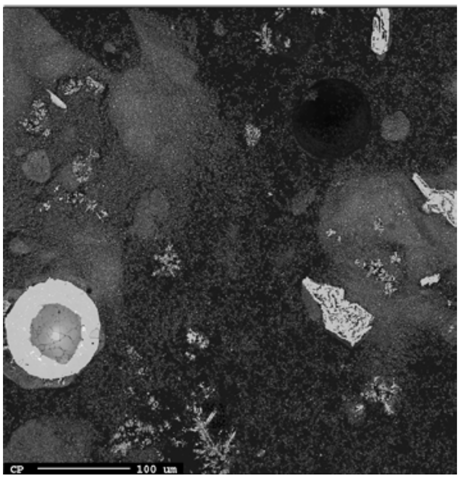


Fig. 5. EPMA image of a hollow MnO-particle gathered in the condensate. The light grey phase is metallic manganese.

MnO, except for the bright phase inside the spherical particle, which as explained above was Mn. The black is the epoxy into which the condensate was cast. It is evident that several different mechanisms have led to the formation of MnO. The finely distributed sub-micron spheres are believed to have originated from the gas-phase. They possibly originate from evaporated MnO that simply re-condenses, but their origin may also have been gaseous Mn. The boiling point of Mn is at *2062 °C*, but the vapour pressure above pure liquid Mn is considerable even at lower temperatures. Thus, liquid Mn will tend to evaporate. There are two paths from gaseous Mn to condensed MnO that does not involve liquid Mn: 1) Mn gas reacts with H_2O above the boiling point of MnO to produce gaseous MnO which later condenses upon cooling; or 2) Mn gas reacts with H_2O at a temperature above the boiling temperature of MnO, which produces solid MnO precipitates at the reaction site.

Observed MnO dendrites, have presumably been created by a different mechanism than the fine powder. Dendritic growth is typical when a solute is abundantly available in a supersaturated atmosphere (in this case gaseous MnO), under conditions where the conditions for growth are more favourable than the conditions for nucleation. It is possible that the dendrites are formed from deposition of supersaturated MnO (either from evaporation of MnO or from reaction of Mn gas with H_2O above the boiling point of MnO), while the fine powder is formed by Mn reacting with H_2O at lower temperatures where it immediately condenses.

Finally, it should be mentioned that in some samples from Experiment 1, significant amounts of copper were detected with EDS. As explained in an earlier section, the MnO “pucks” were completely ablated below the plasma torch, to expose the copper crucible. Hence it is not surprising that copper has entered the system. In samples from Experiment 2, there was much less copper. Copper observed in Experiment 2 is likely to have come from the torch, since the crucible was not exposed to the plasma gas, directly.

4. Conclusions

Small amounts of metallic manganese have been confirmed as parts of the reaction products from experiments with MnO and hydrogen plasma. The reaction mechanisms remain to be adequately explained, but this will be the focus of ongoing work. It is believed that controlling the back-reaction into MnO will always remain of paramount importance. It is thus of considerable importance to determine to what extent the small amounts of Mn found in the experiments described herein was due to small amounts of Mn being initially produced vs. large amounts of produced Mn back-reacting into MnO, as this will dictate where to put our focus in the continuation of this work.

The fact that metallic manganese was found exposed to the atmosphere with no surface MnO-layer indicates that under favourable conditions, the gas flow can perhaps be manipulated to restrict back-reaction.

The results presented here can be viewed with both excitement and apprehension: The demonstration of the production of manganese metal by use of hydrogen carries with it a great promise for sustainable metal production; but only tiny amounts have so far been produced, and the situation around back-reaction is not fully understood. Perhaps both apprehension and excitement are in order.

5. References

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