

Reduction of Zinc Oxide in Manganese Furnace Dust with Tar

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Manganese furnace dust is formed when volatiles and fines are cleaned by wet scrubbers from the off-gases from manganese alloy smelting furnaces. Impediments to the recycling of the manganese furnace dust back to the ferroalloy furnaces are handling due to the presence of tar, and the potential accumulation of zinc in the furnaces, which can cause irregularities in their operation. This paper examines reduction of zinc oxide from manganese furnace dust formed during ferromanganese and silicomanganese production at Tasmanian Electro Metallurgical Company. Zinc oxide was reduced by tar in the furnace dust above 800°C. The reduction rate increased with increasing temperature with almost complete zinc removal at 1100°C. The effects of gas atmosphere, pellet size, pressure applied in pellet preparation, as well as mixing of furnace dust with manganese ore, on zinc oxide reduction and removal were studied.

KEY WORDS: ferromanganese; silicomanganese; manganese furnace dust; zinc oxide; tar; reduction.

1. Introduction

The Tasmanian Electro Metallurgical Company Pty Ltd. (TEMCO), Australia produces about 250 000 tonnes per year of ferromanganese and silicomanganese alloy in three sealed and one semi-sealed ferroalloy furnaces. Wet scrubbing of the off gases from the sealed furnaces produces about 15 500 tonnes of manganese furnace dust per year. This furnace dust is stored in settling ponds, resulting in an environmental liability. About 170 000 m³ of furnace dust has been accumulated in existing settling ponds. TEMCO is developing technologies to utilise the furnace dust and to stop further accumulation and eventually to recover all of the waste.

The manganese furnace dust contains high concentration of manganese oxide. Recycling of manganese furnace dust back into the ferroalloy furnaces would not only reduce an environmental liability caused by its storage, but also decrease manganese ore consumption by utilising the manganese oxide content of the furnace dust. However, manganese furnace dust contains up to 1.5 wt% zinc, which needs to be removed prior to feeding the furnace dust into the furnaces to avoid the detrimental effect of zinc on operation of smelting furnaces.

A few investigations on recycling of manganese furnace dust by sintering were reported in literature. Majercak *et al.*¹⁾ examined sintering of mixtures containing flue dust from the production of high carbon ferromanganese. They achieved a manganese yield of 67–75% and acceptable mechanical strength of the sinter. Chaichenko *et al.*²⁾ reported that addition of 4–6% dry furnace dust or flue dust improved sinter quality and sinter plant productivity. Krivenko *et al.*³⁾ sintered the agglomerated mixture of slime, dust and crushed ferromanganese alloy. The sinter was tested in fer-

rosilicomanganese smelting with positive results. Removal of zinc was also studied by Hjortland and Olsen.⁴⁾ The manganese furnace dust was first micropelletised with addition of calcium dichloride, and then mixed with coke and sintered. They reported more than 20% zinc removal. Further information was however needed on the behaviour of zinc and tar during the sintering of manganese furnace dust.

The characteristics of TEMCO's manganese furnace dust and deportments of zinc balance in ferromanganese and silicomanganese furnaces were reported in an earlier paper.⁵⁾ This paper investigates zinc removal under different sintering conditions. The effects of temperature, gas atmosphere, pellet size, pressure applied in pellet preparation, and mixing of furnace dust with manganese ore, on zinc oxide reduction were examined.

2. Experimental

The sample of TEMCO's manganese furnace dust examined in this paper was taken from the middle of the settling pond, at 30–60 cm in depth. It contained 59 wt% of water. The dried sample contained 32.8 wt% manganese, 1.5 wt% zinc and 19.5 wt% carbon. The furnace dust was dried in oven at 100–105°C for several hours, milled and pressed to form pellets of 15 mm in diameter. In examination of the effect of pellet size, the pellet diameter was changed from 5 to 15 mm. The typical press load was 20 kN; it was changed from 5 to 25 kN to examine the effect of press load on zinc removal rate. Manganese ore was dried, crushed and sieved to examine the effect of its addition to furnace dust on zinc removal. Pellets were formed from manganese ore with size in the range of +45–180 μm mixed with dried and milled manganese furnace dust in different proportions.

Sintering of manganese furnace dust was examined in a vertical tube furnace, a muffle furnace and a thermogravimetric furnace (TGA). In the vertical tube furnace, a pellet was placed in an alumina crucible at the bottom of an alumina tube. Gas flows of air and argon were directed on the top of the crucible through the alumina tube. In the muffle furnace, a sample was placed on an alumina plate, or contained in an alumina crucible, in a static air atmosphere. In the TGA, a pellet was placed in an alumina crucible hanging from the balance and located within the furnace hot zone. A gas flow of air or nitrogen was introduced from the top of furnace tube and ducted out from the bottom. In isothermal sintering, the furnace was preheated to the sintering temperature, and a sample was introduced into the furnace hot zone by lifting the furnace. The furnace was lowered after completion of sintering. In temperature programmed experiments, the sample was located in the furnace isothermal zone at room temperature, and the temperature was ramped to the designated level at a controlled rate. It should be mentioned that the weight loss in the TGA experiments was mainly caused by evaporation and decomposition of tar components, which are volatile and thermally unstable at temperatures above 800°C. This made impossible using the weight loss data for analysis of zinc removal. Zinc removal rate was calculated based on the initial and final zinc contents and the total weight loss after sintering.

The zinc content in a sample was analysed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). About 0.1 g of ground sample was digested into a solution composed of 6 mL HCl, 2 mL HNO₃ and 2 mL H₂O₂ under microwave, and then diluted to an appropriate concentration for analysis. Carbon content was measured by a LECO carbon and sulphur analyser.

3. Sintering of Manganese Furnace Dust

The sintering behaviour of manganese furnace dust was studied in a vertical tube furnace at different temperatures in air with a flow rate of 0.5 L/min. The furnace was heated to the experimental temperatures and a sample was brought into the furnace hot zone. It took approximately 15 min to heat a sample to the furnace temperature where it was further calcined for 5 min. The furnace dust started sintering at approximately 1 000°C. The pellet did not gain strength and could be easily broken when the sintering temperature was lower than 1 000°C. At 1 200°C, the pellet started melting and stuck to the crucible. At 1 400°C the molten furnace dust reacted with alumina crucible, causing the bottom to swell and crack.

Comprehensive sintering tests were also conducted in the sinter pilot plant at the CSIRO Division of Minerals; these results will be reported separately.

Figure 1 shows the appearance of a pellet of manganese furnace dust before sintering, sintered at 1 200°C in a muffle furnace for 15 min, and the section of the sintered sample when it was broken.

At 1 100°C, in both air and argon atmospheres, decomposition and vaporisation of tar components and the decomposition of carbonates resulted in a weight loss of 30–35%. Similar weight losses in both air and argon indicate that combustion of tar inside pellets was not significant.

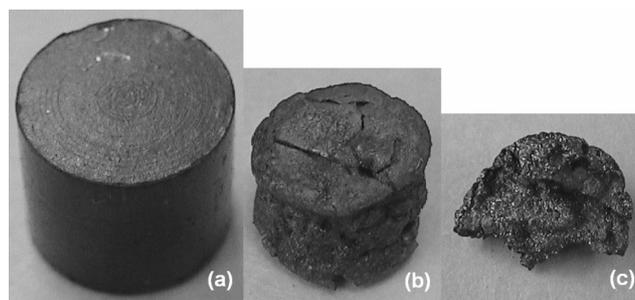


Fig. 1. Appearance of (a) unsintered pellet, (b) pellet sintered at 1 200°C for 15 min, (c) section of broken sintered pellet.

Table 1. Zinc content of manganese furnace dust sintered in a vertical furnace.

Sample	Temperature, °C	Atmosphere	Zn, %
Middle	Ambient		1.50
Pellet	1050	Air	0.072
Pellet	1100	Air	0.034
Pellet	1150	Air	0.029
Pellet	1100	Ar	0.018
Powder	1100	Air	0.528

4. Zinc Removal from Manganese Furnace Dust

Manganese furnace dust contains more carbon (19.5 wt% of carbon, dry basis, most in tar components) than is needed for reduction of zinc oxide (1.5 wt%), presuming that the tar does not combust during heating. Thus no additional reductant was used in the zinc oxide reduction experiments. The effects of temperature, gas atmosphere, pellet size, press load, and addition of fine manganese ore to the furnace dust were examined.

4.1. Effect of Temperature

The effect of temperature on zinc removal from the manganese furnace dust in the vertical furnace is shown in **Table 1**. After 5 min sintering at 1 050°C there was a decrease in zinc content from 1.5 to 0.072 wt%. Increasing temperature to 1 100°C and 1 150°C further decreased the zinc content to 0.034 and 0.029 wt%, respectively.

Results of the effect of temperature on zinc removal experiments conducted in the muffle furnace and TGA are shown in **Figs. 2** and **3**, respectively.

In the muffle furnace, the furnace dust pellets were placed on an alumina or silicon carbide plate or in an alumina crucible for 15–20 min. Zinc removal was negligible at 800°C when the sample was placed on a plate but became significant at higher temperatures (**Fig. 2**). Increasing temperature to 1 100°C resulted in about 60% zinc removal from the pellet on the alumina or silicon carbide plate. There was no noticeable difference between the zinc removal rates obtained using alumina and silicon carbide plates. A remarkable increase in the zinc removal was observed when the sample was contained in a crucible. At 1 100°C, the zinc removal achieved 97.5% after 20 min of sintering and was close to completion after one hour. A similar trend in zinc removal was observed in the TGA, where samples were sintered at different temperatures in air and nitrogen for 10 min. As shown in **Fig. 3**, at temperatures below 800°C, the zinc removal was low at less than 20%. It increased to 90% at 1 000°C and achieved 99% at

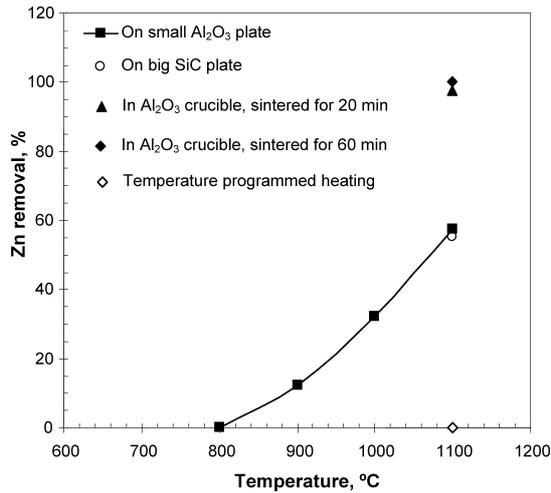


Fig. 2. Effect of sintering temperature on zinc removal. The samples were sintered in a muffle furnace for 15–20 min.

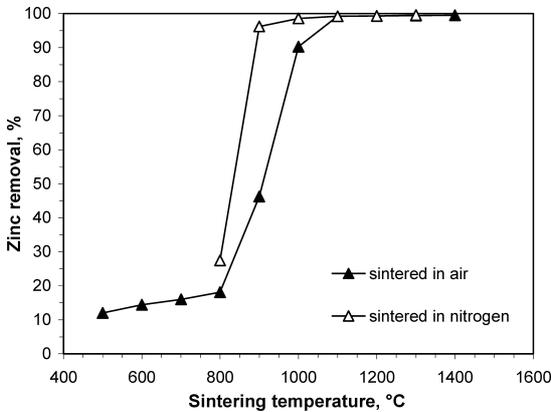


Fig. 3. Effect of sintering temperature on zinc removal. The samples were sintered in a TGA furnace with 0.5 L/min air or nitrogen gas flow for 10 min.

1 100°C. In the temperature interval 800–1 000°C, removal of zinc from furnace dust in nitrogen was faster than in air. At temperatures below 800°C and above 1 000°C, the effect of gas atmosphere was not significant.

4.2. Effect of Gas Flow Rate

The effect of gas flow rate on zinc removal rate is shown in Fig. 4. Experiments were conducted in the TGA furnace at 1 000°C in air and nitrogen with a sintering time of 10 min. The gas flow rate changed from 0.5 L/min to 1.6 L/min. For experiments in nitrogen, the zinc content in a pellet decreased with increasing flow rate, although it was quite low (0.02 wt%) at a flow rate of 0.5 L/min. For experiments in air, increasing air flow rate had a detrimental effect on zinc removal.

4.3. Effect of Addition of Fine Manganese Ore

At TEMCO, fine manganese ore is sintered using a moving strand sinter plant. Utilisation of manganese furnace dust in the sinter plant, if feasible, would include mixing of dust with the ore. The effect of addition of fine manganese ore on the zinc removal rate was examined in the muffle furnace. The pellets with different manganese furnace dust-to-ore ratios were sintered at 1 100°C for 15–20 min. The results are shown in Fig. 5. It can be seen that zinc removal

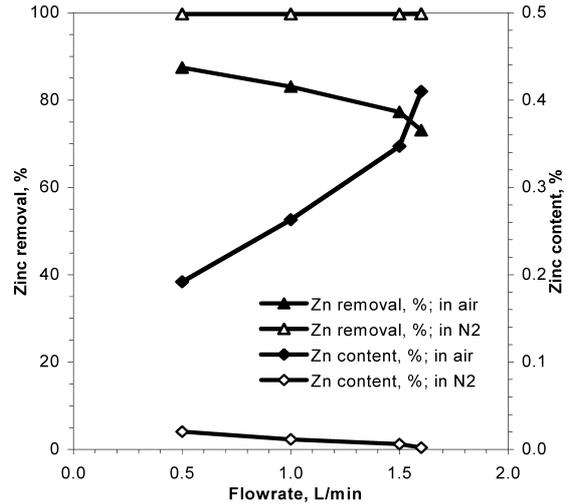


Fig. 4. Effect of gas flow rate on zinc removal of manganese furnace dust pellets. The samples were sintered in a TGA furnace at 1 000°C for 10 min.

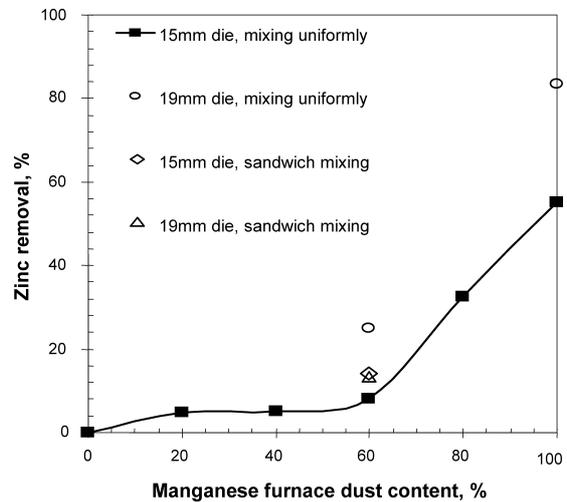


Fig. 5. Effect of manganese furnace dust content in furnace dust-fine manganese ore mixture on zinc removal. The samples were sintered in a muffle furnace at 1 100°C for 15–20 min.

was low when the furnace dust content in pellet was lower than 60%. There was a sharp increase in zinc removal when the furnace dust fraction increased from 60 to 100%. However the removal of zinc was relatively low even for 100% furnace dust pellets because, in these experiments, pellets were placed on an alumina plate. These results are consistent with data presented in Fig. 2.

The effect of furnace dust-to-ore ratios on zinc removal from furnace dust was also investigated in the TGA furnace. The results are shown in Fig. 6. These tests were carried out at 1 300°C for 10 min in air and nitrogen with a gas flow rate of 0.5 L/min. Zinc removal was much higher than in experiments conducted in the muffle furnace. Carbon loss was also recorded. Figure 6 shows that carbon loss rate decreased with decreasing furnace dust content in a pellet when manganese ore content was less than 60%.

4.4. Effect of Pellet Size

The effect of pellet size on zinc removal was studied in the TGA furnace at 1 000°C in air and nitrogen with a sin-

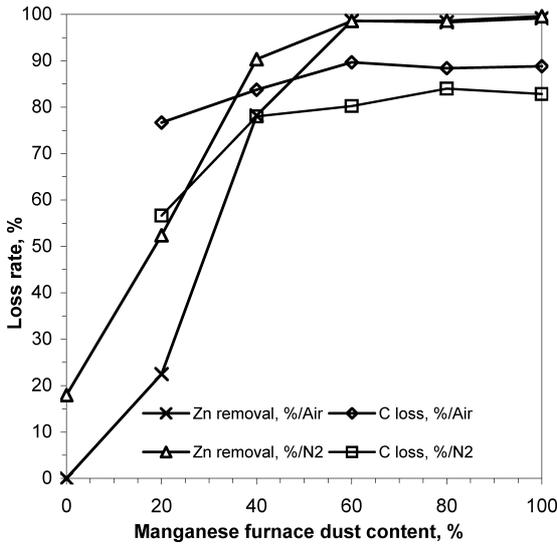


Fig. 6. Effect of manganese furnace dust content in furnace dust-fine manganese ore mixture on zinc removal. The samples were sintered in a TGA furnace at 1300°C for 10 min.

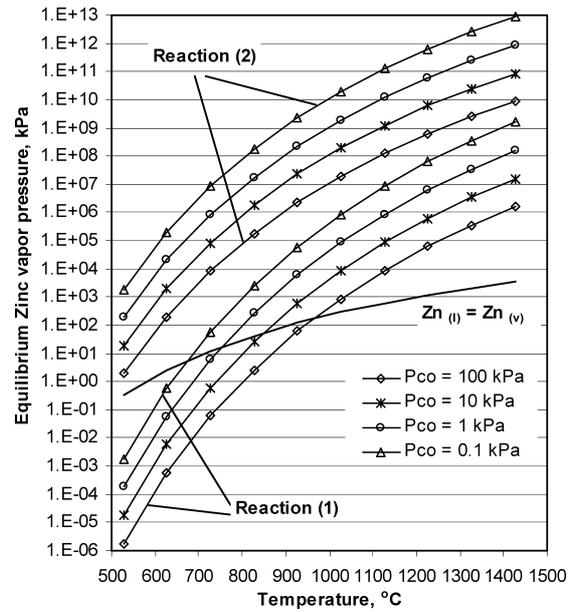


Fig. 8. Equilibrium partial pressure of zinc vapour.

Table 2. Sintering of manganese furnace dust pellets of different diameter in a TGA furnace at 1000°C.

Atmosphere	Pellet diameter, mm	Weight loss, %	C loss, %	Zn removal, %
Air	5	53.6	94.3	61.9
	8	41.9	92.9	69.9
	15	40.3	92.7	87.4
Nitrogen	5	50.9	66.7	99.9
	8	37.9	63.2	99.8
	15	36.2	67.9	99.7

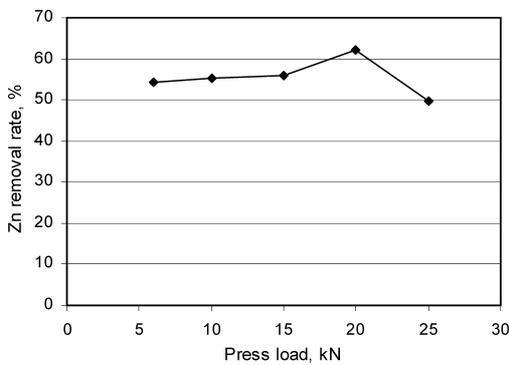


Fig. 7. Zinc removal rates of manganese furnace dust pellets prepared with different press load. The samples were sintered in a muffle furnace for 20 min.

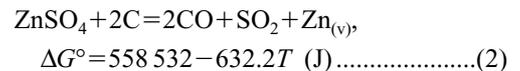
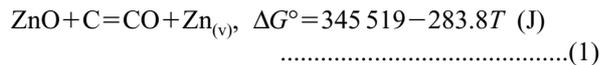
tering time of 10 min. Pellet size was changed from 5 to 15 mm. Results are presented in Table 2. In air, the zinc removal rate increased significantly with increasing pellet size. In nitrogen, the zinc removal was almost complete for all samples between 5–15 mm.

4.5. Effect of Press Load

The effect of the press load in preparing furnace dust pellets on the zinc removal was examined in the muffle furnace at 1100°C. The press load changed from 5 to 25 kN. The results are shown in Fig. 7. No effect on the zinc removal was observed. After 20 min of sintering, the zinc removal was about 57% regardless of the load of pressing.

5. Discussion

Zinc in manganese furnace dust is present in the form of ZnO and ZnSO₄ in the 2 : 1 ratio.⁵⁾ Tar consists of C₁₅–C₂₈ aliphatic hydrocarbons, polyaromatic hydrocarbons with 3–6 rings and their derivatives, and sulphur and oxygen containing compounds.⁵⁾ At the reduction temperatures above 800°C, tar components are volatile and thermally unstable. Carbon from these evaporated tar components and char formed from thermal decomposition of tar acted as a reductant. To simplify the analysis, the activity of the carbon in the tar was considered to be the same as graphite, i.e. unity. Zinc oxide and sulphate are reduced to zinc vapour (Zn_(v)) by Reactions (1) and (2).



The zinc vapour diffuses out of pellets and is removed from the furnace dust. Figure 8 presents the partial pressure of zinc vapour in equilibrium with ZnO or ZnSO₄ and CO calculated from Reactions (1) and (2) at different CO pressures and temperatures. In these calculations the partial pressure of SO₂ was assumed to be the same as zinc vapour pressure. The saturation vapour pressure of liquid zinc is also plotted in this figure. The equilibrium zinc vapour pressure according to Reaction (2) is close to or higher than 100 kPa, what means that Reaction (2) is not limited by thermodynamics. The rate of zinc removal by Reaction (2) is controlled either by ZnO reduction kinetics or by removal of zinc vapour from pellet by diffusion, or their combination.

Reaction (1) is also thermodynamically favoured in a wide range of reaction conditions. For example, at 800°C and CO partial pressure of 10 kPa, equilibrium zinc vapour pressure reaches 10 kPa.

Experimental results are sensitive to the gas atmosphere

and experimental design. For experiments in nitrogen, the sintering atmosphere is reducing. For experiments in air, particularly when a furnace dust sample was kept on a plate, zinc vapour could be reoxidised to ZnO, which could precipitate on the pellet exterior, although in the excess of tar, conditions in the pellet interior were reducing.

Thus temperature and gas atmosphere are major factors affecting the zinc removal.

As shown in Table 1, in a vertical furnace at 1100°C, after sintering in nitrogen a pellet contained 0.018 wt% Zn, while sintering in air under otherwise the same conditions decreased zinc content only to 0.029 wt%. Significantly higher zinc removal rate was observed in nitrogen than in air in experiments in the TGA furnace (Fig. 3): 96% of zinc was removed at 900°C in nitrogen. To achieve the same removal of zinc in air, the temperature had to be 100°C higher.

Removal of zinc from a furnace dust pellet is different from dry furnace dust powder. As shown in Table 1, sintering of furnace dust powder at 1100°C in air decreased the zinc content to 0.53 wt%, while sintering of the furnace dust pellet under the same conditions resulted in decrease in zinc content to 0.034 wt%. Obviously, the major difference in these experiments was sample porosity. Air ingress into the loosely packed furnace dust powder increased the oxygen partial pressure in the sample interior thereby partially reoxidising the zinc vapour.

In a temperature programmed experiment, a furnace dust pellet was heated in the muffle furnace with a ramp rate of 200°C/hour from ambient temperature to 1100°C. As shown in Fig. 2, the zinc content in the sample did not change. In the temperature programmed tests in the TGA furnace, a pellet was heated with a ramp rate of 300°C/h to the final temperature of 1400°C. In air the zinc removal was only 27.1%, while in nitrogen 99.7% of initial zinc was removed. For temperature programmed experiments in air, the tar components were gradually oxidised during the long heating period before the furnace temperature achieved the level at which reduction of zinc oxide started. With the same procedure in nitrogen, tar did not burn-out; char formed in the process of tar evaporation and thermal decomposition was available for reduction of zinc oxide.

Reduction of zinc oxide occurred in both air and nitrogen provided that the gas atmosphere in the sample interior was reducing. In experiments in air it was achieved by pelletising the furnace dust. Indeed in experiments with furnace dust pellets, carbon was not totally consumed. This is shown in Fig. 9 which presents the residual carbon and carbon loss in experiments in air and in nitrogen, in the TGA furnace at different temperatures. The carbon losses in air and in nitrogen were close and not significantly affected by the sintering temperature.

Removal of zinc requires a reducing atmosphere in the furnace. In air, the zinc vapour was reoxidised and deposited on the crucible walls or on the pellet itself if it was on a plate. In experiments in alumina crucibles, deposited zinc oxide formed whiskers. XRD and EDS spectra of whiskers are shown in Fig. 10. Both analyses confirmed that the main composition of the whiskers was zinc oxide. A chemical analysis showed that the whiskers contain up to 77.4% zinc, close to the stoichiometric content of zinc in pure zinc

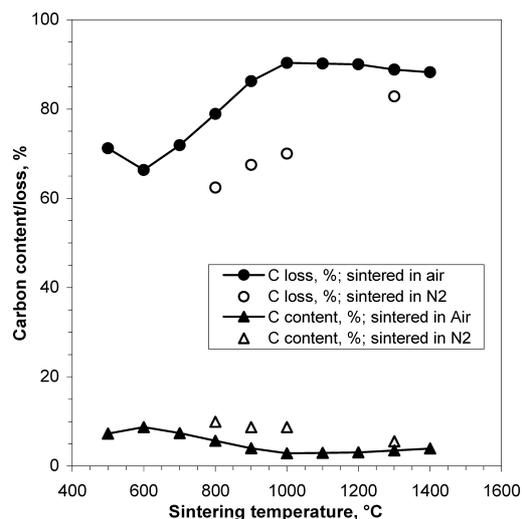


Fig. 9. Effect of temperature on carbon loss of manganese furnace dust. The samples were sintered in a TGA furnace with 0.5 L/min air or nitrogen gas flow for 10 min.

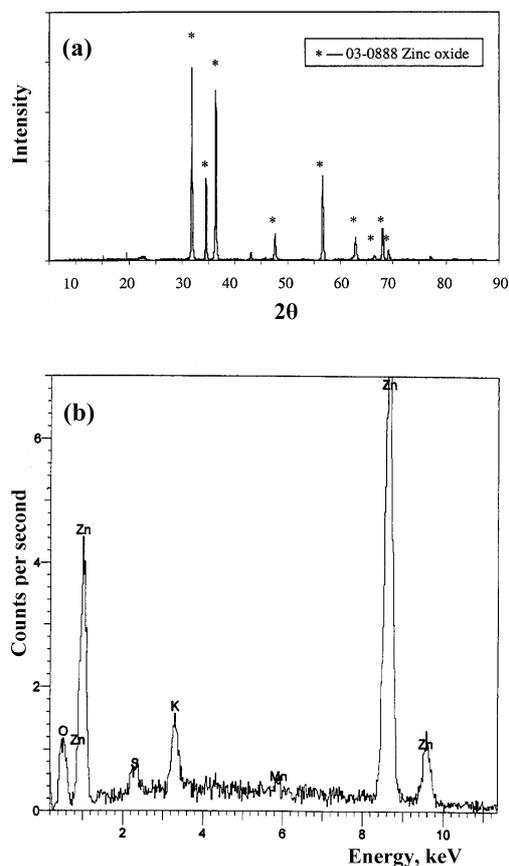


Fig. 10. (a) XRD pattern and (b) EDS spectroscopy of whiskers formed on a crucible during sintering of manganese furnace dust pellet.

oxide, 80.2%.

The effect of adding fine manganese ore to furnace dust on zinc removal is complex. Figure 5 shows a sharp decrease in zinc removal when the fine ore fraction was increased from 0 to 40% at 1100°C in the muffle furnace. In experiments in the TGA furnace at 1300°C, zinc removal was only slightly affected by additions of ore up to 60 wt%, however, it decreased sharply when more than 60 wt% of fine manganese ore was added. This can be explained by

the difference in the calcination temperature and change in porosity of the pellet made from the furnace dust-ore mixture. The pellet porosity increased with increasing ore content, which had a detrimental effect on the zinc removal, particularly in experiments in air, by allowing oxygen to penetrate into the pellet interior and reoxidise zinc. In experiments at 1300°C, when the pellet was partly molten, the pellet porosity was low, and addition of the ore on the porosity was insignificant. When the manganese ore fraction in the pellet exceeded 40–60 wt%, the kinetics of zinc removal slowed down because of lowering zinc concentration in the pellet, and removal of zinc decreased (Fig. 6).

At temperatures used in this research, manganese oxides of the ore can be reduced to MnO and iron oxides to metallic iron.⁶⁾ However, as shown in Fig. 6, carbon loss did not increase along with increase in manganese ore content, perhaps due to relatively low reduction rate and short calcination time. Therefore, reduction of manganese ore was not significant under the experimental conditions of this work. “Dilution” of manganese dust by ore addition and relative decrease of tar did not affect the amount of tar available for the reduction of zinc oxide, with which the tar is intimately mixed in the dust.

6. Conclusions

Manganese furnace dust started to sinter at temperatures above 1000°C. When the temperature was higher than 1200°C, partial melting of manganese furnace dust was observed.

Zinc oxide in manganese furnace dust was reduced to zinc vapour by tar in furnace dust. Temperature and gas at-

mosphere are key parameters affecting the zinc removal from the furnace dust. Reduction of zinc oxide from furnace dust pellets started at 800°C. The zinc removal rate increased with increasing temperature. In the TGA furnace, removal of zinc was close to completion at 1100°C.

Reduction of zinc oxide was observed in air and nitrogen with reduction rates higher in nitrogen than in air under otherwise the same conditions. However, removal of zinc from the furnace dust required a reducing furnace atmosphere.

Optimal conditions for removal of zinc from the furnace dust include: temperature in the range 1000–1150°C, inert gas atmosphere and furnace dust fraction in the furnace dust-manganese ore mixture above 60%.

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