The Behaviour of Selenium Impurities during the Alloying of Aluminum with Manganese Additions

R.I.L.Guthrie
M. Isac
S.A. Sajjadi, and S. Zhao

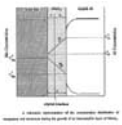
McGill Metals Processing Centre
Montreal, Quebec, Canada

Alloy Briquettes

A schematic of the experimental set-up

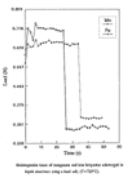
Mn - Al phase diagram

Exothermic reactions and expansion in manganese briquette immersed in melt: a) green briquette, photographs,b, c, d, e, sample withdrawn from the melt, containing its exothermic reactions within the body of the briquette

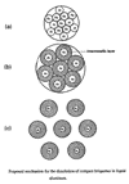


A schematic presentation of the concentration distribution of Manganese and Aluminium during the grouth of an intermatalic layer MnAl

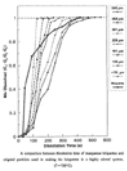
Intermetalic layer which exists around alloying perticles (Mn) during dissolution at high rates of mixing.



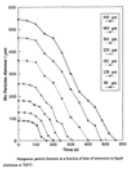
Disintergration times of manganese and iron briquettes submerged in liquid aliminum using a load cell, (T=720 oC)



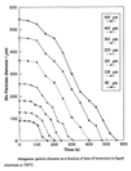
Proposed mechanism for the dissolution of compact briquettes in liquid aliminum.



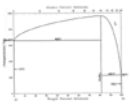
A comparison between dissolution time of manganese briquettes and original particles used in making the briquettes in a stirred system, (T=720 oC).



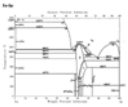
Manganese particle diameter as a function of time of immersion in liquid aluminum at 720oC.



A comparison between experimental dissolution time of iron and manganese in molten aluminum and theorical values predicte based on proposed correlations.



Atomic Percent Selenium



Fe-Se Atomic Percent Selenium

Preliminary tests

Sample No.	Target of %Se	Target of % Mn	% Se analyzed	% Mn analyzed	Smelting Operation	Status of Se addition
1# - solid	0.1	-	BDL	0.002	In air	Pure Se powder
1# - dross	-	-	1.05	0.006	-	-
2# - solid	0.1	-	BDL	0.001	In argon	Pure Se powder
2# - dross	-	-	1.40	0.01	-	-
5# - solid	0.05	7.5	BDL	4.88	In air	0.5%-Se B
5# - dross	-	-	0.49	53.39	-	-
6# - solid	0.01	1.5	BDL	1.08	In air	0.5%-Se B
6# - dross	-	-	0.097	1.14	-	-
7# - solid	0.05	7.5	BDL	5.33	In argon	0.5%-Se B
7# - dross	-	-	0.097	5.91	-	-
8# - solid	0.1	1.4	BDL	1.19	In air	5%-Se B
8# - dross	-	-	0.62	1.32	-	-
9# - solid	0.62	1.4	BDL	0.42	In air	25%-Se B
9# - dross	-	-	2.10	4.44	-	-

COMPOSITIONS OF THE ALLOYING BRIQUETTES

(30 mm dia, 10 mm thick, weight 25-26 gr)

Briquette	Se%	Mn%	Al%
Standard Briquette	0.057	75	25
0.5% Spiked Briquette	0.5	74.62	24.88

EXPERIMENTAL PROCEDURE:

1. Melting temperature 7200C +/_ 50C
2. Add Mn-Al briquettes to 2/20 kg melts of Al
3. After 3 min, stir Al melt for 10 sec
4. Repeat stirring at 10 min and 15 min after the addition of the briquettes

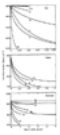
5% Spiked Briquette	5.0	71.25	23.75
25%- Spiked Briquette	25.0	56.25	18.75

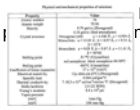
5. Collect dross samples for chemical analysis, and X-ray diffraction
6. Analyze melt samples for Se and Mn
7. Collect fume sample on Cu spiral condenser, and analyze for Se

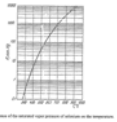
Manganese and Selenium recoveries in aluminum melts and drosses for standard and spiked Mn - Al briquettes

Sample No.	Target Contents of %Se	Target Contents of %Mn	Status of Se addition	%Se Analyzed (AA spectrom)	%Mn Analyzed
11# - solid	0.00114 (11.4ppm)	1.5	0.057%-Se Briquette	0.032	0.83
11# - dross	-	-	-	0.026	0.90
12# - solid	0.01	1.5	0.5%-Se Briquette	0.037	1.05
12# - dross	-	-	-	0.097	1.94
13# - solid	0.1053	1.5	5%-Se Briquette	0.051	1.14
13# - dross	-	-	-	0.32	0.87
14# - solid	0.6667	1.5	25%-Se Briquette	0.13	1.06
14# - solid	-	-	-	2.83	2.09


Melting, vaporization, and
m powder.


Effect of solutes (atom%) on surface tension (dynes/cm, or mN/m) of liquid: iron at 1550oC, copper at 1150oC, and aluminum at about 700oC


Physical and mechanical
nium

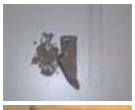

Dependence of the saturated vapor pressure of selenium on the temperature.


1. Adding standard Al-Mn briquettes (0.057% Se)

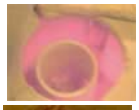

2. Adding spiked Al-Mn briquettes (0.5% Se)


3. Adding spiked Al-Mn briquettes (5wt% Se)

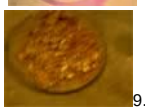

4. Adding spiked Al-Mn briquettes (25% Se)


5. Initial gray colored appearance of dross removed from melt (5% Se spiked briquettes)

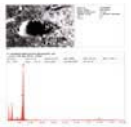

6. Reddish dross on surface of selenium melt -(spiked Mn-Al briquettes (5%Se))


7. Dross formation following addition of Al-Mn spiked briquettes (25%Se)

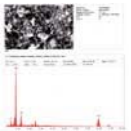

8. Initial gray colored appearance of dross removed from melt (25%Se spiked briquettes)


9. Reddish-Brown appearance of dross after 24 hr contact in air (25%Se spiked briquettes)


10. Reddish-Brown appearance
r contact in air (25%Se spiked


11. 25%Se addition, inclusions, SEM X230 (electron probe microanalysis)


12. SEM of Se deposition on
scale experiment


13. Se deposition on Cu spiral during large scale melting, SEM (5% Se spiked briquettes)


Large scale set-up


Clean copper spiral condenser
Se) briquettes additions to 20 kg


Large scale melting test (20 kg), with -spiked briquettes (5% Se)


Large scale experimental set-up:
enching spiral after test


Examples of acute or chronic Se-intoxication in humans.

Conclusions

1. The dissolution of manganese powder contained in typical Mn-Al briquettes in aluminum melts require about 15 min.

2. For alloying with 'standard' Mn-Al briquettes (0.057%Se),in a small crucible (2Kg), the content of

selenium in the cast aluminum alloy was below the detection limit (50ppm).

3. Preliminary results suggest that the majority of selenium reports to the dross and vapor phases vs cast metal.

4. The concentration of selenium in the dross increased with increasing contents of selenium in the briquettes.

5. SEM of fume deposition during alloy addition indicated the existence of selenium and oxygen (selenium dioxide?). X-rays analyses are in progress.

6. Selenium burns with a blue flame, to form selenium dioxide. The blue colored flame during alloying with Mn-Al briquettes with 5 and 25%Se indicated the presence of selenium dioxide (vapor pressure of selenium dioxide at 317oC is 1 atm).

7. Selenium melts at 217oC and boils at 685oC. The black smoke condensed on the copper spiral indicated the presence of both black amorphous selenium as well as selenium dioxide fume.

8. Selenium dioxide is highly toxic when dust or vapor is inhaled or absorbed through skin.