Molten salt enhanced hydrogen production by using skimmed hot dross from aluminum remelting process

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Content

1 Introduction

2 Experimental

3 Results

4 Conclusions

1.Introduction | hydrogen

◆Current process

1. Natural gas reforming: $CH_4+H_2O=3H_2+CO$

2. Coal gasification: $C+H_2O=CO+H_2$ $CO+H_2O=CO_2+H_2$

Minimization of fossil fuel and consequent carbon footprint

◆Alternative process

Water photolysis

Reforming of biomass

Metallic fuels-aluminum

1. Introduction | hydrogen

$$2Al(s)+6H_2O(I)\rightarrow 2Al(OH)_3(s)+3H_2(g)+16.3MJ/kg \qquad <280^oC$$

$$2Al(s)+4H_2O(I,g)\rightarrow 2AlOOH(s)+3H_2(g)+15.5MJ/kg \qquad 280^oC\text{-}480^oC$$

$$2Al(s,\mathrm{I})+3H_2O(g)\rightarrow Al_2O_3(s)+3H_2(g)+15.1\mathrm{M}J/kg \qquad >480^oC$$

: Problem

Passive oxide layer formed during the reaction

: Solution

Alkaline activation, doping with metals, grinding, etc

1. Introduction | Al/hydrogen

[redacted]: New concept

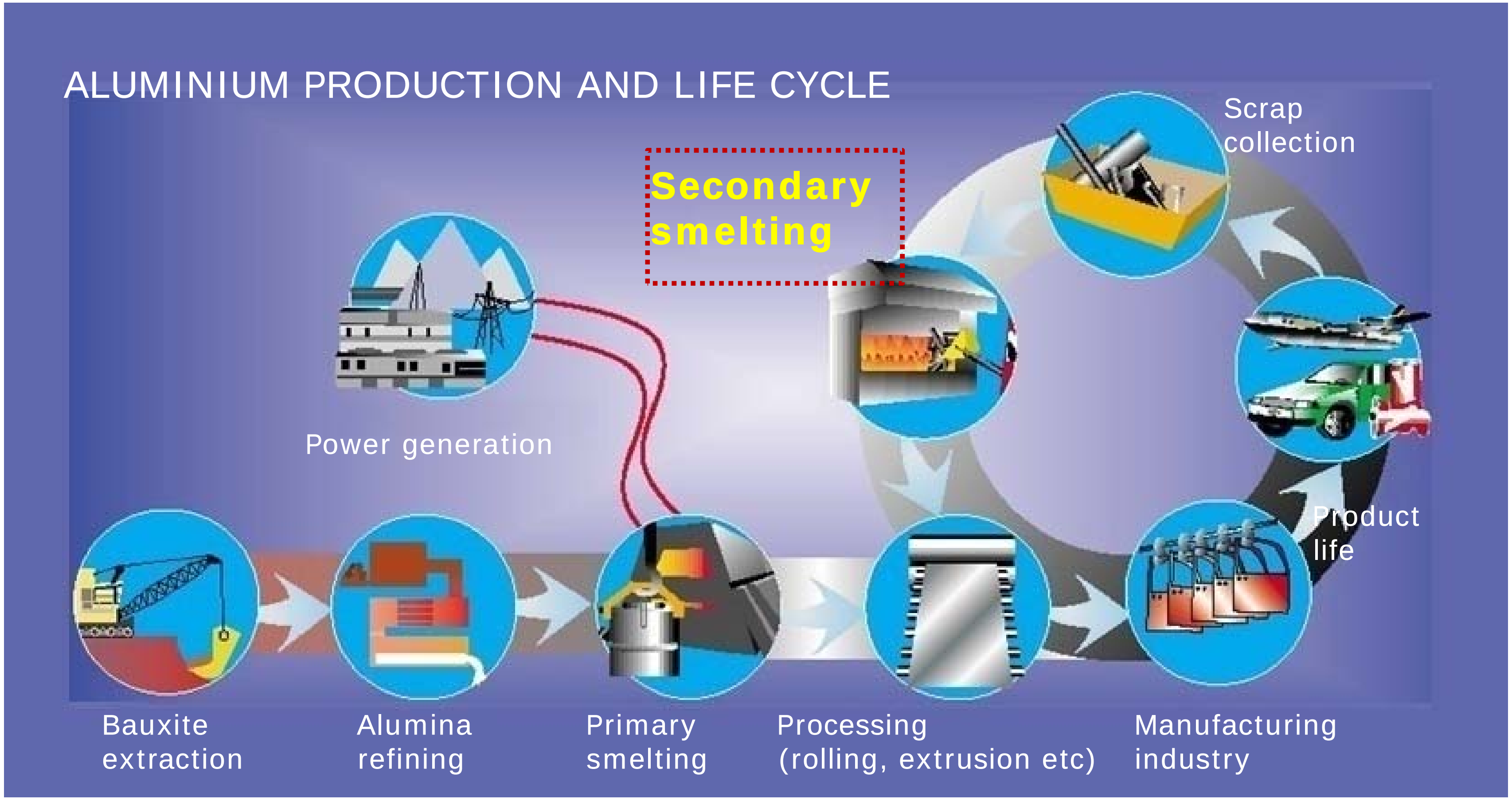
- **High temperature Al/water steam reaction system**

  Additional utilization of Reaction enthalpy to enhance the overall energy efficiency

- **The use of secondary aluminum**

  Utilization of aluminum waste to achieve economical hydrogen production

1. Introduction | Aluminum



1. Introduction | Secondary Aluminum

Abundant metallic aluminum（>45 wt% Al）
and potential heat(> 1.2J/gK)

Low recovery efficiency，aluminum loss within 30-50%！！

1. Introduction | Aluminum dross

Salt flux
- KCl, NaCl, fluroides

aluminum
- Al, AlN, etc

oxides
- Al_2O_3, SiO_2, MgO, etc

Heavy metal
- FeO_x, MnO, TiO_2, CrO_x, etc

→ **pollution**

$$AlN+3H_2O=Al(OH)_3+NH_3$$

$$Al+3H_2O=Al(OH)_3+1.5H_2$$

1. Highly flammable
2. Leachable
3. Increasing disposal costs
4. Environmental regulations

1. Introduction | Features

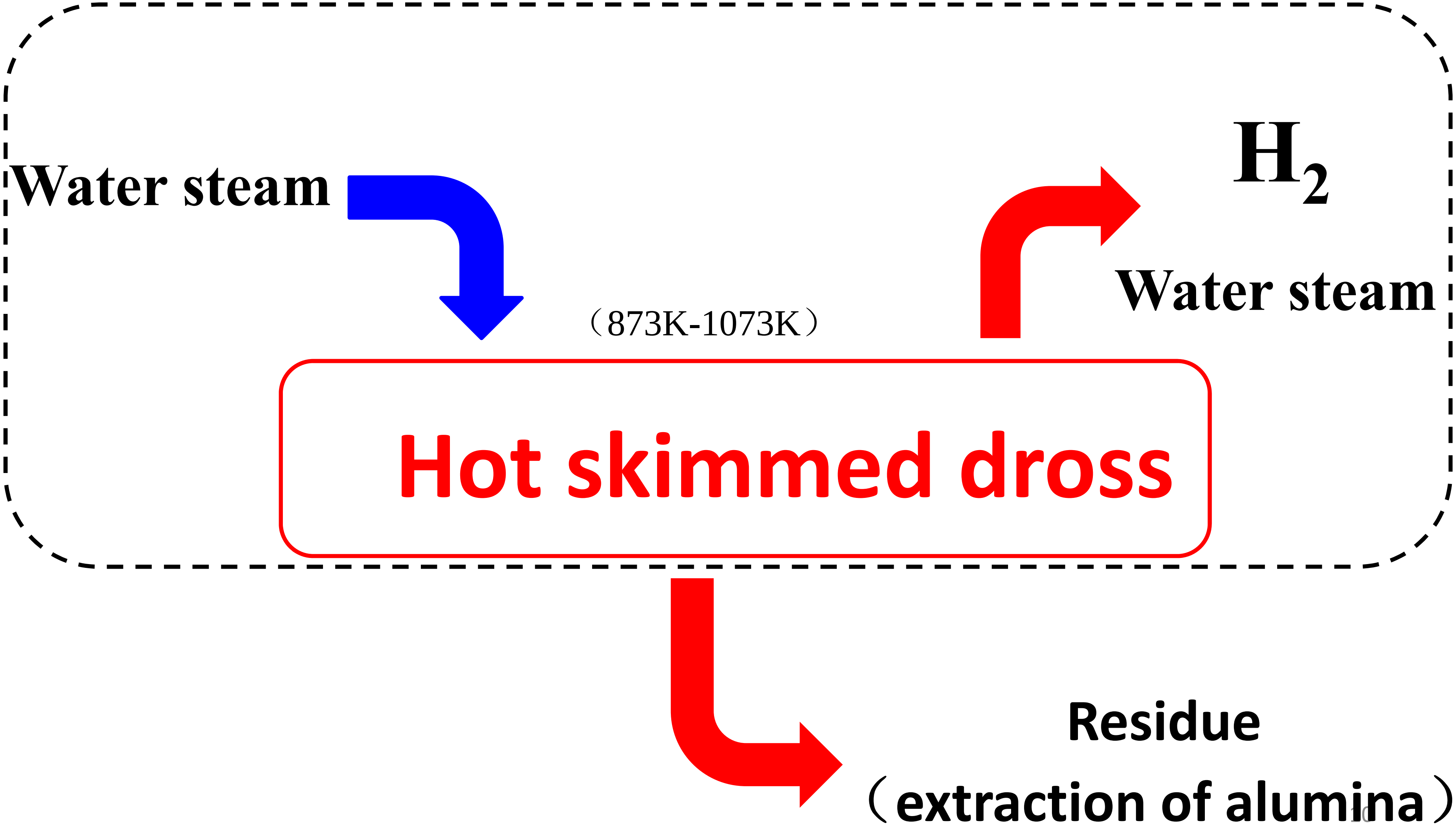
The main features are extracted as follows:

- The skimmed hot dross generated in secondary production of aluminum contains high amount of metallic aluminum and also the potential heat. The conventional recovery with relatively low efficiency causes significant loss of valuable resources and brings environmental concerns.

- The secondary aluminum could be utilized with more beneficial energy efficiency compared with primary aluminum in the hydrogen production.

- The key for Al/water reaction is to ensure continuous hydrogen production by destroying the passive product layer. The salt flux charged during the aluminum remelting process has the ability to remove oxides.

2. Experimental



2. Experimental | Raw material

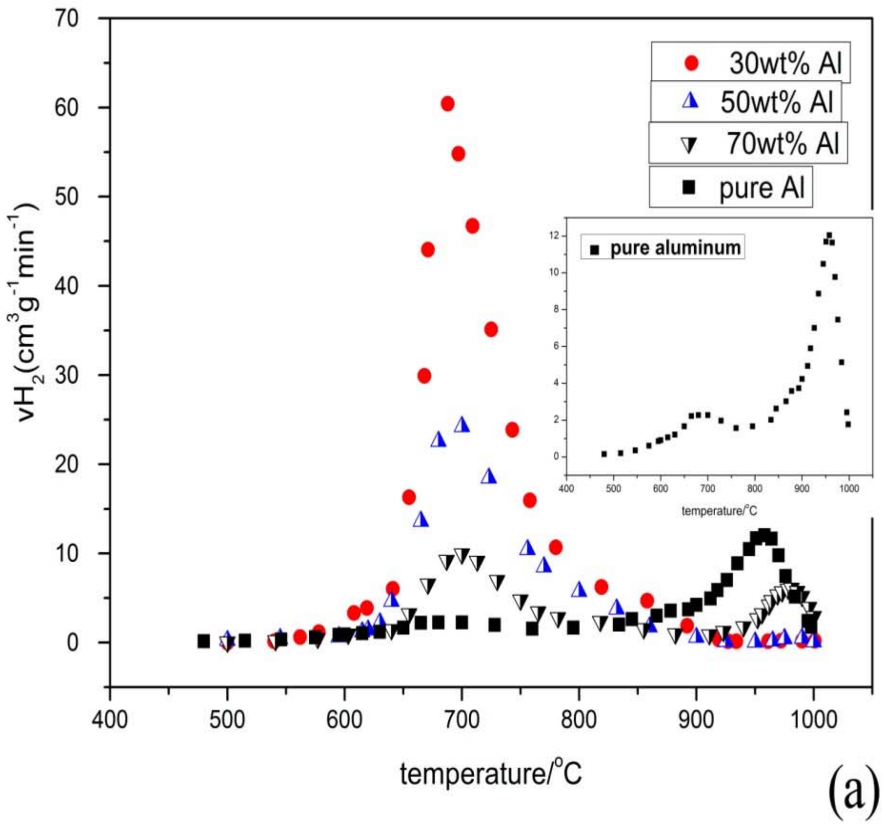
Table 1 Chemical analysis of skimmed dross with 50 wt% Al

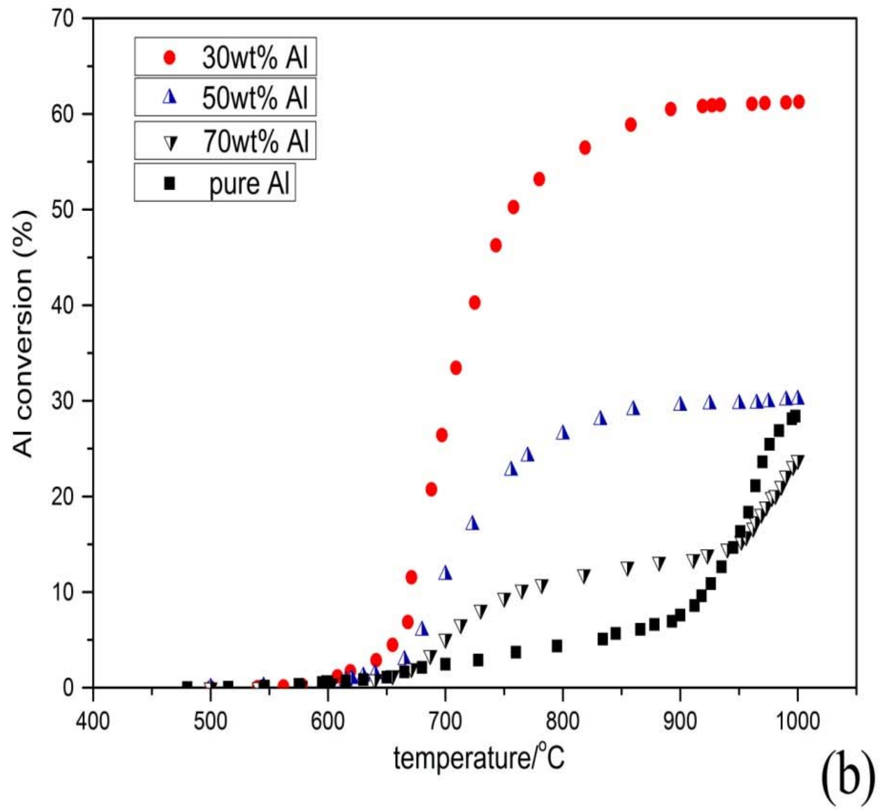
composition	Al_2O_3	AlN	MgO	KCl	NaCl	SiO_2	CaF_2	TFe	Al
wt%	14.58	2.8	1.53	13.5	10.63	2.56	1.11	0.9	50
composition	F	C	S	P	Cu	Mn	Cr	Ti	Zn
wt%	0.12	0.55	0.12	0.25	0.23	0.12	0.02	0.1	0.08

Metallic aluminum 30 wt%, 50 wt%, 70 wt%

salt flux (58.9 wt%, 25.24 wt%, 10.8 wt%)

3. Results | kinetics

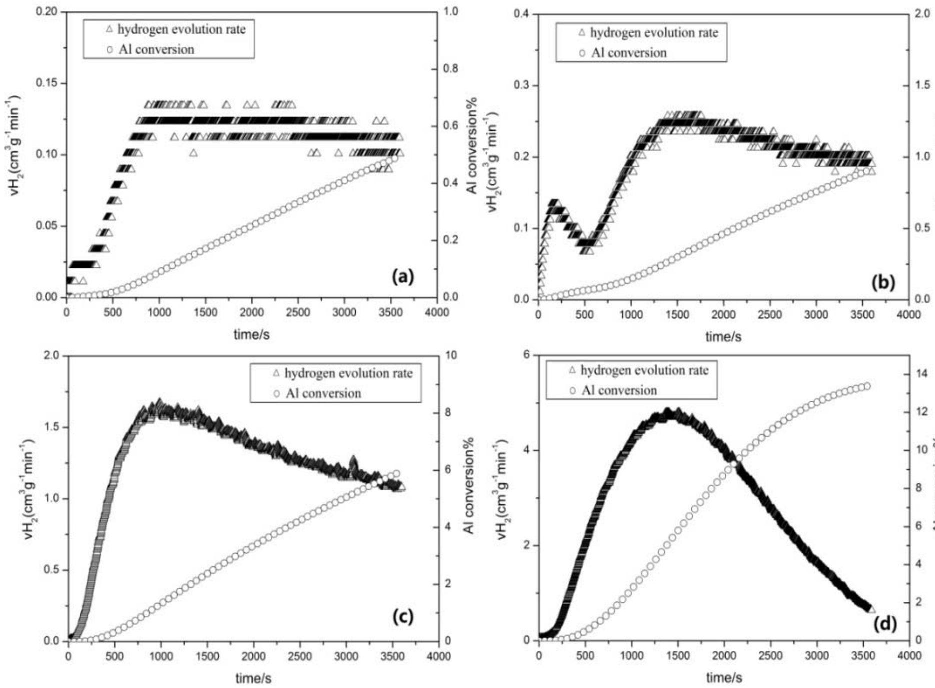




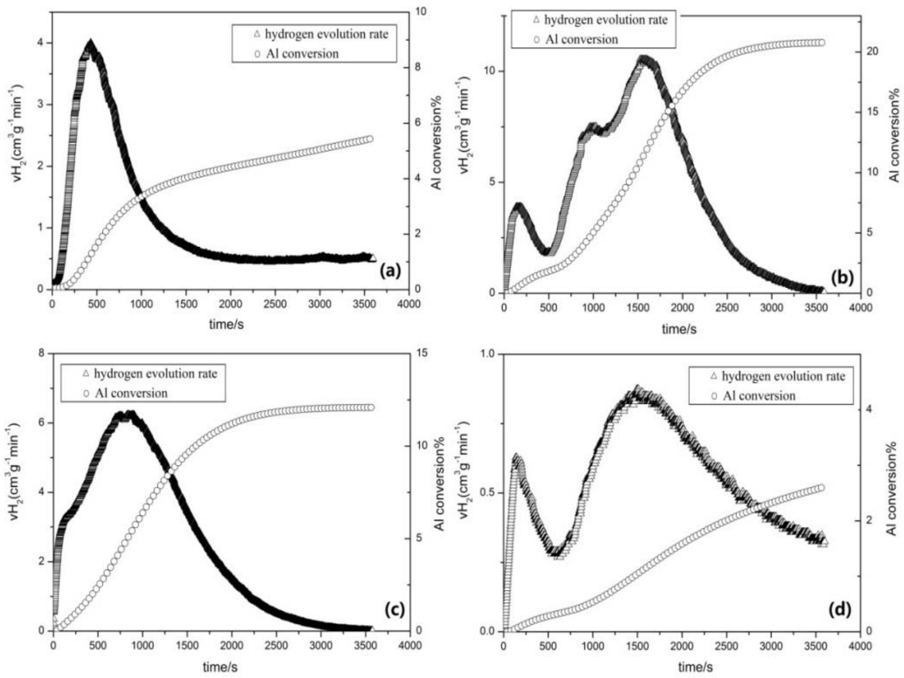
(a) The hydrogen evolution rate and (b) corresponding aluminum conversion of skimmed dross with different amount of metallic aluminum and pure aluminum samples during ramping from 500 °C-1000 °C with a rate of 5 °C min^{-1}.

3. Results | Kinetics

Pure Al



dross



The hydrogen evolution rate and corresponding aluminum conversion of pure aluminum powder and skimmed dross at different temperatures (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C.

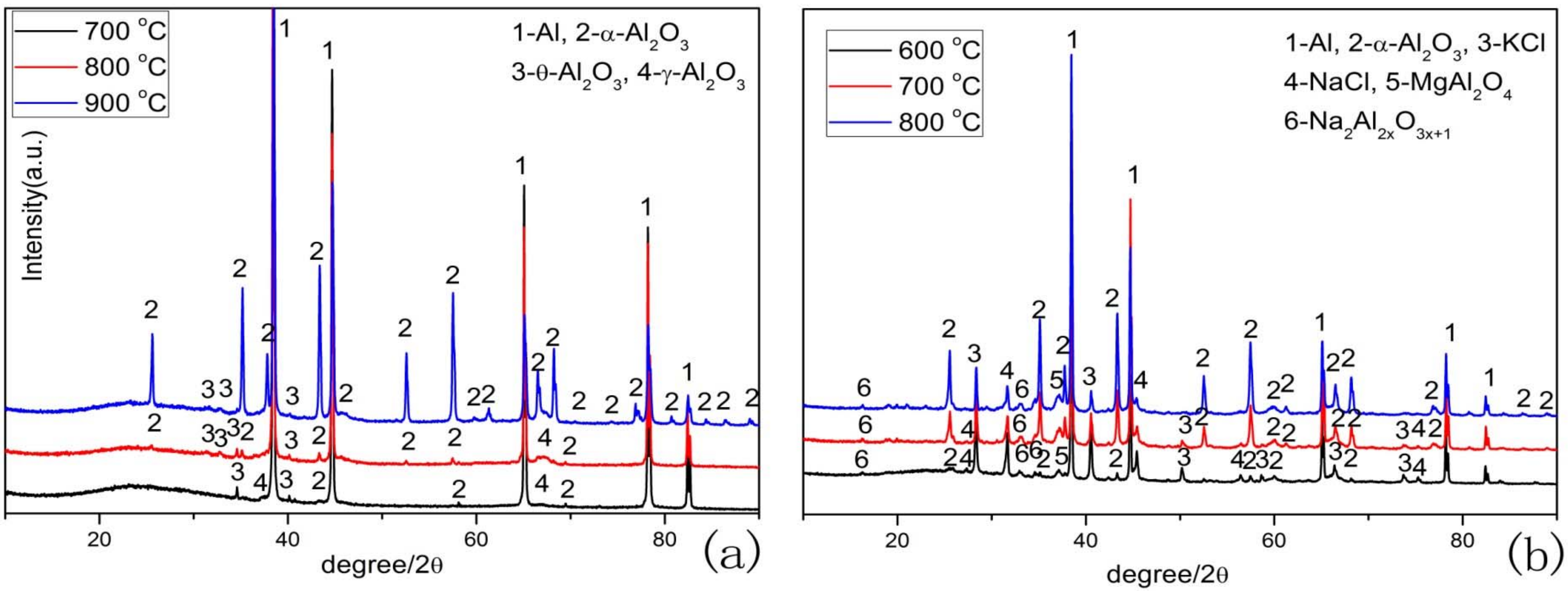
3. Results | Kinetics

1. The presence of salt flux can promote the Al/water reaction greatly in the temperature region of 600-850 ^oC.

2. With addition of salt flux, the Al/water reaction rate is very low in high temperature region of 900-1000 ^oC, as compared to that of pure aluminum.

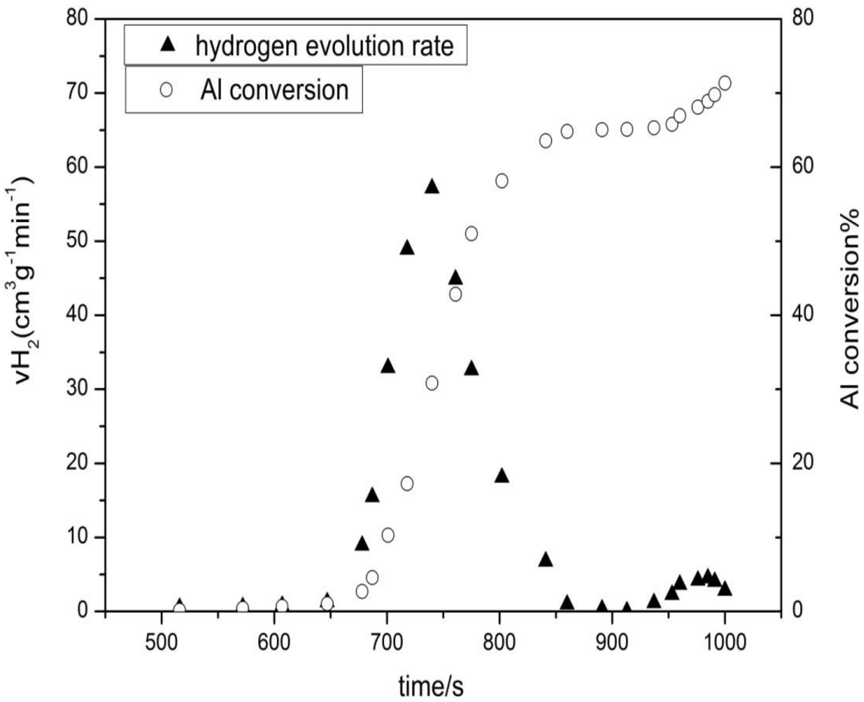
3. The mass ratio of salt/Al present in the skimmed dross has a great influence in the Al/water reaction behavior, more additional salt flux brings more reaction at low temperature region (600-850 ^oC). In the high temperature region (900-1000 ^oC), however, the reaction rate is observed to be lower.

3. Results | Phase evolutions

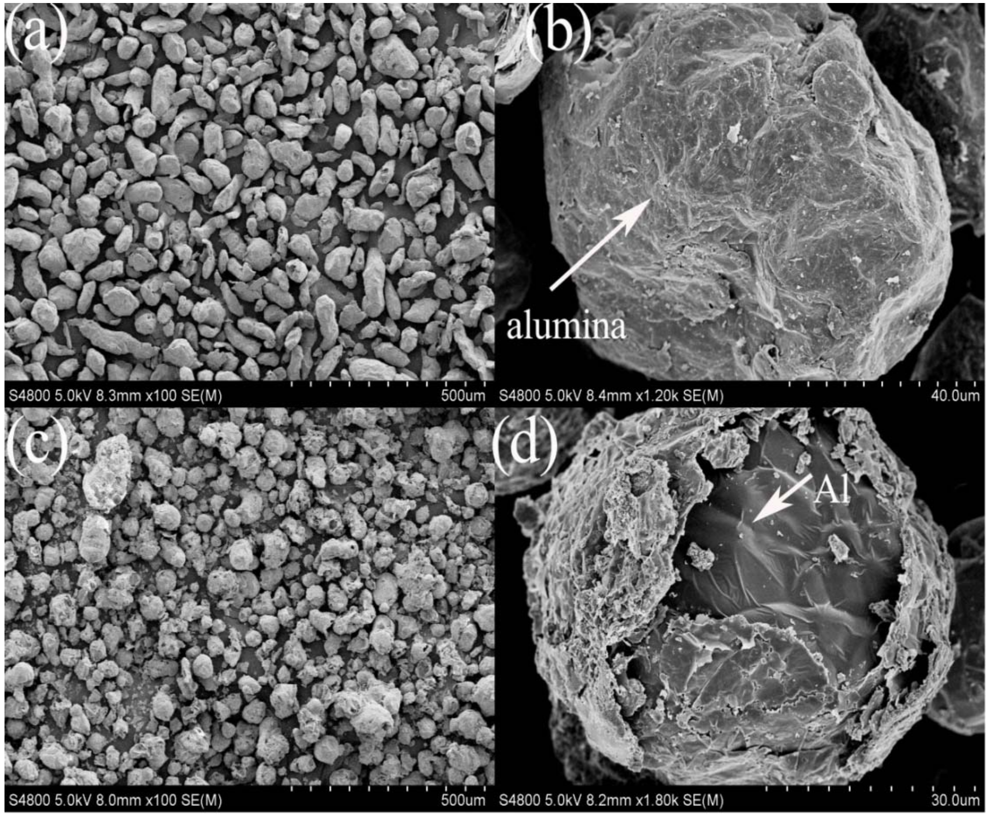


XRD results of (a)pure aluminum and (b)skimmed dross with 50 wt% Al oxidized 1hr in argon-water steam atmosphere at different temperatures.

3. Results | Phase evolutions

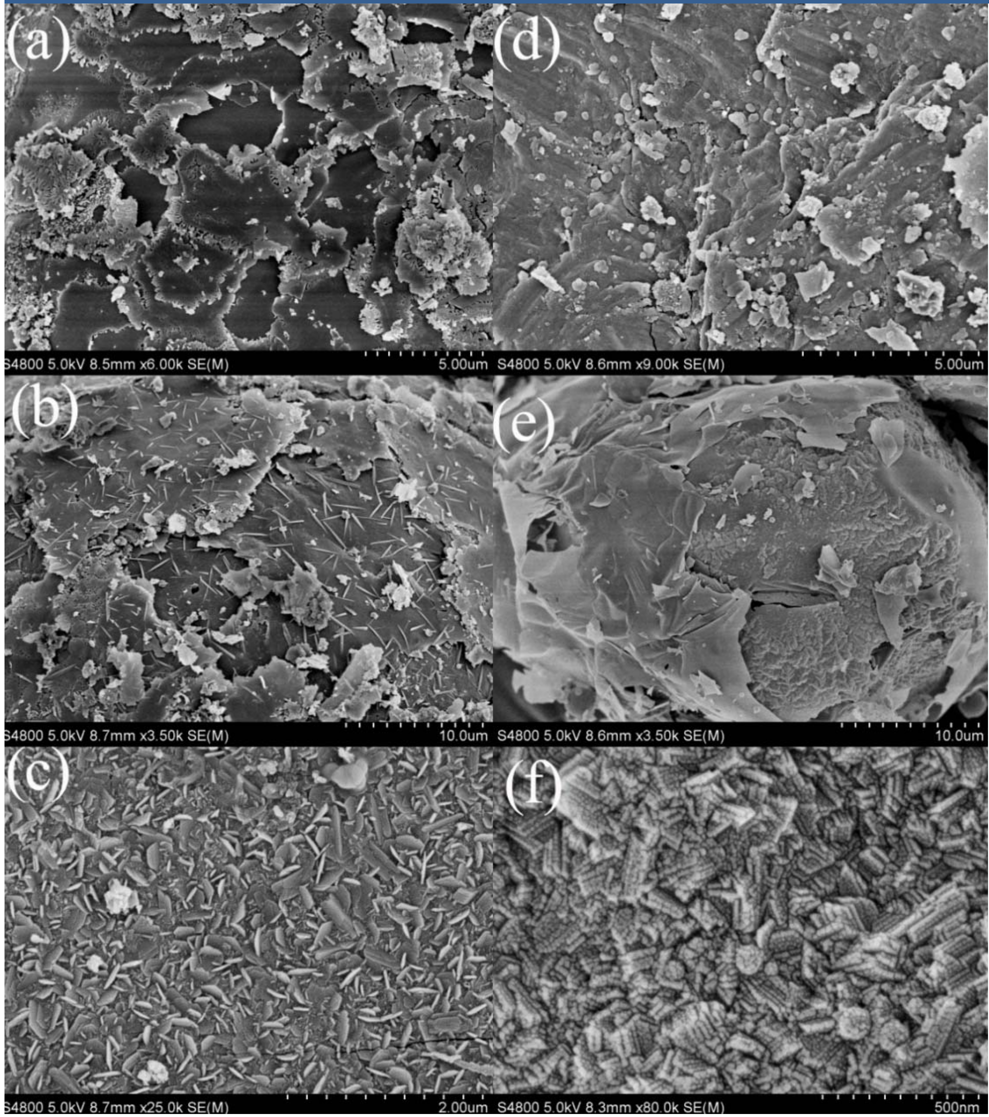


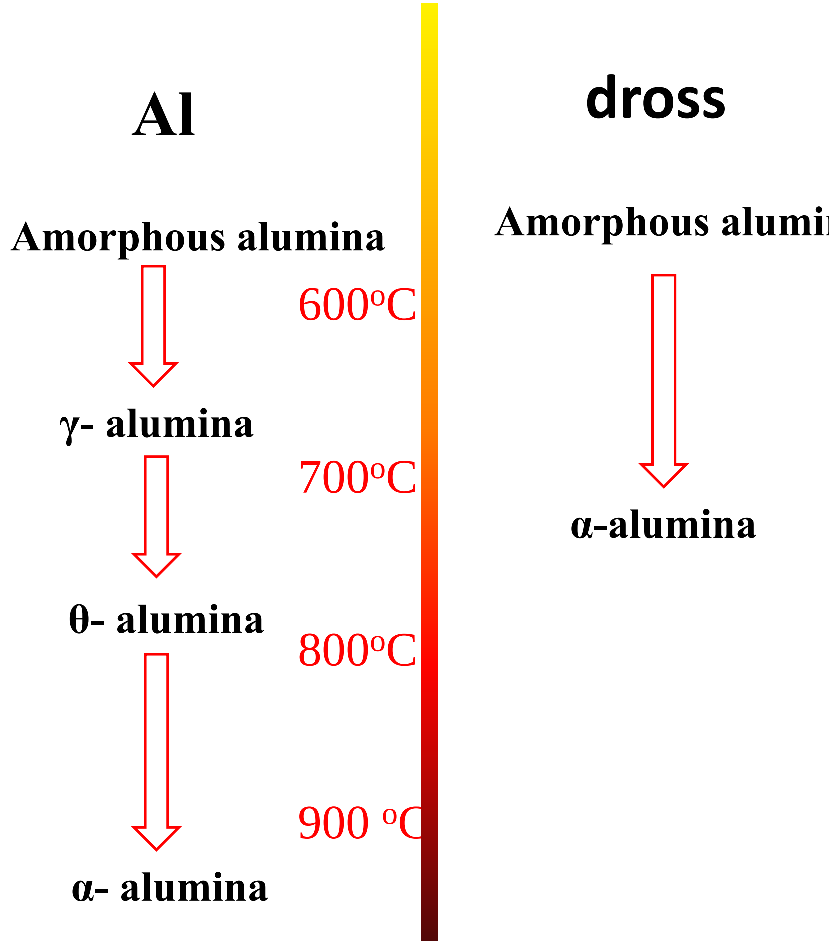
Hydrogen evolution rate and corresponding aluminum conversion of 50 wt% salts-50 wt% Al sample during ramping from 500 ^oC-1000 ^oC with a rate of 5 ^oC min^{-1} in argon-water steam atmosphere.



SEM images of aluminum particles from the reaction of (a, b) pure aluminum and (c, d) 50 wt% salts-50 wt% Al sample in argon-water steam atmosphere after ramping from 500 ^oC to 680 ^oC with a rate of 5 ^oC min^{-1}.

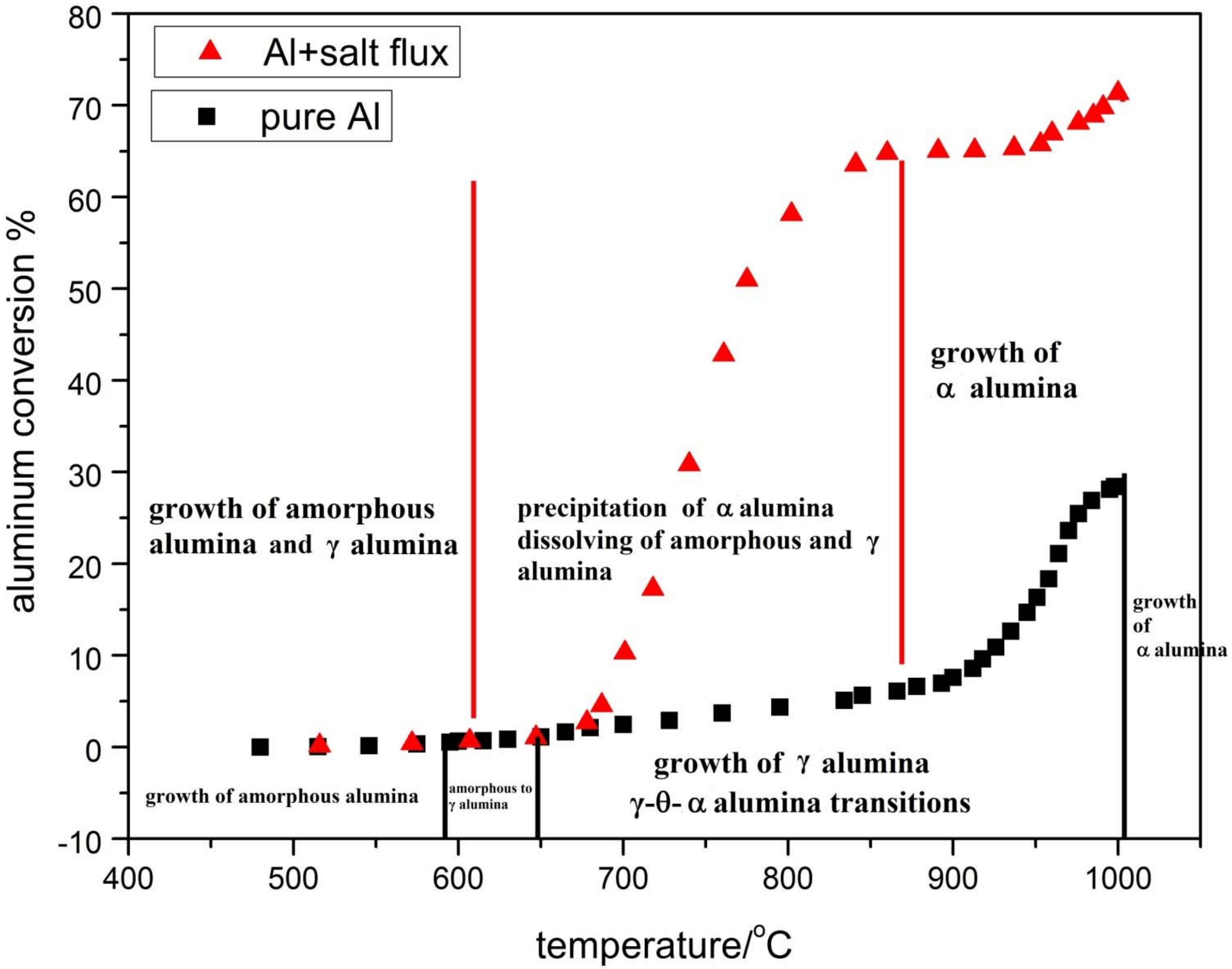
3. Results | Phase evolutions





SEM images of the surface of alumina layer of (a: 600 °C, b: 700 °C, c: 800 °C) skimmed dross with 50 wt% Al and (d: 600 °C, e: 700 °C, f: 800 °C) pure aluminum oxidized by water steam.

3. Results | Phase evolutions



A schematic diagram showing different reaction behavior of Al/water steam at high temperature with or without salt flux addition.

4. Conclusions

water steam

skimmed hot dross

Temperature（650-850 ^oC)

$$2Al(s) + 3H_2O(g) \rightarrow Al_2O_3(s) + 3H_2(g) - 954.8kJ / mol$$

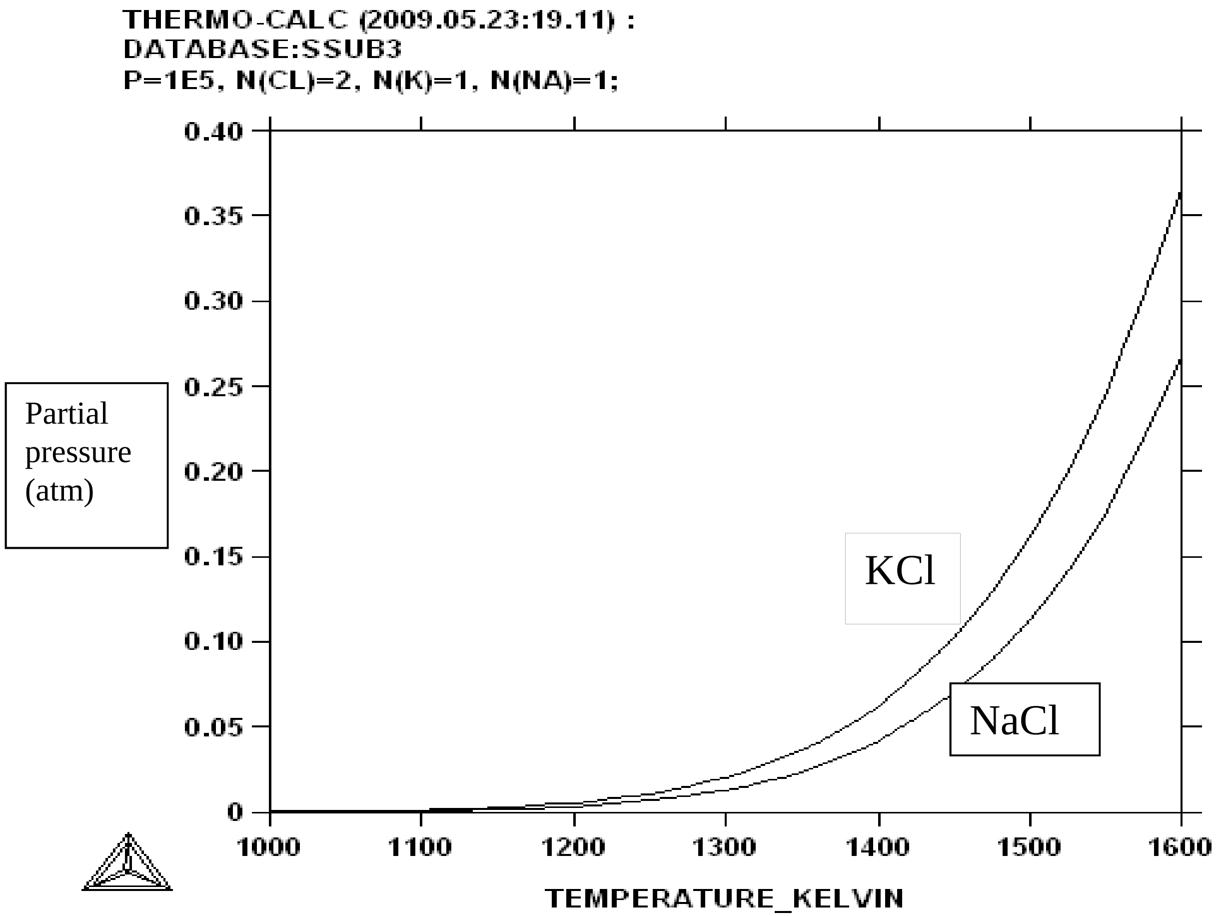
+potential heat

high temperature H_2-water steam → **11.6MJ/kg dross**

alumina rich dross → **1.09kg Al_2O_3/kg dross**


吴韵茶莊

FRASERSUITES


THERMO-CALC (2009.05.23:19.11) :
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P=1E5, N(CL)=2, N(K)=1, N(NA)=1;
Partial pressure (atm)
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0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
KCl
NaCl
1000
1100
1200
1300
1400
1500
1600
TEMPERATURE_KELVIN