白金族金属の新しい分離・回収法の開発

Development of New Separation and Recovery Process of Platinum Group Metals

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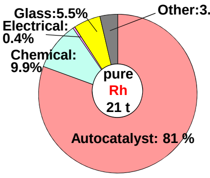
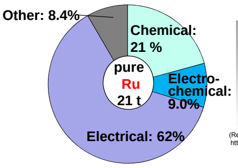
Introduction

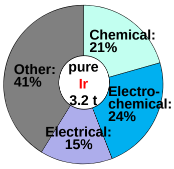
● Demand in the world 2008




Autocatalyst
(Ref. Sumitomo Metal Mining Co., Ltd., http://www.smm.co.jp/product/group/syokubai.html)



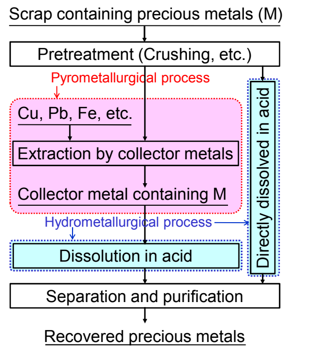

Hard disc drive
(Ref. Fujitsu Co., Ltd., http://pr.fujitsu.com/jp/news/2007/03/14.html)



(Ref: Johnson Matthey, Platinum 2008)


Spark plug
(Ref. Denso Co., Ltd., http://www.denso.co.jp/ja/products/aftermarket/repair_parts/plug/iridiumpower/lineup.html)

● Typical recovery process



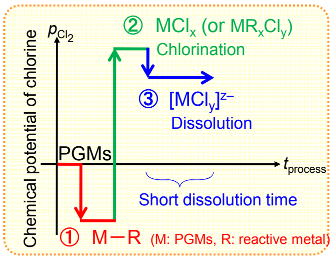
Pyrometallurgical process
- ○ High efficiency & speed
- × High energy cost & large facilities

Hydrometallurgical process
- ○ Low energy cost & easy handling
- × Long processing time & generation of a large amount of waste solution

All recovery processes of PGMs utilizes hydrometallurgical processes.

● Concept of this study

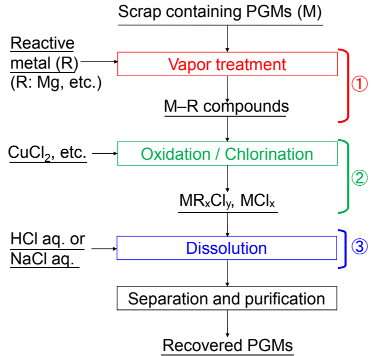
Development of a new process for an effective recovery of PGMs from scrap



① Alloy formation under a highly reducing atmosphere
- ・Pretreatment for selective and efficient chemical reaction of PGMs

② Oxidation / Chlorination
- ・Achieve high dissolution efficiency
- ・Reduce amounts of acids required for dissolution
- ・Pretreatment for fast dissolution

● Flowchart of the new process



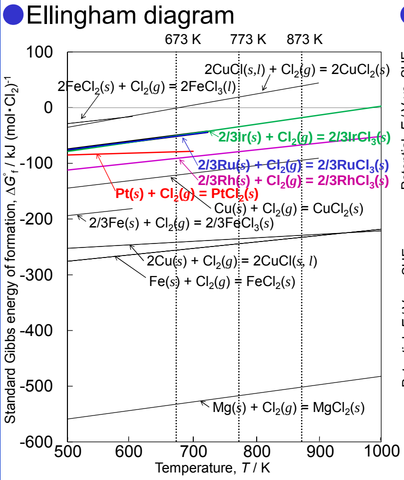
① Alloying (M + R → M–R)
- ・PGMs are reacted with collector metal R supplied through gas phase
- ・The complex chlorides are produced upon chlorination

② Oxidation / Chlorination (M–R + $CuCl_2$ → MR_xCl_y + CuCl)
- ・Oxidation of PGMs to higher valence state

③ Dissolution in solution. (MR_xCl_y → $[RCl_z]^{n-}$)
- ・Dissolve as chloro complex ions into aqueous solution without using any oxidants

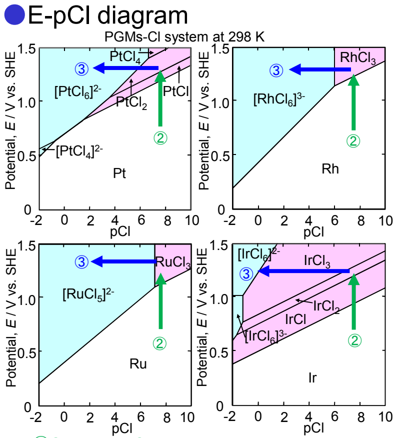
Thermodynamic analysis

● Ellingham diagram



PGMs and Mg can be chlorinated by $CuCl_2$ or $FeCl_3$.

● E-pCl diagram

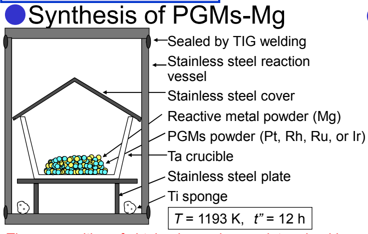


②Oxidation / Chlorination
③Dissolution in Cl^- containing solution

Without oxidizing agent, chlorinated PGMs compounds dissolve in Cl^- solution by forming chloro-complex ions.

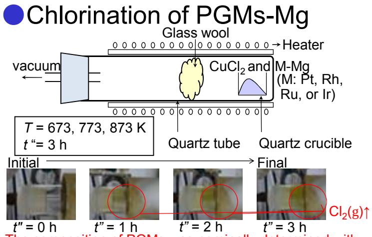
Experimental

● Synthesis of PGMs-Mg



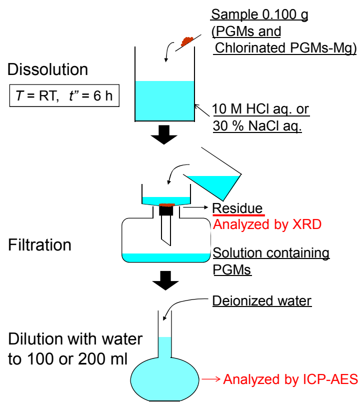
The composition of obtained sample was determined by ICP.

● Chlorination of PGMs-Mg



The composition of PGMs was nominally determined with respect to the mass of the initial PGMs-Mg and obtained sample after chlorination.

● Dissolution experiment



The ratio of dissolved PGMs was determined as follows.

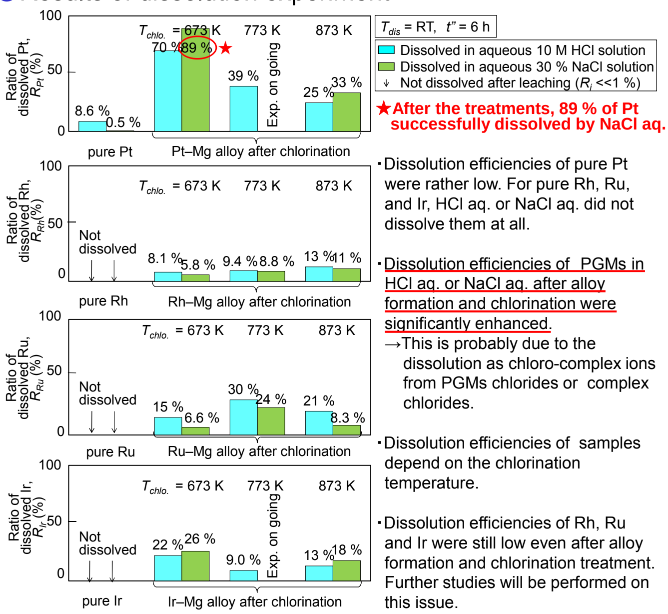
R_{PGMs} (%) = $w_{PGMs,sol}$ / $w_{PGMs,s}$ × 100

$w_{PGMs,sol}$: Weight of PGMs in the solution

$w_{PGMs,s}$: Weight of PGMs in the sample.

Results and Discussion

● Results of dissolution experiment

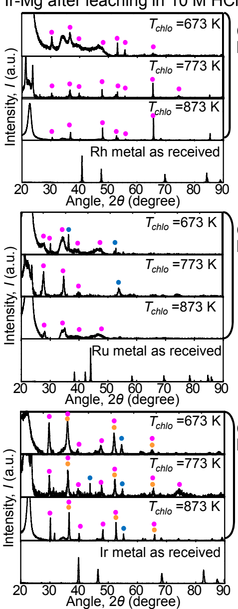


★After the treatments, 89 % of Pt successfully dissolved by NaCl aq.

- ・Dissolution efficiencies of pure Pt were rather low. For pure Rh, Ru, and Ir, HCl aq. or NaCl aq. did not dissolve them at all.
- ・Dissolution efficiencies of PGMs in HCl aq. or NaCl aq. after alloy formation and chlorination were significantly enhanced.
  →This is probably due to the dissolution as chloro-complex ions from PGMs chlorides or complex chlorides.
- ・Dissolution efficiencies of samples depend on the chlorination temperature.
- ・Dissolution efficiencies of Rh, Ru and Ir were still low even after alloy formation and chlorination treatment. Further studies will be performed on this issue.

● Investigation of samples by XRD after leaching

XRD patterns of deposits of chlorinated Rh-Mg, Ru-Mg, and Ir-Mg after leaching in 10 M HCl aq. at RT for 6 h



Chlorinated Rh-Mg after leaching
- ●:$RhCl_3$,

- ・$RhCl_3$ was generated by chlorination experiments.
- ・$RhCl_3$ is insoluble in HCl aq.

Chlorinated Ru-Mg after leaching
- ●:$RuCl_3$,
- ●:not identified

- ・$RuCl_3$ was generated by chlorination experiments.
- ・$RuCl_3$ is insoluble in HCl aq.

Chlorinated Ir-Mg after leaching
- ●:$IrCl_3$, ●:$IrCl_4$,
- ●:not identified

- ・$IrCl_3$ (+$IrCl_4$) was generated by chlorination experiments.
- ・$IrCl_3$ (+$IrCl_4$) is insoluble in HCl aq.

Conclusion

New process for separation and recovery of PGMs by alloy formation and chlorination was investigated.

- ・Dissolution efficiencies of PGMs in HCl aq. or NaCl aq. were significantly enhanced by alloy formation with Mg and chlorination using $CuCl_2$. Formation of PGMs chlorides or complex chlorides probably enhanced the dissolution efficiencies.
- ・Chlorinated Rh-Mg, Ru-Mg and Ir-Mg compounds were dissolved in HCl aq. or NaCl aq. At this stage, dissolution ratios, R_i of compounds were low compared to that of chlorinated Pt-Mg.
- ・Solid residues (e.g. $RhCl_3$, $RuCl_3$ and $IrCl_3$ (+$IrCl_4$)) was obtained after leaching of chlorinated Rh-Mg, Ru-Mg and Ir-Mg compounds after leaching.

Future works

Currently, various chlorination agents and conditions for dissolving PGMs by solutions without strong oxidants are under investigation with the aim of developing a new environment-friendly separation and recovery process.

The future works are as follows.

- ・Select the optimum temperature and chlorination / oxidation agents to synthesize the easily soluble PGMs compounds
- ・Find the effective solution and condition for a successful dissolution of PGMs compounds