Development of New Recovery Process for Rhenium from Nickel-based Superalloy Scraps

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Introduction

Rhenium (Re)

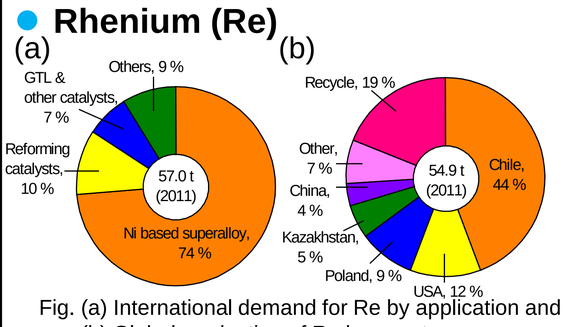
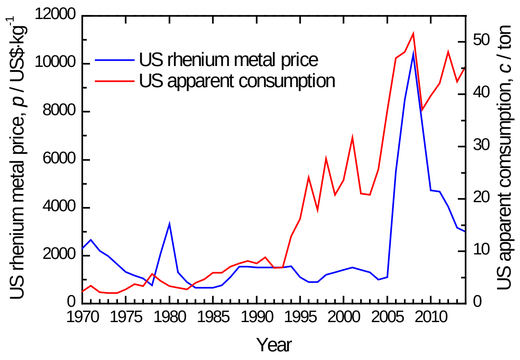


Fig. (a) International demand for Re by application and (b) Global production of Re by country.



Demand for Re has increased rapidly, due to increased Re consumption for Ni-based superalloy production.

Ni-based superalloy

- Excellent mechanical strength
- Creep-resistance at high temperature
- Good surface stability against corrosion

[ref] Honda Motor Co., Ltd, webpage (http://www.honda.co.jp/ tech/new-category/airplane/HF120/)

High pressure turbine blade
⇒Aerospace / Power-generation industries

Superalloy	Compositioin of selected single crystal nickel-base superalloys											
	Re	Cr	Co	Mo	W	Al	Ti	Ta	Nb	Hf	Ru	Ni
CMSX-4	3.00	5.70	11.00	0.42	5.20	5.20	0.74	5.60	-	0.10	-	63
CMSX-10	6.00	2.00	3.00	0.40	5.00	5.70	0.20	7.00	0.10	0.03	-	71
UCSX-1	6.30	2.30	6.00	1.50	7.00	5.80	0.20	8.40	-	0.03	2.00	60
EPM-102	5.95	2.00	16.50	2.00	6.00	5.55	-	8.25	-	0.15	3.00	51
TMS-138	5.00	3.00	12.00	3.00	6.00	-	-	6.00	-	0.10	2.00	63

1) "Global Industry Markets & Outlook 9th Edition 2013", Roskill Information Services Ltd, 2013.

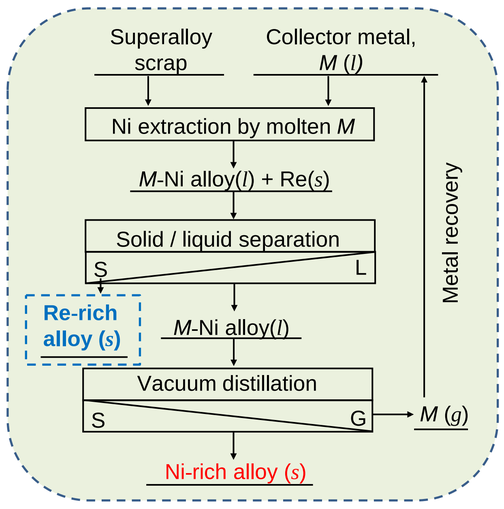
Typical Re concentration is 3 ~ 6 mass%.
(Re concentration in typical ore is only 1 ~ 10 ppm)

Ni-based superalloy is a good source of Re!

Typical recycling process

- **Pyrometallurgical process (current major process)**
  Superalloy scrap is melted with primary alloying metals to produce superalloy ingot.
  ✕ 20 % of Re is lost due to oxidation into Re_2O_7.
- **Cascade use**
  Reuse of superalloy scrap as additive for steel production.
  ✕ Re cannot be recycled.
- **Hydrometallurgical process**
  After dissolution in acid, Re is separated from other refractory metals such as Ta, W and Hf by ion exchange.
  ✕ Toxic waste solution.
  ✕ Long processing time.

New recovery process



- ✓ **No waste solution**
- ✓ **High efficiency**

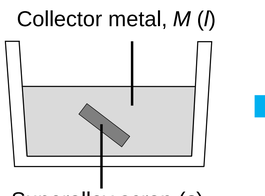
Purpose of this study

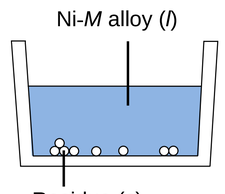
- **To identify the collector metal**
- **To demonstrate the feasibility of the proposed Re-concentrating process.**

Thermodynamic analysis

Collector metal, *M*

Superalloy scrap is immersed in molten *M*,
then Ni-*M* compounds form and Ni is dissolved in molten *M*.

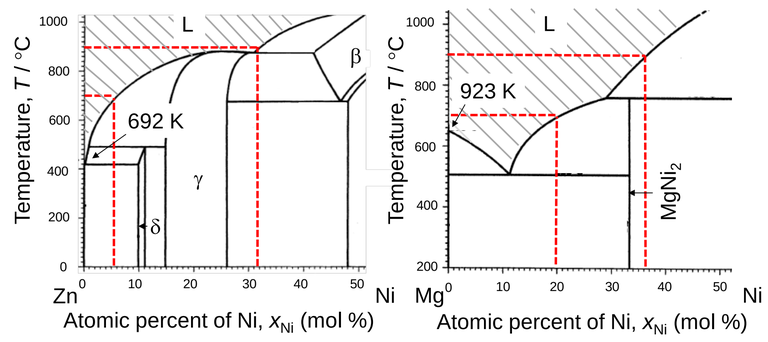


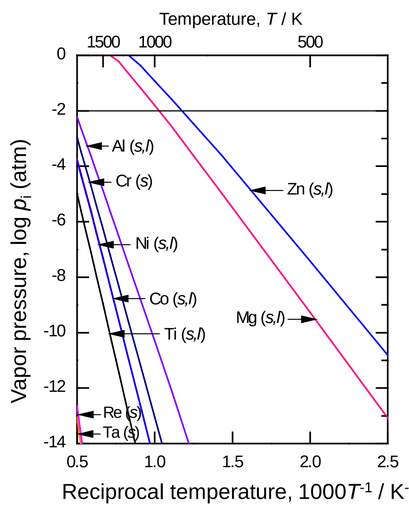


Element, X	M.P., T / K	Intermetallic phase Ni-X	Intermetallic phase Re-X
Cu	1356	×	×
Sm	1345	○	○
Ag	1235	×	×
Ge	1210	○	○
Ca	1112	○	N/A
Ce	1068	○	N/A
Ba	998	×	×
Al	933	○	○
Mg	912	○	×
Sb	903	○	×
Zn	693	○	×
Pb	600	×	N/A
Cd	594	○	N/A
Bi	544	○	×
Sn	505	○	×
Li	453	×	×
In	430	○	○
As	354	○	○
Ga	303	○	×
Hg	234	○	×

Collector metal requirements
- Low melting temperature
- High Ni solubility
- Low Re solubility

Zn and **Mg** were selected as collector metals considering melting temperature, Ni solubility, and Re insolubility





Vapor pressures of Zn and Mg are much higher than that of Ni.

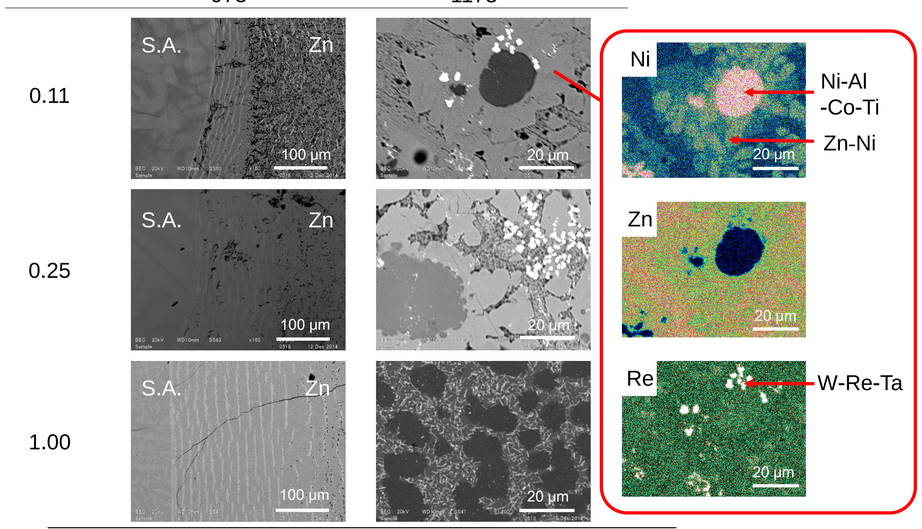
Zn & Mg may be easily separated from Ni by vacuum distillation!

Considering its high vapor pressure and ease of use, Zn seems to be more suitable than Mg as a collector metal.

Re recovery from superalloy

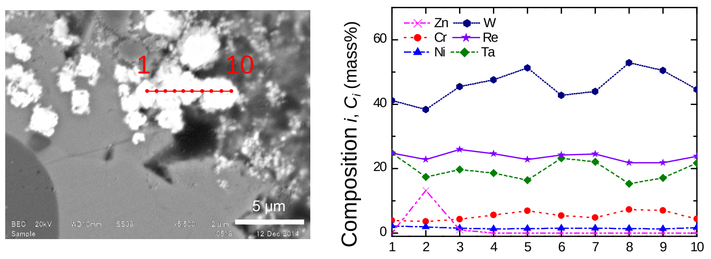
Scrap sample in molten collector metal

Heated with molten Zn for 6 h in a vacuum quartz ampoule



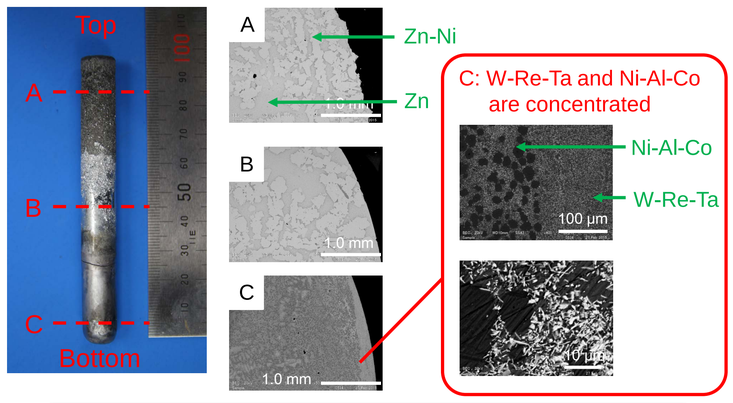
- Zn barely reacted with Ni-based superalloy at 973 K.
- Three intermetallic phases were formed at 1173 K.
  Re can be separated from Ni as W-Re-Ta alloy.
  - Typical Re concentration is 15 ~ 25 mass%.
  - Valuable elements, e. g., Ta and W, can also be collected.

Composition of W-Re-Ta phase



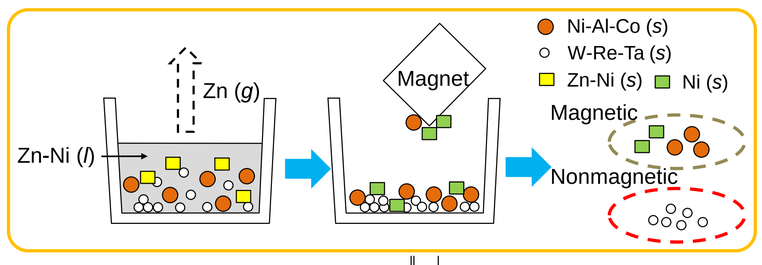
Vertical distribution of intermetallic alloys

Superalloy was heated with Zn at 1173 K for 6 h and then cooled to room temperature in a vacuum quartz ampoule for 12 h.

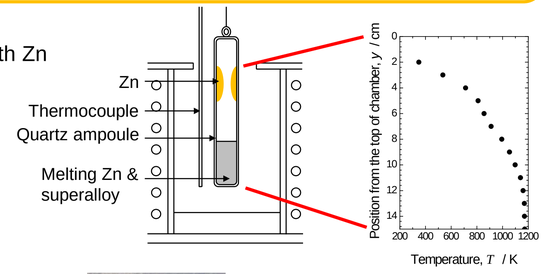


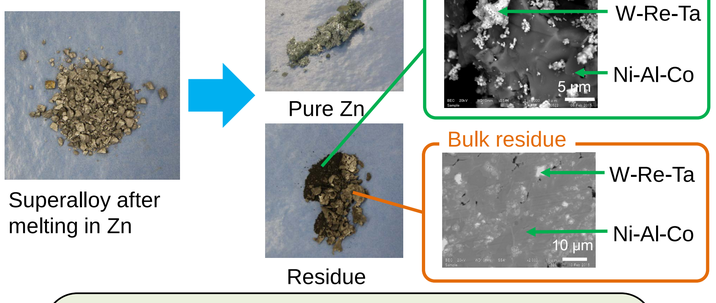
- Heavy alloys such as **W-Re-Ta** are concentrated at the **bottom** of the sample.
- Zn-Ni alloy is concentrated in the upper part.
  ➡ **Separation of Ni and Re was successful.**
  Separation of Ni-Al-Co must be achieved.

W-Re-Ta separation



Heating superalloy with Zn
1173 K, 6 h
⇩
Zn distillation
1173 K, 6 h





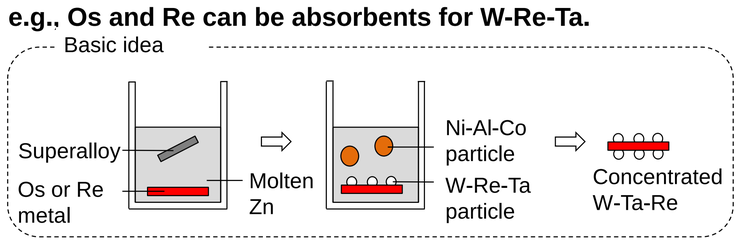
- It was possible to separate Zn in the ampoule by heating with a temperature gradient.
- W-Re-Ta was not separated by magnetic separation because of its strong adhesion to Ni-Al-Co alloy.

Conclusion

- **The feasibility of Re separation from Ni-based superalloy using Zn as a collector metal was demonstrated.**
- **W, Re, and Ta form intermetallic particles in molten Zn. Since these particles have high density, they were concentrated at the bottom of the crucible.**
- **The magnetic separation of W-Re-Ta from Ni-Al-Co following Zn evaporation was unsuccessful. Another method to separate W-Re-Ta from Ni-Al-Co must be considered.**

Future work

- **Re separation process from Ni-Al-Co alloy must be developed.**
  e.g., Os and Re can be absorbents for W-Re-Ta.



- **Ni and Re separation using Mg as a collector metal.**
- **Experimental apparatus to continuously extract Ni and concentrate Re is shown in the right figure.**
  Considering the density difference between Ni and W-Re-Ta, it is possible to obtain concentrated W-Re-Ta particles in the bottom of the upper crucible.