Nickel and rhenium separation from nickel-based superalloy scraps using zinc circulation

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Introduction

Ni-based superalloy

- Excellent mechanical strength
- Creep-resistance at high temperature
- Good surface stability against corrosion
- High melting point (~1700 K)

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

High pressure turbine blade
⇒Aerospace / Power-generation industries

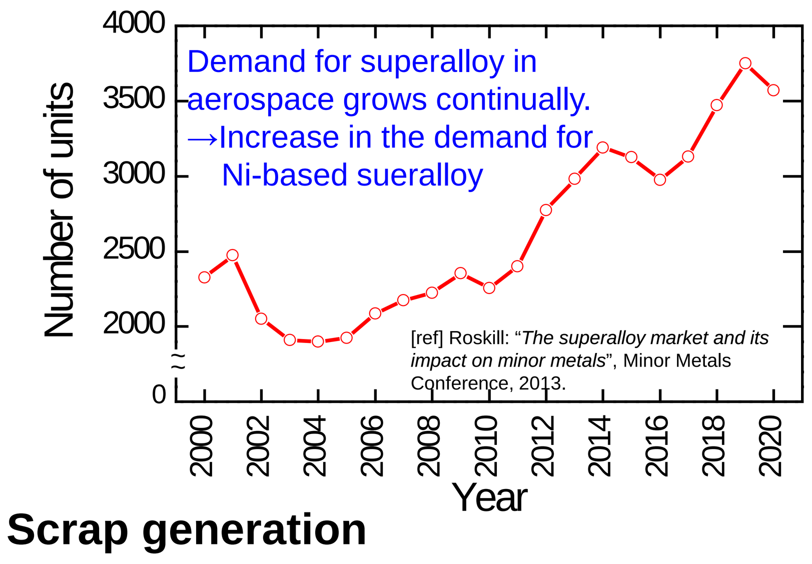
Composition of Ni based superalloy

Superalloy	Concentration of element i, C_i (mass%)								
	Re	Cr	Co	Mo	W	Al	Ta	Ru	Ni
CMSX-4	3.00	5.70	11.00	0.42	5.20	5.20	5.60	-	64
CMSX-10	6.00	2.00	3.00	0.40	5.00	5.70	7.00	-	71
UCSX-1	6.30	2.30	6.00	1.50	7.00	5.80	8.40	2.00	61
EPM-102	5.95	2.00	16.50	2.00	6.00	5.55	8.25	3.00	51
TMS-138	5.00	3.00	12.00	3.00	6.00	-	6.00	2.00	63

Ref) “Global Industry Markets & Outlook 9th Edition 2013”, Roskill

Superalloy contains several rare metals.
Among these metals, rhenium (Re) is one of the rarest and the most expensive metal.
Ni-based superalloy is a good source of Re!

Production of commercial aeroengines



Scrap generation

Primary metals — Superalloy scrap
↓
Remelting
↓
Superalloy ingot
↓
Machining → Scraps
↓
Products
↓
Used products

[ref] O. Çolak: Strojniški vestnik-Journal of Mechanical Engineering, 58.11, 2012, p.683-690.

e.g. Cutting chips

[ref] MBR METALS web page http://mbrmetals.com /products/rhenium-containing-solid-scrap.html

Most of scraps are generated as cutting chips

Recycling process

Remelting process

Superalloy scrap — Primary metals → Remelting → Superalloy ingot

- O Simple
- × Contaminated scrap cannot be used.
- × Quality control is difficult.

Cascade use

Superalloy scrap → Steel production

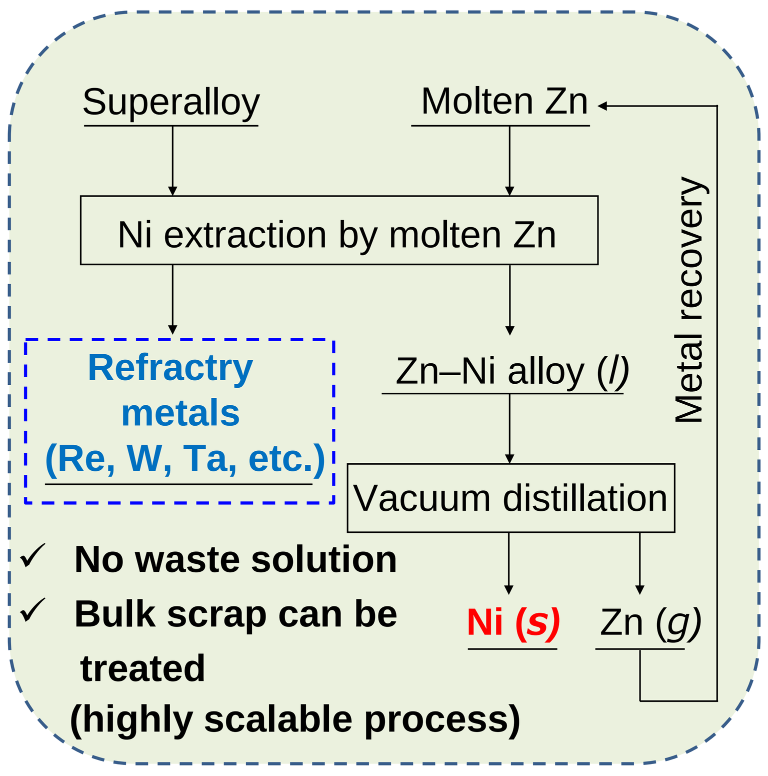
- O Contaminated scrap can be used.
- × Re cannot be recovered and/or recycled.

Hydrometallurgical process

Superalloy scrap → Pulverization → Acid dissolution → Ion exchange etc. → Re

- O Most of elements in superalloy can be separated and recovered.
- × Energy consuming pretreatments are needed.
- × Generation of toxic aqueous waste solutions
- × Long processing time

New recovery process



- ✓ No waste solution
- ✓ Bulk scrap can be treated (highly scalable process)

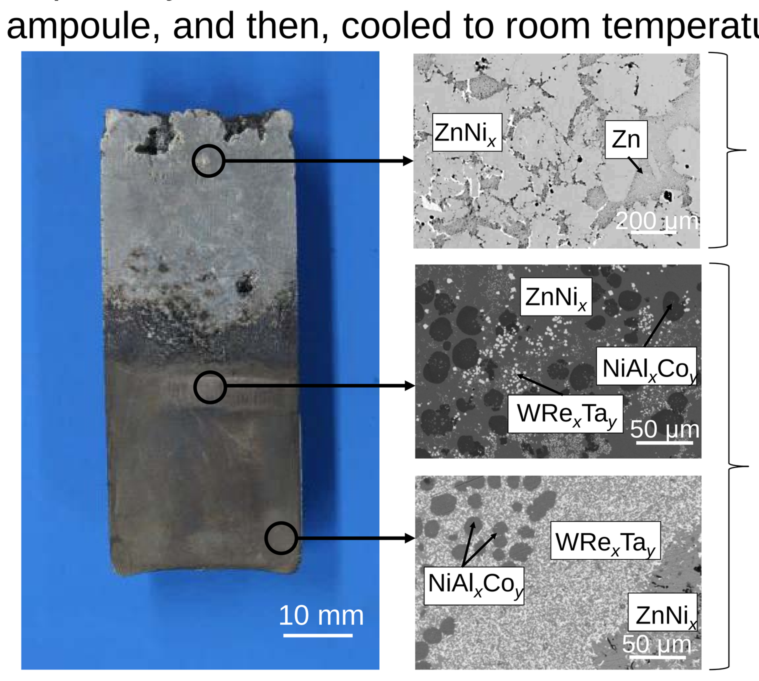
Purpose of this study

- **To demonstrate the feasibility of the proposed Re-concentrating process using Zn circulating reaction chamber.**

Zinc circulation method

Our previous report

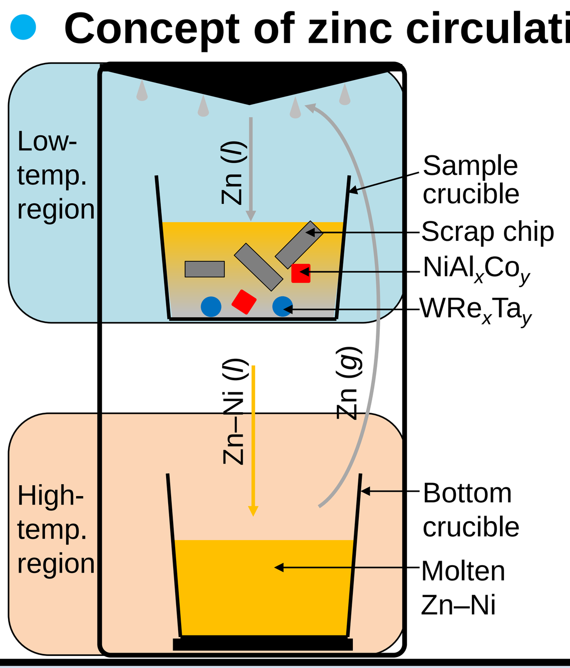
Superalloy was heated with molten Zn at 1173 K for 6 h in a quartz ampoule, and then, cooled to room temperature in the furnace.



Upper part: Zn, $ZnNi_x$ alloy

Middle & bottom part: WRe_xTa_y, $NiAl_xCo_y$, $ZnNi_x$

Concept of zinc circulating reaction chamber



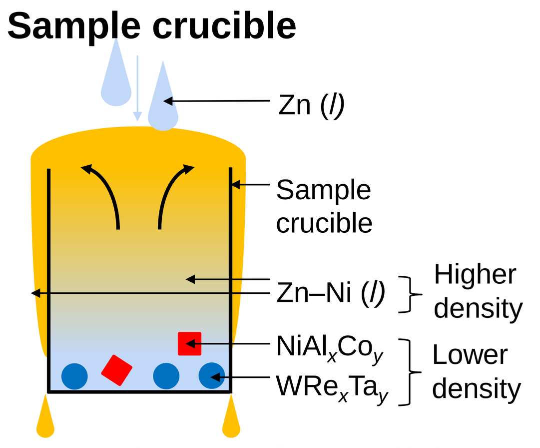
Merit of this method

- **Ni and concentrated WRe_xTa_y can be obtained separately**
- **Continuous Ni extraction from superalloy to molten Zn can be achieved.**

Zinc circulation (in Vacuum)

Mechanism (Zn–Ni transportation by overflow)

Sample crucible

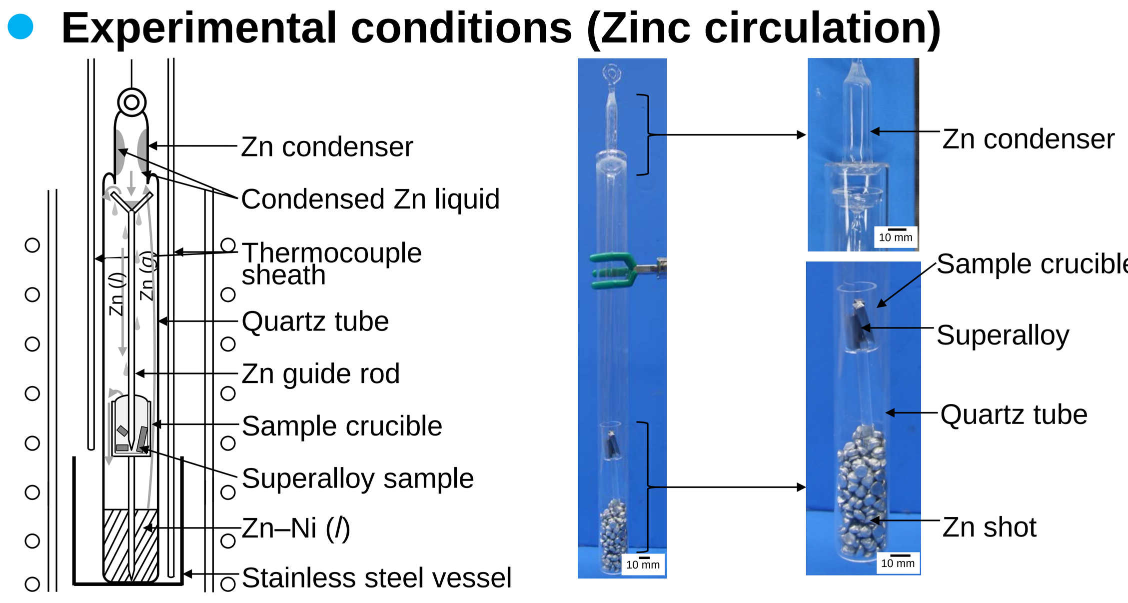


Ni is transported to the bottom with Zn overflow.

WRe_xTa_y alloy remains at the bottom of sample crucible because of its large density.

Separation of Ni and Re can be achieved

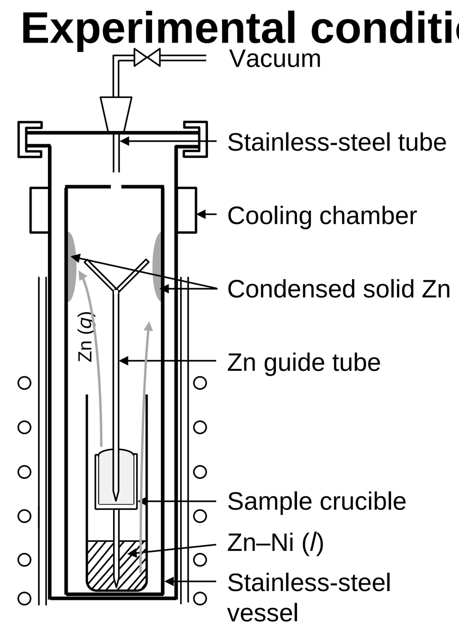
Experimental conditions (Zinc circulation)



Experimental conditions for Zn circulation in vacuum.

Exp. #	Weight of zinc, w_{Zn} / g	Weight of superalloy, w_{SA} / g	Heating temp., T_i / K: Sample crucible	Heating temp., T_i / K: Bottom of chamber	Holding time, t' / h	Height of crucible, h / mm
1	98.0	9.8	1173	1192	6	30
2	99.0	9.9	1173	1179	12	30
3	150.0	15.0	1173	1175	6	60
4	150.0	10.0	1173	1179	12	60

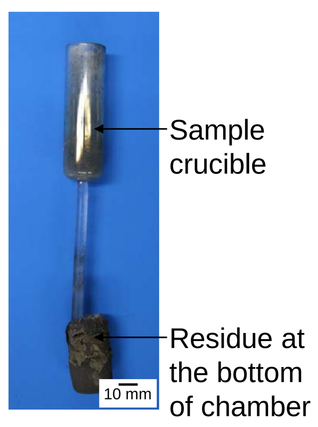
Experimental conditions (Zinc distillation)



Experimental conditions for Zn distillation.

Sample	Heating temp., T_i / K: Sample crucible	Heating temp., T_i / K: Bottom of chamber	Holding time, t' / h
1	1135	1173	12
2	983	1031	12
4	983	1031	12

Result



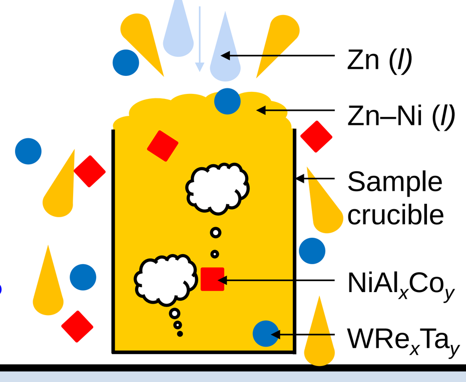
Analytical results of residues obtained at the bottom of the chamber after Zn-circulation and distillation experiment.

Sample	Heating temp., $T_{crucible}$ / K	Ni	Al	Co	Cr	W	Ta	Re	Zn	Fe
		Concentration of element i, C_i (mass %)								
	Superalloy	60.0	5.6	9.5	6.4	6.3	6.3	2.9	0.2	n.d.
1	1135	26.5	6.5	2.9	14.7	2.7	2.1	0.8	0.9	42.8
2	983	57.5	0.5	10.7	6.7	11.7	8.5	2.7	1.4	0.3
4	983	57.2	0.5	9.0	7.6	12.1	8.8	3.0	1.8	n.d.

Analyzed by XRF. n.d.: Not detected. Below the detection limit of the XRF (< 0.01 mass %).

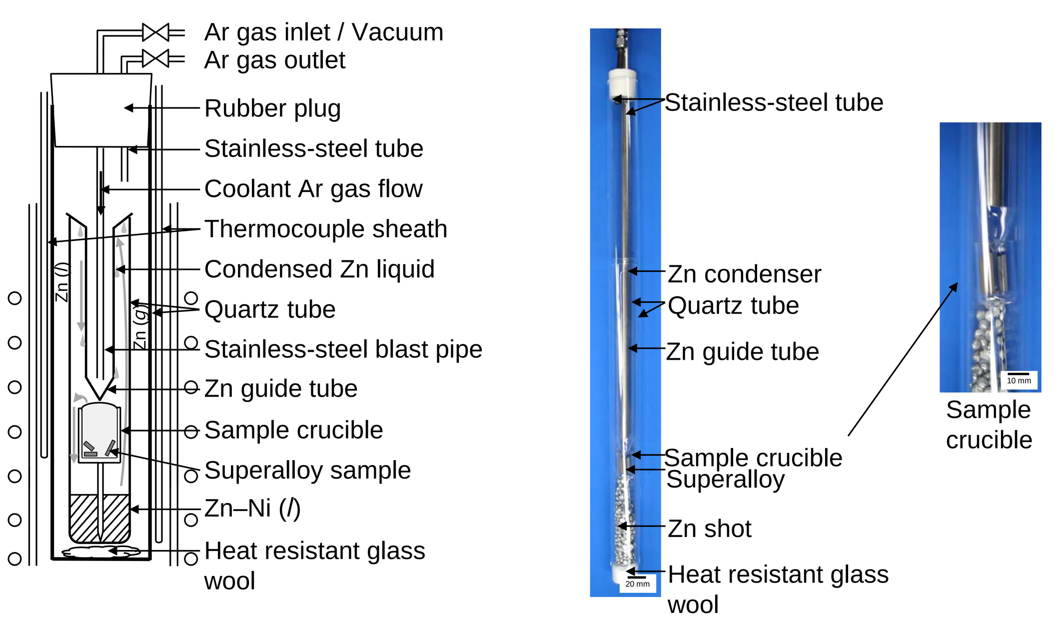
WRe_xTa_y alloy also transported with Zn circulation

Zn boiled violently in sample crucible
→Molten Zn alloy flew out with WRe_xTa_y?



Zinc circulation (in Argon gas)

Experimental conditions



Experimental conditions for Zn circulation in Ar gas.

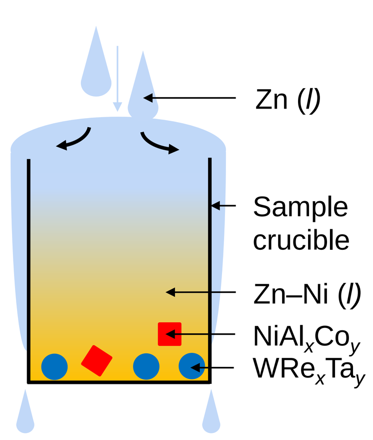
Exp. #	Weight of zinc, w_{Zn} / g	Weight of superalloy, w_{SA} / g	Heating temp., T_i / K: Sample crucible	Heating temp., T_i / K: Bottom of chamber	Holding time, t' / h
5	151.0	15.1	1173	1220	3
6	151.0	15.1	1173	1216	6
7	149.0	14.9	1179	1203	12
8	150.0	15.0	1176	1201	18

Result

Analytical results of residue (~100 g) obtained at the bottom of the chamber after Zn-circulation experiment.

Exp. #	Holding time, t' / h	Ni	Al	Co	Cr	W	Ta	Re	Zn
		Concentration of element i, C_i (mass %)							
5	3	0.7	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	99.2
6	6	1.3	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	98.5
7	12	0.9	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	99.1
8	18	0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	100.0

Analyzed by XRF.
n.d.: Not detected. Below the detection limit of the XRF (< 0.01 mass %).

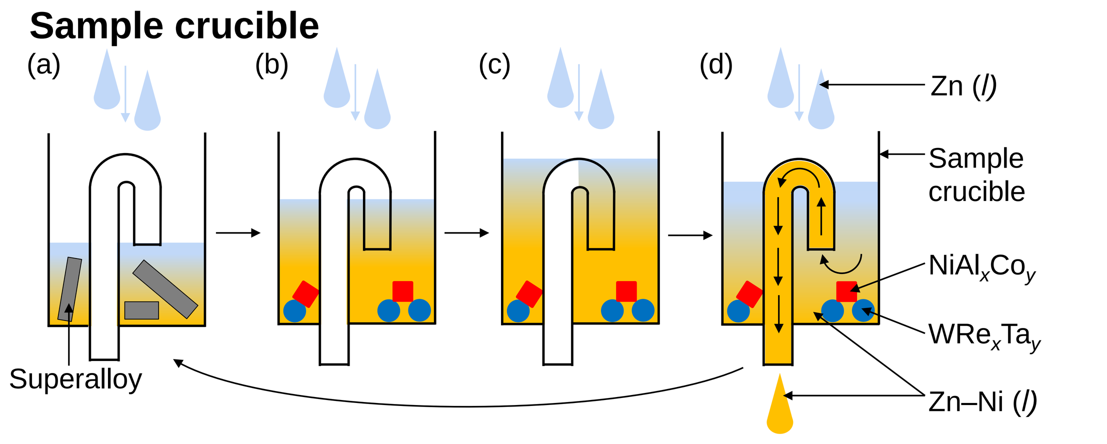


The amount of Ni transported to the bottom was low.

Zinc circulation using siphon

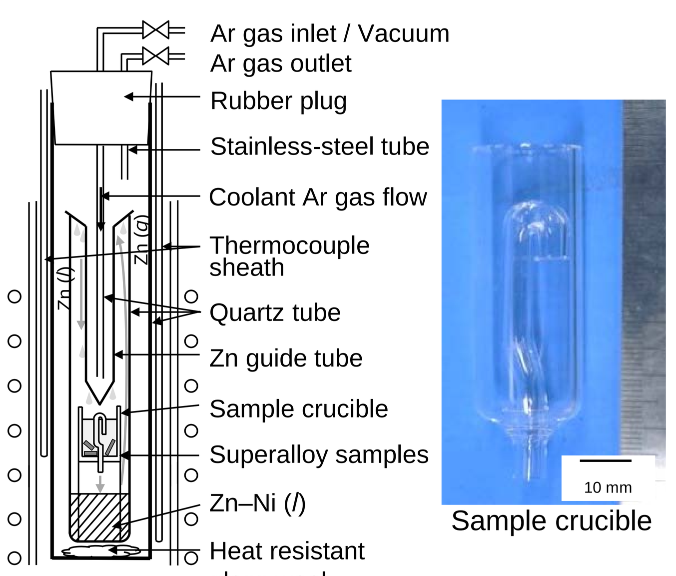
Mechanism
(Zn–Ni transportation based on the principle of the siphon)

Sample crucible



Experimental conditions

Zinc circulation

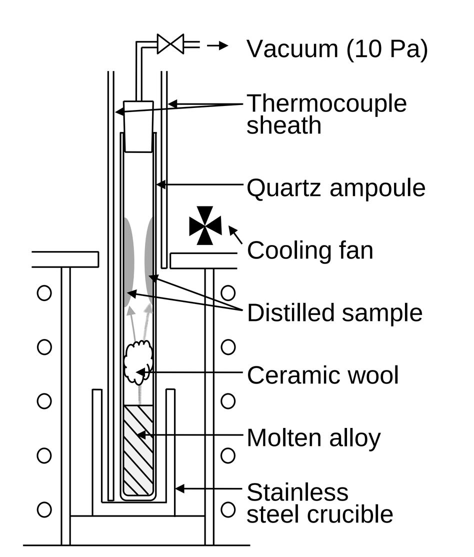


Sample crucible

Experimental conditions for Zn circulation using the principle of the siphon.

Exp. #	Weight of zinc, w_{Zn} / g	Weight of superalloy, w_{SA} / g	Heating temp., T_i / K: Sample crucible	Heating temp., T_i / K: Bottom of chamber	Holding time, t' / h
9	154.0	15.4	1173	1212	24

Zinc distillation

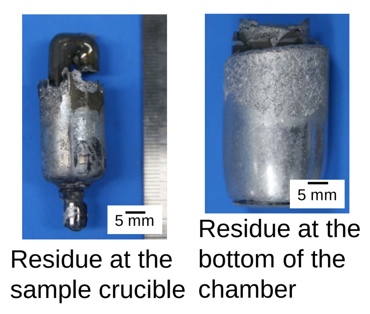


Experimental conditions for Zn distillation.

Exp. #	Sample	Weight of sample, w_{before} / g	Heating temp., T / K	Holding time, t' / h
10	crucible	13.0	1173	6
	bottom	41.9	1173	6

Result

After Zn circulation



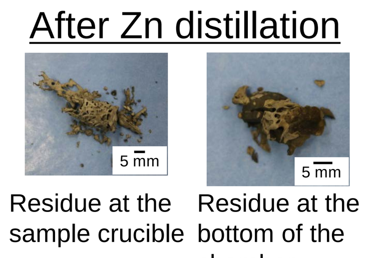
Residue at the sample crucible — Residue at the bottom of the chamber

Analytical results of residue (~100 g) obtained at the bottom of the chamber after Zn-circulation experiment.

Exp. #	Sample	Ni	Al	Co	Cr	W	Ta	Re	Zn
		Concentration of element i, C_i (mass %)							
9	Bottom	5.6	n.d.	0.5	0.5	n.d.	n.d.	n.d.	93.4

Analyzed by XRF.
n.d.: Not detected. Below the detection limit of the XRF (< 0.01 mass %).

After Zn distillation



Residue at the sample crucible — Residue at the bottom of the chamber

Analytical results of residues obtained after Zn-distillation experiment.

Exp. #	Sample	Ni	Al	Co	Cr	W	Ta	Re	Zn
		Concentration of element i, C_i (mass %)							
	Superalloy	60.0	5.6	9.5	6.4	6.3	6.3	2.9	0.2
10	Crucible	43.7	5.9	8.2	5.9	14.2	13.8	6.5	1.9
	Bottom	77.9	4.0	9.2	6.4	0.7	0.9	0.4	0.6

Analyzed by ICP.

In the sample crucible: Ni ↓ Refractory metals ↑
At the bottom : Ni ↑ Refractory metals ↓

Re and Ni could be separated by using Zn-circulation.

Summary

- **The feasibility of the proposed Re-concentrating process using Zn circulating reaction chamber was experimentally demonstrated.**
- **Three types of Zn circulating reaction chamber were used.**
  - **Vacuum type: W, Ta, and Re were transported to the bottom of chamber, and thus, could not be separated from Ni.**
  - **Ar type: The amount of Ni transported to the bottom of the reaction chamber was low**
  - **Siphon type: Re and Ni could be separated effectively.**