Development of Novel Recycling Techniques for Nickel-based Superalloy Scraps

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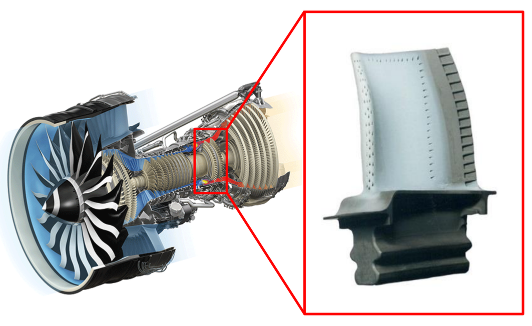
Introduction

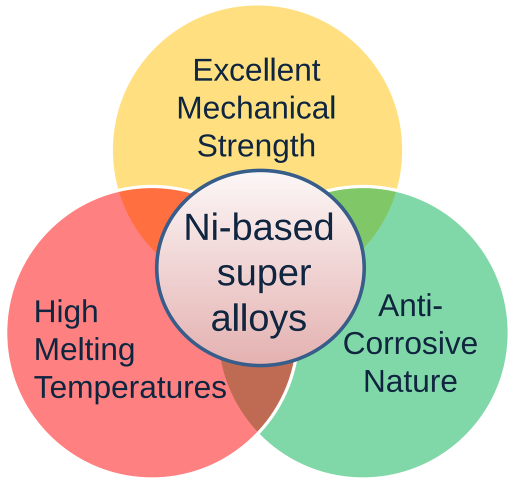
Future demand of airplanes

Unit of airplanes in service in year 2015, U_1	Future demand of airplanes in year 2035, U_2	Percentage increase in 2035, X_i (%)
22,510	45,240	201

Demand of airplanes is expected to be double increase in the next 20 years

Nickel (Ni)- based superalloy turbine blade





Values of elements in Ni-based Superalloy

Element, i	Standard alloy composition, C_i (mass%)	Value of the element in 1 kg alloy, p'_i / US$/kg	Rate of value of the element r_i (%)
Ni	61.7	7.3	6.6
Co	9.0	2.6	2.4
Cr	6.5	0.1	0.1
Ta	**6.5**	**15.3**	**14.0**
W	6.0	2.3	2.1
Al	5.6	0.1	0.1
Re	**3.0**	**81.0**	**73.9**
Ti	1.0	0.1	0.1
Mo	0.6	0.1	0.1
Hf	0.1	0.6	0.6
	Total	109.6	

Ref) T. D. Kelly, and G. R. Matos: "Historical statistics for mineral and material commodities in the United States: U.S. Geological Survey Data Series 140", *U.S. Geological Survey*, (2014).

A superalloy contains rare (scarce) and expensive "**refractory metals**" such as **Rhenium (Re), Tungsten (W) and Tantalum (Ta)** for their high-temperature strength.

The recovery of refractory metals is important

Conventional recycling process

Process	Description	Disadvantage
Remelting	High quality scraps are remelted for superalloy production	× Contaminated scraps cannot be recycled by this process, owing to the possible impurities that might be found in the superalloy ingot × Quality control is difficult
Cascade use	Scrap is downgraded for use in stainless steel and low grade superalloy	× Refractory metals such as Re and Ta cannot be recovered and/or recycled
Acid dissolution	Uses aqueous solutions to dissolve superalloy	× Energy-consuming pretreatments are required × Generation of toxic aqueous waste solutions × Long processing time

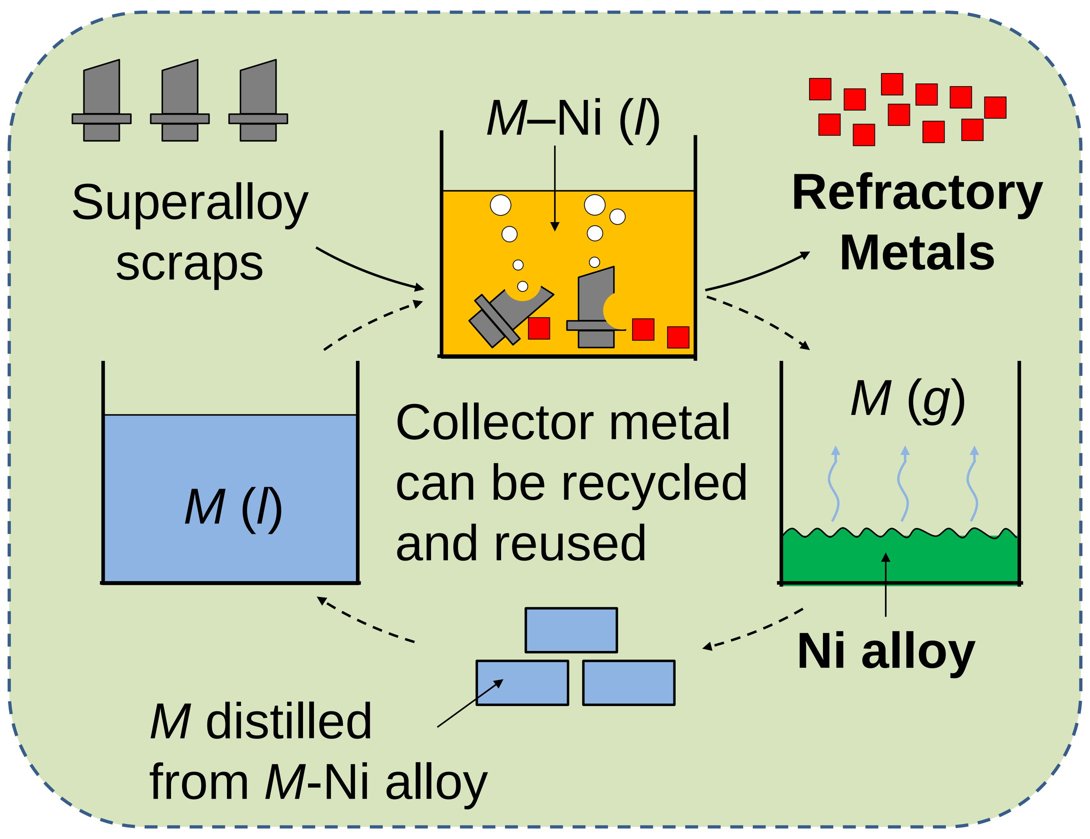
New recycling process for superalloy

A new environmentally sound recycling process has to be developed

- **Efficient recovery of refractory metals**
- **High-speed / low energy consumption**
- **No waste solution containing strong acid is generated**

Separation of refractory metals from superalloy scraps by using molten metal

Concept of separation of refractory metals by using molten metal



- **Ni and refractory metals can be separated and recovered to their metallic state.**
- **No waste solution is generated**
- **Bulk scraps can be treated (highly scalable process)**

Purpose of this study

To demonstrate the feasibility of the proposed recycling process for superalloys using molten Bi–Zn.

Dissolution of superalloy in molten zinc (Zn)

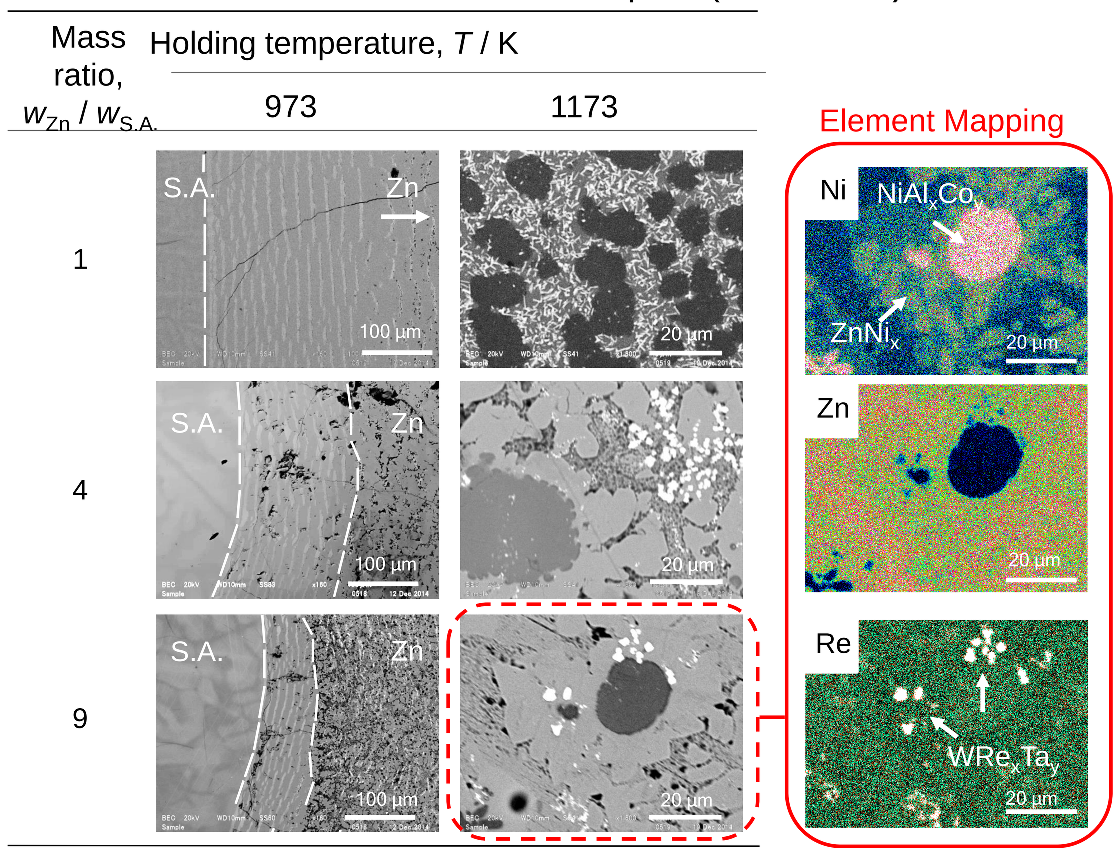
・Large Ni solubility
・Zero or little solubility for refractory metals

Experimental conditions

Superalloy ingot was heated with molten Zn at 973 K or 1173 K for 6 h in a quartz ampoule, and then quenched to room temperature.

Result

Microstructures of the obtained samples (SEM-EDS)



- 973 K: The Ni-based superalloy hardly dissolved in molten Zn
- 1173 K: The Ni-based superalloy disappeared in molten Zn
- **Refractory metals can be separated from Ni in the form of a WRe$_x$Ta$_y$ alloy**

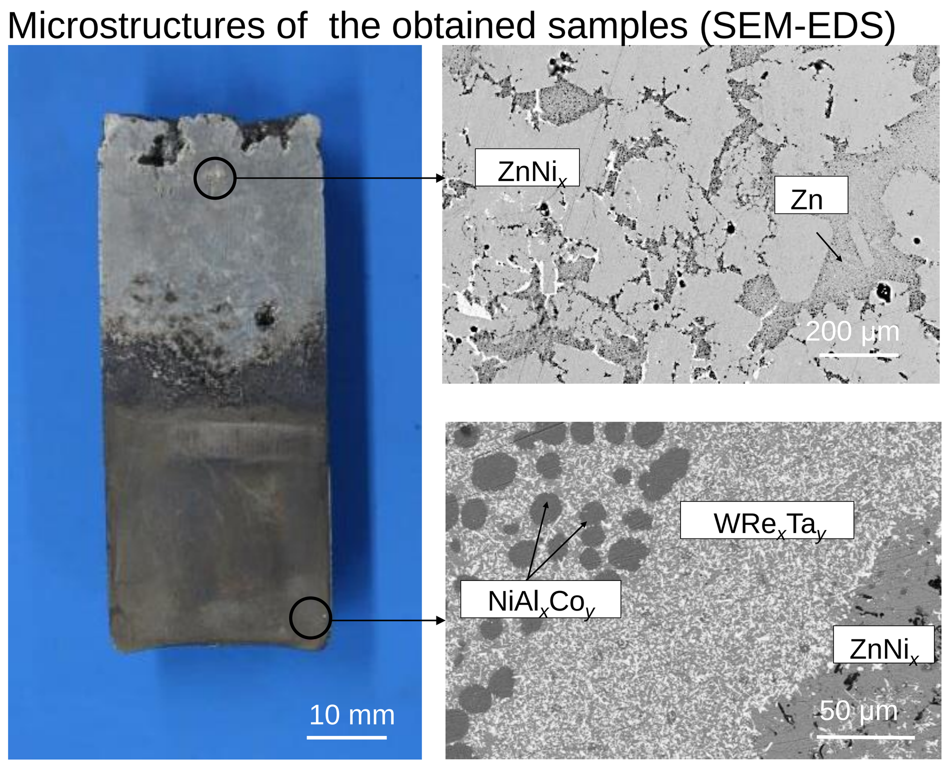
Separation of ZnNi$_x$ alloy from refractory metals

Experimental conditions

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. The mass ratio of Zn to superalloy was 4 : 1.

Result

Microstructures of the obtained samples (SEM-EDS)

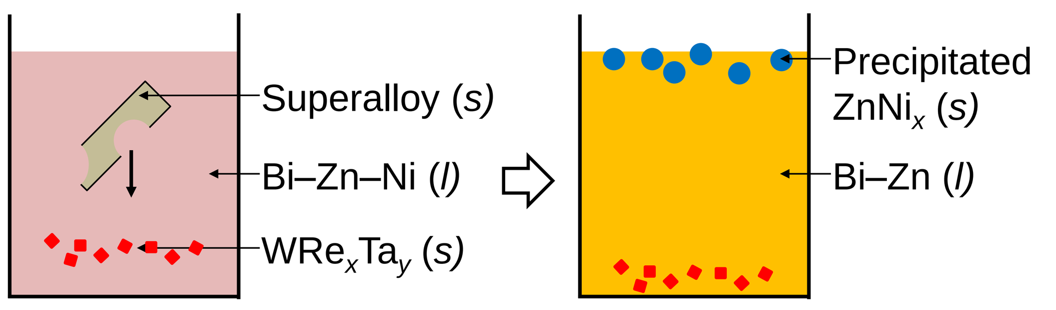


- Major percentage of the precipitated ZnNi$_x$ alloy was concentrated at the lower part of liquid Zn matrix because of its higher density.
- Separation of ZnNi$_x$ and WRe$_x$Ta$_y$ alloys could not be achieved because both alloys are accumulated at the bottom.

Gravity separation of Ni using molten Bi–Zn

Concept of Ni separation by using bismuth (Bi)–Zn

Two steps to recover refractory metals

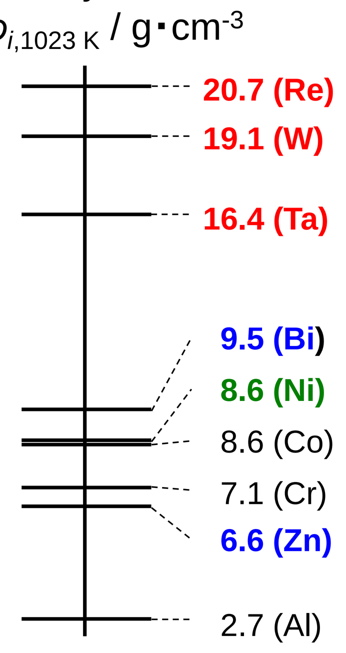


Heating at high temp.
⇒Ni in superalloy dissolves in molten Bi–Zn, while Re forms alloy with W and Ta.

Cooling
⇒ZnNi$_x$ alloy is precipitated from molten Bi–Zn, after which it floats because of its smaller density.

Why Bi–Zn (*l*) was used?

Density at 1023 K, $\rho_{i,1023\ K}$ / g・cm^{-3}



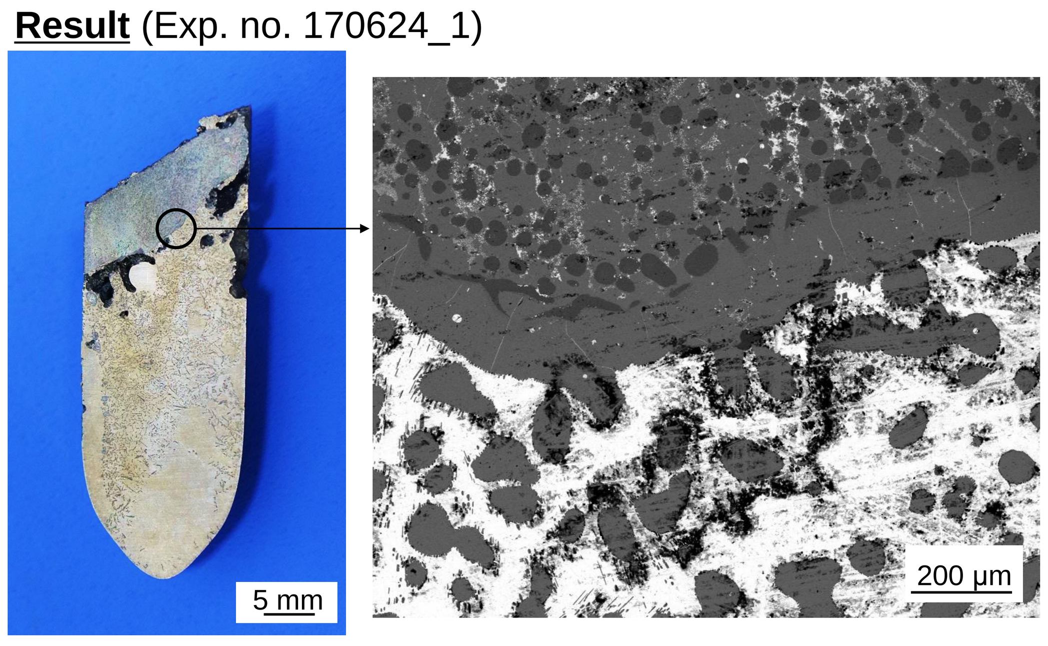
- When molten Zn–Bi–Ni alloy is cooled to 1023 K, ZnNi$_x$ intermetallic alloy and molten Bi–Zn alloy are formed.
- Precipitated ZnNi$_x$ intermetallic alloy floats on the liquid surface of the molten Bi–Zn alloy because of its lower density.
- Refractory metals (W, Re, Ta) are more likely to accumulate at the bottom of Bi–Zn alloy as a result of their relatively high densities and weak chemical affinities with Bi and Zn.

Gravity separation of Ni and refractory metals

Experimental conditions

Superalloy was heated with molten Bi–Zn alloy at 1173 K for 24 h in a quartz ampoule, and then cooled to 1023 K. The alloy was heated at 1023 K for 12 h. Mass ratio of superalloy to Zn and Bi was m_{SA} : m_{Zn} : m_{Bi} = 1 : 4 : 8.

Result (Exp. no. 170624_1)



Upper phase
- **Solid matrix (Grey) : $Zn_{78}Ni_{19}Co_2$**
- Black deposit : $Ni_{39}Al_{27}Zn_{18}Co_{13}Ta_2Cr_1$

Lower phase
- **Liquid matrix (White): $Bi_{91}Zn_8Re_1$**
- Gray deposit : $Zn_{78}Ni_{19}Co_2$

(Alloy particles containing refractory metals were dispersed in the entire area, but their composition could not be measured because of their relatively small size.)

Large percentage of ZnNi$_x$ alloy floated on the liquid surface of Bi–Zn alloy. This results shows the possibility of gravity separation of Ni and refractory metals!

Summary

- **In order to develop a new recycling process for superalloys, the reactions between a superalloy and molten Zn and Bi–Zn alloy were investigated.**
- **The superalloy fully dissolved in the molten Zn at 1173 K. However, the separation of ZnNi$_x$ and WRe$_x$Ta$_y$ alloys could not be achieved.**
- **After the dissolution of the superalloy in the molten Bi–Zn alloy, the obtained alloy was cooled. The ZnNi$_x$ alloy was then precipitated and floated on the molten Bi–Zn alloy.**
- **More experimental study is needed in order to understand the behavior of refractory metals in molten Bi–Zn alloy.**

Industrial application