NEW PRODUCTION PROCESS OF NIOBIUM POWDER BY PREFORM REDUCTION PROCESS

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Introduction

Miniaturization and high performance of mobile equipment

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Miniaturization and high capacity of electronic parts

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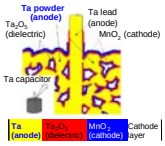
Demand of Ta capacitor is expanding.

・small ・high capacitance ・high thermal stability

Capacitance (C)

$$C = \frac{\varepsilon_0 \cdot \varepsilon_r \cdot S}{d}$$

C : capacitance
ε_0 : absolute permitivity of free space
ε_r : relative permitivity of dielectric
S : specific surface area
d : plate distance (dielectric thickness)



Higher specific surface area would result in higher capacitance.

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Fine particles are necessary to fabricate high-capacitance capacitor.

Table Comparison between niobium and tantalum

	Niobium		Tantalum	
Symbol of element	Nb		Ta	
Atomic number	(VB) 41		(VB) 73	
Atomic weight	92.9		180.9	
Density	8.56	g/cm³	16.65	g/cm³
Melting point	2468	℃	2980	℃
Boiling point	4758	℃	5534	℃
Resistivity (20℃)	12.5	Ω・cm	12.4	Ω・cm
Clarke number	2×10^{-3} (34th)		1×10^{-3} (40th)	
Annual world production[a]	23000	ton	2300	ton
	(21000)[b]	ton	(1400)[c]	ton
Demand in Japan	3900	ton	550	ton
	(3900)	ton	(270)	ton
Price (in round numbers)	55	$/kg[d]	700	$/kg[e]
Major applications	Microalloy element for steel		Solid electrolytic capacitors	
Commercial production process	Aluminothermic reduction (ATR) (Nb/FeNb bar)		Sodiothermic reduction (Hunter) (Ta powder)	

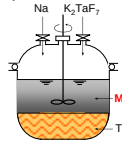
a: Year 2000, Converted into pure metal.
b: Converted quantity of pure niobium used as ferroniobium (Fe-65%Nb).
c: Powder for capacitors
d: Aluminothermic reduction (ATR) niobium, by three times electron beam (EB) melted, purity: 99.8%.
e: At least 30,000 yen/Kg heavily varies with powder purity and morphology.

・Similar to Ta in physical and chemical property (homologous element)
・Ample resources
・Low price

→ Nb is emerging as a material that can substitute for Ta in capacitors.

Current production process of Ta powder

Hunter process



K_2TaF_7 + 5 Na → Ta + 5 NaF + 2 KF (in molten salt)

Huge environmental load

Fig. Schematic illustration of tantalum powder production for electric device by using metallothermic reduction.

○ High purity and fine powder obtainable
× Batch type process →low productivity
× Large amount of fluorides wastes →environmental problem
× Use of Na as a reductant →high reactivity

Current Niobium production process

ATR(Alumino-Thermic Reduction) process

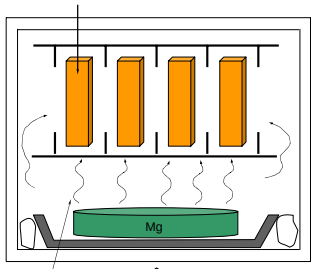
$3\,Nb_2O_5 + 10\,Al \rightarrow 6\,Nb + 5\,Al_2O_3$

Fig. Schematic illustration of Alumino-Thermic Reduction(ATR).

This process is not suitable for capacitor because the form of Nb produced by ATR process is bulk.

Preform reduction process (PRP)

Feed prefrom (Nb_2O_5 powder + flux)



Reduction by Mg vapor

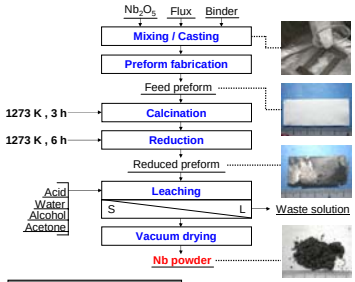
Chemical reaction:
$Nb_2O_5 + 5\,Mg \rightarrow 2\,Nb + 5\,MgO$

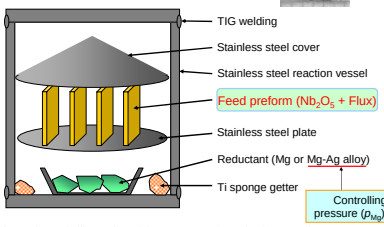
<Features>

・Fine and homogeneous powder obtainable
・No emission of waste solution containing fluorine
・Flexible scalability
・Small amount of molten salts required
・(semi-) Continuous and high-speed process

Experimental 1

Preform Reduction Process (PRP)



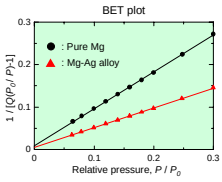


Controlling Mg vapor pressure (p_{Mg}) by using alloy

Fig. Schematic illustration of the apparatus for reduction experiment.

Result 1

Specific surface area measurement



$$\frac{1}{Q\left[\left(P_0/P\right)-1\right]} = \frac{C-1}{Q_m C}\left(\frac{P}{P_0}\right) + \frac{1}{Q_m C}$$

P : equilibrium pressure of adsorption
P_0 : saturation pressure of gas
Q : amount of adsorption at P
Q_m : amount of monolayer adsorption
C : BET constant

Reductant, R	Specific surface area, S / m²·g⁻¹
pure Mg	4.98
Mg-Ag alloy	9.21

Mg vapor pressure in the reaction system was reduced by the alloying process, and the supply rate of Mg was suppressed.

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Specific surface area increased when Mg-Ag alloy was used.

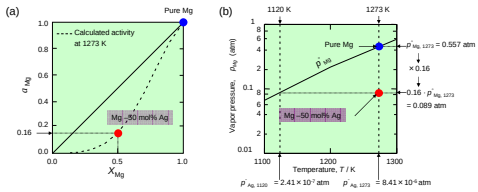
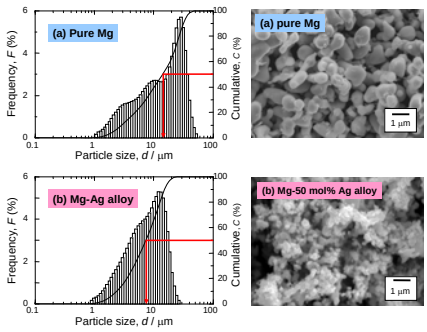


Fig. (a) Activity of Mg in Mg-Ag alloy at 1273 K.
(b) Vapor pressure of Mg as a function of temperature.

Particle size distribution and SEM images



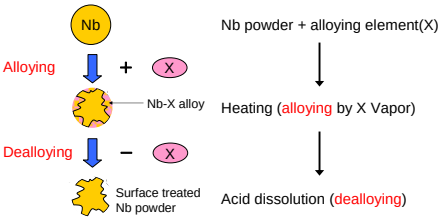
Reductant, R	Particle size distribution D_{10} / μm	D_{50} / μm	D_{90} / μm
Pure Mg	2.91	14.13	31.46
Mg-Ag alloy	2.40	7.37	15.16

Particle size decreased when the Mg-Ag alloy was used as a reductant.

Experimental 2

Alloying-dealloying treatments

Outline of this process



Nb powder + alloying element(X)

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Heating (alloying by X Vapor)

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Acid dissolution (dealloying)

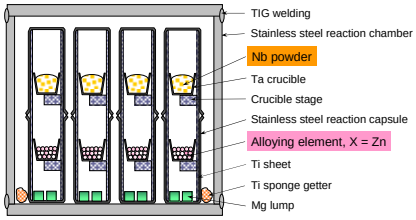


Fig. Schematic illustration of the apparatus for alloying experiment
T = 1273 K, t = 6 h

Result 2

XRF analysis

	Concentration of element i, C_i (mass%)						
	Nb	Zn	Fe	Cr	Ni	Ti	Ta
after alloyng Zn	76.0	23.7	0.06	<0.01	0.02	<0.01	0.22
after acid dissolution	99.6	0.05	0.02	0.03	0.03	<0.01	0.23

Zn was dissolved and removed by leaching.

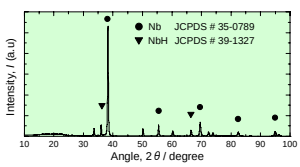
Specific surface area measurement

sample	Specific surface area, S / m²·g⁻¹ before treatment	after treatment
A	1.61	2.65
B	7.25	7.28

When the Nb powder with low surface area was used as starting material, the specific surface area increased predominantly.

XRD analysis

After alloying and dealloying treatment



Some peaks were detected besides Nb and NbH.

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Need to remove impurities

Conclusion

New production process of fine Nb powder by Preform Reduction Process (PRP) was investigated.

- Nb powder with low particle size distribution and high specific surface area was obtained by this process when Mg-Ag alloy was used as a reductant.
- The specific surface area of the Nb powder was increased by alloying with Zn vapor and dealloying with acid.

Future work

More efficient process for producing Nb powder with higher specific surface area by alloying and dealloying treatment are being investigated.
Simultaneous process for preform reduction and alloying for producing high performance metal powders will be investigated.