Application of Disproportionation Reaction to Surface Treatment

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Disproportionation reaction is very important and interesting reaction to be applied to such surface treatment as metal, alloy, compound coating, a surface etching and so on. In gaseous system, the reaction of Al chloride is applied to Al and Al alloy coating, and the similar reaction of Ti chloride is also used for Ti, Ti alloy and Ti compound coating. As for aqueous system, this reaction is utilized to such metal coat as Sn etc. and metal etching such as Cu, Fe and so on.

Also in molten salts system, this reaction has many application for surface treatment like metal, alloy and compound coatings for corrosion, wear, heat resistance and so forth. For instance, carbide film, nitride film, boride film, alloy film, quite new different film from the components of substrate material are coated in single and multiple component film system by the disproportionation reaction.

INTRODUCTION

Disproportionation reaction is the reaction which occurs each other for one ionic state to make elemental and ionic states or two ionic states, and also backward reaction in the case of metal or element, whose ionic valency shows more than two states, like the following reactions.

$$M^{a+} \rightleftarrows M^0 + M^{c+}$$

$$M^{b+} \rightleftarrows M^{a+} + M^{c+} \qquad (0<a<b<c)$$

For instance, there are in gaseous state system,

$$3AlCl(g) \underset{>1273k}{\overset{<973k}{\rightleftarrows}} 2Al(l\ or\ s) + AlCl_3(g)$$

$$2TiCl_2(g) \underset{>1273k}{\overset{<873k}{\rightleftarrows}} Ti(s) + TiCl_4(g)$$

or

$$2TiCl_3 \rightleftarrows TiCl_2 + TiCl_4$$

$$2CO \rightleftarrows C + CO_2$$

in aqueous state system,

$$2Sn^{2+} \rightleftarrows Sn^{0} + Sn^{4+}$$
$$2Cu^{+} \rightleftarrows Cu^{0} + Cu^{2+}$$

and also in fused salts system

$$3Al^{+} \rightleftarrows 2Al^{0} + Al^{3+}$$
$$2Ti^{2+} \rightleftarrows Ti^{0} + Ti^{4+}$$
$$3B^{2+},(B^{+}) \rightleftarrows B + 2B^{3+}$$

and so on.

In the case of Ti, the film can be coated by the reaction,

$$2Ti^{2+} \rightarrow Ti^{0} + Ti^{4+}$$

where at appropriate conditions (temperature, reactivity etc.) Ti alloy and Ti compound can be deposited as a film on the substrate. If the alloy or compound formation reaction occurs under these condition, the alloy on compound film can be coated or deposited at the same reaction temperature according to the following total reaction.

$$\begin{array}{lll} \text{Ti(source)} \rightarrow & \text{Ti(alloy or compound on substrate)} & \\ (\text{activity, } a_1) & (\text{activity, } a_2) & [a_1 > a_2] \end{array}$$

This reaction process, where the disproportionation reaction concerns as a intermediate stop, can be called chemical transportation process.

GASEOUS AND AQUEOUS SYSTEM

In gaseous disproportionation reaction of Al chloride, pure Al can be originally deposited to make a thin film of Al, Al-alloy and Al-compound on substrate as follows;

$$3AlCl_3(g) \xrightarrow{<973k} 2Al(s \text{ or } l) + AlCl_3(g)$$

In the case of Ti, the following disproportionation reaction can be applied to make Ti, Ti alloy or Ti compound thin film[1],

$$2TiCl_2 \rightarrow Ti^{0}(\text{as metal, alloy or compound}) + TiCl_4$$

where the formation reaction of alloy or compound will occur easily at diffusion temperature. As for aqueous disproportionation reaction, the reaction between Cu and $CuCl_2$ in solution is very important in Cu-etching process for printed circuit board processing. Recently, the electroless plating of Sn can also be performed by using the disproportionation reaction, mainly, in alkaline solution[2] as follows;

$$2Sn^{2+} \rightarrow Sn^{0} + Sn^{4+}$$

where Sn^{2+} exists in form of $HSnO_2^-$ or $Sn(OH)_3^-$ in 0.2~0.4 mol Sn^{2+}/l, 4~5 mol/l NaOH at 353 K (deposit rate is 6 μm/h)[3, 4]. In this case, Sn state in deposit at the beginning is Cu_6Sn_5 to become β-Sn layer as a growth step.

FUSED SALTS SYSTEM

Molten salt is a very convenient media in a reaction system, because proper fused salt system can be chosen in wide range of reaction temperature to let diffusion reaction occur at interface between deposited metal and substrate and purge effectively oxygen(in air) from substrate material etc.

In the first utilization of disproportionation reaction, Ni substrate was siliconized in the system of KCl-NaCl-NaF-Na_2SiF_6+Si molten salts [5] as follows;

$$Si^0(\text{source}) + Si^{4+} \rightarrow 2Si^{2+}$$
$$4Si^{2+} + 5Ni \rightarrow Ni_5Si_2 + 2Si^{4+}$$

(1) Metal Carbide Film Formation (Cr-C, TiC, VC, ZrC, TaC etc.)

Thin metal carbide film can be coated by the disproportionation reaction in molten salts (5% Metal fluoride-KCl-NaCl-Metal system) to be deposited on the substrate which contains carbon in it.

Basic principal reactions are as follows;

$$\text{Cr-C}: 2CrF_4^- \rightarrow \text{Cr-C film(on substrate)} + F^- + CrF_7^-$$
$$\text{TiC}: 2TiF_6^{4-} \rightarrow \text{TiC film(on substrate)} + 6F^- + TiF_6^{2-}$$
$$\text{VC}: 3VCl_4^{2-} \rightarrow \text{VC film(on substrate)} + 2VCl_6^{3-}$$
$$\text{ZrC}: 2ZrF_6^{4-} \rightarrow \text{ZrC film(on substrate)} + 6F^- + ZrF_6^{2-}$$
$$\text{TaC}: 5TaF_5^{2-} \rightarrow \text{2TaC film(on substrate)} + 4F^- + 3TaF_7^{2-}$$

In these cases of metal carbide film formation, as for Cr-C thin film on C-steel, hardness of deposited Cr-C is in range of 1255~2188 Hv depending on C content, as for ZrC film, 1490 Hv, as for TiC film, 1750 Hv, as for VC film, 3400 Hv and as for TaC film, 2800~3000 Hv. [6]

(2) Metal Boride Film Formation (Fe-B, Cr-B, Ti-B, V-B, Zr-B etc.)

The disproportionation reaction of boride ion in fused salts will be shown as follows;

$$3B^{2+} \text{ or } 6B^{+} \rightarrow 2B^{3+} + \text{metal boride (on substrate)}$$

In KCl-$BaCl_2$-NaF-B_2O_3 + B(or Fe-B), the boriding reaction will occur according to the following reactions. In usage of Boron, FeB-Fe_2B double film can be coated, and in usage of FeB, Fe_2B film only can be coated respectively,

$$B(\text{or FeB}) + 2B^{3+} \rightarrow 3B^{2+} \text{ or } 6B^{+} + (Fe)$$
$$3B^{2+}(\text{or } 6B^{+}) + Fe(\text{substrate}) \rightarrow FeB\text{-}Fe_2B(\text{or } Fe_2B) + 2B^{3+}$$

In the case of usual stainless steel, Cr-boride film can be coated, which has 3200 Hv, as for Ti containing material, TiB_2 film has 4200 Hv, as for V containing material, VB_2 has 3700 Hv, as for Zr containing material, ZrB_2 film has 3000 Hv.

(3) Metal Nitride Film Formation (CrN, TiN, ZrN, VN etc.)

Nitrogen containing material like nitrided steel can be coated by metal nitride film through disproportionation reaction in similar molten salts (5% Metal fluoride 15% Ferrometal-KCl-NaCl) as follows;

$$\begin{aligned} CrN &: Fe\text{-}N + Cr \rightarrow CrN + Fe(\text{or } Fe\text{-}Cr) \\ TiN &: Fe\text{-}N + Ti \rightarrow TiN + Fe(\text{or } Fe\text{-}Ti) \\ ZrN &: Fe\text{-}N + Zr \rightarrow ZrN + Fe(\text{or } Fe\text{-}Zr) \\ VN &: Fe\text{-}N + V \rightarrow VN + Fe(\text{or } Fe\text{-}V) \end{aligned}$$

By using the disproportionation process, the hardness of deposited thin film can be controlled in range of 1500~3000 Hv. [6]

(4) Metal Silicide Film Formation (Fe-Si, Cr-Si etc.)

The disproportionation reaction of silicon ion in molten salts is as follows;

$$2SiF_6^{4-} \rightarrow Si(\text{in substrate material}) + 6F^- + SiF_6^{2-}$$

Using the siliconizing process through disproportionation reaction in molten salts to coat Fe-Si, Cr-Si, Mo-Si, NiSi, TiSi etc., that is very important as super heat resistant coating for gas turbine system. [7]

CONCLUSION

As shown in above lines, the disproportionation reaction of transition metal or element is very useful and better applicable for the thin film formation on the substrate to modify the surface of substrate to be effectively functional. By this process, many kind of alloy film (Fe-Si, Fe-V, Fe-Ti, Fe-Zr etc.) and new ceramic film (like metal carbide, metal nitrides, metal borides, metal silicides etc.) can be coated very easily.

REFERENCES

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[4] V. P. Pilnikov et al ; Prot. Met(Eng. Trans), V.17, No.1, 116~117. ('98)
[5] A. J. Gay et al ; J. Less Comm. Met., 40(1975)21.
[6] T. Oki ; Memoirs of Eng of Nagoya Univ., 40(1994)115.
[7] T. Oki ; Japan Inst. Metal, 32(1993)29.

Table Standard composition of molten salts for various film formation

Salts(wt%)	KCl	$BaCl_2$	NaF	Others
Metal Boride	30.9	41.2	15.5	2.0wt%B_2O_3, 10.4wt%ferroboron
Cr Nitride	31.7	31.7	15.9	4.8wt%CrF_3, 15.9wt%ferrochromium
Ti Nitride	31.7	31.7	15.9	4.8wt%K_2TiF_6, 15.9wt%ferrotitanium
V Nitride	31.7	31.7	15.9	4.8wt%V_2O_3, 15.9wt%ferrovanadium
Zr Nitride	31.7	31.7	15.9	4.8wt%$ZrCl_4$, 15.9wt%ferrozirconium
Cr Silicide	32.7	32.7	12.7	12.7wt%Na_2SiF_6 , 9.1wt%Si powder

Functional Electroless Nickel Plating

MATSUDA Yoshiki

Electroless Nickel Bath Composition

$NiSO_4$	０．１ mol/L
NaH_2PO_2	０．３ mol/L
Complex agent	
$Pb(NO_3)_2$	２ mg/L
Bath temperature	８０℃

Complex Agent in Electroless Nickel Bath Composition

Sodium Malate	0.1 mol/L
Sodium Succinate	0.1 mol/L

Glycine	0.2 mol/L
Sodium Acetate	0.1 mol/L

Glycine	0.1 mol/L
Sodium Citrate	0.1 mol/L

Sodium Citrate	0.1 mol/L
Sodium Acetate	0.1 mol/L

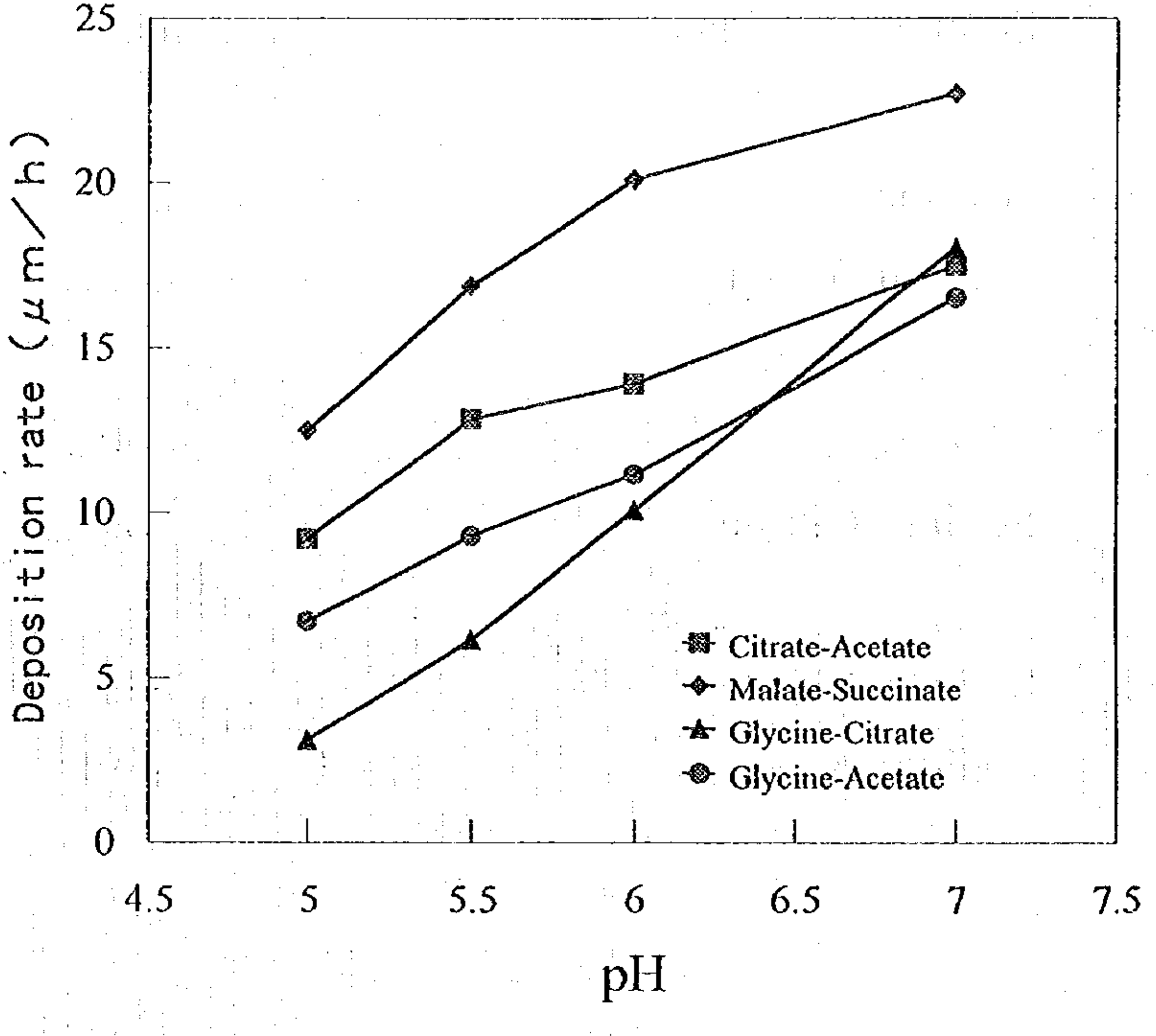


Fig. Deposition Rate

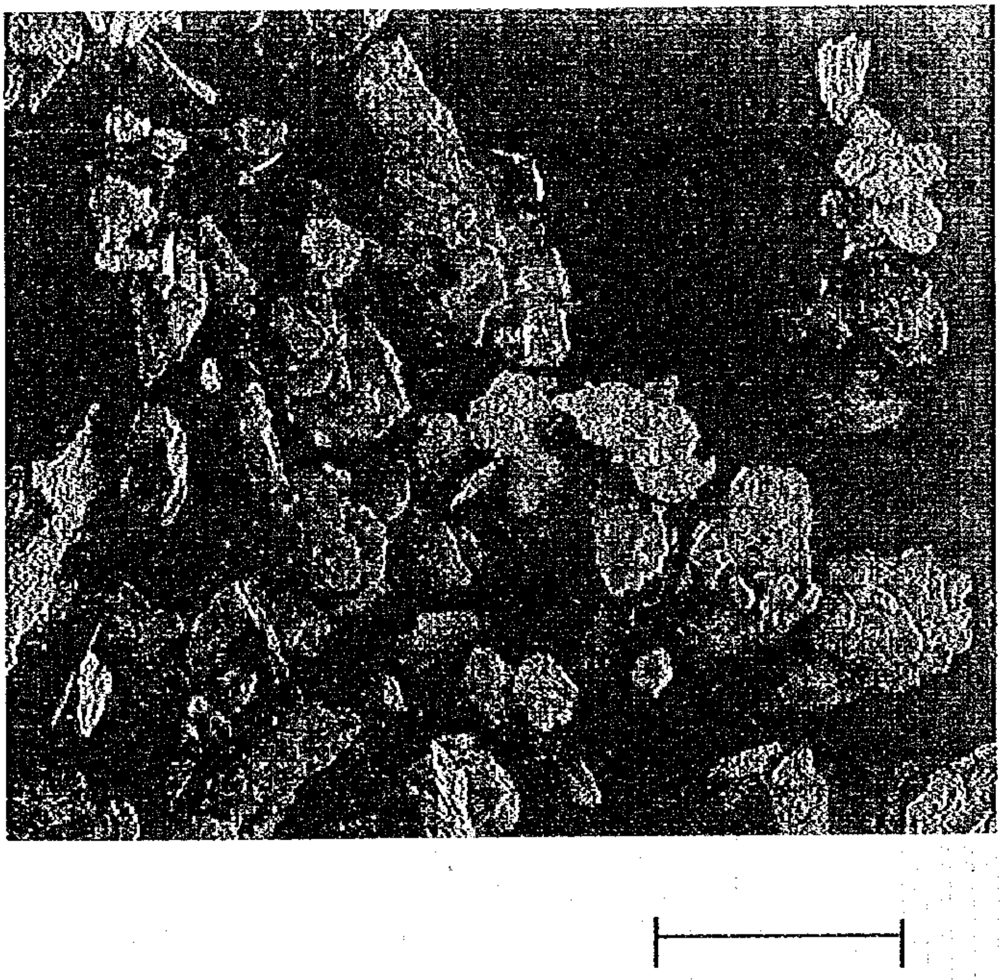


Fig. Sericite Particles

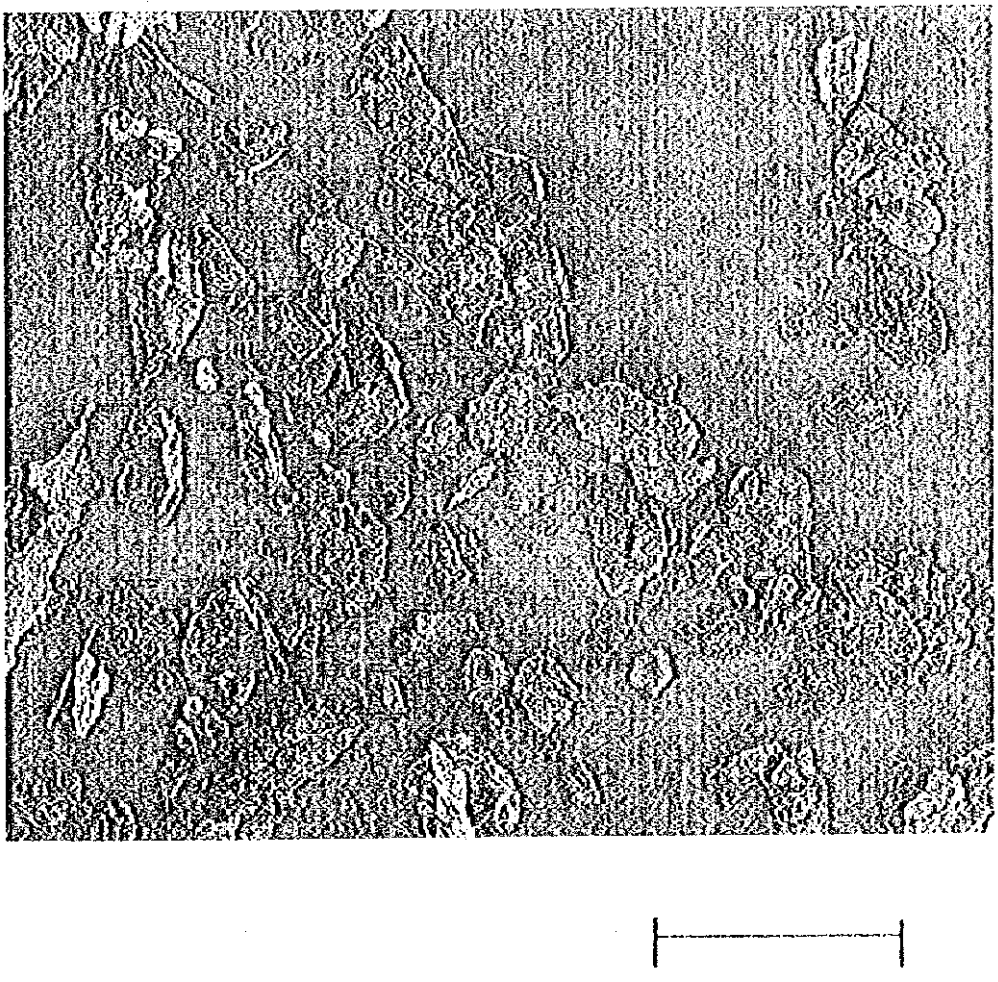


Fig. Sericite Particles

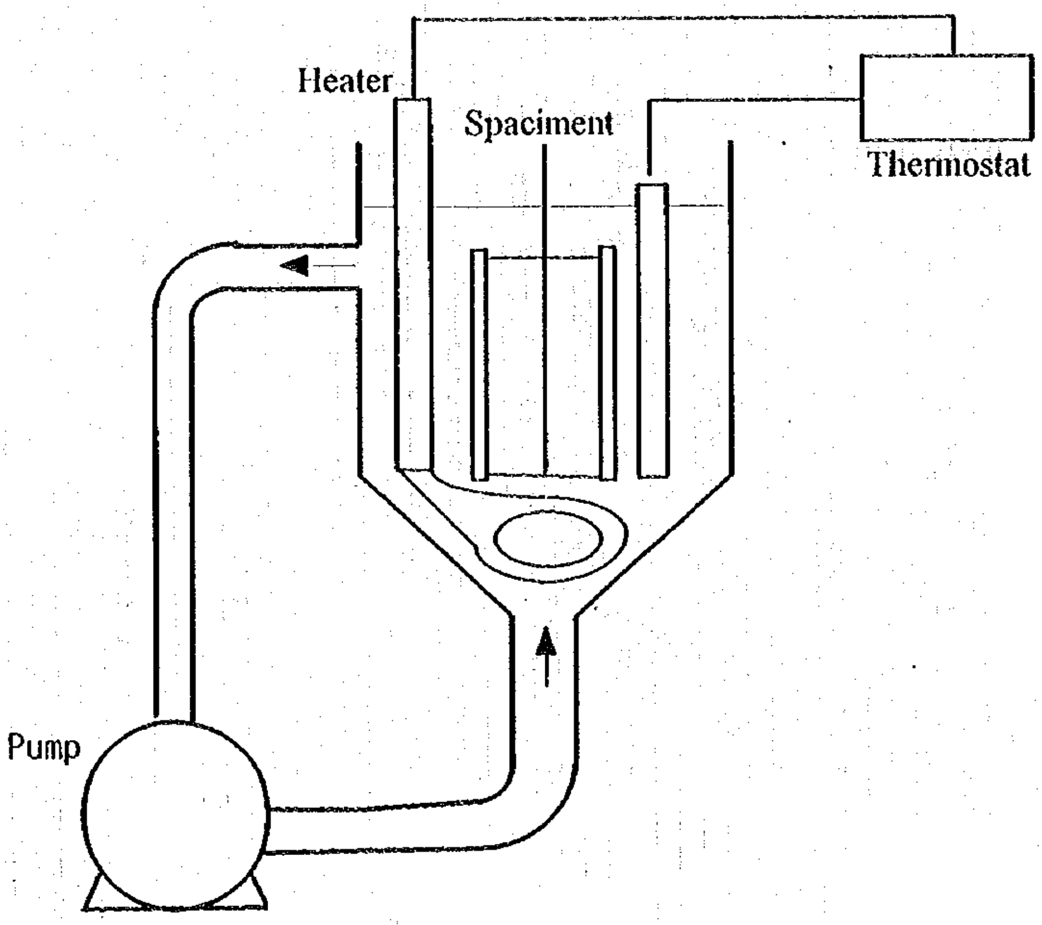


Fig. Composite Plating System

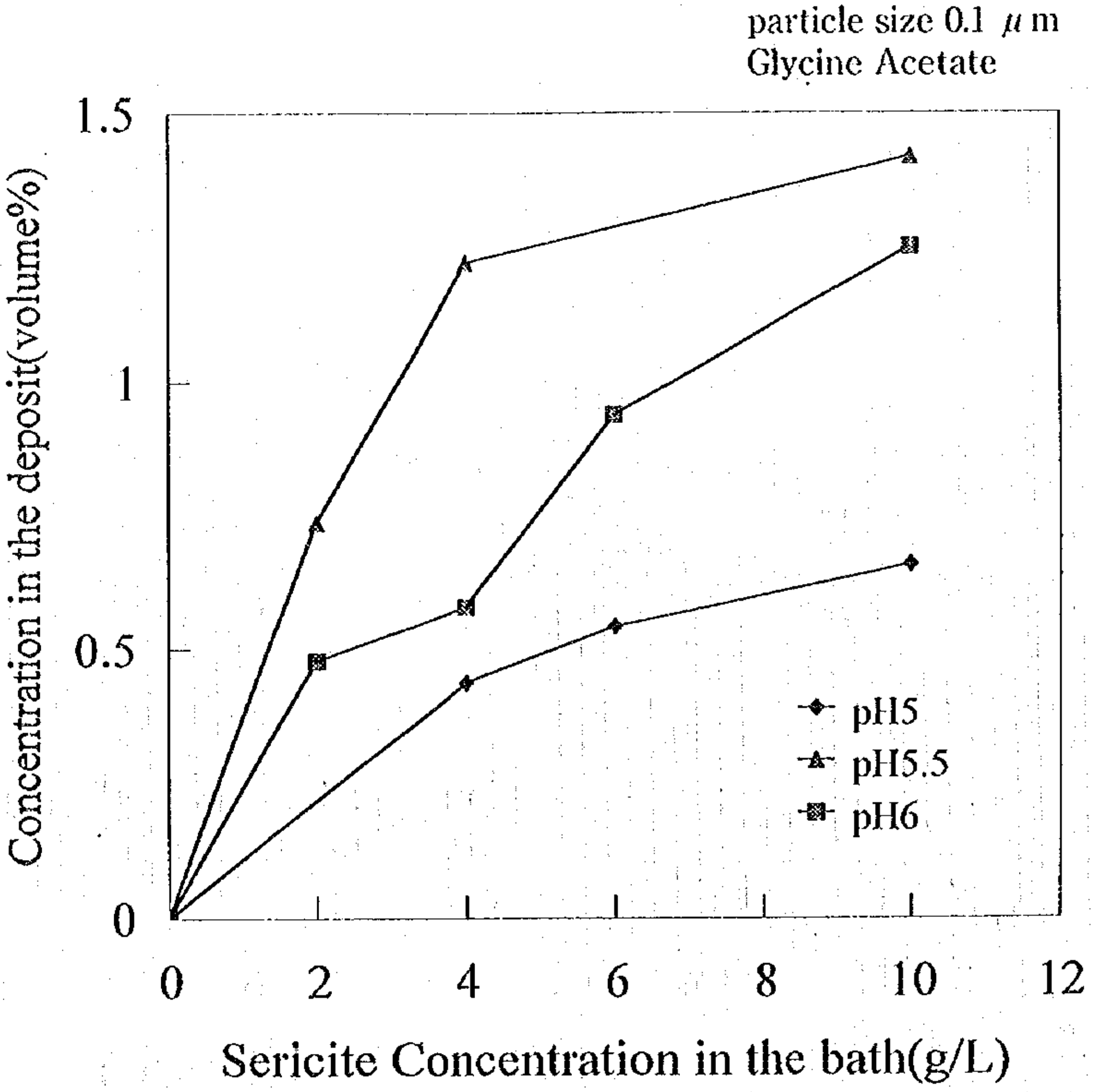


Fig. Effect of Sericite Concentration

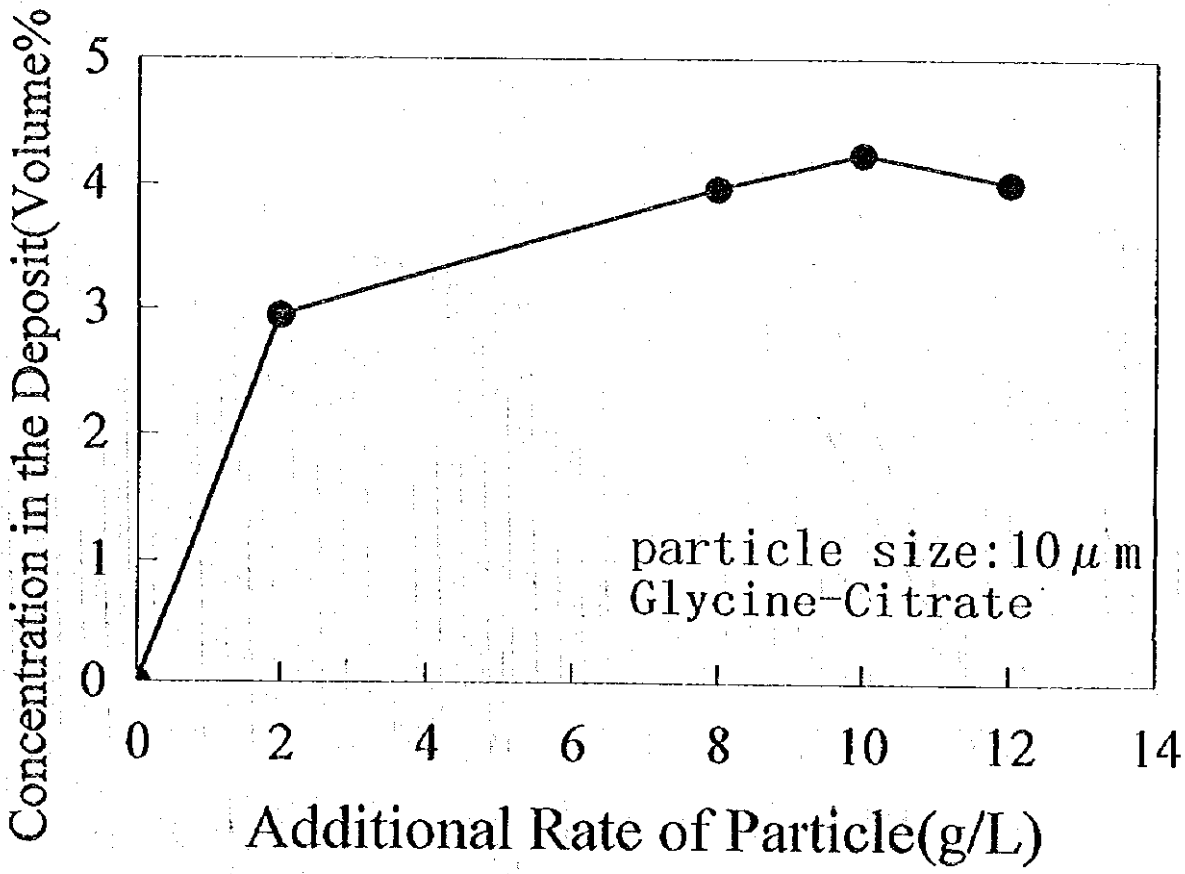


Fig.Addition and Composition

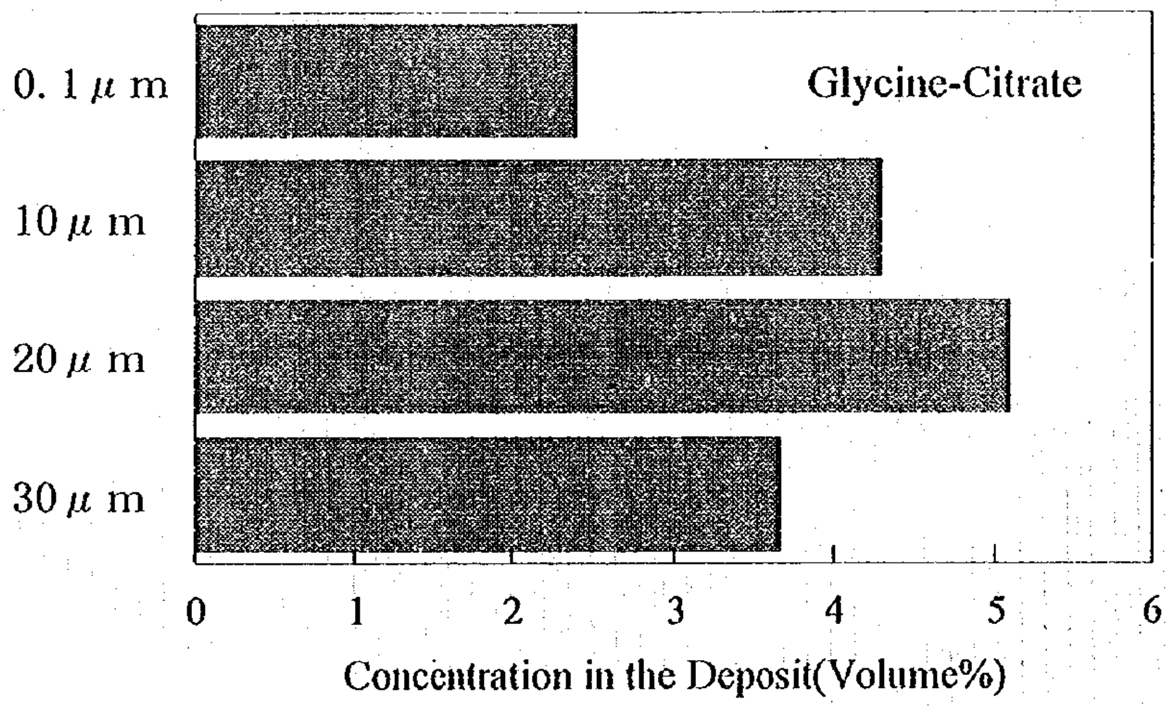
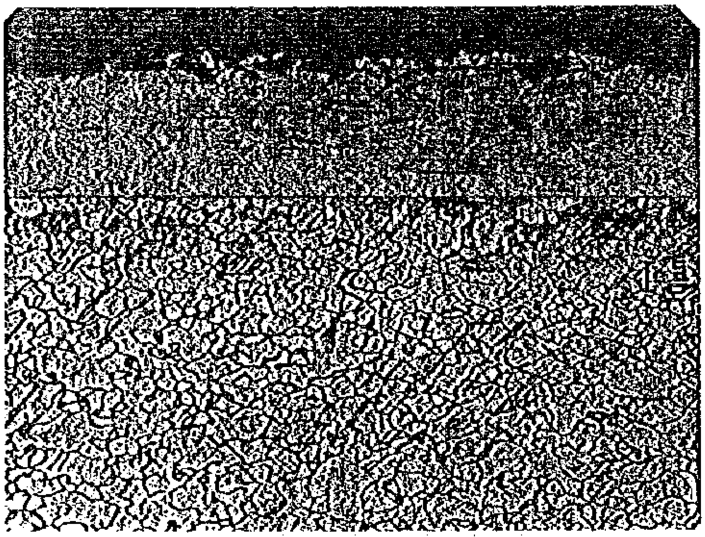
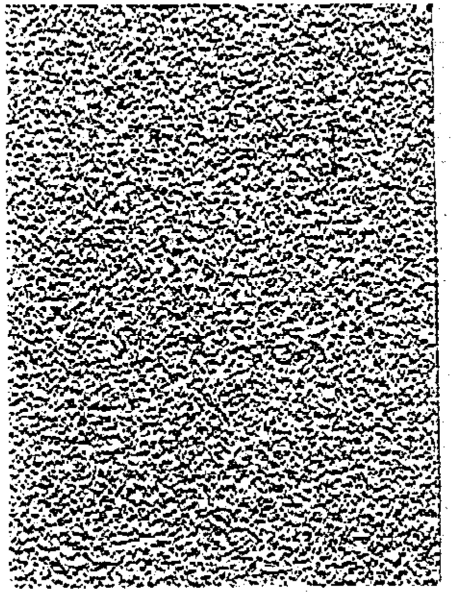


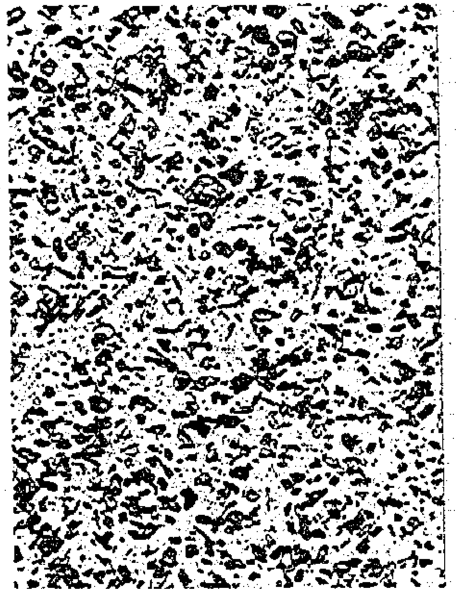
Fig.Particle Size and Composition



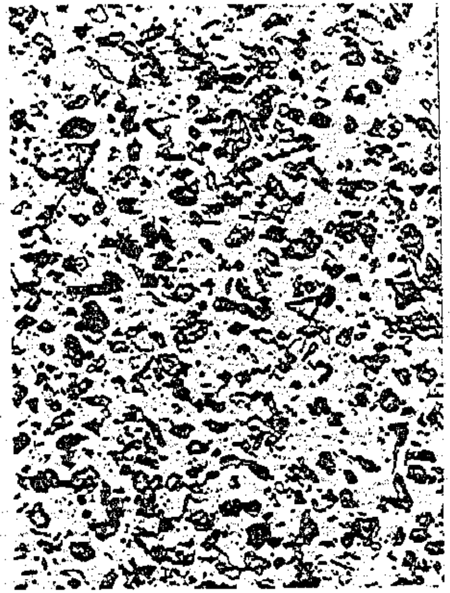


平均粒径　0．1μm

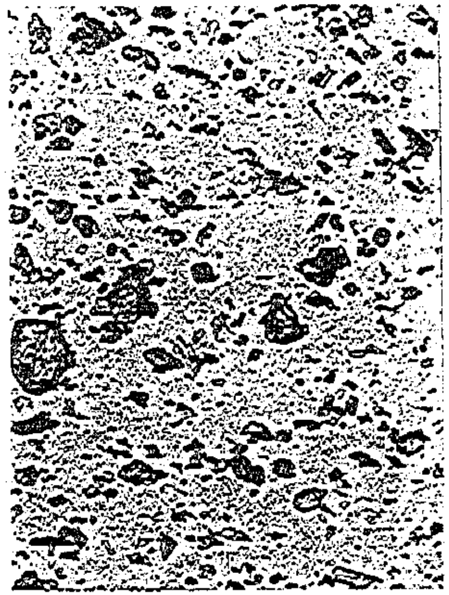
particle size
(average)



10μm



20μm



30μm

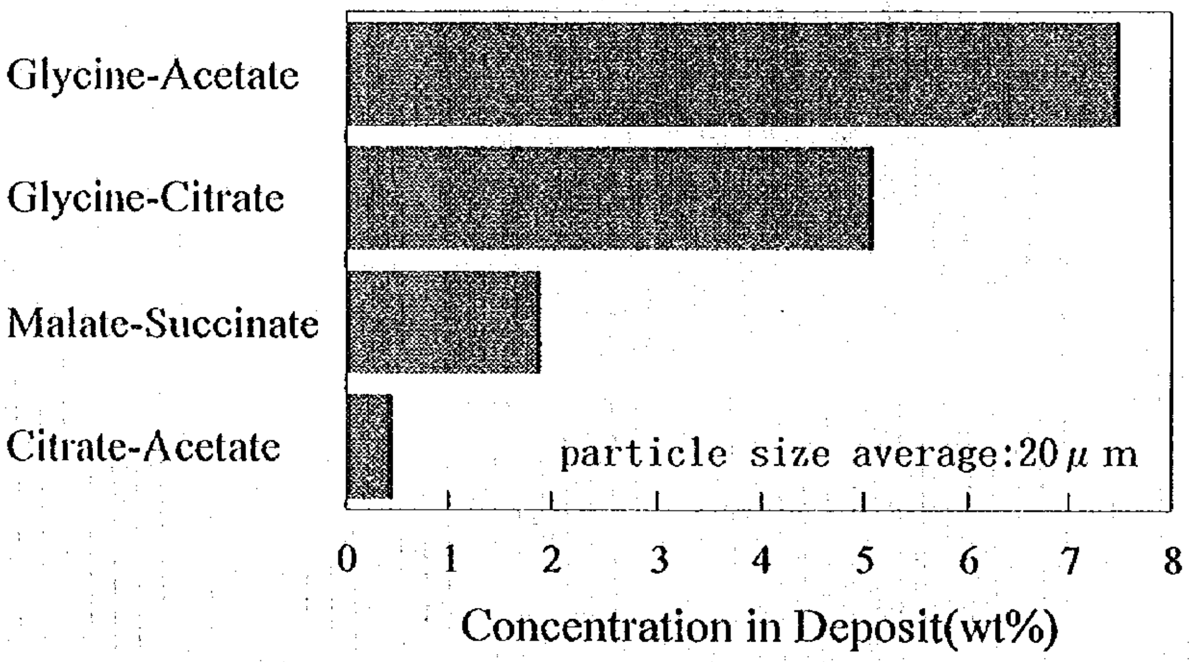


Fig. Sericite Concentration

			molecular weight	$-NH_2$
n-propylamine	(PA)	$CH_3CH_2CH_2NH_2$	59.11	1
ethylenediamine	(EDA)	$H_2NCH_2CH_2NH_2$	60.10	2
diethylenetriamine	(DETA)	$H_2NCH_2CH_2NHCH_2CH_2NH_2$	103.17	3
triethylenetetramine	(TETA)	$H_2N(CH_2CH_2NH)_2CH_2CH_2NH_2$	146.24	4
tetraethylenepentamine	(TEPA)	$H_2N(CH_2CH_2NH)_3CH_2CH_2NH_2$	189.31	5
pentaethylenehexamine	(PEHA)	$H_2N(CH_2CH_2NH)_4CH_2CH_2NH_2$	232.37	6

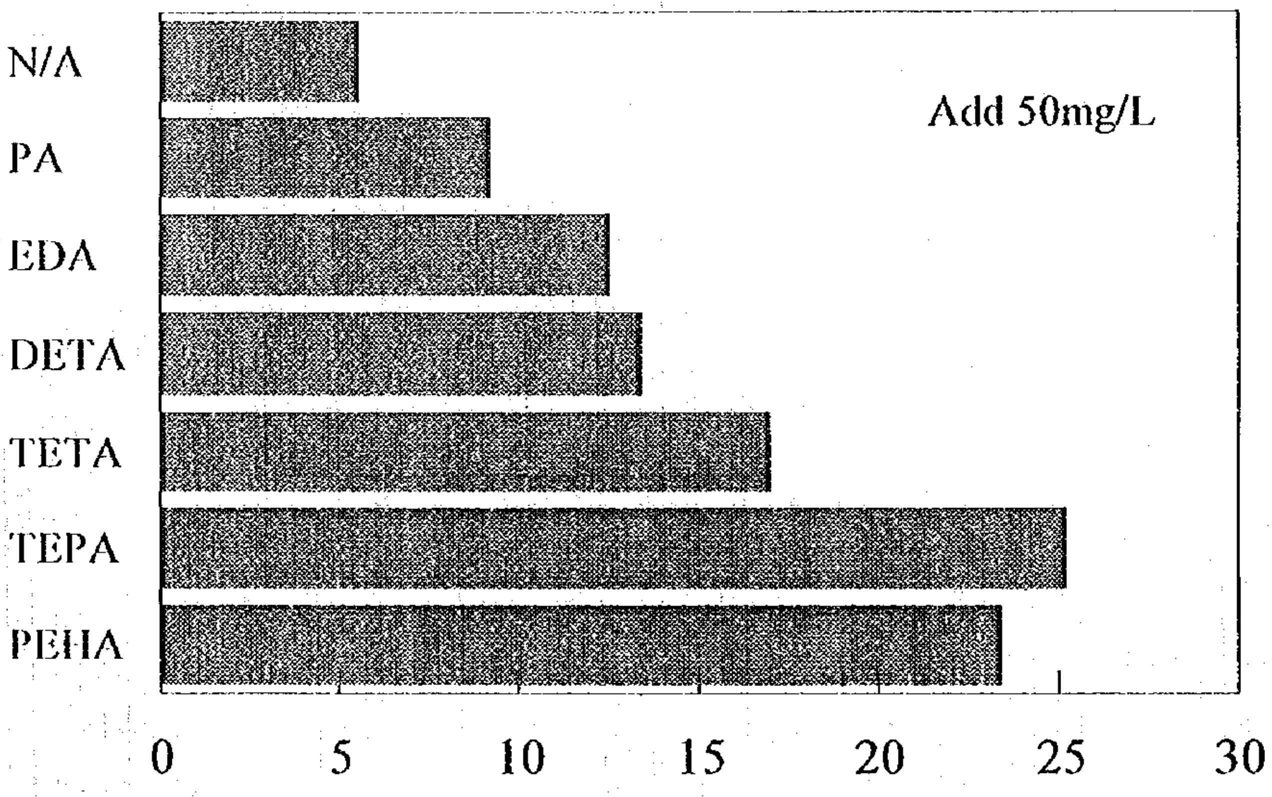


Fig.Addisiton and Composition

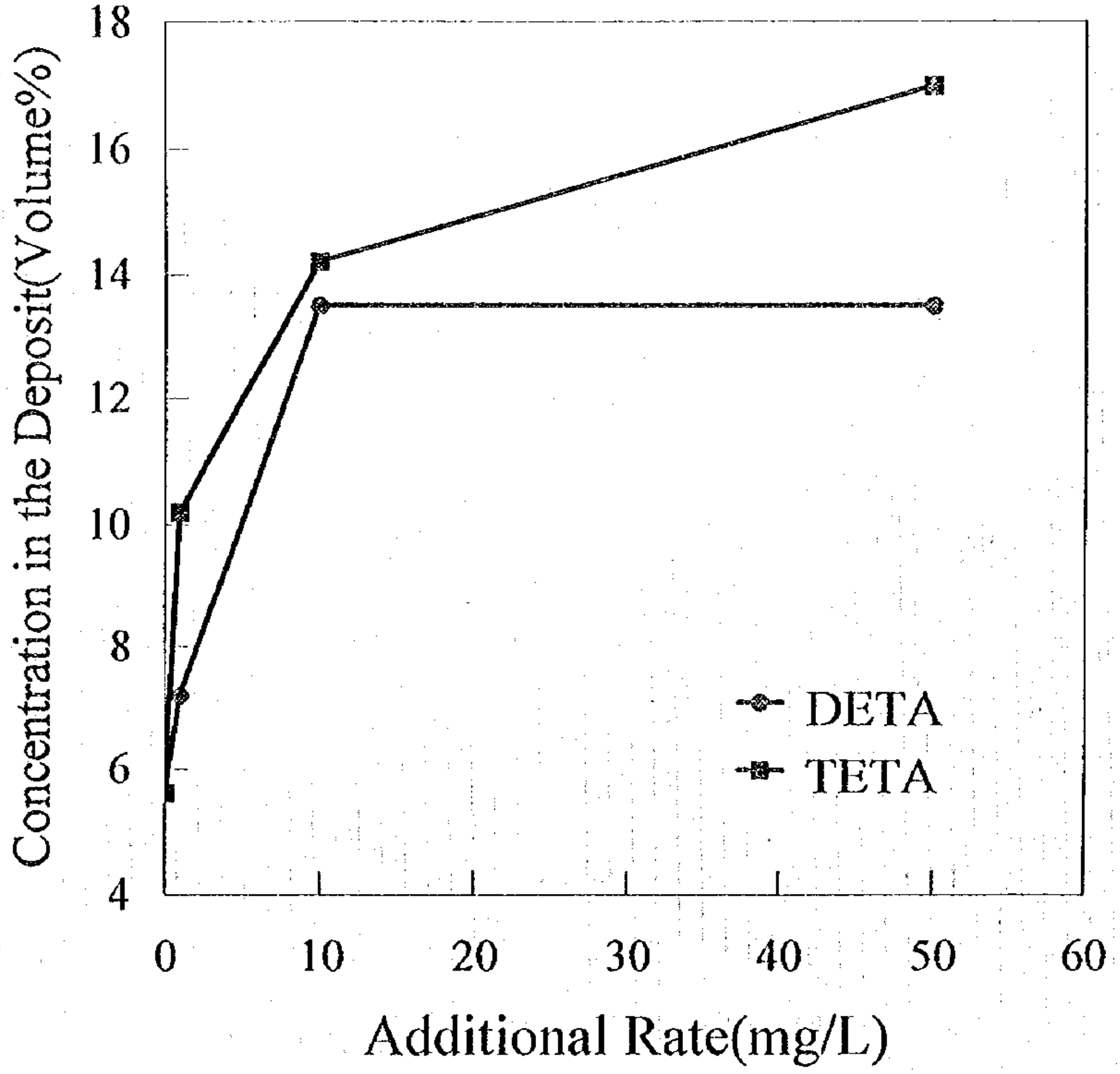


Fig. Effect of Additional Rate

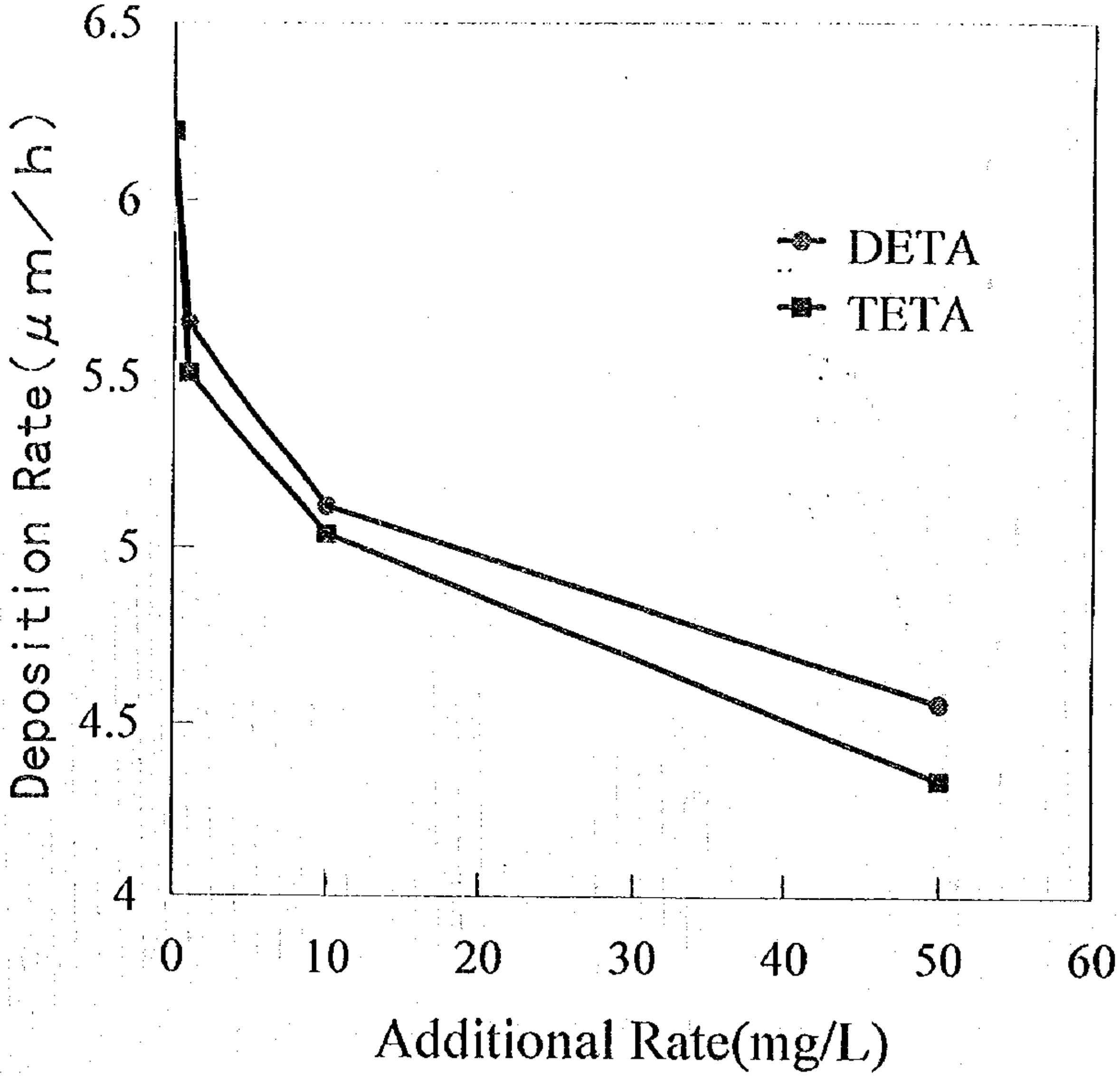


Fig. Effect of Deposit Rate by Addition

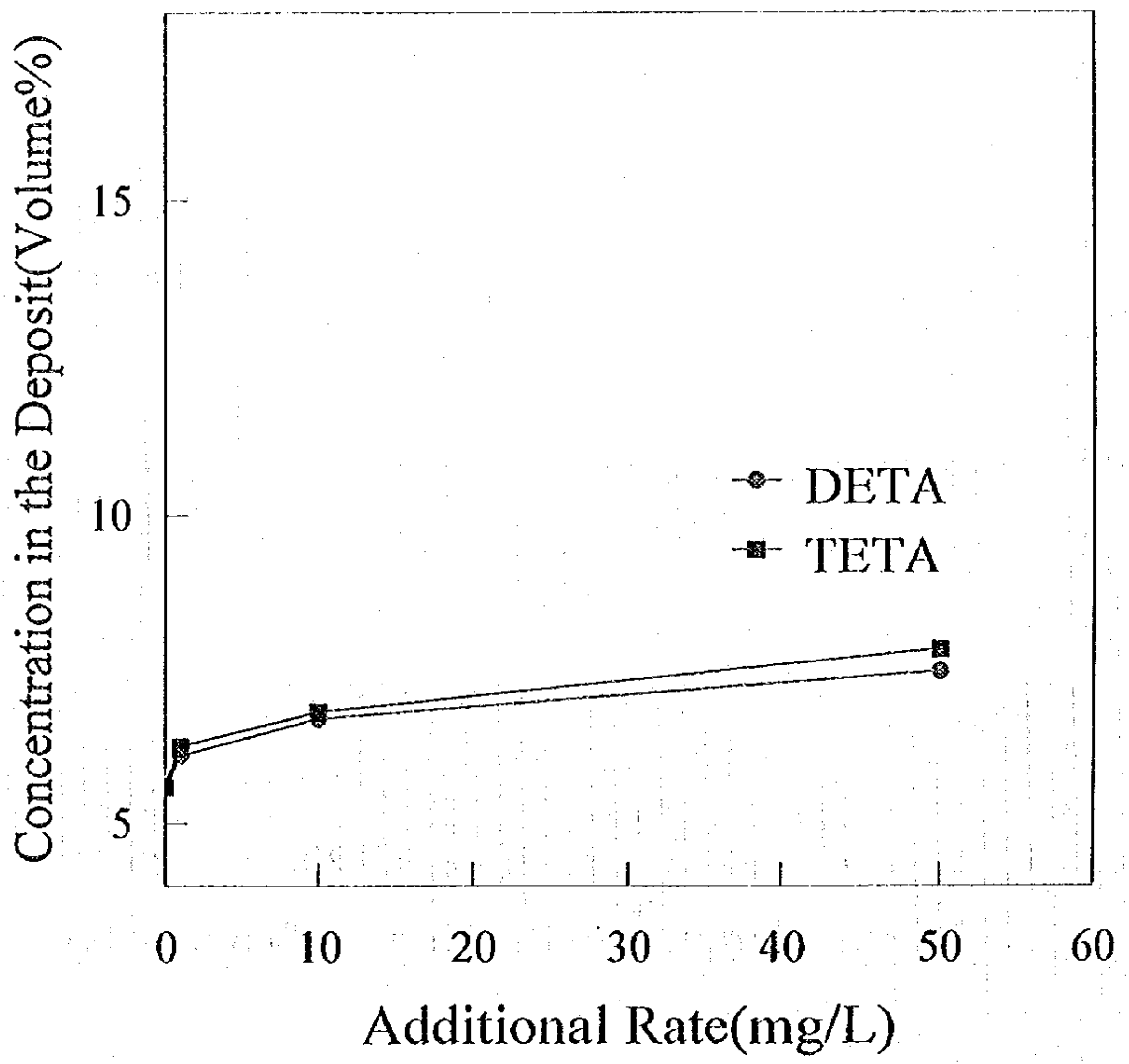


Fig.Calculative Concentration
Transformed Deposition Rate

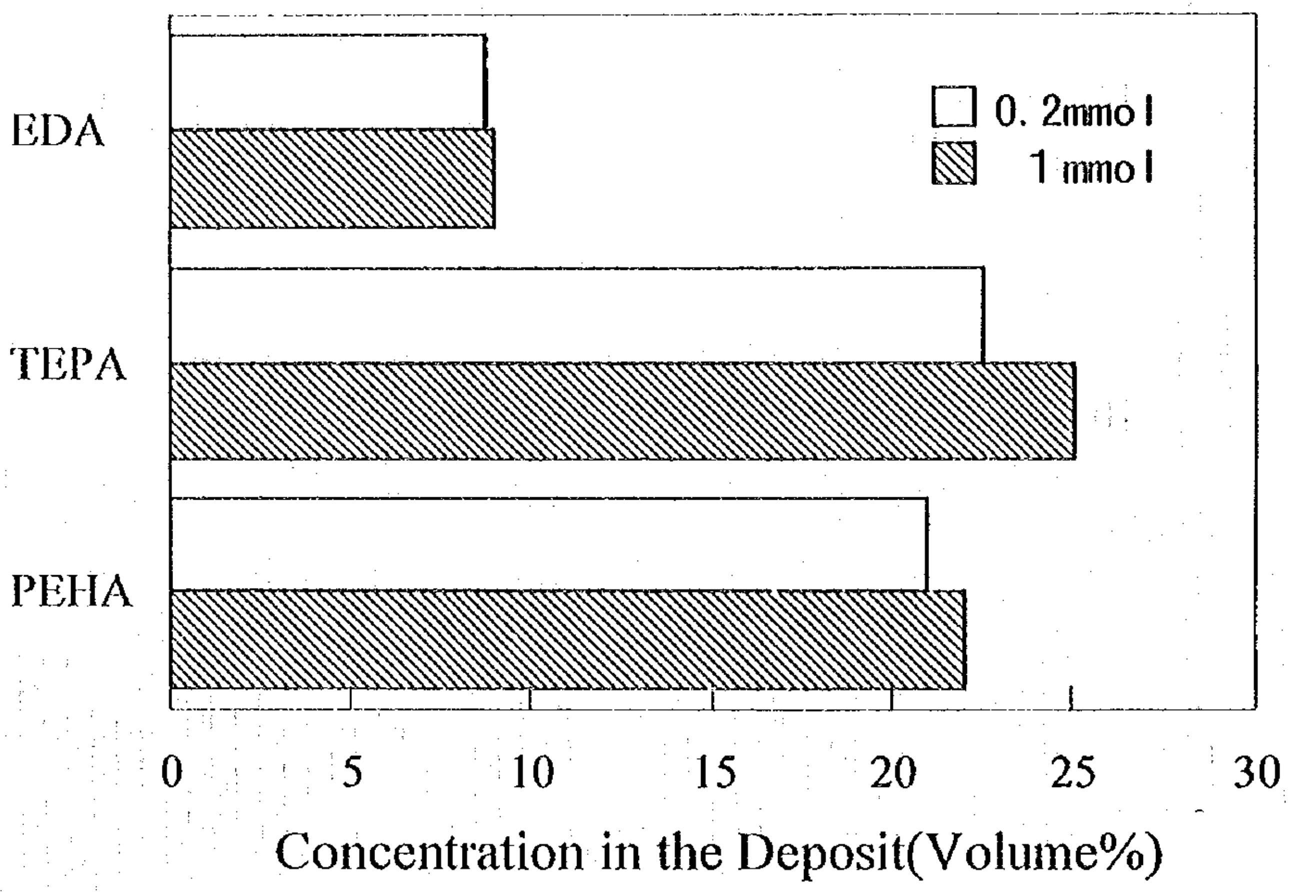


Fig.Effect of Addition

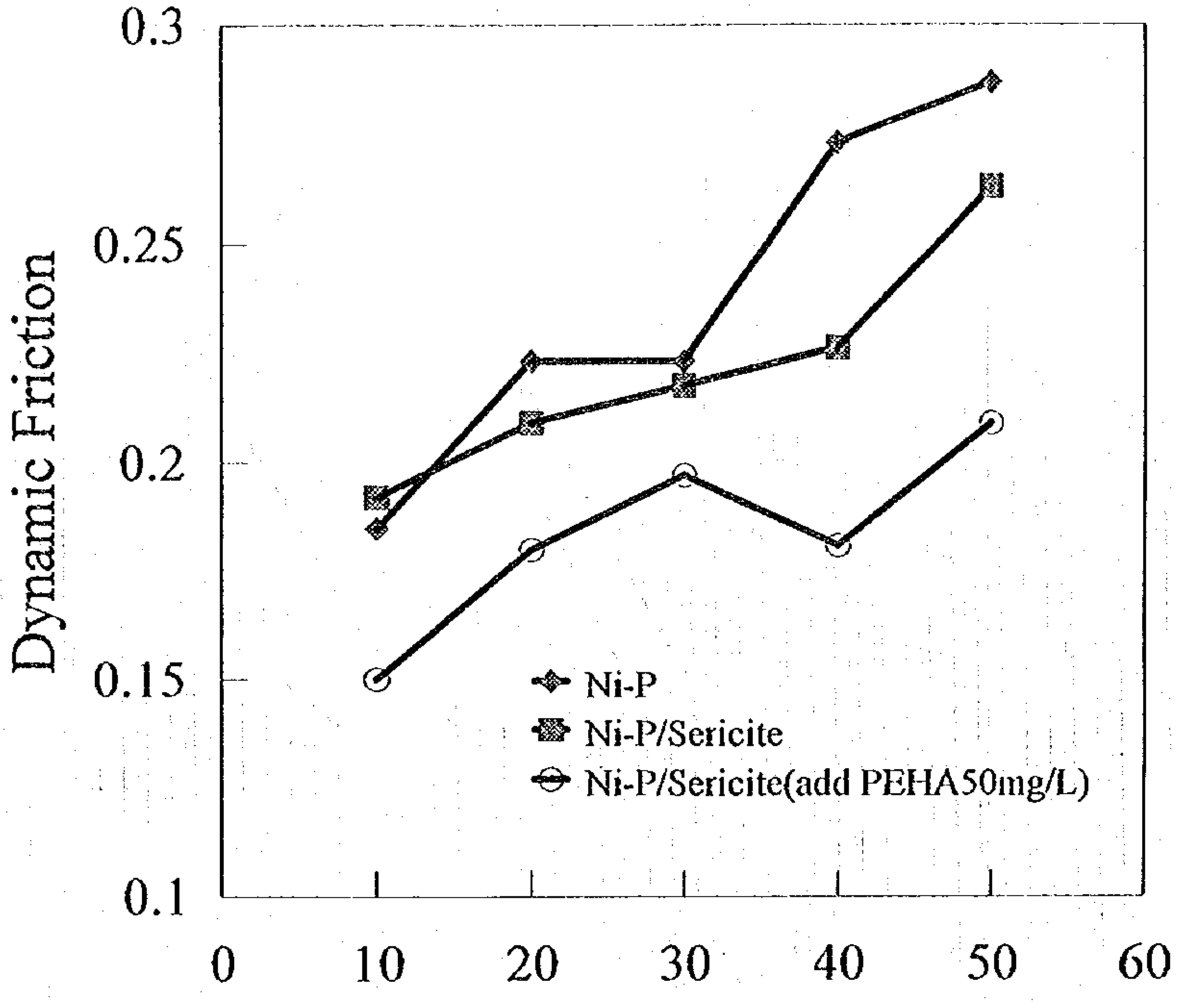


Fig. Coefficient of friction

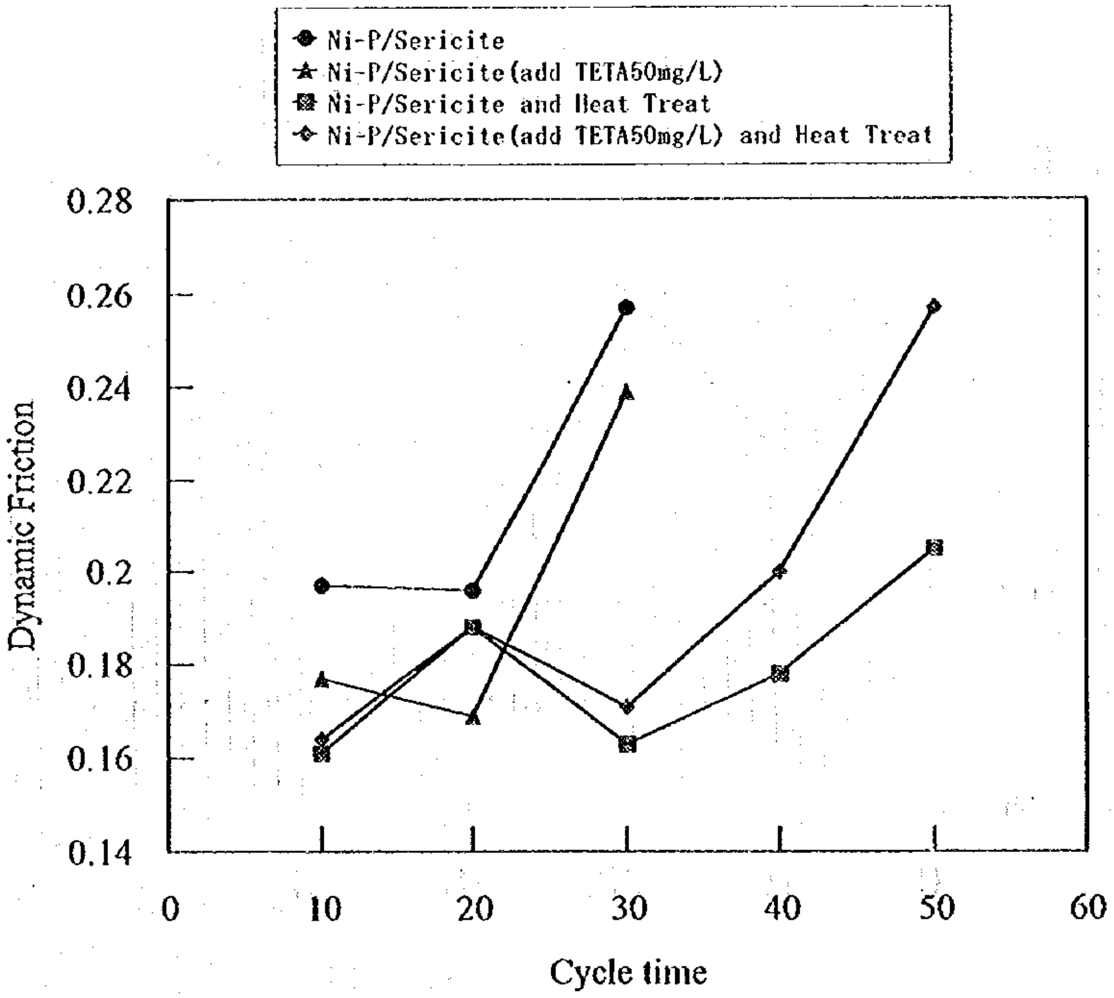


Fig. Effect of Dynamic Friction after Heat Treatment

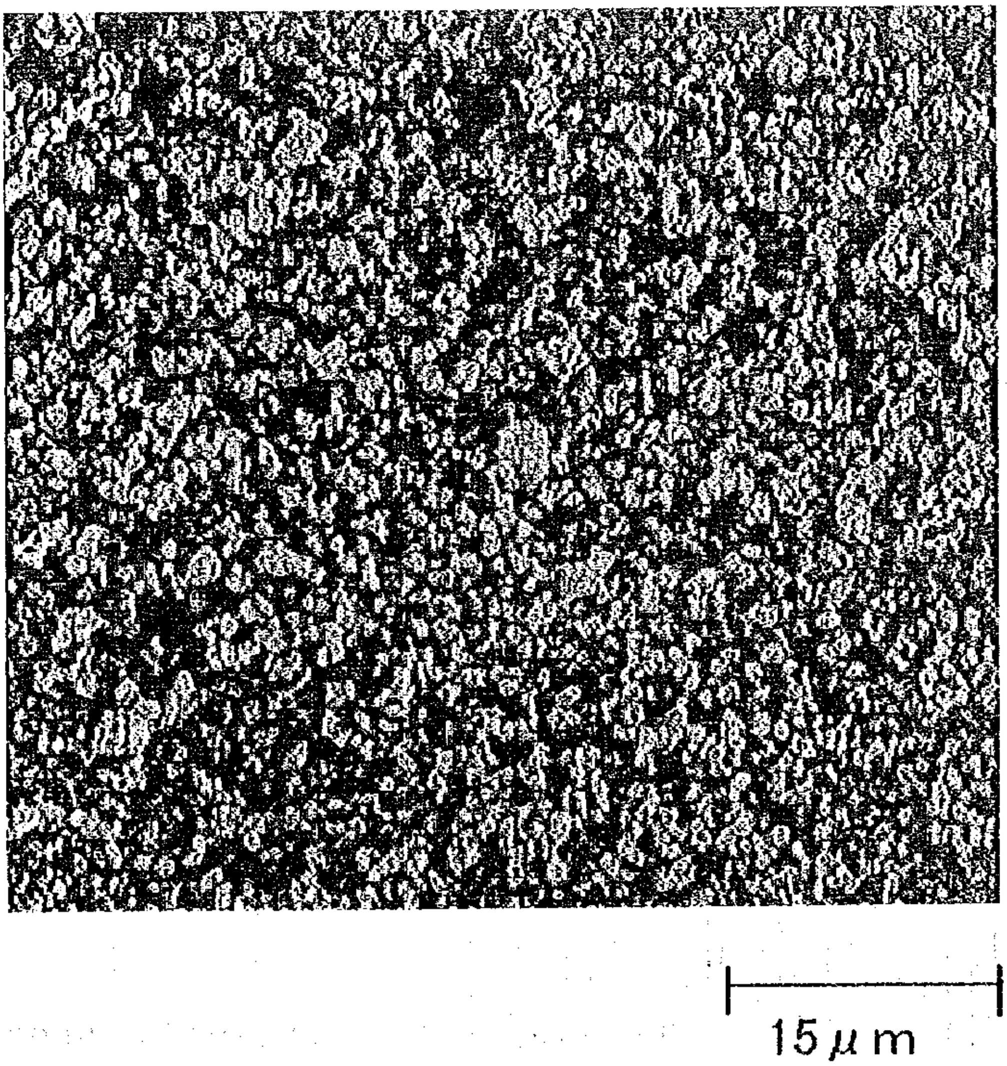


Fig. TiN Particles

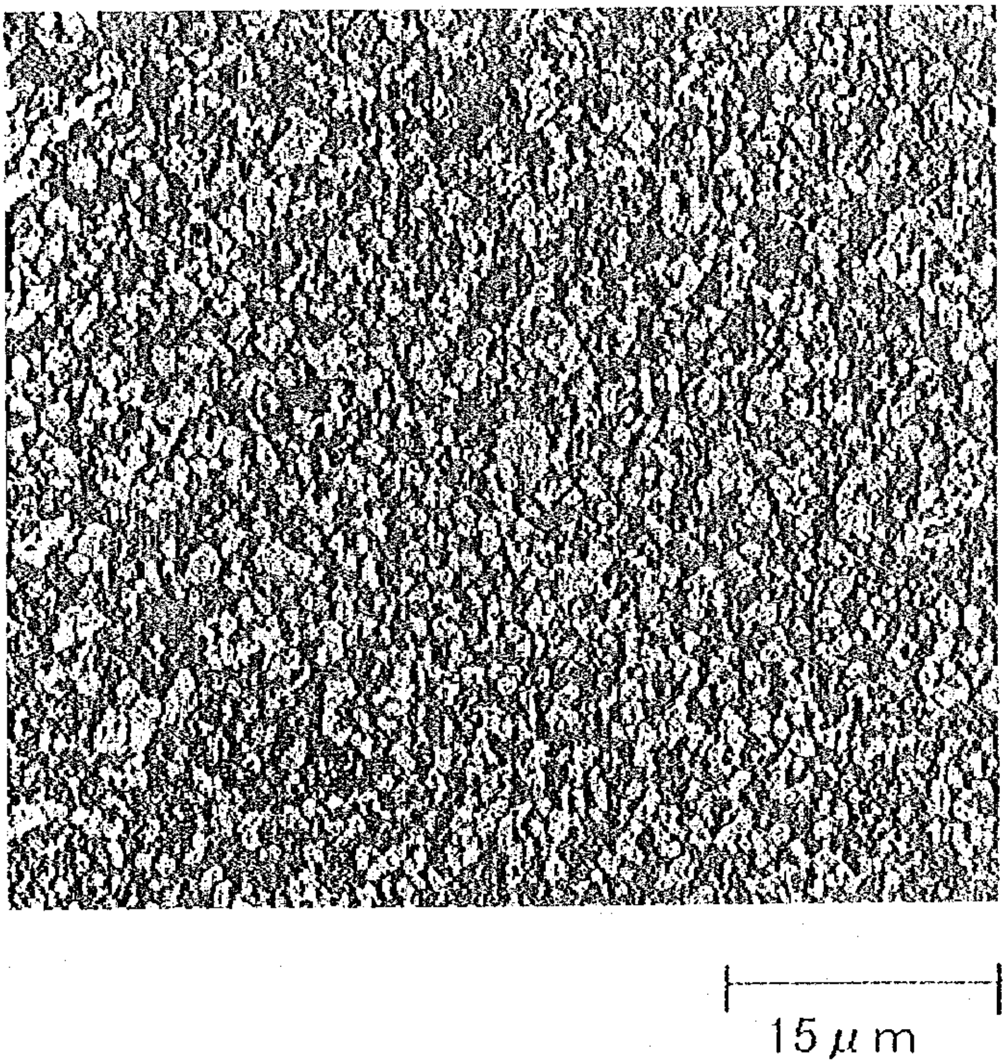


Fig. TiN Particles

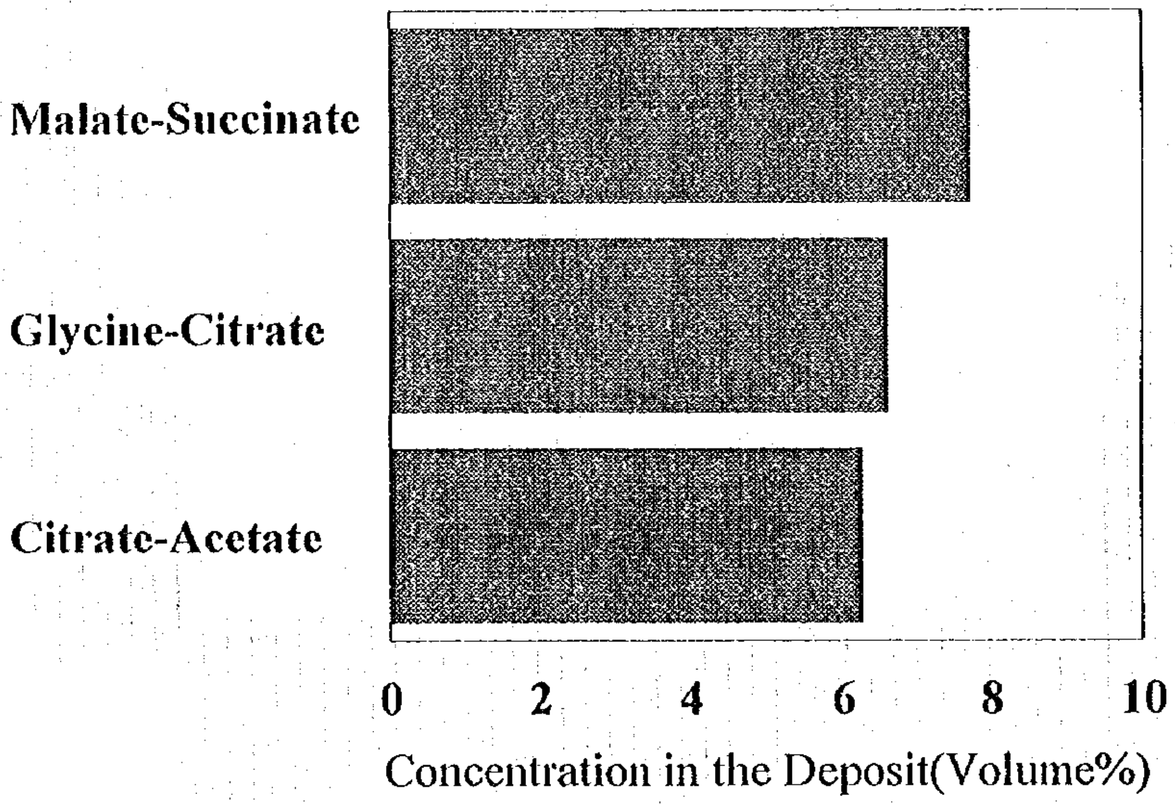


Fig.TiN Concentration in the Deposit

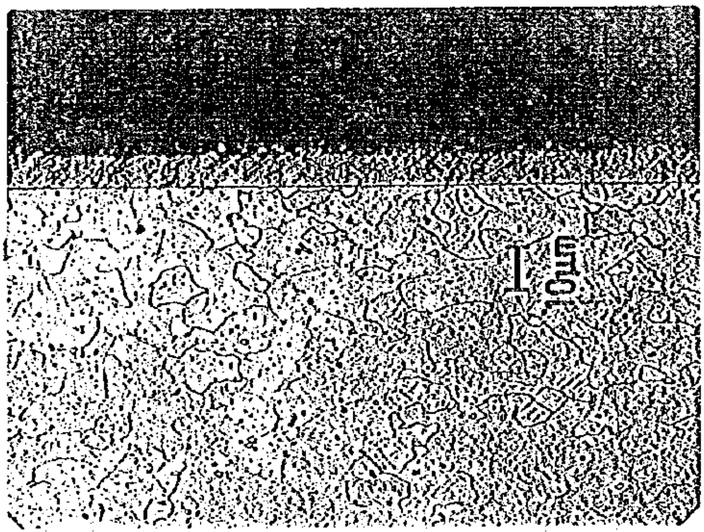
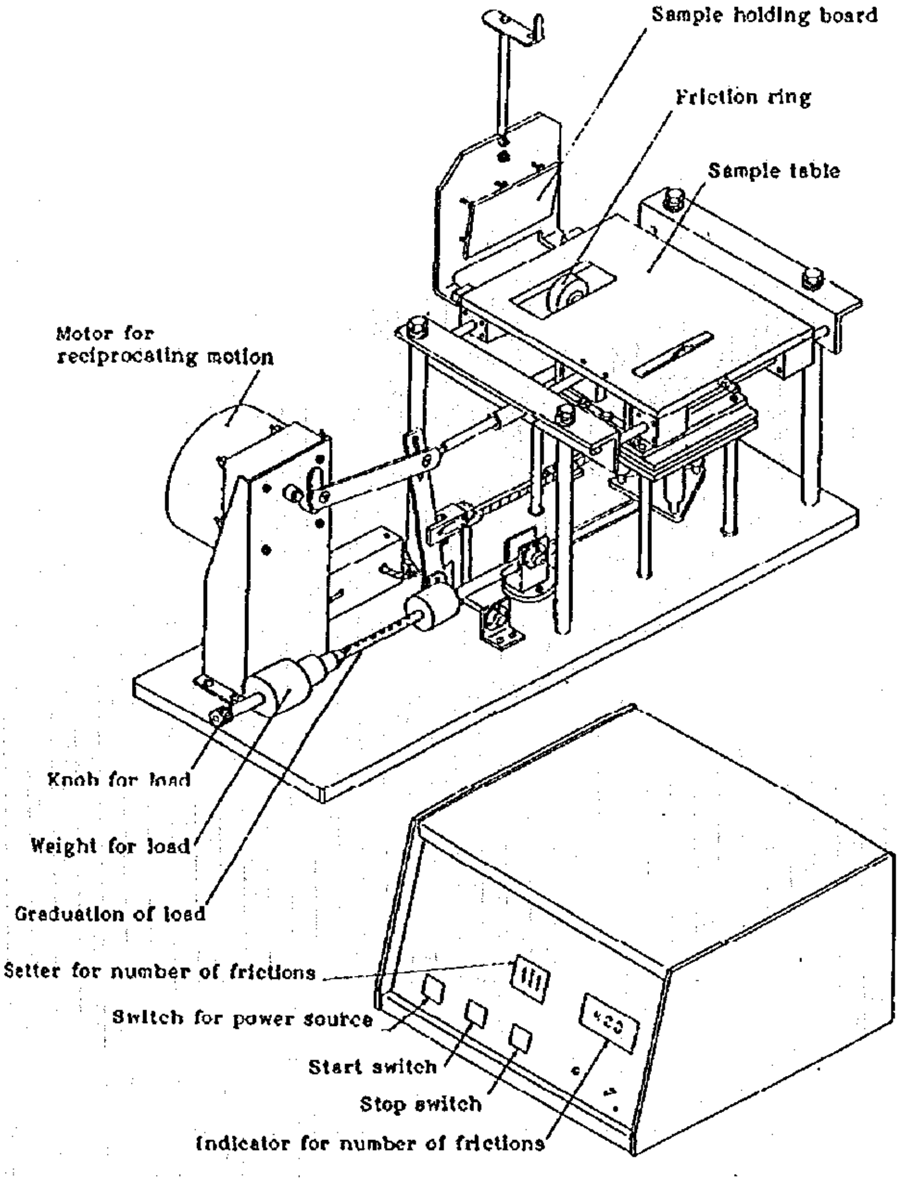

10μm

Fig.Example of Apparatus for Reciprocating Motion Wear Resistance Test



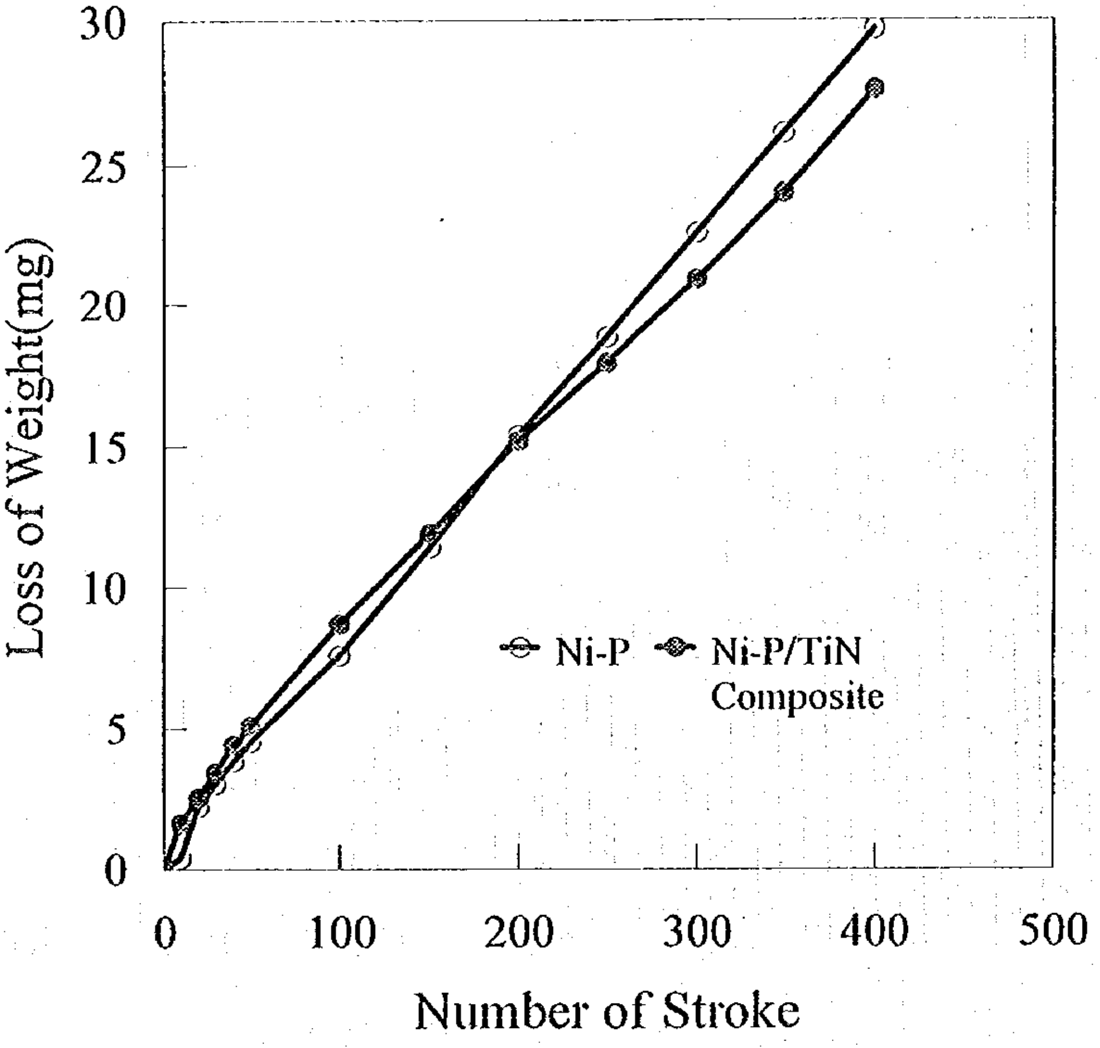


Fig. Result of Wear Resistance Test

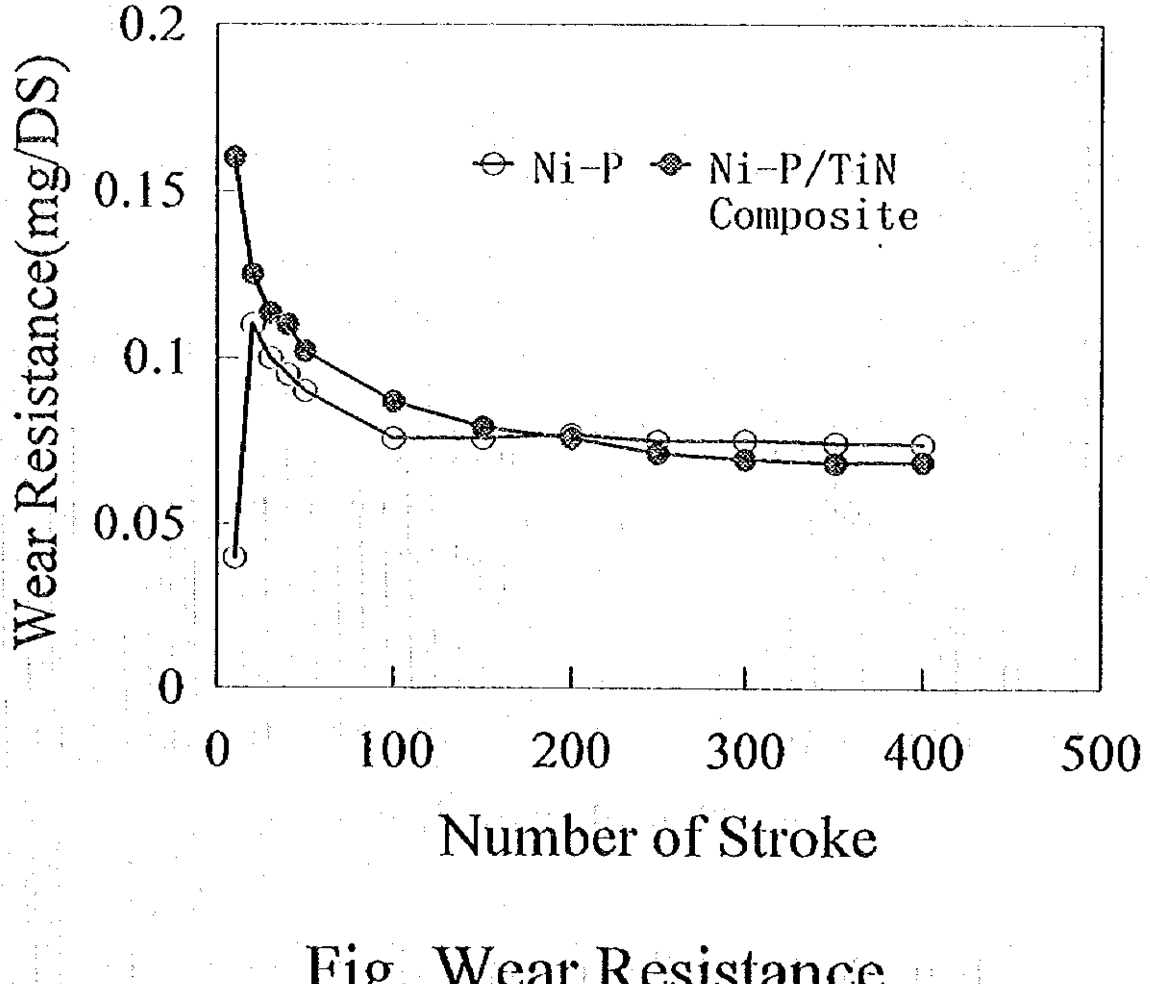


Fig. Wear Resistance

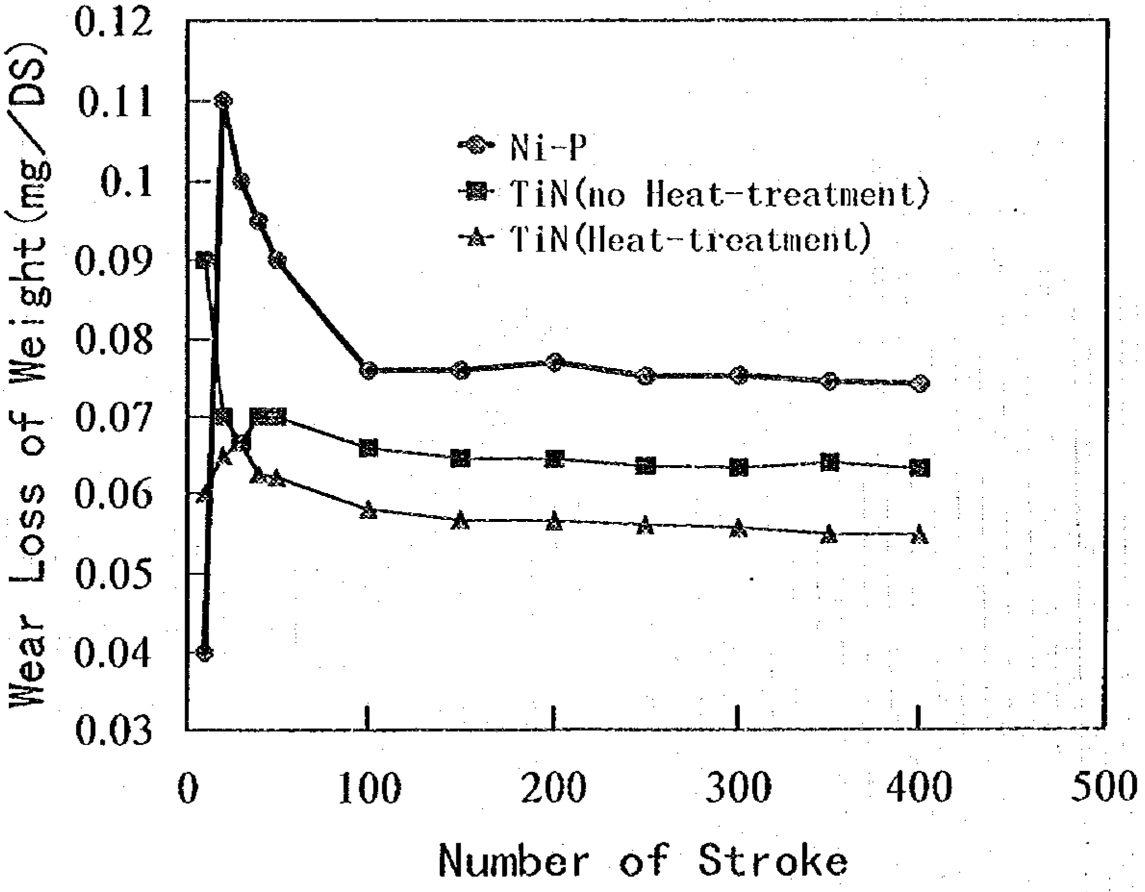
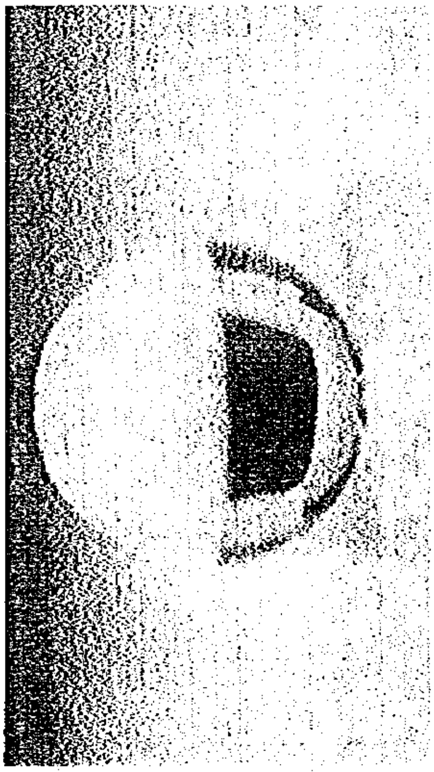
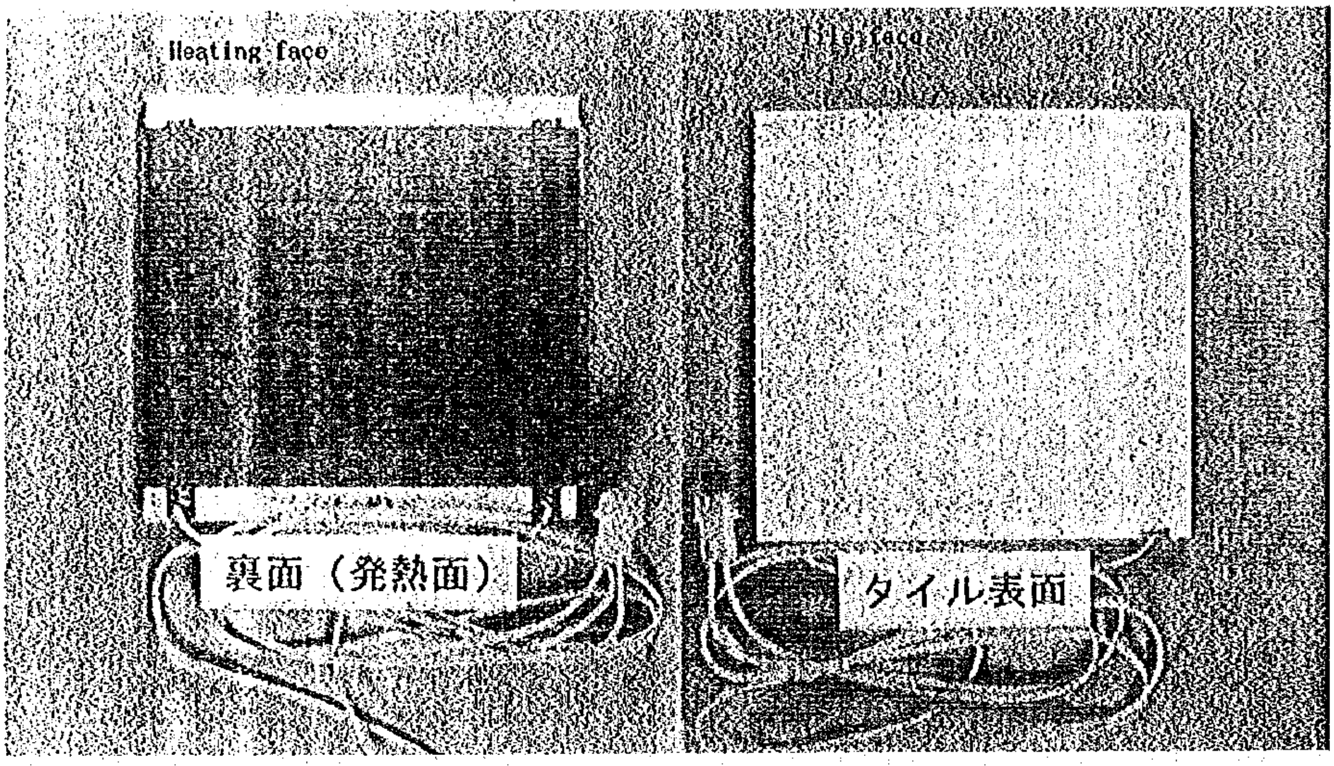


Fig. Reciprocating Motion Wear Resistance Test




Heating face
裏面（発熱面）
Tile face
タイル表面

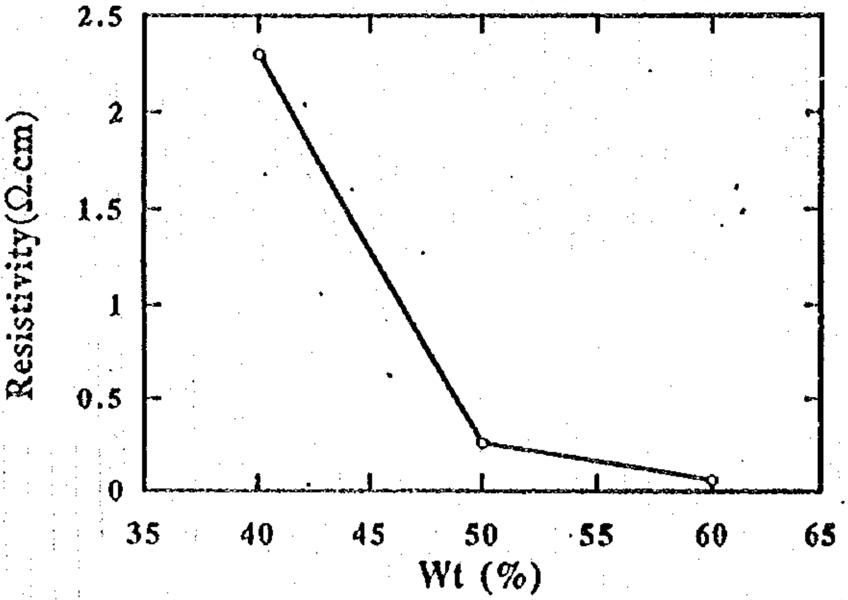


Fig.5 Resistivity and Ni-sericite Wt% with Phenol Resin

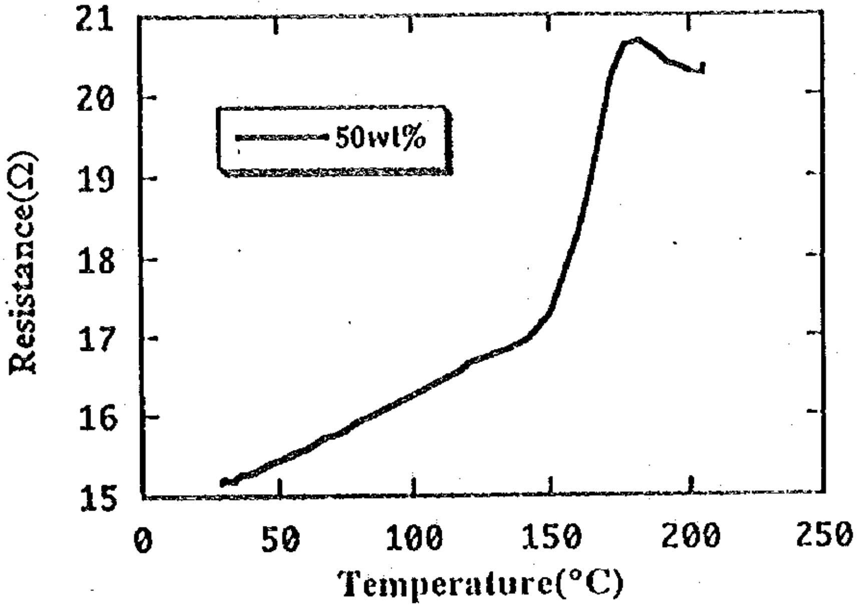


Fig.6 Internal Heating and Resistance

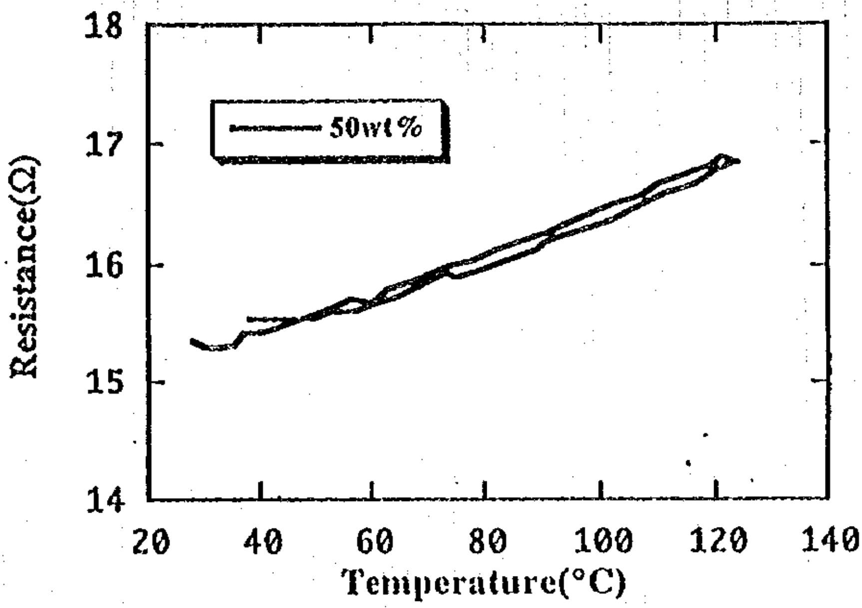


Fig.7 Internal Heating and Resistance