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APPLICATION OF DISPROPORTIONATION REACTION TO SURFACE TREATMENT

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ABSTRACT

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.

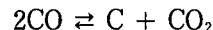
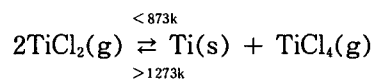
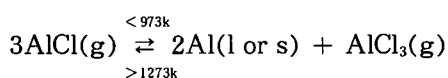
Also in molten salts system, this reaction has many application for surface treatment like metal, alloy and compound coatings for corrosion, wear, heat resistance and so forth. For instance, carbide film, nitride film, boride film, alloy film, quite new different film from the components of substrate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

INTRODUCTION

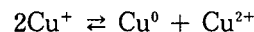
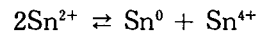
Disproportionation reaction is the reaction which occurs each other for one ionic state to make elemental and ionic states or two ionic states, and also backward reaction in the case of metal or element, whose ionic valency shows more than two states, like the following reactions.



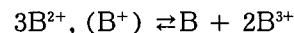
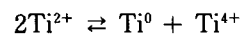
For instance, there are in gaseous state system,



in aqueous state system,

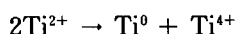


and also in fused salts system

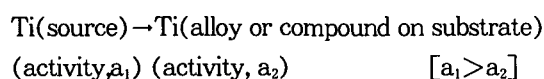


and so on.

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



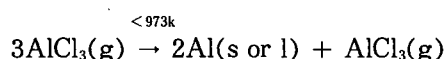
where at appropriate conditions (temperature, reactivity etc.) Ti alloy and Ti compound can be deposited as a film on the substrate. If the alloy or compound formation reaction occurs under these condition, the alloy on compound film can be coated or deposited at the same reaction temperature according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



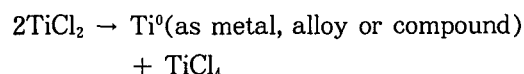
This reaction process, where the disproportionation reaction concerns as a intermediate stop, can be called chemical transportation process.

GASEOUS AND AQUEOUS SYSTEM

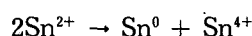
In gaseous disproportionation reaction of Al chloride, pure Al can be originally deposited to make a thin film of Al, Al-alloy and Al-compound on substrate as follows;



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



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;



where Sn^{2+} exists in form of HSnO_2^- or $\text{Sn}(\text{OH})_3^-$ in 0.2~0.4 mol Sn^{2+}/l , 4~5mol/l NaOH at 353 K (deposit rate is 6 $\mu\text{m}/\text{h}$)^[3, 4]. In this case, Sn state in deposit at the beginning is Cu_6Sn_2 to become β -Sn layer as a growth step.

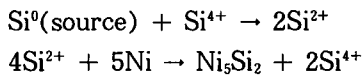
FUSED SALTS SYSTEM

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.

Table 1 Standard composition of molten salts.

| Film | Salts | | |
|--------------|----------------------------------|---------------|---|
| Boride | 2.0wt% B_2O_3 | 10.4wt% Fe-B | Standard supporting salts |
| Chromizing | 4.8wt% CrF_3 | 15.9wt% Fe-Cr | |
| Titanizing | 4.8wt% K_2TiF_6 | 15.9wt% Fe-Ti | |
| Vanadizing | 4.8wt% V_2O_5 | 15.9wt% Fe-V | |
| Zirconizing | 4.8wt% ZrCl_4 | 15.9wt% Fe-Zr | |
| Siliconizing | 12.7w% Na_2SiF_6 | 9.1wt% Si | |
| | | | 31.7% KCl- BaCl_2^- 15.9% NaF |

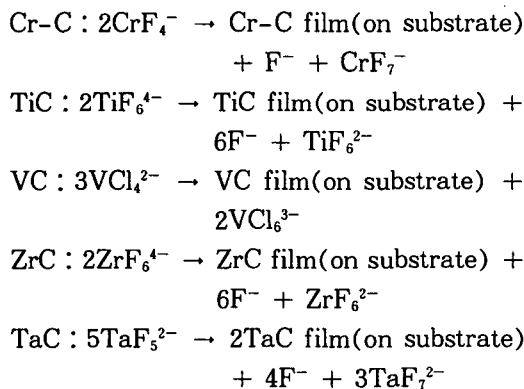
In the first utilization of disproportionation reaction, Ni substrate was siliconized in the system of $\text{KCl-NaCl-NaF-Na}_2\text{SiF}_6+\text{Si}$ molten salts^[5] as follows;



(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.

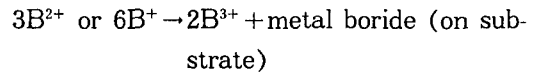
Basic principal reactions are as follows;



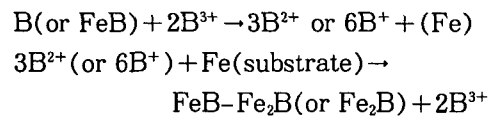
In these cases of metal carbide film formation, as for Cr-C thin film on C-steel, hardness of deposited Cr-C is in range of 1255~2188 Hv depending on C content, as for ZrC film, 1490 Hv, as for TiC film, 1750 Hv, as for VC film, 3400 Hv and as for TaC film, 2800~3000 Hv.^[6]

(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;



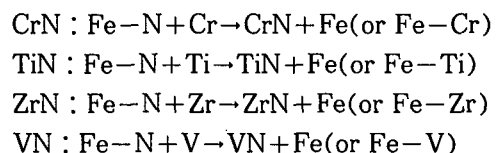
In $\text{KCl-BaCl}_2-\text{NaF-B}_2\text{O}_3+\text{B}(\text{or Fe-B})$, the boriding reaction will occur according to the following reactions. In usage of Boron, FeB-Fe₂B double film can be coated, and in usage of FeB, Fe₂B film only can be coated respectively,



In the case of usual stainless steel, Cr-boride film can be coated, which has 3200 Hv, as for Ti containing material, TiB₂ film has 4200 Hv, as for V containing material, VB₂ has 3700 Hv, as for Zr containing material, ZrB₂ film has 3000 Hv.

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

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

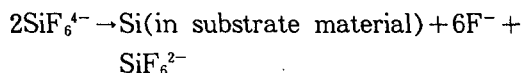


By using the disproportionation process, the hardness of deposited thin film can be controlled in range of 1500~3000 Hv.^[6]

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

The disproportionation reaction of silicon

ion in molten salts is as follows;



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.

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