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Osaka University

Fundamentals of Ceramic(Glass)-Metal Bonding (I)†

Nobuya IWAMOTO*

Abstract

To proceed the study of ceramic-metal bonding, effects of various factors such as adherence-promoting additive, atmospheric conditions, pretreatment of base metal on obtaining good adherence were summarized. Especially the state of iron ion at interface between ceramic and metal works effective on adherence and the solubility of oxide film formed at interface in ceramic was discussed from fundamental result obtained with the use of physical and chemical means.

KEY WORDS: (Ceramic) (Interface) (Bonding) (Metal)

1. Introduction

Since energy crisis it is being called exploitation of new energy such as nuclear fusion, sunshine, liquification of coal and so on. It is an important matter to solve material problem for a development of these processes. From the standpoint to operate vessel at high temperature above 500°C, we should pay attention on the problems as for thermal conduction and corrosion from an oxidation. When we consider refractiveness and corrosiveness from oxidation, ceramics such as oxide or nitride is recommended.

However as regards heat conduction and good machinability metal has superior property.

Before now the development of cermet has been carried on for space material. However it has weak point for an oxidation characteristic as well as carbide

On the other side the use of metal is limited till 1000°C and the use of cobalt must be avoided from the radioactivity in nuclear- and fusion reactor. Molybdenum and tungsten have property of high hardness but scarce toughness.

Accordingly it becomes necessary to make combined material, from metal and ceramic, having refractiveness and good heat conductivity by making the best use of each characteristics.

Furthermore ceramic-metal bond can be used for severe environments such as high temperature engine, ocean development, requirement of high reflectivity in the case of space technology or sunshine utilization, protection of high velocity missile by aero-dynamical

heating, printed circuit for electronics and the possibility of welding between different sort of metals instead of usual fusion bonding.

Hereafter ceramic-metal bonding will be powerful process in each field

There exist many processes in ceramic-metal bonding.

- 1) ceramic (solid) – metal (solid) by pressure bonding
- 2) ceramic (gas) – metal (solid) by wire-explosion, plasma spraying, or CVD
- 3) ceramic (liquid) – metal (solid) by enamel or brazing
- 4) ceramic (solid) – metal (gas) by evaporation, spraying or CVD
- 5) ceramic (solid) – metal (liquid) by sintering or brazing

In this review, the author would like to treat the means, (1), (2) and (3).

2. Mechanisms of the adherence of porcelain enamels

Theories concerning mechanisms of the adherence of porcelain enamels can be broadly divided into six categories as follows:

1) Mechanical gripping theory

The theory was presented by Clawson⁽¹⁾ and it was supported by Richmond et al⁽²⁾. The theory is grounded on that enamel corrodes iron as base during enameling and the bonding between enamel and base comes in effect to well because the surface of base becomes roughly.

2) Dendrite theory

The theory was proposed by King⁽³⁾ and it is based on

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that metal dendrite can be formed from the reaction of the components such as CoO and NiO containing in enamel. This is proved from the experiment using α -iron⁴⁾. Further the theory is supported⁵⁾ from simultaneous reactions with oxidation and reduction combined with



3) Galvanic theory

Staley presented the theory that with the electrolytic action of iron base during enameling metal precipitated, such as Co, Ni or Sb, facilitates good bonding between enamel and iron base when metal oxide, whose metal is ranked intermittent between iron and copper in a series of electromotive force, is contained in enamel⁶⁾. Moreover such metals as Co, Ni, and Sb have intermittent expansion coefficient between those of enamel and iron base, and thereupon mechanical bonding with the form of dendrite is formed.

On the other hand Dietzel⁷⁾ thought that CoO or NiO in enamel can be reduced and therefore electrolytic precipitation can promote the bonding between enamel and iron base. Further he thought that mechanical grip can occur because enamel entered into the cavity induced from strong selective corrosion on iron surface at high temperature by flowing an electric current. Moore et al.⁸⁾ supported this thought.

4) Oxide layer theory

The theory was given by Cooke⁹⁾. This thought is based upon that there occurs oxidation of iron base during enameling and the oxide formed dissolves continuously in enamel and accordingly transition layers changing the chemical composition can be originated. The effect brings about good result for bonding.

Kautz¹⁰⁾ considered that FeO layer equal to 0.00003 inch thickness can be formed at the interface between enamel and metal during enameling, and this layer is composed from FeO as chief component and small quantities of Fe and Fe₃O₄¹¹⁾. CoO in enamel was considered to promote the dissolution of iron oxide into enamel and to work as oxidizing agent. On the other hand Vielhaber¹²⁾ thinks that CoO in enamel lessens the solubility of iron oxide in enamel.

5) Chemical bond theory

Howe¹³⁾ presented this theory. It is thought that CoO in enamel increases the solubility of FeO and chemical bonding between enamel and iron base occurs because of the action of oxidizing agent. Douglas et al.¹⁴⁾ intended that oxygen must be continuously kept at the interface between enamel and metal to obtain good bonding and

CoO can be behaved as oxidizing agent.

6) Hydrogen theory

In general porcelain has inherent ability for bonding with iron as well as copper. The difference in bonding strength with iron or copper can be reduced to an existence of hydrogen. Hydrogen generated during enameling prevents to wet the surface of iron but an existence of iron oxide at the interface between enamel and iron can extend hydrogen as water by oxidation. CoO in enamel acts as oxidizing agent to form iron oxide necessitated at the interface.

When various theories as to the mechanisms of the adherence of porcelain enamels were summarized, the following classification can be induced:

- CoO in enamel accelerates the bonding between enamel and iron base as oxidizing agent. (Kautz¹¹⁾, Howe¹³⁾, Douglas & Zander¹⁴⁾, and Deringer¹⁵⁾)
- CoO in enamel increases the solubility of iron oxide in enamel. (Clawson¹⁾, Kautz¹⁰⁾, and Howe¹³⁾)
- CoO in enamel accelerates the formation of iron dendrite. (King³⁾)
- CoO in enamel has an effect to precipitate Co metal on iron. (Staley⁶⁾, and Dietzel⁷⁾)

Every theories were deduced from the fact that good result as for bonding between porcelain enamel and iron base could be obtained when CoO was contained in enamel.

3. Experimental certification of the effect of additive for obtaining good adherence

Harrison et al.¹⁶⁾ certified the following reaction using radioisotope.



Moore and Eubanks¹⁷⁾ compared the adherence-promoting effect of CuO and Co₃O₄ in enamel on stainless steel.

In **Figure 1**, the result is shown. It will be seen that, in both systems, the adherence index increases with increasing the oxide content and nearly same tendency can be shown.

Eubanks and Moore¹⁸⁾ studied the effect of MnO₂ added as an oxidizing agent in enamel on the adherence index. As shown in **Figure 2**, adherence value becomes slightly better with an addition of MnO₂ in enamel.

King, Tripp and Duckworth¹⁹⁾ summarized the free energy of formation of oxide at the enameling temperature. The values are compared in **Table 1**.

They studied the phases precipitated from glass-metal mixtures containing CoO, PbO, As₂O₃, or CuO which is

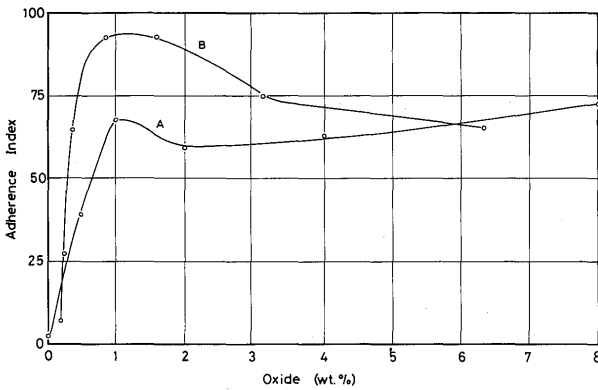


Figure 1: Comparison of adherence-promoting oxide as CuO and Co₃O₄ (firing at 1550°F for 5 min.)¹⁷⁾
 (A) CuO on stainless steel
 (B) Co₃O₄ on iron

Table 1 Free energies of formation of metal oxides at 1292°C¹⁸⁾

Oxide	Energy (kcal/mole O ₂)
2Ca + O ₂ → 2CaO	-256
Zr + O ₂ → ZrO ₂	-219
4/3 Al + O ₂ → 2/3 Al ₂ O ₃	-217
2Ti + O ₂ → 2TiO	-203
Ti + O ₂ → TiO ₂	-182
Si + O ₂ → SiO ₂	-166
4/3 B + O ₂ → 2/3 B ₂ O ₃	-162
2Mn + O ₂ → 2MnO	-148
4Na + O ₂ → 2Na ₂ O	-139
4/3 Cr + O ₂ → 2/3 Cr ₂ O ₃	-138
2Zn + O ₂ → 2ZnO	-110
4/5 V + O ₂ → 2/5 V ₂ O ₅	-102
4/5 P + O ₂ → 2/5 P ₂ O ₅	- 94
2Fe + O ₂ → 2FeO	- 94
W + O ₂ → WO ₂	- 94
Mo + O ₂ → MoO ₂	- 94
Sn + O ₂ → SnO ₂	- 94
4/3 Fe + O ₂ → 2/3 Fe ₂ O ₃	- 90
2Co + O ₂ → 2CoO	- 80
2/3 Mo + O ₂ → 2/3 MoO ₃	- 79
2Ni + O ₂ → 2NiO	- 76
4/3 As + O ₂ → 2/3 As ₂ O ₃	- 73
4/3 Sb + O ₂ → 2/3 Sb ₂ O ₃	- 72
2Pb + O ₂ → 2PbO	- 63
2Bi + O ₂ → 2BiO	- 60
4/3 Bi + O ₂ → 2/3 Bi ₂ O ₃	- 50
4Cu + O ₂ → 2Cu ₂ O	- 48
2Cu + O ₂ → 2CuO	- 35

below FeO in free energy of formation. The results obtained are given in Table 2.

The reduction behavior satisfied with the prediction from free-energy-of-formation data except the oxidation of Cu by arsenic glass. The important facts observed in this experiment are as follows:

- a) The reactions, between Fe and CoO glass and between Cr, or Fe and As₂O₃ glass, were completed in less than 10 minutes.
- b) Cr worked more sluggish than Fe as a reducing agent.

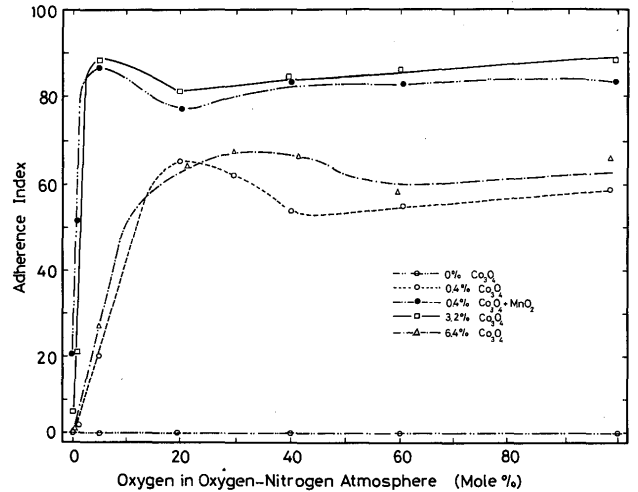


Figure 2: Effect of oxygen content of firing atmosphere and various metallic oxide additions on adherence.¹⁸⁾

Table 2 Phases precipitated from glass-metal mixtures¹⁹⁾
 (1500°F, 2 hrs in Ar)

Oxide addition to basis glass	Metal additive	Precipitated phase	
		Expected	Observed
None	Chromium	None	None
None	Iron	None	None
None	Copper	None	None
ZrO ₂	Chromium	None	None
ZrO ₂	Iron	None	None
ZrO ₂	Copper	None	None
CoO	Chromium	Cobalt	Cobalt
CoO	Iron	Cobalt	Cobalt
CoO	Copper	None	None
As ₂ O ₃	Chromium	Arsenic	Arsenic
As ₂ O ₃	Iron	Arsenic	Arsenic
As ₂ O ₃	Copper	None	None
PbO	Chromium	Lead	Lead
PbO	Iron	Lead	Lead
PbO	Copper	None	None
CuO	Chromium	Copper	Copper
CuO	Iron	Copper	Copper
CuO	Copper	Cuprous oxide	Cuprous oxide

4. Effect of atmosphere on an adherence

As mentioned before, the role of oxygen from oxidizing agent added in enamel is important on adherence.

In the next place, an effect of atmospheric conditions on adherence should be considered from the standpoint of oxygen migration into interface between enamel and base metal.

Zackay, Mitchell, Mitoff and Pask studied wetting behavior of sodium silicate glass on some group I and group VIII metals when atmosphere, in vacuum, helium, hydrogen, oxygen, or air, was changed²⁰⁾.

In Table 3, effect of metal composition and atmosphere on contact angle with sodium silicate glass at

was affected most by atmospheres of water vapor, carbon monoxide, hydrogen, and oxygen. On the basis of Young's equation only changes in the glass-metal interfacial tension, e.g., those brought about by absorption of gas, oxygen and hydrogen, at the interface, would be expected to affect the strength.

In Table 4, effect of atmosphere on contact angle of sodium silicate on Pt is given. Further effect of gas mixtures on contact angle of sodium silicate on Pt is given in Table 5.

Table 3 Effect of metal composition and atmosphere on contact angle with sodium silicate glass at 900°C

Atmosphere	Copper	Silver	Gold	Nickel	Palladium	Platinum
Helium	60	70	60	55	55	60
Hydrogen	60	73	45	60	40	43
Air	0	0	55	0	25	0
Oxygen	0	0	53	0	20	0

900°C is given.

They considered various causes such as compound formation, gas solubility, and polarizing power of metal to explain the difference in contact angle given in Table 3. However these problems remain unsolved.

Further Fulrath, Mitoff and Pask²¹⁾ studied the wetting behavior of sodium silicate on metals such as Fe, Ti, Zr, Mo, W, or Ta. Although the consideration using interfacial energy in the glass-metal was given, it is not clear. Volpe, Fulrath and Pask²²⁾ studied the wetting of sodium silicate on Au and Pt at 1000°C with the use of various atmospheres such as oxygen, nitrogen, carbon dioxide, helium, argon, water vapor, carbon monoxide, hydrogen, and several mixtures of some of these gases. Especially they found new evidence that wetting of Pt was only affected by these atmospheres and the contact angle

Table 4 Effect of atmosphere on contact angle of Na₂O·2SiO₂ glass on platinum (Pressure in 10⁻³ mm. of Hg)

Gas	10	100	1000
O ₂	15°	13°	10°
N ₂	22°	21°	32°
CO ₂	20°	29°	—
Ar	17°	—	37°, 22°
He	—	—	24°
H ₂ O	58°	63°	—
CO	40°	55°	66°
H ₂	56°	51°	49°

Table 5 Effect of gas mixtures on contact angle of Na₂O·2SiO₂ glass on platinum

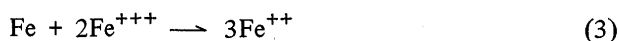
H ₂ O(%)	100	60	20	0
Gas mixture				
H ₂ O + O ₂	60°	17°	15°	13°
H ₂ O + N ₂	60°	60°	60°	20° - 30°

These results suggest that oxygen has a greater effect on the glass-metal interfacial tension than on the surface energy of the metal because absorption on the metal alone would have caused an increase in contact angle, and oxygen can move to the glass-metal interface through metal.

Cline, Fulrath and Pask²³⁾ studied contact angle of sodium silicate on iron in vacuum and in oxygen at 900° to 1000°C. In vacuum contact angle of 55° ± 2° was obtained and the adherence was poor. On the other hand, contact angle of sodium silicate on oxidized iron was about 24° and then rose to almost 55° as the oxide was dissolved and the glass came into contact with the clean iron.

Adams and Pask²⁴⁾ studied contact angle of sodium silicate containing various content of iron oxide on iron at 1000°C in vacuum. Depending on X-ray analysis of glass initially containing 28.5 mole% Fe, the iron in glass was considered as ferrous state. With the reaction between ferrous iron in glass and the iron entering the glass at its interface, ferric iron in glass could be reduced to be ferrous iron. The adherence becomes better with the proceeding of this reaction. They thought that the result

can be originated by roughning effect of base metal.



Pask and Fulrath²⁵⁾ summerized a series of their investigation as for wetting of sodium silicate glass on several metals. In Table 6, the results are given.

They thought the reason for the occurrence of strong chemical bond between glass and metal as follows:

Table 6 Contact angle of drops of Na₂Si₂O₅ glass on several metals at 1000°C

	Vacuum	Ar, He N ₂ , CO ₂	O ₂	H ₂	H ₂ O	CO
Au	62°	62~65°	35°	65°	65°	65°
Pt	22°	17~24°	15°	52°	60°*	60°
Fe	55°	n.d. +	12~24°#	n.d.	n.d.	n.d.

*Pt in (H₂O + O₂), 15°; Pt in (H₂O + N₂), 60°

+n.d. = not determined

#Fe in O₂ becomes oxidized; indicated contact angle is on oxidized iron, on solution of oxide, angle rises to approximately 55° (afore-mentioned)

Metal is covered by a layer of oxygen held by covalent-ionic bonds created by partial transfer of electrons from the surface atoms to the oxygen atoms. To lower the internal energy of glass by increasing the screening of the silicon in the glass, the dissolution of oxide layer on metal occurs.

Accordingly when the surface of the glass comes in direct contact with the metal atoms and the surface oxygens of the glass are already bonded, only a weak bond of the van der Waals type can be formed and worce adherence can be induced.

They emphasized the wetting behavior is chiefly governed by high surface energy of metals, which are generally sensitive to the atmosphere because the surface tension of soda-lime-silica glass is relatively unaffected by various atmospheres which was determined by Parikh²⁶⁾.

Further they checked the correspondence between an adherence behavior of sodium silicate on metals and some thermodynamic and physical properties of metals.

In Table 7, several data are given.

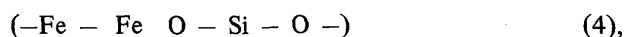
Table 7 Some thermodynamic and physical properties of several metals and compounds

Material	Melting point (°C)	Props. at 1200°K			
		Vapor Pressure (mm of Hg)	ΔH° Sublimation (kcal/mole)	ΔF° Sublimation (kcal/mole)	Coeff. of ther. exp. (in/in °C)
Pt	1774	3.4×10^{-14}	134	92	8.9×10^{-6}
Au	1063	1.55×10^{-8}	83	48	1.42×10^{-6}
Fe	1535	2.9×10^{-8}	96	57	12.3×10^{-6}
FeO	1420	1.58×10^{-12}			
Na ₂ Si ₂ O ₅ glass, up to 350°C					$\sim 15 \times 10^{-6}$

The conclusions obtained are as follows;

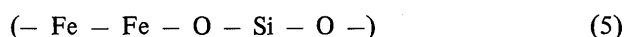
- Bond energies, Pt > Fe > Au
- Stabilities of the bulk metal oxides, Fe > Pt > Au
- Coefficient of thermal expansion, Fe \approx sodium silicate

When transition zone can be represented as following,



poor adherence with van der Waals type of bond will be developed.

On the other hand when a chemically bonded type of transition zone such as



was formed, good adherence can be obtained.

King, Tripp and Duckworth¹⁹⁾ studied about nature of porcelain enamels in detail. The following subjects were systematically studied:

- Role of CoO and NiO added in enamel
- Effect of iron oxide, FeO, Fe₃O₄ or Fe₂O₃, in enamel
- Effect of atmospheric oxygen and iron oxides in enamel
- Effect of nickel dip on an iron surface
- Effect of nickel added in enamel

As for the role of CoO or NiO added in enamel, they appreciated as

- during a temporary deficiency of atmospheric oxygen small amount of oxygen available intimate contact between enamel and metal can be given, and
- the addition of these oxides make effective in accelerating the removal of the scale. Further it was shown that Fe₃O₄ was more soluble in enamel than either FeO or Fe₂O₃. Accordingly it is favorable that CoO and NiO change to Fe₃O₄ from FeO which is the major constituent of scales on iron.

Iron oxides added, even if the constituent was changed as FeO, Fe₃O₄ or Fe₂O₃, in enamel did not prove to be effective roughning agents in the absence of atmospheric oxygen.

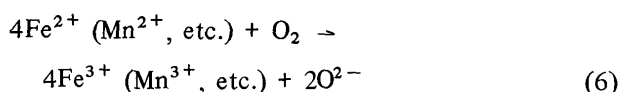
When enamel are fired on iron in air, all the oxides of iron were effective as corrosion accelerators. Particularly Fe_3O_4 behaved most readily as a corrosive oxide.

Nickel dip operated effective in decreasing the oxidation of the iron and maintained a more uniform degree of roughness over long firing times.

Nickel added in enamel worked to be an extremely active agent in promoting surface roughness in the presence of atmospheric oxygen.

Depending on the experimental evidence, they presented new adherence mechanism between enamel and iron as following:

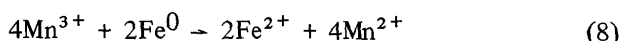
1) At the enamel-air interface,



2) At the enamel-iron interface,



or



They suggest that "oxygen transport" is a misnomer and that the true mechanism may be one of cation diffusion or even of electron transport.

In Figure 3, the schematic representation of enamel-metal interface is shown.

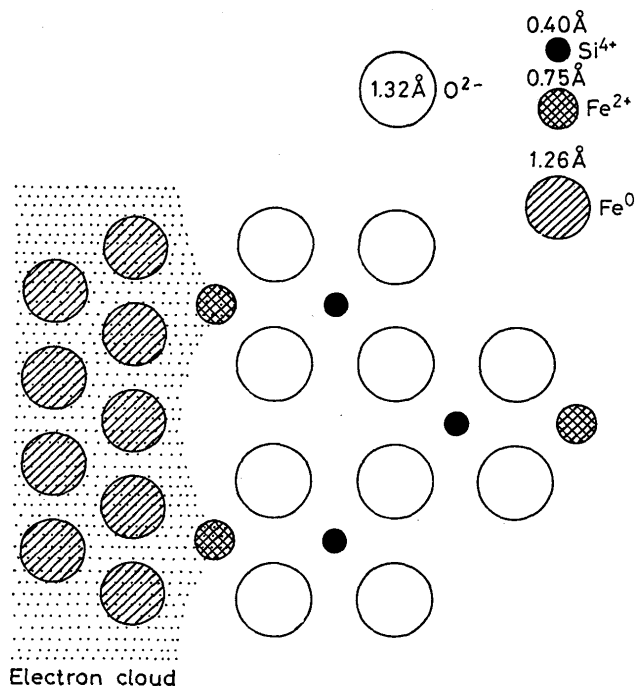
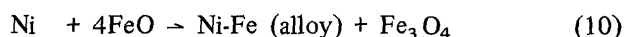
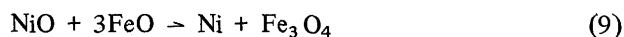


Figure 3: Schematic representation of glass-iron interface¹⁹⁾

5. Pretreatment of iron base

Since old time, nickel flash in iron has received much attention for obtaining good adherence between enamel and metal. Kautz¹⁰⁾, Wainer and Baldwin,²⁷⁾ and others have reported that the nickel flash inhibits the excessive formation of oxide between the enamel and the metal during firing. Douglas and Zander²⁸⁾ performed X-ray diffraction study for identifying the constitution of iron oxide when nickel flashed iron specimen was fired, and concluded that nickel not only reduced the oxide film formed during the initial stages of firing but favored the formation of Fe_3O_4 rather than FeO . They considered the following reactions to explain the occurrence of iron-nickel alloy.



Further they continued X-ray diffraction study about oxidation film formed when enamel containing TiO_2 was used.²⁹⁾

In Figures 4, 5 and 6, adherence meter count, amount

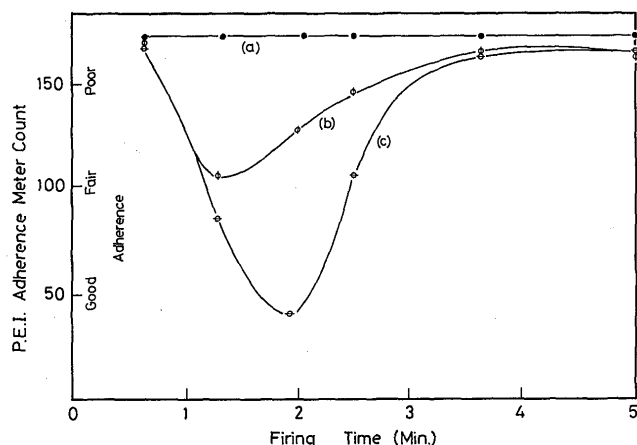


Figure 4: Effect of firing time on adherence meter count²⁹⁾
 (A) no nickel deposit, (B) 0.086g nickel/ft² metal deposited (C) 0.142g nickel/ft² metal deposited

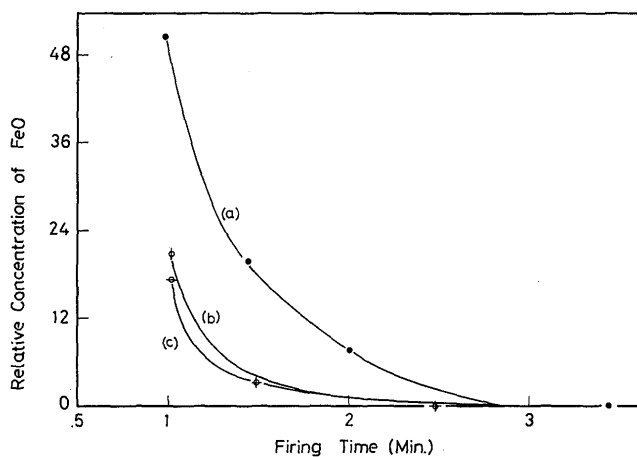


Figure 5: Effect of firing time on FeO content in oxide layer²⁹⁾
 (A), (B), and (C) are same to those in Fig. 4

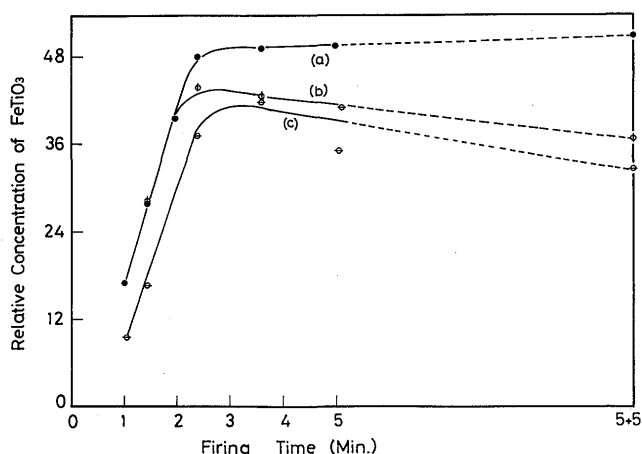


Figure 6: Effect of firing time on the content of FeTiO₃ formed²⁹⁾ (A), (B), and (C) are same to those in Fig. 4

of FeO formed, and relative concentration of FeTiO₃ are shown,

Nickel pickling decreases the initial amount of iron oxide formed, and the amounts of FeTiO₃ formed is also decreased.

Fussell and Hadley³⁰⁾ disagreed with the finding by Douglas and Zander²⁸⁾ that the nickel pickling favored the formation of Fe₃O₄ rather than FeO. They found that the nickel flash may reduce the rate of oxidation by slowing down the rate or number of Fe ions diffusing outward. Further they indicated controversial point that the relative amounts of each oxide were based on the relative heights of peaks of X-ray diffraction data, but the effects, either the presence of large crystals or preferred orientation due to cold-rolled iron, should be considered.

It is an important matter that the rate of diffusion of the nickel inward, however, was much slower than the iron outward, and when oxidation continued for a longer time all the nickel would eventually have been contained in the FeO phase.

6. Electrochemical studies on the system between glass and transition metal oxides

Lacy and Pask in a series of papers^{31)~33)} studied the solubilities of transition metal oxides such as NiO, FeO and CoO in sodium silicate glass using solid electrolyte and obtained various thermodynamical values.

As for the solubility of FeO, King et al¹⁹⁾ already introduced solubility factors for FeO as shown in Table 8.

Depending on the following steps the solubility of FeO in glasses can be obtained except when the glass contains MnO.

- 1) Multiply the weight per cent of each oxide in the glass by its factor.
- 2) Add products from (1) algebraically.

Table 8 Solubility factors for FeO

Oxide	Factor
Na ₂ O	-0.63
K ₂ O	-0.45
CaO	-0.40
BaO	-0.11
MgO	-0.92
MnO	-0.00
Al ₂ O ₃	-1.21
TiO ₂	-1.34
ZrO ₂	-0.75
B ₂ O ₃	+1.70
SiO ₂	+1.20
P ₂ O ₅	+2.23

- 3) If this sum is a positive value, it represents the parts of FeO soluble in 100 parts of glass. A negative value means that the glass will dissolve no FeO.

In Figure 7, an experimental apparatus is shown. Cell

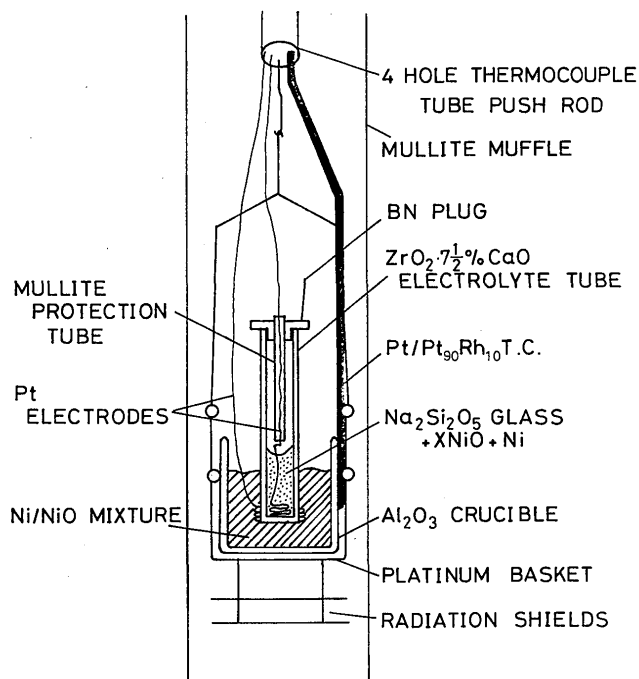
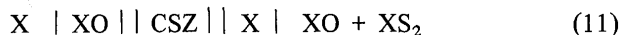


Figure 7: Diagram of experimental assembly³¹⁾

is composed from the following departments.



where, X denotes Fe, Co, or Ni, CSZ the CaO stabilized ZrO₂, and S the sodium silicate respectively.

In reversible cell, the free energy of this reaction may be related to the cell potential by the expression.

$$\Delta F = -n\zeta E = RT (2.303) \log (a_{NiO}) \quad (12)$$

where ζ = Faraday constant (23,061 cal/V), E = the cell output (V), R = the gas constant (1.987 cal/°C), T = absolute temperature, and n = the number of electrons

transferred in the cell reaction.

As an example, a_{FeO} is plotted in the case of $Na_2Si_2O_5$ glass containing various amounts of FeO as a function of temperature in Figure 8.

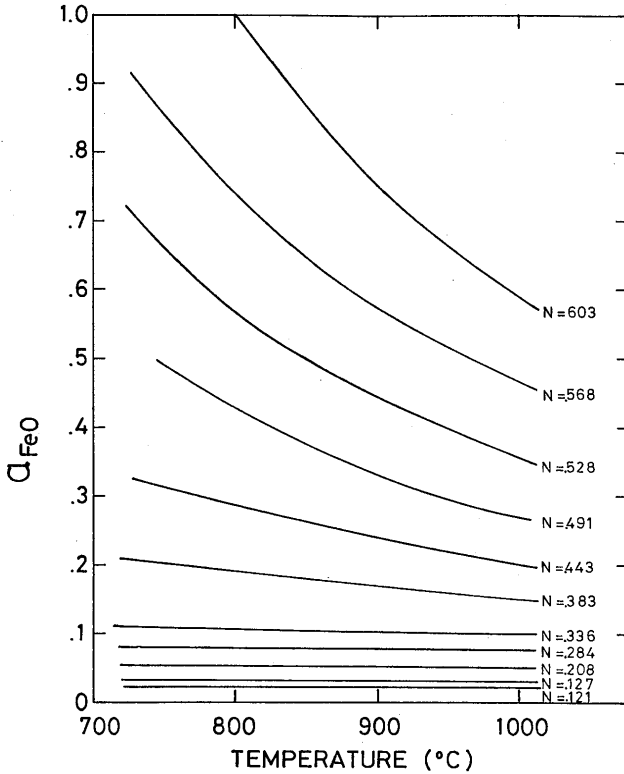


Figure 8: Variation in activity of FeO (referred to pure solid standard state) with temperature for each composition studied.³¹⁾

With the diagram, saturation solubility of FeO can be obtained by extrapolating to $a_{FeO} = 1$. In Figure 9, the summerized result concerning FeO, NiO, and CoO is shown.

It is understood that FeO can be dissolved in sodium silicate glass with great quantities than NiO and CoO.

From the standpoint of ceramic-metal bonding, it is interesting matter that sodium silicate glass can dissolve a great quantity of FeO such as 56 weight percentage at 1000°C. When the oxide layer is thinner and the reaction time is longer, it has a danger to weaken the bonding strength between ceramic and metal by dissolving FeO in ceramic.

7. Diffusion behavior of oxide in ceramic

Dissolving velocity of oxide film on metal base is governed by diffusion velocity of iron ion in ceramic.

Borom and Pask³⁴⁾ measured interdiffusivities of iron oxides, FeO, Fe₃O₄ and Fe₂O₃, with the use of Boltzmann-Matano method, and the result is shown in Figure 10. The diagram indicates that FeO which is most defective oxide can diffuse easily than Fe₃O₄ or Fe₂O₃.

We should pay an attention that the diffusion velocity depends upon atmospheric conditions on heat treatment, temperature and chemical composition of base metal.

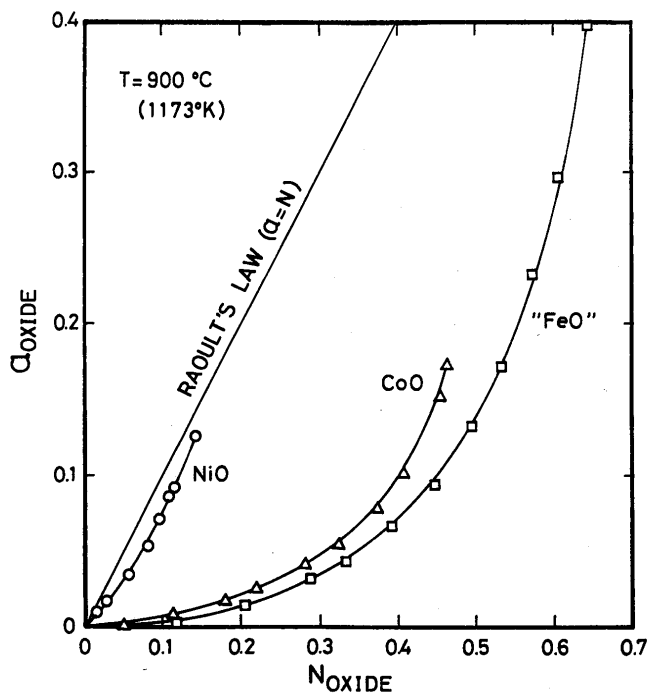


Figure 9: Activity values of FeO NiO and CoO³¹⁾ in $Na_2Si_2O_5$ glass.

8. State of iron ion in glass and the wetting

Bhat and Manning³⁵⁾ studied wetting and adherence behaviors of sodium silicate glass when the amount of iron oxide added and the state of iron ion were changed.

In Table 9, the chemical compositions of glasses used for experiment are given. In Table 10, the room temperature adherence values by push off tests are given. Further contact angles for glasses on steel are given in

Table 9 Chemical compositions of glasses

Number	Composition (wt%)				Ignition loss
	SiO ₂	Na ₂ O	Feo	Fe ₂ O ₃	
305	61.4	32.1		3.8	2.7
315	56.8	28.8		11.4	3.0
318	55.9	28.6		13.8	2.7
325	52.1	26.1		19.1	2.7
205	64.8	28.2	1.7	3.5	1.8
220	53.0	26.5	8.9	9.9	1.7
243	41.1	20.5	19.5	17.3	1.6

Table 10 Room temperature adherence of glasses in Contact with steel

Number	Push-off strength (psi) for the intervals at test temperature		
	15 min	30 min	60 min
305	0	0	0
315	460	60	0
318	520	120	0
325	NTR	>1670	>2160
205	0	0	0
220	1390	320	310
243	NTR	>470	>2110

Table 11.

From these results, the following conclusions were derived:

- 1) Contact angle in equilibrium decreases as the Fe content in glasses is increased.
- 2) To obtain better wetting glasses must hold iron ion as Fe^{3+} rather than a combination of the Fe^{2+} and Fe^{3+} .
- 3) Always the good correspondence between wetting and adherence behaviors was not observable, but the glass nearly saturated with iron oxide showed good correspondence.

Table 11 Contact angles for glasses on steel

Number	Contact angles (degrees) Equilibrium, θ_0
305	43.5
315	34
318	32.5
325	15
205	48.5
220	29
243	25

9. Application of Mössbauer spectroscopy

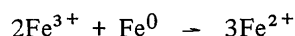
Bhat, Manning and Bowen³⁶⁾ applied Mössbauer effect to solve the state of iron ion in glass.

The effect is a convenient means to determine the state of iron, Fe^{3+} or Fe^{2+} , and the configuration site against oxygen ions surrounding iron ion, tetrahedral or octahedral, in glass or mineral. With the information about quadrupole splitting we can obtain the knowledge about symmetrical configuration surrounding an iron ion.

In **Table 12**, iron ion contents of glasses before and after experiments determined by Mössbauer effect are given. It was noted that the state of iron ion changed after wetting experiment. In **Table 13**, Mössbauer parameters for glass samples before and after experiments are given.

The conclusions obtained are as follows:

- 1) It was confirmed that the reaction shown in eq. (3) occurred between wetting experiment. Also the quantity of Fe^{2+} increased with increasing of reaction time.



- 2) There seems correlation between configurational symmetry of iron ion in glasses and the adherence behavior.
- 3) After wetting experiment state of iron ion, Fe^{2+} and Fe^{3+} , in glasses occupies octahedral configuration.

10 Key to solve adherence problem between ceramic and metal

It has been indicated that there are many factors governing adherence behavior between ceramic and metal.

We must know the effects of variables such as atmospheric conditions, sort of steel, heat treatment, cooling velocity, and the way of bonding.

Further the knowledges concerning characteristic of oxide layer, diffusion behavior of element, and formation of compound at the interface must be gathered.

Therefore new analyzing means such as ion probe mass analyzer, Auger-, Mössbauer-spectroscopy and ESCA (Electron Spectroscopy for the Chemical Analysis) must be applied to solve the problems at the interface.

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