

A CONTRIBUTION TO THE STUDY OF THE PHASE BOUNDARY BETWEEN METAL AND VITREOUS ENAMEL

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A study of the phase boundary between the metallic and the vitreous phase showed that the intermediate layer on which the mutual adhesion depends, consists of glass-metallic clustered complexes. The adhesive power is primarily provided by metals of the transient group which constitute the centres of polynuclear clustered complex compounds.

INTRODUCTION

At present, there is an increasing demand for development of new types of materials, especially composite ones, which would resist corrosion and erosion even at elevated temperatures. Such novel materials also include glass-metallic and ceramo-metallic materials as well as various types of vitreous and glass-ceramic coatings on metals.

As far as the coatings are concerned, one of the main problems is concerned with creating perfect joining of the physically quite dissimilar materials. On the other hand, a minimum cohesion between the glass-ceramic and the metallic material is sometimes required, e.g. in the case of submerged-arc welding. The present contribution has the purpose to present some new findings based on experimental data and elucidating the mechanisms involved in the creation of bonds between the glassy and the vitreous phase.

In spite of a number of theories which have been suggested for explaining the formation of bonding between metal and glass, a consistent conception of the whole problem is still lacking.

According to Dietzel [1], Rickman [2], King [3], adhesion of vitreous enamels to steel sheet is associated with the formation of iron oxides which mediate the bond between glass and the metal. The adhesion was found to depend on the formation of a thin layer of Fe_3O_4 oxides which is created over a relatively short period of time during the heat treatment of the vitreous coating.

According to the electrochemical theory worked out by Dietzel [4], the so-called adhesive oxides CoO and NiO at the metal-vitreous enamel boundary produce local galvanic microcells, while bringing about strong corrosion of the metal surface which makes it rough and provides satisfactory anchoring for the vitreous coating.

Litvinova [5] points out the electron theory of adhesion between the glassy and the metallic phase, based on the finding that the adhesion is a product of an interaction at the phase boundary which yields products with a strong covalent bond.

According to our findings, the adhesion between the metallic and the glassy phases is mediated by cluster-type complex compounds that form an intermediate layer at the phase boundary [6].

EXPERIMENTAL

The phase boundary between the metal and the vitreous enamel was studied on specimens of cold-rolled steel sheet to ČSN 41 1320 (ingot-cast steel) provided with a coat of the KZ ground enamel, and on specimens of the same sheet with a single cover enamel.

Before enamelling, the sheet specimens were subjected to chemical pretreatment consisting of alkaline degreasing, pickling in sulphuric acid, and with some of the specimens for single-coat enamelling, to induction pickling and chemical nickeling.

The enamel slip was applied by wet spraying; after drying, the coat was heat treated at 820—840 °C for 5 minutes.

The specimens were first tested for adhesive strength by forcing through a spherical cap in a defined way (the Eirchsen apparatus).

The adhesion of the ground coat was classified as degree 1—2, that of the single cover coat enamel as degree 2 (a 1—5 scale, degree 1 — the best adhesion, degree 5 — no adhesion). Transverse polished sections were then prepared for examining the phase boundary under the JEOL 50 A scanning electron microscope. The EMX-SM electron microanalyzer was employed for quantitative phase microanalysis.

On enamelled sheet specimens 20×30 mm in size the phase boundary was separated by dissolving the metallic phase in 3 % bromine solution in methanol (50 °C, magnetic stirrer, 20—30 r.p.m.). To facilitate the dissolving, the specimen thickness was locally reduced by milling.

Spectra of electron paramagnetic resonance were measured on the Varian E4 instrument first at room temperature and then at lower temperatures of down to —170 °C.

Samples of the enamel separated from the intermediate phases were further subjected to measurements by the ESCA (XPS) method, both in the as received state and after removal of a surface layer approx. 50 to 150 nm in thickness by ionic etching. The XPS spectra of the specimens were measured on the ESCA 3 Mk II electron spectrometer made by VG Scientific; the pressure of residual gases in the analytic chamber was about $5 \cdot 10^{-7}$ Pa and the AL K α line ($h\nu = 1486.6$ eV) was used for X-ray excitation. The spectra were stored in the Nicolet 1072 multi-channel analyzer. The 0—1300 eV spectral range of bond energy was measured.

The phase boundary was also analyzed qualitatively and semiquantitatively by the SIMS method. The purpose of the analysis was to determine the elements present including the changes in their representation by volume, and to study the occurrence of type FeNiCo polyatomary ions. The samples were analyzed in a dynamic atomization schedule under identical experimental conditions (primary ionic current $jp = 0.1$ mA cm⁻², energy of primary argon ions 4.5 keV, the dimension of the elliptical trace of the primary beam approx. 2 mm, the angle between beam and surface normal line was 60°, the chamber pressure $6 \cdot 10^{-6}$ Pa). The surface of each specimen was atomized for altogether 380 minutes, and during that time the beam of primary ions penetrated into a depth of approx. 1.5 μ m. Prior to the first recording, the surface contamination was eliminated by vertically swinging the argon ion beam over the point of analysis with an amplitude of approximately 2 mm for 5 minutes. The layer removed was about 5 nm in thickness. The electrostatic surface charging during the analysis was compensated by a beam of electrons emitted by an electron nozzle. The gravimetric spectra of secondary

ions were recorded at 20-minute intervals and for the respective elements and selected polyatomic combinations, subsequently evaluated with respect to relative intensities of the secondary ionic current and then processed numerically.

Results

The phase boundary was first studied on scanning electron micrographs (Fig. 1) showing the adhesive intermediate layer 10–25 μm in thickness. The subsequent microanalysis revealed the presence of a metallic phase in the enamel, with concentrations increasing towards the phase boundary (Fig. 2).

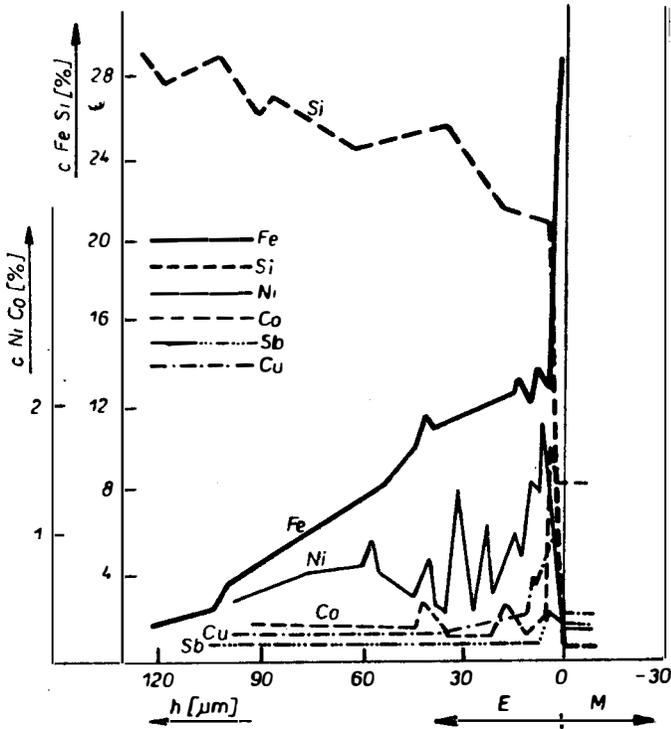


Fig. 2. Concentrations of Fe, Ni, Co, Sb close to the phase boundary (EMX-SM electron micro-analyzer); E — enamel, M — metal.

Measurements of electron paramagnetic resonance, carried out on a separated layer of vitreous enamel, indicated the presence of coordinated bonds in the complex compounds occurring at the phase boundary (Fig. 3). Samples 1, 3 and 4 are those of the metal-enamel phase boundary, while sample 2 corresponds to the enamel frit.

The ESCA method was further employed in qualitative and semi quantitative analyses of the KZ ground enamel and the white single-coat cover enamel B, separated from the phase boundary. Table I lists the results of the qualitative analyses.

Table I
Bonding energies of the individual elements found in the enamel samples [eV]
(related to line C1s = 285.0 eV)

Sample	C1s	O1s	Na1s	Si2p	Fe2p	C12p	B1s	Mn2p
B-as rec.	282.7	532.5	1072.5	103.4	711.4			
B-pow. Ar	282.6	532.3	1072.5	103.2	707.2	109.4	193.1	
KZ-as rec.	282.8	531.7	495.7*	102.8	710.6 711.6			641.4

* The position of the Na KLL Auger line in the scale of bonding energies

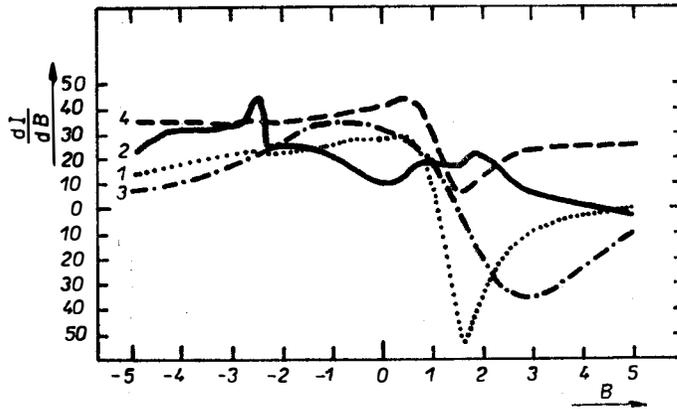


Fig. 3. Spectra of electron paramagnetic resonance of an enamel coat separated from intermediate phases (Varian E4 spectrometer); 1, 3, 4 — enamel separated from the phase boundary, 2 — frit of the KZ ground enamel.

Table II.

Relative intensities of secondary ionic current established for selected X^+ ions in samples of white and ground enamel at a depth of approx. (1) 20 nm and (2) 1.5 μm

X^+	I^+ arb. u.				I^+x/I^+_0			
	B		KZ		B		KZ	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
^{16}O	4.7	7.2	3.2	4.5	1.0	1.0	1.0	1.0
^{27}Al	600	740	360	520	127	103	112	116
^{28}Si	920	580	440	490	195	81	138	109
^{52}Cr	3.5	5.2	1.2	4.1	0.74	0.72	0.38	0.91
^{56}Fe	460	760	190	240	98	106	59	53
^{58}Ni	1.2	1.1	0.2	0.4	0.26	0.15	0.63	0.089
^{59}Co	1.7	1.8	0.73	0.98	0.36	0.25	0.23	0.22
^{72}FeO	17	16.5	4.8	6.3	3.6	2.3	1.5	1.4
$^{100}\text{FeSiO}$	4.2	5.6	1.7	2.6	0.89	0.78	0.53	0.58

The SIMS method was likewise used in qualitative and semiquantitative analyses of the metal-glassy phase boundary.

The elements found in both samples by qualitative analysis were divided during semiquantitative assessment into four groups and the concentrations C were estimated as follows for the ground enamel specimen:

- (a) C 10 % : O, Na, Fe;
- (b) C 10 — 1 % : Li, B, Al, Si;
- (c) C 1 — 0.1 % : H, C, F, Mg, Cl, K, Cu, Ti, Mn;
- (d) C 0.1 % : Cr, Ni, Co, Ba.

Table II lists a comparison of relative intensities I^+ of selected secondary ions obtained at a depth of approx. 20 nm and 1.5 μm . The value of I^+ (Ni) was determined by subtracting the superposition with I^+ of the ^{58}Fe isotope, the value of I^+ (Co) being affected by superposition with I^+ (TiB).

DISCUSSION

The phase microanalysis (Fig. 2) showed the enamel to contain a metallic phase whose concentration increased in the proximity of the phase boundary. Local concentration peaks of Fe, Ni, Co and Sb arise close to the interface. The planar microanalysis likewise indicates that in the glassy phase the phase boundary is bordered with metallic inclusions in sizes of the order of μm units.

The resonance peaks of the electron paramagnetic resonance spectra indicate the presence of glass-metallic complex compounds with ligand bonds in octahedral symmetry.

Separated samples of the phase boundary were further subjected to qualitative and semiquantitative analyses by the ESCA and SIMS methods. The presence of metallic phases at the boundary was confirmed. For example, the bonding energy values of $2p$ iron electrons corresponded to trivalent iron (711.4 eV) and metallic iron (706.9—707.6 eV). There was also contaminating carbon with the bonding energy of C 1s electrons of 285.0 eV and carbon corresponding to the carbidic form with a bonding energy of 282.6—282.8 eV. The intensities of secondary ionic current I^+ established allowed the concentrations of the individual elements to be assessed and the occurrence of polyatomic ions to be discussed. For example, polyatomic cluster anions Fe_3^- and Fe_3O_m^+ were identified ($m = 1.3$).

It may be assumed that the layer of molten enamel containing SiO_2 , B_2O_3 , Al_2O_3 , forms ligand bonds coordinating with transient metals (Co, Ni, Fe, Ni, Cu, Mn) producing glass-metallic cluster complex compounds with a coordinating bond (Fig. 4).

In the course of enamel firing, the activity of atoms in both the base metal and the glassy phase tends to increase. The oxides of the base metal dissolve in the enamel, the nascent Fe^{2+} atoms, jointly with the ions of metals contained in the enamel, Me^+ , produce polyatomic ions $\text{Me}^+\text{Fe}^{2+}$, thus creating the centre of a polynuclear complex group. This centre comprises several ions of transient metals joined by delocalized metal—metal bonds; the atoms can be arranged trigonally, tetrahedrally, octahedrally, or in more complex structures. The properties of the base metal and those of the cluster metal are similar, e.g. the trigonal arrangement in the dense packing of atoms in the metallic cluster is similar to plane (100) in the metal. As the cluster gives up or accepts electrons quite readily,

- Рис. 1. Граница раздела фаз металл-эмаль (электронный микроскоп JEOL, JSM-50 A).*
- Рис. 2. Концентрации Fe, Ni, Co, Sb вблизи границы раздела фаз (электронный микроанализатор EMX-SM), E — эмаль, M — металл.*
- Рис. 3. Спектры электронного парамагнитного резонанса эмалевого покрытия, выделенного из промежуточных фаз (спектрометр Varian E 4); 1, 3, 4 — эмаль, выделенная из раздела фаз, 2 — фритта основной эмали KZ.*
- Рис. 4. Модель стеклометаллического кластерного комплекса в октаэдрической симметрии, тригональное упорядочение центрального иона.*

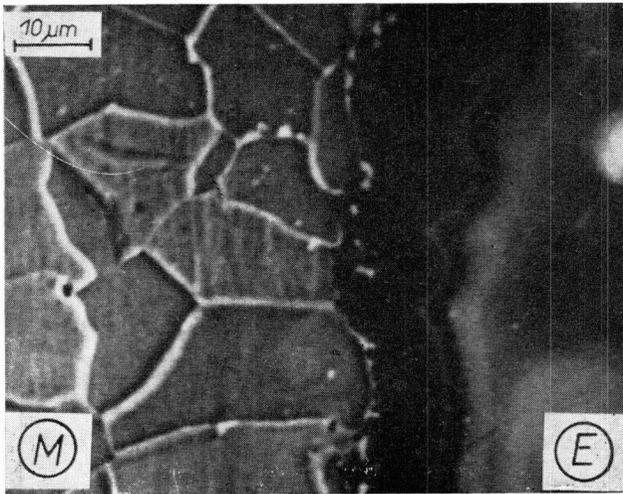


Fig. 1. Phase boundary metal-vitreous enamel (JEOL JSM-50 A electron microscope).