CONTRIBUTION TO THE STUDY OF THE PHASE BOUNDARY BETWEEN THE VITREOUS AND METALLIC PHASE

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PŘÍZPĚVEK KE STUDIU FÁZOVÉHO ROZHRANÍ MEZI SKLOVITOU A KOVOVOU FÁZÍ

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Abstrakt

Práce se zabývá studiem fázového rozhranní mezi kovovou a sklokeramickou fázi a studuje vznik spojením mezi nimi. Experimentálně bylo zjištěno, že v průběhu tepelného zpracování dochází na fázovém rozhraní k fyzikálně chemickým reakcím řízeným přenosem tepla při kterých se vytváří přechodová přídržná mezivrstva. Nositelem adheze jsou kovy přechodové skupiny, které vytvářejí středy polynukleárních klasterových komplexů, vytvářejících přechodovou adhezní mezivrstvu.

Abstract

A study of the phase boundary between the metallic and vitreous phase showed that the intermediate layer upon which mutual adhesion depends, consists of glass-metallic cluster complexes. Experimental work showed that, during heat treatment, physically chemical reactions controlled by heat transfer occur at the phase boundary, resulting in the creation of a transient adhesive intermediate layer. The adhesive force is primarily provided by metals of the transient group which constitute the centres of poly-nuclear cluster complex compounds.

Key words: phase boundary; metal; vitreous enamel; intermediate layer; cluster complex

1. Introduction

The study of phase boundaries between vitreous and metallic phases enables, for example, monitoring of adhesion of vitreous enamel coatings to steel, or ceramic materials to metal substrates. On the other hand, these results can be used in formulating the composition of welding slags.

Numerous authors have studied the origin of joining between vitreous enamel coatings and base metal. Adhesion of vitreous enamel to steel sheet is related to the production of iron oxides which apparently mediate joining between glass and iron. It was found that adhesion depends on the production of a thin layer of Fe_3O_4 oxides which is formed in a relatively short time interval during enamel firing [1]. King [2] defined conditions for production of satisfactory vitreous enamel adhesion as follows:

enamel must perfectly wet the metal,

enamel must be saturated with base metal oxides at the phase boundary,

the metal oxide must not be reduced by the metal.

Rickmann [3] confirms the requirement that satisfactory adhesion is conditioned by a contact angle of 1 - 2° between vitreous enamel and iron. Similar conclusions are made by Pask [4].

Since conditions for satisfactory adhesion of enamel, in connection with conditions formulated by Dietzel, King and Rickmann [1, 2, 3], change with a leap, it is necessary, for reasons of technological reliability in practice, to ensure satisfactory adhesion of vitreous enamel using so-called adhesive oxides which include, amongst others, CoO and NiO. According to Dietzel [5], during firing the following reactions take place in the enamel with dissolving of oxides:

$$Fe_3O_4 \rightarrow Fe^{2+} + 2\ Fe^{3+} + 4\ O^{2+} \qquad \text{(dissolved in enamel)}$$

$$2\ Fe^{3+} + Fe \rightarrow 3\ Fe^{2+}$$

$$2\ Fe^{2+} + Co^{2+} \rightarrow 2\ Fe^{3+} + Co$$

Another very important reaction between metallic iron and remaining Co from the enamel begins in places where the layer of oxides dissolves:

$$Fe + Co^{2+} \rightarrow Fe^{2+} + Co$$

According to the electrochemical theory, so-called adhesive oxides CoO and NiO react at the metal - enamel phase boundary accompanied by production of local galvanic microcells, while bringing about strong corrosion of the metal surface which causes its roughening and thus satisfactory anchoring of enamel.

Litvinova [6] points out the electron theory of adhesion between vitreous enamel and metal, based on the finding that adhesion is the product of an interaction at the metal - enamel phase boundary which yields products with a strong covalent bond.

The above cited theories of adhesion between vitreous enamel and metal do not sufficiently explain the production of a glass-metallic system at the metal - enamel phase boundary which we proved experimentally and which produces an intermediate layer mediating adhesion between the metal and vitreous phase [7, 8].

2. Experiment results and their discussion

Various methods were used during experiments, for example, microanalysis, X-ray diffraction analysis, ESCA method, SIMS method, electron paramagnetic resonance. Experiments were performed on samples of Kosmalt steel sheet manufactured by Východoslovenské železárny (East Slovakian Ironworks). Ground and cover enamels (P 1092, P 1192, K536) produced by Mefrit s.r.o. Mělník were also used.

Experimental work showed that an adhesive intermediate layer is produced at the phase boundary between metal and vitreous enamel - Fig.1. This intermediate layer is composed of an adhesive glass-metallic complex.

A layer of molten enamel which contains, amongst others, SiO_2, B_2O_3, Al_2O_3 creates ligand bonds which coordinate with transient metals Co, Ni, Fe, Mo, Cu, Mn and produce glass-metallic cluster complexes with a ligand-type coordinating bond. Adhesion is achieved mainly because, under certain conditions, the field of ligands causes splitting of orbital energy levels of adhesive metal (Co, Ni, Fe) ions which are found in the vitreous phase.

Fig.1 Adhesive intermediate layer of glass-metallic complex at the metal - vitreous enamel phase boundary (steel ČSN 417242 and enamel Ž01) - magnification 1000x

The split orbit then linearly combines with electron orbits of ions from vitreous phase compounds which results in the production of molecular orbits of polynuclear cluster compounds. The cluster centre is formed by several transient metal ions, in-between which delocalised metal-metal bonds exist; atoms can be arranged trigonally, tetrahedrally, octahedrally or in more complex structures, see Fig.2.

Fig.2 Model of the glass-metallic cluster complex in octahedral symmetry.

Trigonal arrangement of the central ion.

The properties of the base metal and those of the cluster metal are similar, for example, the trigonal arrangement in the dense packing of atoms in the metallic cluster is similar to the plane (100) in the metal. As the number of atoms in the cluster increases so its properties approach those of the crystal. Distribution of cluster energy levels is close to Fermi´s level; some levels are occupied by electrons and some levels are free, so the cluster easily gives up or accepts electrons and offers suitable conditions for elctron transfer.

These facts support production of a metallic bond between the base metal and cluster, involving formation of alloyed inclusions, e.g. Co - Fe, Ni - Co, Ni - Fe, Cu - Fe, etc.

During heat treatment of a vitreous enamel coating, the activity of base metal ions as well as vitreous phase central ions is increased which accelerates electron transfer and creates conditions for coordination of ligands and formation of cluster complexes. Base metal oxides are dissolved in the vitreous phase which comes into contact with nascent metal Fe^{2+}, and alloy $M^{+}Fe^{2+}$ is formed together with metal M^{+}, thus forming the centre of the polynuclear complex group. In this way a base is created for production of the metal cluster complex $Fe^{+}[Fe^{(m-n)+}.Fe^{2+}.M^{+}(SiO_4)^{-}]$.

Adhesion is mediated by transient group metals - Mn, Fe, Co, Ni, Mo - and some group B metals such as Sb, Sn and their combinations. FeC, which reacts with oxygen accompanied by production of Fe^{+} and CO, is also involved mediation of adhesion. FeO oxide dissolved in enamel reacts with carbon monoxide thus producing highly active nascent Fe^{2+}. Due to electron transfer, Fe^{+} and Fe^{2+} easily combine by means of metallic bond, while Fe^{2+} acts a the central ion and provides joining of glass molecules by means of oxygen bonds. Fe atoms can occupy free locations in the metallic cluster complex and provide a direct bond with the base metal. The CO ions, found in the system under the effect of the ligand field, activate the metallic cluster and accelerate its joining with the base metal.

Phase boundary microanalysis proved increased concentrations of metals in the vitreous phase, see Fig.3. This figure shows distinct local peaks in Fe, Ni, Co, Sb concentrations in the immediate proximity of the phase boundary.

Fig.3 Concentrations of Fe, Ni, Co, Sb in the vitreous phase close to the phase boundary

(electron microanalyser EMX-SM), E - enamel, M - metal

Coordination of bonds of complexes occurring at the phase boundary was evaluated from measurement of a separated layer of vitreous enamel under spectra of electron paramagnetic resonance. It showed the position of Fe in tetrahedral and octahedral symmetry, see Fig.4.

Fig.4 Spectra of electron paramagnetic resonance of the phase boundary.

(1,3,4 - separated enamel, 2 - vitreous enamel frit)

A - Fe in tetrahedral symmetry characteristic of glass

B - Fe in octahedral symmetry - occurrence at separated phase boundary

Studies of the metal-vitreous enamel coating phase boundary found the occurrence of physically-chemical reactions controlled by heat transfer during heat treatment of the vitreous enamel coating, and these reactions involve production of a glass-metallic adhesive intermediate layer (30 - 50 μm) at the phase boundary, in the presence of glass-metallic cluster complexes with co-ordinating bonds mediating adhesion between the metal and vitreous enamel phases. [7, 8]

Transient group metals form the centres of cluster complexes at the phase boundary of the metal-vitreous enamel phase. By affecting the composition of this intermediate layer it is possible to control the adhesive force which is very significant for the formulation of vitreous and glass-metallic coating systems, and metal base materials - steel sheets.

To achieve perfect adhesion between metal and the vitreous enamel coating it is essential to perform pre-preparation of the metal surface that will ensure removal of greases, impurities, corrosive products, etc. Another very important factor is the time delay between completion of metal surface pre-preparation and application of a vitreous enamel coating. Observance of the time delay is very significant especially in the case of pre-preparation by blasting; immediately after blasting of the metal surface in atmospheric conditions, an oxide layer is formed due to high reactivity of the blasted surface with the surrounding environment.

Pre-preparation of the metallic material as the base for the vitreous enamel coating has a significant influence on creation of a metal - enamel phase boundary which affects not only adhesion between metal and enamel but also vulnerability of the system to defects in the vitreous enamel coating [9].

If the metal surface is not cleared of the oxide layer completely prior to enamelling, see Fig.5, the remains are involved in a reaction at the metal-enamel phase boundary during enamel firing, and thereby affect the properties of the adhesive intermediate layer as well as adhesion of the vitreous enamel coating to the metal.

During studies of the effect of metallic material/ steel sheet surface reactivity on adhesion of the vitreous enamel coating to metal, it was found that steel sheet with a coherent oxide layer (rust), see Fig.6, contains metallic inclusions in the adhesive intermediate layer that is much greater in quantity and distance from the metal - enamel phase boundary than in the case of steel sheet without such an oxide layer, see Fig.7. According to our experimental work, adhesion of the vitreous enamel coating to metal increases with a growing quantity of oxide layer remains. This is reflected in the thickness of the adhesive intermediate layer which increases, see Fig.8, 9, 10.

The effect of oxide layer remains on production of the adhesive intermediate layer, after pre-preparation by blasting, is depicted in figures 8, 9, 10.

The quantity of metal inclusions in the adhesive intermediate layer and thickness of this layer affect not only adhesion of the vitreous enamel coating to metal but also the fracture properties of the intermediate layer and time of hydrogen penetration through the integrated metal - vitreous enamel coating system. [10]

Fig.5 X-ray diffraction spectrum of a non-blasted (upper picture) and blasted steel sheet surface

3. Conclusion

Studying of the metal-vitreous enamel phase boundary found that the adhesive intermediate layer is formed by glass-metallic cluster complexes with ligand-type coordinating bonds, where cluster complex centres are formed by transient group metals. Main components (SiO_2, B_2O_3, Al_2O_3) of vitreous enamel form cluster complexes together with central ions of transient metals (Fe^{3+}, Fe^{2+}, Mn^{3+}, Ti^{3+}, Co^{3+}, Ni^{2+}).

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