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A comparative study of a vitreous biological composition suitable for coating steel prostheses

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A correlation between composition and quality of a biological glass used as a bioglaze and an industrial glaze for sheet-steel coating was carried out. Apart from the extremely different conditions, particularly relative to the temperature for application of the coating to the metallic substrate, it was noted that the compositions are not very much different; this led us to think that the doping of the vitreous system with substances favouring the bonding of glaze to support (according what has been suggested by enamellists) is trustworthy in this case too. Some hypotheses relative to the role of nickel and the fluidity of the vitreous system were made to explain the observations, and to suggest the best way to improve the adhesion of metal to glaze.

1. Introduction

The present study involved consideration of the problem of adhesion at glass–metal interfaces with the specific aim of using bioactive glass to coat AISI 316L steel prostheses. In particular, one of the most promising glass compositions we developed for coating metal prostheses was considered for this study. On the basis of the similarity between glass coatings on metal to be used as prostheses and glass coatings (enamels) on sheet steel produced commercially, the results obtained in this study were compared with those for one of the commercial enamel systems involving a glass composition similar to the composition of the glass we developed for use in fabricating prostheses. It should be remembered, however, that such a comparison is only qualitive since the coating of the metal by the two glasses takes place under quite different conditions. The industrial enamel has a low melting temperature (about 400° C) and the bioactive glass considered for this study melts at about 1250° C.

2. Experimental details

Analyses of the samples were carried out using a scanning electron microscope (SEM) equiped with an energy-dispersive X-ray (EDX) microprobe. In order to obtain greater and more detailed information on the morphology of the interface, oblique rather than orthogonal metallographic sections were prepared. The samples were fixed on a suitable support so as to obtain an angle of about 2° with the polishing surface and then the usual metallographic preparation cycles were carried out (Fig. 1).

The test samples consisted of small 4 cm × 2 cm × 0.05 cm plaques of steel coated with bioglass. The bioactive glass used was made using the following method: an initial mixture of chemicals (SiO_2: 45.0%, CaO: 24.5%, Na_2O: 24.5%, P_2O_5: 6.0%) was fired for 6 h at 1350° C to form the base frit. Then, to 100 g of this frit, finely ground, the following compounds were added: 2 g Al_2O_3, 1 g NiO, 6 g Fe_2O_3, 0.6 g Cr_2O_3, 1 g Ta_2O_5 and 0.5 g La_2O_3. This second mixture was carefully homogenized and then re-fired at 1300° C for 4 h to give a melt into which the steel test samples were dipped at about 1250° C. In all cases, firing of the vitreous mixes was carried out in platinum crucibles to avoid any contamination. The final composition obtained corresponds to the composition No. 15 reported in a previous paper [1]. The glass composition gave monoaxial tensile strength up to 280 $kg\,cm^{-2}$ when coated on AISI 316L stainless-steel test samples.

Two methods for pretreating the metal surfaces of the test pieces were used and are reported in Fig. 2. The steps indicated in the diagram of this figure are followed by drying in a furnace at 150° C for 4 h and then a preheating oxidation process at 550° C at the time of immersion of the metal substrate in the molten bioactive glass. The results obtained were the same from both methods; however, the first method (the one using HF) was preferred because of both its simplicity and speed of execution. This was the method used for all the samples in the photographs shown in this report.

The samples of industrially produced enamelled

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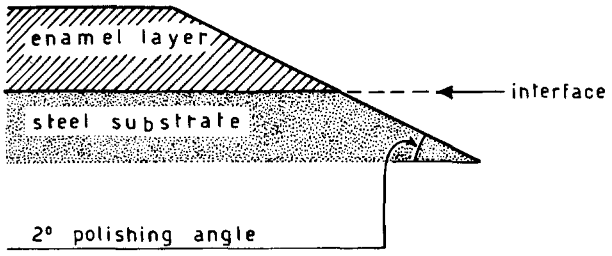

Figure 1 A schematic representation of the 2° angle obtained by polishing for magnification of SEM analyses.

steel used in the comparative study were obtained by cutting test pieces from household appliances presently on the market.

Sometimes untreated metal surfaces are used in the industrial enamelling processes for the production of household applicances. In this case, both the polishing of the metal surface and the composition of the vitreous coating become particularly important. Generally very strong degreasing agents are used (e.g. alkaline treatments at 90° C with brushing or ultrasound treatments with trichloroethylene or Henkel 669 solutions). Such treatments, particularly for the metals not treated in any other way, serve to avoid the problems which would arise from the presence of a layer (about 2 to 3 nm thick) of oily carbon-based residues which forms on the surface of sheet steel and prevents a good reaction between glass and steel*. Such thorough preparation of the metal surface is necessary because of the low degree of etching which must be used in order to assure reliability for such systems.

3. Results

Mapping and area analyses on the same portion of sample were carried out on test pieces like those shown in Fig. 3a for the system using bioactive glass, and in Fig. 4a for the industrial one. To allow immediate comparison of the results, even if only qualitative, the same operating conditions were used for analysing all the samples.

The distributions of calcium, silicon, nickel, iron and chromium in the samples coated with bioactive glass are shown in Figs. 3b, c, d, e and f; the distributions of nickel, chromium, titanium and iron for the industrial enamelled steel are shown in Figs. 4b, c, d and e. The results of EDX area analyses for the bioactive glass-coated AISI 316L steel and for the industrial system are reported in Figs. 5 and 6 respectively. The specific results presented here can be considered representative of the results obtained on all samples examined, since analogous data were found for all the samples studied.

Etching and acid treatments of the metal surface facilitate intergranular reactivity, and consequently the possibility for intergranular penetration of a reactive and sufficiently fluid glass increases. In the specific case of this study, Figs. 3 and 4 clearly show that the system with the bioactive glass gives rise to a predominantly intergranular attack with excessive penetration of the glass into the metal substrate, characterized in particular by roots of penetration which flow into the interior of the metal alloy to a depth of around 3 or 4 layers of grains. In Fig. 2 it can be seen that some of the penetration roots are interconnected in triple or even multiple points, a condition which destabilizes the homogeneity of the metal sheet and consequently reduces the metallic hold of the layer involved. An analogous situation was found for the distribution of silicon (Fig. 3c): in some zones of the metal alloy, the boundaries of the silicon distribution correspond to the shallow grooves around the grains. With regard to calcium, silicates seem to form with a greater concentration of calcium silicate in the zones where the concentrations of nickel, chromium and iron are lowest. The nickel distribution seems to be quite uniform with the exception of a streak in close contact with the metal.

Experimentally, it was observed that the quality of the glass-to-metal adhesion obtained could be related to a bluish green–brown colour occurring on the metal surface after the completion of the prefiring operation. This could correspond to the surgical enrichment of a particular atomic species that is a component of the metal alloy. This may be explained by the commonly accepted belief that a very thin, green–brown surface covering corresponds to a network-type surface film of deposited nickel atoms, as schematically sketched in Fig. 7, generally upon a further wüstite molecular layer. When properly dispersed in such a sieve-like structure, homogeneous over a relatively large microsystem, the nickel behaves

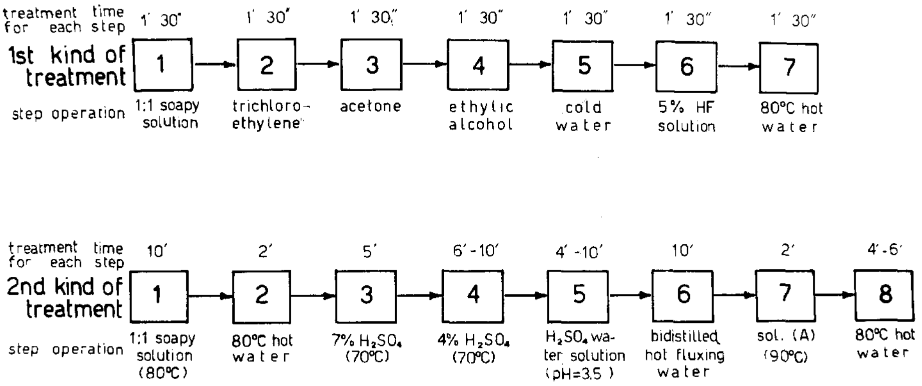

Figure 2 Schematic representation of the two methods used for pretreating the metal surfaces (AISI 316L stainless steel) before coating with the bioactive glass. Solution A indicated in this figure for use in the second method is formed by dissolving 0.4 ml of a 3 : 1 (vol) solution of saturated NaOH and saturated borax in 100 ml of distilled water.

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*For the production of glass-coated prostheses, it will probably be necessary to carry out preliminary cleaning of the steel as well as the standard treatments reported here.

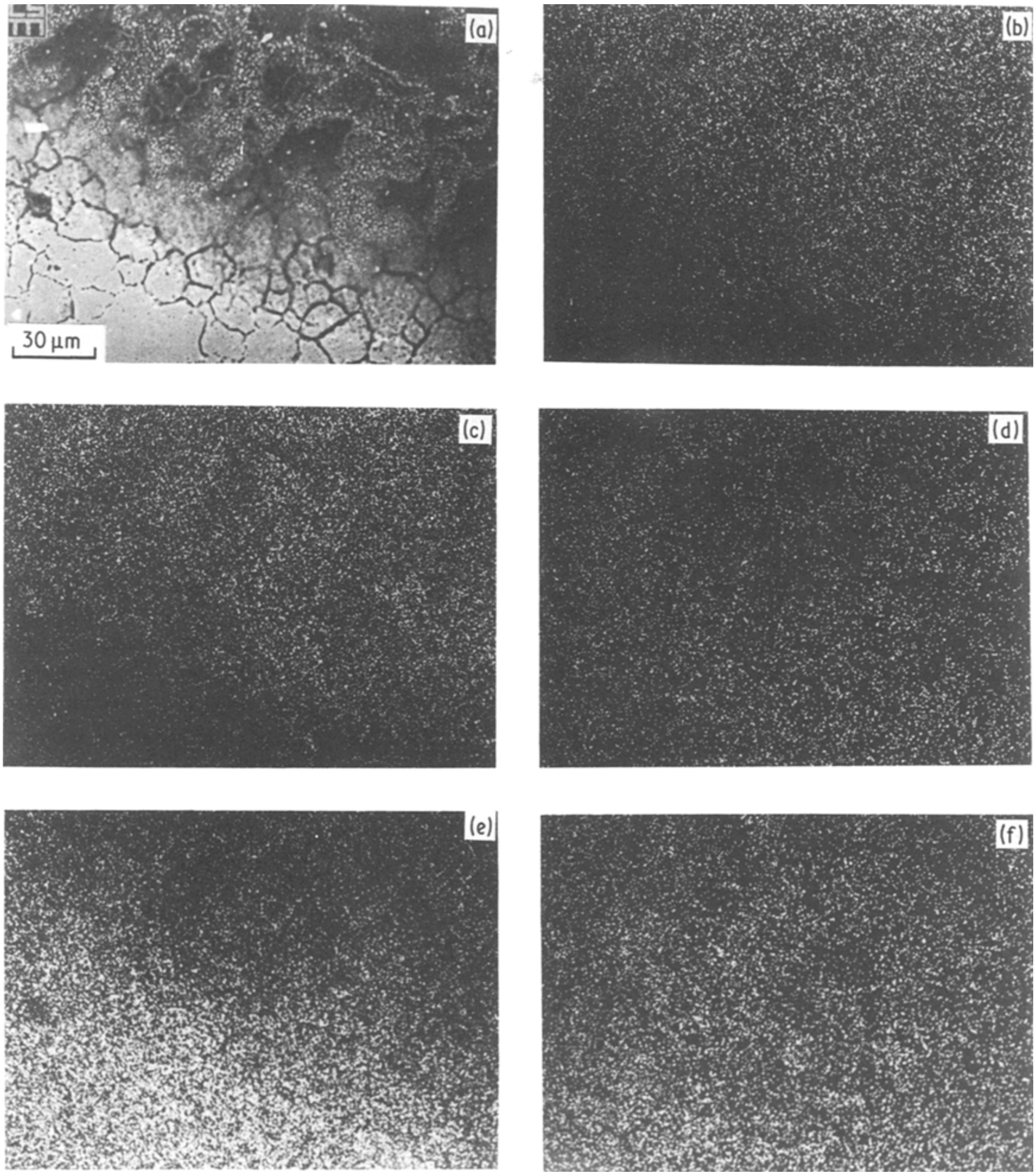

Figure 3 Sample covered with bioactive glass. (a) Morphology of the interface between bioactive glass and steel as seen on an oblique 2° section; the metal side is the lower left one and the glass side is the upper right one. EDX spot mapping of (b) calcium, (c) silicon, (d) nickel, (e) iron, (f) chromium, for the zone represented in Figure 3a.

as a permeable membrane regulating the diffusion of Si^{4+} (as silicate groups) and Fe^{2+} originating from the glass system and the metal substrate, respectively. It seems clear that this phenomenon will be regulated by the dimensions of the individual points of deposited nickel, by the dimension of the mesh of the network formed and the degree of homogeneity in the distribution of the nickel microsystems formed. In addition, if the various points (generally of the dimension of 100 nm or less) of the network are sufficiently oxidized, such a network structure serves as an ideal "container" of the oxygen atoms which are necessary for redox reactions.

4. Discussion

The results obtained in this study may be interpreted with the aid of some general considerations. The mechanisms of adhesion of the bioactive glass to metal substrates are many, just as it is well known to be true for any other type of enamel. The model for the anchoring mechanism based on bridging oxygens between the metallic and vitreous systems (at a molecular level), reported in a previous study [2], may be involved only at the level of the alloy grains. Further phenomena, at a higher dimensional scale, occur. So, the so-called "good chemical adhesion" suffers the interference of such other phenomena. Indeed, the coating procedures of a steel with glass (as in enamelling) involve ionic diffusion and redox processes in which nickel and iron are in competition with each other for oxidation. Since nickel is a semi-noble metal, its oxides tend to favour the oxidation of iron atoms. One of the more important regulator mechanisms is based on the enrichment of the metal surface with oxides of noble or semi-noble metals, since their presence makes oxygen atoms available for the surface oxidation processes.

The ideal condition is that of obtaining a mono- or

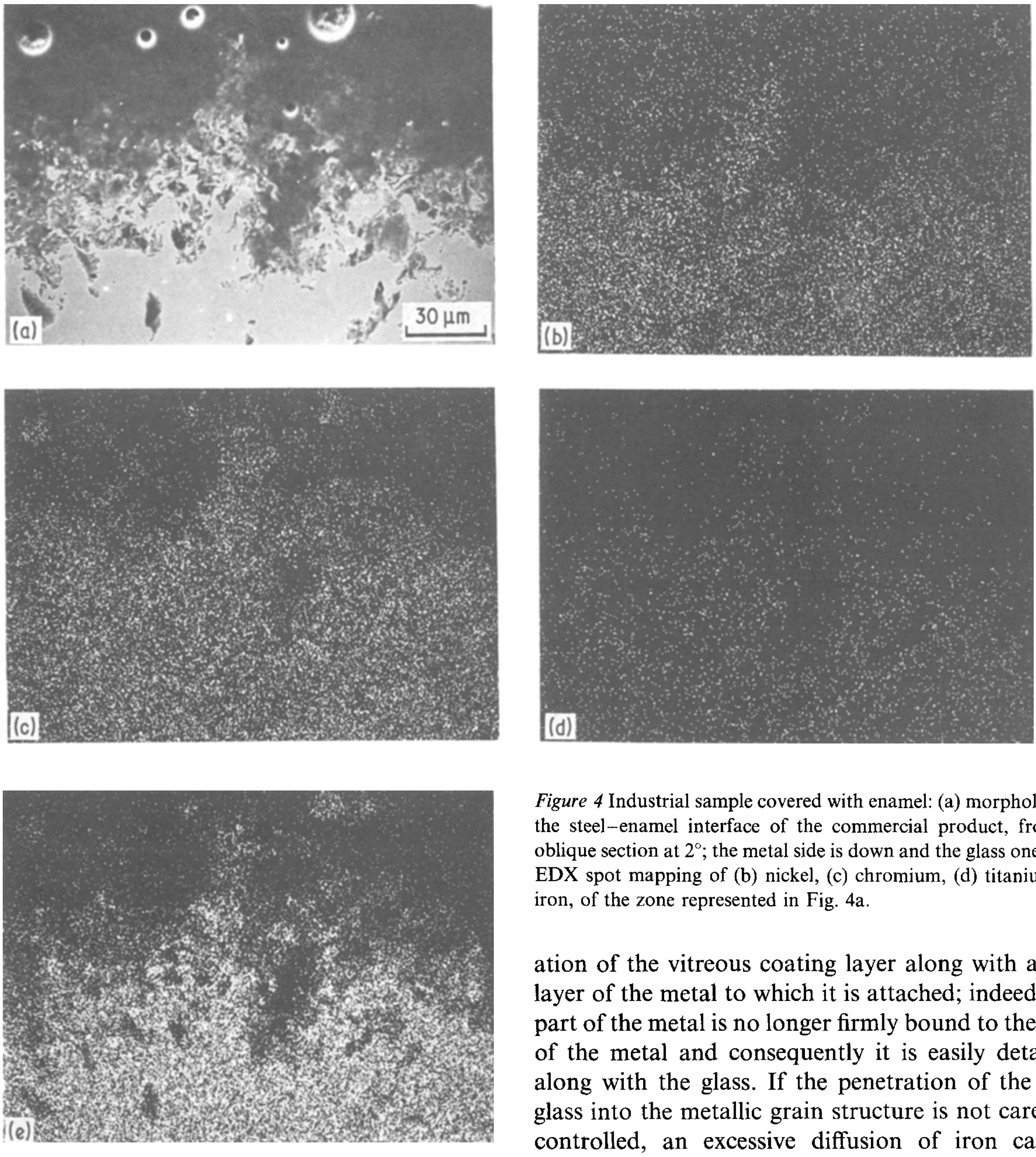

Figure 4 Industrial sample covered with enamel: (a) morphology of the steel–enamel interface of the commercial product, from an oblique section at 2°; the metal side is down and the glass one is up: EDX spot mapping of (b) nickel, (c) chromium, (d) titanium, (e) iron, of the zone represented in Fig. 4a.

bi-molecular film of nickel atoms which could support the formation of bridging oxygens between the iron atoms at the steel grain surface and the silicate compounds in the glass. If the amount of nickel at the surface is too high, its dissolution in the glass becomes difficult and at the same time the formation of an excessively thick layer of FeO (wüstite) is favoured, which in turn can lead to exfoliation of the enamel, as observed also by us. In contrast, if the amount of nickel at the surface is too small, the controlled limitation of the amount of NiO under the nickel layer does not occur and consequently the nickel layer is attacked and dissolved by the vitreous system. In addition, if the amount of nickel at the metal surface is too small and if the glass is not sufficiently fluid, an excessively thick fayalite ($FeO \cdot SiO_2$) layer may form, which is brittle and not very consistent and which may give rise later on to detachment of the vitreous coating from the metal substrate. On the other hand, if the glass is too fluid as shown here, it may attack the grain structure of the metal alloy and thus weaken the surface of the substrate, and allow the possiblity of exfoliation of the vitreous coating layer along with a thin layer of the metal to which it is attached; indeed, this part of the metal is no longer firmly bound to the bulk of the metal and consequently it is easily detached along with the glass. If the penetration of the fluid glass into the metallic grain structure is not carefully controlled, an excessive diffusion of iron can be

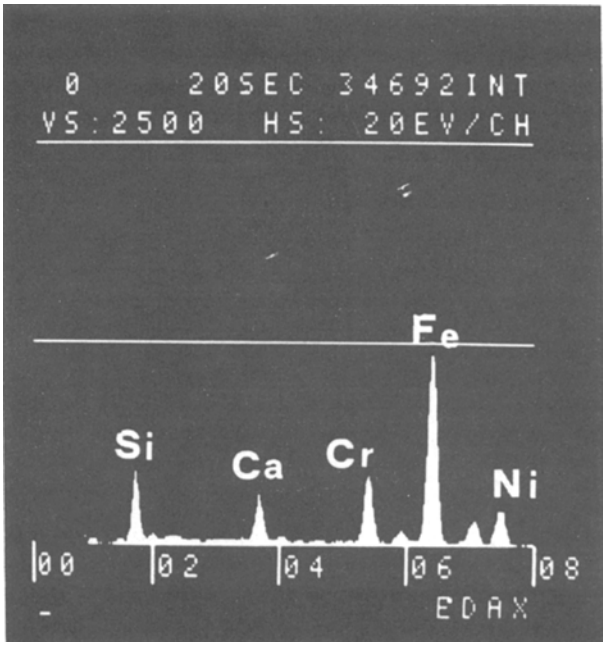

Figure 5 EDX analytical spectrum of the area shown in Fig. 3a.

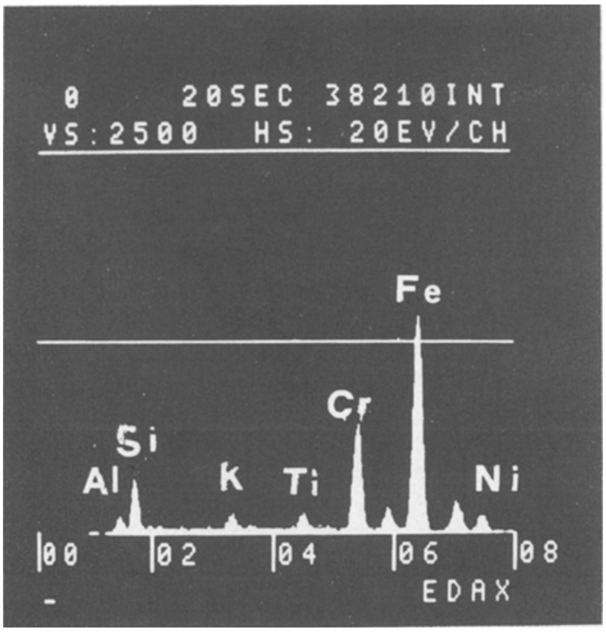

Figure 6 EDX analytical spectrum of the area shown in Fig. 4a.

expected and excessive deposition of nickel may appear at the interface because of redox reactions.

Such considerations make clear the necessity of paying careful attention to the control of the deposition of nickel on the metal surface to be enamelled. Usually preferential deposition of nickel occurs in the rough areas of the surface and on the crests of any ridges present.

The metal pretreatment method which we used, and subsequent thermal treatment of the metallic sample before its dipping in the glass melt, favour the interstratification of different atomic species at the metal surface, with selected deposition on its rough regions and along the grain boundaries. Details of the specific local situations are difficult to establish, and it is also difficult to define what really occurs in the presence of nickel before dipping. In the samples examined, a thin network of deposited nickel is probably formed as previously described, but because of either the destruction of the original network or its limited consistency in relation to the requirements during immersion of the metal in the melted glass, the nickel network formed was not sufficient to control the excessive attack of the glass on the granular structure of the metal alloy. The excess of nickel, however, is clear, as seen from the two spectrograms of Figs. 5 and 6 where the amount of nickel per unit area is greater in the case of the bioactive-glass– steel system than in the industrial enamel–steel system. This excess of nickel is probably due more to the diffusion of nickel from the steel alloy (favoured by the high temperature of dipping) than to the diffusion of nickel from the coating glass.

With the exception of the presence of calcium (necessary for a bioactive glass) and the absence of potassium in the bioactive glass, the distribution of the fundamental components of the composition was more or less the same for the two systems, the bioactive glass and the industrial enamel, indicating that such a distribution is a necessary condition for attaining the best values of adhesion. The excessive fluidity of the bioactive glass, one of the reasons for its excessive intergranular penetration, is favoured not only by the high melting temperature (1250° C) but also by the presence in the glass composition of Na^+ and PO_4^{3-} ions, chemical species which promote the solvent and breaking-down actions of the silica on the metal alloy. In order to avoid this phenomenon, it is evidently necessary to carry out a further correction of the doping composition of the bioactive glass. For example, the nickel ion activity may also be predetermined through controlling its presence in the bioactive glass.

One means of controlling the excessive penetration rate of the very fluid vitreous system (which cannot however be modified beyond certain limits and still maintain the properties of a bioactive glass) may be through the presence of TiO_2, which can possibly regulate ionic diffusion to promote the formation of a needle-shaped network, useful for improving the nickel network and suitable for checking the excessive penetration of the bioactive glass into the interior of the granular structure of the metal alloy. It seems possible, therefore, that the ionic and molecular flux at the interface could be reduced by (i) decreasing the etching times and thus limiting the activation of the intergranular surfaces, and (ii) adding "regulating" substances to the glass composition which promote the action of the network of deposited nickel. If this

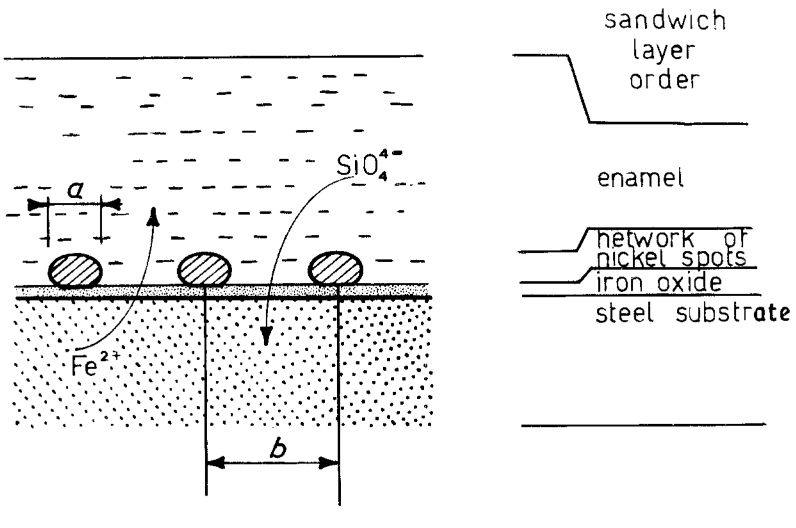

Figure 7 Schematic representation of the network-type surface structure of nickel deposition on the metal surface under conditions of the prefiring operations leading to the best coating on the metal surface. The best distribution of such nickel deposition on the metallic surface of the substrate at the interface is the one that consists of a layer of spheruloidal precipitate of nickel spots. These metallic granules, each having diameter *a*, must be uniformly dispersed to give rise to an arrangement like a network. The average distance between two nearby spots, corresponding to the average width of the meshes forming the network, is shown as *b*. The figure also illustrates the nature and the probable diffusive progress of the fundamental ionic species.

can be achieved it would then seem possible that at the same immersion times and temperature used in this study, the intergranular rooting of the bioactive glass coating may be decreased.

5. Conclusions

The bioactive glass which the results of a previous study [1] had indicated as being most suitable for coating metal prostheses was found to have good adhesion, as shown by SEM micrographs obtained in this present study. The micrographs, however, also show that the agressiveness and wetting power of the bioactive glass on the metal are relatively high. This means that even though the bioactive-glass–metal system studied here corresponds relatively well to the requirements of such a system, it will be worthwhile to carry out further studies directed towards improving the workability of the components in order to obtain a still more suitable system. The results obtained from the tests carried out in this study provide a useful basis for further studies directed towards improving the nature of glass–metal reactivity, which in the present system is excessive. It is clear from these studies that a high wetting power of the glass alone is not sufficient to achieve the best results, but rather a compromise is necessary between the wetting power of the glass and maintaining good cohesion between the grains of the metal substrate. Based on the results obtained here, the steps necessary to improve the physicochemical characteristics of the bioactive-glass–metal system are the following:

(a) decrease the etching time when pretreating the metal substrate;

(b) add an appropriate component to the glass composition which will form a microcrystalline precipitate suitable for reducing the flux at the glass–metal interface;

(c) seek ways to improve the distribution of the nickel concentration at the glass–metal interface.

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