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Conference Director

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Foreword

A Message from the Technical Forum Chairman

Again this year, as has become the pattern each autumn since the first PEI Technical Forum back in 1937, a banner group with an active interest in porcelain enameling met in a two-day conference on a midwestern university campus. This year more than 200 technical representatives gathered at the University of Illinois to hear and discuss a variety of porcelain-enamel-related topics.

Many people contribute to the success of each of our Technical Forums. The committee, the host university, the Forum speakers, and panel participants—and, importantly, an active and interested audience—are all vital elements.

For this year’s meeting, it all started when the Technical Forum Committee assembled last spring and began to make plans for the meeting. Countless candidate topics were weighed and considered, and finally, more than 30 papers and panel presentations were selected and prepared for the Forum audience. The spirited discussions following each paper and in the informal gatherings between sessions underline the value of the efforts of all of those who made the Forum possible.

This year’s Technical Forum led off with the A. I. Andrews Memorial Lecture presented by Professor Wendell S. Williams of the University of Illinois. Dr. Williams discussed some of the many new analytical tools that are available for research and analysis today.

A series of papers and panel discussions devoted to the developments in ground coats followed. Experiences with low cobalt systems were reported. Next, attention was given to the growing successes throughout the industry with no-nickel-no-pickle systems.

The advances in porcelain-enamel powder were next highlighted. The developing trends were noted, and the numerous plant experiences in which companies have moved to powder-application production occupies an important part of the discussion. Attention was then directed at the new equipment now available for improved application of porcelain enamel, both in powder processes and in the use of robots for a variety of operations. Metal preparation received its share of attention as cost-effectiveness of detergent concentrates was considered.

On Wednesday, furnace innovation was an important part of the program. Design concepts were discussed, and experiences with various types of furnaces were explored. Examples of cost savings both by fuel conversion and by the use of ceramic-fiber insulation were cited.

As the Forum drew to a close, a paper describing the reaction of various enameling systems to direct firing was presented, and experience in cast-iron enameling by the wet process was reported. There followed several papers on the subject of improved frit utilization; both frit conservation in the plant and recycling were included. Finally, environmental aspects were explored, touching on the environmental audits, hazardous wastes, and responses to the various Environmental Protection Agency waste-water regulations.

I enjoyed very much the opportunity to serve as chairman of the PEI Forum Committee this year. I am grateful for the support of the officers and staff of the Porcelain Enamel Institute, and we all owe a deep debt of gratitude to our excellent...
hosts at the University of Illinois, especially to Clifton Bergeron.

I want to again thank members of the Committee, the speakers, and the session chairman for their efforts in making this Forum possible. We look forward to seeing all of you at next year's Technical Forum which will be held at Ohio State University on October 26 and 27.

James F. Quigley, Chairman
1982 Technical Forum Committee
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The techniques of scanning electron microscopy, energy-dispersive X-ray analysis, transmission electron microscopy, electron diffraction, electron energy-loss spectroscopy, and Auger electron spectroscopy are discussed as means for analyzing coating/metal interfaces, precipitates, and grain-boundary phases. Examples are drawn from systems involving cobalt, nickel, titanium, tungsten, carbon, and boron.

I. Introduction

This lecture on modern instrumental methods for materials analysis will be delivered from the perspective of a materials scientist rather than an analytical chemist. Therefore, the methods themselves will be described only briefly, with emphasis on fundamental principles and the range of applicability, rather than details of operation or competing models. Applications have been selected which lie close to the interests of the porcelain-enamel industry although they are not drawn specifically from that source. The topics are coating/metal-interface chemistry, precipitates in metals, and grain-boundary phases — problem areas in a number of basic and applied materials fields.

II. Instrumental Methods

A list of new techniques for materials analysis includes at least a dozen entries, such as scanning electron microscopy (SEM), energy-dispersive X-ray analysis (XES, EDS, or EDXA), transmission electron microscopy (TEM), scanning-transmission electron microscopy (STEM), electron energy-loss spectroscopy (EELS), selected-area diffraction (electron) (SAD), reflection high energy electron diffraction (RHEED), Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS), and X-ray photoelectron spectroscopy (XPS or ESCA).

The most immediately useful instrument in the materials laboratory today is the scanning electron microscope (SEM) combined with energy-dispersive X-ray analysis (EDX or XES). With its great depth of focus for visualizing textures of...
surfaces — steels pickled for enameling, for example — the SEM has greatly extended our ability to look at materials. Although this instrument is not new, it has been refined and the resolution has increased to 70 Å in the last few years.

In the SEM, an electron current is emitted by a hot cathode or cold field-emission source, accelerated through 50 kV, and focused by electromagnetic lenses to impinge on the surface of a solid specimen. An image is formed on a cathode ray tube (CRT) from the current of secondary electrons or back-scattered electrons coming from the specimen surface as the focused beam is scanned across it. The successful resolution of details only tens of angstroms across depends not only on the precise control of the microscope’s parameters but also on a principle of physics: the wavelength of the moving electron is smaller than the detail being examined.

To extract chemical information produced by the electron beam, the typical SEM is equipped with a detector (usually Li-drifted Si) which responds to impinging X-ray photons produced by the electrons hitting atoms in the specimen with a current pulse proportional to the energy of the individual photon. Thus, elements can be identified by their characteristic X-ray energy, \( E \), which is related to the X-ray wavelength, \( \lambda \), by the expression \( E = \frac{hc}{\lambda} \), where \( h \) is Planck’s constant and \( c \) is the velocity of light. Elements beyond and including sodium in the periodic table can be analyzed to a precision of 0.1% if they are present in amounts greater than \( \approx 1\% \). The study of specimens by SEM/XES is particularly attractive in a busy laboratory or plant, as little specimen-preparation time is required, and in some models, fairly large objects can be inserted directly.

Despite its general utility, the SEM/XES combination is limited to visualization of surface detail only and to near-surface chemical analysis, does not respond to light elements, and cannot detect elements in low concentrations.

For study of microstructural features in the bulk of a specimen, and with resolution now approaching atomic dimensions, the transmission electron microscope (TEM) is available. Microscopic defects, such as dislocations, precipitates, and individual grain boundaries, can readily be visualized by TEM. This capability is important for a porcelain-enamel laboratory, as the quality of the product is in large part determined by the quality of the underlying steel, which is often not obvious without detailed microscopic examination.

In TEM a high voltage beam of electrons (100 keV to 1 MeV) penetrates a thin foil (200–1000 Å) and forms a contrast image on a photographic plate or phosphor screen or on a solid-state detector which converts the electron impact to signals to control the beam of a CRT. The last method is used with the scanning-transmission electron microscope (STEM) which is particularly useful for analytical studies. It generally includes both an energy-dispersive X-ray detector and an electron energy-loss spectrometer.

The method of electron energy-loss spectroscopy (EELS) is the complement of the analysis of X-rays emitted by a foil through which an energetic electron beam has passed (XES). Instead of measuring the number of X-ray photons produced, EELS measures the number of electrons which have lost the energy required to excite those X-rays. One advantage is that the chemical information comes from a region of the specimen not much larger than the diameter of the electron-beam focal spot (as small as 5 Å on some models). In the case of XES, by contrast, the effective area can be ten or even a hundred times as large as the beam because of multiple scattering and fluorescence in the foil specimen. The superior spatial resolution of EELS is sometimes very advantageous, as we shall
Another advantage of EELS is its sensitivity to light elements, e.g., carbon, boron, and silicon.

For crystal-structure information, as opposed to elemental analysis, it is necessary to use diffraction. The TEM and STEM instruments are equipped with the capability of producing electron-diffraction patterns, using either transmission with a mask to examine small regions (selected-area diffraction (SAD)), or in grazing incidence (reflection high energy electron diffraction (RHEED)).

Another approach to analyzing solid surfaces is the study of the energy distribution of electrons emitted when the surface is excited by an electron beam. Excited atoms can lose energy either by emitting photons or electrons; the latter process is called radiationless or Auger de-excitation, after a French physicist who discovered the effect. These Auger electrons have energies characteristic of the atoms emitting them and thus permit elemental identification (Auger electron spectroscopy (AES)). A scanning Auger microprobe (SAM) allows such analysis with lateral spatial resolution of $<1000$ Å with a sensitivity of 0.1 at.%, including light elements (e.g., C, N, and O). Furthermore, by sputtering the surface away with an argon-ion beam while the Auger analysis is in progress, the instrument can obtain elemental profiles with a spatial resolution of the order of one atomic distance normal to the plane of the specimen.

III. Applications

We now turn to several examples of the application of modern instrumental methods to the analysis of materials which have counterparts in the porcelain-enamel industry.

For good adherence, any coating must make a chemical bond with the substrate. Texturing the surface before coating is also helpful because of improved mechanical interlocking and greatly increased effective surface area for chemical interaction. In the case of porcelain enamels on steels, pickling the surface with H$_2$SO$_4$ to roughen it followed by electroless deposition of nickel or cobalt layers prior to enameling is generally practiced to improve both chemical bonding and mechanical interlocking.

Here, we will examine a similar system in which cobalt interaction with both substrate and coating is critical for coating adherence, although in this case the participating nonmetal species is carbon rather than oxygen. The system is WC-cobalt with a coating of TiC. This combination is widely used in the cutting-tool industry, as the cemented carbide provides mechanical toughness for interrupted machining of steel, and the TiC coating provides some oxidation protection for the WC and reduces the chemical interaction between the cobalt binder and the ferrous workpiece. Note the parallel with the protection against oxidation and other forms of chemical degradation of the substrate provided by porcelain enamel on steel.

The TiC coating can be applied in several ways: chemical vapor deposition, activated evaporation, or sputtering. For understanding tool failure in which spalling of the coating is the problem, it is essential to characterize the interface between the substrate and coating, in particular, the gradients of chemical composition near the interface. Since each coating method involves a different substrate temperature and atmosphere, substantial differences might be expected.

How can the chemistry of an interfacial region be analyzed on the scale of a few hundred angstroms? Effective use of wavelength-dispersive X-ray analysis in conjunction with scanning electron microscopy for this purpose was reported to this forum in 1980 by Kim. Here, we will examine a different technique, Auger
electron analysis, which has the advantage of greater spatial resolution normal to the plane of the specimen. Hence, the method can do microchemical analysis very close to the boundary between coating and substrate. The technique, described above, permits continuous removal of surface coating, atomic layer by atomic layer, by sputtering with an argon beam while the atomic species uncovered on the surface are identified by the characteristic energies of electrons emitted following excitation by an incident electron beam. The characteristic line shape or signature of species of particular interest can also be examined periodically to follow changes in chemical bonding.

A specimen of commercial cutting tool coated by chemical vapor deposition was studied by Auger microscopy and other techniques by Sharma and Williams. Figure 1(A) shows the microstructure of the cemented carbide visualized by scanning electron microscopy. The material is complex, containing hard particles of both cubic and hexagonal carbides and a binder phase. Etching of the predominantly cobalt binder phase reveals the particles more distinctly. Mapping of the individual elements of interest—tungsten, cobalt, and titanium—was carried out by energy-dispersive X-ray analysis on the scanning electron microscope. The results are shown in Figs. 1(B)–1(D). It is clear that some diffusion of tungsten from the substrate WC particles into the TiC coating has occurred at the high temperatures (1100°C) used in the CVD process. (The tungsten goes into solid solution with the TiC.)

Although the carbon species is not detected by energy-dispersive X-ray analysis, its participation in the coating process is critical and has many ramifications. The carbon for combining with the titanium supplied from the vapor species (TiCl4) to make TiC is supposed to come from a hydrocarbon gas which is cracked on the substrate at 1100°C. However, initially the deposited Ti picks up carbon from the substrate, thus depleting the surface of carbon. Further, the atmosphere is hydrogen-rich and decarburizing. As a result, carbon is removed from the cobalt binder phase, where it is in solid solution along with tungsten, and a new phase, η-Co6W6C, forms from the binder. This eta phase is brittle and detrimental to mechanical properties. Thus, two of the important questions for microchemical analysis of the interfacial region will be whether eta phase has in fact formed and whether the carbon concentration is low in this region.

If another phase has formed at the interface, it will be very thin and difficult to detect. The approach used in this case was reflection high energy electron diffraction (RHEED), performed in a transmission electron microscope but with the specimen (a cross section) positioned for grazing incidence rather than transmission of the electron beam. The resulting electron-diffraction pattern, shown in Fig. 2, includes not only the appropriate diffraction spots for small crystals of WC, but also a smaller diameter ring, indicating a larger lattice constant, which corresponds to W6Co6C. Thus, the presence of eta phase at the interface is confirmed even though the thickness of the layer is probably <1 μm.2

The presence of the eta phase at the coating/substrate interface could only have come about through the depletion of the cobalt binder of a few tenths of a percent carbon as explained above. How can we detect directly such a carbon deficiency? For this purpose we employ Auger electron analysis. Figure 3(A) shows the concentration profiles for carbon, tungsten, titanium, and cobalt near the original interface of the specimen already described. A minimum in the carbon concentration at the interface is clearly illustrated. Continuous spatial variations in the concentrations of the other three elements are also shown. The abscissa is given in units of sputtering time in the Auger spectrometer rather than depth of pene-
tration, as the precise correlation is not known. However, through comparison with the SEM image and X-ray map shown earlier, 100 min corresponds to \( \approx 5 \mu \text{m} \).

On the same scale of sputtering time or distance penetrated, the activated reaction evaporation process, which is conducted with the substrate at a somewhat lower temperature, leads to less interdiffusion. There is still some carbon depletion at the interface, however (Fig. 3(B)).

The least interdiffusion and hence weakest bonding is exhibited by the sputter-coating process in which the substrate is essentially at room temperature. Even on the expanded scale shown, the profiles are almost square waves. (Note in this case a small oxygen-contamination signal.) This profile would also be typical of TiC coatings applied to steel substrates by sputtering (Fig. 3(C)).

We have seen how Auger electron spectroscopy can do microchemical analysis of the critical interfacial region between coating and substrate. In addition, the method can give limited information about the state of chemical bonding of the atoms studied. In Fig. 4, we see not only the concentration profiles of the elements of interest but also the characteristic signature (in the derivative mode) for carbon. Note the slight difference between carbon combined with tungsten for form WC, and carbon combined with titanium to form TiC; in the former case there is an additional wiggle in the lower right loop. As the sputtering in the Auger spectrometer proceeds to remove surface for analyzing what lies beneath, the Auger signature for carbon changes gradually from that typical of C in the TiC coating to that typical of C in the WC particles forming the bulk of the substrate. As this example shows, it is sometimes possible to identify the chemical environment of a particular atomic species by close inspection of its Auger signature and comparison with standards.

Having illustrated the utility of Auger electron spectroscopy, scanning electron microscopy, energy-dispersive X-ray analysis, and reflection high energy electron diffraction in studying coating/substrate interfaces — techniques which are applicable to the porcelain-enamelledsteel interface as well — we turn to the study of the chemical composition of minute precipitates and grain boundaries. The examples will again be drawn from the refractory hard metals — cemented carbides and single crystal carbides and borides — but contact with problems in the porcelain-enamelledsteel industry is straightforward, as the steels being coated contain grain-boundary constituents and even, in some cases, TiC precipitates.

In the cemented-carbide industry, a matter of continuing debate has been whether the carbide particles are separated by a thin film of binder phase following liquid-phase sintering or whether there is a continuous skeleton of carbide/carbide contact. This issue is important in interpreting plastic deformation in these materials.

An approach taken by Sharma\(^3\) and by Ruchlewicz\(^4\) was to prepare thin foils of cemented carbides and examine them with a scanning-transmission electron microscope, detecting with an energy-dispersive system the X-rays emitted by the transmitted electrons interacting with atoms in the foil. Because of the fine focus of this instrument (spot diameter, 5–10 Å), even 20-Å grain boundaries could be probed.

There is one important qualification, however. Because of multiple scattering and fluorescence in the foil (emitted X-ray photons excite nearby atoms on the way out, leading to X-ray production some distance from the electron-beam focal spot) the actual region from which the X-ray information comes is considerably larger than 5–10 Å. Sharma determined the effective diameter by placing the beam at the apex of a wedge-shaped grain of cobalt in a cemented carbide and translating

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the specimen in steps until the cobalt X-ray signal leveled off, as seen in Fig. 5.3

The question of whether there is cobalt in the very narrow grain boundary was then answered with some confidence by comparing the cobalt/tungsten ratio in the center of a grain with the value in the grain boundary. Sharma, Ward, Fraser, and Williams found considerable cobalt in the grain boundary with this approach (Fig. 6).5

A study using the same instrument was done on an alternative cutting-tool material, nickel-bonded TiC, by Ruchlewicz.4 Figure 7(A) shows the energy-dispersive X-ray spectrum from a single grain of TiC. The dominant peak is titanium with a small amount of nickel (probably fluorescence from the binder) and molybdenum (added to improve binding and in solid solution with the TiC). The grain boundary, by contrast, has a considerable amount of nickel, as shown in Fig. 7(B).

These two examples show that the spatial distribution of nickel and cobalt—elements much used in the porcelain-enamel industry—can be determined on the scale of hundreds of angstroms with a scanning-transmission electron microscope fitted with an energy-dispersive detector for analyzing the emitted X-rays.

An even more refined method for determining chemical composition in small volumes is electron energy-loss spectroscopy (EELS). For detection of light elements—often the nonmetallic constituents of minute precipitates in metals—EELS can be dramatically successful. As explained above, this method when used with extremely thin specimens does not suffer from degradation of the information by multiple scattering of electrons as they pass through the specimen, nor does X-ray fluorescence perturb the study, as the X-rays are thrown away in favor of the transmitted electrons which excited the atoms to emit X-rays. Using this method, Sharma3 and Allison4 studied thin foils of TiC to determine the feasibility of the approach. As shown in Fig. 8, the principal component of the electron current in the detector is the directly transmitted and elastically scattered beam, as most of the electrons pass through the foil without losing energy at all. However, a few will lose characteristic amounts of energy by knocking core electrons from atoms. These electrons can be separated from the direct beam by an energy-analyzing spectrometer. The electronics then count and display the number of electrons having lost a given amount of energy. Figure 8 also shows the (much smaller) electron energy-loss peaks corresponding to the characteristic X-ray edges of elements X and Y in the specimen.

With the feasibility of EELS for TiC analysis demonstrated, Mochel, Allison, and Williams used the method to identify a mysterious precipitate in another refractory compound, TiB2.7 As seen in Fig. 9, an optical micrograph of an etched surface, even single crystals of TiB2 contain precipitates of some unknown material. These precipitates reduce the fracture stress of the diboride, but without knowing what they are, one is at a loss to prevent or remove them. By transmission electron microscopy (TEM), the precipitates are seen to be extremely thin, perhaps 20 Å (Fig. 10), but the focal spot of the electron beam in the scanning transmission electron microscope is even smaller, 5–10 Å, so chemical analysis within the precipitate alone can be performed. As shown in Fig. 11, the precipitate contains only titanium and carbon, whereas the bulk material, known to be TiB2, shows energy-loss peaks for only titanium and boron. The clean separation of the signals from the precipitate and surrounding material illustrates the ability of electron energy-loss spectroscopy to identify light elements with a few angstroms of lateral resolution.