

Walther N. KOHL
Consultant, Materials, Techniques and Devices
Belmont Massachusetts, USA

Materials selection and compatibility*

While the remarks made in the first lecture [Ref. 1] established the frame within which Materials Science developed and showed that technology must at all times be closely interwoven with societal needs, we shall now address a more specific problem that must be solved when materials interact in a given device.

Electronic devices in the conventional sense, where the free flight of electrons is involved, require that a high vacuum or rarefied gas be maintained within an evacuated envelope, while solid-state devices are free of this restriction. In all cases, however, materials must be chosen on the basis of their suitability for the performance of the intended function and their compatibility with other materials that serve as electrodes, supports, gas dispensers, or the envelope.

Environmental conditions to which the device may be exposed in operation, or during fabrication and testing, can further restrict the available choice of materials. High temperature, low temperature, vibration and shock, and penetrating radiation are some of the variables that must be considered. A more complete list of parameters that affect the selection of materials is given in Table 1. Not all these parameters necessarily apply in each case, and their relative importance will shift with the intended function of the device under consideration, but the first five items determine whether a vacuum can be maintained for a prolonged period. One must also consider how readily a material can be fabricated into a desired shape, whether it is easily joined to other materials, and whether its cost, both for acquisition and fabrication, is acceptable.

* Presented at the International Summer School on subject electronics materials (Herceg-Novi 1975)

PARAMETERS AFFECTING THE SELECTION OF MATERIALS

Chemical stability
 Vapor pressure
 Outgassing rate
 Gas permeation
 Gettering rate
 Sputtering rate
 Mechanical strength
 Resistance to shock and vibration
 Low and high-temperature stability
 Resistance to nuclear radiation
 Electrical conductivity
 Thermal conductivity
 Thermal emissivity
 Magnetic permeability
 Primary electron emission
 Secondary electron emission
 Field emission
 Dielectric properties
 Optical properties
 Thermoelectric properties

As pointed out in an earlier paper [Ref.2], several categories of compatibility must be distinguished:

1. compatibility of one material with its environment;
2. compatibility of materials with each other and with their environment;
3. compatibility of materials with a desired function of adjacent components;
4. compatibility with prescribed processing and test procedures;
5. compatibility of materials with the health and comfort of the operator;
6. compatibility with market economics.

It cannot be too strongly emphasized that materials selection on the basis of these compatibility requirements and the parameters listed in Table 1 must take place at the design stage. Unless a consensus is established between the designer, the materials engineer, and the production engineer while the project is still on the drawing board, costly alterations and substitution of materials may become necessary later on when hardware has already been produced. At least, the chances are that such needed alterations are drastically reduced by this team approach. A model of the device or a pilot production run will usually show up faults that have been overlooked so that the design has to go "back to the drawing board". In this sense, design is always an iterative process, and a more detailed flow chart of it will be shown in the third lecture [see also Ref.3].

Information on Materials Properties on the basis of which a reliable selection of materials for design purposes can be made is often inadequate. Published data rarely take into account the influence of environmental conditions or that of the earlier treatment to which the material may

Table 2

PARTIAL LISTING OF THE CHARACTERISTICS OF A CRYSTAL*

Elemental composition

1. Precise ratios of major elements (i.e. exact stoichiometry)
2. Concentration of all foreign elements
3. Characterization of outermost electron shell of crystal constituents and impurities
4. Distribution of inhomogeneities and impurities

Defect characteristics of the crystal lattice

1. Characterization and concentration of vacancies, interstitials, and substitutional defects
2. Dislocation concentration, nature, and distribution
3. Grain boundary structure

Structural characteristics

1. Structure type
2. Precise lattice parameters
3. Location of atoms within the unit crystal cell

Surface characteristics

1. Chemical nature of the crystal surface: Are impurities concentrated or diluted?
2. Structural nature: surface defects; Which atoms are exposed?
3. Depth and nature of the natural surface layer
4. Depth and nature of the surface damage caused by cutting, polishing, etc.
5. Gas and moisture absorption on the surface: How fast do surface layers respond to environment

have been subjected. These variables can have a profound effect on the property norms appearing in handbooks and tables. Unless it is known from prior experience which of these variables can be neglected and what the relative importance is for the remainder, the designer must conduct evaluation tests that closely simulate the conditions to be encountered in service. This can be a time-consuming and costly undertaking, especially when it includes failure analysis and the determination of reliability levels.

The Characterization of Materials is a concept that imposes a stricter specification of materials in terms of Composition, Structure and Defects (C-S-D). These three parameters were recognized as basic

*After Laudise and Nassau [Ref.5]. Reproduced by permission of the authors and of the Alumni Association of the Massachusetts Institute of Technology.

for the determination of ensuing properties, after an exhaustive study had been conducted by the Materials Advisory Board (MAB) of the National Academy of Sciences (NAS) and the National Academy of Engineering (NAE) in 1964-1967 [Ref.4]. Laudise and Nassau [Ref.5] have recently tabulated some of the characteristics that should be known for a crystal (Table 2) and point out that similar summaries could be prepared for glasses and ceramics. Indeed, the properties of all materials, and therefore their performance in a given environment, are determined not only by C-S-D but also by the methods used for the preparation of the materials, since these, in turn, affect composition, microstructure, and the number and type of defects observed.

Table 3

METHODS USED FOR COMPOSITIONAL AND STRUCTURAL ANALYSIS OF MATERIALS (Arranged alphabetically by letter codes)

AES	Auger electron spectroscopy
AS	Absorption spectroscopy
EM	Electron microscopy
EPM	Electron probe microanalysis
EPR	Electron paramagnetic resonance
ES	Emission spectroscopy
ESCA	Electron spectroscopy for chemical analysis
FES	Flame emission spectroscopy
FIEM	Field ion emission microscopy
GC	Gas chromatography
GDMS	Glow discharge mass spectrometry
GDOS	Glow discharge optical spectrometry
HEED	High energy electron diffraction
IEM	Ion emission microscopy
IMMA	Ion microprobe mass analysis
IMPS	Ion microprobe spectroscopy
INS	Ion neutralization spectroscopy
ISS	Ion scattering spectroscopy
LC	Liquid chromatography
LEED	Low energy electron diffraction
LM	Light microscopy
MS	Mass spectroscopy
NAA	Neutron activation analysis
NMPS	Nuclear microprobe spectroscopy
NMRS	Nuclear magnetic resonance
PES	Photoelectron spectroscopy
REM	Reflection electron microscopy
RHEED	Reflection high energy electron diffraction
SAM	Scanning auger microprobe
SCANNIR	Surface composition by analysis of neutral and ion impact radiation

SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectrometry
TEM	Transmission electron microscopy
UPS	Ultraviolet photoelectron spectroscopy
XFA	X-Ray fluorescence analysis
XRD	X-ray diffraction

A large body of literature has accrued over the past 10 years that addresses this important field of Materials Characterization (MC). The Symposium on "Ceramic Microstructures, their Analysis, Significance, and Production" [Ref.6], held at the University of California, Berkeley, is an example of the extension of these concepts to ceramics. The published Proceedings of this Conference run to 1008 pages. A more recent text on "Characterization of Solid Surfaces" is that by Kane and Larrabee [Ref.7] in which the instrumental techniques for its achievement are described in detail. A set of four volumes on "Systematic Materials Analysis" [Ref.8], edited by Richardson and Peterson, is in preparation, and two volumes of this set have appeared at this time of writing.

It would lead us too far afield in this presentation to attempt an evaluation of the many instrumental procedures that are being used for MC in given situations, but Table 3 presents an outline that shows how far-reaching, and how expensive, any serious attempt at Materials Characterization can be. In a condensed review of this field, Cosgrave [Ref.9] lists the methods primarily applicable to Compositional Analysis and those used for Structural Analysis, Defect and Surface Characterization as follows:

1.1. Methods for Composition Analysis

- Emission Spectroscopy
- Mass Spectroscopy
- Flame Emission and Absorption Spectroscopy
- X-Ray Spectroscopy
- Activation Analysis
- Electron Probe Microanalysis
- Infrared Spectrophotometry
- Gas Chromatography
- Liquid Chromatography

1.2. Methods for Structure- Defect or Surface Characterization

- X-Ray Diffraction
- Electron Diffraction
- X-Ray Diffraction Microscopy
- Light Microscopy
- Electron Microscopy
- Scanning Electron Microscopy

In evaluating these different methods of analysis, the most important parameters are Sensitivity, Accuracy, and Precision. The meaning of these terms is not sharply defined, but varies somewhat with the method under consideration. On the whole, Sensitivity stands for the ultimate detection limit, but it also implies that concentration gradients can be determined. It may be of interest, for example, to know how small a particle of one species can be detected adjacent to another species in a given sample; Resolving Power would be an appropriate term in this case, although it has a somewhat different meaning in optical instruments. Accuracy usually refers to the stability of instrument calibration and the freedom from error, and Precision involves the repeatability of measurements.

Standard Reference Materials [Ref. 10] are available from the National Bureau of Standards (NBS) that assist the experimenter in correlating properties with chemical composition, and, in some cases, with microstructure.

The difference between the analysis of bulk materials, even on a very small scale, and that of surfaces is illustrated by comparing the Electron Microprobe (EMP) with Auger Electron Spectroscopy (AES). While the EMP has the unique capability of performing chemical analysis on a micron scale and of detecting as small an amount of material as 10^{-15} gram in a volume of one cubic micron (10^{-12} cc), this is essentially a depth analysis involving thousands of atomic layers. AES on the other hand explores only the first three or four atomic layers and can detect and identify most elements in $1/10$ of a monolayer.

For AES a much better vacuum (10^{-10} Torr) must of course be maintained to extend the time during which a contaminating monolayer is formed from constituents of the vacuum atmosphere. For an EMP this is not a prime consideration, so that it may be operated at an ambient pressure of 10^{-4} Torr or better. Needless to say, these requirements are reflected in the cost of the instruments.

2. EXAMPLES OF COMPATIBILITY CONSIDERATIONS IN DESIGN

The remarks made, so far, suggest that Materials Compatibility is an important consideration whenever solids, liquids, and gases have an opportunity to react with each other, and that materials to be used in a physical structure must be selected on the basis of such an appraisal. This summary statement highlights the fact that there cannot be "sound design" of any device without giving prior consideration to the possible reactions of materials with their environment in the broadest sense, be these other materials in any of the possible phases, or imposed operational conditions, as enumerated at the beginning of this discussion.

As a consequence, the number of possible examples of judicious selection of materials on the basis of compatibility is as large as the number of successful designs. The few cases to be mentioned will be drawn from the author's experience in this field and include some that have recently been brought to his attention.

A large body of literature is available on this subject, and those interested in specific details are referred to the Proceedings of the several International Conferences on "The Reactivity of Solids", the Conferences on "High Temperature Technology" organized by Stanford Research Institute (SRI), and numerous publications by the "Defense Metals Information Center" (DMIC) of Battelle Memorial Institute, the National Aeronautics and Space Agency (NASA), and the Society for the Advancement of Materials and Process Engineering (SAMPE). The present author's Handbook M3 [Ref. 11] contains many references to the literature on this subject up to 1966, including the important contributions by workers in the U.S.S.R., such as Samsonov and his collaborators.

Interaction of materials at high temperatures is of particular concern in the design of high-temperature furnaces, in thermionic energy converters, in nuclear reactor design, and that of Nuclear Auxiliary Power Systems for space propulsion (SNAP).

In some of these cases, the device must operate in the presence of cesium vapor and in others liquid alkali metals are used as the thermodynamic working fluid or heat transfer medium. Corrosive attack becomes a serious problem in these environments. It has been shown, for example, that alumina bodies used for "Bore Seals" in alternators for "SNAP Systems" operating at 900°C in a mercury or alkali metal vapor atmosphere must not contain more than 0.05 per cent silica. This investigation conducted some ten years ago at EIMAC, Division of Varian Associates, has been described in the literature [See Ref. 11, p.84]. The present author prepared at that time, while a consultant to the project, a bibliography on the "Compatibility of Ceramic/Metal Seals with Alkali Metals" [Ref. 13].

Similar remarks apply to the operation of Heat Pipes that serve to transfer thermal energy from a remote point to a desired interaction zone, such as a thermionic cathode heated by a radioactive isotope source located at some distance from it. This distance between evaporator and condenser may be as large as 25 cm, and the diameters of such heat pipes range from 6 mm to 15 cm, Working temperatures extend from zero to 2000°C, and the vapor pressures from 0.03 to 10 atm. Only small temperature differences, on the order of 1°C, are required between the hot and cold end. Large amounts of energy, from a few Watts to 17 kW, can be transferred in this manner. Two lengthy articles on Heat Pipes by Asselman and Green [Ref. 12] appeared in 1973 and describe both theory and applications. Heat Pipes are commercially available in the U.S.A. in a wide range of sizes for different power levels to suit the many possible applications. Among these are equalization of furnace temperatures, cooling of electron device assemblies, and transfer of heat from the bombarded area of rotating anode x-ray tubes.

Serious problems of materials compatibility can arise in an attempt to match the material for the pipe itself to the selected working fluid. At the lower temperatures, aluminum tubes have been used with a filling of ammonia, using a stainless steel mesh for the return of the condensed vapor along the

wall; stainless steel (S.S.) tubes filled with ammonia or methyl alcohol and copper tubes filled with water find application to the level of 150°C. A nickel shell has been used with a filling of potassium in one case, but refractory metals and their alloys are generally required at the higher temperature levels where liquid metals (Pb, Bi, Ag, K, Na, Li) act as working fluids. Frequently a ceramic transition separates the heat pipe from the interaction zone, so that ceramic/metal seals are needed that withstand the adverse environment.

The problems encountered are many. Since the wall of the heat pipe has to be thin to facilitate thermal heat transfer from the external source, the vapor pressure of the working fluid at the operating temperature must not be so high as to endanger the stability of the envelope. This consideration eliminates the use of sodium at 1450°C, for example. Lithium is incompatible with alumina at this temperature and therefore cannot be used as a filling for ceramic-insulated structures. Johnson [Ref. 12] has reported on "Corrosion Studies of Liquid Metal Heat Pipe Systems at 1000 to 1800°C".

Another example where the interaction of ceramics with refractory metals is of critical importance is illustrated by a unique furnace insulation that is being marketed under the Tradename "Multi-Foil" by Thermo Electron Corporation in Waltham, Mass. While the benefit of multiple radiation shields has been recognized for a long time, the number of concentric shields on cylindrical furnaces has rarely exceeded a dozen for the simple reason that the overall volume becomes too large when conventional insulation and shield materials are being used. This difficulty is avoided in "Multi-Foil" structures by using very thin (25 μm) refractory metal foil in as many as 200 layers (typically about 60) that are spirally wrapped and insulated from each other by sprayed on ceramic powder having a particle size of about 25 μm . Very low thermal conductivity (2×10^{-5} Watt/cm °C at 2400°C) across the wrapped layers is thereby achieved, resulting in substantial (10x) reduction of power consumption when compared with furnaces insulated in a more conventional manner. It is of course essential that no chemical reaction or sintering between the ceramic particles and the shield metal occurs at the operating temperature. A careful appraisal of materials compatibility is therefore necessary. Tungsten foils have successfully operated with thoria powder for many thousands of hours, and molybdenum, tantalum, and tungsten-rhenium foils have been used with zirconia and yttria powders at lower temperature levels where bonding does not occur as readily.

These few examples have indicated that the Materials Engineer is often confronted with situations where very low impurity levels cause incompatibility and lead to failure if they are disregarded. In electroplating, for example, substrate surface contamination will affect the uniformity of the deposit and its adherence and cause porosity and stress. This observation puts into focus the requirement of carefully controlled cleaning procedures for electron device fabrication.

Permissible impurity levels in solders use for the production of Printed Circuit Boards (PCB) are very low for some elements. As little as 0.001 per cent b.wt. of either zinc or aluminum may cause lack of adhesion and brittleness, as well as a tendency toward "hot-short-cracking", a term describing mechanical weakness of soft solders below the solidus temperature and extending to about 140°C.

On the other hand, small additions of foreign elements can at times turn incompatibility into compatibility. Thus the wellknown "tin pest", observed with pure tin solders, is avoided by the addition of 0.5 per cent antimony or 0.1 per cent bismuth, or 5 per cent lead [Ref. 11].

We shall have occasion to discuss the implication of these last-mentioned incompatibilities on "Joining Techniques" which will be the topic for the third lecture in this series. At the same time, members of the audience will no doubt provide other important examples where compatibility is a limitation imposed on the selection of materials.

References

1. Kohl W.H.: Materials Science, Technology and Society. Lecture No 1 presented at the '75 Conference on "Materials in Electronics" at Herceg Novi, Yugoslavia, July 7-16, 1975
2. Kohl W.H.: The Compatibility of Materials, IEEE Spectrum, 6, No 1 Jan. 1969, 67-74
3. Ruskin A.M.: Materials Considerations in Design, Prentice Hall, Inc., Englewood Cliffs, N.H. 1967
4. Materials Advisory Board, Characterization of Materials, Publication MAB-229-M, National Academy of Sciences, Washington D.C. 1967
5. Laudise R.A., Nassau K.: Electronic Materials of the Future: Predicting the Unpredictable, Technology Review MIT, Oct/Nov. 1974, 61-69
6. Fulrath R.M., Pask J.A.: Ceramic Microstructures, Their Analysis, Significance, and Production. Proceedings of the Third International Materials Symposium held at the University of California, Berkeley, June 13-16, 1966. John Wiley and Sons, Inc., New York, 1968
7. Kane P.F., Larrabee G.B.: Characterization of Solid Surfaces, Plenum Press, New York, 1974
8. Richardson J.H., Peterson R.V., ed's: Systematic Materials Analysis, Academic Press, New York, N.Y. 1974
9. Cosgrove J.F.: Materials Evaluation at GTE Labs, GTE Laboratories Profile, 3, 1973. A well chart comparing 28 available methods for the determination of chemical composition was prepared by D.J.Bracco and J.F. Cosgrove and became available in January 1974
10. Catalog of Standard Reference Materials, Special Publication 260, 1970. National Bureau of Standards, Washington, D.C. 20234
11. Kohl W.H.: Handbook of Materials and Techniques for Vacuum Devices M3, Van Nostrand Reinhold, New York, 1967
12. Johnson G.D.: Corrosion Studies of Liquid Metal Heat Pipe Systems at 1000°C to 1800°C, in Proc. of AIME Conference on Liquid Metals, Philadelphia, Pa. Oct. 13-16, 1969
13. Kueser P.E. et al.: Bore Seal Technology Topical Report, NASA-CR-54093 Dec. 1964; prepared by Westinghouse Electric Corporation, Aerospace Electrical Division, Lima, Ohio