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A study of the nature of solderless metal–ceramic bonds by reflectivity measurements

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The bonding mechanism between surfaces of tantalum and sapphire, aluminium and sapphire as well as copper and sapphire, was studied using optical reflectivity measurements and electro-reflection. In the tantalum-sapphire system, a reaction layer could be detected, but no indication of such a layer could be found in the other systems. The bond strengths observed in these systems are related to free valency states in the surfaces of the oxides.

1. Introduction

The mechanism by which two solid bodies adhere to each other has not been understood for special systems until recently. Metal-to-ceramic bonds are frequently used in seals for electronic components and are needed for high temperature composite materials. The processes used at present for making metal-to-ceramic seals such as the well-known Mo–Mn and the so-called active metal processes are complicated, but their bonding mechanisms are well understood [1, 2]. The intermediate layers occurring with these systems influence the loss phenomena in electronic components and the compatibility and stability of high temperature composite materials.

It is expected that many of the problems related to these intermediate layers, however, will be avoided by directly sealing metals onto ceramics at elevated temperatures. However, little is known about the bonding mechanism in such direct, solderless bonds. Some theoretical considerations and a literature survey have been given earlier [3].

2. Experimental procedure

Bonding of sapphire (alumina single crystals) to tantalum, copper, and aluminium were studied. The samples consisted of polished sapphire plates (cut perpendicular to the optical axis, 15 mm diameter, 2 mm thick) onto which Ta–, Cu–, and Al–plates (14 mm diameter, 1 mm thick) had been pressed at 850 N cm^{-2} in a reducing atmosphere at 1400, 980, and 600° C, respectively. Further experimental details can be found in [3].

With light micrographs using cuts forming an angle of almost zero with the plane of adherence and thus giving a resolution of up to 50 nm [4], no intermediate layers could be detected.

In order to study the bonding mechanisms further, optical reflectivity measurements were performed making use of the translucency of sapphire over a large part of the spectrum. This method is experimentally simple and the only one whereby possible intermediate layers with thicknesses in nanometers can be detected directly without breaking the composite. These methods have been described in detail by Harrick [5].

The principle of the measurement is shown in Fig. 1. In this example two different layers are assumed. The penetration depth, and thus the reflectivity, can be varied by altering the wavelength as well as the incidence angle of the light. Fig. 2 shows a schematic drawing of the apparatus. The wavelength can be selected with the monochromator, and the reflectivity deter-

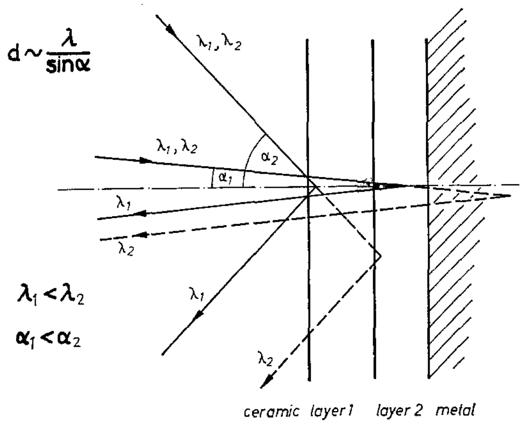


Figure 1 Schematic representation of the depth of penetration of light for different wavelengths and different angles of incidence.

mined in comparison to a standard (aluminium) reflector. The three components on the right hand side will be explained later.

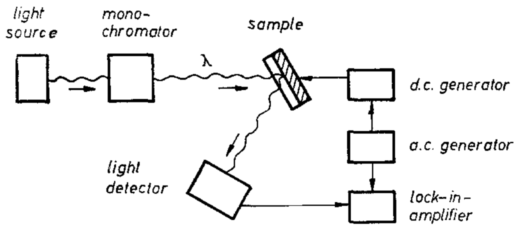


Figure 2 Schematic drawing of the experimental apparatus.

Whilst it is well appreciated that ellipsometry is the most precise means for measuring the thickness and optical constants of thin films [6], it was not used here because the primary object was to find changes in the reflectivity at different pressing times in order to seek some conclusions about the formation of reaction layers. There are three other reasons for this confinement to pure detection of such layers:

(1) The oxide films with which the metals are primarily covered are not destroyed simultaneously over the whole contact area during pressing; therefore, some averaging of the reflectivity is necessary and the precision is low.

(2) The optical constants, from which the reflectivity can be deduced, vary locally perpendicular to the reaction layer because of the concentration gradients of the reactants.

(3) In layers with thicknesses of 10 nm or less, the optical constants are strongly thickness dependent ([7], p. 233).

In order to obtain some idea about the thickness dependence of the reflectivity for layers between sapphire and metal, computer calculations have been performed. Fig. 3 shows the reflectivity, as a function of wavelength, with the thickness of the layers as a parameter for different coefficients of absorption k_1, the dispersion being kept constant. The optical values of sapphire (n_0), copper and aluminium (n_2, k_2) were taken from the literature [8-10], as well as a reflectivity equation for normal incidence [10].

3. Results and discussion

3.1. Tantalum-sapphire

The change in the reflectivity of a tantalum-sapphire bond is shown in Fig. 4, after a pressing time of 15 min. The steep slope at 1.75 eV or 710 nm, results in a red colouration. After longer pressing times, a nucleation in the layer can be clearly detected, leading to diffuse reflections. In this case, the equations taken from [10], pp. 6 to 120, are no longer valid, thus no systematic thickness dependence of the reflectivity could be detected.

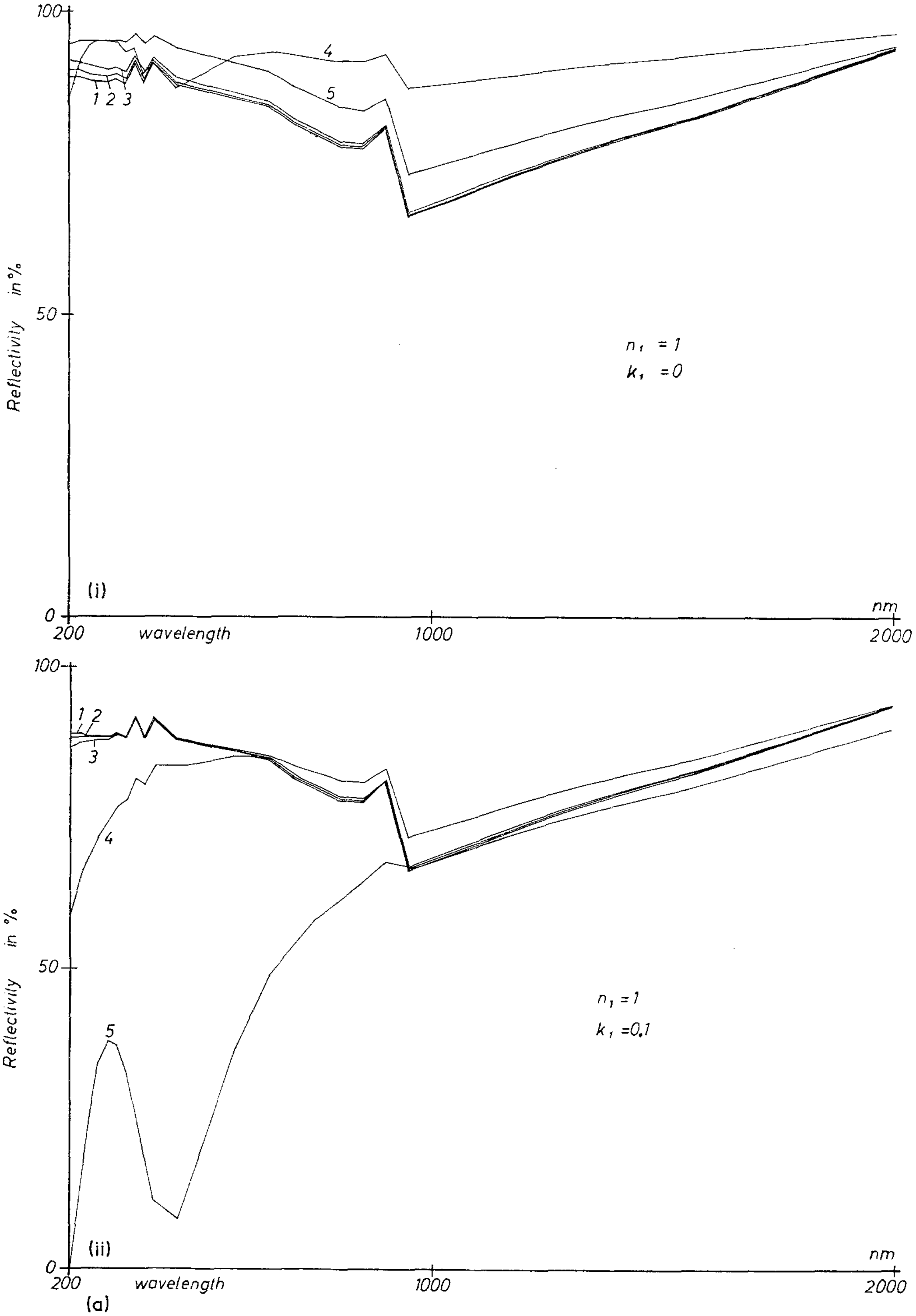
The red colouration mentioned above cannot be caused by interference effects because of the lack of the periodicity of interference spectrograms; also, the film thickness would need to be in the order of half the wavelength (λ/2). The formation of a reaction layer in this system must also be expected from thermodynamic considerations [3]. Therefore, the bond strength can be explained by the assumption of a reaction layer of the composition $Ta_xAl_yO_z$.

3.2. Aluminium-sapphire and copper-sapphire

The reflectivities of an aluminium-sapphire bond are shown in Fig. 5, and those of a copper-sapphire bond in Fig. 6, for two pressing times. These figures also show the reflectivities of these systems without intermediate layers according to

$$R = \frac{(n_0 - n_2)^2 + k_2^2}{(n_0 + n_2)^2 + k_2^2}.$$

For the aluminium-sapphire system, a comparison of the curves of Fig. 5 with the computer


100
50
0
Reflectivity in %
1 2 3
4
5
$n_1 = 1$
$k_1 = 0$
(i)
200
wavelength
1000
2000
nm
100
50
0
Reflectivity in %
1 2
3
4
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$n_1 = 1$
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(ii)
200
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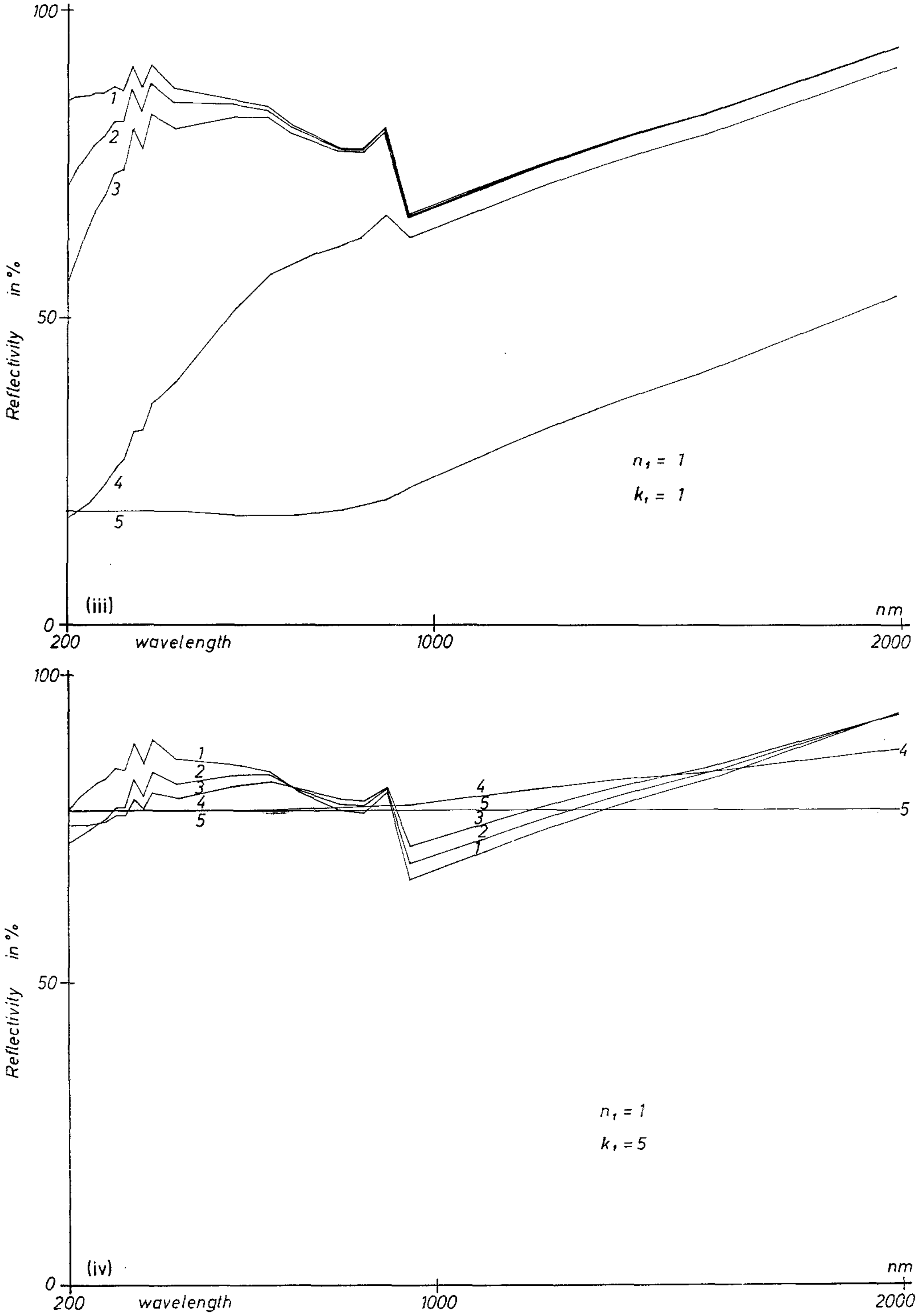
nm
(a)

Figure 3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Reflectivity in %
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Reflectivity in %
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$n_1 = 1$
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(a)

Figure 3

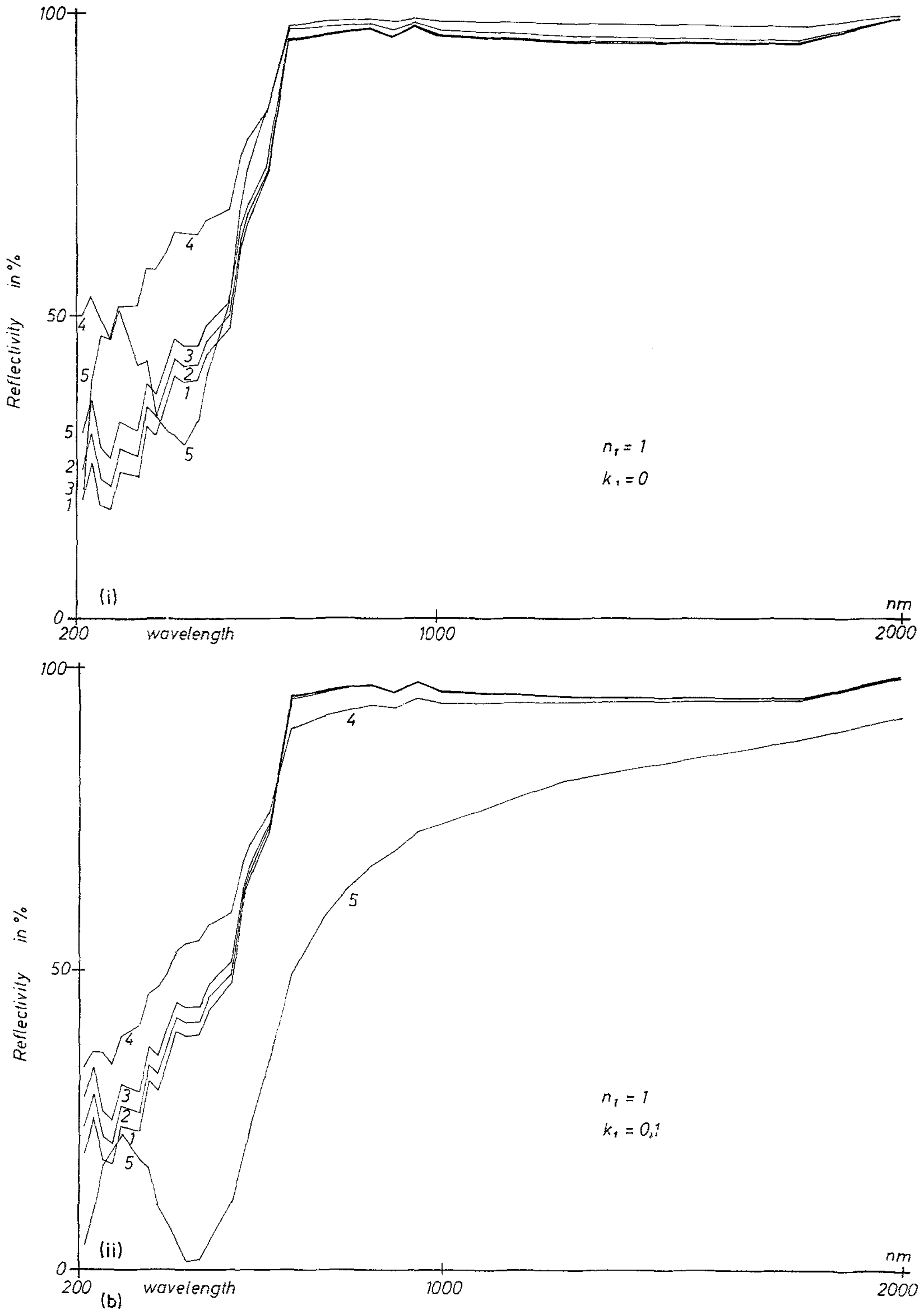
(i)
Reflectivity in %
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Figure 3

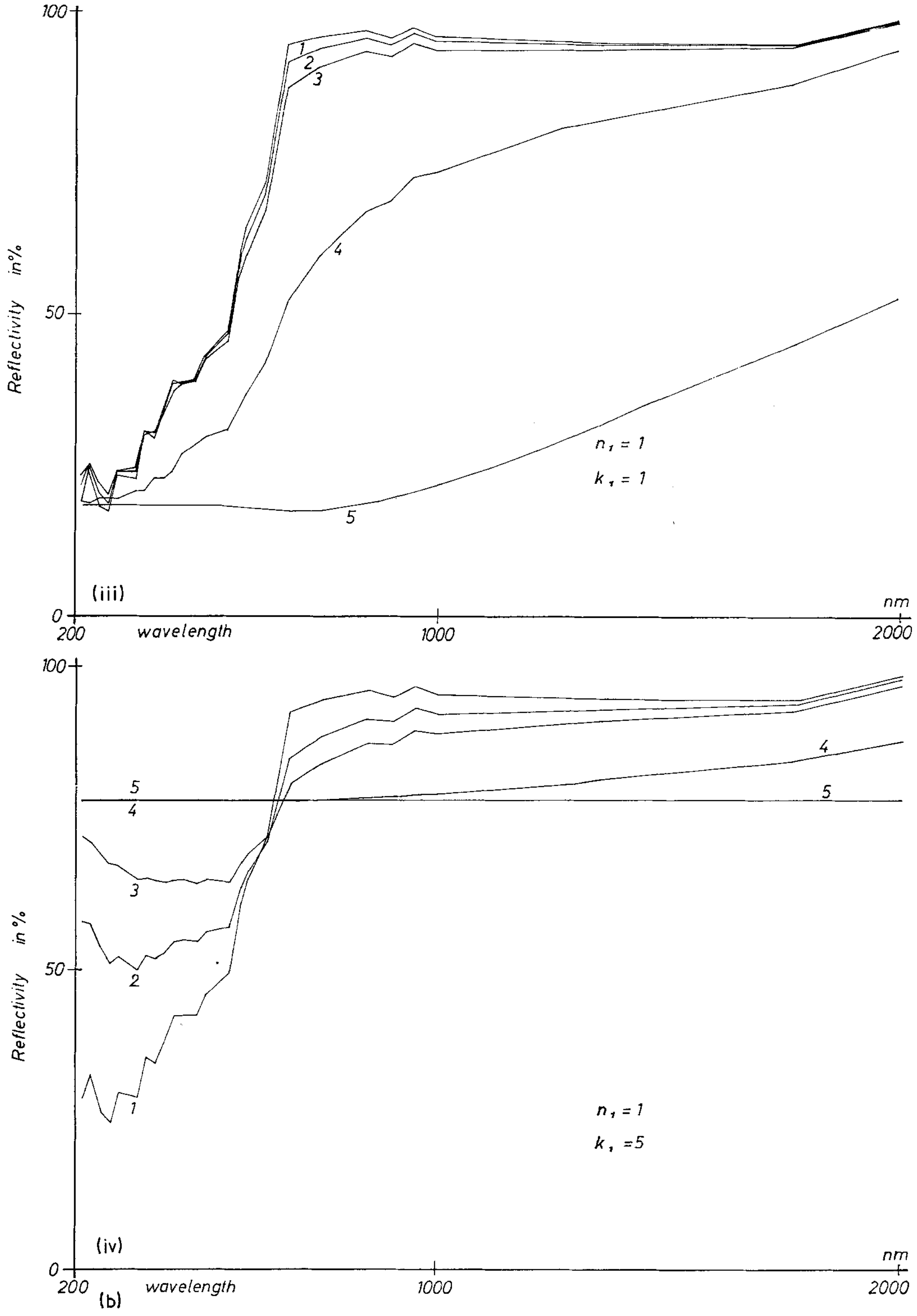

Figure 3 Computer calculations of the reflectivity as a function of the wavelength for normal incidence for the three-phase system, sapphire–intermediate layer–metal, for different thicknesses of the intermediate layers (parameter) and different coefficients of absorption (different figures) for (a) aluminium and (b) copper. (Thickness of intermediate layers: (1) 1 nm, (2) 5 nm, (3) 10 nm, (4) 50 nm, (5) 200 nm.)

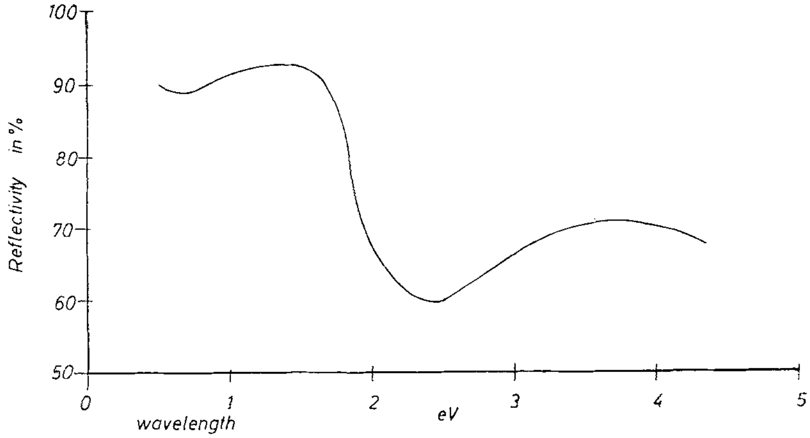

Figure 4 Reflectivity versus wavelength of the Ta–sapphire system.

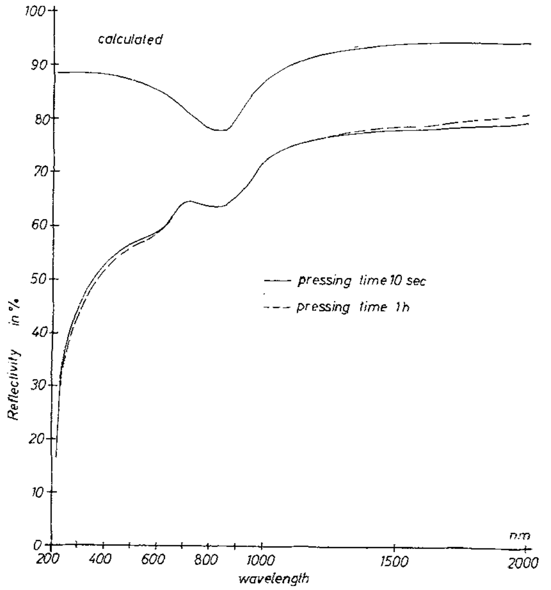

Figure 5 Reflectivity versus wavelength of the Al–sapphire system for two different pressing times and a calculated curve for zero layer thickness.

calculated curves of Fig. 3a leads to the assumption that an intermediate layer of thickness 50 nm and optical values $n_1 = 1$, $k_1 = 1$ exists. However, the lack of any detectable pressure-time dependence of the reflectivity in Fig. 5 (the two curves for 10 sec and 1 h are practically identical) indicates a constant thickness of the intermediate layer over the whole pressing operation, thus excluding the formation of a reaction layer during pressing. Therefore, the 50 nm intermediate layer is assumed to consist of contaminations formed as a film before or at the initiation of the pressing operation. (From Fig. 3a it can be deduced that a pressure-time or thickness-dependent layer resulting in identical curves, within experimental accuracy, could only be translucent with $k_1 = 0$, as with a single crystal, and have a thickness of < 10 nm. However, this possibility can be excluded because of the conditions of formation of the composite.)

For the copper–sapphire system the experimental study is more complicated because of bond instability in samples with short pressing times and low bond strengths. Whilst with aluminium–sapphire composites the bond strength increases with time if the samples are kept at room temperature [3], copper–sapphire composites lose their bond strength rapidly after cooling from the pressing temperature due to the fact that the low yield strength of copper cannot compensate for the shear forces resulting from the different thermal contraction of the copper and the sapphire on cooling. The formation and propagation of an air gap from the circumference of the sample towards its centre can be directly observed by the movement of Newton rings.

A comparison of the experimentally deduced curves of Fig. 6 with the computer curves of Fig. 3b leads to similar conclusions for the copper–sapphire system as those mentioned above for the aluminium–sapphire composite.

Measurements with larger angles of incidence (up to $\alpha = 45°$) also showed a pressure-time independent reflectivity, thus also supporting the

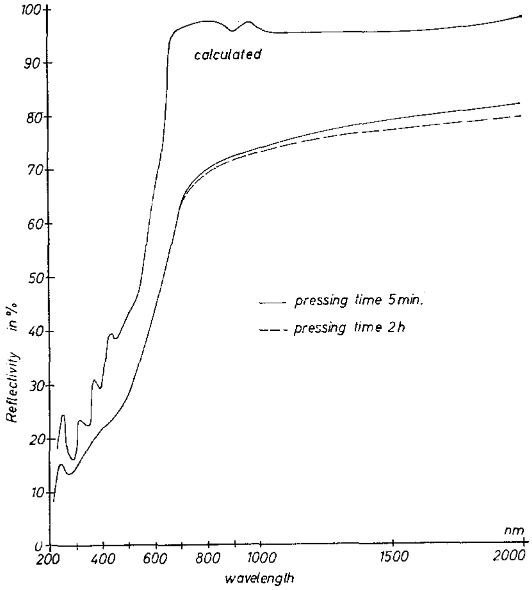

Figure 6 Reflectivity versus wavelength of the Cu–sapphire system for two different pressing times and a calculated curve for zero layer thickness.

assumption of the absence of a reaction layer. In addition, thermodynamic considerations of the systems concerned also tend to exclude the possibility of reaction layers [3].

A reduction in surface energy or more precisely the boundary energy by diffusion seems to be another possibility. Values of diffusion coefficients between that of the single crystal and those of the polycrystalline materials can be expected because the sapphire surface is heavily disturbed by polishing. The diffusion coefficients for temperatures between about 600 and 1000°C, however, are in the order of 10^{-20} to 10^{-15} cm^2 sec for the systems concerned, thus excluding this possibility for the pressing times used.

These considerations lead to the conclusion that the bond strengths found in these systems cannot be attributed to a reaction layer. Therefore, in order to understand these phenomena, short range forces, acting over a few atomic layers only, must be assumed.

4. Electroreflection

Electrostatic forces resulting from different work functions or Fermi energies of the materials concerned, must be considered. The theory of electrostatic double layers has been discussed, particularly by Derjaguin [12].

In the system Al Al_2O_3, bond strengths of more than 10 000 N cm^{-2} have been found [3]. To explain these, electrostatic surface charges of about 10^{14} cm^{-2} must be present according to $H = \sigma^2/2\epsilon$ where H is the bond strength per unit area, σ the surface charge, and ϵ the dielectric constant (between 1 and 10 depending on the Debye length).

In the CdS–Au system, these forces could be shown to be the main source of the bond strength [13]. This was demonstrated by "electroreflection" as described in detail by Cardona [14].This method consists of applying an electric a.c. field to the boundary, thus deforming the energy bands and creating population changes in the energy levels. Charge densities of 10^{10} cm^{-2} can be detected with a single step reflection [5].

The experimental apparatus for such a study is shown schematically on the right hand side of Fig. 2. By combining d.c. and a.c. fields, reflectivity changes as low as 10^{-5} can be detected. With an applied field of 10^4 V cm^{-1}, a surface charge density of 10^{11} cm^{-2} could be measured. In both systems (Al–sapphire and Cu–sapphire), however, no signal could be found at any wavelength. This must be taken as an indication that the bond strength in these systems can only be related to forces which are not influenced by an electric field. The surface of aluminium oxide is mainly occupied by cation vacancies. These vacancies can be replaced by metal ions, thus filling the free surface states and resulting in the high bond strengths found experimentally. Because of the higher affinity of aluminium to oxygen than of copper to oxygen, this leads to the assumption that a higher bond strength exists in the aluminium–sapphire than in the copper–sapphire system in accordance with results reported in [3].

5. Conclusions

Using optical reflectivity measurements, it has been shown that the bonding in the system tantalum–sapphire is caused by a reaction layer. No such layers could be detected in the aluminium–sapphire or copper–sapphire systems. Electrostatic forces may also be excluded from the bonding mechanism in these systems. The bond strengths are related to the action of free surface valency states of the oxide.

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References

1. J. T. KLOMP, *Powder Met. Int.* **3** (1971) 142.
2. *Idem, Sci. Ceramics* **5** (1971) 501.
3. G. HEIDT and G. HEIMKE, *Ber. Dt. Keram. Ges.* **50** (1973) 303.
4. K. HERFF and E. ROEDER, *Prakt. Met.* **9** (1972) 615.
5. N. G. HARRICK, "Internal Reflection Spectroscopy" (John Wiley, New York, 1967).
6. J. SHEWCLUN and E. C. ROWE, *J. Appl. Phys.* **41** (1970) 4128.
7. H. MAYER, "Physik dünner Schichten" (Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1950).
8. I. H. MALITSON, *J. Opt. Soc. Amer.* **52** (1962) 1377.
9. P. P. JOHNSON and R. W. CHRISTY, *Phys. Rev. B* **6** (1972) 4370.
10. D. E. GRAY, ED. "American Institute of Physics Handbook" (McGraw-Hill, New York, 1972).
11. J. H. CHRISTIAN and H. L. TAYLOR, *J. Appl. Phys.* **38** (1967) 3843.
12. B. V. DERJAGUIN and V. P. SMILGA, *ibid* **38** (1967) 4609.
13. W. SCHNABEL, *Batelle Informationen Frankfurt* **1** (1970) 35.
14. M. CARDONA, in *Modulation Spectroscopy, Solid State Physics, Supplement 11*, edited by F. Seitz, D. Turnbull and H. Ehrenreich. (Academic Press, New York, 1969).

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