to remain locked in the $NaNO_3$ during thermal cycling. Other solids which undergo reversible thermal transformations (e.g. quartz [11] at 575° C) would be expected to behave in a manner similar to $NaNO_3$.

Acknowledgements

Support for this work from the Ministry of Technology, the encouragement of Professor S. Peat, and the kindness of Dr R. G. Di Martini (Stevens Institute of Technology, Hoboken, New Jersey) are gratefully acknowledged.

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22 May 1967

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The Number of Components Required in a Composite Material

One of the aims of research in composite materials is to reduce or eliminate the empirical approach, in order to design a composite material, the physical properties of which have been specified in advance, from a knowledge of the physical properties of available individual components; for example, to specify values for properties such as specific gravity, moduli of elasticity, and thermal conductivity in the final composite, and to calculate how these may be obtained by combining individual components, and what will be the effect of the geometrical arrangement of the latter upon these properties. The question to which we direct our attention is: what is the minimum number of components required to achieve the desired result?

This question is only concerned with "relevant" physical properties. This distinction between "relevant" and "irrelevant" physical properties in a given application is of great importance in materials science. It is obvious that, under any given circumstances, certain properties are relevant and the remainder irrelevant. Thus, in a milk bottle, certain mechanical properties like impact strength are important in use, whilst others such as dielectric constant are unimportant. It follows that, in the selection of materials for the design of composites, attention need only be focused on a relatively small number of properties.

We define a composite material as a solid which is made by physically combining two or more existing materials to produce a multiphase system with different physical properties from the starting materials. A chemical reaction may occur during or after the process of manufacture, so that in certain cases a phase in a composite material may differ from the starting material (for example, the rubber phase in high impact polystyrene has different mechanical properties from the original rubber; another example is the matrix in concrete). However, this point is not central to the argument, since we are concerned with the finished composite and hence the relationship between: (i) the physical properties of the finished composite; (ii) the geometrical structure of the composite; and (iii) the physical properties of the constituent phases. For the purpose of this discussion, the individual phases are assumed to be uniform and isotropic.

We wish to deal with the problem: if it is desired to specify n properties in a composite material (this will usually be a small number – say <6), how many single materials or components are required to attain the desired result? (This is an idealised form of the problem, since it states that a given property in the composite should have a specific value; for example, a Young's modulus E of 100 000 lbf/in.^{2} ($1\ \text{lbf/in.}^2 = 7 \times 10^4\ \text{dyn/cm}^2$). In practice, a range of 100 000 to 120 000 lbf/in.^{2} may be satisfactory, or E should be $>100\,000$ lbf/in^2.)

The composite material M_c will be described as follows (where the subscript c refers to the composite and p_1, p_2, etc. are physical properties):

$$M_c \text{ having } p_{1c}, p_{2c}, p_{3c} \ldots\ldots\ldots p_{nc}$$

$p_{1c} \ldots\ldots\ldots p_{nc}$ are the n relevant physical properties which it is wished to specify. Each component r has an appropriate value for the corresponding physical properties $p_{1r} \ldots\ldots\ldots p_{nr}$, which will, in general, be different from the corresponding values for the composite.

We now wish to know whether it is possible to combine m starting materials to produce a composite having n specified physical properties, and whether there is a relationship between m and n. It is at once apparent that a necessary, but not sufficient, condition to be satisfied for a feasible solution, where the relevant function or boundary functions relating the property to the composition are monotonic, is:

$$\begin{gathered}\text{Minimum } p_{ir} < p_{ic} < \text{maximum } p_{ir} \\ r = 1 \ldots . m \\ i = 1 \ldots . n\end{gathered} \tag{1}$$

i.e. the value required of a property in the composite material must lie between the lowest and highest of the corresponding component values. For the sake of simplicity, the following discussion is confined to monotonic functions of property and composition.

Case A The property is independent of structure There is a clear distinction between those properties which are dependent upon, and those which are independent of, the geometrical configuration of the composite. Certain physical properties (e.g. density or specific heat) depend only upon the concentration or volume fraction of the components and are independent of the geometry of the system. Such properties may be additive (e.g. density) or non-additive.

If, for example, they are additive, then

$$p_{ic} = \sum_{r=1}^{r=m} p_{ir} V_{ir} \tag{2}$$

where

$$\sum_{r=1}^{r=m} V_r = 1 \tag{2a}$$

where p_{ic} is the property p_i of the composite M_c, p_{ir} is the same property of a component r, and V_r is the volume fraction of the same component.

For additive or non-additive (but monotonic) properties uniquely defined by concentration, the relationship between m and n is:

$$m = n + 1 \tag{3}$$

since there are n equations of the type (2) in addition to equation 2a.

This is illustrated in fig. 1 for two additive properties P and p and two components. It will be seen that, having specified P_c at a given value, a given volume fraction V_c is required which, in turn, determines p_c. If it is necessary to specify p_c at an independent value, an additional component is needed.

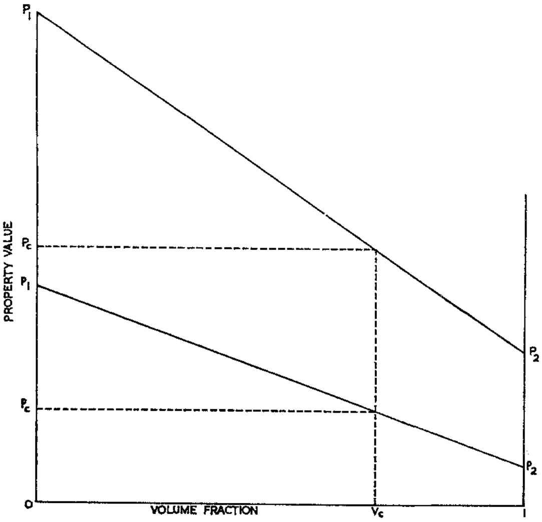

Figure 1 Property as a function of volume fraction – two components and two properties uniquely defined by *V*.

Case B The property is structure-dependent This is a more usual case, and applies to such properties as elastic moduli, and thermal and electric conductivity. Since this class of property is dependent on structure, it is *not* uniquely defined by the concentrations of the components, i.e.:

$$p_{ic} = f(p_{i1}, p_{i2} \ldots . p_{im}, V, G) \tag{4}$$

In this relation, V is the volume fraction of the components and G embraces the geometrical variables of the components such as phase continuity, orientation of particles, size and size distribution of particles [1-4] which independently influence p_{ic}. It will be seen below that the influence of G is controlled by the upper and lower bounds of p_{ic}, which are themselves a function of the individual values of p_{i1}, p_{i2}, etc.

The physical significance of G is seen if we consider the simple two-component case for an elastic modulus, or thermal or electrical conductivity (which show identical relationships). This is shown in fig. 2.

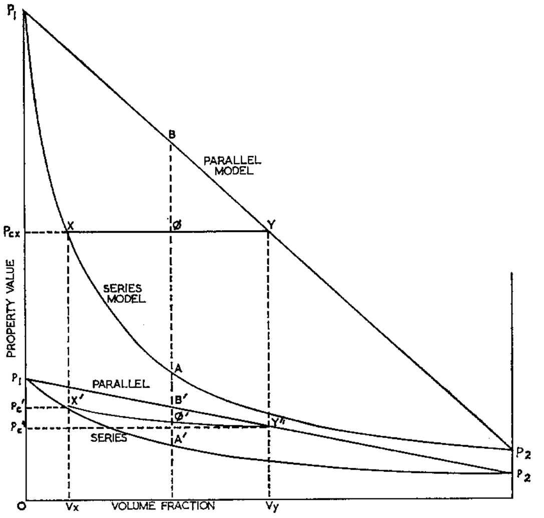

Figure 2 Property as a function of volume fraction – two components and two properties not uniquely defined by *V*.

The upper bound is given by the "parallel" model:

$$p_c = p_1 (1 - V) + p_2 V \qquad (5)$$

where V is the volume fraction of component 2.

The lower bound is given by the "series" model:

$$\frac{1}{p_c} = \frac{V p_1 + (1 - V) p_2}{p_1 p_2} \qquad (6)$$

Fig. 2 shows a plot of equations 5 and 6 for two cases, where the individual component properties are shown by P_1 and P_2, and p_1 and p_2, and where:

$$p_1/p_2 < P_1/P_2$$

to indicate the way in which the bounds diverge as this ratio increases; P_1 and P_2, for example, might be bulk moduli, and p_1 and p_2 thermal conductivity.

A given value of P may, in theory, be arrived at over a range of volume fractions for structure-dependent properties, and this is shown in fig. 2 for the value P_c as the line XY. Not only does the volume fraction vary in going from X to Y, but so also does the geometrical arrangement of the phases. It should be emphasised that, although this is theoretically possible, it may not be practical for many systems with our present state of knowledge. There are relatively few methods of producing alternative phase arrangements (reference 2, chapter 1).

Similarly, a range of values of P may be obtained for a given value of V, as shown by the line AB. Since P is a function of the geometrical arrangement G (equation 4), the significance of G may be seen by evaluating $P_{cB} - P_{cA}$ at constant volume-fraction:

$$P_{cB} - P_{cA} = P_1 (1 - V) + P_2 V - \left[\frac{P_1 P_2}{P_1 V + P_2 (1 - V)}\right] \qquad (7)$$

which reduces to

$$P_{cB} - P_{cA} = (P_1 - P_2)^2 \Big/ \left(\frac{P_1}{1 - V} + \frac{P_2}{V}\right) \qquad (8)$$

Following this introduction, we now wish to show the way in which a second property p_c will vary for a constant value of P_c shown in the diagram as P_{cx}. The limits are immediately evident as p'_c and p''_c, which represent the intercepts of V_x and V_y on the series and parallel models respectively. Thus for every value P_c there is a range of values of p_c, and, if it were independently required that p_c should fall between p'_c and p''_c (i.e. $p'_c > p_c > p''_c$), then we could obtain two specified values of properties P and p with two components. In this case:

$$m = n \qquad (9)$$

which should be compared with equation 3.

In order to establish the relationship between p and V between the limits p'_c and p''_c, we make the assumption that, for each point ϕ on the straight line XY, there is a corresponding point ϕ' on a curve $X'Y''$, which can be obtained as follows:

$$\frac{A'\phi'}{A'B'} = \frac{A\phi}{AB} \qquad \text{(in fig. 2)} \qquad (10)$$

or

$$\frac{p_{\phi'} - p_{A'}}{p_{B'} - p_{A'}} = \frac{P_\phi - P_A}{P_B - P_A}$$

i.e.

$$p_{\phi'} = \left(\frac{P_\phi - P_A}{P_B - P_A}\right)(p_{B'} - p_{A'}) + p_{A'}$$

or

$$p_\phi' = \left[\frac{P_{cx} - \left(\dfrac{P_1P_2}{VP_1 + P_2(1-V)}\right)}{P_2V + P_1(1-V) - \left(\dfrac{P_1P_2}{VP_1 + P_2(1-V)}\right)}\right] \left[p_2V + p_1(1-V) - \left(\frac{p_1p_2}{p_1V + p_2(1-V)}\right)\right] + \frac{p_1p_2}{p_1V + p_2(1-V)} \quad (11)$$

in which P_1, P_2, p_1, p_2, and P_{cx} are constants, since P_{cx} has been given a particular value.

We conclude that the geometrical variables represented by G in equation 4 lead to an additional limited degree of freedom where the property is structure-dependent. As mentioned above, if the desired second physical property p_ϕ' of the composite falls between p'_c and p''_c (having previously first specified a value P_{cx} for the first property), only two components are needed to permit two physical properties to be specified. The probability of this increases if P_{cx} or p_ϕ' are given upper and lower limits instead of being given unique values as above.

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23 May 1967

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