i.e. "it slows down". In fact, we are uncertain about the detailed behaviour of the crack tip relative to the cleaving of a complete band. However, in stating this, we do note that Doyle et al. [3] have adduced good evidence from secondary fracture markings in PS that crack acceleration occurs in one part of the band and also that Doyle now states that a sudden jump was observed under the microscope in the same region. Our usage of the word "jump" referred to the observed coalescence of the crack tip with an advanced microcrack. These distinctions may appear to be rather refined but they are made in order to deny any commitment concerning questions of crack acceleration which are regarded by Doyle et al. as important in deciding between their mechanism of band formation, by craze wedge splitting, and one which they attribute to Hull [4].

The main criticism offered by Doyle is that the mechanism of crack tip jumping *cannot* explain band periodicity. This criticism is valid although it would be more judicious to state that the phenomenon *does not* explain periodicity. However, it can be incorporated with additional observations and assumptions to provide explanations along the lines suggested, for example, either by Hull or by Doyle et al. This, in fact, is what Doyle has done in a revision of the craze wedge mechanism. Our own reticence to enter into this level of detail is due to an inability to explain certain phenomena at a gross level including periodic band formation in polymethyl methacrylate. In this case microstructural details apparently similar to those documented in PS appear as a special case observed only within a narrow range of molecular weights [5]. This observation would appear to call for a more general mechanism which would explain all cases and, more critically, account for a dependence of band spacing on molecular weight [6]. The need to explain this latter relationship was pointed out previously by Benbow [7]. It would be helpful to know whether any dependence on molecular weight is observed in PS and other glassy polymers.

Finally, apology must be made for the discursive nature of this exchange of views. To some extent this is due to a primitive means of communication involving descriptions of pictures of fracture surfaces. There is not yet any agreement about terminology and redundance in the use of terms such as "striations", "bands", "ribs" etc. Neither is there agreement about which experimental variables should be specified, chemical composition, molecular weight, sample geometry, strain rate etc. These matters seem ripe for discussion at some future conference on fractography.

Acknowledgement

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On the thermal oxidation resistance of some Intermetallic compounds

In a recent systematic study [1], Stone has reported on the thermal oxidation behaviour of several intermetallic compounds. As in his previous work on the oxidation of metals [2], he chose a parameter T_p as the index of the oxidation resistance of the material. T_p is the temperature which yields a weight change of 1 mg cm^{-2} over 4 h on thermal oxidation of the material in air. Higher T_p values would thus indicate higher resistance to oxidation and vice versa. The classification of the oxidation behaviour of various intermetallic compounds was attempted in terms of the ratio of T_p to the melting point of

the material or its oxidation product and some interesting trends were shown to exist. On the basis of the oxidation data and the estimated hardness of the intermetallic compounds, some useful comments were developed on the nature and incidence of binary intermetallic compounds.

The purpose of the present note is to analyse Stone's data [1] with regard to another important matter, namely, the origin of the differences (e.g. for a given metal such as Al) in the magnitude of the T_p values observed for its intermetallic compounds formed with various metals such as V, Mn, Ni, Ti and La; metalloids such as Sb will not be considered because of their intinsically different nature from metals. In other words, the changes in the T_p values of Al (or Zn) brought about by the intermetallic formation with a series of different metals will be related to some fundamental properties of the oxides of the latter.

In the data reported by Stone [1], *extensive* series of intermetallic compounds of only two metals, Al and Zn have been examined. The following discussion will, therefore, be limited to the oxidation of intermetallic compounds of these metals only.

During thermal oxidation, the growth of an oxide occurs by the thermally-assisted movement of ions (and vacancies) so that high ionic conduction should lead to facile oxide growth. However, if the presence of an element in, for example, an intermetallic compound of Al provides a path of high *electronic* conduction, the ionic conduction is retarded (or becomes more difficult). In general low electronic conduction is a necessary condition for high ionic conduction (either under thermal or field gradients) as, for example, in alkali halides. On the other hand, materials showing high electronic conduction (e.g. germanium) tend to support low ionic conduction. This is because under the conditions of thermally- or field-assisted movement of charge carriers (electrons, holes, ions, vacancies, etc.) in a material, electronic and ionic conduction are *parallel* processes; hence high electronic conduction would lead to low ionic conduction and vice versa. We now note that the exothermic value of the heat of formation per *equivalent* of an oxide (i.e. $- \Delta H_e$) is equal to half its band gap [3, 4]. Hence low $- \Delta H_e$ values mean low band gap and hence high electronic conduction with the consequent retarded oxide growth. If the metal other than aluminium in the binary compound has an oxide of low $-\Delta H_e$ value, it
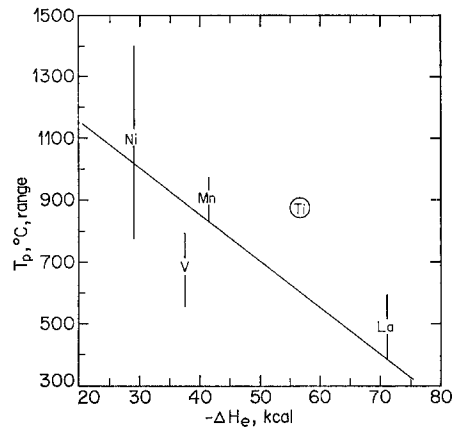

Figure 1 A plot of T_p for the oxidation of intermetallic compounds of Al with Ni, V, Mn, Ti and La against the heats of formation per equivalent, $- \Delta H_e$, values of the oxides of the latter metals.

would tend to give the intermetallic compound a high T_p value, i.e. oxide growth not facile because of electronic conduction. On the other hand, an intermetallic compound of Al with a metal such as La, whose oxide has a high $- \Delta H_e$ and hence high band gap would have an oxide with little electronic conduction and, therefore, facile ionic conduction and grain growth (low T_p). This line of argument may now be tested for the case of Al and Zn as follows.

The range of T_p values observed for the intermetallics of V, Mn, Ni, Ti and La with aluminium [1] are plotted in Fig. 1 here together with the $- \Delta H_e$ values [5] of the oxides of the shown metals. For a given metal, e.g. V, Stone
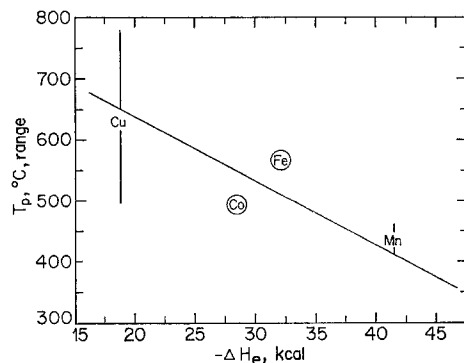

Figure 2 A plot of T_p for the oxidation of intermetallic compounds of Zn with Cu, Co, Fe and Mn against the heats of formation per equivalent, $- \Delta H_e$, values of oxides of the latter metals.

has reported the T_p data for several inter-metallics. However, since the $- \Delta H_e$ values of the oxide of vanadium cannot be "adjusted" for every composition of Al–V compounds, one is obliged to lump the T_p values for all Al–V compounds. As argued above, a general trend in Fig. 1 is quite clear, in that metals whose oxides have low $- \Delta H_e$ values (e.g. Ni) give inter-metallics with high T_p values whereas the opposite obtains for metals such as La, the oxide of which has a very high $- \Delta H_e$ value.

In Fig. 2, appropriate data on the inter-metallic compounds of Zn with four metals are presented and the various quantities have the same significance as in Fig. 1. Once again one observes that metals such as Cu (whose oxide has a low $- \Delta H_e$ value) give intermetallics with high T_p values whereas those with relatively high values of $- \Delta H_e$ for the oxides (e.g. Mn) tend to impart low T_p values to the intermetallics.

It is realized that the conceptual basis for Figs.

1 and 2 can be discussed very qualitatively only. However, it is clear that Figs. 1 and 2 provide a rough guide line for the prediction of the effect on the T_p of a series of intermetallics formed by combining one metal with a series of other metals.

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Vacancy ordering in cobalt sulphide

Although the structure of cobalt sulphide (CoS) is nominally of the NiAs-type, the compound does not exist at the stoichiometric one-to-one atomic ratio but is found within a limited range of composition near $CoS_{1.15}$. In view of the cobalt deficiency it is expected that ordering of the cobalt atoms and vacancies would occur, similar to that observed in other transition metal sulphur systems, e.g. Cr–S [1], Fe–S [2].

Various compositions of cobalt sulphide were prepared by direct combination of the elements at $1000°C$ in sealed silica tubes. After annealing at different temperatures, thin foils for examina-tion in a JEM 200 electron microscope were prepared by grinding the specimens in a mortar and collecting the fragments on a copper grid. The electron diffraction patterns from specimens annealed below $450°C$ (Fig. 1) show the presence of extra reflections besides those characteristic of an NiAs-type cell. All the reflections could be indexed in terms of an hexagonal supercell with dimensions,

$$a_s = 2a_h, c_s = 3c_h,$$

where the subscripts h and s refer to the basic NiAs and superstructure cells respectively.

Figure 1 Electron diffraction patterns from Co_7S_8. Indices of reflections and beam directions refer to the basic NiAs-type cell.