Heat diffusivity criterion for the entrapment of particles by a moving solid–liquid interface

Recently, Omenyi and Neumann [1] have proposed a thermodynamic criterion for the entrapment of particles by solidifying melts based on interfacial tension. According to them the criterion for particle entrapment by the solidifying melt is

$$\Delta G_{\text{net}} < 0$$

where

$$\Delta G_{\text{net}} = \gamma_{\text{ps}} - \gamma_{\text{pl}}.$$

ps and pl are particle–solid and particle–liquid interfacial tensions. They derived the values of γ_{ps} and γ_{pl} are particle–solid and particle–liquid They have predicted the rejection or entrapment of glass spheres, siliconized glass spheres, teflon, polystyrene, nylon and acetal particles by napthalene and biphenyl organic matrix material, and found good agreement with their actual experimental results for slow rates of interface movement (a few micrometres per second). The good agreement between their predictions and experimental observations indicates that the thermodynamic criterion is satisfactory for predicting rejection or entrapment of particles ahead of the freezing interface.

While the thermodynamic criterion appears to be satisfactory, it could be difficult to compute the values of ΔG_{net} in certain other systems where the surface tension values at the melting points are not readily available. Hence an attempt has been made to identify a simpler empirical calculation (involving more readily available properties of materials) which could be used in preliminary predictions of the rejection or entrapment of particles by growing crystals. Initially the ratio of thermal conductivities of the particles and the crystal were examined since, recently, Zubkov *et al.* [2] have proposed thermal conductivity criterion to predict the entrapment or the rejection of foreign particles by growing crystals. According to the criterion of Zubkov *et al.* [2], at low growth rates (i.e. $VR/\lambda \ll 1$ where V is the rate of growth of the crystal, R is the particle radius and λ is the thermal conductivity of the melt) if the value of λ_p/λ (the ratio of the thermal conductivity of the particle and that of the liquid) is less than one the particles will be rejected. Under such conditions just beneath the particle (in a vertical freezing system) the interface develops a bump due to reduced heat flow to the interface, over which the particle will roll and is thus prevented from being entrapped. If the value of λ_p/λ is greater than one, just beneath the particle a depression is formed in the interface, as a result of which the particles will be captured more readily even at very slow growth rates.

The predictions based on thermal conductivity criterion of Zubkov *et al.* [2], have been compared with the experimental observations of Omenyi and Neumann [1] who used a horizontal cell for crystal growing. Table I shows that the thermal conductivity criterion of Zubkov *et al.* [2] is able to successfully predict several experimental observations of Omenyi and Neumann, however, the observations are contrary to the prediction in the case of polystyrene particles.

TABLE I Change in free energy for the process of particle engulfment. Predictions, based on (a) thermodynamic criterion and (b) thermal conductivity criterion for the biphenyl and napthalene systems

Matrix/particle	ΔG_{net}	Prediction based on thermodynamic criterion	$\frac{\lambda_p}{\lambda}$	Prediction based on thermal conductivity criterion	Results of actual experiments
Biphenyl/siliconized glass	negative	Engulfed	6.3	Engulfed	Engulfed
Biphenyl/Teflon	negative	Engulfed	1.4	Engulfed	Engulfed
Biphenyl/polystyrene	negative	Engulfed	0.92	Rejected	Engulfed
Biphenyl/nylon	positive	Rejected	0.04	Rejected	Rejected
Biphenyl/acetal	positive	Rejected	0.05	Rejected	Rejected
Napthalene/siliconized glass	negative	Engulfed	6.2	Engulfed	Engulfed
Napthalene/Teflon	negative	Engulfed	1.3	Engulfed	Engulfed
Napthalene/polystyrene	negative	Engulfed	0.90	Rejected	Engulfed
Napthalene/nylon	positive	Rejected	0.041	Rejected	Rejected
Napthalene/acetal	positive	Rejected	0.052	Rejected	Rejected

0022–2461/81/020562–03$02.30/0

TABLE II Thermal conductivities, specific heats and densities of different particles and growing crystals [5–10]

Materials	Thermal conductivity (in CGS)	Specific heat (in CGS)	Density ($\mathrm{g\,cm^{-1}}$)
Napthalene	0.000 78	0.281	1.14
Nylon	0.000 03	0.43	1.15
Teflon	0.001	0.28	2.1
Acetal	0.000 41	0.4669	0.821
Glass	0.004 54	0.117	2.5
Polystyrene	0.000 64	1.09	0.40
Biphenylene	0.000 72	0.385	0.992

In view of this, a modified criterion, namely, the ratio of $\sqrt{(\lambda_p c_p \rho_p)}$ to $\sqrt{(\lambda c \rho)}$, is proposed as a first indicator of particle behaviour ahead of freezing interfaces. In the solidification literature [3] the product $\sqrt{\lambda c \rho}$, where λ is thermal conductivity, c is specific heat and ρ is density, refers to heat diffusivity (whereas $\lambda/c\rho$ is thermal diffusivity) and it is therefore proposed to name the criterion as the heat diffusivity criterion. According to the heat diffusivity criterion, when the heat diffusivity of the particles $\sqrt{(\lambda_p c_p \rho_p)}$, is greater than the heat diffusivity of the liquid $\sqrt{(\lambda c \rho)}$ the particle will be captured by the solid–liquid interface whereas when the heat diffusivity of the particles is lower than the heat diffusivity of the liquid the particle will be rejected by the interface. However, the heat diffusivity criterion is likely to be valid only at very slow growth rates (i.e. $VR/\lambda \leqslant 1$) and under conditions where other factors such as body forces [4] do not override the heat flow effects. In order to verify the applicability of the heat diffusivity criterion, the values of $\sqrt{(\lambda c \rho)}$ have been computed for the various crystal particle systems studied by Omenyi and Neumann [1]. The values of thermal conductivity (λ) specific heat (c) and density (ρ) of different crystals and particles used in computing heat diffusivity values are listed in Table II [5–10]. The predictions of rejection or entrapment of particles based on heat diffusivity criterion have been compared with the experimental observations of Omenyi and Neumann [1] in Table III. It is clear from Table III that there is complete agreement between the predictions based on the heat diffusivity criterion and the experimental observations of Omenyi and Neumann [1]. Thus it is felt that the heat diffusivity criterion could be a simple indicator of entrapment or rejection of particles by growing crystals, deserving of further examination.

References

1. S. N. OMENYI and A. W. NEUMANN, *J. Appl. Phys.* 47 (1976) 3956.
2. A. M. ZUBKOV, U. G. LOBANOV and V. V. NIKONOV, *Soviet Phys. Crystall.* 18 (1973) 239.
3. M. C. FLEMINGS, "Solidification Processing" (McGraw-Hill, New York, 1974) pp. 9–10.
4. K. H. CHEN and W. R. WILCOX, *J. Cryst. Growth* **40** (1977) 214.
5. C. J. SMITHELLS, "Metals Reference Book" (1976).
6. "Thermophysical properties of Matter". The TPRC Data Series (Plenum Press, New York, 1970).
7. J. B. CLARK, "Physical and Mathematical Tables" (1966).
8. A. T. DIBENEDETTO, "The Structure and Properties of Materials" (McGraw-Hill, New York, 1967).

TABLE III Heat diffusivity of the particles suspended in the melt and growing crystals and the results of the experiments on the interaction of particles with the melt [1]

Crystals	$\lambda c \rho$	Particle	$\lambda_p c_p \rho_p$	$\frac{\lambda_p c_p \rho_p}{\lambda c \rho}$	$\frac{\sqrt{\lambda_p c_p \rho_p}}{\sqrt{\lambda c \rho}}$	Predicted result	Result of experiment
Napthalene	0.000 25	Teflon	0.000 59	2;36	1.53	Capture	Capture
		Siliconized glass	0.001 33	5.32	2.30	Capture	Capture
		Polystyrene	0.000 28	1.12	1.05	Capture	Capture
		Nylon	0.000 01	0.04	0.2	Rejected	Rejected
		Acetal	0.000 16	0.64	0.8	Rejected	Rejected
Biphenyl	0.000 27	Teflon	0.000 59	2.36	1.53	Capture	Capture
		Siliconized glass	0.001 33	4.925	2.21	Capture	Capture
		Polystyrene	0.000 28	1.039	1.01	Capture	Capture
		Nylon	0.000 01	0.037	0.19	Rejected	Rejected
		Acetal	0.000 16	0.592	0.17	Rejected	Rejected

9. J. A. DEAN, "Long's Handbook of Chemistry" (McGraw-Hill, New York).
10. ZBIENIEWO and JASTRZEBSKI, "Nature and Properties of Materials" (John Wiley, New York, 1959).

*Received 30 April
and accepted 10 June 1980*

M. K. SURAPPA
P. K. ROHATGI
*Regional Research Laboratory,
Council of Scientific and Industrial Research,
Trivandrum 695019,
India*

F-band absorption and thermoluminescence in X-ray irradiated NaI single crystals

The properties of colour centres formed in alkali halides by ionizing irradiations have been studied [1, 2]. Such studies gave considerable insight into the electronic processes taking place in these solids. Though much work has been reported on KCl and NaCl, other crystals particularly NaI received very little attention. An absorption band with a peak of 588 nm is identified as being due to the F-centres [2]. Luminescence of free and self trapped excitons in NaI has been discussed by Luschik *et al.* [3]. It is our purpose to report in this paper results of our investigations on (i) the absorption bands produced in NaI single crystals by X-ray irradiation, (ii) the growth of the F-band with time of irradiation (i.e. X-ray dosage), (iii) thermal bleaching characteristics of the F-band and (iv) thermoluminescence of these X-ray irradiated NaI crystals. As NaI is highly hygroscopic, X-ray irradiation was carried out and all measurements were taken at an elevated temperature of 40° C (room temperature is about 25° C).

Some of the NaI single crystals used in the present work were supplied by Bhabha Atomic Research Centre, Bombay. Flame photometric

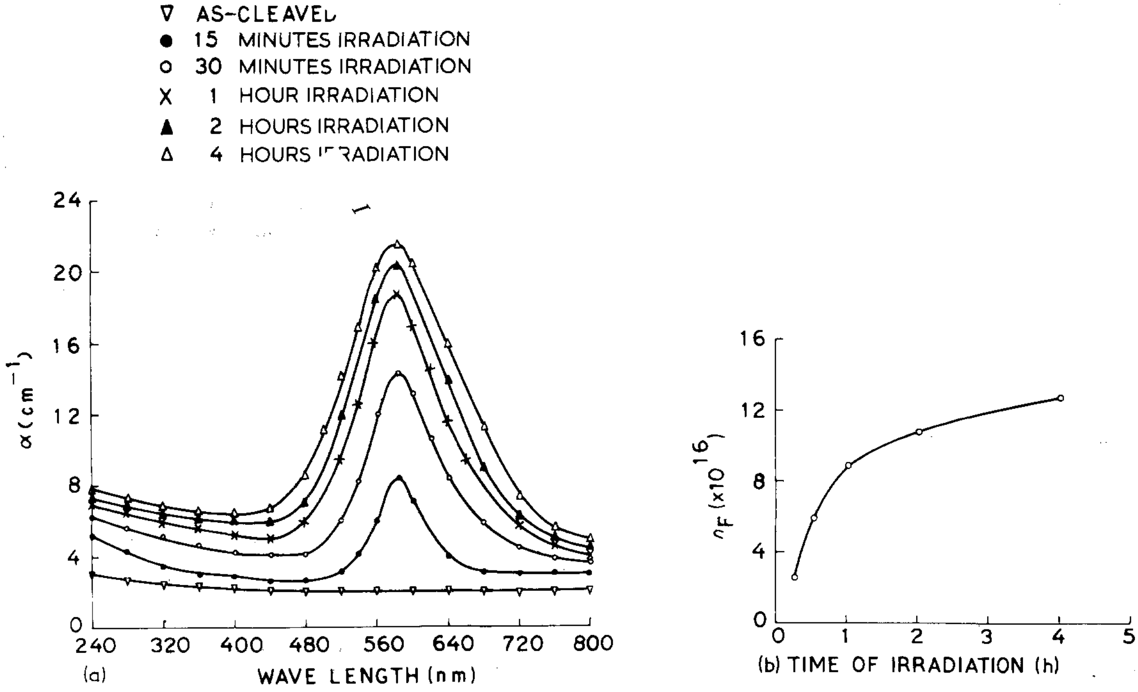

Figure 1 (a) Absorption coefficient (α) as a function of wavelength for NaI crystals for different X-ray irradiation times at 40° C. (b) Growth of F-band in X-ray irradiated NaI crystals.

0022–2461/81/020564–04$02.40/0