ments of silicon powder compacts under vacuum, or argon, are certainly feasible, a more simple procedure from the point of view of obtaining rapid reaction initiation might be the injection of a few vol% hydrogen into the nitriding gas during the furnace warming-up stage, nitridation being completed under 100% nitrogen. To what extent this type of two-stage process would affect the microstructure and properties of the resulting material needs to be investigated.

Subsequent to the reaction initiation stage the continuing presence of hydrogen in the nitriding atmosphere also gives rise to larger values of the reaction rate constants for both the α- and β-phase formation reactions compared with those for reaction in nitrogen alone. This second effect, the existence of which is apparent from the data of Dawson and Moulson [1], has now been studied in some detail [10] and the results will be published shortly.

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D. CAMPOS-LORIZ
F. L. RILEY
Department of Ceramics,
Houldsworth School of Applied Science,
The University of Leeds,
Leeds, UK

Surface energies of high explosives PETN and RDX from contact angle measurements

Recently, the fracture surface energies of PETN (pentaerythritol tetranitrate) and RDX (cyclotrimethylene trinitramine) have been determined by Hagan and Chaudhri [1], using a micro-indentation fracture mechanics approach. This technique involves measuring the work required to cleave a crystal creating two new surfaces and is advantageous because it provides the most direct determination of surface energy. Obreimoff [2] first reported the crystal cleavage method for measuring surface energy in experiments on mica. Later Gilman [3] added several refinements reducing uncertainty. However, the crystal cleavage method for obtaining surface energy has several difficulties.

The most serious problem with this technique is the irreversible nature of cleavage. Reversibility can only be approached for exceedingly low velocity crack propagation in an environment where gas adsorption does not occur. Plastic deformation and heat flow to the surroundings provide additional dissipative processes. To minimize the effect of dislocation motion some experiments have been done at cryogenic temperatures. Despite these difficulties, reasonably consistent results have been obtained [3] for a number of brittle materials, including LiF, MgO, CaF_2, BaF_2, and $CaCO_3$.

Another method for determining surface energy, involving contact angle measurements, has been described by Rhee [4]. The most common method for measuring the contact angle is the sessible drop technique [5]. In this experiment,

the contact angle, θ, is related to the solid surface energy, γ_{SV}, the liquid surface tension, γ_{LV}, and the liquid–solid interfacial energy, γ_{LS}, by the equation

$$\gamma_{SV} = \gamma_{LS} + \gamma_{LV} \cos \theta. \qquad (1)$$

There are four unknowns in this expression and only θ and γ_{LV} can be determined directly from the experiment.

For a system of homologous liquids on a solid surface, an empirical linear relation has been found between θ and γ_{LV}, which is given by the expression

$$\cos \theta = 1 + b (\gamma_c - \gamma_{LV}), \qquad (2)$$

where b is the slope of the line and γ_c is the critical surface energy for spreading [6]. These two equations were combined [4], with the assumption that γ_{LS} is zero at the minimum of a plot of γ_{LS} versus $\cos \theta$, to yield

$$\gamma_{SV} = \frac{(b\gamma_c + 1)^2}{4b} \qquad (3)$$

This equation has been shown to be valid for calculating the surface energy of a variety of polymers and ceramics, including polytetrafluoroethylene, n-hexatriacontane, paraffin, polyethylene, polystyrene, polyethylene terephthalate, 6,6-nylon, MgO, UO_2, and BeO. Care must be exercised to avoid sessile drop materials that are soluble in the substrate, which could dramatically alter the surface and interfacial energies.

A number of years ago, Fox and Levine [7] performed wettability studies at 20° C on natural faces of PETN and RDX single crystals. Contact angles for liquids having a variety of surface tensions were measured. Complete listings of the original data obtained [7] for PETN ({1 1 0} and {1 0 1} surfaces) and RDX are given in Tables I and II respectively. Plots of $\cos \theta$ versus γ_{LV} for these two explosives appear in Figs. 1 (PETN) and 2 (RDX), where the solid straight lines were obtained by least-squares analysis. In performing this analysis for RDX, the contact angle measurements using formamide and thiodiglycol were omitted since the deviation from the remaining data was considerable. The values for b and γ_c allowed γ_{SV} to be calculated using Equation 3, and these results are summarized in Table III for

PETN and RDX. The fracture surface energies reported by Hagan and Chaudhri {1} are included for comparison purposes.

TABLE I Contact angle data* for PETN crystal surfaces at 20° C

Liquid	Surface tension, γ_{LV} ($J\,m^{-2}$)	{1 1 0} contact angle θ (deg)	{1 0 1} contact angle θ (deg)
Water	0.0728	77	72
Glycerol	0.0634	67	61
Formamide	0.0582	56	45
Thiodiglycol	0.0540	48	32
Methylene iodide	0.0508	41	31
Sym-tetrabromoethane	0.0497	34	18
Aroclor 1242[†]	0.0453	25	10
Phosphen-3[‡]	0.0452[¶]	30	12
α-Bromonaphthalene	0.0446	34	11
Aroclor 1248[§]	0.0442	25	
1,5-Bis (γ-phenylpropyl-mercapto) pentane	0.0432	24	
Bis (2-phenylethyl)-β-methyl adipate	0.0413	8	
Tricresylphosphate	0.0409	12	

*Data taken directly from work by Fox and Levine [7].
[†] Trichlorodiphenyl.
[‡] Mono (o-chlorophenyl) diphenylphosphate from Dow Chemical percolated through activated Florisil.
[§] Tetrachlorodiphenyl.
[¶] Value determined at NRL by capillary rise method.

The surface energy values determined from contact angle measurements were substantially lower than the fracture surface energies. In addition, the difference between the values for PETN and RDX was small compared to the pronounced variation in the fracture energies. The reason for the differences in the surface energies obtained by these two techniques is not totally understood. One possible explanation is that the fracture surface energy values include a significant plastic flow contribution, that has not been accounted for, and this would result in an overestimate as the authors indicate. It is also possible that the fracture surfaces had different crystallographic orientations from the surfaces in the contact angle studies, and that there is a large variation in surface energy with orientation.

It is evident that additional work is needed to resolve the differences in the values obtained using the two techniques. However, this is welcomed

TABLE II Contact Angle Data* for RDX at 20° C

Liquid	Surface tension, γ_{LV} ($J\,m^{-2}$)	Contact angle
Water	0.0728	65
Glycerol	0.0634	55**
Formamide	0.0582	34††
Thiodiglycol	0.0540	19**
Methylene Iodide	0.0508	34
Aroclor 1242†	0.0453	19
Phosphen-3‡	0.0452¶	13
α-Bromonaphthalene	0.0446	6
Aroclor 1248§	0.0442	18
1,5-Bis (γ-phenylpropylmercapto) pentane	0.0432	5
Bis (2-phenylethyl)-β-methyl adipate	0.0413	Spreads
Tricresylphosphate	0.0409	Spreads

*Data taken directly from work by Fox and Levine [7].
†Trichlorodiphenyl.
‡Mono (o-chlorophenyl) diphenylphosphate from Dow Chemical percolated through activated Florisil.
§Tetrachlorodiphenyl.
¶Value determined at NRL by capillary rise method.
**Value identical to that obtained in dry nitrogen at 20° C with a liquid sample purified by percolation through activated Florisil in dry air immediately prior to use.
††Value identical to that obtained in dry nitrogen at 20° C with a sample of formamide purified by percolation through activated Florisil and silica in dry air immediately prior to use.

TABLE III Compilation of values for b, γ_c and γ_{SV} in homologous organic liquids on PETN and RDX substrates at 20° C along with Hagan and Chaudhri's [1] results (γ_{SV}^F)

Substrate	b	γ_c ($J\,m^{-2}$)	γ_{SV} ($J\,m^{-2}$)	γ_{SV}^F ($J\,m^{-2}$)
PETN {1 1 0}	2.43×10^{-2}	0.0402	0.0402	0.11
PETN {1 0 1}	2.51×10^{-2}	0.0454	0.0458	
RDX	1.99×10^{-2}	0.0429	0.0432	0.07

because characterization of explosives from a materials science viewpoint is long overdue.

Acknowledgement

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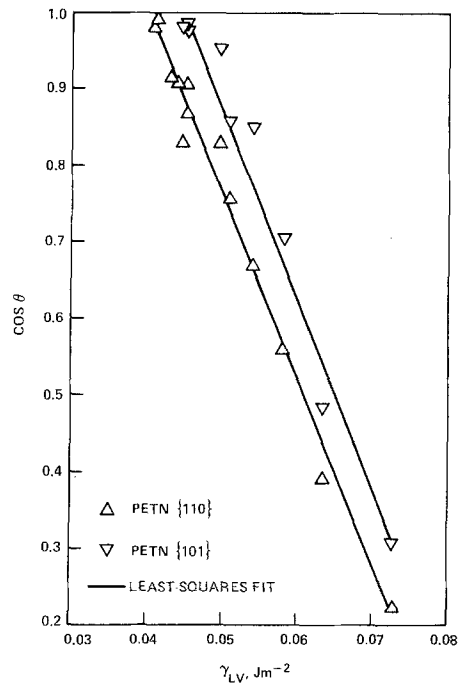
Figure 1 cos θ versus γ_{LV} for PETN.
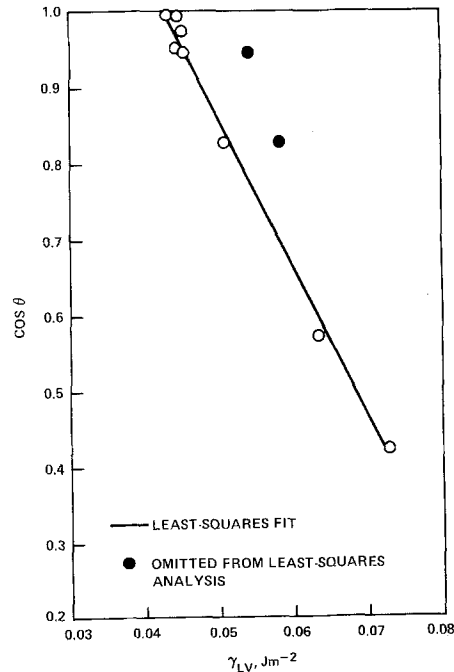

Figure 2 cos θ versus γ_{LV} for RDX.

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WAYNE L. ELBAN
Naval Surface Weapons Center,
Silver Spring, Maryland 20910, USA

Decomposition of $CaCO_3$ and formation of Ca_3SiO_5

The lowering of the decomposition temperature of $CaCO_3$ with the addition of a mineraliser (NaF) and the formation of Ca_2SiO_4 [1] and Ca_3SiO_5 [2] with the additions of mineralisers (NaF in the case of Ca_2SiO_4 and CaF_2, etc., in the case of Ca_3SiO_5) coupled with rapid heating of the raw mixes (stoichiometric proportions of silica gel and $CaCO_3$) were reported in earlier communications [1, 2]. The effect of the cations (mineraliser) appears to play a significant role as observed during continued study in this area of research.

The decomposition of $CaCO_3$ in a mix containing silica gel and $CaCO_3$ (1:3) and 2% LiF, CaF_2, SrF_2 and BaF_2 studied using differential thermal analysis (DTA), is shown in Table I and Fig. 1.

In general, the drop in the decomposition temperature of $CaCO_3$ with increasing amount of mineraliser (2 to 6%) was more pronounced in the case of NaF, LiF and BaF_2 than for SrF_2 and CaF_2. Evidently, the cations have an effect on the decomposition process and it is interesting to observe the distinct grouping among the mineralisers, i.e., CaF_2, SrF_2, BaF_2 and NaF, LiF.

The mechanism of the decomposition process appears to be different, i.e., with higher atomic number, ΔT increases while the reverse is true in the cases of NaF and LiF.

The ionic radii of the cations ($Li^+ - 0.78$, $Na^+ - 1.01$, $Ca^{2+} - 1.06$, $Sr^{2+} - 1.20$ and $Ba^{2+} - 1.40$ Å) is an important parameter, as can be seen in Fig. 2. At higher percentage of additions (6%), the mechanism of decomposition is distinctly different. The effect of the cations (as shown by the line marked 4% with respect to Ca; this is
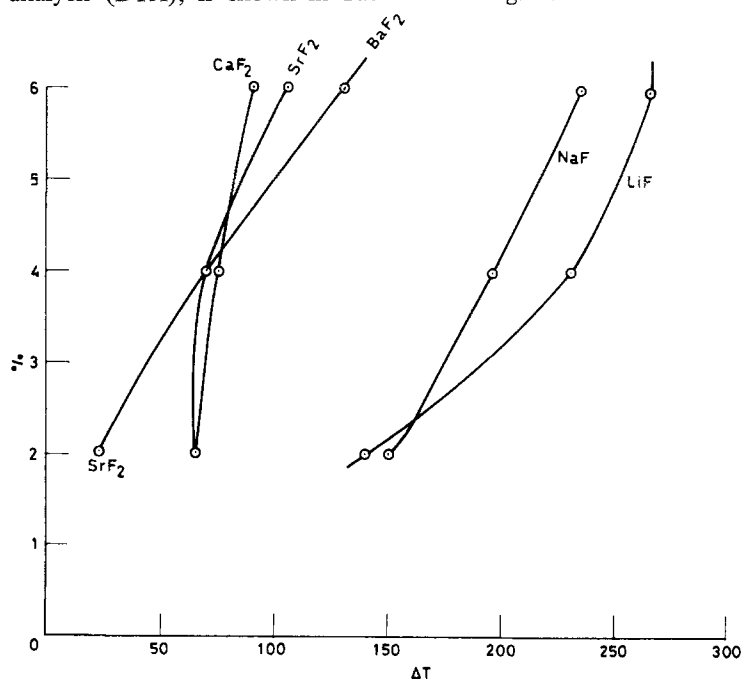

Figure 1 The variation in decomposition temperatures ($\Delta T = T CaCO_3 - T CaCO_3$ + mineraliser) of $CaCO_3$ with amount (%) of mineraliser in the mixes containing silica gel and $CaCO_3$ (1:3).