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REPORT

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GROWTH OF CREAMED TNT ON THERMAL CYCLING

Robert P. Parker and William S. Wilson

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(14) MRL-R-720

GROWTH OF CREAMED TNT ON THERMAL CYCLING

Robert P. Parker and William S. Wilson

(11)

ABSTRACT

Growth or irreversible thermal expansion of creamed TNT on thermal cycling is described. Growth of TNT charges appears to correlate with the quantity of impurities present, and increases linearly with the maximum temperature experienced in a manner which suggests the existence of a critical upper temperature which must be exceeded for any growth to occur. This temperature is close to the eutectic temperature for a ternary mixture of 2,4,6-TNT, 2,3,4-TNT and 2,4-DNT.

On the basis of these results and changes in the external appearance of TNT specimens subjected to thermal cycling, a 'ratchet' mechanism to account for growth is proposed, in which the stresses generated by anisotropic thermal expansion of TNT are relieved above the eutectic temperature by a mass transfer process such as grain boundary sliding or dynamic recrystallisation.

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Growth or irreversible thermal expansion of creamed TNT on thermal cycling is described. Growth of TNT charges appears to correlate with the quantity of impurities present, and increases linearly with the maximum temperature experienced in a manner which suggests the existence of a critical upper temperature which must be exceeded for any growth to occur. This temperature is close to the eutectic temperature for a ternary mixture of 2,4,6-TNT, 2,3,4-TNT and 2,4-DNT.

On the basis of these results and changes in the external appearance of TNT specimens subjected to thermal cycling, a "ratchet" mechanism to account for growth is proposed, in which the stresses generated by anisotropic thermal expansion of TNT are relieved above the eutectic temperature by a mass transfer process such as grain boundary sliding or dynamic recrystallisation.

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GROWTH OF CREAMED TNT ON THERMAL CYCLING

INTRODUCTION

α- or 2,4,6-trinitrotoluene (TNT) occurs commonly as rods, tablets and plates. The crystal system is not unequivocal, and both orthorhombic and monoclinic forms, and variants of each, have been described [1,2]. However the deviation from orthorhombic symmetry is slight, and for most practical purposes the symmetry may satisfactorily be regarded as pseudo-orthorhombic, the unit cell having dimensions of approximately 4.0, 0.6 and 1.5 nm and containing 16 molecules. Predictably, TNT also shows a marked anisotropy of thermal expansion. Scott quotes coefficients of thermal expansion of 5.16×10^{-5}, 5.56×10^{-5} and 15.36×10^{-5}/°C, along the major crystallographic axes [3], while Grabar, Hession and Rauch found values of 4.96×10^{-5}, 5.05×10^{-5} and 18.1×10^{-5}/°C [4]. Unfortunately, however, there is disagreement over the assignment of these values to specific crystal axes.

In common with other materials such as tin, cadmium and zinc [5], uranium [6-12] and zirconium [13], which also exhibit anisotropic thermal expansion, polycrystalline charges of TNT and TNT-based compositions show a cumulative, permanent and irreversible expansion on thermal cycling in addition to the more familiar reversible thermal expansion. This irreversible expansion, which occurs in all directions, results in an increase in volume (and decrease in density) of the charge, and is commonly termed growth. Growth of TNT is illustrated in Figure 1 as axial elongation of a cylindrical specimen, and can have important consequences for explosive-filled munitions. "Natural" thermal cycling during storage other than in temperature-controlled magazines can cause bare or lightly cased charges of TNT-based explosives to grow beyond tolerance specifications, or to buckle and distort to such an extent that components can no longer be correctly assembled. This type of failure has been noted in the burster XM83 filled with Composition B and the Mk 44 torpedo warhead filled with Torpex. Such a problem has not been encountered in more heavily cased stores such as artillery rounds. Moreover, such ammunition which *has* experienced extensive *natural* thermal cycling appears to be less prone to filling prematures than similar rounds which have not. It was proposed that this desensitisation might be a result of the explosive expanding irreversibly to fill the voids, cracks and base-gaps which occur during the filling process, and which are known to contribute to the incidence of filling prematures. A programme of work was initiated at Picatinny Arsenal (now U.S. Army Armament Research and Development Command) to investigate this and related phenomena [14].

The present report records the results of some experiments carried out at MRL in relation to growth in TNT. It discusses the effects of the cycling range and the impurities present on the growth of creamed TNT, and suggests a mechanism which might account for the growth process.

EXPERIMENTAL

1. Apparatus

In investigations into the growth of uncased TNT-based compositions reported previously, the specimens of explosive have simply been placed in an oven, subjected to the appropriate thermal cycling process, and their volumes measured at suitable intervals, either by liquid displacement or by direct mensuration. Although this method has demonstrated the existence and extent of growth, it has been unable to shed much light on the mechanism responsible for the phenomenon. To obtain this information the specimen must be monitored throughout the cycle, and to this end a dilatometer was constructed to record axial elongation of a cylindrical specimen. A fuzed quartz tube, 13 mm inside diameter and 250 mm internal length, was secured in a stainless steel supporting bracket. The cylindrical explosive specimen 50.8 mm long and 12.7 mm in diameter was placed inside the tube, and a hollow quartz plunger 200 mm long and 12.7 mm in diameter was inserted in the tube on top of the explosive. A Philips displacement pick-up PR 9310/03, connected to the appropriate carrier wave measuring bridge PR 9304, was mounted in a bracket to allow displacement of the plunger, and therefore axial expansion and contraction of the explosive, to be monitored. No correction was made for the expansion and contraction of the dilatometer tube; the coefficient of linear expansion of fuzed quartz ($5.5 \times 10^{-7}/°C$) is two orders of magnitude smaller than that of TNT, and its effect on the overall displacement measured by the pick-up will be negligible. The dilatometer, illustrated in Figure 2, was suspended in a Colora KT 50S ultracryostat bath modified by the addition of two 500 watt booster heaters. The temperature of the bath was varied by a temperature cycling unit operating a stepping motor, driving in turn the mercury contact thermometer which controls the bath. The temperature of the bath, measured by a copper/constantin thermocouple, and the elongation of the explosive were recorded using a Moseley 7100 B two-pen strip recorder.

2. Materials

Studies into growth in metals have indicated a pronounced dependence on grain orientation. A grain "texture" contributes to the growth of uranium [6,7], but samples of zirconium with random crystal orientation grow at about three times the rate of those with preferred orientation [13]. The influence of grain orientation was less clear in tin, cadmium and zinc, but growth seems to be greater in specimens with random orientations [5]. Previous studies have not revealed any such effect in TNT or TNT-based explosives, and this parameter will be examined in a later report. To eliminate the effects of grain orientation in the current work specimens were machined from creamed TNT; this material is an array of small, randomly oriented grains prepared by casting a slurry of molten and solid TNT, poured at the melting point of the explosive.

In order to investigate the effect of sample purity on the growth of TNT, specimens were prepared from three different lots of TNT. Two of these were commercial material, containing 2,4-DNT, 2,3,4-TNT and 2,6-DNT impurities; the third was TNT which had been purified by an extension of the industrial bisulphite process and recrystallised twice from ethanol [15], giving a product with a melting point of 80.7°C and containing no detectable impurities (i.e. less than 0.01% by g.l.c.). The amounts of impurities in each material are given in the results section below.

RESULTS

Three series of thermal cycling experiments have been carried out on various samples of creamed TNT. Since the results are influenced by such factors as the impurities present and, possibly, minor variations in the crystal structure, the three series are initially best considered separately.

Series 1

Cylinders of creamed TNT, containing 0.13% 2,4-DNT, 0.03% 2,3,4-TNT and a trace (less than 0.01%) 2,6-DNT, were subjected to 40 six-hour cycles (three hours heating and three hours cooling) between two predetermined temperatures*. The axial elongation and contraction were followed dilatometrically, and the observed growths are recorded in Table 1.

TABLE 1

Temperature Cycle	Axial Growth (%)
4 to 59°C	0.51
14 to 68°C	0.68
4 to 39°C	0.12
14 to 49°C	0.22
24 to 59°C	0.30
24 to 59°C	0.34

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* The temperature cycling control unit was designed to give ranges of 20, 40, 60, 80 and 100°C amplitude. However subsequent calibration and analysis of chart records revealed that the temperature ranges were somewhat smaller than intended. This was probably the result of some variability in the screw-thread pitch of the contact thermometers used. However the temperature ranges were selected somewhat arbitrarily, and the changes are immaterial.

Several points emerge from these results. The cylinder cycled 14-68°C grew more than did that cycled 4-59°C, and the cylinder cycled 24-59°C grew more than that cycled 14-49°C, which in turn grew more than that cycled 4-39°C. Also, cycling 4-59°C and 14-68°C caused greater growth than did cycling 4-39°C and 14-49°C respectively. Finally, the cylinder cycled 4-59°C grew more than that cycled 24-59°C. Thus it can be seen that the growth of creamed TNT increases with both the upper temperature limit and the temperature range.

Series 2

Cylinders of creamed TNT containing 0.20% 2,4-DNT, 0.03% 2,3,4-TNT and a trace (less than 0.01%) of 2,6-DNT were subjected to 40 six-hour thermal cycles of ca. 54°C* (three hours heating and three hours cooling) to various upper temperature limits between 40°C and 75°C. The axial elongation and contraction were followed dilatometrically, and the growths observed are recorded in Table 2 below and plotted as a function of the upper temperature limit of the cycle in Figure 3.

TABLE 2

Temperature Cycle	Axial Growth (%)
-14 to 43°C	0.25
1 to 55°C	0.88
4 to 59°C	1.01
8 to 61°C	1.14
14 to 68°C	1.43
17 to 70°C	1.56

Two features of these results are immediately noteworthy. First, the growth of these samples on cycling 4-59°C and 14-68°C is significantly greater than that after cycling specimens from Series 1 over the same temperature ranges. Factors which might contribute to this sample dependence include the orientation of the grains in the polycrystalline assembly (randomised in creamed TNT) and the impurities present in the TNT. The second prominent feature of the results is the direct linear dependence of growth on the maximum temperature experienced during cycling. The axial growth observed is related to this temperature by the equation (derived using a least-squares method) :

$$\text{Elongation (\%)} = 0.0471\,T - 1.753 \quad (\text{Correlation coefficient } r = 0.998)$$

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* See footnote, previous page.

where T is the maximum temperature measured in °C. This relationship suggests that thermal cycling will only cause growth in this material if a temperature of about 37°C is exceeded.

Relevant data from Series 1 (creamed TNT containing 0.13% 2,4-DNT, 0.03% 2,3,4-TNT and a trace (less than 0.01%) 2,6-DNT) are also presented in Figure 4. Extrapolation of these results, assuming that a linear dependence of growth on the highest temperature experienced in the thermal cycle is also valid in this case, also indicates a critical temperature in the range 30-35°C.

It is interesting to note that a eutectic temperature of about 36.5°C has been observed for a ternary mixture of 2,4,6-TNT, 2,3,4-TNT and 2,4-DNT [16]. The presence of other impurities, even in very small quantities, might be expected to lower the eutectic temperature still further.

Series 3

Cylinders of creamed "ultrapure" TNT containing no detectable amount of 2,4-DNT, 2,3,4-TNT or 2,6-DNT were also subjected to 40 six-hour thermal cycles nominally 60°C. The specimen cycled 3-57°C showed no growth, while those cycled 13-66°C and 18-69°C grew by 0.04% and 0.10% respectively. These results indicate that there is a qualitative correlation of growth in creamed TNT with the presence of impurities. The relationship between impurities present and the growth resulting from 40 six-hour cycles between about 4 and 58°C is illustrated in Table 3 below.

TABLE 3

TNT Sample	Impurities (%)			Growth (%)
	2,4-DNT	2,3,4-TNT	2,6-DNT	
Ultrapure (Series 3)	0	0	0	0
Series 1	0.13	0.03	Trace*	0.51
Series 2	0.20	0.03	Trace*	1.01

* Detectable amounts less than 0.01%

Observations from Dilatometer Records

The dilatometer was used to monitor expansion and contraction of the specimen throughout the thermal cycle in an attempt to gain some insight into the mechanism of the growth process. The records obtained reveal two pertinent features. First, the expansion and contraction of the commercial (impure) TNT are not linear throughout the cycle. To illustrate this point, the first cycle 4-59°C of Series 2 is reproduced in Figure 5. The coefficient of thermal expansion is initially $6.8 \times 10^{-5}/°C$, but increases to 10.9 x 10^{-5}/°C. During the cooling portion of the cycle the coefficient of thermal expansion, initially 10.9 x 10^{-5}/°C, decreases to 6.8 x 10^{-5}/°C by about 35°C. The implication is that different processes take place above and below that temperature. It is interesting to note that in the 3-57°C cycle for pure TNT, in which growth was *not* observed, the expansion and contraction appear to be linear. The second interesting feature is that growth seems to be the result of additional expansion during the heating phase of the cycle. Thus, as Table 4 below reveals, the expansion during the first cycle of Series 2 increases as the upper temperature limit increases, but the contraction remains essentially constant.

TABLE 4

Thermal Cycle	Expansion*	Contraction*	Growth*
-14 to 43°C	2.85	2.65	0.20
1 to 55°C	3.09	2.59	0.50
4 to 59°C	3.25	2.69	0.56
8 to 61°C	3.37	2.68	0.69
14 to 68°C	3.42	2.66	0.76
17 to 70°C	3.50	2.75	0.85

* Arbitrary units from chart records.

Surface Changes Accompanying Growth

Thermal cycling of creamed TNT results in changes to the surface texture, in addition to the phenomenon of growth which is the subject of this report. The explosive specimens, prepared by turning down castings on a lathe, exhibit the typical smooth finish associated with good quality machined samples. After thermal cycling, however, these specimens had developed a distinctly crystalline appearance. This surface change resembles the "plastic deformation" which occurs when tin, cadmium and zinc are subjected to thermal cycling [5] and the surface "wrinkling" of uranium [6,7].

In order to investigate these surface changes more closely, a flat surface was prepared on one of the cylindrical specimens by means of a microtome, and that surface was polished mechanically and etched with bromoform [17]. An area of this etched surface was selected at random for microscopic examination, and a composite photographic "map" was prepared which showed the surface consisting of randomly oriented elongated crystals with straight, sharply defined edges. This specimen was then subjected to thermal cycling 5-65°C and examined periodically, and composite "maps" of the same area were prepared. Two changes were observed. The grain boundaries, initially sharply defined straight lines with distinct angular corners, became more rounded as the grain boundaries of adjacent crystals were redistributed. This is the phenomenon of thermal etching. In addition, small but distinctive regular crystals appeared. The extent of grain boundary etching and the growth of these regular crystals both continued with thermal cycling, and it was concluded that material was melting preferentially at the grain boundaries at higher temperatures and recrystallising again elsewhere. No suggestion of either grain boundary migration or grain boundary sliding was detected.

DISCUSSION OF RESULTS

Previous investigations into growth of TNT-based compositions have done little to clarify the mechanism by which it occurs. Schimmel and Lowell, who discussed expansion of TNT and Composition B in XM83 bursters, simply reported the phenomenon, indicating that they were unable to eliminate growth but that it was tolerable if the tubes were not fully loaded [18]. No attempt was made to explain the process. Kegler and Baumann observed a permanent reduction of density of vacuum cast RDX/TNT 65/35 dependent on both the temperature range and the number of thermal cycles [19]. They reported that growth increased with the upper temperature limit, and that the growth continued even after 235 cycles 20-70°C, although the growth per cycle decreased with the number of cycles. These authors suggested that growth was caused by the difference between the thermal expansion characteristics of RDX and TNT and the strongly anisotropic thermal expansion of both materials. It was proposed that "mutual interactions between crystals" develop during temperature changes, "crushing the TNT" and "loosening the structure" of the crystalline matrix, thereby causing the charge to grow. On the other hand, Rauch and Wainwright suggested that the growth phenomenon might result from the expansion of liquid eutectics and the expansion and expulsion of trapped or dissolved air [14]. This proposal does not fit with the growth of vacuum castings observed by Kegler and Baumann, since such charges should not contain entrained air.

Although they might account for permanent expansion during the first cycle, such mechanisms as simple relief of stresses (pre-existing or induced by thermal expansion) and expansion or expulsion of entrained air do not explain how the driving force is regenerated during subsequent cycles. The problem seems to be better understood by metallurgists than it is by explosives materials technologists [10,11,20] and it is clear that the mechanism must involve both a driving force to generate the appropriate stress, and a mass transfer process by which that stress may be relieved, coupled together in a "ratchet" fashion. The driving force is provided by the anisotropic thermal expansion, but several mass transfer processes are possible, such as grain boundary migration, grain boundary sliding, or recrystallisation. For example, in the classical ratchet mechanism demonstrated by Burke and Turkalo for a zinc bicrystal [20] and proposed by them for polycrystalline uranium [10], grain boundary sliding or flow is the mass transfer process.

It is probably worthwhile to outline the mechanism described by Burke and Turkalo for the regeneration of stresses on thermal cycling of a zinc bicrystal [20]. Consider the bicrystal assembly shown schematically in Figure 6, where the coefficient of expansion of grain 1 parallel to the grain boundary is greater than that in grain 2. Assume for convenience that there is initially no stress in the grain boundary. (This will be the case only if particular pains are taken to ensure it, but it is not important to the argument.) As the temperature is increased grain 1 attempts to expand more rapidly than grain 2, but is constrained by the crystal interface. A compressive stress is generated in grain 1 with a corresponding tensile stress in grain 2, and a shearing stress is set up across the grain boundary. This shearing stress increases until the elastic limit is reached, whereafter additional stress is accommodated by crystallographic slip in the grain which has the greater stress resolved on its slip planes. The stress then remains constant until a temperature T*, at which grain boundary sliding (flow) allows relaxation of the shearing stress. Further temperature increase causes independent expansion of the individual grains, unimpeded by the grain boundary. The differential contraction of the grains as the bicrystal is cooled is also accommodated by grain boundary sliding until movement becomes impossible again at T*. The shearing stress is then set up in the opposite sense with grain 1 in tension and grain 2 in compression, and when the elastic limit is reached additional stress is again relieved by crystallographic slip. When the temperature increases again during the second cycle the stresses decrease, pass through zero and then increase to the elastic limit. The essential features of the ratchet are, then, the generation of a shearing stress at the grain boundary by the different thermal expansions, and the abrupt relief of that stress above the temperature T* by grain boundary sliding.

It is proposed that a similar ratchet mechanism causes the growth of TNT-based compositions. Certainly anisotropic thermal expansion takes place to generate the necessary intercrystalline stresses, while grain boundary migration, grain boundary sliding or some form of dynamic recrystallisation each might afford the mass transfer process.

The data obtained in this study give some clues to the identity of this mass transfer process. First, the conclusion that thermal cycling of commercial TNT will only result in growth if a critical temperature in the range 30-35°C is reached, and the observation from dilatometer records that the coefficient of thermal expansion changes at about the same temperature suggest that the mass transfer process commences in this region. The fact that 2,4,6-TNT and its major commercial impurities, 2,4-DNT and 2,3,4-TNT, form a ternary eutectic of melting point 36.5°C [16] suggests that the presence of a liquid eutectic is important for this mass transfer. This hypothesis derives support from the direct correlation of growth with the upper temperature limit of the thermal cycle, and the qualitative correlation with the quantity of such impurities present, since both parameters can be expected to influence the volume of liquid eutectic present. (It is interesting to note that, while little attempt has been made to identify a dependence of growth in metals on purity, such results as are available suggest an inverse dependence, i.e. that the presence of impurities inhibits growth in these materials [5,10].)

If the presence of a liquid eutectic facilitates the mass transfer process, it is important to understand the distribution of impurities in polycrystalline TNT. Castings are not homogeneous, but rather the TNT crystals growing from the melt are relatively free from impurities which tend to be driven ahead of the advancing crystal front. (This is the basis for the zone refining technique used for the purification of metals and certain organic solids.) As a consequence, the impurities in a cast, polycrystalline charge tend to be concentrated at the crystal boundaries.

Grain boundary migration, proposed as the mass transfer process involved in the growth of zirconium [13], has been observed during microscope studies on thin films of TNT [4,21,22]. In the case of purified TNT, a thin film which remained unchanged after 71 hours at 60°C showed pronounced grain boundary migration after only 3 hours at 65°C; the phenomenon could not be detected in commercial TNT below 55°C [22]. Thus, while grain boundary migration might possibly participate in the growth of pure TNT above about 65°C and that of commercial TNT above 55°C, it clearly cannot contribute below these temperatures.

The microscope studies have suggested the occurrence of melting at the grain boundaries during thermal cycling. The presence of liquid at crystal boundaries would clearly facilitate grain boundary sliding, acting as a lubricant as the crystals move one across the other. Alternatively, the presence of the eutectic liquid at the grain boundaries would provide the solvent necessary for dynamic recrystallisation, in which TNT dissolves from one crystal and recrystallises simultaneously at another. No sign of grain boundary sliding has been detected, but some evidence of recrystallisation was obtained during microscopic examination. However, it is appreciated that events observed at the surface of the specimen need not necessarily occur in the bulk, and the reverse may also be true. On the other hand, indirect support for recrystallisation as the mass transfer process, rather than grain boundary sliding, may perhaps be inferred from the apparent dependence of growth on the volume of eutectic present, which is increased by both the temperature of the sample and the quantity of impurities present capable of forming eutectic mixtures with TNT. While it is apparent that the rate and extent of recrystallisation will depend directly on the volume of solvent present, it would seem that, provided sufficient liquid is present for grain boundary sliding to occur at all, the presence of additional liquid should have little or no effect. For these reasons dynamic recrystallisation is favoured as the mass transfer process, although grain boundary sliding has not been positively discounted.

It is proposed that the growth of creamed TNT occurs by means of a ratchet mechanism similar to that characterised by Burke and Turkalo in a zinc bicrystal [20]. Thus, the anisotropic thermal expansion of the TNT generates stresses at the crystal boundaries, where the impurities are concentrated. These stresses may be relieved above the eutectic temperature by a mass transfer process such as grain boundary sliding or dynamic recrystallisation from a molten eutectic. (The latter process is that currently favoured.) Boundary stresses caused by further heating are relieved by the same mass transfer process, as are those generated on cooling until the grain boundary can support a stress once again, this time in the reverse direction, below the eutectic temperature. On the following cycle the stress first decreases to zero and is set up again in the original direction, before being relieved again above the eutectic temperature by the mass transfer process.

CONCLUSIONS

Creamed commercial TNT undergoes growth or cumulative irreversible thermal expansion as a consequence of thermal cycling. This growth appears to be dependent on "sample parameters", but increases linearly with the maximum temperature experienced in a manner which suggests the existence of a critical upper temperature which must be exceeded for any growth to occur. This temperature is close to the eutectic temperature of a ternary mixture of 2,4,6-TNT, 2,3,4-TNT and 2,4-DNT. Further, the extent of growth appears to correlate with the quantity of these impurities present, and creamed purified TNT shows no growth when cycled 4-58°C, although slight growth was observed after cycling to higher temperatures.

In addition to growth, thermal cycling of a creamed TNT cylinder causes the initially smooth, machined surface to develop a pronounced crystalline appearance. This change has also been observed after thermal cycling of uranium rods, and has been termed "wrinkling". A flat surface machined, polished and etched on the side of a TNT cylinder indicated melting at the intercrystalline boundaries (thermal etching), and small but regular crystals were observed growing on this surface as a consequence of thermal cycling.

A "ratchet" mechanism to account for the growth of creamed TNT is proposed, in which the stresses generated by the anisotropic thermal expansion of TNT during thermal cycling are relieved above the eutectic temperature by a mass transfer process such as grain boundary sliding or dynamic recrystallisation.

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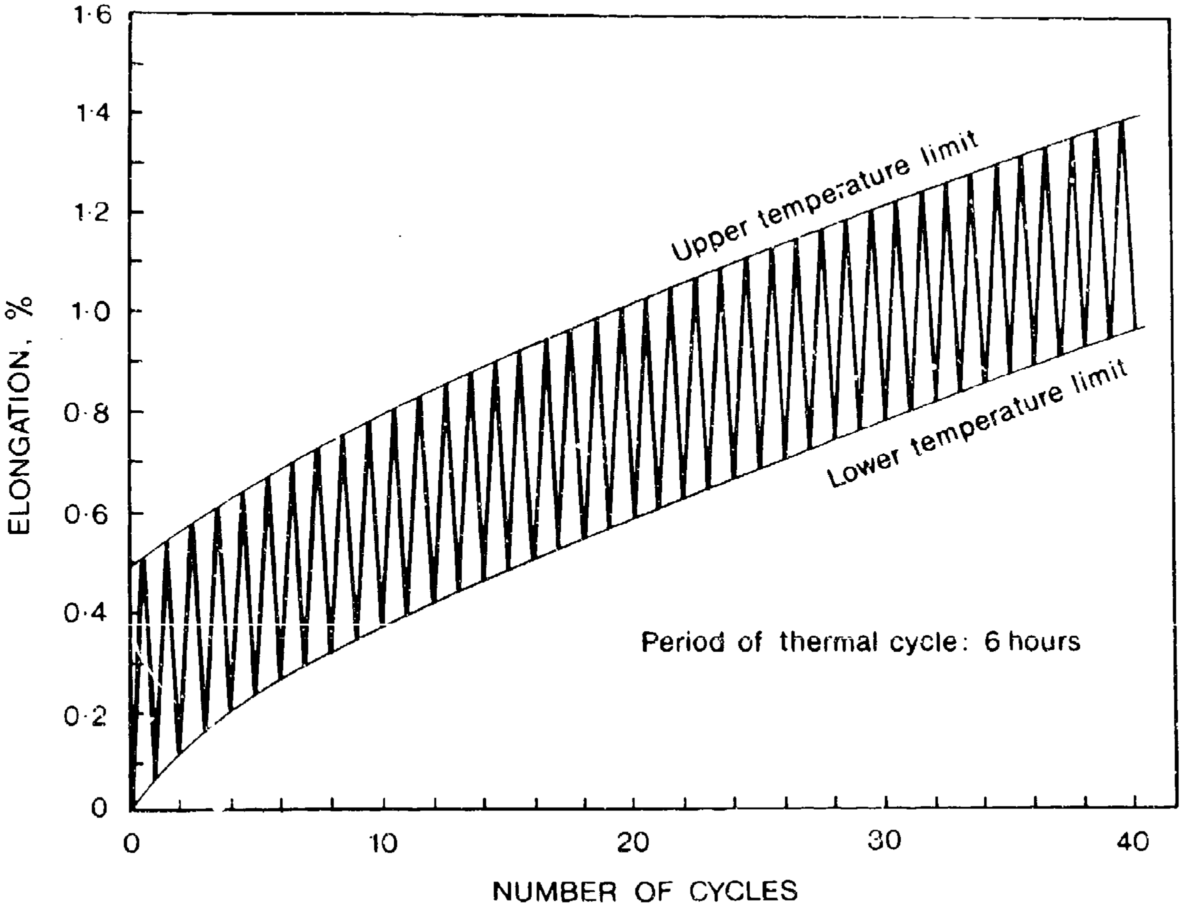

FIG. 1 – Growth of creamed TNT, cycled 4-59°C.

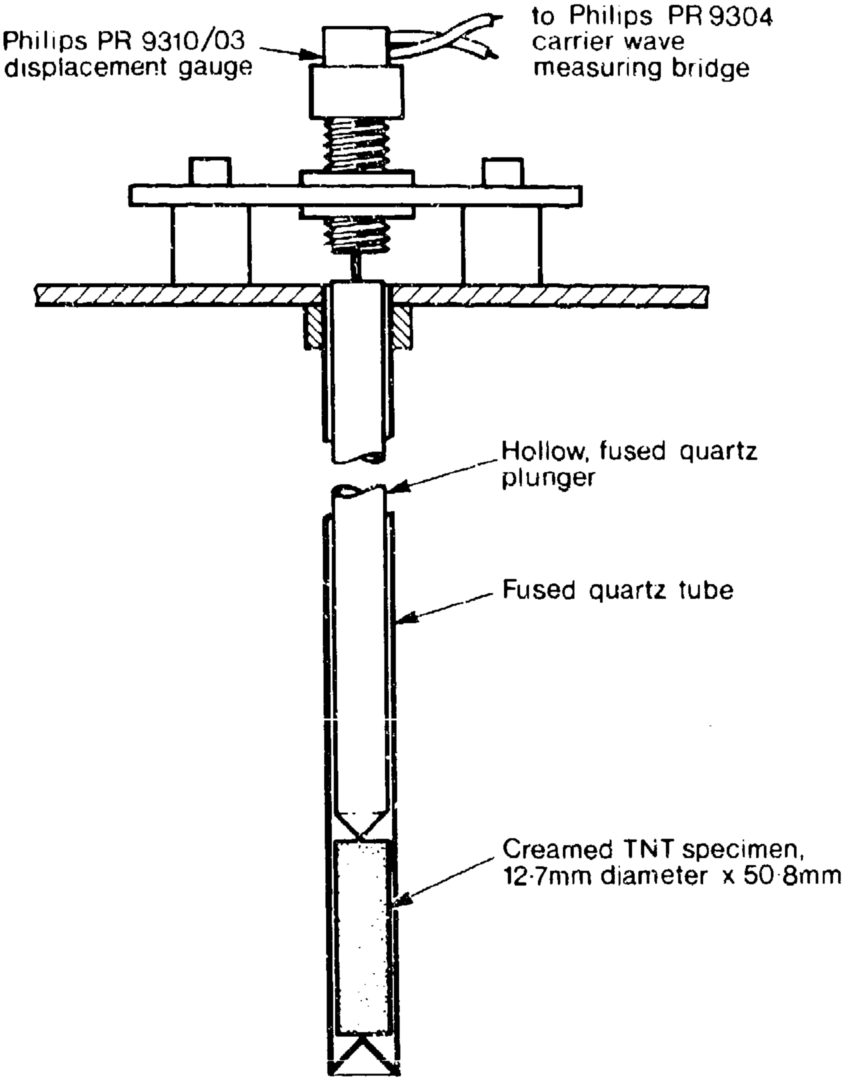

FIG. 2 - Dilatometer for measurement of axial elongation of TNT cylinders.

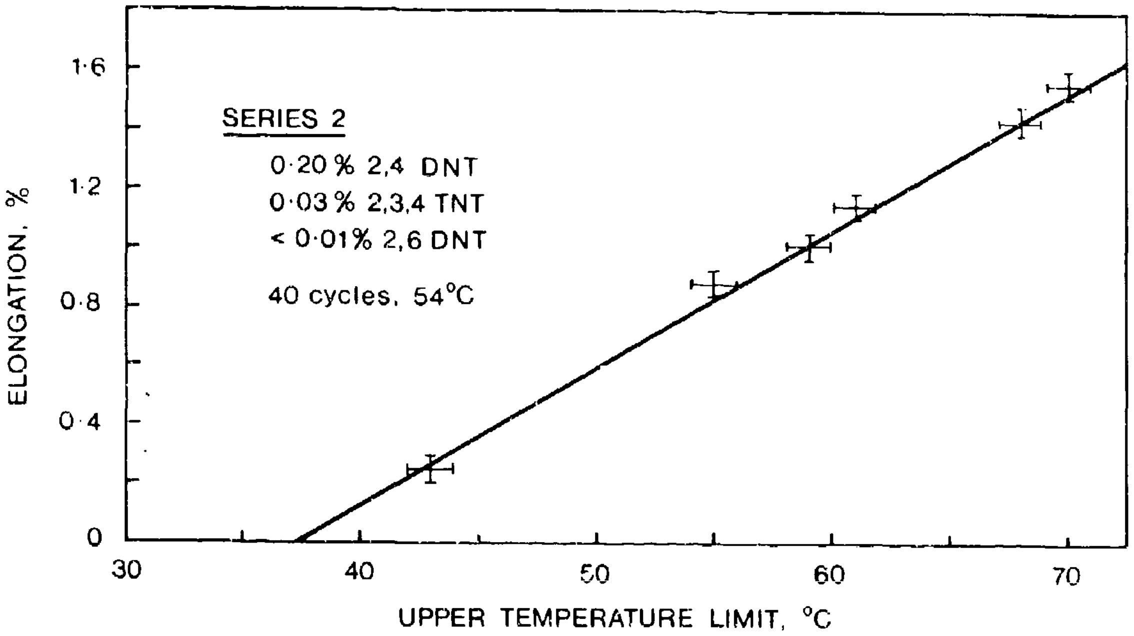

FIG. 3 - Growth of creamed TNT samples from Series 2.

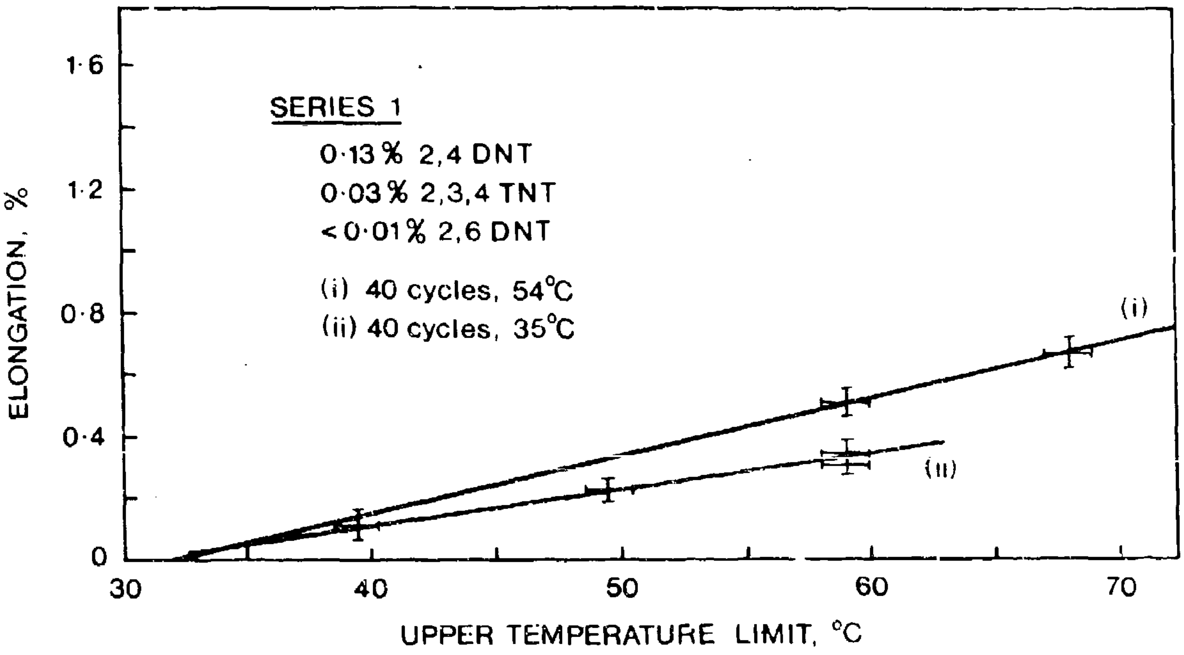

FIG. 4 - Growth of creamed TNT samples from Series 1.

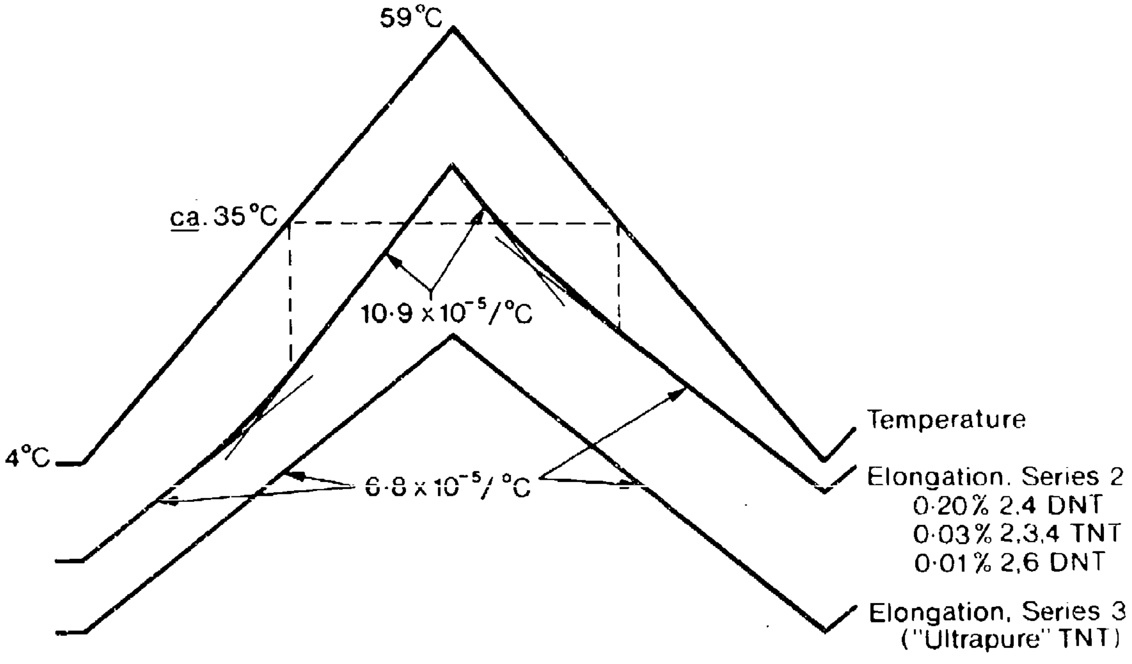

FIG. 5 - Axial expansion of creamed TNT during the first thermal cycle, 4-59°C.

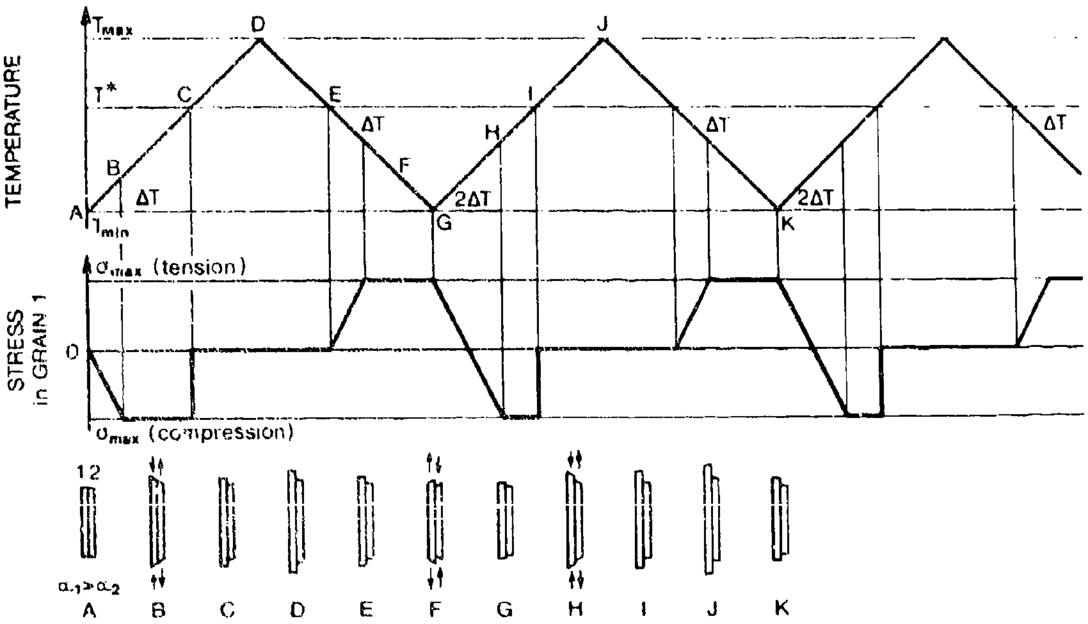

FIG. 6 - Burke and Turkalo's model for growth in a zinc bicrystal.

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