Advanced Materials XII

Edited by
Shaheed Khan, Iftikhar us Salam and Karim Ahmed

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The Advanced Materials XII is the compilation of selected peer reviewed papers from the 12th International Symposium on Advanced Materials held from September 26-30, 2011, Islamabad, Pakistan. As a Secretary of ISAM-2011, I feel immense pleasure that this symposium has ended up with a great success. The ultimate aim of this publication is to present latest information and new findings/innovations in the field of advanced materials. The ever-increasing changes and complexities that characterize present day needs of the industry have forced a growing demand for technical information on advanced materials. Such a demand presents a strong challenge to the researchers in this field to disseminate useful material information readily. It is hoped that the technical data available in this publication is likely to help young scientists and researchers working in the field of advanced materials. In the five-day deliberation of the symposium, nearly one hundred and eighty contributory and invited papers, comprising of seventeen (17) technical sessions and two (02) poster sessions, were presented. Renowned scientists and researchers from foreign and local institutes have shared their ideas with their counterparts on the topics of common interest.

I am personally thankful to the Symposium Chairman for his continuous guidance and assistance, without which it would not have been possible to make this event of international standard. I am also greatly indebted to the technical, secretariat and organizing committees of ISAM-2011 for putting all their efforts in composing the Advanced Materials XII. I am also thankful to the Trans. Tech. Publications (ttp), Ltd., Switzerland for accepting the papers of ISAM-2011 for publication in the journal.

I am also thankful to our distinguish participants, session chairpersons, co-chairpersons and reviewers of the papers for showing their keen interest and providing their assistance/cooperation which turned this event to be a brilliant success.

I owe a special thanks and appreciation to the entire organizing committee for playing their active role in every sector of this event, which has led to achieve the ultimate goal. Finally yet importantly, my gratitude goes to the sponsors of ISAM-2011 for providing financial support for this event.

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New Developments in NdFeB-based Permanent Magnets

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Keywords: NdFeB permanent magnets; sintering; bonding; nanocrystalline alloys

Abstract: NdFeB based alloys have been used as permanent magnets for almost thirty years. The recent researches aim at optimizing the composition, microstructure and properties, reducing cost, and developing new processes. The demand for sintered magnet is increasing. Efforts are directed towards improving properties by controlling grain boundary diffusion, minimizing the rare earth (RE) content and also improving production yield. As for bonded magnets, to enhance remanence and energy product, nanocrystalline powders are employed. High thermal stability has been realized by mixing NdFeB with hard ferrite powders. For nanocrystalline and nanocomposite NdFeB based alloys, both compositional modification and microstructural optimization have been carried out. New approaches have also been proposed to prepare NdFeB magnets with idea structure. Surfactant assisted ball milling is a good top-down method to obtain nanosized hard magnetic particles and anisotropic nano-flakes. Synthesis of NdFeB nanoparticles and NdFeB/Fe(Co) nanocomposite powders by bottom-up techniques, such as chemical reduction process and co-precipitation, has been successful very recently. To assemble nanocrystalline NdFeB powders or nanoparticles into bulk magnets, various novel consolidation processes including spark plasma sintering and high velocity press have been employed. Hot deformation can be selected as the process to achieve anisotropy in nanocrystalline magnets.

Introduction

Our daily environment has been significantly dependent on the materials with outstanding magnetic properties. The trend for hard magnets is directed towards smallest and most powerful magnets, particularly in technologies where miniaturization is required. Although being emerged for almost 30 years, NdFeB based alloy is still the best room temperature permanent magnet now. The excellent magnetic properties result from the Nd\textsubscript{2}Fe\textsubscript{14}B phase with high saturation magnetization (M\textsubscript{s}) and high anisotropy field. The maximum energy product (BH\textsubscript{max}) has reached over 450 kJ/m\textsuperscript{3} early this century. Despite this progress, with the increasing demand for more powerful magnets in electric and magnetic devices, the effort towards improving properties has never been stopped. The production of NdFeB magnets starts from alloys preparation and powdering. The subsequent processes include sintering, bonding or hot-deformation. The magnetic properties of the magnets are closely related to the composition and processing parameters. To develop magnets with new structures or low cost, new process is also in need. In this paper, the recent progresses on NdFeB based magnets are discussed.

Sintered NdFeB magnets: The demand for sintered NdFeB has been increasing during last 20 year and it is expected to continuously increase for next ten years, as shown in Fig.1 [1]. The REFeB (RE=Nd, Pr, etc.) alloys that are highly enriched in RE are suitable for sintering magnets. During the sintering process a paramagnetic RE-rich intergranular phase develops between the micro-sized highly oriented hard magnetic RE\textsubscript{2}Fe\textsubscript{14}B grains, yielding a more or less magnetic isolation of the grains which promotes large coercivities. The average grain size is about 20 µm and most of the grains exhibit a multidomain state well-oriented along the texture axis.[2] To promote coercivity and thermal stability, up to 10 wt.% Dy (or Tb) is generally added in sintered magnet for substituting Nd. This, however, increases the product cost. Current work on sintered NdFeB magnets is directed towards low Dy content, high coercivity H\textsubscript{C} and high thermal stability. Improving the yield of the production is another important goal for all manufacturers. Research
A group from Japan has set a target to meet the demand of 100,000 tons/year of the NdFeB magnets. Based on their recent report[1], the technologies they developed include a pressless process (PLP) and a grain boundary diffusion technique (GBD). They are conducting these two technologies to attain two objectives, one is to obtain $H_C=30$ kOe with Dy content less than 2 wt.%; another is to achieve production yield (output/input) of 95%, which is much higher than 60% by conventional process. The latter can also save RE. GBD can effectively improve the distribution of RE-rich phase and enhance the $H_C[1,3]$.

![Fig. 1. A forecast on the world demand for the NdFeB sintered magnets [1]](image)

**Nanocrystalline NdFeB permanent magnets:** Nanocrystalline NdFeB hard magnets are suitable for tailoring magnets with defined microstructure and properties. Based on the composition, three types of nanocrystalline REFeB magnets with different microstructures have been developed by melt-spinning method, i.e. RE-rich magnets (decoupled magnets), single phase magnets and RE-lean magnets (composite magnets).

**High-coercive RE-rich nanocrystalline magnets** or decoupled magnets have RE-rich composition. The phase structure is similar to that of the sintered magnets where single crystallites of the RE$_2$Fe$_{14}$B phase are magnetically decoupled by a paramagnetic RE-rich boundary phase. However, the grain size is only 50 to 200 nm now, which guarantees that mainly single-domain particles exist. The isotropically distributed easy directions result in a $J_r$ of maximum one-half of the spontaneous polarization $J_S[4]$.

**Remanence enhanced single-phase magnets** are received for the stoichiometric composition RE$_2$Fe$_{14}$B. In such magnets the hard magnetic grains are directly connected without any intergranular phase and therefore they are magnetically coupled by exchange interactions. A significantly enhanced remanence and a slightly reduced coercivity are observed as a consequence of the exchange coupling. However, as the exchange interaction is a very short-range interaction its influence is largest at the grain boundary and disappears inside the grain. Since only the exchange coupled volume fraction can bring about the remanence enhancement, the grain size should be smaller than 50 nm [5]. With diminishing grain sizes $J_r$ increases. The exchange coupling between the grains is also the reason for the smaller $H_C$ values compared to decoupled magnets.

**Exchange coupled nanocomposite magnets** [6,7] can be obtained in Fe-rich compositions, showing a further significant increase of the remanence, accompanied by a further reduction of $H_C$. In such two-phase nanocomposite magnets soft magnetic $\alpha$-Fe grains arise in addition to the hard magnetic RE$_2$Fe$_{14}$B grains. The remanence enhancement is due to the exchange coupling among the grains but also to the very large $J_S$ of the $\alpha$-Fe grains (2.15 T). However, to obtain excellent hard magnetic properties, it is imperative that the soft $\alpha$-Fe grains are completely exchange-coupled with the hard grains. Therefore, their size may not exceed a certain limit which is in the order of the Bloch wall width $d_B$ of the hard magnetic phase [8]. Otherwise, the hysteresis loop would show a two-step demagnetization behavior with drastically deteriorated hard magnetic properties.
The typical microstructures and hysteresis loops for three types of magnets are shown in Fig.2 and Fig.3a. With decreasing RE content, the $J_r$ increases and the $H_C$ decreases. The recent work found that nanocomposite alloys have better thermal stability than RE rich alloys, manifested by low temperature coefficients (Fig.3a) and irreversible losses [9]. Fig.4 summarizes the relationships between $J_r$, $H_C$ and $(BH)_{max}$ for a wide range of nanocrystalline alloys with various composition produced by melt spinning[10]. The results show that, for isotropic nanocrystalline NdFeB magnets, there is a limit of the combination of the magnetic properties.

**Fig. 2.** Microstructure of RE-rich (a), single phase (b) and nanocomposite (c) NdFeB based alloys

**Fig. 3.** The hysteresis loops for three types of alloys (a) and temperature coefficients for NdFeB alloys with various RE contents (b)

**Fig. 4.** $J_r$, $H_C$ and $(BH)_{max}$ for nanocrystalline NdFeB alloys with a wide range of compositions

**Bonded NdFeB magnets:** Nanocrystalline RE-Fe-B based alloys are suitable for the fabrication of polymer-bonded magnets due to their high $(BH)_{max}$ values and their low RE content, which reduces the cost of the raw materials and improves the corrosion resistance. Bonded magnets are made by powderizing the ribbons, mixing the powder with a polymer, followed by compression or
injection-moulding. In the case of bonded magnets, any final shape can be prepared easily without expensive after-treatment like sawing or grinding. The major drawback to bonded magnets is the reduction in their magnetic properties relative to their fully dense counterpart. The magnetic hysteresis loops for optimally quenched ribbons, over-quenched and annealed ribbons and bonded magnet are characterized in Fig. 5a. The reduction of $J_r$ is due to the existence of nanomagnetic binder. A bonded hard magnets consisting of NdFeB and hard ferrites are proposed for improving the thermal stability of the bonded magnets based on the fact that hard ferrites have positive temperature coefficient of coercivity. Fig. 5b shows the hysteresis loops for nanocrystalline NdFeB powders, hard ferrite powders and NdFeB-Ferrite composite powders. The temperature coefficient of $H_C$ is only -0.252 %/K, which is much lower than sintered magnets, indicating that the bonded composite is ideal magnet with good thermal stability and mediate $(BH)_{max}$.

**New approaches for preparing nanocrystalline NdFeB magnetic powders:** To prepare Nd$_2$Fe$_{14}$B based bonded magnets, sintered magnets or magnetic elastomers for engineering applications, magnetic powders are essential. To synthesize nanocrystalline NdFeB powders, both top-down and bottom-up approaches have been carried out.

**Surfactant assisted ball milling:** (SABM) has become a hot topic for preparation of NdFeB nanocrystals during last few years[11,12]. It has been found that both nanoparticles and nanoflakes can be produced. Fig. 6 shows the morphology and hysteresis loops for SABMed NdFeB powders. Very small hard magnetic particles can be produced in this way and with increasing milling time the $H_C$ reduces. A $H_C$ value more than 300 kA/m can be still obtained in the nanoparticles with mean size of 20 nm. A very promising characteristic of this process is that it can produce anisotropic nanostructured flakes with easy axis lying in the flake plane by controlling milling agents and parameters. These anisotropic powders are suitable for preparing anisotropic bonded magnets.

![Figure 5](image1.png)

**Fig. 5.** Magnetic hysteresis loops for optimally quenched ribbons, over-quenched and annealed ribbons and bonded magnet (a) and for selected nanocrystalline NdFeB powders, hard ferrite powders and NdFeB-Ferrite composite magnet (b)

![Figure 6](image2.png)

**Fig. 6.** The morphology for of NdFeB nanoparticles milled for 8 h and hysteresis loops for the nanoparticles after milling for 2, 4 and 8 h by surfactant assisted ball milling
NdFeB nanopowders prepared by chemical method has also attempted recently [13,14]. The most commonly used process for producing Nd$_2$Fe$_{14}$B magnetic alloys, such as powder metallurgy methods and rapid quenching techniques, are energy intensive and require high purity elements as starting materials. Synthesis of Nd$_2$Fe$_{14}$B magnets by chemical routes has shown advantages. However, due to a high negative reduction potential of the RE elements, it is quite difficult to co-reduce REs and transition metals simultaneously. Nd$_2$Fe$_{14}$B alloys are reactive and oxidation prone, making synthesis of nanoparticles challenging. Our recent work [15] found that the Nd$_2$Fe$_{14}$B nanoparticles can be produced by sol-gel followed by reduction-diffusion. The sol-gel technique was used to synthesize a chemically homogenous oxide, and reduction-diffusion of this oxide can produce Nd$_2$Fe$_{14}$B magnetic nanoparticles. As a result, fine Nd$_2$Fe$_{14}$B nanoparticles of ~25 nm size were successfully synthesized. As-synthesized powders had a $H_C$ of 6.5 kOe and a $M_S$ of 21.1 emu/g (Fig. 7a). After removal of the byproduct CaO, the $M_S$ increased to 102 emu/g but the $H_C$ decreased to 3.9 kOe. This technique can be readily extended to the synthesis of exchange-coupled magnetic nanoparticles to obtain high energy product magnets.

NdFeB composite magnets could be as high as 1 MJ/m$^3$, but this has never been achieved in the experiment so far. The main reason may be that the conventional techniques are hardly to control both hard and soft phases at the nanometer scale. Recently, we report a new wet chemistry approach to synthesize the nanocomposites of NdFeB/nano-Fe(Co) with controllable compositions and sizes of both phases [16]. The synthesis was based on the precipitation of Fe and Co ions from their aqueous solutions on the NdFeB powders. Melt spun NdFeB powders were used as the substrates on which Fe, Co or FeCo nanoparticles were deposited. Fig. 8a shows the micrograph of the surface layer of the nanocomposite powders. The coating layers are comprised of Fe nanoparticles with average particle size of ~61 nm. The hysteresis loops of NdFeB/Fe composite powders synthesized with various Fe$^{2+}$ concentrations are shown in Fig. 8b with uncoated powders. Smooth
demagnetization curves for all nanocomposites suggest that the magnetic hard and soft phases are well exchange-coupled. Coating of Fe nanoparticles layer leads to an obvious increase of $J_r$. Using a high Fe$^{2+}$ concentration solution (0.17 M FeSO$_4$), a high $J_r$ was obtained, which gives a remanence enhancement of around 6.5%. A layer of Fe$_{65}$Co$_{35}$ alloy can further increase $J_r$ of the nanocomposite since Fe$_{65}$Co$_{35}$ alloy has higher $J_s$ than Fe or Co at room temperature. This work provides an easy approach to prepare exchange-coupled nanocomposites with controllable compositions and sizes of both hard and soft phases.

**Densification technology**

**Spark plasma sintering (SPS)** has been suggested [17] as a consolidation technique to achieve nanostructure in the bulk magnets from nanocrystalline powders. One of the important advantages of the SPS is the high sintering speed, which can effectively restrain the grain growth and allow preparation of high-density fine crystalline materials [18]. It is also possible to compact NdFeB magnet without Nd-rich phase, such as nanocomposite [19]. SPS process utilizes a momentary local high-temperature field generated by pulse energy, and Joule heating to heat the specimen. The Joule heating is mainly located at the particle boundaries. This leads to grain growth at the particle boundaries, while the grains inside the particles have a less tendency for growth. Two distinguished zones with various grain sizes, thus, were observed. We refer the two zones as the coarse grain zone and fine grain zone [20] due to the obvious difference in grain size, as indicated in Fig.9a inset. For a quantitative analysis. Fig.11a shows the dependences of the average width of the fine grain zone and the average ratio of fine grain zone area on the sintering temperature. It is very clear that the width of the fine grain zone increase with the decreasing SPS temperature. SPS at 600-650°C does not lead to significant grain growth and large area of coarse grain zone in the sintered magnets and uniform grain structure can be obtained. The variations of mean grain sizes $d_g$ with SPS temperature are plotted in Fig.9b. Both mean sizes in fine grain zone and coarse grain zone increase with the SPS temperature, but the growth of grain is more obvious in coarse grain zones.

![Fig. 9. The fine grain zone width and ratio (inset: SEM image for the typical structure of SPSed magnet) (a) and the mean grain sizes in coarse grain zone and in fine grain zone (b) for NdFeB magnets SPSed at various temperatures ($P_{\text{SPS}} = 50 \text{ MPa}; t_{\text{SPS}} = 5 \text{ min}$)](image)

The SPS parameters including $T_{\text{SPS}}$, $P_{\text{SPS}}$ and $t_{\text{SPS}}$ have important effects on the density. The effects of SPS temperature on the density and magnetic properties of NdFeB magnets are plotted in Fig.10. Not surprisingly, in the temperature range 600°C-800°C, the density of the magnet increases with the increase of SPS temperature. With increase of $T_{\text{SPS}}$, the coercivity $J_H$ increases first and decreases after the temperature reaches 700°C. Since there is no heavy rare earth elements, such as Dy or Tb, in our rare earth -rich isotropic sample, the obtained magnetic properties with $(BH)_{\text{max}}$>110 kJ/m$^3$ are indeed very promising. The results also show that, even SPSed at 800°C, the SPSed magnet still have good magnetic properties due to the high ratio of fine grain zone in the magnet (>60%), which indicates the obvious advantages of SPS process for inhibiting grain growth.
Using the NdFeB/nano-Fe composite powders synthesized by chemical method, bulk nanocomposite NdFeB/nano-Fe magnets with density of 7.2 g/cm$^3$ were fabricated by spark plasma sintering (SPS). The sample and hysteresis loops are shown in Fig.4. With increase of the Fe content, the magnetization increases at the expense of coercivity. The results also showed the existence of exchange coupling interaction between soft and hard phases. The results indirectly demonstrate that the nanocomposite structure obtained by chemical method can be maintained after advanced sintering process.

![Fig. 10. The density and magnetic properties for NdFeB magnets SPSed at various temperatures (P_{SPS} = 50 MPa; t_{SPS} = 5 min) (b) and the hysteresis loops for bulk composites sintered from the NdFeB/nano-Fe powders prepared with two Fe$^{2+}$ concentrations by chemical co-precipitation](image)

### High velocity press (HVP), as a shock compaction technique, has been emerged as a promising technique for powder consolidation although it did not applied for preparing NdFeB magnets. We recently fabricated the NdFeB magnet by HVP (Fig.11a inset) without using any binding agent. Good magnetic properties have been obtained. The microstructure (Fig.11b) shows that dense consolidation can be realized and the ultrafine grain structure can be maintained in the magnet. Hence, we believe that HVP can be extended for nanocrystalline NdFeB magnet preparation.

![Fig. 11. Hysteresis loops for starting powders and high velocity pressed magnet (a) and SEM of high velocity pressed magnet (b)](image)

### Anisotropic nanocrystalline magnets: To enhance magnetic properties, it is important to achieve anisotropy in nanocomposite magnets. The combination of SPS and hot deformation process has been quite successful recently [21,22]. Fig.14a is a low magnification SEM image of HDed magnet, showing densified deformed grain structure. Fig.14b shows the hysteresis loops for SPS+HDed magnets parallel to the compression direction under various compression rates, indicating an obvious magnetic anisotropy behavior. Excellent magnetic properties have been obtained at the temperature of 300 K in the magnets along the easy direction, including $J_r = 1.32$ T, $J_{Hc} = $ kA/m, and $(BH)_{max} = 303$ kJ/m$^3$. Here the $(BH)_{max}$ is almost tripled after HD, indicating that current process provides a good approach to improve the magnetic properties of isotropic nanocrystalline NdFeb alloy.
Fig. 12. Microstructure (a) and hysteresis loops along easy axis (b) for SPS+HDed magnet

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References

Computational Model of Phase Transformations in Thermo-Chemical Cathodes Using Kinetic Approach

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Keywords: Phase transformation, Thermo-chemical cathodes, Mathematical model

Abstract: The paper presents the results of modeling of the processes of phases transformations occurring in cathode of plasmatron with zirconium insertion. Model describes temperature and liquid-solid phase transformation in cathode considering kinetics of transformation in accordance with a state diagram. The comparison between one-dimensional mathematical models was exploited for estimation of the kinetics coefficient. First model is based on well-known heat equation with Stefan’s condition on the free boundary between liquid and solid phases [1]. The standard analytical self-similar solution for two-phase case is applied. In the second model, for heat equation instead of Stefan’s conditions, differential equations of kinetics are used.

\[
\frac{dP_{hi}}{dt} = k_i (\text{sign}(P_{hi} - P_{i,eq}) \cdot |P_{hi} - P_{i,eq}|^\nu);
\]

where \(k_i\) are kinetic coefficients of \(P_{hi}\), phase transformation, \(P_{i,eq}\) - the equilibrium contents of \(P_{hi}\) for given temperature, which can be defined from steady state diagram [2,3,4]. After choosing proper value of kinetic coefficient (that ensures identical results of both solutions), it can be used for computation of heat and phase transformation processes in more complex geometry of both two-three-dimensional domain and shape of free boundary, where use of classical Stefan’s model represents more difficult task. Finally, results of numerical solutions are discussed.

Task Description

The mathematical model of thermo-chemical processes in the cathode of plasmatron [5], which is being heated by an electric arch, is investigated. The model describes temperature and phase states taking into account kinetic of phase transformation in accordance with a state diagram. As an example the case of copper cathodes with the zirconium insertion is considered as shown in Fig.1.

\[
\rho \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( \lambda(T) \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( \lambda(T) \frac{\partial T}{\partial z} \right) - L_s \frac{dX}{dt}, \quad \left( t > 0, \ 0 < r < r_k, \ 0 < z < z_0 \right).
\]
\[ \frac{dX}{dt} = K \cdot \text{sign}(X - X_{eq}) \cdot |X - X_{eq}|^\nu; \quad (t > 0, 0 < r < r_k, 0 < z < z_0), \]  
\[ (2) \]

where \( T = T(t, r, z) \) - the temperature °C; \( X = X(t, r, z) \) - relative quantity of liquid phase \( Zr \), in unit of volume, \( C_p \) – specific heat \([\text{J/kg} \cdot \text{K}]\), \( \rho \)- density \([\text{kg/m}^3]\) \( \kappa \) – thermal conductivity \([\text{W/m} \cdot \text{K}]\), \( L_{S,L} \) - latent heat of fusion \([\text{J/m}^3]\), \( K \) – kinetic coefficient \([1/\text{sec}]\), \( X_{eq} \) - equilibrium content of phase, in accordance with state diagram.

Initial and boundary conditions were

\[ T(0, r, z) = T_0 < T_{\text{melting}}; \quad T_R(t, 0, z) = 0; \]
\[ (3) \]

\[ T(t, r, 0) = T_r; \quad T(t, r, z_0) = T_1(r, z) = T_2(r, z) < T_{\text{melting}}, \]

where \( T_b, T_1, T_2 \) – known functions

\[ X(0, r, z) = 0; \quad X_{eq} = \begin{cases} 1, & T < T_{\text{melting}} \\ 0, & T > T_{\text{melting}} \end{cases}. \]
\[ (4) \]

There is a melting of metal at heating a surface of an electrode and, simultaneously there is a rise in the temperature which results in the border dividing solid and liquid phases moves ahead deep into the electrode.

The above model is simpler than the Stefan’s approach of describing an analogical phase transformation \([2,3,4]\), because eliminates problem with calculation of coordinates of the free boundary \( S(t, r, z) \) from nonlinear Stefan’s equation:

\[ \lambda_1 T_{xN}(S) - \lambda_2 T_{xN}(S) = L_{S,L} V_{S,N}; \quad (r, z) \in S, \quad t > 0, \]

where index \( N \) means normal direction to boundary \( S(t, r, z) \), \( V_{S,L} \) – velocity of boundary motion in direction \( N \). But offered approach demands determination of the phase transformation kinetic coefficient \( K \).

**Kinetic Coefficient \( K \) Estimation:** The numerical results by above mentioned kinetics approach (using different values of \( K \)) were comparing with the known exact solution of self-similar two-phases one-dimensional Stefan’s problem and proper value of kinetic coefficient was chosen (that ensures closest results of both solutions). Mathematical descriptions of tasks are as follows:

**One-Dimensional Two-Phases Stefan Problem:** Let \( x \) and \( t \) be the dimensional and time coordinates respectively. One must find \( T_1(x, t), T_2(x, t), \alpha(t) \) which satisfy following conditions:

\[ T_1' = \alpha^2 T_{xx} \quad ; \quad -\infty < x < \alpha(t), \quad T_2' = \alpha^2 T_{xx} \quad ; \quad \alpha(t) < x < \infty, \]
\[ (5) \]

After substitution \( T_i(x, t) = T(x, t) - T_{\text{melting}} \), initial conditions at \( t = 0 \) are:

\[ \alpha(0) = 0, \quad T_1 = T_1^0 < 0, \quad \forall x < 0, \quad \text{and} \quad T_2 = T_2^0 > 0, \quad \forall x > 0, \]

Boundary conditions are:

\[ T_1\big|_{x=-\infty} = T_1^0, \quad T_2\big|_{x=\infty} = T_2^0, \quad (\forall t > 0), \]

On \( x = \alpha(t) \), free boundary conditions are:

\[ T_1(\alpha(t), t) = T_2(\alpha(t), t), \quad T_1(\alpha(t), t) = T_2(\alpha(t), t) = L_{S,L} \frac{d\alpha(t)}{dt}, \]
\[ (6) \]

where \( \alpha^2 \) are the thermal diffusivity coefficients \((\kappa/c_p\rho)\), other parameters are the same as in task (1-4). A known solution of task (7)-(12) can be written as follows [1]:

\[ \alpha(t) = \alpha_0 \sqrt{t}, \]
\[ (7) \]
\[ T_i(x,t) = T_i^0 \left(1 - \text{erfc} \left( \frac{(-1)^i x}{2a_i \sqrt{t}} \right) \right) \left/ \text{erfc} \left( \frac{-(-1)^i x_0}{2a_i} \right) \right), \quad i = 1, 2, \]

where

\[ \text{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^{\infty} e^{-y^2} dy, \]

The value of \( \alpha_0 \) is defined from nonlinear Stefan condition (6), which can be written as follows:

\[ \frac{\exp(-z^2)}{\text{erfc}(-z)} - A_2 \frac{\exp(-A_2^2 z^2)}{\text{erfc}(A_2 z)} = A_2 z, \quad (8) \]

where

\[ z = \frac{\alpha_0}{2a_i}, \quad A_1 = \frac{a_1}{a_2} = \sqrt{\frac{a_1^2}{a_2^2}} > 0, \quad A_2 = -A_1, \quad A_3 = -\sqrt{\pi a_i^2} L_{S,L} > 0, \]

Existence of solution of Eq. 8 is obvious because left side of the equation goes to \(+\infty\) by \( z \to -\infty \) whereas it goes to \(-\infty\) by \( z \to \infty \). At the same time right part of the equation changes from \(-\infty\) to \(+\infty\).

**Non-Stefan Approach:** Now we want to compare solution (7) with solution of non-Stefan model of the same process [2,3,4]:

\[ T_i = a^2(T) T_{xx} + F(x,T), \quad -\infty < x < \infty, t > 0, \quad (9) \]

where \( a^2(t) \) is the heat diffusivity coefficient which depends on temperature only.

\[ a^2(T) = \begin{cases} a_1^2 & \text{for } T < T_{melting} (\text{solid phase}) \\ a_2^2 & \text{for } T > T_{melting} (\text{liquid phase}) \end{cases} \]

where \( T_{\alpha} \) is the average temperature of phase transformation.

Initial conditions are as follows:

\[ T(x,0) = \begin{cases} T_i^0 < T_{melting} (\text{solid phase}) \\ T_i^0 > T_{melting} (\text{liquid phase}) \end{cases} \quad (10) \]

Boundary conditions are:

a) \( T(-\infty, t) = T_i^0 \), \quad b) \( T(\infty, t) = T_2^0 \), \quad (11)

\( F(x,T) \) represents heat source (or sink) from latent heat of phase transformation, which is \( F(x,T) = R X_i \),

where \( X_i = X_i(x,T) \) is the content of \( i-th \) phase in a substance (e.g. \( X_1 \) is the content of solid phase, \( X_2 \) is the content of liquid phase), \( R = L_{S,L}/c_p \). We suppose that

\[ X_1 + X_2 = 1; \quad \forall(x,t), \quad (12) \]

\( X_i \) are to be determined from usual equations of kinetics:

\[ \frac{dX_i}{dt} = K \cdot \text{sign}(X - X_{eq}) \cdot |X - X_{eq}|^\nu; \quad (13) \]

where \( K \) is the kinetic coefficient of phase transformations, \( X_{eq} \) are the equilibrium contents of \( X_i \) as given \( T \) which can be defined from steady state diagram.

For our case:
We use one Eq. 14 together with Eq. 13 to avoid violation of the mass conservation law, especially by numerical solution of task (9)-(14).

**Numerical Solution Results**

Now a two phase problem is considered to compare the solution of (7) with the solution of (9)-(14). In this problem one phase is solid and second phase is liquid Zr. For these substances the parameters of processes are as follows [5, 6]:

Thermal diffusivities:
\[ a_1^2 = 1.34 \times 10^{-2} m^2 / s, \quad a_2^2 = 1.3 \times 10^{-4} m^2 / s; \]

thermal conductivities (close to melting point):
\[ \lambda_1 = 37.5 W / m.K; \quad \lambda_2 = 36.5 W / m.K, \quad T(\alpha,t) = 0; \quad (15) \]

\[ L_{L,S} = 1.7 \cdot 10^4 J / mol \approx 1.2 \cdot 10^9 J / m^3, \]

and we used interpolation: \( a^2(T) = a_1^2 X_1 + a_2^2 \cdot (1 - X_1) \), in accordance with condition (12).

Initial conditions for temperature (after substitution: \( T = T - T_{melting} \)) were as follows:
\[ T(x,0) = -1 \quad for \ x < 0, \quad solid \ phase; \quad T(x,0) = +30 \quad for \ x > 0, \quad liquid \ phase, \]

Using those parameters the value of unknown \( \alpha_0 \) has been calculated by the Eq. 8:
\[ \alpha_0 = -2.7 \cdot 10^{-6} m / \sqrt{s} = -2.7 \cdot 10^{-4} cm / \sqrt{s}. \]

The standard difference approximation of task (10)-(15) was obtained using the forward-difference method [4]. Results of numerical calculations of \( \alpha(t) \) for different values of kinetic coefficient \( K \) given in a Table 1 and on Fig.2.

It is quite expected that the width of zone which contains mix of both phases grows by decreasing of \( K \) and \( \alpha_{calc} \) becomes closer to \( \alpha(t) \) by greater values of \( K \) (see Fig.2). But there was not significant increasing of accuracy of calculations for values \( K \) above 0.3-0.5.
Table 1. Values of free boundary coordinate $\alpha(t)$ (Stefan’s solution (8)) and calculated $\alpha_{\text{calc}}$ coordinate of point where $T(\alpha_{\text{calc}}, t) = 0$ for task (10)-(15) by different values time $t$ and kinetic coefficient $K$. $\Delta \text{mix}$ – width of zone which contains mix of both solid phase 1 and liquid phase 2.

<table>
<thead>
<tr>
<th>K</th>
<th>$t = 25$ [sec]; $\alpha(t) = 0.0014$ [m]</th>
<th>$t = 100$ [sec]; $\alpha(t) = 0.0027$ [m]</th>
<th>$t = 250$ [sec]; $\alpha(t) = 0.0043$ [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha_{\text{calc}}$</td>
<td>$\Delta \text{mix}$</td>
<td>$\alpha_{\text{calc}}$</td>
</tr>
<tr>
<td>0.01</td>
<td>0.0043</td>
<td>0.008</td>
<td>0.0045</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0017</td>
<td>0.002</td>
<td>0.0031</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0016</td>
<td>0.001</td>
<td>0.0029</td>
</tr>
</tbody>
</table>

Figure 2. Values of $\alpha(t)$: 1 - exact values,(13); 2, 3, 4 - numeric calculations for $K=0.01; 0.1; 0.3$, respectively.

After estimation of $K$, solution of initial two-dimensional task (1)-(4) was found, using value of kinetic coefficient $K = 0.3$, [1/s]. Functions $T_1$ and $T_2$ in boundary condition (3) were defined from conditions of experimental data:

1. The temperature in the center of a cathode spot $T(t, 0, 0)$ is close to temperature of boiling of zirconium (~ 3500 °C), [2]
2. The temperature in a zone of contact between the zirconium insert and a body of the cathode $T(r_k, 0)$ should be a little below melting point of copper, i.e. about 1000 °C
3. Initial temperature $T_0 = 300$ °C, $T_{\text{melting}} = 1855$ °C, $r_k = 0.002$ m, $z_0 = 0.005$ m,

In accordance with those conditions function $T_1$ was chosen as

$$T_1(t,r,0) = A \left( B^2 + r^2 \right)^{-\frac{1}{2}},$$

where $A = 2.024$, $B = 0.578 \times 10^{-3}$. 

Some results of numerical calculations of $\alpha(t)$  (where $T(t,r,z) \approx T_{\text{melting}} = 1855^\circ C$) with using forward-difference approximation of task (1)-(4) for different values of kinetic coefficient $K$ is shown as Fig. 3. Width of mix-zone is about 15% of value $\alpha(t)$ for 1,2 variants and less than 5% for variant 3, which is close to steady state solution.

References

Recent Advances in Fatigue Crack Growth

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Keywords: Fatigue crack growth, fatigue crack closure, non-propagating cracks, short fatigue cracks, fatigue notch sensitivity, very high cycle fatigue (VHCF)

Abstract: Many of the recent advances in the understanding of the fatigue crack growth process have resulted from an improved realization of the importance of fatigue crack closure in the crack growth process. Two basic crack closure processes have been identified. One of which is known as plasticity-induced fatigue crack closure (PIFCC), and the other is roughness-induced fatigue crack closure (RIFCC). Both forms occur in all alloys, but PIFCC is a surface-related process which is dominant in aluminum alloys such as 2024-T3, whereas RIFCC is dominant in most steels and titanium alloys.

A proposed basic equation governing fatigue crack growth is

\[
\frac{da}{dN} = A(\Delta K_{eff} - \Delta K_{th})^2
\]  

where \( \Delta K_{eff} = K_{max} - K_{op} \) where \( K_{max} \) is the maximum stress intensity factor in a loading cycle and \( K_{op} \) is the stress intensity factor at the crack opening level. \( \Delta K_{th} \) is the range of the stress intensity factor at the threshold level which is taken to correspond to a crack growth rate of 10-11 m/cycle. The material constant \( A \) has units of (MPa)-2, and therefore Eq. 1 is dimensionally correct. Eq. 1 has been successfully used in the analysis of both long and short cracks, but in the latter case modification is needed to account for elastic-plastic behavior, the development of crack closure, and the Kitagawa effect which shows that the fatigue strength rather than the threshold level is the controlling factor determining the rate of fatigue crack growth in the very short fatigue crack growth range.

Eq. 1 is used to show that

1. The non-propagating cracks observed by Frost and Dugdale resulted from crack closure.
2. The behavior of cracks as short as 10 microns in length can be predicted.
3. Fatigue notch sensitivity is related to crack closure.
4. Very high cycle fatigue (VHCF) behavior is also associated with fatigue crack closure.

Introduction

Some forty years ago Elber [1] discovered the phenomenon known as crack closure. Crack closure can be defined as the contacting of the opposing faces of a fatigue crack during the unloading portion of a fatigue cycle before the minimum load of the cycle is reached. There is also a crack opening level during the loading portion of a cycle when the opposite faces of a fatigue crack separate. Elber considered that the only effective portion of the cycle in propagating a crack was that portion of the cycle between the opening level and the maximum of the cycle, as expressed in the following equation:

\[
\Delta K_{eff} = K_{max} - K_{op}
\]

The crack closure process has been used for example to account for R effects in fatigue crack growth, where R is the minimum load divided by the maximum load, as well as for the retardation that occurs after an overload.
It is now recognized that there are two inherent types of fatigue crack closure [2]. One is referred to as plasticity-induced crack closure (PIFCC), and the other as roughness-induced fatigue crack closure (RIFCC). In a plane specimen, PIFCC is a surface related event brought about by the movement of material in the thickness direction from the surface toward the interior of a specimen due to the lateral contraction of the specimen at the crack tip during the loading process. This lateral contraction is indicated in Fig. 1a. (Figure 1b will be discussed later.) In this figure, the loading direction is vertical. The line outlines the shape of the crack tip plastic zone, with material moving laterally from the right to the left in the thickness direction. The material transported to the subsurface from the surface prevents the crack from closing completely during unloading and results in PIFCC. As the crack grows and \( \Delta K \) increases the magnitude of \( K_{\text{op}} \) also increases as more excess material is accumulated in the wake of the crack tip. This is the explanation for the PIFCC which Elber investigated in structural aluminum aircraft alloys. That PIFCC is a surface-related phenomenon can be shown by determining the \( K_{\text{op}} \) level before and after machining away the surface layers as indicated in Fig. 2 [2]. Note that after each machining step there is a significant drop in \( K_{\text{op}} \).

The other form of inherent closure, RIFCC, differs from PIFCC in that it is through-thickness in nature. This can be shown by machining away the surface layers and finding no change in \( K_{\text{op}} \) [2]. RIFCC occurs in steels and in titanium alloys. This type of closure results from the contact of asperities on mating fracture surfaces and, in contrast to PIFCC, is independent of the \( \Delta K \) level. Fig 1b shows that for a low-carbon steel the degree of lateral contraction is more diffuse and much less than for an aluminum alloy. In this case, any PIFCC is dominated by the RIFCC.

With this background in crack closure we can next proceed to the analysis of fatigue crack growth.

**Fatigue Crack Growth**

The following equation will be used in the analysis of fatigue crack growth:

\[
\frac{da}{dN} = A(\Delta K_{\text{eff}} - \Delta K_{\text{eff}})^2
\]  

(2)

Where \( a \) is the crack length, \( N \) is the number of cycles, \( A \) is a material constant of dimensions \((\text{MPa})^{-2}\), and \( \Delta K_{\text{eff}} \) is the effective range of \( \Delta K \) at the threshold level which is taken to correspond to a growth rate of \( 10^{-11} \) m/cycle. It is noted that Eq. 2 is dimensionally correct. Figure 3 shows an example of the use of Eq. 2 in the linear elastic fracture mechanics (LEFM) analysis of long cracks as a function of \( R \) in the titanium alloy Ti-6Al-4V. In this example fully developed RIFCC is involved, and a term \( \left(1 + \frac{\Delta K_{\text{eff}}}{K_c - K_{\text{max}}} \right) \) has been added to Eq. 2 to account for the occurrence of static
modes of fracture at high $\Delta K$ levels. From Fig. 3 we can conclude that Eq. 2 describes the crack growth behavior rather well, and as Elber suggested, the use of $\Delta K_{\text{eff}}$ eliminates the effect of $R$ on the rate of fatigue crack growth. Note that there is a region of transition in the plot. It is thought that this transition occurs on increase in $\Delta K$ when the mode of growth changes from Mode II (shear mode) to Mode I (the opening mode). This change may occur when the plastic zone size in Ti-6Al-4V exceeds the alpha grain size and two slip systems can then act at the crack tip to propagate the crack.

![Graph showing crack growth behavior](image)

**Fig. 2.** The effect of surface machining on the $K_{op}$ level in a 6061-T6 aluminum alloy [2]

A perhaps more interesting analysis has to be made to account for the growth behavior of short cracks. Short cracks differ from long cracks in three important ways [3]:

1. The fatigue strength may be close to the yield strength, so that elastic-plastic behavior rather than linear-elastic behavior may be involved.
2. As a new crack develops, initially there is no crack wake and no crack closure. The $K_{op}$ level increase from zero to the level associated with a long crack, $K_{opmx}$, over a distance of 0.5 mm or so.
3. For cracks of only some ten microns in length, the fatigue strength rather than the threshold level becomes a controlling factor (Kitagawa effect [4]).
Eq. 2 has to be modified in order to deal with the above three items. The resulting equation is:

\[
\frac{da}{dN} = A \left[ \left( \sqrt{2\pi r_c F} + Y \sqrt{\pi a F} \right) \Delta \sigma - \left( 1 - e^{-k\lambda} \right) \left( K_{op\max} - K_{min} \right) - \Delta K_{effth} \right]^2
\]

(3)

Where \( r_c \) is a material constant of the order of one micron in length, \( F \) is the elastic-plastic correction factor, \( Y \) is a geometrical factor, being 0.73 for a semi-circular crack, and 1.12 for a through crack in a plate, \( k \) is a material constant which governs the rate of crack closure development with a value of 6000 m\(^{-1}\) for many steels, and \( \lambda \) is the length of the crack measured from the surface or from the tip of a notch. A detailed explanation of the derivation of Eq. 3 is available in ref. [3]

**Applications**

**Non-propagating cracks from notches [5]:** In 1957 Frost and Dugdale [6] published a paper in which it was shown that for notches in a steel plate of 0.1 - 0.5 mm radius and 5 mm depth, fatigue cracks were able to propagate to failure only at stress amplitudes above 50 MPa, independent of the notch radius. Below this stress amplitude non-propagating cracks of the order of 1 mm in length were formed. These non-propagating cracks formed because of the development of crack closure in the wakes of the crack tips. In order for a fatigue crack to grow to failure it must overcome two barriers. One of these is \( \Delta K_{effth} \), which for steels is about 3.0 MPa\(\sqrt{\text{m}}\), and the other is crack closure. The amount of crack closure depends upon the material constant \( k \) and the magnitude of \( K_{op\max} \), the crack opening level for a long crack, which in this case was taken to be 4.7 MPa\(\sqrt{\text{m}}\).

The solid line in Fig. 4 indicates the stress amplitude required to propagate a crack at 10-11 m/cycle, the threshold level where the driving force equals the resisting force, as a function of \( \lambda \), the crack length. Because the crack closure level increases from zero to a maximum, the stress amplitude required to propagate a crack at the threshold level increases to a maximum and then decreases as the driving force becomes greater than the resisting force.

**Analysis of Short Crack Behavior:** Figure 5 is a plot of the stress amplitude at the fatigue strength level (10-11 m/cycle) as a function of crack length for R -1 loading [7]. It is noted that the shortest crack is but 10 microns in length. In deriving these results, Eq. 3 modified for R -1 loading was used. Note that the increase in stress amplitude above the \( \Delta K_{effth} \) level is due to the development of crack closure. This example together with Fig. 3 shows that the computational procedures developed are able to deal with both long and short cracks within the same framework of analysis.

Fig. 4. A plot of the stress amplitude required to propagate a crack in a notched plate as a function of the crack length \( \lambda \) measured from the tip of a notch. The notch depth, \( a_0 \), was 5.0 mm
Fatigue Notch Sensitivity [3]: It is well known that the fatigue notch factor, $K_F$ (the ratio of the fatigue strength of an unnotched specimen to that of a notched specimen), is less than the value of KT, the theoretical stress concentration factor. For specimens of notch radii less than several millimeters this effect is due to crack closure. For example, consider Fig.6. Crack growth at the threshold level begins from holes of differing radii at a stress range of 200 MPa, but for hole radii of 0.20 mm and 0.48 mm the stress range must be increased to offset the effects of crack closure. The fatigue strength of the specimens corresponds to the peak stress and results in $K_F$ being less than KT.
Very High Cycle Fatigue (VHCF) [9]: In recent years VHCF has been a topic of interest. Why do some materials such as die steels and Ti-6Al-4V alloys fail after $10^8 - 10^9$ cycles of loading at stress amplitudes below the nominal (in-air) fatigue strength? In such cases why is the fatigue fracture origin subsurface? We are still seeking answers to these questions, but some new ideas have been put forth. For example, the stress amplitudes in VHCF are so low that crack closure provides a barrier to fatigue crack growth somewhat similar to the case of non-propagating cracks. Surface oxides may make the surface layers resistant to fatigue crack initiation, and sub-surface sites become favored. Yet the crack closure barrier remains. In the case of Ti-6Al-4V alloys Oguma [10] has shown there is evidence of wear of the fracture surfaces in the case of VHCF which is not found in the case of surface-nucleated fatigue cracking in air. Figure 7 [9] indicates just how wear can affect the crack closure level to allow a fatigue crack to propagate. At a maximum stress of 750 MPa ($R = 0.1$) a cleavage facet is formed at a subsurface locale. Initially the crack would not be able to propagate, but as wear takes place in subsequent cycles just ahead of the facet and the crack closure level is reduced, the fatigue crack will be able to advance an increment. This wear-and-growth process is repeated over and over again until the crack is of sufficient length that crack closure is no longer a barrier. After this point is reached the crack can propagate relatively rapidly to failure. Most of the VHCF lifetime is spent in the wear process.

![Figure 7](image-url)  
**Fig. 7.** The stress required for fatigue crack propagation at $R = 0.1$

At a maximum stress of 825 MPa (Fig. 7) a fatigue crack can propagate at a relatively rapid rate to failure. At 750 MPa the crack cannot propagate because the driving force, $D$, is less than the resisting force, $R$. When the wear process reduces the crack closure level, $R$, to that of the driving level, $D$, an increment of growth can occur at the crack tip. This process is repeated over and over until the crack propagates past the closure barrier, thereby accounting for VHCF.

**Concluding Remarks**

In this paper crack closure has played an important role in providing a clearer understanding of the factors involved in both long and short fatigue crack growth. It is urged that researchers determine the crack closure levels in their experimental work, for this will then focus attention on $\Delta K_{effth}$, the real driving force for fatigue crack growth.
References


Viscoelastic Response of HTPB Based Solid Fuel to Horizontal and Vertical Storage Slumping Conditions and It’s Affect on Service Life

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**Abstract:** Frequent use of solid fuels as thrust generating energy source in modern day space vehicle systems has created a need to assess their serviceability for long term storage under various conditions. Solid fuel grain, the most important part of any solid fuel system, responds viscoelastically to any loading condition. For the assessment of the service life of any solid fuel system, the solid fuel grain has to be structurally evaluated in applied storage conditions. Structural integrity of the grain is exceptionally significant to guarantee the successful operation of the solid fuel system. In this work, numerical simulations have been performed to assess the mechanical stresses and strains induced in an HTPB based solid fuel grain during service life employing ABAQUS standard FEA software using 4-node bilinear quadrilateral elements. For finite element analysis (FEA), typical 2-D and \( \pi/n \) axisymmetric section of 5-point (n) star grain geometry is considered. Mechanical loads include the horizontal or vertical 1-g (solid fuel weight) storage condition. The simulation results are compared with the analytical results for the same grain geometry. Analytically measured slump deflections in grain segment at various storage times have been found in good relation with the FEA based simulation results. This proves the validity of the procedure adopted and is helpful in assessment of the service life of solid fuel systems.

**Introduction**

Ready-to-use state of solid fuel systems provides an opportunity to store/deploy them in various modes/schemes for long durations [1]. Mostly a solid fuel system is stored in vertical or horizontal position, however, the deployment scheme could be horizontal, vertical or in an inclined plane for various reasons. The most important fundamental part of a solid fuel system is the solid fuel charge which is a polymeric material (usually a solid high polymer) and hence exhibits a viscoelastic behavior [2]. Therefore, long term storage of a solid fuel system in any position (vertical or horizontal) means steady application of load on the solid charge structure which results in the deformation (small or large) of this polymeric material [1–5]. Although the loads in storage condition are always below yield-point, but the creep behavior of the solid fuel grain converts small loads imposed for longer duration into large deformations [4–6, 15–17]. In addition, handling of the solid fuel system during repositioning or deployment phase, e.g., from vertical to horizontal, creates a tip-over loading [4] which can also contribute to generate a significant effect on the damage evolution in solid fuel (specifically for larger systems) [4–8].

Guarantee of a safe operation of the system during storage period of time requires a complete evaluation of the structure of solid fuel casted in the system [1–5, 9, 10, 15–17]. This includes structural and thermo-mechanical analysis of the casted solid high polymer (the solid fuel) and its bond-line strength [3, 16]. Only an accurate prediction of the resulting state of stress and deformation in the grain and in the case will allow an appraisal of the effect of such storage on the performance of the rocket [3]. In this regards, the determination of the state of stress and strain existing in a cylindrical grain, bonded to a motor case and subjected to a transverse body force, was initially considered by Blatz et al [2]. Work has also been done in generating empirical relationships for the estimation of slumping in solid charges subjected to gravity loadings [4, 5, 16]. However, it has been classified as a tedious and less accurate a job to do [4, 5], especially when complex shape solid fuel geometry has to be considered for assessment [5]. The advent of high performance finite