



Initial Studies of Gun Tube Erosion Macroscopic Surface Kinetics

by Paul J. Conroy, Michael J. Nusca, Cary Chabalowski,
and William R. Anderson

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Abstract

Current theories concerning gun tube erosion consider that erosion can occur under various conditions. The worst condition occurs when the melting temperature of the gun steel is exceeded for the tube's inner surface. This causes the tube to grossly melt. This melt wipe mechanism is not as simple as once thought because the propellant product gases are known to react with the surface, resulting in an altered surface material. This altered material may have a lower melting temperature than that of the gun steel and/or weakened mechanical properties. Previous surface reaction studies by the authors used a generalized equilibrium scheme with a control volume analysis to represent surface reactions occurring during a cannon firing. This led to a postreaction treatment at the interface which incorporated the subsurface diffusion of species to limit the surface reaction. In this study, the surface reactions and rates are specified explicitly with published rates and guidance from fundamental molecular modeling results. The results demonstrate the utility of the surface reaction mechanism presently employed and the incorporation of finite rate surface kinetics in the fundamental physical representation of erosion.

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1. Introduction

In consideration of the development of the Future Combat System, it is necessary to understand the physics and chemistry of the interior ballistic erosion problem in order to focus mitigation efforts. This study focuses on incorporating and applying generalized finite rate kinetics to the gun tube erosion problem. Previously, a melt wipe model (Weinacht and Conroy 1996; Conroy et al. 1997) was documented, followed by the inclusion of generalized equilibrium (Conroy et al. 1997, 1998, 1999b). The melt wipe description enabled very severely eroding systems to be modeled (Conroy et al. 1997, 1999a). However, it did not account for the erosion in systems which apparently did not reach the melting temperature of the gun steel. These systems at the time were thought to have some form of augmented heat transfer due to projectile blowby (Gerber and Bundy 1994) or heat release at the surface due to chemical reactions. It was initially thought that the oxidation of the surface was releasing sufficient energy to melt the oxidized material. This material along with its energy was subsequently blown out of the gun tube in the product gases. Thus the tube effectively did not experience any additional heating, as might be evidenced experimentally. Chemical phenomena were investigated initially due to unusual behavior of RDX-containing propellants. The adiabatic flame temperature of M43, which contains RDX, is lower than that of M30, which does not contain RDX, while the erosivity was typically higher (Ward et al. 1981). This behavior conflicts with previously held beliefs and correlations which used the flame temperature to identify erosivity (Jones and Breitbart 1959; Frankle and Kruse 1967; Lawton 1984). Possible causes for this behavior were hypothesized after the inclusion and application of equilibrium chemistry to the erosion problem (Conroy et al. 1999b). The equilibrium chemistry required the definition of a specific control volume for the reaction which was defined by the diffusion depth of carbon into the surface. The premise was that no more steel could react with carbon or oxygen; therefore, the limiting factor was diffusion.

Although equilibrium chemistry continues to be applied for reaction of materials which diffuse into the substrate in this work, including finite rate kinetics at the surface has resulted in an elimination of many of the assumptions from the equilibrium calculations. Finite rate kinetics also allows the inclusion of many erosion reaction inhibition concepts which can lead or direct investigations of mitigating additives or chemical surface alterations.

2. Physical Description

Figure 1 describes the physical result of gun firings on a coated gun tube. The cracks inherent in the chrome, produced by either residual stresses from the manufacturing process or from thermomechanical cycling during gun firings, enable gases to reach the substrate where they react with the surface altering it from virgin gun steel. This altered surface is much easier to remove. A critical description of the loss of surface coatings was pointed out by Conroy et al. (1999b), namely in that the erosion preferentially traverses laterally under the coating following the conductive energy transported through the coating to the substrate. Thus, the interface between the substrate and the surface material is the hottest location at the bottom of the pit or crack and therefore the most reactive. This causes coating undermining and subsequent removal by high pressure gas in this region after the passage of the rarefaction wave during gun tube blowdown.

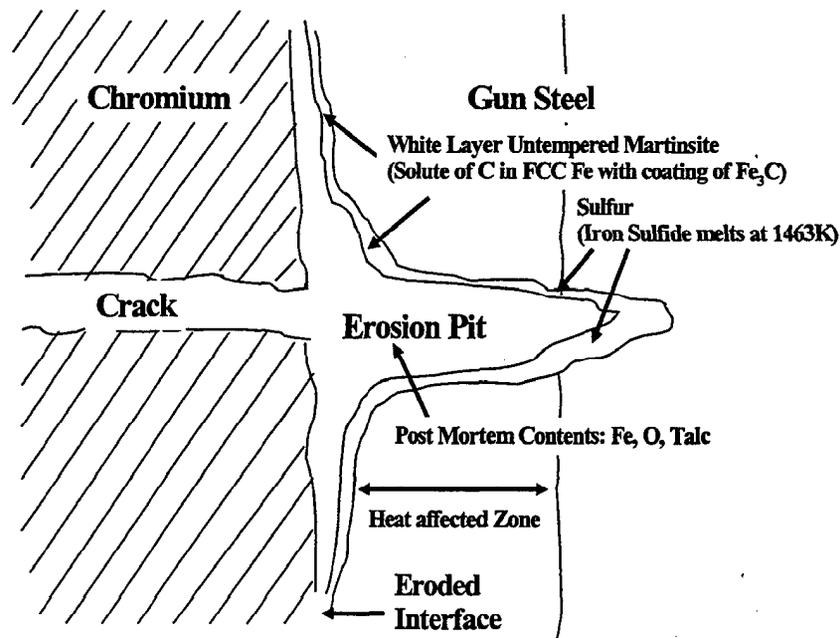


Figure 1. Description of postmortem erosion pit (Cote and Rickard 2000).

Figure 2 describes the physical representation that has been incorporated into the erosion model. Included in the figure and representation are the core flow species which supply both heat and mass transfer to the surface. Considered in the coating and the substrate is the calculation of stress resulting from both the surface boundary condition of pressure, as well as the mismatch in coefficients of thermal expansion between the coating and substrate. When the stress in the

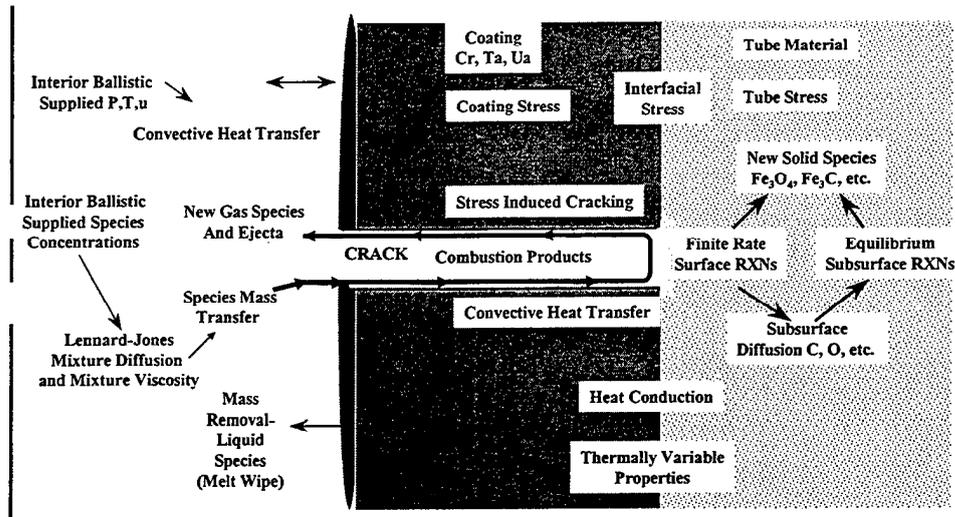


Figure 2. Analytical description including kinetics and coatings.

coating exceeds the ultimate strength, a crack is assumed to form. This produces a crack distribution within the coating. Excessive interfacial shear stress would cause the coating to delaminate and subsequently be removed. Convective heat transfer imparts energy to the surface of the coating as well as in the crack where it is augmented. Energy is transported through both the coating and substrate material. Further details are described in previous reports (Conroy et al. 1998, 1999b).

Surface kinetics have been included in the following manner. The species transported down into the crack are determined through multicomponent diffusion with Wilke's mixing rule to account for interactions. The quantity of surface iron available for reaction is determined from the thermally variable diffusion depth $\sqrt{\alpha dt}$ for carbon over the computational time step at the crack base surface temperature, where alpha is the diffusivity and dt is the time-step. The reaction mixture temperature is determined through a weighting function between the gas and solid phase materials. Given the specific heats, average molecular weight, identity and quantity of reactants, and the user-supplied reactions, the nonequilibrium kinetic subroutine models the reaction of the species through the macroscopic hydrodynamic time step. By specifying the maximum kinetic time step (which is much smaller than the hydrodynamic time step) to at least 1/25 but no more than 1/500 iterations per hydrodynamic time step, the product species from one kinetic computational sweep through the reaction mechanism can interact as reactants for all the other reactions in the mechanism.

When the kinetics routine calculation is completed for the hydrodynamic time step, the integrated quantity of carbon and oxygen, which diffused into the steel

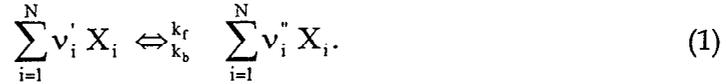
from the dissociation of CO, is subsequently reacted with the substrate through equilibrium chemistry as guided from previous work with the model. In the current model, binary diffusion of species into the solid phase is assumed. This approach does not account for cross terms of additional species. Inclusion of full multicomponent subsurface diffusion is planned as a future effort. The quantity of material diffused appears to be small in comparison to the surface reacting material, although during the cooling portion of the ballistic cycle the diffusion continues for quite some time after the surface passes the melting temperature of Fe₃C. The period of time between the time when the interface temperature decreases below the melting temperature of Fe₃C and the temperature at which diffusion stops is what potentially makes diffusion important. During this time, material is being inserted into the steel and the following shot will experience a loaded substrate which will be removed.

Once both the surface and subsurface systems have reacted, the postreacted products are prepared for carryover to the next time step. This step allows for determining whether energy released was positive or negative, as well as whether surface material was lost or gained. This energy is incorporated as a surface source term.

3. Nonequilibrium Chemical Kinetics

The nonequilibrium (or finite-rate) chemical kinetics subroutine has been adapted from the NSRG computational fluid dynamics code written at ARL (Nusca 1998), and recently applied to propulsive reacting flow systems (Nusca et al. 1999) as well as an open-air, high-speed chemically reacting jet (Nusca et al. 2000). In the NSRG code, this subroutine is used to compute the chemical source term that appears on the right-hand side of each species conservation equation in the Navier-Stokes equation set. For the present effort, this subroutine has been adapted so that it is patterned after the equilibrium subroutine, documented previously in Conroy et al. (1999b). As a result, the Army Research Laboratory Gun Tube Erosion Code (ATEC) determines the local flow conditions (density, temperature, and species mass fractions) and numerical conditions (time step or interval), while the nonequilibrium subroutine (using an appropriately smaller chemical time step) returns the new chemical constituency based on a predetermined set of chemical reactions and rates (i.e., the chemical mechanism). In this section, a general review of the nonequilibrium routine is given.

Chemical reactions can be expressed in a general fashion (where X_i represents the symbol for species i , for example H₂O) with stoichiometric coefficients, ν , for each species in these reactions:



A chemical kinetics mechanism consists of L such reactions. For each reaction, a general reaction rate equation is written, as in

$$\frac{dC_i}{dt} = \sum_{i=1}^L (v_i'' - v_i') \left(k_f \prod_i C_i^{v_i'} - k_b \prod_i C_i^{v_i''} \right), \quad (2)$$

where C_i represents the concentration of species i . This equation relates the time rate of change of this concentration for a particular species (the left-hand side) to the current values of concentrations for all N species, raised to powers of either the reactant coefficient (v -prime) or product coefficient (v -double-prime). In equation 2, the reaction rates (k) and the stoichiometric coefficients for the reaction (v) multiply the product sums. In order to compute the total change in C_i , this equation represents a sum over every reaction (total of L) in the reaction mechanism. The nonequilibrium routine determines the largest physical time step (dt in equation 2), which is also smaller than the fluid time step from ATEC, and computes the new species concentrations (using dC_i/dt) for all N species. Concentrations can be converted to mass fractions for convenience. In general, tens or hundreds of chemical time steps will have to be taken per one fluid time step. Nusca (1998) provides more details.

The forward reaction rate is usually defined using the Arrhenius form,

$$k_f = A T^n \exp(-E_a / kT), \quad (3)$$

where the rate data A , E_a , and n are determined from physical chemistry (k is Boltzmann's constant and is used to express E_a/k in temperature units). The backward rate can either be specified in the same form as the forward rate (above) or can be computed using the equilibrium constant for each reaction,

$$k_b = k_f / K_e ; K_e = \exp\left(-\frac{\Delta G}{RT}\right), \quad (4)$$

where K_e is the equilibrium constant for a particular reaction computed from the change in Gibbs energy (ΔG) for that reaction (see Nusca 1998 for details). Gibbs energy for each species is computed using the NASA Lewis database (Gordon and McBride 1971).

There are many situations for which reaction rates are of the additive type (wherein two rates are computed and added together for the final rate) or the pressure dependant "falloff" type (wherein the final rate is the product from three factors—two separate rates and a function based on the local flowfield temperature, pressure, and mixture). The nonequilibrium routine will accept

special coding for these cases. In other situations, certain reactions involve a "third-body" or a "collision partner" (often denoted M). The species M can stand for any of the N species being considered in the mechanism; thus, a single reaction involving M-type species is actually N reactions with the same reaction rate. For these N reactions, there is usually specified a third-body collision efficiency for a particular collider species. These efficiency factors are multiplied by the concentration of the collider species in the product summation terms of equation 2. The nonequilibrium routine is set up to automatically handle third-body reactions. For an example of these situations (i.e., non-Arrhenius reaction rates and third-body reactions), the reader is directed to Nusca et al. (2000).

4. Chemical Kinetics Mechanism

A finite rate chemical reaction module has been incorporated into the erosion package as described. Before using the package, a series of numerical experiments were made to insure that the correct information was passed to and returned from the module. One of the numerical validating experiments involves a simple set of reactions to test various areas of kinetics involving both temperature sensitivity as well as possible third body reactions, presented in Table 1.

Table 1. Example kinetics validation reaction set.

	Reaction	A (cm ³ /mole s) or (cm ⁶ /mole ² -s)	n (-)	Ea/k (K)	Third Body
1	H ₂ (g) + O ₂ (g) ⇌ 2OH (g)	1.7e13	0.0	24169	no
2	OH (g) + H ₂ (g) ⇌ H ₂ O(g) + H	2.2e13	0.0	2593.	no
3	OH(g) + H(g) ⇌ H ₂ O(g)	2.2e22	-2.0	0.0	yes

Table 2 describes the results for the validation kinetic reaction calculation, presented in Table 1, using the module as a stand-alone package (which has been extensively tested) (Nusca 1998) and the integrated version of the module in the erosion package. Both the stand alone and integrated versions produce identical results without the reverse reactions. However, if the reverse reactions are enabled, then the integrated package depends on the older version of the NASA Lewis database which is automatically read in, while the stand-alone package uses a newer NASA Lewis database. The differences observed with the reverse calculations implemented are due to the different versions of the thermochemical

Table 2. Mass fraction production rates for kinetics validation reaction set.

Integrated Kinetics (With and without backward reactions)				Stand-Alone Kinetics Module (With and without backward reactions)			
species	g/cm ³ -s			species	g/cm ³ -s		
1	-0.16962E+05	H		1	-0.16962E+05	H	
2	0.00000E+00	H ₂		2	0.00000E+00	H ₂	
3	0.00000E+00	O ₂	Without	3	0.00000E+00	O ₂	Without
4	-0.28622E+06	OH	Backward Rate	4	-0.28622E+06	OH	Backward Rate
5	0.30318E+06	H ₂ O		5	0.30318E+06	H ₂ O	
1	-0.16962E+05	H		1	-0.16962E+05	H	
2	0.18858E+00	H ₂		2	0.19973E+00	H ₂	
3	0.29935E+01	O ₂	With	3	0.31805E+01	O ₂	With
4	-0.28623E+06	OH	Backward Rate	4	-0.28623E+06	OH	Backward Rate
5	0.30318E+06	H ₂ O		5	0.30318E+06	H ₂ O	

database. If this ultimately causes large discrepancies, the older database could be updated; however, the effect appears to be orders of magnitude smaller than what would be considered an issue.

A proposed set of reactions between the primary propellant combustion products (H₂, CO, CO₂, H₂O) with the surface of the gun tube is presented in Table 3. Although the reverse reactions could have been included at this time, only the forward reactions are considered. The coefficients and exponents in Table 3 are literature values, except for the coefficient of reaction no. 2, which was not available from the literature. Fortunately, the exponent for reaction no. 2 was available. This provided a starting point from which to develop some estimates for the coefficient. A parametric study involving many calculations was performed on the coefficient, a few of which are presented in Figure 3. As the coefficient A₂ is increased from 3.8e14 to 6.0e14, the effect of reaction temperature and duration on pit growth is immediately clear. This modification affects the quantity of material removed in the forcing cone region. Farther down bore there is a gradual asymptote to a common amount of material removed.

A substantial difference exists between the previous calculation using infinite rate (equilibrium) chemistry and the finite rate chemistry results. The previous results do not take reaction rates into account; therefore, the pit growth rate results are much higher down bore than they apparently should be. The chemical reaction rates control the amount of product formed, as well as the supply of potential reactants for intermediate reactions. The depth of material typically removed from the base of a pit is between 0.7μ and 1.5μ per shot for this particular APFSDS round (Hubbard and Gilley 1998). This magnitude is verified by micrographs (Cote and Pickard 2000), such as those shown in Figure 4. This

Table 3. Proposed reaction mechanism.

	Reaction	A (cm ³ /mole-s) or (cm ⁶ /mole ² -s)	n (-)	Ea/k (K)	Third Body
1	CO(g) + O(ads) + (Surface) → CO ₂ (g) + (Surface) (Tsang and Hampson 1986)	6.17e14	0.0	1510.0	yes
2	CO(g) + (Surface) → C(ads) + O(ads) + (Surface) (Grabke 1964) (Collider)	5.2e14 (Estimate)	0.0	23903.0	no
3	O(ads) + O(ads) + (Surface) → O ₂ (g) + (Surface) (Tsang and Hampson 1986)	1.89e13	0.0	-900.0	yes
4	H(g) + OH(ads) + (Surface) → H ₂ O(g) + (Surface) (Baulch et al. 1992)	8.35e21	-2.0	0.0	yes
5	H ₂ (g) + (Surface) → 2H(g) + (Surface) (Tsang and Hampson 1986)	4.57e19	-1.4	52530.0	no
6	H(g) + O(ads) + (Surface) → OH(ads) + (Surface) (Tsang and Hampson 1986)	4.71e18	-1.0	0.0	yes
7	CO(g) + O ₂ (ads) + (Surface) → CO ₂ (g) + O(ads) + (Surface) (Tsang and Hampson 1986)	5.06e13	0.0	31800.0	no

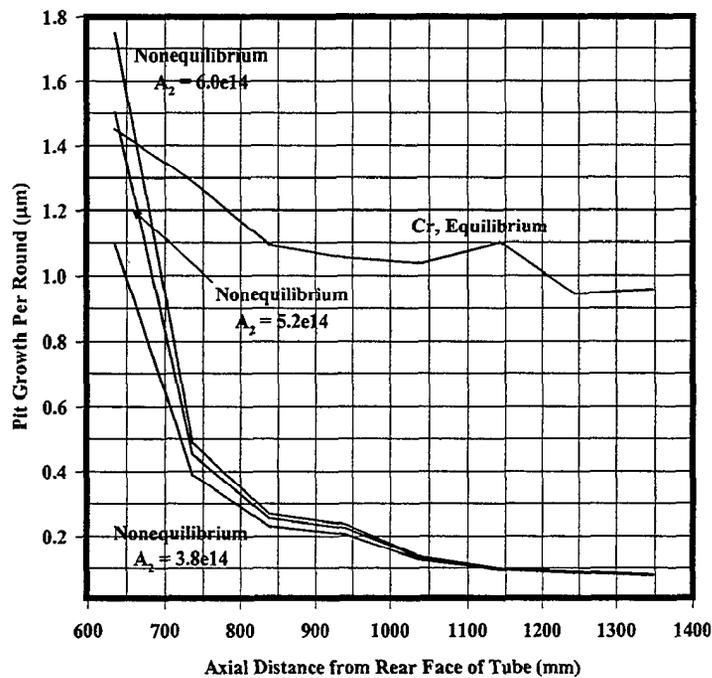
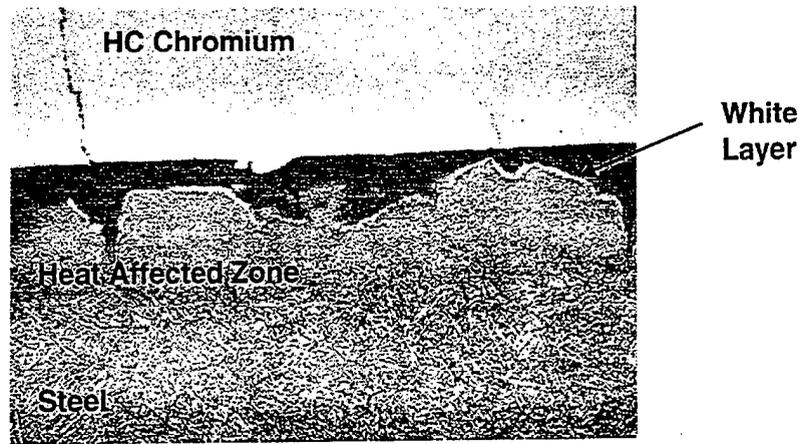


Figure 3. Pit growth rate for chrome coated steel, 120-mm M256 barrel firing, and APFSDS round with various reaction rate coefficients.



Original 500X

Figure 4. Substrate erosion beneath "older" cracks showing lateral distribution (Cote and Rickard 2000).

leads to assigning $5.2e14$ to the coefficient value A_2 . Whether this assigned value is correct or not is purely speculation at this time. One item which the equilibrium calculations provided is the resultant chemical constituency involving iron carbide. Therefore, the resultant carbon from reaction no. 2 in Table 3, was enabled to react with the iron at the surface to produce iron carbide through the prescribed surface reactions.

5. Results

Figure 5 compares the previous equilibrium assumption to the present nonequilibrium assumption for a 0.010-in chromium (Cr) plated M256 120-mm tank canon firing an APFSDS round. Also presented is data from a M68 nonchromed tank cannon firing a similar round but reduced by a factor of ten (Ward and Brosseau 1980). The difference in predictions between the equilibrium and nonequilibrium assumptions is striking. The equilibrium assumption produces more erosion down bore than the nonequilibrium assumption. Closer to the forcing cone for the M68 data and the nonequilibrium calculation, we see that the higher temperatures guide the reaction rate. Although the nonequilibrium resultant eroded depth should be less than that of the equilibrium, this is not necessarily the case since the computational scheme is somewhat different between the two. The equilibrium scheme was based on a fixed control volume with a finite amount of iron, while the nonequilibrium scheme enables iron to be consumed as needed by the surface reaction.

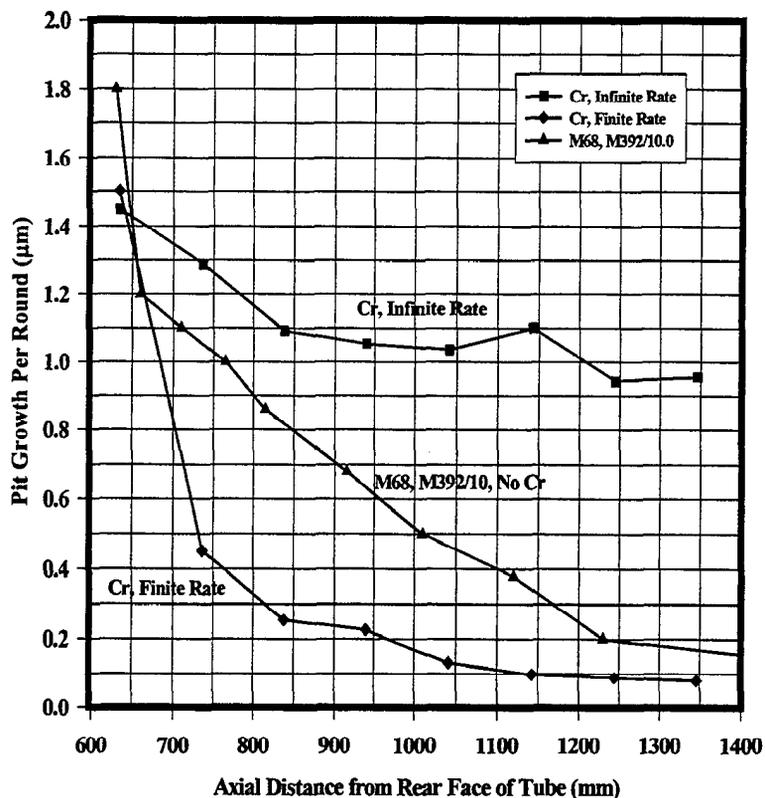


Figure 5. Single firing pit growth for 0.010-in chrome coated steel compared to M68 nonchromed gun firing m392/10 APFSDS round.

Using the previously determined value for A_2 , calculations for a similar tantalum (Ta) coating were made and presented in Figure 6. The only modifications were to the physical properties of tantalum. Figure 6 also compares equilibrium as well as nonequilibrium results for both chromium as well as tantalum coated tubes. The large difference between Cr and Ta in the potential pit growth rate at the forcing cone is due to the inherent higher temperature experienced with the tantalum coating, as seen in Figure 7. The peak temperature experienced by the pit interface is almost 200 K higher for the tantalum than for the chromium. This drives the exponent in the Arrhenius reaction rates, as well as the substrate diffusion of the species. This implies that if there was a crack or other type of pit formed in a tantalum coating of equal thickness as chromium, then the tantalum coating would not tend to have the longevity of the chromium coating in similar circumstances.

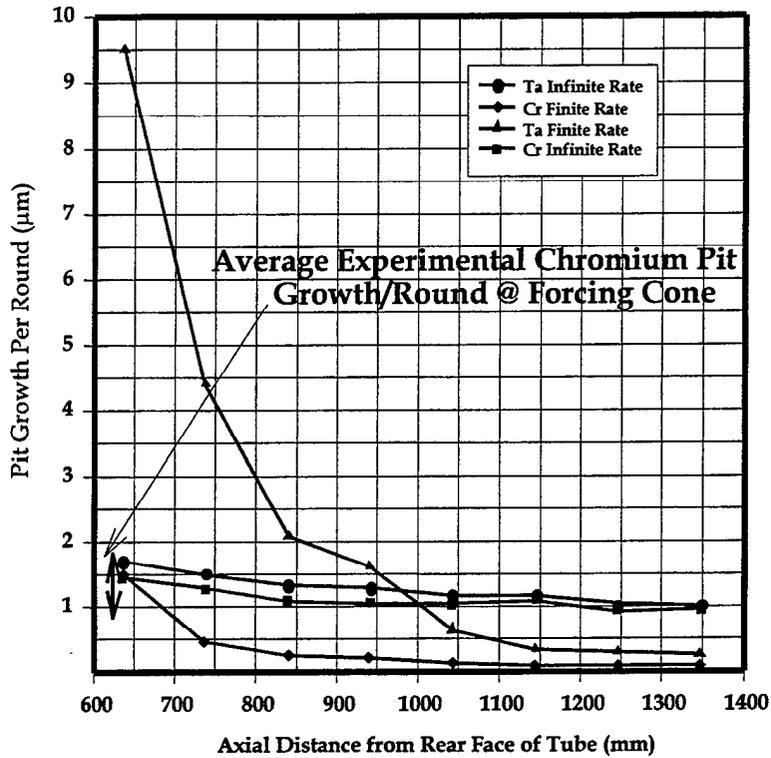


Figure 6. Single firing pit growth rate for 120-mm, M256, Cr, and Ta coated steel 0.010 in thick, firing and APFSDS round.

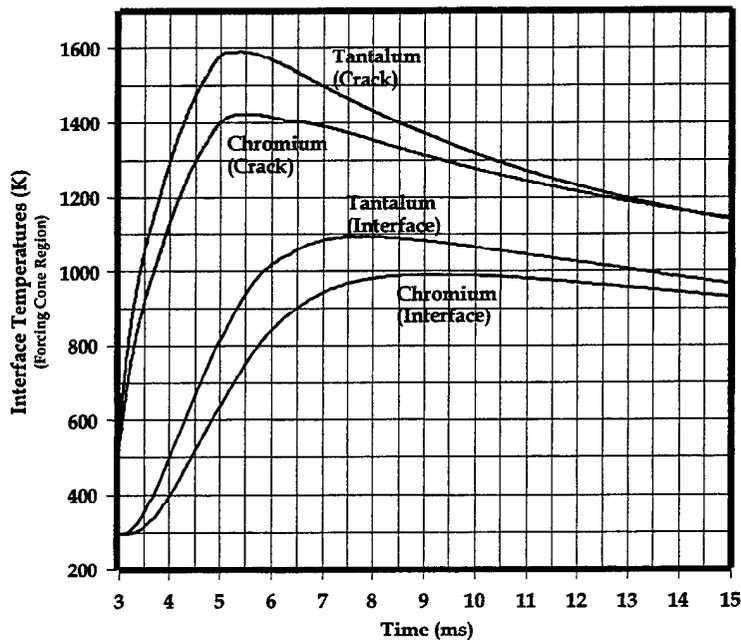


Figure 7. Interfacial and crack base temperatures for 0.010-in chromium coating compared to 0.10-in tantalum coated 120-mm M256 firing an APFSDS.

6. Nitrogen Hypothesis

Considering that the primary driving reaction of the chemical mechanism is the dissociation of the carbon monoxide, ways to possibly mitigate erosion would include methods to suppress this dissociation or suppress the production of carbon monoxide in the first place. Interestingly, Ponec and van Barneveld (1979) suggest that the surface dissociation of CO on an iron surface is spoiled by nitrogen intrusion or nitriding the surface, but they do not state specifically why this occurs. This leads to the possibility that increasing the nitrogen content of the propellant products may diminish the CO dissociation and thereby the erosion. Leveritt et al. (2000) have discovered that some advanced propellants, with similar flame temperatures as older propellants such as JA2, do not erode as much as the older double base propellant. Complicating matters is the fact that these advanced propellants have a much higher CO/CO₂ ratio than do the double base propellants. One would expect these higher ratios to exacerbate the carburization mechanism. Fortunately, Ponec's explanation may be applied to these new propellants because their nitrogen content is approximately three times that of conventional propellants.

The M242 Bushmaster barrel may be nitrided or chrome plated. If it is chrome plated, access for erosion is through the cracks to the substrate (Conroy et al. 1999b). Considering the hypothesis of Ponec and van Barneveld (1979), investigation into nitriding surfaces before they are chrome plated or even afterward may lead to technological breakthroughs to increase the service life by mitigating the erosion at the base of the cracks. The authors do not believe that the nitrided chemical process involved for nitriding to mitigate erosion was previously understood, other than that it increased the surface hardness. We now have a possible chemical rationale for nitriding gun barrels in that the nitrogen appears to either interfere with the dissociation of the carbon monoxide on the surface, or perhaps interfere with the diffusion of carbon into the substrate steel, or both.

7. Discussion

Nonequilibrium chemical kinetics have been incorporated in the erosion calculations. The user may input externally the reaction mechanism desired with standard kinetic rate parameters. For the iron-gas system, a potential mechanism was investigated. One reaction coefficient was unknown for the mechanism and was estimated through a parametric study. Fortunately, Grabke (1964)

investigated the specific dissociation of CO on the iron surface and reported the activation barrier. This enabled the inclusion of the reaction, while an estimate of the reaction coefficient was made through a parametric study.

Nonequilibrium and equilibrium chemistry erosion computational results were presented. The differences are striking in that the equilibrium calculation shows much more downbore erosion than the nonequilibrium calculation and is also limited near the forcing cone by the control volume description. The nonequilibrium calculations show a larger influence of the reaction temperature than do the equilibrium results when comparing tantalum to chromium. Tantalum may erode more than chromium under similar circumstances due to its physical properties.

The dissociation of CO is important, and ways to mitigate it were investigated in the literature. Ponc and van Barneveld (1979) provided a clue that nitrogen or nitriding the surface may inhibit this dissociation. Experimentally, this may have been observed by Leveritt et al. (2000) in new high energetic propellants.

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Current theories concerning gun tube erosion consider that erosion can occur under various conditions. The worst condition occurs when the melting temperature of the gun steel is exceeded for the tube's inner surface. This causes the tube to grossly melt. This melt wipe mechanism is not as simple as once thought because the propellant product gases are known to react with the surface, resulting in an altered surface material. This altered material may have a lower melting temperature than that of the gun steel and/or weakened mechanical properties. Previous surface reaction studies by the authors used a generalized equilibrium scheme with a control volume analysis to represent surface reactions occurring during a cannon firing. This led to a postreaction treatment at the interface which incorporated the subsurface diffusion of species to limit the surface reaction. In this study, the surface reactions and rates are specified explicitly with published rates and guidance from fundamental molecular modeling results. The results demonstrate the utility of the surface reaction mechanism presently employed and the incorporation of finite rate surface kinetics in the fundamental physical representation of erosion.

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