Some characteristics of fine beryllium particle combustion

D.A. Davydov [a], O.V. Kholopova [a], B.N. Kolbasov [b,*]

[a] *Bochvar Institute for Inorganic Materials, Moscow, Russia*
[b] *Russian Research Centre 'Kurchatov Institute', Nuclear Fusion Institute, Pl. Kurchatova 1, 123182 Moscow, Russia*

Abstract

Beryllium dust will be produced under plasma interaction with beryllium armor of the first wall in ITER. Exothermal reaction of this dust with water steam or air, which can leak into the reactor vacuum chamber in some accidents, gives concern in respect to reactor safety. Results of studies devoted to combustion of fine beryllium particles are reviewed in the paper. A chemically active medium and elevated temperature are prerequisite to the combustion of beryllium particles. Their ignition is hampered by oxide films, which form a diffusion barrier on the particle surface as a result of pre-flame oxidation. The temperature to initiate combustion of particles depends on flame temperature, particle size, composition of combustible mixture, heating rate and other factors. In mixtures enriched with combustible, the flame temperature necessary to ignite individual particles approaches the beryllium boiling temperature.
© 2007 Elsevier B.V. All rights reserved.

1. Introduction

Beryllium (Be) will be used in the International thermonuclear experimental reactor (ITER) and in some demonstration fusion power reactors (DEMO) as protective cladding (armor) on the first wall and neutron multiplier. It is expected that plasma interaction with Be armor during reactor operation will result in the formation of fair quantity of Be dust. Under some accidents ingress of air and water into the vacuum chamber and their exothermic chemical reaction with Be dust are possible. Therefore possible ignition of Be dust gives concern for fusion reactor safety.

Due to high toxicity of beryllium, experimental studies of its ignition, combustion and detonation are fraught with contamination of the premises and are dangerous. Therefore their number is much smaller than the number of similar studies with non-toxic metals.

Studies conducted earlier by the Russian, US and JAERI research teams [1–6] in the frames of ITER International Project addressed Be safety issues and focused on the chemical interaction of beryllium with air and steam at relatively low (<1000 °C) temperatures. In this temperature range, the main hazard is the formation of potentially explosive hydrogen by the reaction between Be and steam.

In this paper studies of combustion initiation of beryllium particles at higher temperatures (up to 2900 K) are reviewed and analyzed and role of such factors as oxide film, flame temperature, particle

* Corresponding author. Tel.: +7 095 1967583; fax: +7 095 9430073.
E-mail address: kolbasov@nfi.kiae.ru (B.N. Kolbasov).

size, composition of combustible mixture, heating rate, chemical activity of ambient medium and heat-exchange of Be particles with ambient medium is considered.

2. Role of oxide film in metal oxidation and combustion

Uncontrolled combustion implies a thermal equilibrium disruption leading to a self-accelerating growth of the particle temperature. In the case of Be particles, it is severely hampered by an oxide film forming on the particle surface as a result of pre-flame oxidation and serving as a diffusion barrier.

Temperature (T) dependence of the Be-oxidation rate constant (K) is exponential and is described by either the Arrhenius equation: $K = B\exp(-E/RT)$ or the transient state theory: $K/T = C\exp(-E/RT)$, where E is activation energy, $C = \alpha\exp(\Delta S/R)$, ΔS is entropy change and R is gas constant [7].

Protective properties of the oxide films forming on the surface of metal particles are to a considerable degree characterized by the Pilling–Bedworth factor $\beta = M\rho/nA\rho_{ox}$, where M is the oxide molecular weight, ρ_{ox} is the oxide density, ρ is the metal density, A is the metal atomic weight, and n is the number of metal atoms within the oxide molecule.

Very simplified interpretation of the Pilling–Bedworth rule [8] allows to state that, if the volume of the metal oxide produced by the reaction of metal and oxygen is less than the volume of the consumed metal ($\beta < 1$), a metal oxide film may be discontinuous and cannot safely protect the metal from subsequent high-temperature oxidation; if the volume of the metal oxide is greater than the consumed metal volume ($\beta > 1$), the produced oxide film can impede further metal oxidation, provided that the oxide boiling temperature is high enough.

For Be, the ratio of the metal oxide (BeO) volume to the consumed metal volume $\beta = 1.68$ at 20 °C. For other temperatures, tabulated data are adjusted using the thermal expansion coefficients [9]. Factors other than β, such as oxide ductility, adhesion to metal, ability to flake off and solubility within the metal also affect protective characteristics of the oxide films.

At high temperatures, an oxide's key thermal characteristics are the melting point, thermal expansion coefficient, heat capacity, thermal emissivity and heat conductivity.

The loss of the protective ability of oxide film is a prerequisite to the ignition of beryllium particles.

The big difference between the specific volumes (V) and thermal expansion coefficients of Be and its oxide ($V_{BeO}/V_{Be} = 1.7$) causes a compressive stress in BeO and the film cracking. The stress is growing with increasing oxide film thickness, i.e. with increasing temperature and time. Therefore, oxide film loses its protective properties with time. The lower the temperature, the more time is required for a film to be destroyed. At temperatures below 970 K, cracks can skin over in air or O_2, while at temperatures above 1020 K cracking becomes dominant and films lose their protective properties. Gas penetration through cracks to the metallic surface (either clean or covered with a very thin film) speeds up the reaction rate.

The temperature at which an oxide film loses its protective properties was referred to as 'transient' temperature by Mellor and Glassman [10].

Above 920 K moisture impairs the protective properties of oxide films. At constant temperature, the time preceding the oxide film fracture shortens with increasing partial pressure of steam, while at constant partial pressure it shortens with increasing temperature. The oxidation rate in steam, in contrast to dry gases, is very pressure-sensitive. In gas/steam mixtures, the oxidation rate increases with increasing total pressure.

3. Ignition temperature and combustion induction period

From the energy standpoint, beryllium is one of the most reactive metals. Like aluminium, it is classed with 'volatile metals' [11]. Beryllium boiling temperature ($T_{boil} = 2750$ K) is lower than that of its oxide BeO (4393 K) and slightly lower than BeO melting temperature (2823 K). Beryllium melting temperature $T_{melt} = 1556$ K.

Beryllium flame ignition at temperatures close to 2700 K (lower than the Be boiling temperature) was reported by Macek et al. [11], who studied the combustion of individual Be particles. However, the ignition may occur at temperatures below 1300 K [12] if the particles are very small, their concentration is high, amount of oxidant is high, heating rate is high and heat loss from oxidized particles is small enough. In this case due to exothermal reaction, particle temperature significantly exceeds flame temperature.

Be particle ignition has been analyzed quantitatively under specific gas burner blaze conditions ($P = 1$ atm, oxygen partial pressure was 0.16–

0.43 atm, CO_2 partial pressure was 0.42–0.46 atm, ignition temperature $T_{ign} = 2400$–2920 K) [13]. Under combustion of condensed systems, the duration of a pre-burn lag (or combustion induction period τ_{ip}) is largely determined by the difference between the ambient temperature and the particle T_{ign}, as well as by particle size. It decreases with decreasing T_{ign} and, accordingly, with increasing ambient temperature [14].

According to Kyul [14], each Be particle undergoes three heating stages: (1) heating up to the melting temperature, (2) isothermal melting, and (3) heating of the molten droplet to the ignition point. Theoretical study was performed under the following assumptions: (a) heating is provided by heat-exchange with surroundings, (b) chemical reaction is not taken into account, (c) the difference between the particle speed and the gas flow speed is constant, (d) changes in the diameter and density of a melting particle are not small. Fig. 1 shows calculated particle temperature behavior with time and induction period lengths during the heating of a particle to a predetermined temperature.

4. Effect of particle size and concentration as well as of heat exchange with ambient medium and heating rate

The ignition temperature (T_{ign}) depends on the size (d) of metal particles. The growing protective oxide film decreases the oxidation rate, making larger particles ignite at higher temperatures [15].

If a particle is heated during the pre-flame period from the surrounding gas solely through the heat conductivity and subsequently burns down in a diffusion mode in the vapor phase, then combustion time τ_{cmb} and induction period τ_{ip} must be proportional to d^2 [16]. This dependence correlates with the relationship between the particle size and their heating-up time. In fact, the measured τ_{ip} is proportional to $\sim d^{2.5}$.

The greater the concentration of metal particles, the lower their T_{ign} due to the 'collective' effect. This T_{ign} reduction is larger for smaller particles since at higher substance concentrations, heat removal intensifies with decreasing size of particles, causing a rise in ambient temperature and making a type of adiabatic shell around each particle [17].

T_{ign} is also strongly affected by the heating rate of the particles that determines the thickness and density of the oxide film. A slow heating-up is accompanied with the formation of a dense protective film, any crack would be 'skinned over' with a newly formed oxide, and the particle T_{ign} reaches maximum values. This explains why metals ignite more readily at high heating rates [18].

5. Effect of oxidant concentration and chemical activity of ambient medium

A chemically active medium and elevated temperature are prerequisite to the combustion of Be particles. In media with low (less than 16%) oxygen content, the transition from the induction period to combustion has no strongly pronounced boundary and is practically indiscernible. This causes some uncertainty regarding the establishment of quantitative characteristics of the Be particle ignition point.
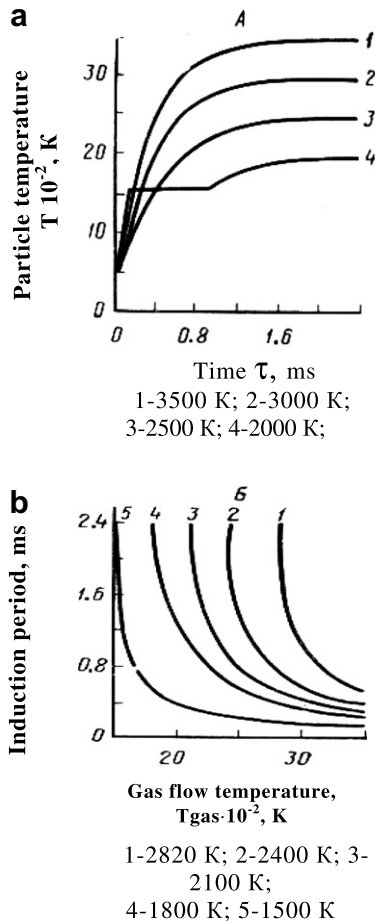

Fig. 1. (a) Be particle ($d = 20$ μm at $T_o = 500$ K) temperature versus time and (b) induction period τ_{ip} versus gas flow temperature: difference between the particle speed and the gas flow speed $\Delta V = 58$–61 m/s [14].

The effect of oxidant concentration on the temperature, at which finely-dispersed Be particles ignite, was studied experimentally in [19]. Where the hydrogen–oxygen ($O_2 < 20\%$) flame temperature was within 2600 K, particles of 30–35 μm in diameter practically did not ignite. At lower O_2 concentrations, flame temperature level for particle ignition was higher, gradually approaching T_{boil}. However, even at elevated oxygen concentrations of flame ($O_2 > 20\%$), there is no limit, in a strict sense, on the critical flame temperature – as in the case of Al. At 2600–2800 K, the fraction of ignited particles was no greater than 30%. In a dry atmosphere, all other conditions being equal, the total percentage of ignited particles is higher than in the presence of H_2O [13]. In a hydrogen–oxygen atmosphere at 2900 K, the Be particle combustion percentage is practically 100%.

Such ignition data are very scarce. They are validated, however, by experimental evidence – albeit also very limited – for the combustion of fine (35–45 μm in diameter) Be particles in a compound ammonium perchlorate–trioxymethylene flame [11]. The total pressure within the facility varied between 2.4 and 50 atm. The particles started to ignite at about 2380 K, if the oxygen partial pressure exceeded 4–6 atm. As the oxygen concentration in flame decreased, the Be ignition became more difficult. At $P_{O_2} < 0.1$ atm, the combustion sometimes could not occur even at temperatures close to 2650 K.

Thus, in mixtures, enriched with combustibles, the flame temperature necessary for the ignition of

Be particles is approaching Be boiling temperature (T_{boil}) (Fig. 2). The temperature shown in the figure is working fluid temperature (T_o), not the temperature of particles at the moment of ignition [11].

The minimum ambient temperature for Be particles combustion is determined by working fluid chemical activity and properties. However, there is no way to bring Be specimens to vapor-phase burning mode or, at least, to raise their temperature to $T \geqslant 2200$ K in a H_2O (steam) atmosphere.

6. Physical model of metal particle combustion

Particle ignition characteristics determined by the peculiarities of the metal oxidation kinetics were investigated by Khajkin et al. [15].

Combustion initiation conditions for spherical metal particles are determined by simultaneously solving the heat-balance equation (1) and the kinetic oxidation law equation (2):

$$\frac{1}{3}c\rho r_o \frac{dT}{dt} \approx Q\rho \frac{d\delta}{dt} - \frac{\lambda}{2r_o} Nu(T - T_o), \tag{1}$$

$$\frac{d\delta}{dt} = \frac{k'_n c_{ox}^m}{\delta^n} \exp(-E/RT), \tag{2}$$

where r_o is the particle radius, k'_n is the pre-exponential, m is the reaction order for the oxidant in the corresponding metal oxidation law, c_{ox} is the oxidant concentration at the particle surface, c is the metal specific heat, λ is the coefficient of gas thermal conductivity, Q is the reaction thermal effect as per 1 g oxide, multiplied by the oxide/metal density ratio, Nu is the Nusselt number, t is time.

The n factor determines the oxidation rate to oxide film thickness relationship, that is, the oxidation law ($n = 0$ – linear law, $n = 1$ – parabolic law, $n = 2$ – cubic law, etc.). The authors restrict their discussion only to power-law oxidation patterns, assuming that a distinctive feature of the logarithmic (stronger) oxidation patterns is stronger dependence of the oxidation rate on δ, while the oxidation regularities are similar to those observed in the case involving a large n factor.

The conditions enabling metal particle ignition are determined by the rate of oxidation-induced heat generation and a high-speed heat removal from a particle to the ambient gas under the following initial conditions: at $t = 0$, $T = T_I$, and $\delta = \delta_I$, where δ_I is the initial oxide film thickness and T_I is the initial temperature of the particle. For small particles, i.e., for small Re numbers, $Nu \approx 2$.
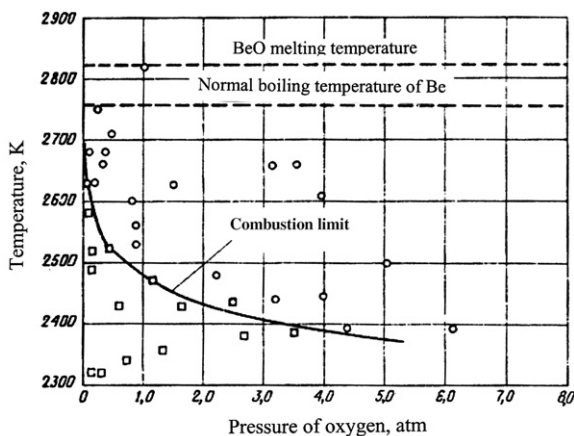

Fig. 2. Flame temperature, at which Be particles ignite, as a function of P_{O_2} [11]. The solid line corresponds to the combustion limit; □ – no ignition; ○ – ignition.
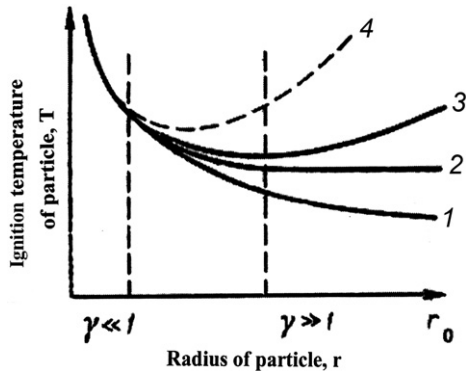
Fig. 3. Combustion temperature against particle radius for different patterns of oxidation: $1 - n = 0$; $2 - n = 1$; $3 - n = 2$; $4 - n \gg 1$. $\gamma = \frac{r_0}{3\delta_1} \frac{cRT_0^2}{EQ}$ [15].

By replacing the variables, the set of equations is transformed to a dimensionless form, formally resembling the equation system describing a thermal explosion [20].

Equation for the linear oxidation pattern ($n = 0$) can be reduced to the ordinary heterogeneous combustion regularity, and T_{ign} decreases with increasing particle size. Where the oxidation rate follows the parabolic law ($n = 1$), the opposite factors may balance each other, in which case T_{ign} is independent on the particle size over a certain size range. Where an oxidation rate is more strongly dependent on δ than on the parabolic oxidation rate pattern (follows the cubic or logarithmic law, $n > 1$), T_{ign} of sufficiently large particles rises with increasing particle size and the dependence of T_{ign} on the metal particle diameter is described by a curve with a minimum (Fig. 3) [15].

7. Conclusions

1. In many cases, a preliminary destruction of the oxide film is necessary to initiate ignition and combustion of Be. Like Al, Be develops a highly-protective oxide film. This explains why in adverse thermal conditions Be particles ignite at higher temperatures (~ 2700 K). The 'transient' temperature for Be coincides with its boiling point, which is lower than the BeO melting temperature. However, Be particles may ignite at temperatures below 1300 K, if the particles are very small, their concentration is high, amount of oxidant is high, heat loss from particles is small and heating rate is high.

2. Beryllium particles ignite only in chemically active media at elevated temperatures. In media with low (less than 16%) oxygen content, the transition from the induction period to combustion has no strongly pronounced boundary. This hinders the quantitative detection of the Be particle ignition parameters.

3. Ambient temperature enabling the combustion of fine Be particles depends upon oxidant concentration. Where the hydrogen–oxygen ($O_2 < 20\%$) flame temperature is within 2600 K, particles of 30–35 μm in diameter practically remain non-flammable. For flames with lower free oxygen concentrations, the critical ambient temperature level is higher, gradually reaching $T_{boil} = 2750$ K. However, even at high oxygen concentrations of flame ($O_2 > 20\%$), there is no limit, in a strict sense, on the critical ambient temperature, as there is in the case of Al. At 2600–2800 K, the percentage of ignited particles is no greater than 30%. In a dry atmosphere, all other conditions being equal, the percentage of ignited particles is higher than in the presence of H_2O. In a hydrogen–oxygen atmosphere at 2900 K, the Be particle combustion percentage is practically 100%. Particles start to ignite at ~ 2380 K, if the oxygen partial pressure exceeds 4–6 atm. As the oxygen concentration of flame decreases, the Be combustion becomes more difficult. At $P_{O_2} < 0.1$, ignition can not occur even at temperatures close to 2650 K. In enriched combustible mixtures, critical flame temperature necessary for ignition of individual particles approaches the Be boiling temperature.

4. There is no way to bring Be specimens to vapor-phase combustion mode or, at least, to raise their temperature to $T \geqslant 2200$ K while burning them in a H_2O (steam) atmosphere. Nevertheless, the metal oxidation in this medium is very active and is accompanied by the formation of a complex double-layer oxide (a thick and porous upper layer and a thin dense lower layer which protects the particle from oxidation).

5. A physical model of ignition and combustion of metal particles has been considered. Required conditions for spherical metal particles are determined by solving the heat-balance equation (1) and the kinetic oxidation rate equation (2).

References

[1] D.A. Davydov, V.A. Gorokhov, V.K. Kapyshev, S.I. Sorokin, in: Problems of Atomic Science and Engineering,

Ser. 'Materials Science and New Materials', Bochvar Institute, Moscow, 1995, vol. 1 (52), p. 74 (in Russian).

[2] B.N. Kolbasov, A.Yu. Biryukov, D.A. Davydov, M.I. Guseva, B.I. Khripunov, S.N. Korshunov, Yu.V. Martynenko, P.V. Romanov, V.I. Vasiliev, Fusion Eng. Des. 54 (2000) 451.

[3] S.I. Sorokin, D.A. Davydov, Plasma Devices Oper. 11 (4) (2003) 257.

[4] K. McKarthy, R. Anderl, D. Petti, G. Smolik, H.-W. Bartels, S. Morozov, D. Davydov, B. Kolbasov, V. Shestakov, I. Tazhibaeva, A. Vurim, A. Chekhonadskikh, in: Fusion Energy, 1998, Proceedings of 17th International Conference, Yokohama, Japan, 1998, C&S Papers Series No. 1/C, IAEA, Vienna, 1999, CD-ROM file EX8/1 and <http://www.iaea.org/programmes/ripc/physics/fec1998/html/fec1998.htm>.

[5] R.A. Anderl, R.J. Pawelko, G.R. Smolik, F. Scaffidi-Argentina, D.A. Davydov, Fus. Technol. 38 (3) (2000) 283.

[6] H. Yoshida, K. Ashibe, K. Ono, M. Enoeda, Measurements of breakaway reaction between beryllium and water vapor for ITER blanket design, Report of Japan Atomic Energy Research Institute, Naka, Japan, JAERI – M92-083, 1992.

[7] P.F. Pokhil, A.F. Belyaev, Yu.V. Frolov, V.S. Logachev, A.I. Korotkov, Burning of Powder-like Metals in Active Media, Nauka Publishers, Moscow, 1972 (in Russian).

[8] I.L. Knunyants (Ed.), Chemical Encyclopedia, vol. 1, Sovetskaya Entsiklopediya Publishers, Moscow, 1988 (in Russian).

[9] A. Kubashevsky, B. Hopkins, Oxidation of Metals and Alloys, Metallurgiya Publishers, Moscow, 1965 (in Russian).

[10] A.M. Mellor, I. Glassman, Pyrodynamics 3 (1–2) (1965) 43.

[11] A. Macek, P. Fridman, J. Semple, in: V.A. Ilyinskij, I.N. Sadovskij (Eds.), Heterogeneous Combustion (compiled papers translated from English), Mir Publishers, Moscow, 1967, p. 21 (in Russian).

[12] V.M. Maltsev, M.I. Maltsev, L.Ya. Kashporov, Basic Characteristics of Combustion, Khimiya Publishers, Moscow, 1977 (in Russian).

[13] A. Macek, J. Semple, in: 12th International Symposium on Combustion, Pittsburg, 1969, p. 14.

[14] D.K. Kyul, Rocket Eng. Astronaut. (12) (1965) 83 (in Russian).

[15] B.I. Khaikin, V.Ya. Bloshenko, A.G. Merzhanov, Combust. Explo. Phys. 6 (4) (1970) 474 (in Russian).

[16] M.A. Gurevich et al., Combust. Explo. Phys. 5 (3) (1969) 441 (in Russian).

[17] E.N. Rumanov, B.I. Khaikin, Combust. Explo. Phys. 5 (1) (1969) 129 (in Russian).

[18] E.I. Popov, A.L. Breiter, Powder Metall. (5) (1973) 101 (in Russian).

[19] A. Macek, in: 11th International Symposium on Combustion, 1967, The Combustion Institute, Pittsburg, p. 20.

[20] D.A. Frank-Kamenetsky, Diffusion and Heat Transfer in Chemical Kinetics, Nauka Publishers, Moscow, 1967 (in Russian).