

Review

Thermite reactions: their utilization in the synthesis and processing of materials

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A class of exothermic reactions between, typically, a metal and an oxide, commonly referred to as thermite reactions, is reviewed with emphasis on their utilization in the synthesis and processing of materials. Theoretical and experimental results relating to ignition and combustion (self-propagation) characteristics of these reactions are presented.

1. Introduction

The word “thermit” was first coined by Goldschmidt in 1908 [1] to describe exothermic reactions involving reduction of metallic oxides with aluminium to form aluminium oxide and metals or alloys. This type of reaction is characterized by a large heat release which is often sufficient to heat the product phases above their melting points. For example, the thermite reaction $2\text{Al} + \text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe} + \text{Al}_2\text{O}_3$ can attain a temperature higher than 3000 °C which is above the melting points of both iron and Al_2O_3 . Currently, the term thermite reaction is used to describe a much broader class of reactions and can be defined as an exothermic reaction which involves a metal reacting with a metallic or a non-metallic oxide to form a more stable oxide and the corresponding metal or non-metal of the reactant oxide. This is a form of oxidation–reduction reaction which can be written in a general form as



where M is a metal or an alloy and A is either a metal or a non-metal, MO and AO are their corresponding oxides, and ΔH is the heat generated by the reaction. Because of the large exothermic heat, a thermite reaction can generally be initiated locally and can become self-sustaining, a feature which makes their use extremely energy efficient. The fact that many thermite reactions yield a molten product that consists of a heavier metallic phase and a lighter oxide phase which can be separated by gravity, makes these reactions potentially useful in a variety of metallurgical applications [2–20]. Because the self-sustaining nature of thermite reactions can be adjusted by the addition of an inert diluent, they are often used as experimental models for solid combustion studies [21–35] and for pyrotechnic uses [36, 37]. More recently, thermite re-

actions have become important in the synthesis of refractory ceramic and composite materials [38–57], and in the preparation of ceramic linings in metallic pipes [58–70]. There are also many other materials-related processing and heat-generation inventions which utilize thermite reactions [71–85]. While most of the focus is on the beneficial aspect of thermite reactions, accidental explosion in chemical plants and mines involving such reactions are of great safety concern [86, 87]. This brief review demonstrates the importance of this class of industrial reactions. We provide a review of the theoretical and experimental work relating to thermite reactions and discuss the important examples of their utilizations.

2. Thermodynamic considerations

As indicated above, thermite reactions are oxidation–reduction processes. There are a number of factors involved in the selection of a reducing agent for a particular oxide. The tendency for a metal to reduce an oxide depends, of course, on the free energy of formation of its oxide. Fig. 1 presents the Gibbs free energy of formation as a function of temperature for a series of possible reducing metals (Al, Mg, Ca, Zr, Zn and Ti) and several other common reducing agents (Si, C and H_2) [88, 89]. All the reactant metals show negative Gibbs free energies of oxide formation over a wide temperature range. Most of the metals have higher reducing tendency than the non-metal reducing agents, and the extent of their reducing tendency decreases as temperature increases. Both calcium and magnesium have higher Gibbs free energies of oxide formation at low temperatures, but their reducing tendency decreases more sharply at elevated temperatures. In addition, both calcium and magnesium are more volatile, boiling at 1757 and 1363 K, respectively

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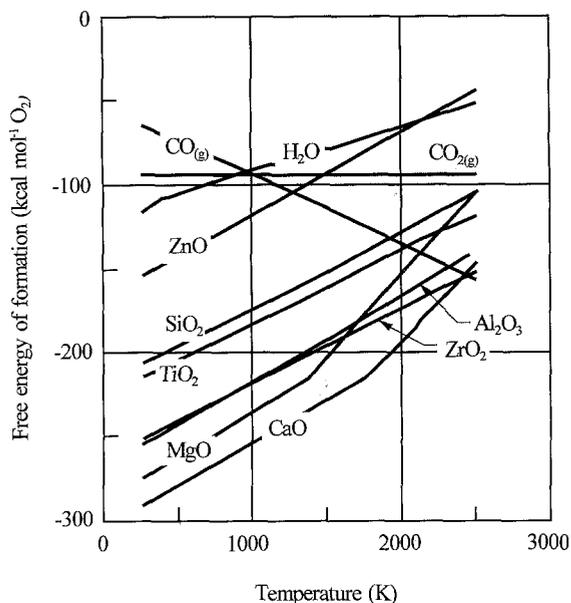


Figure 1 Free energy of formation for oxides.

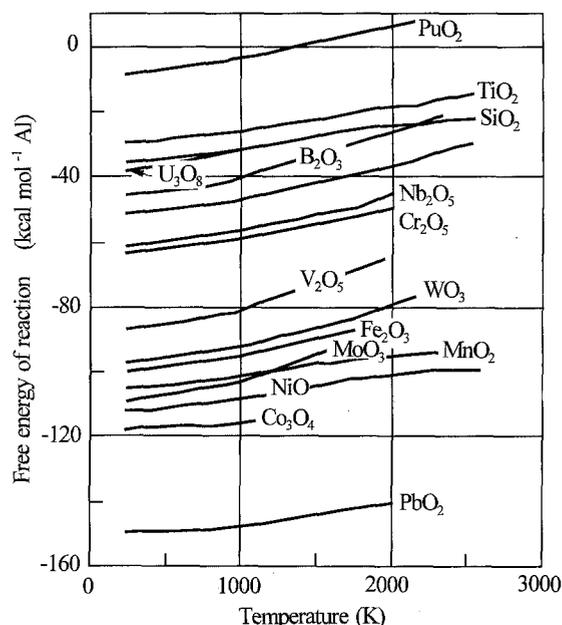


Figure 2 Free energy of thermite reactions with aluminium as the reducing agent.

(at 1 atm pressure), and thus are less desirable for certain applications because of high reaction pressure and vaporization losses [8]. Both aluminium and zirconium have comparable reducing tendency, but aluminium is more commonly used, because it is more readily available. Its physical properties and those of its oxides are more suitable for the requirements of several metallurgical applications [5], as will be discussed later.

Another factor is the consideration of the exothermicity of the thermite reactions. The heat released from the reaction heats up the product to the

adiabatic temperature which can be calculated from the enthalpy of the reaction and the heat capacity of the product phases with the assumption of adiabatic conditions. A large number of oxides can be reduced by aluminium up to relatively high temperatures (2500 K), as shown in Fig. 2. These aluminium-based thermite reactions result in production of Al_2O_3 and the elemental components corresponding to the reactant oxides. Using the usual thermodynamic approach [90, 91], the adiabatic temperatures, T_{ad} , for these thermite reactions were calculated and are presented in Table I. In many cases, the adiabatic temperature

TABLE I Adiabatic combustion temperatures and melting points of the product metals

Reaction	$T_{\text{ad}}(\text{K})^{\text{a}}$	T_{mp} of metal (K) ^b
I. Formation of common structural metals		
$\text{Al} + 1/2\text{Fe}_2\text{O}_3 \rightarrow \text{Fe} + 1/2\text{Al}_2\text{O}_3$	3622	1809
$\text{Al} + 3/2\text{NiO} \rightarrow 3/2\text{Ni} + 1/2\text{Al}_2\text{O}_3$	3524	1726
$\text{Al} + 3/4\text{TiO}_2 \rightarrow 3/4\text{Ti} + 1/2\text{Al}_2\text{O}_3$	1799	1943
$\text{Al} + 3/8\text{Co}_3\text{O}_4 \rightarrow 9/8\text{Co} + 1/2\text{Al}_2\text{O}_3$	4181	1495
II. Formation of refractory metals ^c		
$\text{Al} + 1/2\text{Cr}_2\text{O}_3 \rightarrow \text{Cr} + 1/2\text{Al}_2\text{O}_3$	2381	2130
$\text{Al} + 3/10\text{V}_2\text{O}_5 \rightarrow 6/10\text{V} + 1/2\text{Al}_2\text{O}_3$	3785	2175
$\text{Al} + 3/10\text{Ta}_2\text{O}_5 \rightarrow 6/10\text{Ta} + 1/2\text{Al}_2\text{O}_3$	2470	3287
$\text{Al} + 1/2\text{MoO}_3 \rightarrow 1/2\text{Mo} + 1/2\text{Al}_2\text{O}_3$	4281	2890
$\text{Al} + 1/2\text{WO}_3 \rightarrow 1/2\text{W} + 1/2\text{Al}_2\text{O}_3$	4280	3680
$\text{Al} + 3/10\text{Nb}_2\text{O}_5 \rightarrow 6/10\text{Nb} + 1/2\text{Al}_2\text{O}_3$	2756	2740
III. Formation of other metals and non-metals		
$\text{Al} + 1/2\text{B}_2\text{O}_3 \rightarrow \text{B} + 1/2\text{Al}_2\text{O}_3$	2315	2360
$\text{Al} + 3/4\text{PbO}_2 \rightarrow 3/4\text{Pb} + 1/2\text{Al}_2\text{O}_3$	> 4000	600
$\text{Al} + 3/4\text{MnO}_2 \rightarrow 3/4\text{Mn} + 1/2\text{Al}_2\text{O}_3$	4178	1517
$\text{Al} + 3/4\text{SiO}_2 \rightarrow 3/4\text{Si} + 1/2\text{Al}_2\text{O}_3$	1760	1685
IV. Formation of nuclear metals		
$\text{Al} + 3/16\text{U}_3\text{O}_8 \rightarrow 9/16\text{U} + 1/2\text{Al}_2\text{O}_3$	2135	1405
$\text{Al} + 3/4\text{PuO}_2 \rightarrow 3/4\text{Pu} + 1/2\text{Al}_2\text{O}_3$	796	913

^a The calculation of T_{ad} does not take into account vaporization of the product phases.

^b T_{mp} of Al_2O_3 is 2315 K.

exceeds both melting points of the product phases. These include reactions that reduce Fe_2O_3 , NiO , Co_3O_4 , Cr_2O_3 , V_2O_3 , MoO_3 , WO_3 , PbO_2 , MnO_2 , and Nb_2O_5 , while the reaction to reduce B_2O_3 reaches the melting point of Al_2O_3 . Only in a few cases (e.g. reduction of TiO_2 and PuO_2 by aluminium) is the adiabatic temperature below the melting point of both product phases. The adiabatic temperature provides not only a quantitative measure of the exothermicity of the reaction, but also a quick determination of the propensity of the reaction to self-propagate. In self-propagation, the reaction proceeds in a combustion form in which the heat generated from the locally ignited region can subsequently trigger the reaction in the adjacent reactant layer, thus the reaction zone moves in the form of a wave until all the reactants are consumed. As a rule, the reaction can self-propagate if the T_{ad} exceeds 2000 K [91]. Moreover, the information of T_{ad} also provides some insight to the possible states of interaction, whether in solid, liquid, gas, or a combination of these. The high reaction temperatures of thermite systems ensure the possibility of achieving equilibrium conditions. It is, therefore, suitable to use thermodynamic calculations based on minimization of the total Gibbs free energy of the system to obtain equilibrium distribution of product phases and the corresponding reaction temperature under adiabatic conditions [38, 92]. This analysis is especially applicable in predicting the possible product phases in more complicated starting thermite mixtures in which multiple oxides and/or multiple reducing metals are present.

3. Ignition of thermite reaction

The physical and chemical stability of the reactant oxides has important effects on the ignitability of the thermite mixtures [93]. Chernenko *et al.* [93] classified the oxides according to the following criteria: (1) chemically and physically stable oxides, (2) chemically stable but physically unstable oxides, (3) chemically unstable oxides that decompose, and (4) chemically unstable oxides that undergo further oxidation. In their experimental study, it was found that the oxides which fall under Class 1 (e.g. NiO , TiO_2 , Cr_2O_3 , Al_2O_3 , Ta_2O_5 , and Nb_2O_5) are essentially inert up to the moment of ignition. When such thermite reactions are carried out in air, the oxidation of aluminium by atmospheric oxygen initiates the combustion of the mixtures. In the case of Class 2 oxides (e.g. B_2O_3 which melts at 450°C , MoO_3 which sublimates, and WO_3 , which also sublimates) the appearance of a liquid oxide phase may increase the rate of the oxidation-reduction reaction and thus enhance system ignition. It may also hinder ignition in air by eliminating the influence of the external oxygen, if the rate of chemical interaction of the aluminium with the liquid oxides is low. Moreover, with volatile reactant oxides, the reaction between aluminium and the gaseous oxides can become the step that initiates ignition. In the case of Class 3 oxides (e.g. V_2O_3 , CrO_3 , Li_2O_2 , BaO_2), the ignition process is more complex because the oxygen liberated from the decomposition of the oxide can

play a significant role in initiating the combustion reaction. For example, the ignition of the CrO_3 -Al mixture can occur at as low a temperature as about 170°C , which is the decomposition temperature of CrO_3 . Finally, with the Class 4 oxides, further oxidation takes place in air, and the heat liberated from this reaction can heat the specimen to the ignition point of the thermite reaction. An example of such a case is the ignition of FeO -Al in air, which is initiated by the reaction of FeO with oxygen to form a higher oxide.

The initiation of thermite reactions can be accomplished in a variety of methods. They can be ignited by a combustion wave from a chemical reaction (or igniter) [21–25], an electrical current [94, 95], radiation energy from a heat source or a laser beam [96, 97], or by mechanical impact [86, 87]. The ignition process of a thermite reaction by a combustion wave has been most intensely studied, both theoretically and experimentally [21–24]. The investigation of this ignition process is not only of great interest as a theoretical problem of the interaction between two reactive systems, but also for a number of practical applications, such as in the choice of optimum composition of the igniter for pyrotechnical uses [36, 37].

The electrical energy required to ignite thermite mixtures has been investigated [94]. From this study, the time-independent ignition energies were obtained for the systems $\text{Al-Cu}_2\text{O}$, $\text{Al-Si-Cu}_2\text{O}$, and $\text{Al-Mg-Cu}_2\text{O}$ as 6.60, 2.81 and 3.03 J, respectively [94]. Using a laser as the ignition source has also been attempted on the $\text{Al-Fe}_2\text{O}_3$ system [96, 97]. In this investigation, the laser impingement on the samples is simultaneously coupled with measurement of the temperature distribution in the sample by a high-speed thermographic method. Finally, it has also been demonstrated that a thermite reaction can be initiated by mechanical means [86]. Striking an aluminium smear on a piece of rusty mild steel with a hammer can create a spark which has been blamed for initiating explosions in chemical plants [86] and mines [87]. In this case, the occurrence of thermite reactions constitutes an industrial fire hazard.

4. Combustion of thermites

4.1. Intrinsic and materials parameters

The high exothermic energy associated with thermite reactions and, in general, the condensed nature of the reactants and products at the reaction temperature make many thermite systems examples of reactions in the gasless combustion regime. The criterion for defining gasless combustion is [98]

$$P(T_c) \ll P_0 \quad (2)$$

where P is the vapour pressure of the most volatile component (or dissociation pressure of the products) at the combustion temperature T_c , and P_0 is the external gas pressure. The Fe_2O_3 -Al thermite mixture diluted with the end product (Al_2O_3) has been shown to proceed as a gasless combustion [28]. As illustrated in Fig. 3, the combustion rate of the Fe_2O_3 -Al- Al_2O_3 system is independent of the inert gas pressure (up to

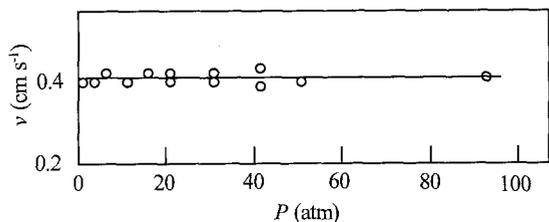


Figure 3 The combustion velocity of (2Al + Fe₂O₃): 30 wt% Al₂O₃ system as a function of the inert ambient gas pressure [28].

~100 atm). However, as indicated above, some thermite systems react with gas evolution resulting from the decomposition of oxides or the vaporization of reactants. In these cases, the combustion model becomes more complicated because mass diffusion is no longer negligible when compared with the thermal diffusion. The combustion rate can be significantly affected by pressure, as will be seen in some thermite systems discussed below. The theoretical model for the partial gas evolution cases is not well studied [99].

Numerous experimental studies have been conducted to determine factors affecting the combustion rate of thermite systems. These factors included particle size of reactants [100–102], addition of inert diluent [25, 28, 102], pre-combustion compact density [101], salt addition [100], centrifugal force [103, 104], ambient inert gas pressure [99, 105, 106], and the physical

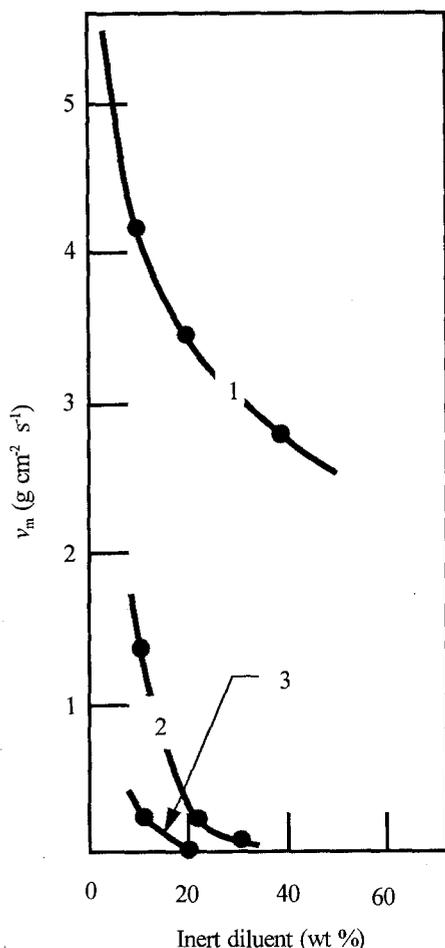


Figure 4 Dependence of the mass combustion rate, v_m , of the Co₃O₄-Al system on the type of diluent added: (1) Al₂O₃, (2) CaF₂, (3) CaO [102].

and chemical stability of oxide reactants [102, 107]. In general, decreasing the reactant particle size increases the combustion rate [100–102]. Balakir *et al.* [102] observed that increasing the aluminium particle size to larger than 100 μm can result in difficulty in the initiation of the thermite reactions (Al-Co₃O₄ and Al-NiO). Addition of inert diluents also effectively reduces the combustion rates [28, 102] because of the production of less heat and the longer transport distances between reactants. Different types of inert diluent also produce different degrees of reduction in the combustion rate as shown in Fig. 4 [102]. This can be related to the difference in the thermophysical properties (e.g. thermal conductivity and heat capacity) of the diluents [25]. Dubrovin *et al.* [101] conducted an extensive study of the effect of compact density and particle size on the mass combustion rate of aluminothermic compositions which are mixtures of Cr₂O₃, crushed iron ore (89.7 wt% Fe₂O₃:8.7 wt% SiO₂), and aluminium. The mass combustion rate of the mixture as a function of the bulk density of the mixture for different iron ore particle sizes is shown in Fig. 5. For a fixed bulk density, the mass combustion rate increases with decreasing particle size, consistent with the observations of others [100, 102]. In the low-density range, the combustion rate decreases as bulk density increases reaching a minimum and then increases again. Dubrovin *et al.* [101] related this behaviour of the combustion rate to the effective thermal conductivity of pressed mixture which has been found to exhibit a similar bulk density dependence [108].

Addition of salts of alkali metals (e.g. NaF, KF, NaCl and KCl), alkaline earth metals (e.g. AlF₃, MgF₂), and cryolite (NaAlF₆) can effectively increase the mass combustion rate of a thermite mixture as

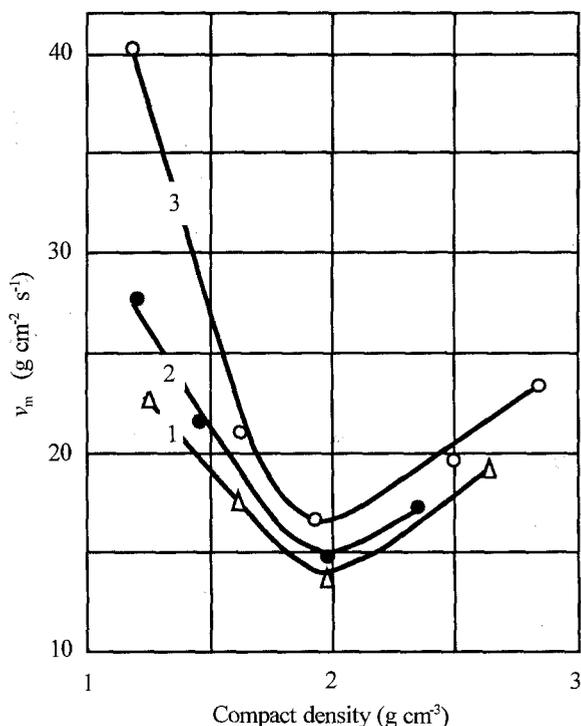


Figure 5 Mass combustion rate versus compact density (average particle size of iron ore, μm : (1) 57, (2) 50, (3) 40) [101].

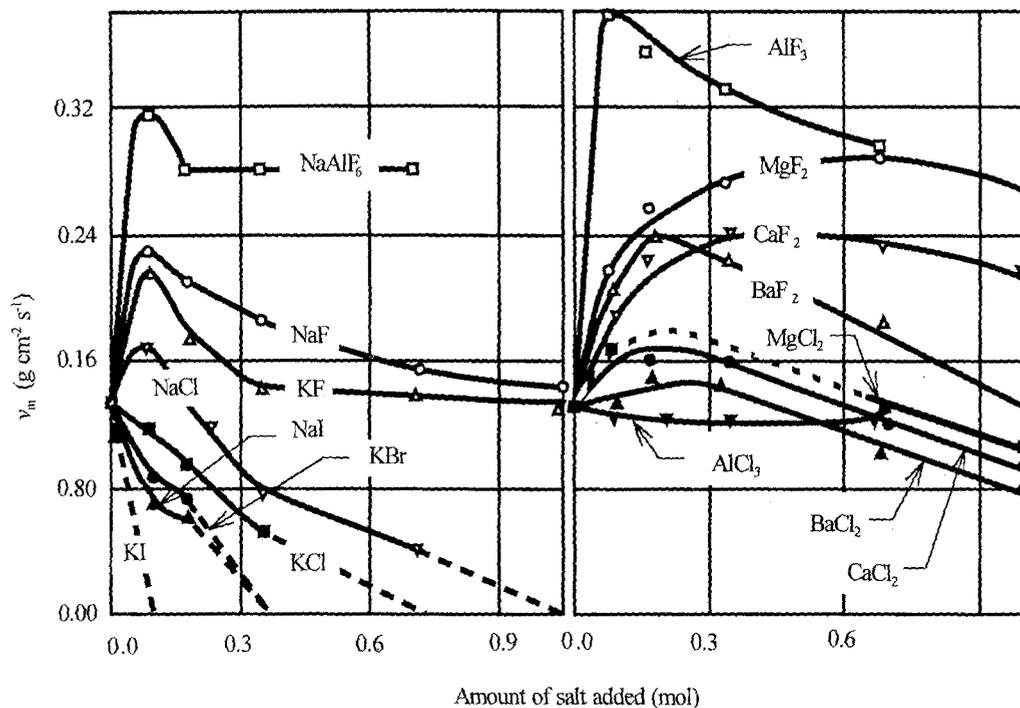


Figure 6 Influence of the addition of various salts on the mass combustion rates of the $2\text{Al} + \text{Cr}_2\text{O}_3$ thermite [100].

shown in Fig. 6 [100]. The effect of salt addition is most prominent with the addition of small amounts, and the highest combustion rate was found in the compositions containing aluminium fluoride (AlF_3) and cryolite (NaAlF_2). It is proposed that salt additives reduce the temperature at which the reaction between the oxide and the aluminium commences. The oxide film on the aluminium particle, which acts as a barrier to the interaction, can be disintegrated by the alkali metal or alkaline earth metal salts at a temperature significantly lower than the ignition temperature of the thermite, and consequently, the ignition temperature of the thermite mixture with salt addition is notably reduced [100].

4.2. The effect of pressure and centrifugal force

The effect of centrifugal force, reported as the ratio of the centrifugal acceleration, a , to the gravitational acceleration, g , on the combustion rates of several thermite systems has been investigated [103, 104]. Serkov *et al.* [103] used the thermite system 81.5 wt% (20 wt% Al:80 wt% FeO):18.5 wt% Al_2O_3 which yields a condition that all components (start and end) are in the molten state at the combustion temperature, and studied the effect of centrifugal force in the range of 0–895 a/g . In this range, the burning rate was found to increase by a factor of approximately 6, as seen in Fig. 7. The increase in burning rate was suggested to be due to the presence of molten aluminium, which is driven by the acceleration force into the pores of the still unreacted substance ahead of the wave [103]. More recently, Karataskov *et al.* [104] investigated the influence of a centrifugal force on the two thermite-based systems, $\text{CrO}_3\text{--Cr}_2\text{O}_3\text{--Al--C}$ and $\text{CrO}_3\text{--Cr}_2\text{O}_3\text{--Al--C--NiO}$. The effect of the centrifugal force on combustion rate in these two systems has

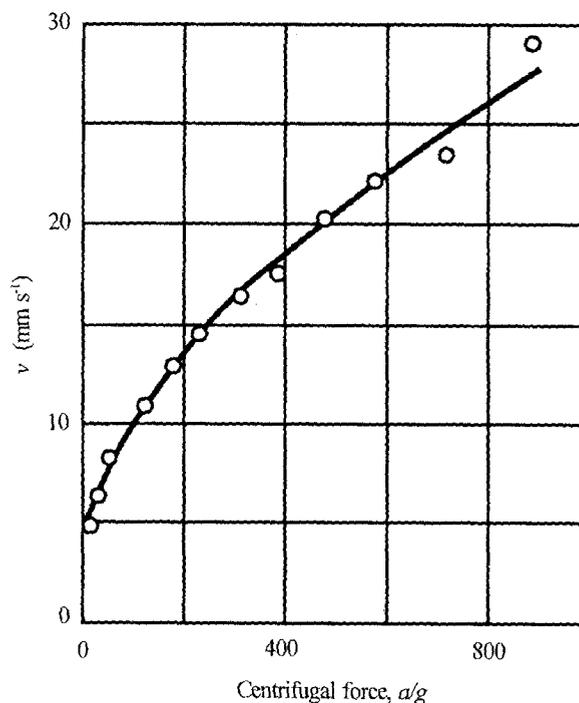


Figure 7 Combustion velocity of ferro-aluminium thermite as a function of centrifugal force [103].

a strong dependence on the nature of the carbon used, Fig. 8 [104]. The combustion rate of the mixture containing carbon black increased by a factor of 1.5–2.5 with an increase in the acceleration force (0–800 a/g). On the other hand, for the compounds containing graphite the velocity first increased slowly at low acceleration forces, but with a further increase in the acceleration force, the velocity increased sharply, by a factor of 7–12. As in the previous study, the increase in rate as a result of the application of a centrifugal force is attributed to the forced penetration of the

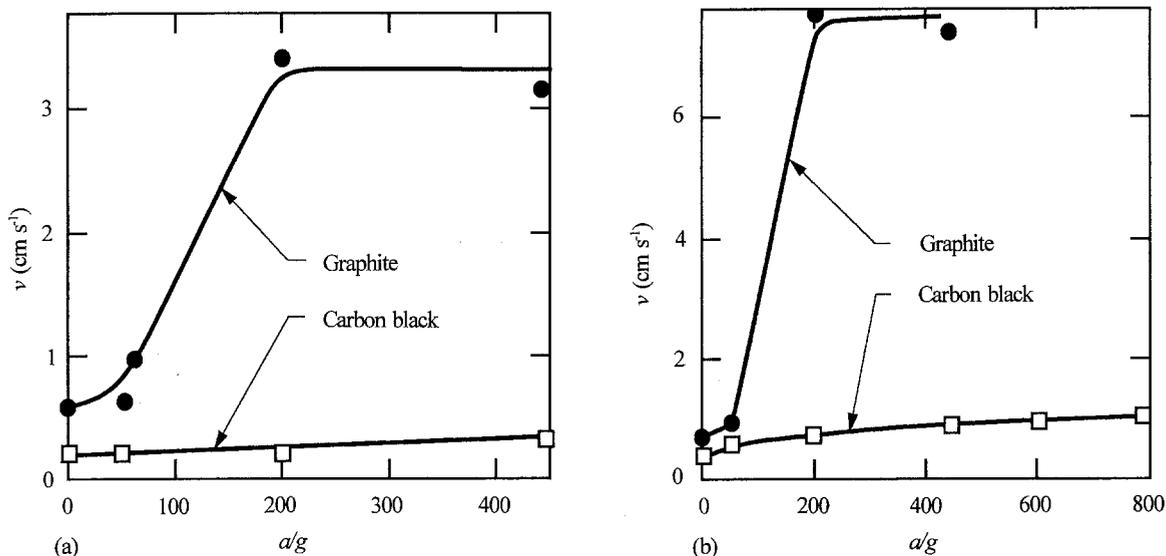


Figure 8 Influence of the centrifugal force and the nature of the carbon used on the combustion velocity for (a) 37% CrO_3 + 27% Cr_2O_3 + 27% Al + 9% C mixture, and (b) 33% CrO_3 + 24% Cr_2O_3 + 9% NiO + 27% Al + 8% C mixture (the percentages are wt%) [104].

liquid into pores of the unreacted materials [104]. In this regard it is worth noting that the increase in velocity of the reaction containing nickel in the product is significantly higher than that without nickel and is consistent with the proposed role of a centrifugal force. Presumably, the molten nickel penetrates the pores and reacts with aluminium.

For some thermite systems the burning rate depends on the ambient pressure. This has been associated with vaporization of the starting components at the temperature reached in the combustion front [106]. Romodanov and Pokil [106] studied the effect of pressure, in vacuum range, on the combustion of the thermite mixture, Fe_2O_3 -Al- Al_2O_3 . The combustion of this mixture has been shown earlier to be independent of inert gas pressure for pressures higher than 1 atm [28]. However, as the pressure decreases, the boiling point of aluminium can become lower than the combustion temperature (e.g. at $P = 10^{-2}$ mm Hg, the boiling point of aluminium is 1148 °C). Combustion rate of this thermite system at low ambient gas pressure was found to depend on the level of pressure, Fig. 9 [106]. Combustion under vacuum proceeds in the presence of a gas phase (aluminium vapour). In certain thermite systems, the combustion rate increases with pressure, reaching a maximum, and then decreases with further pressure increase, as shown in

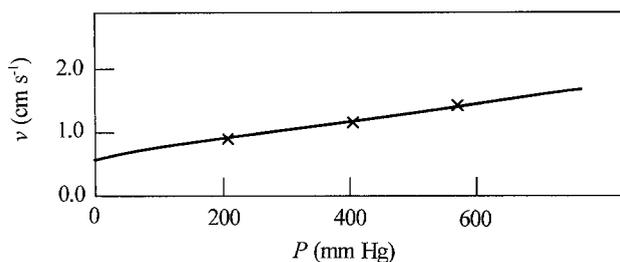


Figure 9 Pressure dependence of combustion velocity of (2Al + Fe_2O_3): 30 wt % Al_2O_3 system under vacuum [106].

Fig. 10 for three thermite systems: BaO_2 -Zr, MoO_3 -Mg, and PbO_2 -Zn [99]. Ivanov *et al.* [99] attempted to explain this anomalous pressure dependence of the combustion rate on the basis of the physical properties of the reactants and the selective wetting of the liquid. Both magnesium and zinc have low melting points (650 and 417 °C, respectively) and low normal boiling points (1107 and 906 °C, respectively), while BaO_2 has a low melting point (450 °C), and liquid BaO_2 can readily decompose at a lower temperature as the pressure decreases. For all three systems shown in Fig. 10, because of the high volatility

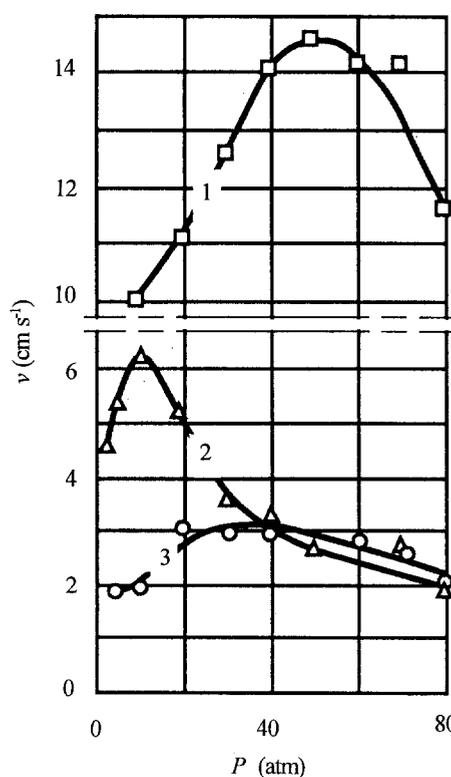


Figure 10 Effect of pressure on the combustion velocity of thermite mixtures: (1) BaO_2 -Zr, (2) MoO_3 -Mg, (3) PbO_2 -Zn [99].

of reactants, vapours are formed resulting from the heat of combustion. The rise of combustion rate at the low range of pressure is associated with the rise in the extent of the vapour phase penetrating the pores as the ambient pressure increases. However, at a higher pressure the gas formation is suppressed, and the melt formed in the combustion process can selectively wet the pores resulting in inhibition of reaction. The effect of pressure on combustion rate was also investigated on the following thermite and thermite-based mixtures: (1) $\text{WO}_3\text{-CoO-Al-C}$, (2) NiO-Ti , (3) $\text{CrO}_3\text{-Al-B}$, (4) $\text{WO}_3\text{-Al-C}$, and (5) $\text{CrO}_2\text{-Cr}_2\text{O}_3\text{-Al-C}$ [105]. In all five systems, the calculated theoretical combustion temperatures are high and exceed the melting points of the initial components and final products [41]. The combustion rates, v_0 , of all five systems were found to increase with increase in the argon pressure, P_0 , as shown in Fig. 11. The dependence of combustion velocity, v_0 , on pressure, P_0 , is described by the formula $v_0 = BP^u$, where $u_3 = u_4 = u_5 = 0.2$, $u_1 = 0.4$, $u_2 = 0.6$ (the subscripts refer to the reactions as stated above). The pressure dependence of the combustion rate indicates the presence of gas phase in the combustion process: this is evident from the nature of oxides. As discussed previously, WO_3 sublimates, and CrO_3 and CrO_2 easily decompose to O_2 and Cr_2O_3 . Moreover, it is possible to form gaseous product phases at high temperatures as demonstrated by the equilibrium calculation of the final product compositions [105]. Because, in the report [105], the unit of the product gas concentrations was not specified, the equilibrium calculation for the $\text{WO}_3\text{-CoO-Al-C}$ system (in weight fractions: 0.66, 0.124, 0.182 and 0.034, respectively) was repeated by using CSIRO thermochemistry system software. The calculated adiabatic combustion temperature and the total product gas concentration (in mole fraction) as a function of pressure are presented in Fig. 12. The calculated results agree qualitatively with those obtained by Yuxhvid *et al.* [105] and show significant amounts of gaseous products mainly

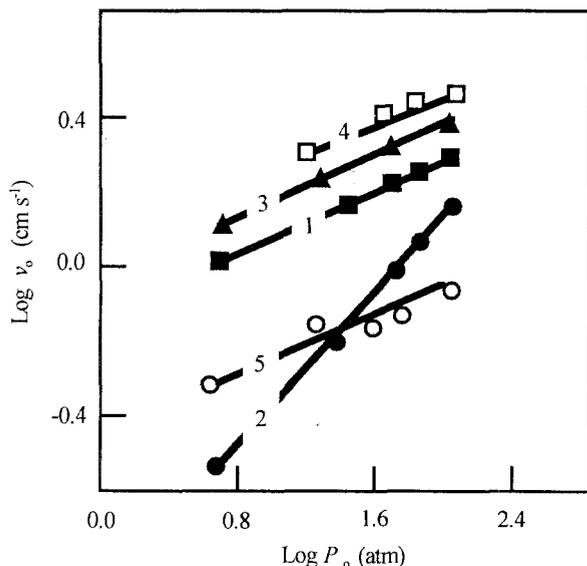


Figure 11 The dependence of the combustion velocity of various thermite reactions on pressure: (1) $\text{WO}_3\text{-CoO-Al-C}$, (2) NiO-Ti , (3) $\text{CrO}_3\text{-Al-B}$, (4) $\text{WO}_3\text{-Al-C}$, (5) $\text{CrO}_2\text{-Cr}_2\text{O}_3\text{-Al-C}$ [105].

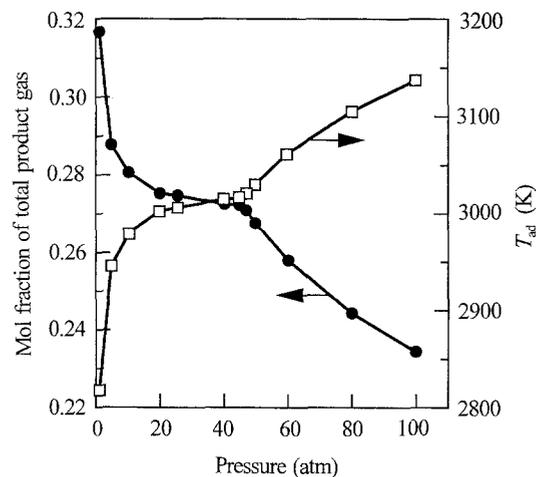


Figure 12 The effect of ambient pressure on the calculated adiabatic combustion temperature, T_{ad} , and total product gas concentration of the $0.66 \text{WO}_3 + 0.124 \text{CoO} + 0.182 \text{Al} + 0.034 \text{C}$ system (the coefficients are weight fractions).

CO , Al_2O , Al , and some Co . The combustion temperature increases with an increase in the ambient pressure while the total product gas concentration decreases as the ambient pressure decreases. The strongest dependence of v_0 on P_0 was observed for the mixture $\text{NiO} + \text{Ti}$ and may be attributed to the dissolved hydrogen and nitrogen gas in titanium particles [105]. The dissolved gases are liberated into the reacting melt and then form a gas phase. In general, increase in v_0 with increasing P_0 may occur on the account of increase in combustion temperature and the reduction in the gas volume generated. The pressure dependence of the combustion velocity of the stoichiometric $6\text{Mg} + 2\text{B}_2\text{O}_3 + \text{C}$ system has also been observed [46]. The combustion velocity increased with an increase in the argon pressure in the low-pressure range (1–13 atm), remained relatively constant in the mid-pressure range (30–150 atm), and decreased with a further increase in the argon pressure (200–1020 atm). At low pressure, significant amounts of the reactant loss due to vaporization decreases the combustion temperature, thus lowering the combustion velocity. As the argon gas pressure increases, the amount of heat loss to the surrounding argon gas also increases due to an increase in the density and thermal conductivity of the argon gas. This, in effect, decreases the temperature gradient in the combustion front, thus lowering the driving force for the propagation of the combustion front.

4.3. The role of oxide stability

The dependence of the combustion rate on the physical and chemical stability of the oxides has been investigated for a variety of thermite systems [102, 107]. Balakir *et al.* [102] studied the following thermite systems: $\text{WO}_3\text{-Al}$, $\text{MoO}_3\text{-Al}$, $\text{Nb}_2\text{O}_5\text{-Al}$, $\text{Cr}_2\text{O}_3\text{-Al}$, $\text{W}_2\text{O}_5\text{-Al}$, and $\text{Co}_3\text{O}_4\text{-Al}$ and found that oxidizers with high vapour pressure (e.g. WO_3 and MoO_3) gave the greatest rates of combustion. This is consistent with the results shown in Fig. 11 in which the mixtures

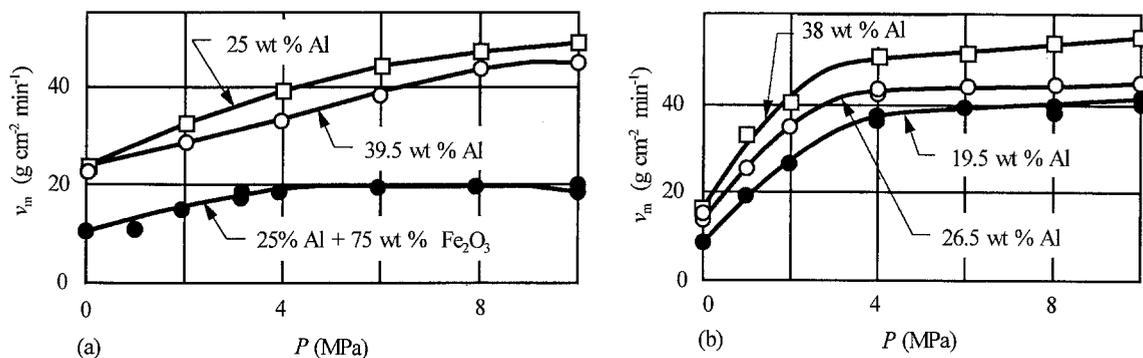
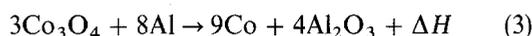
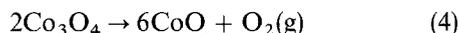


Figure 13 Influence of the pressure on the mass combustion rate of the mixtures (a) Al–Ni₂O₃ and (b) Al–NiO containing various amounts (wt%) of aluminium in the reactants [107].

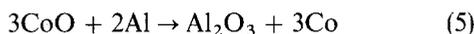
containing WO₃ exhibited higher combustion velocities. It is concluded that in these systems the interaction proceeds primarily with the participation of the gas phase [102]. For example, in the case of the thermite system Co₃O₄–Al, the mechanism begins by the step



The liberated heat raises the temperature of the system and as it reaches 900 °C, the reactant oxide becomes unstable with respect to dissociation, i.e.



The next step then involves the reaction of the oxygen gas with aluminium to form additional Al₂O₃ and the continuation of the thermite reaction, but now as



In other systems, where the oxide is stable relative to dissociation, other factors may play a role. For example, in the case of the Nb₂O₅ + Al thermite, the adiabatic temperature exceeds the melting point of Nb₂O₅ (1783 K) and thus at least part of the process involves the reaction between the molten oxide and liquid aluminium. Obviously, for systems in which the oxide does not dissociate or undergo a phase transformation (e.g. Cr₂O₃–Al), the thermite process is between a solid oxide and the liquid aluminium.

The combustion rates of Cr₂O₃–M (where M = Zr, Mg, and Al) thermites [102] were found to correlate well with the binding energy of the resulting oxides (ZrO₂, MgO and Al₂O₃). The combustion rate was found to decrease with decreasing binding energy. In the study by Shidlovskii and Gorunov [107], the combustion of the Ni₂O₃–Al and NiO–Al thermites was studied and compared with that of Fe₂O₃–Al for the following reasons: Ni₂O₃ is less stable than Fe₂O₃ (the more common oxidizer used), and it decomposes with the formation of NiO, even at 570 K. Also, there is a strong tendency for the liberated nickel to react with aluminium to form the intermetallic compound AlNi. The mass burning velocities, defined as the product of density and wave propagation velocity (g cm⁻² s⁻¹), of Ni₂O₃–Al and NiO–Al thermite mixtures with varying amounts of starting aluminium are presented in Fig. 13 along with results for the stoichiometric 2Al + Fe₂O₃ system. In the nitrogen

pressure range 0–4 MPa, the mass burning velocity of all three thermites increases with increasing pressure; however, above 4 MPa only the mass burning velocity of Ni₂O₃–Al was observed to increase with pressure. Presumably, the vaporization of aluminium at 4 MPa is sufficiently suppressed, and with further increases in pressure, the reactions of NiO–Al and Fe₂O₃–Al take place in the gasless regime so that their combustion velocities are independent of pressure, whereas the combustion of Ni₂O₃–Al continues to involve the decomposition of Ni₂O₃ to oxygen and NiO. The higher combustion rate of Ni₂O₃–Al and NiO–Al relative to Fe₂O₃–Al at all pressures was suggested to be the result of the additional contribution of the interaction of aluminium and the product nickel.

4.4. Mechanistic investigations

In the area of mechanistic studies of thermite combustion, two other experimental approaches have been attempted. One involved using high-temperature diffraction electron microscopy [109], and the other employed a programmed heating method [110]. High-temperature diffraction electron microscopy permits the study of the structure and composition of the products being formed at the interface. Examination of the interaction of Fe₂O₃ particle on aluminium film revealed that three intermediate reaction zones exist between the ferric oxide and the aluminium film, as seen in Fig. 14 [109]. In this study, the detection of traces of Fe₃O₄ led to the proposal that the decomposition of Fe₂O₃ (Fe₂O₃ → Fe₃O₄ → FeO) precedes the interaction between iron oxide and aluminium. The presence of FeO leads to the formation of FeAl₂O₄

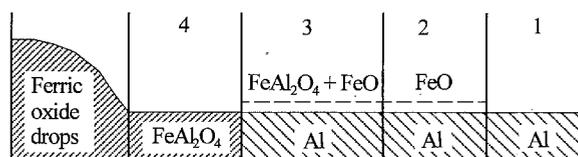
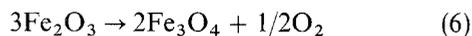


Figure 14 Interaction zones between Fe₂O₃ and aluminium films: (1) pure aluminium film, (2) finely dispersed FeO particles on the aluminium film, (3) fine particles of FeAl₂O₄ with traces of FeO on the aluminium film, (4) FeAl₂O₄ layer [109].

according to



Although this approach provides a direct examination of the structure and chemical composition changes, the heat-transfer condition of the sample examined can be very different from that in the combustion process. As pointed out elsewhere [111, 112], different heating conditions can result in different controlling mechanisms.

In the programmed-heating method developed by Miller [110], a cylindrical sample of the thermite mixture is heated at a constant rate up to the point at which the entire sample proceeds to react all at once (thermal explosion). Based on the thermal explosion theory developed by Frank-Kamenetskii [113] for gasless systems, the maximum difference between the sample centre temperature, T_c , and sample wall temperature, T_w , $\Delta T_m = T_c - T_w$, just prior to the reaction is given by [110].

$$\Delta T_m = 1.38 RT_0^2/E \quad (9)$$

where R is universal gas constant, T_0 is the initial temperature, and E is the activation energy. Using this method to study the gasless thermite reaction $3\text{Cu}_2\text{O}(\text{s}) + 2\text{Al}(\text{s}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) + 6\text{Cu}(\text{s}) + 2406\text{ J g}^{-1}$, Miller [110] obtained an activation energy of 658 kJ mol^{-1} . This high activation energy value was rationalized in terms of the high-temperature requirement for ignition of the thermite reaction and its high reaction rates, once ignition has occurred.

5. Utilization of thermite reactions

5.1. Metallurgical applications

5.1.1. Preparation of metals and alloys

The use of self-propagating high-temperature synthesis (SHS) reactions to synthesize intermetallic compounds has been demonstrated relatively recently. Such reactions, which typically involve the use of metallic reactants, have been adequately described elsewhere [39, 91], and because they do not include an oxide phase, they will not be covered in this review. One of the early industrial applications of thermite reactions is in the preparation of metals and alloys. Because of the large amount of heat generated from the reaction, the products are often in the liquid state, and thus the metallic phase, which has a higher specific gravity, can be separated from the lighter oxide phase (commonly referred to as slag). As early as 1898, Goldschmidt and co-workers [2, 3] reported using aluminium as the reducing agent for thermite reactions to prepare chromium, manganese, iron, vanadium, niobium and ferroalloys. Although there are other reducing agents, such as calcium and magnesium, that can be used in thermite reactions (see Section 2), aluminium is still by far the most preferred reducing agent in metal and alloy preparation because of several important advantages [5]. Aluminium provides a good reducing potential, as shown in Fig. 1.

Moreover, the oxide of aluminium (Al_2O_3) has a lower melting point (2051°C) than those of calcium (T_{mp} of CaO is 2580°C) and magnesium (T_{mp} of MgO is 2800°C). This lower melting point facilitates phase separation of metal from the oxide. Aluminium also has lower vapour pressure and when reacted at 1 atm does not usually boil at the reaction temperature. Thus, the use of aluminium, unlike calcium or magnesium, does not require pressure-tight reaction vessels. From a cost standpoint, aluminium is cheaper than calcium and magnesium. Although aluminium is more expensive than silicon and carbon, the use of aluminium produces purer metals and alloys because silicon and carbon can react with the product metals to form stable silicides and carbides. Thermite reactions that use aluminium as the reducing agent are commonly called aluminothermic reduction reactions [5]. Pure metals that have been produced by aluminothermic reduction processes in either large- or small-scale include refractory metals (Cr, V, Ta, Mo, W, Nb) and common structural metals (Fe, Ti) [4–8]. Ferroalloys, which are alloys of iron containing a sufficient amount of one or more additional elements for use as additives to steel, are produced principally by aluminothermic reduction processes [5–8]. Ferroalloys are obtained by co-reducing the oxides of the desired alloying elements with iron ore by aluminium. This reduction process can proceed to form such important commercial alloys as ferrotitanium, ferroniobium, ferrotungsten, ferromolybdenum, ferrovandium, and ferroboration. Preparation of nuclear metals (Pu, U) and alloys (Pu–Al, U–Al) by aluminothermic reduction process has also been investigated in several studies [114, 115]. The interest here is primarily generated by the desire to develop stable nuclear fuels. Although preparation of alkaline earth metals (Group IIA) and alkali metals (Group IA) are often done by reduction of their oxides by aluminium [8], these aluminothermic reductions are mostly endothermic and are carried out at elevated temperature and in vacuum; therefore, they do not fit the general exothermic criterion associated with thermite reactions.

The important requirement for effective thermite process of preparing metals and alloys is to achieve good separation of the metallic phase from the oxide phase. The reaction temperature, first of all, must be sufficiently high to melt both phases. For less energetic thermite reactions, thermal boosters (such as sodium chlorate (NaClO_4) and potassium nitrate (KNO_3) which react exothermically with aluminium) can be added to the thermite mixture to increase the heat evolution, or the mixture can be preheated prior to ignition [5]. Alternatively, fluxing additives such as CaO can be added to the mixture to form lower melting slags (e.g. $2\text{CaO} \cdot \text{Al}_2\text{O}_3$ which melts at $<1400^\circ\text{C}$, considerably lower than the melting point of Al_2O_3). Goldschmidt had employed this approach by using intermetallic reactants (Ca–Si, Ca–Al, and Mg–Si) instead of aluminium as reducing agents in order to form lower melting compounds [2]. Another important criterion regarding separation is the time during which the oxide is in the liquid state. This time can be controlled by both the reactant particle size

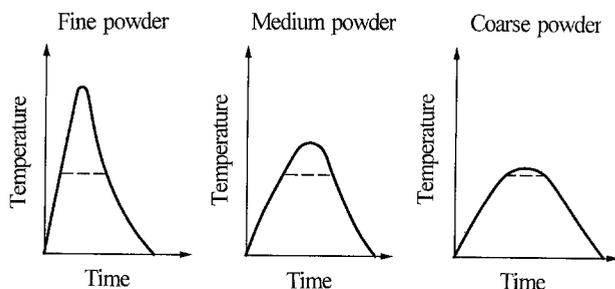


Figure 15 Schematic illustration of the effect of aluminium particle size on temperature–time profile during aluminothermic reduction [6].

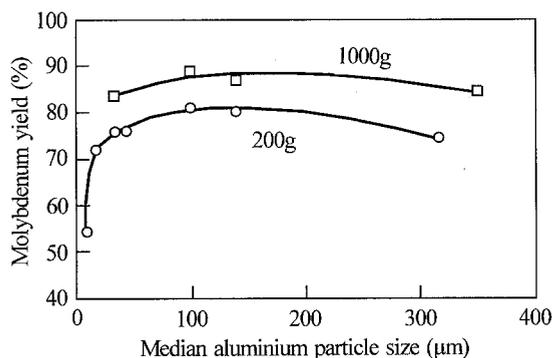


Figure 16 Effect of aluminium particle size and batch size on molybdenum yield in the aluminothermic reduction of MoO_3 [6].

and the batch size [6]. The viscosity of molten high alumina slags does not vary linearly with temperature, but decreases abruptly with relatively small increases in temperature only slightly above their melting points [116]. The effect of aluminium particle size on this molten duration is illustrated in Fig. 15 [6]. Reaction with a fine aluminium powder is so rapid that the reaction is completed before appreciable heat is conducted away to the colder reaction vessel. Therefore, a high peak temperature is produced, but because no additional heat is generated after all the aluminium is oxidized, the temperature drops rapidly and the time (depicted by the dashed line) above the temperature required for a highly fluid slag is short. With a medium-fine aluminium powder, the reaction is slower so that the peak temperature is lower because heat generation and heat loss are occurring simultaneously, but the time above the temperature required for a highly fluid slag is longer. With a coarse powder, reaction is so slow that the temperature is never much higher than the required temperature, and metal–slag separation is not as good as with a medium-fine powder. Increasing the batch size of the thermite mixture also increases the separation yield of the metal product because of the smaller heat loss resulting from the smaller surface area to volume ratio of the larger mixture charge. The effects of aluminium particle size and batch size on the product metal yield for the $\text{Al}-\text{MoO}_3$ system is shown in Fig. 16 [6].

5.1.2. Welding

The other important metallurgical application of thermite reactions is welding. At the beginning of this

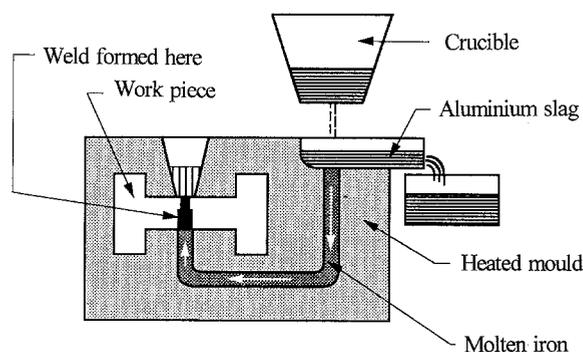


Figure 17 Schematic representation of the thermite welding process [10].

century, Goldschmidt also demonstrated the use of the metal produced from thermite reactions for welding metal parts [9]. As illustrated in Fig. 17 [10], the apparatus for thermite welding is relatively simple and consists of a reaction crucible and a heated mould in which the workpieces to be welded are placed. The thermite mixture is packed in the crucible and ignited, typically by burning magnesium [11]. Once the reaction is complete, the molten metals formed settle to the bottom and are allowed to flow by gravity to the gap between the metal pieces. As the thermite metal solidifies, it joins the two metal pieces together. Because of the relatively low cost of the equipment and materials used, thermite welding is still the most widely used field-welding process for rails [11, 12]. Most thermite welding processes use iron produced from the aluminium–iron oxide mixtures [13–16] or alloys of iron from the aluminium–iron oxide mixture with addition of other oxides such as NiO [14] and MnO_2 [16]. Thermite mixtures with copper oxides as the principal oxidizing agents are also employed [17, 18]. Instead of aluminium, titanium and magnesium are also used as the reducing agents in some cases [16, 19, 20]. Arc welding, another common form of welding, is achieved by using an electric arc as the heat source to melt and join the metals. In an arc welding process using a consumable electrode, thermite mixtures are often bound to the electrode to add additional heat to the arc and provide additional filler metal [19, 20, 117, 118]. Arc welding, with the use of a thermite mixture, has been shown to improve the speed of welding and the rate of metal deposition [19, 20, 118].

5.2. Synthesis of materials

The use of thermite-based reactions to synthesize ceramic and composite materials under self-propagating conditions has gained attention in recent years [38]. These reaction processes can be classified under the materials synthesis method commonly referred to as self-propagating high-temperature synthesis (SHS), or combustion synthesis. The method is an energy-efficient way of synthesizing many refractory materials [38, 39]. Many SHS reactions start with elemental components to form the refractory compounds. Thermite reactions have the advantage over these elemental reactions in that they start with naturally occurring

TABLE II Examples of thermite-based reactions for synthesis of refractory phases [41]

System	Original mixture	Desired product	T_c , (K) (calculated)	T_{mp} , (K) (of desired product)
1	2MoO ₃ + 4Al + C	Mo ₂ C	5200	2573
2	3CrO ₃ + 6Al + 2C	Cr ₃ C ₂	6500	2168
3	WO ₃ + 2Al + C	WC	3800	3058
4	3V ₂ O ₅ + 10Al + 6C	VC	3400	2921
5	2MoO ₃ + 6Al + B ₂ O ₃	MoB	3800	2823
6	CrO ₃ + 4Al + B ₂ O ₃	CrB ₂	4100	2473
7	2WO ₃ + 6Al + B ₂ O ₃	WB	3600	3073
8	3V ₂ O ₅ + 22Al + 6B ₂ O ₃	VB ₂	3500	2673
9	3MoO ₃ + 14Al + 6SiO ₂	MoSi ₂	3200	2293
10	3CrO ₃ + 14Al + 6SiO ₂	CrSi ₂	3600	1748
11	3WO ₃ + 14Al + 6SiO ₂	WSi ₂	3000	2433
12	3V ₂ O ₅ + 10Al + 3N ₂	VN	3400	2323

Note: Reducing agent aluminium. By-product Al₂O₃, $T_{mp} = 2300$ K. Calculation was performed in the approximation of complete suppression of vaporization of volatile components for the given composition of products. The extremely high temperatures listed for Systems 1 and 2 are evidently very difficult to realize.

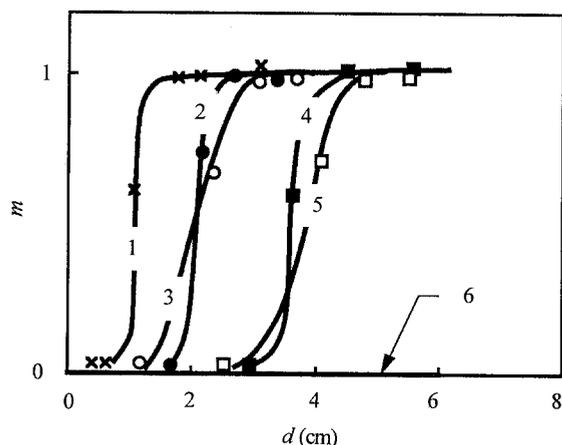


Figure 18 Yield of cast refractory compounds, m , as a function of the diameter of the reaction volume, d . (1) Mo₂C, $a/g = 1000$; (2) WC + Co, $a/g = 1000$; (3) WC, $a/g = 1000$; (4) VC, $a/g = 1000$; (5) WC, $a/g = 1$; (6) W, $a/g = 1$. ($T_0 = 300$ K for all except (5) where $T_0 = 800$ K) [41].

oxides which are less expensive and more readily available than elemental reactant powders [38].

Generally, there are two sequential chemical reactions in thermite-based synthesis reactions: (1) reduction of the oxides to form the element, and (2) interaction of the reduced element to form the desired compound. Examples of this type of synthesis of inorganic refractory phases, such as borides, carbides, nitrides and silicides, are presented in Table II [41]. The adiabatic combustion temperatures, T_{ad} , of these reactions exceed the melting points of both product phases. It is, therefore, possible to form cast refractory compounds which can be separated from the lighter oxide (Al₂O₃) by gravity or with use of a centrifuge. Critical conditions for phase separation were found with respect to the vessel diameter, d , Fig. 18, which presents the completeness of phase separation (yield of cast refractory phase in the ingot, m) as a function of vessel diameter, for various systems. For each system, a specific centrifugal acceleration, a (in g), is used. With $d < d_c$ (critical diameter), solidification of the

system is faster than phase separation, and the combustion product consists of a fused but unseparated mass. With $d > d_c$, the phase separation time is shorter than the time of thermal relaxation of the combustion products. In this case, the cast refractory and oxide phases in the combustion products will be completely separated, forming a clean boundary between the layers. The magnitude of d_c was found to decrease with increasing centrifugal acceleration and increasing initial temperature. Depending on the ratio between the diameter and height, L , of the melt, the crystallization may be unidimensional or in all directions. With $d > L$, uniformity in grain size is typically found. With $d < L$, the grain size increases from the periphery to the centre, and in the central part there are shrinkage blisters and cracks [41].

In the reactions presented in Table II, aluminium is used as the reducing metal. The use of an alternative reducing metal, magnesium, on the other hand, often results in product phases (MgO and the refractory phases) of solid forms because the adiabatic combustion temperature is less than the melting points of the product phases. In this case, separation of the desired refractory phases is readily achieved by dissolving the MgO phase with a dilute acid solution. These processes with magnesium as the reducing agent have been applied to synthesis of submicrometre SiC [42, 43] and B₄C [44–46] powders.

With the simultaneous production of multiple phases in the thermite-based reactions, it is possible to produce composite materials with phases uniformly distributed in the materials [47, 48]. Over the past three decades, various investigators have used thermite-based reactions to produce composite materials, and a partial list of these is given in Table III. The first known composite material synthesis application was done by Walton and Poulos [47] in 1959 to produce ceramic-metal composites (e.g. Al₂O₃-Cr), or cermets. They also demonstrated the feasibility of producing MSi-Al₂O₃, MB-Al₂O₃, and MC-Al₂O₃ composites (M = Cr, Zr and Ti) by heating the preforms of thermite mixtures in the furnace to the

ignition temperature. Other recent studies of synthesizing composites by thermite reactions include the work done by Cutler *et al.* [42], Holt [45], Wang and co-workers [40, 46], and Logan and co-workers [49–53]. Cutler *et al.* explored the possibilities of using self-propagating thermite reaction processes (Reactions 6–10 in Table III) to synthesize $\text{Al}_2\text{O}_3\text{-SiC}$, $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$, $\text{Al}_2\text{O}_3\text{-Mo}_2\text{C}$, and $\text{Al}_2\text{O}_3\text{-TiC}_x\text{N}_{1-x}$ composites. The predicted phases were found in the products. Holt and Wang and co-workers demonstrated the possibility of forming $\text{Al}_2\text{O}_3\text{-B}_4\text{C}$ and $\text{MgO-B}_4\text{C}$ composites by a combustion process (Reactions 7 and 11 in Table III). Fig. 19 shows the distribution of the Al_2O_3 and B_4C phases in the combusted product starting with the stoichiometric reactant mixture ($4\text{Al} + \text{B}_2\text{O}_3 + \text{C}$), and Fig. 20 shows the distribution of the MgO and B_4C phases in the combustion product starting with the stoichiometric reactant mixture ($6\text{Mg} + 2\text{B}_2\text{O}_3 + \text{C}$) [46]. In the latter mixture,

noticeable amounts of magnesium borate phase were also found in the combusted product. Since the early 1980s, Logan and co-workers [49–53] began a series of studies to understand the reaction process of forming $\text{TiB}_2\text{-Al}_2\text{O}_3$ composites starting with a mixture of TiO_2 , B_2O_3 , and aluminium. Their studies resulted in a qualitative model describing the interaction between the reactant particles. Because the $\text{TiB}_2\text{-Al}_2\text{O}_3$ products under the self-propagating process are often porous, attempts have been made to simultaneously hot-press [119] or hot-roll [120] the mixture during the reaction in order to densify the product. Rusanova *et al.* [54] developed a process for producing $\text{Al}_2\text{O}_3\text{-Cr-Al}$ composites by first using $\text{Al-Cr}_2\text{O}_3$ thermite reaction to form $\text{Al}_2\text{O}_3\text{-Cr}$ preform. The preform is then infiltrated with aluminium. This process is deemed advantageous over equivalent powder metallurgy methods in producing finely dispersed and uniformly distributed product phases. Park *et al.* [55]

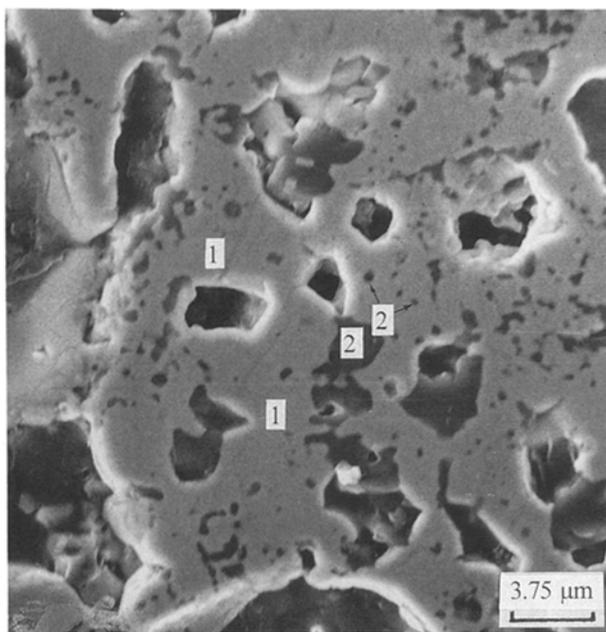


Figure 19 Spatial distribution of (1) Al_2O_3 and (2) B_4C in the $4\text{Al} + 2\text{B}_2\text{O}_3 + \text{C}$ samples combusted at 1 atm (secondary electron image) [46].

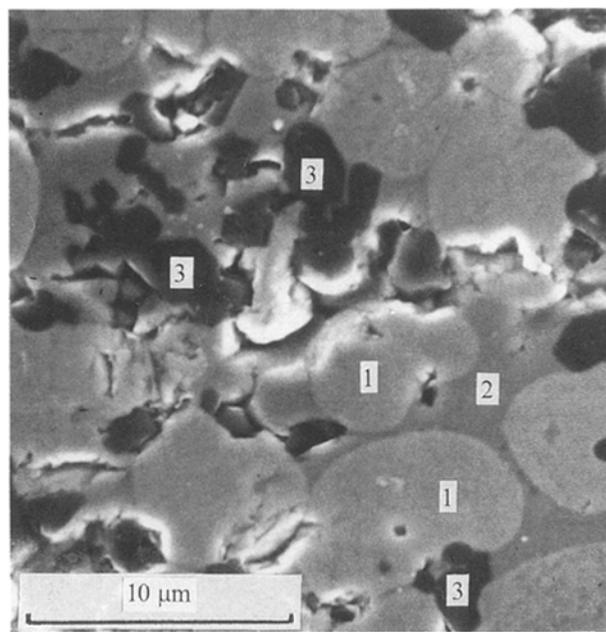


Figure 20 Spatial distribution of (1) MgO , (2) B_4C and (3) $\text{Mg}_3(\text{BO}_3)_2$ in the $6\text{Mg} + 2\text{B}_2\text{O}_3 + \text{C}$ samples combusted at 1020 atm (secondary electron image) [46].

TABLE III Reactions for synthesizing composite materials

Reaction	Reference
1. $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3$	[97, 54]
2. $2\text{ZrO}_2 + 2\text{SiO}_2 + 16/3\text{Al} \rightarrow 8/3\text{Al}_2\text{O}_3 + \text{ZrSi}_2 + \text{Zr}$	[47]
3. $\text{TiO}_2 + \text{B}_2\text{O}_3 + 10/3\text{Al} \rightarrow \text{TiB}_2 + 5/3\text{Al}_2\text{O}_3$	[47, 49]
4. $\text{TiO}_2 + 4/3\text{Al} + \text{C} \rightarrow \text{TiC} + 2/3\text{Al}_2\text{O}_3$	[47]
5. $3\text{Fe}_3\text{O}_4 + 8\text{Al} \rightarrow 4\text{Al}_2\text{O}_3 + 9\text{Fe}$	[58]
6. $\text{SiO}_2 + 4/3\text{Al} + \text{C} \rightarrow \text{SiC} + 2/3\text{Al}_2\text{O}_3$	[42]
7. $2\text{B}_2\text{O}_3 + 4\text{Al} + \text{C} \rightarrow \text{B}_4\text{C} + 2\text{Al}_2\text{O}_3$	[42, 45, 46]
8. $2\text{MoO}_3 + 4\text{Al} + \text{C} \rightarrow \text{Mo}_2\text{C} + 2\text{Al}_2\text{O}_3$	[42]
9. $3\text{TiO}_2 + 4\text{Al} + 3/2\text{C} + 3/4\text{N}_2 \rightarrow 3\text{Ti}(\text{C}_{0.5}\text{N}_{0.5}) + 2\text{Al}_2\text{O}_3$	[42]
10. $3\text{TiO}_2 + 4\text{Al} + 1.5\text{NaCN} \rightarrow 3\text{TiC}_{0.5}\text{N}_{0.5} + 2\text{Al}_2\text{O}_3 + 1.5\text{Na}$	[42]
11. $6\text{Mg} + 2\text{B}_2\text{O}_3 + \text{C} \rightarrow 6\text{MgO} + \text{B}_4\text{C}$	[45, 46]
12. $\text{SiO}_2 + \text{Al} \rightarrow \text{Si} + \text{Al}_2\text{O}_3 + \text{N}_2 + \text{heat} \rightarrow \beta\text{-sialon, 15R-sialon, Al}_2\text{O}_3, \text{AlN}$	[55]
13. $\text{Al} + \text{SiO}_2 + \text{C} + \text{N}_2 \rightarrow \text{SiC, AlN, AlON, Al}_2\text{O}_3$	[56]

Note: All reactions are balanced assuming the given starting compositions on the left side of the equations, except Reactions 12 and 13.

synthesized sialon materials by first reacting the Al-SiO₂ thermite to form silicon and Al₂O₃. The Si-Al₂O₃ mixture was then nitrized at elevated temperature for an extended period of time to form sialon materials. The phase composition of the product was found to depend on the nitrizing temperature. At lower nitrizing temperatures (1400–1600 °C), a mixture of β-sialon, 15R-sialon, Al₂O₃ and AlN results. At a higher temperature (1750 °C), only β-sialon and 15R-sialon were found in the product. Lisachenko *et al.* [56] investigated the effect of initial composition and the ignition method on the phase composition of the combustion product obtained by reacting the SiO₂-Al mixture either with or without the addition of carbon in a nitrogen atmosphere. The three ignition methods studied were by: (1) a thermite reaction (Fe₂O₃-Al or Fe₂O₃-Mg), (2) plasma, and (3) heating to self-combustion (i.e. heated to 1853 K). By changing the method of initiating the combustion, the composition of the batch composition, and the composition of the atmosphere, it is possible to regulate the phase composition of the combustion product, and in combination with a subsequent nitrizing process, it is then possible to obtain various nitride-containing or sialon-containing ceramic materials. Using thermite reactions to synthesize materials can also be carried out by mechanical means. Schaffer and McCormick [57] demonstrated that it is possible to form β' brass by ball milling a mixture of CuO, ZnO and calcium powders. Hida and Lin observed that grinding can induce the thermite reaction $3\text{SiO}_2 + 4\text{Al} \rightarrow 3\text{Si} + 2\text{Al}_2\text{O}_3$ [121].

5.3. Coating by centrifugal thermite process

An interesting utilization of thermite reaction to produce industrial products is the centrifugal thermite process (C-T) of lining metal pipes with a ceramic material (e.g. Al₂O₃) [58–61]. Many industrial applications require pipes and vessels with a corrosion-resistant, abrasion-resistant, and heat-resistant ceramic bonded to the metallic body. The centrifugal thermite process, which provides a rapid and economical method for producing such metal-ceramic composite pipes, is illustrated in Fig. 21. It involves first packing a powdery thermite mixture, such as the Al-Fe₂O₃ mixture, against the inner surface of the pipe and then igniting the mixture at one point while

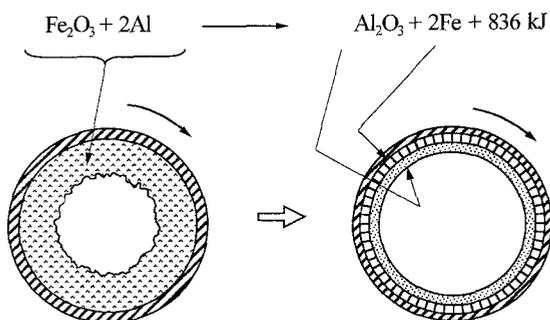


Figure 21 Schematic representation of the centrifugal-thermite process [63].

the pipe is being rotated about its axis. Because of the large amount of heat released by the thermite reaction, the product phases are in the liquid state and, therefore, can undergo separation due to the difference in their densities. The centrifugal force assists the speed of separation and also the effective expulsion of trapped and impurity gases. The result is the formation of bonded low-porosity layers of Al₂O₃ on top of the higher density iron layer, which bonds to the inside of the pipe.

Much of the research and development work of the process has been carried out by Odawara and co-workers [58, 61–70]. Several process parameters that affect the composites were investigated, and these included thermal insulation [64], centrifugal force [65], environmental gas content [66], and gas pressure [67], and the additives to thermite powders [68]. It was confirmed by temperature measurements along the pipe length that the reaction proceeds along the inner surface of the hollow body first, and then into the layer in the radial direction, resulting in a homogeneous quality in the direction of pipe length [63]. The schematic illustration of temperature at a hollow surface measured by an infrared-radiation thermometer during the centrifugal thermite reaction process is shown in Fig. 22 [63, 70]. The temperature first increased around the point of ignition (1) and then decreased as the reaction proceeded to propagate in the longitudinal direction. The temperature rose acutely when the whole interior surface had reacted. It then dropped rapidly when the fume generated was being blown off (2). The reaction proceeded to propagate in the radial direction (Stage B), and subsequently reached the highest temperature when all the packed thermite powder had reacted. The cooling process then followed (Stage C). The microstructure of the composite lining is dictated by the thermal history of the cooling process [70]. As the duration of ceramic molten state becomes longer, a denser and more uniform ceramic layer, but with larger grains, is obtained. As the duration of metal in the molten state becomes

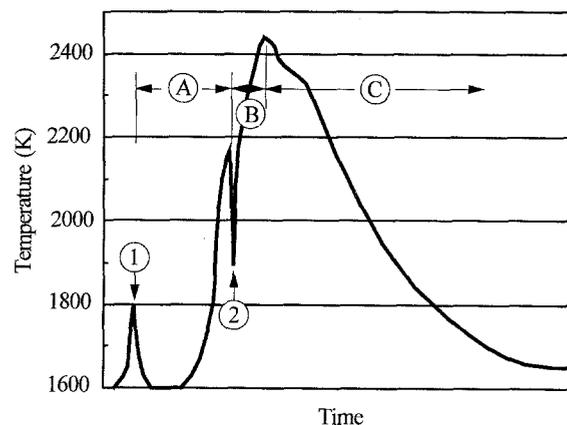


Figure 22 Schematic illustration of the temperature profile of the hollow surface measured by an infrared radiation thermometer during the centrifugal thermite process: (1) ignition; (2) blow-off of fumes; A, propagation of reaction along the hollow surface; B, propagation of reaction in the radial direction; and C, cooling process [63].

longer, wetting between the product metal and the outer pipe improves. This longer molten metal duration, however, results in slower cooling, thus thermal shrinkage of the outer metal pipe will be larger, causing the product ceramic layer to compress more and resulting in microcrack formation in this layer. Therefore, a balance of these two stages is needed in order to obtain a desirable microstructure. This centrifugal thermite process has also been extended to forming ceramic-ceramic composite pipes [69]. Such composites are demonstrated by the following reactions



The process results in the formation of the oxide (Al_2O_3), which has a lower density, as the inner layer and the carbide or boride, which has a higher density, as the outer layer. Because this outer ceramic layer does not wet the inner surface of the mould, the ceramic composite pipe could be easily removed from the mould.

5.4. Other novel applications

Cost-effective methods of storing radioactive wastes in the solid product from thermite reactions have been developed by several investigators [71–73]. The method developed by Spector *et al.* [71] involves first mixing radioactive wastes into a thermite mixture and then igniting the mixture to form highly water insoluble polysilicates which fix the radioactive materials. The principal thermite reaction for this process is

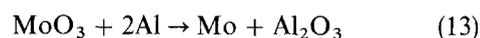


with a heat of reaction of -245 cal. Because part of the heat required for the formation of molten silicates is derived from the chemical reaction, only relatively low-temperature furnace facilities (600°C) are required to preheat the mixture before ignition. Moreover, both silicon and Fe_2O_3 are readily available, relatively inexpensive and thus, economically suitable for large-scale industrial processing. Another thermite method proposed by Rudolph *et al.* [72] involves using aluminium as the reducing agent to react with metallic oxidants (Fe_2O_3 and/or MnO_2). The product of the thermite reaction is reported to be a solid containing several crystalline phases, and possibly also vitreous phases, and has comparable leaching characteristics as the glass from the conventional vitrification process for storing radioactive waste. In the third method [73], radioactive waste-containing metal oxides generated from nuclear power plants is mixed with aluminium powder and ignited to reduce the metal oxides. The product mixture is melted by the heat generated from the thermite reaction and thus can be cast into shape. The method is reported to reduce the waste volume with low cost.

The high energy generated from the thermite reaction is an excellent heat source for many other special applications. For example, the thermite reaction ($8\text{Al} + 3\text{Fe}_2\text{O}_3 \rightarrow 4\text{Al}_2\text{O}_3 + 9\text{Fe}$) has been considered as the fuel for heating the motive fluid in a gas turbine

to be used for torpedo propulsion [74]. The considerable energy that can be released by a thermite reaction at a high rate for a limited period of time, the compactness of the thermite mixture, and the quietness of the thermite reaction make it suitable for such an application. Another application was demonstrated by Mohler *et al.* [75]. They employed a thermite mixture ($2\text{Al} + 3\text{CuO}$) to develop small torches for applications where the amount of space is limited. In applications where, momentarily, production of high-pressure and high-velocity gases is required, such as in the demolition of concrete, thermite mixtures with additions of substances that decompose into gases at high temperature can be ignited to result in such a condition [76, 77]. A thermal cell employing a thermite reaction can be activated when the external gas reaches above the ignition temperature of the thermite mixture [78]. In this application, the thermite reaction, once reacted, can generate sufficient heat to melt a solid electrolyte, which in molten form is conductive, thus completing a circuit. The heat of thermite reactions has also been applied to sintering ceramic powders [79, 80] and for relieving localized stress in welds. [81]. The thermite mixture $\text{Al}-\text{WO}_3$ can be vacuum deposited as thin layer on a substrate underlying or overlying a thin-film circuit, and this thermite layer can be ignited by electrical current to self-destruct the circuit [82].

In addition to utilizing the heat generated by the thermite reaction, many other interesting applications also use the substances produced by the thermite reaction to achieve certain overall material properties. Thermite compositions such as $\text{Si}-\text{MoO}_3-\text{WO}_3$ can be incorporated into the starting powder mixture used to produce thin-layer passive electronic components (e.g. resistors) [83]. This method reduces the baking temperature and time typically needed to produce these components. A MoSi film on a silicon wafer can be formed by irradiation of CO_2 laser on a thin powder layer of MoO_3-Al mixture applied on the wafer surface [84]. According to this study, the CO_2 laser initiates the following sequential reactions



Metal silicides have low resistivity, good thermal and chemical stability, and are desirable materials for many electronic applications [122, 123]. Lastly, thermite reactions can be used to provide the oxide hardeners (such as Al_2O_3 , ZrO_2 , TiO_2 , SiO_2 and ThO_2) in the process of making dispersion-hardened ferrous alloys. Such a process has been shown to provide finer dispersion hardeners ($< 1 \mu\text{m}$) and more uniform distribution of these hardeners over the conventional powder metallurgy approach [85].

6. Conclusion

This paper presents a general review of thermite reactions which are exothermic oxidation-reduction reactions involving a metal and an oxide. The reducing tendency and the physical properties of the metal and the physical properties of its corresponding oxide

are important considerations in the selection of a suitable thermite system. Because of the large heat release, once initiated, thermite reactions are capable of self-propagation. The reactions can be ignited by an energy source such as a combustion wave from a chemical reaction, electrical current, radiation energy, or a mechanical impact. The physical and chemical stability of the reactant oxides affects the initiation of the combustion reaction. Several factors that affect the combustion rate and combustion mode of thermite systems are also discussed. Thermite reactions have long been important in the preparation of many metals and alloys and in welding. In recent years, thermite reactions have gained increasing utilization in the synthesis of materials such as cast ceramics, cermets, and ceramic-ceramic composites. Because of the low cost of the reactant materials and the energy efficiency of the reactions, various material processes, for example, forming a ceramic lining in a pipe and storage of nuclear waste, have been developed based on thermite reactions. This review also surveys other material-related inventions based on thermite reactions.

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Received 7 May
and accepted 12 November 1992