



Self ignition of layers of metal powder mixtures



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ABSTRACT

The availability of models that predict the thermal stability and spontaneous ignition of metal powders is of great importance to the nuclear industry and powder handling systems in general. The present paper describes the application of a previously published two-dimensional axisymmetric model to the ignition characteristics of zirconium (Zr), tantalum (Ta) and Zr/Ta deposits on a hot surface. Their minimum ignition temperatures and oxidation behavior were investigated by validating the model against extensive experimental data. A nonlinear increase of the minimum ignition temperature was observed for Zr/Ta layers as a function of Zr content. The more reactive material, Zr, determines the thermal sensitivity of Zr/Ta mixtures, even when the Zr content is as low as 30 wt.%. The model successfully predicts the ignition sensitivity of such mixtures with average deviations of $\pm 4\%$ for Ta loads amounting to less than 80 wt.%. Three main aspects have been highlighted by SEM observations and XRD analyses: i) the diffusion of oxygen through the upper layers is the rate limiting step of the combustion reaction, ii) mechanical stresses are important for tantalum oxide layers and modify oxygen diffusion, and iii) due to lack of oxygen at the bottom of dust deposits, nitration reactions occur.

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1. Introduction

Since the industrial age and extensive use of coal, self-heating of combustible dust has been recognized as a major industrial hazard. However, the industrial landscape has changed considerably and the industrial use of metal powders, as pure compounds or mixtures, has grown significantly in recent decades. Statistics show that such materials are frequently involved in accidents due to self-heating, fire and explosion, during crushing, pneumatic transport, storage, etc. Giby analyzed 197 incidents related to combustible dust over 25 years and concluded that 24% of them were caused by metal dusts against only 10% for coal [1].

In order to assess the risk related to the self-ignition of metal powders, quantitative safety parameters such as the minimum ignition temperature or ignition delay have to be estimated. Such data are available for pure compounds in the literature [2–4]. However, for powder mixtures, which can be encountered in raw materials as well as in finished products or waste, it is often not the case [5].

In the nuclear field, the recovery and conditioning of old waste from the first generation of nuclear reactors, consisting of structural elements in zirconium, magnesium or graphite, are concerned with such ignition phenomena. The thermal stability of the metal elements mentioned above varies as a function of their particle size distribution and can

even lead to pyrophoricity (i.e. their thermal instability at room temperature). This, in particular, is the case of fine uranium or uranium compounds [6] which can be encountered in association with zirconium or magnesium.

Moreover, among the material and fuel candidates for certain types of nuclear reactors of the future, non-oxide compounds such as carbides or nitrides of actinides (uranium carbide [7], uranium or plutonium nitrides, etc.) can lead to thermal instability in industrial synthesis and waste recycling. In addition, such materials are often encountered as powder layers of variable thickness (deposits due to shearing of structural elements, filter cakes...) or containers (hoppers, silos ...).

Due to the number of applications and substances, this relative lack of data can be justified by the magnitude of the work that the experimental characterization of each mixture under various conditions would represent and cost. Therefore, the development of a numerical model dedicated to the prediction of the thermal instability of such mixtures is essential.

In this paper, a two-dimensional axisymmetric model has been developed for predicting the thermal behavior of layers of metal powder mixtures in contact with a hot surface. In order to validate this model, an experimental study has been carried out. First, various tests have been done in order to choose the most appropriate and the most representative materials for such industrial applications in the nuclear field. Secondly, the thermal stability of pure dusts and of solid/solid mixtures has been determined. Finally, results of ignition tests have been compared with those of the numerical model.

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2. Choice of the metal powders

In order to study the self-heating of metal powder mixtures, the dusts have been chosen with regard to two main criteria: their minimum ignition temperatures must be significantly different and these materials must have distinct “thermal signatures” (strong exothermicity on a short period of time). Tests have been carried out on a heating plate consisting on an Inconel square plate of 280 mm length. Powder beds of 5 mm thickness were put on the plate and heated at a rate of 40 °C/min to a maximum temperature of 480 °C. Oxidation onset temperatures and the temperature at which the maximum oxidation rate has been recorded (T_{oxi}^+) have also been determined by thermogravimetric analyses using a Setaram thermobalance (Setsys Evolution TGA).

At first, various powders have been tested with a maximum diameter of 44 µm (Table 1). However, only zirconium and niobium powders ignited at a temperature close to 300 °C. It was then decided that powders having a lower particle size distribution (ranging from 1 to 6 µm) be used. Only four powders ignited during such tests: iron, niobium, tantalum and zirconium. Table 1 shows the results of these tests as well as the values of Pilling and Bedworth's ratios (RPB) related to the main oxide which is produced [8]. When “self-heating” is specified, it means that no ignition has been observed within the meaning of the IEC 1241-2-1 standard [9], but that a significant increase of temperature has been recorded (ranging from 50 to 200 °C).

In order to guide the material choice, thermogravimetric analyses have been performed under air atmosphere with a 5 °C/min heating rate up to 1000 °C (Table 2) and confirm the results shown in Table 1. The remaining powders can be categorized into two kinds of materials: those with a high reactivity such as fine iron and zirconium, and those with a low reactivity as niobium, tantalum and coarse zirconium. Iron will not be considered for further tests because its exothermicity leads to powder temperatures of approximately 300 °C with no significant ignition peak (low “thermal signature”). Tests carried out with niobium have demonstrated that the oxidation of this powder leads to a high volume expansion, which will be difficult to model (Fig. 1). As a consequence, fine tantalum and zirconium have been used in this study.

3. Determination of pure dust properties

3.1. Physical properties of the powders

The powders were dried under dynamic vacuum during 24 h before testing. Zirconium and tantalum powders were chosen with narrow particle size distributions and similar mean particle sizes in order to avoid segregation during the dust layer formation [10]. Particle size distributions were determined in ethanol by using a laser diffraction particle size analyzer (Mastersizer, Malvern). The results were quite different from the diameters indicated by the suppliers as can be seen in Table 3. Zirconium dusts being delivered in water, the particles

Table 2

Temperature at which the maximum oxidation rate has been recorded T_{oxi}^+ for some of the tested powders.

Powders	Iron	Niobium	Niobium	Tantalum	Zirconium	Zirconium
Particle size (µm)	1–6	1–5	44	2	2–3	44
T_{oxi}^+ (°C)	281	444	460	550	346	488

were larger than expected due to the formation of agglomerates during the drying of the powders [10]. The particle size distribution of tantalum exhibits a secondary peak, which confirms the presence of agglomeration for this powder. Scanning Electron Microscopy (SEM) and BET analyses have also been performed on the dust samples. In the case of zirconium, SEM observations corroborate the presence of small spherical particles from 300 nm to 1.7 µm, frequently arranged in aggregates (Fig. 2). They also show the porous structure of zirconium agglomerates, which is verified by BET experiments with an open porosity of 67% (Table 3). Tantalum exhibits a porous coral-like structure with an open porosity of 88%, which is consistent with the SEM observations carried out by Matsuda and Yamaguma (Fig. 3) [11]. The results obtained by BET and SEM analyses are more consistent with the particle sizes indicated by the suppliers, i.e. 2 µm for tantalum and 2–3 µm for zirconium. Differences between BET diameter and SEM diameter are notably due to the fact that the BET diameter has been estimated by assuming that the particles were identical and spherical, which is obviously not the case. With the particle size distributions being not unimodal and the powder densities being strongly different, segregation necessarily takes place. Thus, dusts were homogeneously mixed by means of a Turbula chaotic stirrer (T2F – GlenMills) before the tests.

3.2. Determination of the oxidation kinetics

The oxidation kinetics of zirconium and tantalum has been studied by thermogravimetric analysis, using a Setaram thermobalance (see Section 2). The experiments were realized under the following conditions: the samples were kept at 20 °C under air during 2 h, then heated at 5 °C·min⁻¹ to set point temperatures ranging from 150 to 450 °C and kept for 20 h at constant temperature, before cooling at 20 °C·min⁻¹. The weight variations with respect to the set point temperatures were used to correlate various kinetic laws and determine the kinetics parameters. Classical shrinking core models with film-diffusion, ash diffusion and chemical reaction limitations as well as Ginstling and Brounshtein, and Jander models, which are diffusion controlled models, were tested [12,13]. The rate of these gas–solid reactions can be generally described by the following equation:

$$\frac{dX}{dt} = A_0 \cdot e^{-\left(\frac{E_a}{RT}\right)} \cdot f(X) \quad (1)$$

Table 1

Characteristics of the tested metal powders.

Powders	Particle size (µm)	Main oxide	RPB (–)	T_{ignition} (°C)	Observations	Providers
Aluminum	44	Al ₂ O ₃	1.29	–	No ignition	Alfa Aesar
Iron	1–6	Fe ₂ O ₃	2.14	155	Ignition	Goodfellow
Iron	44	Fe ₂ O ₃	2.14	–	Self-heating	Sigma-Aldrich
Magnesium	44	MgO	0.80	–	No ignition	Alfa Aesar
Niobium	1–5	NbO	1.38	293	Ignition	Alfa Aesar
Niobium	44	NbO	1.38	304	Ignition	Alfa Aesar
Tantalum	2	Ta ₂ O ₅	2.44	334	Ignition	Alfa Aesar
Tantalum	44	Ta ₂ O ₅	2.44	–	Self-heating	Alfa Aesar
Titanium	44	TiO ₂	1.78	–	No ignition	Alfa Aesar
Tungsten	44	WO ₂	2.09	–	No ignition	Alfa Aesar
Zinc	44	ZnO	1.59	–	Self-heating	Merck
Zirconium	2–3	ZrO ₂	1.55	181	Ignition	Alfa Aesar
Zirconium	44	ZrO ₂	1.55	290	Ignition	Alfa Aesar

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