

INVESTIGATION OF THERMAL PROPERTIES OF HIGH-TEMPERATURE (1000–4000 K) SYSTEMS BY AN ARC SPECTROSCOPIC METHOD*

(DECOMPOSITION OF TRICALCIUM PHOSPHATE)

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An arc spectroscopic method was developed on the analogy of thermogravimetry. Using spectrographic recording, line intensity vs. arcing time relations were determined and transformed to weight loss vs. time curves for the components evaporated from a carbon electrode cavity. The temperature of a spot 3 mm below the bottom of the cavity was followed with a thermocouple and temperature of the bottom was calculated. As a first attempt the decomposition of tricalcium phosphate was investigated. It was estimated that in the reductive surroundings of the cavity the temperature at which the rate of decomposition was maximum, was about 2000°.

Since 1950 increasing interest has been shown in the reactions taking place in the carbon electrode cavity [1–5]. Compounds formed during a given arcing period have been identified by X-ray diffraction and the temperature of the outer part of the electrode measured by optical pyrometry [4, 5]. The aim of these studies was primarily to promote the formation of volatile or non-volatile compounds in a controlled manner, and indirectly to increase the analytical sensitivity of arc spectrochemical methods.

On the basis of published observations and our own experience an attempt has been made to develop an arc spectroscopic method on the analogy of thermogravimetry: in the latter case the weight of the residual sample is measured, and in the former case the relative amount of the fraction removed can be determined. With "arc spectroscopic thermal analysis" one may expect to extend the measuring range to 3700°, the sublimation point of carbon. Further, the method can give information about the thermal properties of minor constituents of the sample as well.

As a first attempt, an investigation of tricalcium phosphate was chosen, for in this case it is possible to compare the results of different methods.

Results and discussion

The experimental set-up for the arc spectroscopic investigation is illustrated in Fig. 1. The cavity of the carbon anode contains only 1 mg of sample. With this set-up it is thought that the majority of the heat transfer is effected through

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the bottom of the cavity, which has a temperature T_1 . The temperature T_2 of the surface 3 mm below the bottom of the cavity was measured with a platinum/platinum-rhodium thermocouple. A spring between the electrode clamp and the ceramic tube of the thermocouple ensured good contact with the measuring spot.

Before analysis of the sample it was treated with solutions of noble metals, which acted as internal references for temperature estimation. After drying and homogenization the concentrations of Ag, Au and Pd were each 0.04% and that of Pt 1%.

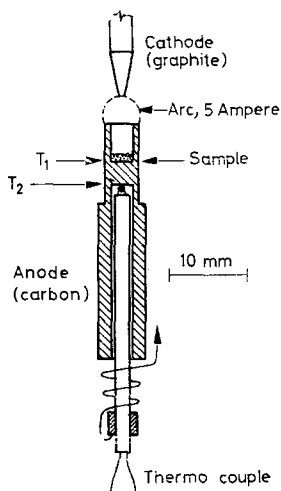


Fig. 1. Experimental set-up for the arc spectroscopic investigation (T_2 measured, T_1 calculated temperatures)

During the arcing the thermocouple voltage was recorded; this is shown in Fig. 2, with the corresponding temperature curve. It can be seen that a fairly fast initial temperature rise was followed by a nearly linear rate of increase due to the smooth combustion of the wall of the cavity. At the moment of the final jump in temperature a small globule of the residual sample could be seen to drop from the electrode, which by this time had practically no cavity.

The temperature of the bottom of the cavity, denoted as T_1 (Fig. 1), which is in direct contact with the sample, was calculated using the Fourier law of heat conduction. It is obvious that calculation with this equation can be simplified if the thermal conductivity is not dependent on temperature. According to Euler [6], the thermal conductivity of carbon not containing crystalline graphite is practically non-variant in the range 25–3200°. It was therefore important to use a carbon electrode material with microcrystalline-structure. The thermal conductivity of the selected carbon (type Ringsdorff RW II) was guaranteed by the manufacturer to be $0.06 \text{ cal s}^{-1} \text{ degree}^{-1}$.

The rate of heat flow was determined by calorimetric measurement and related to the arcing period. For this, in a separate experiment the lower tip of the carbon electrode was immersed in a glass beaker containing stirred water. The results of the calorimetric measurements were corrected for the radiant heat transmission.

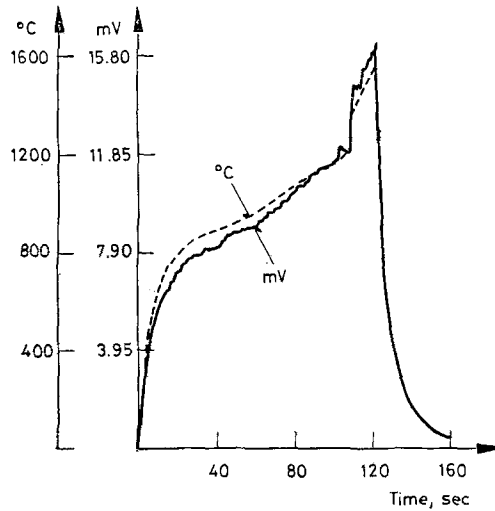


Fig. 2. Recorded thermocouple voltage during the arcing, and the corresponding temperature curve

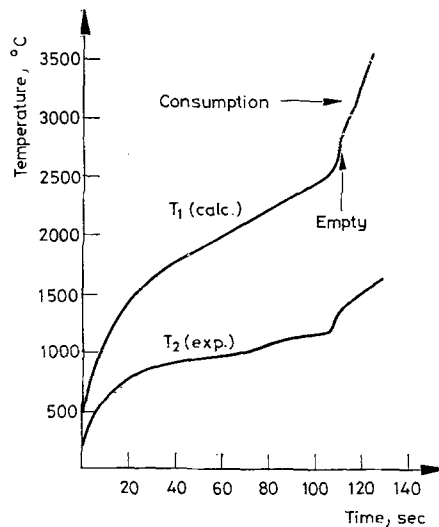


Fig. 3. Variation of the measured (T_2) and calculated (T_1) temperatures during the arcing. (The moment at which the cavity became empty and the moment of consumption of the cavity wall are marked)

In Fig. 3 the measured T_2 and the calculated T_1 are plotted as a function of arcing time. The point when the cavity became empty and that at which the cavity was completely consumed are marked. Euler's measurements [6] show that the temperature of a layer 0.5 mm below the anode spot is 3200° for a pure carbon electrode 3 mm in diameter. Our calculations indicate that the temperature is very close to this value at the moment of the final consumption of the cavity. The agreement seems acceptable.

The emission of the vapour entering the arc plasma was measured spectrographically in order to detect all the species of interest simultaneously. From racking plate spectra, with successive 6 s exposures, the line intensity vs. excitation time curves commonly used in analytical spectrochemistry could be constructed. For the investigations discussed here it is more expedient to apply a normalized and integrated "evaporation curve", which can be transformed to a weight loss vs. time curve as follows.

If the amount of sample is small, and the spectral lines used are invariant and free from self-absorption [7], we may write:

$$I(t) = a\Phi(t) \quad (1)$$

where I is the line intensity, Φ is the rate of evaporation and a is a constant. Integrating the intensity over the total evaporation of the relevant species, we get:

$$H = \int_0^{t'} I(t) dt = a \int_0^{t'} \Phi(t) dt = aQ \quad (2)$$

where H is the radiant exposure and Q is the total amount of the element loaded. To eliminate the unknown constant a , normalization should be performed:

$$I(t)/H = I_n(t) = \Phi(t)/Q \quad (3)$$

where $I_n(t)$ is the normalized intensity. As a last step the normalized intensity is integrated until the moment of inspection (t):

$$\int_0^t I_n(t) dt = H_n(t) = \frac{q(t)}{Q} \quad (4)$$

where $q(t)$ is the fraction of the species evaporated during time t .

With this interpretation it can easily be seen that the normalized radiant exposure (H_n) times a hundred is the weight loss in per cent.

Fig. 4 illustrates the normalized radiant exposure vs. time relationships. The upper part shows the curves of sample constituents, and the lower part the curves of the added noble metals. The spectral lines used are also marked. From the combined data of Figs 3 and 4 the weight loss vs. temperature curves could be plotted according to thermoanalytical practice, and are shown in Fig. 5. On the curve for calcium the formation and decomposition temperatures of calcium car-

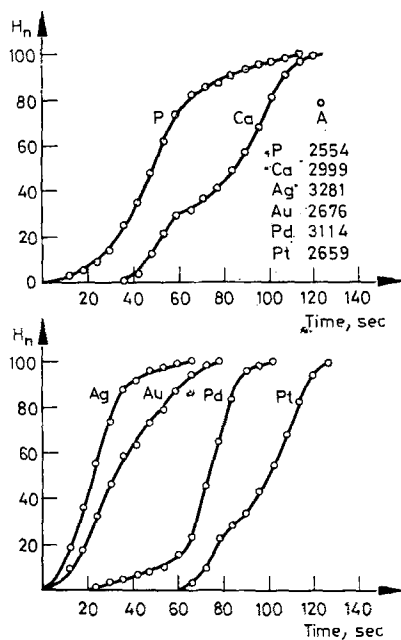


Fig. 4. Normalized radiant exposure ($\times 100$) vs. arcing time curves for the constituents and the added noble metals

bide [4] and the melting and boiling points of calcium oxide [8] are indicated. The latter data are also denoted on the curves of the noble metals.

The noble metal curves permit some conclusions on the accuracy of the temperature measurement. The solutions of noble metals were each added to the sample and dried separately. Thus, it was thought that during the arcing these metals would be present in a separate molten phase. Furthermore, the noble metals are not likely to form any compound with the sample and electrode material. The weight loss curves of noble metals are therefore considered independent of each other and of the sample. In spite of the reasonable prediction that below the melting point the weight loss should be negligible, the curves show 8%, 3% and 1% losses for silver, gold and palladium, respectively. Accordingly, the error becomes smaller in the vicinity of the inflection point of the phosphorus curve where the heating range is also constant (Fig. 3).

In Fig. 5 it can be seen that the temperature at which the maximum rate of evaporation of phosphorus occurs (the inflection point is marked by a dotted line) is about 2000° , which may be considered the decomposition temperature of tricalcium phosphate.

The weight loss curve for calcium (Fig. 5) shows two inflection points. The first is closely coincident with the inflection point of phosphorus, while the second is above the decomposition temperature of calcium carbide. During the final part

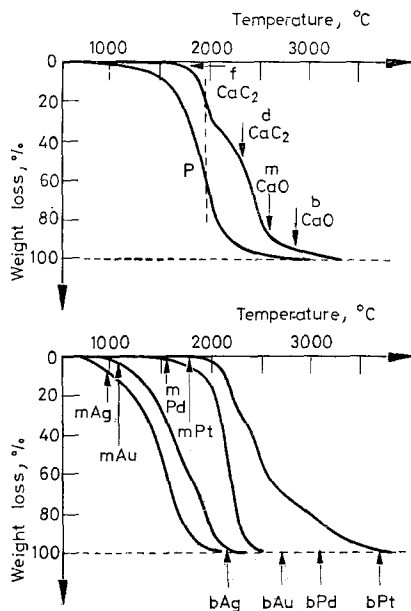


Fig. 5. Weight loss vs. temperature curves; *m* melting, *b* boiling, *f* formation, *d* decomposition temperatures according to the literature

of the arcing period the presence of calcium oxide might well account for the curve shape, because in this range the wall of the cavity is consumed and there is no reducing atmosphere. Since the calcium oxide falls off the electrode tip, the ordinate values for the calcium curve may not be taken as accurate.

Conclusion

The thermal stability of tricalcium phosphate differs markedly in environments of different oxidizing powers [9]. Under non-reducing or oxidative conditions it melts at 1700°. However, when heated up to about 2000° with an oxyhydrogen flame, its decomposition is practically negligible. In a graphite furnace its behaviour is completely different. Reduction starts in the solid phase at 1050° and phosphorus escapes. Then at 1600° the system melts and calcium oxide, calcium carbide and calcium phosphide can be detected in the melt.

In analytical flame photometry the decreasing effect of the phosphate anion upon the emission or absorption of calcium species is a long and much investigated question [10]. The amount of interference differs markedly in oxidizing and reducing flames. A good comparison may be made between the behaviour in oxyacetylene and in acetylene-nitrous oxide flames, which have about the same temperature, 2900°. Phosphate interference occurs in the non-reducing oxyacetylene

but in the case of the reducing acetylene-nitrous oxide flame it is completely eliminated [11]. This means that the refractory calcium-phosphorus compounds are decomposed below 2900° under reducing conditions.

In the carbon electrode cavity used by us the environment was also reductive because of the presence of carbon and the formation of carbon monoxide [12]. According to Fig. 5, the formation of volatile phosphorus (compound) starts at about 1000°, has a maximum rate at about 2000° and is finished at about 2700°. These results are in agreement with the observations cited above.

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RÉSUMÉ — On a mis au point une méthode de spectroscopie d'arc, analogue à la thermogravimétrie. Elle repose sur la détermination de l'intensité des raies en fonction de la durée d'excitation et sur la transformation de ces données en courbes de pertes de masse en fonction du temps pour les constituants provenant de la cavité de l'électrode, en carbone. Un thermocouple disposé 3 mm au-dessous du fond de l'électrode permet d'évaluer la température. Comme premier essai, on a étudié la décomposition du phosphate tricalcique. La décomposition atteint sa vitesse maximale à 2000 °C environ dans les conditions d'atmosphère réductrice de la cavité.

ZUSAMMENFASSUNG — In Anlehnung an die Thermogravimetrie wurde eine bogenspektroskopische Methode entwickelt. Der Zusammenhang zwischen Linienintensität und Zeit wurde durch spektrometrische Beobachtungen bestimmt und bezüglich der aus dem Kohlen-elektroden-Kelch verflüchtigten Substanz in eine Gewichtsverlust — Zeit Kurve transformiert. Die Temperatur der 3 mm unterhalb der Bodenplatte des Elektrodenkelches befindlichen Fläche wurde mit einem Thermoelement gemessen und die Temperatur der Bodenplatte berechnet. Als erster Versuch wurde die Zersetzung von Tricalciumphosphat studiert. Es wurde festgestellt, daß unter den reduzierenden Bedingungen des Kelches die Zersetzung um 2000 °C die maximale Geschwindigkeit erreicht.

Резюме — Разработан спектроскопический метод на аналогии термогравиметрии. Спектроскопически детектирована зависимость интенсивности линии от времени электрической дуги. Эта зависимость трансформирована в кривую потери веса — времени. Методом исследовалось расход фосфата кальция. Установлено, что при восстановительных условиях скорость распада при 2000° максимальна.