PRINCIPLES OF THE OPTICAL DIFFERENTIAL THERMAL ANALYSIS (ODTA)

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ABSTRACT

Optical differential thermal analysis (ODTA) can operate in the 490-3600°C range, using infrared pyrometers for the temperature detection of both the Black-Body and the sample. Hence, the method is called "optical." Infrared detection of any phase transition is a result of two cooperative effects: ΔH and the emissivity change. Such cooperation leads to a high sensitivity thereby permitting ODTA measurements at temperature rates as low as 0.1°C/min. Hence, phase transitions can be studied at almost equilibrium conditions. In order to detect emissivity changes, single color pyrometers have to be used. Problems associated with simultaneous use of the Black-Body as a temperature reference source and a heater are discussed. Use of the ODTA at high temperatures is demonstrated on a study of the melting behavior of a sapphire single crystal. The feasibility of computing emissivities as a function of temperature from the gathered data is indicated.

INTRODUCTION

The term "thermal analysis" is reserved for techniques in which physical or chemical changes of a system are determined as a function of temperature. The principal techniques under this definition are thermogravimetry and differential thermal analysis (DTA).[1,2] In DTA, thermocouples are used most frequently to determine the temperature at which heat of reaction is either evolved or absorbed. Thermocouples limit the use of the DTA to temperature ranges below 1600°C and to a noncorrosive atmosphere. At temperatures over 1400°C, thermocouple wires are mechanically weak and have to be reinforced by refractory materials. Due to the high temperature, the increased electrical conductivity of refractory materials causes an electrical leakage which, together with the air atmosphere in the furnace, may cause problems in measurements. Hence, a noncontact technique is preferable for high temperature measurements.

Emissivity is a thermochemical and thermophysical property of materials. Its value changes when a material undergoes a chemical or a physical change. In turn, emissivity variation is reflected in the amount of the infrared radiation (IR) emitted by such material. A method for thermal analysis based on IR radiation detection was designed and named, the Optical Differential Thermal Analysis (ODTA).[3] The ODTA operates in the temperature range from 800 to 2200°C and in any atmosphere tolerated by the material of the furnace.

The concept of temperature measurement by infrared radiometry differs significantly from the measurements done by thermocouples. Elements of infrared radiometry, pertinent to the ODTA, shall be reviewed first.

Principles of Temperature Measurements by the Infrared Radiometry

Part of the radiant energy which strikes an object is transmitted through, part is reflected from, and yet another part absorbed by that object.

If the total energy reaching the object is defined as unity, then:

$$t + r + a = 1 \tag{1}$$

where $\underline{t}$, $\underline{r}$, and $\underline{a}$ are the object's fractional transmittance, reflectance and absorptance, respectively. If a major part of the radiant energy is transmitted through the object, such material is regarded as transparent. By contrast, if $\underline{r}$ is very high, the object behaves like a mirror. Materials with high $\underline{a}$, on the other hand, are good absorbers. An important principle of infrared radiation is expressed by the Kirchhoff's law for the emissivity ϵ:

$$a = \epsilon \tag{2}$$

which describes the consequence of the fact that at a thermal equilibrium the energy radiated by an object must be equal to the energy absorbed. This is the fundamental law on which the design of the ODTA apparatus is based. (ϵ is a number between zero and one which expresses the emissive characteristics of a material surface.) The Kirchhoff's law is valid for any material and for any wavelength:

$$a\lambda = \epsilon\lambda. \tag{3}$$

The Black-Body (Bl-B) is a perfect absorber, thereby it is the most powerful radiator possible. Since absorptivity is quantitatively equal to emissivity, a small aperature in the black-body cavity (BBC) yields a radiant energy flux that has almost the same properties as a thermal field within a completely enclosed cavity, hence represents the temperature of the BBC.

A small object or sample (an imperfect absorber) situated within the BBC has the same temperature as the BBC. However, the pyrometer focused on the sample will read temperature T_S approximated by:

$$\frac{1}{T_B} - \frac{1}{T_S} = \frac{\lambda_0}{C_2} \quad \ln \epsilon_S \tag{4}$$

where T_S is temperature of the nonperfect radiator, T_B is temperature of the BBC, λ_0 is the central wavelength of the pyrometer response range, C_2 is the second radiation constant and ϵ_S is the emissivity of the imperfect radiator.[4]

The emissivity is a thermochemical and a thermophysical property of a material; therefore it varies abruptly at a phase change. The enthalpy and the emissivity changes are reflected in the temperature differential between the sample and BBC. A small aperature in the cylindrical wall of the BBC, detailed description of which will be given elsewhere, exits Bl-B's radiation while the pyrometer focused on the sample through the aperture in the lid of BBC is predominantly exposed to the sample radiation. The temperature from the BBC pyrometer is the temperature reference source. By plotting the reference temperature on the X axis and the sample temperature on the Y axis, the temperature curve shown in Figure 1 is obtained. The accurate temperature of onset of the thermal arrest is difficult to determine from the temperature curve. A change of the slope of temperature curve can be better resolved by plotting temperature differences between sample temperature and temperature reference source on the Y axis DTA curve, Figure 2. The practically undetectable thermal arrest on the thermal curve, indicated by arrow b) in Figure 1, can be well resolved by the derivative of the temperature curve of Figure 1, as seen in Figure 3, DTA curve.
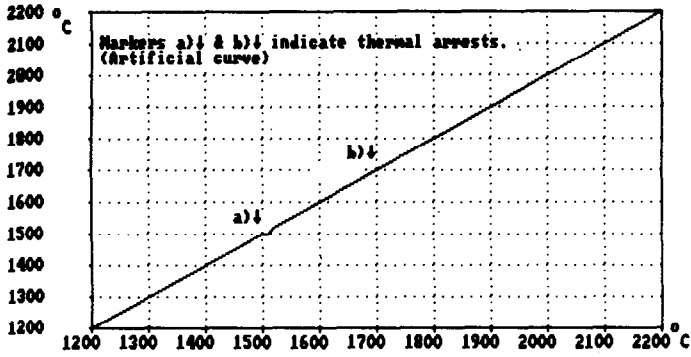
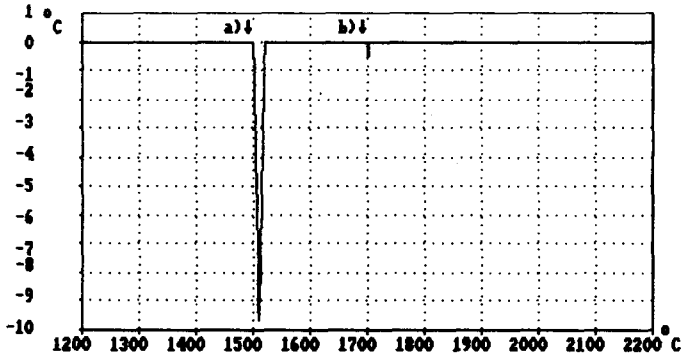FIGURE 1. ODTA temperature curve.

FIGURE 2. DTA curve of temperature curve from Fig. 1.
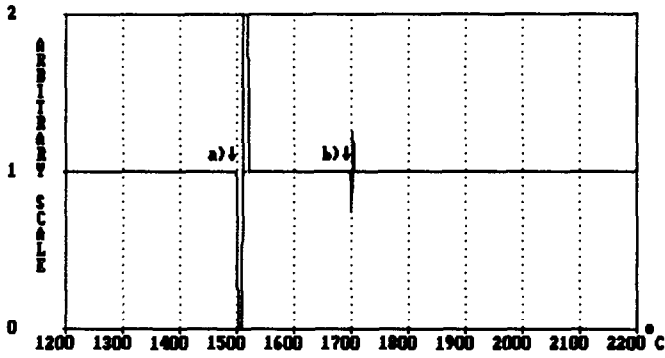

FIGURE 3. dTA curve of temperature curve from Fig. 1.

Thus far the discussion has been concerned only with the total radiant emission into a hemisphere. For obvious reasons the pyrometers cannot be mounted coaxially. Consequently, due to the directional property of the radiation, the area of the BBC viewed by each radiometer is different and the magnitude of radiation reaching each radiometer depends on the angle θ. The directional property of radiation is described by a radiant brightness concept. Radiant brightness is the radiant flux emitted per unit area per solid angle. This quantity is called radiance which has dimensions of watt/cm^2. Lambert's law for radiation emitted in the hemisphere is:

$$N\theta = N_0 \cos\theta \qquad (5)$$

N_0 is radiance and θ is the angle which the radiometer forms with the axis of BBC.

Errors, arising from the nonaxiality of the pyrometers and a particular geometry of the BBC used in the ODTA apparatus can be almost eliminated by either "specific calibration" or more practically by computer data refinement; both will be discussed elsewhere.

Data Acquisition

Linearized IR pyrometers yield digital signals which are acquired by a computer in tables of the following forms: x,y; x,x-y; t,y; and t,x-y, where x and y are the data from the BBC and the sample, respectively, and t is the real time. The x-y terms are differential data which can be generated either directly or from the digital data. The advantage of the latter is in the fact that the data can be simultaneously corrected for inaccuracy arising from the difficulty of applying correctly the Lambert's law and from other incidental experimental errors. The x,y data are used for calculation of the emissivity. Differentiation of x,y data can also be carried out with respect to the "experimental furnace background." Data collected with respect to t are useful in calculations of the reaction kinetics.

The possibility to display simultaneously three types of data from a single experiment gives the ODTA a unique flexibility. A theoretical x,y temperature curve, of two consequent hypothetical isothermal arrests, is shown in Figure 1, while its differential form x,x-y (DT curve) is depicted in Figure 2. In Figure 3, derivative form (dT curve) of the temperature curve is shown.

PRINCIPLES OF MEASUREMENTS

The shape and the area of ΔT_{max} and ΔT_{min} in the DTA depends on both intrinsic and extrinsic factors. The extrinsic, i.e., experimental factors, which are most determinative, are the heating rate, the temperature reference source and the relative positioning of the temperature reference source to the sample. In the ODTA, the dual function of the BBC eliminates temperature reference source along with the thermocouple assembly. As a consequence, the heating rate in the ODTA is quite domineering.

For example, ΔT peaks of sapphire heated at 5.0°C/min and at 0.5°C/min are dissimilar as seen in Figure 4.
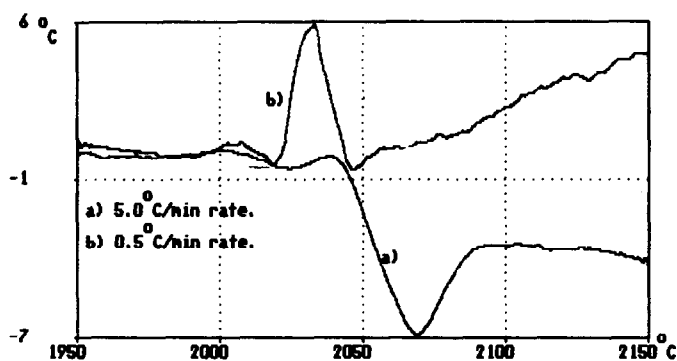
FIGURE 4. ODTA curves of sapphire melting in argon atmosphere.

In the ODTA concept the sample mass is always small compared to that of the BBC, hence, any abrupt enthalpic change in the sample will not effect the BBC temperature itself; but,when the sample melts,the liquid phase has greater reflectivity, thereby the emissivity will decrease. This effect results in a lower radiation transfer between the BBC and the sample according to Equation 6:

$$q_{B \rightleftharpoons S} = A_1 \sigma (T_B^4 - T_S^4) \cdot 1/[(1/\epsilon_B)+(1/\epsilon_S)-1] \qquad (6)$$

where $q_{B \rightleftharpoons S}$ is the net radiation interchange between the surfaces of the BBC and the sample, T_B and T_S are the absolute temperatures of the BBC and the sample, ϵ_B and ϵ_S are emissivities of the material of the BBC and the sample, respectively, A is a shape factor and σ is the Stefan-Boltzmann constant.

Simultaneous decrease of both the heat transfer and the emissivity enhances the visibility of the thermal-arrest resulting in the good distinguishability of the melting temperature on the differential curve. This principle allows $\Delta T/t$ to be as low as $0.1^\circ C/min$. At low $\Delta T/t$ rates the resolvability of the melting point can be further enhanced by the use of large samples. At the beginning of the melting a small amount of liquid is formed. Owing to the fact that the entire top surface of the sample has nearly uniform temperature, the liquid phase, upon reaching the melting temperature, forms almost uniformly throughout an entire thin surface layer and the melting proceeds downward from the surface. This makes it possible to measure the temperature of melting with samples whose weight can range from 2g to even more than 2000g.

Sapphire melt has higher reflectivity than solid sapphire, hence, after melting, due to the lower emissivity, the baseline departs downward, DTA curve a) in Figure 4.

The ODTA curves a) and b), as seen in Figure 4, show dissimilarity. In this case the only factor which can cause such an effect is the difference in $\Delta T/t$ rates. The explanation of ΔT_{max} observed on curve b) can be inferred from the sapphire weight loss when the sample is maintained at temperatures 50 to 20°C below its melting temperature. Mass spectroscopy under such conditions detected Al_2O in the furnace atmosphere. This agrees with Repko's[5] findings which have shown that from the three possible alumina suboxides, Al_2O is the thermodynamically favored species.

The kinetics of the reaction:

$$Al_2O_3(S) \iff Al_2O(g) + O_2(g) \tag{7}$$
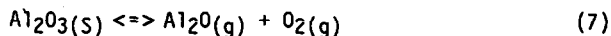
was measured. Disks of sapphire single crystals (5 cm^2) weighing 12g, were placed in a moly crucible and heated to 2040°C in argon ambient atmosphere. The loss of 0.008g/cm^{2}hr was found to be independent of the sample weight but directly proportional to its surface area, and time. This means that when sapphire is heated at the 5°C/min rate over an interval from 2000 to 2100°C, 0.012g of sapphire will be lost, while at the 0.5°C/min rate, 0.13g of Al$_2$O$_3$ will be evaporated from the sapphire disk. Consequently, the thickness of the disk heated at 0.5°C/min rate will be lowered by some 10 percent. Since sapphire transmittance in the 0.7 to 1.1 μm range is high and also a function of the thickness; the pyrometer sees a greater portion of the moly radiation, thereby the baseline rises. The ΔT_{max} observed on the DTA curve of sapphire heated by 0.5°C/min rate may indicate that the free energy of formation (ΔH) in Equation 7 is negative. This can be substantiated by observations made during the study of the Al$_2$O$_3$-Y$_2$O$_3$ system where yttria-rich compositions, i.e., mixtures with high melting points, lost selectively higher amounts of alumina when heated above 1950°C in an argon atmosphere.

CONCLUSION

Principles of the ODTA method were discussed in the view of infrared radiation laws. The capability and operation of the ODTA is demonstrated by a study of the sapphire melting. It is demonstrated that the ODTA technique can in a short time solve quite complex problems at high temperatures.

ACKNOWLEDGMENT

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