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ROLE OF SURFACE CHEMISTRY IN THE IGNITION OF PYROTECHNIC MATERIALS

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ABSTRACT

Due to the interaction of fresh metal surfaces with oxygen of the atmosphere, native oxides always form on reactive metals, such as titanium and aluminum. In this paper, the chemistry of the native oxide will be discussed in light of its role in pyrotechnic ($Ti/KClO_4$) and thermite (Al/Cu_2O) reactions. Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) were used to characterize the surface chemistry of the native oxide at ambient (25°C) and at elevated (<1000°C) temperatures. From the AES data it was concluded that the oxide on titanium began dissolving at 300°C, and above 350°C the data showed the presence of "free" metal on the surface. XPS data showed the dissolution process to proceed through the formation of titanium suboxides. Similar AES data recorded on the native oxide of aluminum indicated that no dissolution occurs over the temperature range of 25°C to >660°C (the melting point of aluminum metal). However, AES analysis of Al/Cu_2O pellets revealed the presence of an interfacial reaction zone between the aluminum fuel and the Cu_2O particles. These AES and XPS results were found to complement the thermal property measurements, such as DSC and DTA, on the $Ti/KClO_4$ pyrotechnic and Al/Cu_2O thermite mixtures. A reaction mechanism is presented for the $Ti/KClO_4$ pyrotechnic mixture illustrating the role of the surface oxide in the ignition process. A model is also presented for Al/Cu_2O ignition.

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INTRODUCTION

The basic chemical mechanisms which control the thermal ignition of pyrotechnic materials are not well known. A series of studies to determine these mechanisms for a limited number of pyrotechnic blends is presently underway at the Mound Facility. As part of this effort, a study of the surface chemistry of $TiH_x/KClO_4$ ($0.15 \leq x \leq 1.9$) pyrotechnic compositions began in 1975 followed by studies on Al/Cu_2O thermites a year later (Ref. 1 to 7). Early results established that the titanium subhydride particles are coated with thin layers of titanium oxide, suboxide, and/or hydroxides with Ti^{+4} as the primary oxidation state. Also, a contaminant layer of carbon was always present on the fuel surface. In more recent studies, it was shown that simply mixing titanium powder with the $KClO_4$ oxidizer lowered the surface concentration of titanium suboxides (or hydroxides). The surface oxides were shown to dissolve upon heating through a process which increased the surface concentration of the suboxides followed by an increase in free titanium metal at the surface at higher temperatures. These surface processes have been related to the electrostatic and thermal initiation mechanisms for the $TiH_x/KClO_4$ system (Ref. 8 and 9).

The surface chemistry of aluminum fuel, Cu_2O oxidizer, and both powdered and compacted Al/Cu_2O thermites has been investigated at the Mound Facility (Ref. 3 to 7). The native oxide coating on the Al powders as received from the manufacturer was found to increase by approximately 20% after mixing with the Cu_2O oxidizer at room temperature. Pressing the mixture for 15 minutes at 425°C doubled the thickness of the aluminum oxide coating on the fuel. It was also shown that the surface of the Cu_2O contained small concentrations of CuO that disappeared upon heating.

For most applications, the Al/Cu_2O thermites are pressed at elevated temperatures and pressures to form special shapes and densities required to meet specific needs. This hot pressing utilizes temperatures of 425° to 500°C and pressures in excess of 10,000 psi. These conditions plastically deform the fuel so that a matrix of Cu_2O oxidizer is established in a continuum of aluminum. An interfacial region of at least 100 Å between the Al and Cu_2O is produced by the pelletizing process which was examined by scanning Auger microscopy (Ref. 7).

In this study, the surface chemistries of $Ti/KClO_4$ and Al/Cu_2O are related to thermal data for these systems. Mechanisms to explain the roles of the surface oxides in the ignition of these pyrotechnics are proposed for each system.

EXPERIMENTAL

The titanium based pyrotechnic materials used in this study have previously been described in some detail (Ref. 8 and 9). Polycrystalline titanium and aluminum foils were used for both the AES and XPS experiments to minimize the influence of surface roughness on the measurements.

Theoretically stoichiometric thermite mixtures (11 wt % Al and 89 wt % Cu_2O) were produced by dry mixing Reynolds XD28 aluminum flake and Cerac "Pure" cuprous oxide in a V-blender for one hour (Ref. 10). Aluminum flake was used as received while Cu_2O powders were sieved through a 400 mesh screen prior to blending. Thermite pellets about 6 mm in diameter, 2 mm in height, and at 90% of theoretical density were pressed from powders with preheated graphite dies under dry nitrogen at 425°C and 12,000 psi for 15 minutes (Ref. 12).

Thermal data were generated with a DuPont 990 thermoanalyzer using the 1200° high temperature DTA cell, the DSC cell and the 951 thermogravimetric analyzer. A Varian Auger spectrometer (Model 981-2707) having a maximum electron beam energy of 10 keV and a minimum spot size of 5 μm was used for the AES measurements. A beam energy of 5 keV and a beam current density of 20 mA/cm^2 (2 μA beam rastered over $10^4 \mu m^2$) was selected. The XPS data were obtained with an extensively modified AEI ES-100 photoelectron spectrometer. Modifications to this instrument include the addition of a 220 l/sec turbomolecular pump and a 110 l/sec ion pump for evacuation of the sample chamber. The heater assembly in the AES and XPS systems has been used in cathode studies and is described elsewhere (Ref. 11). In both cases, the temperature of the foil was measured using a chromel-alumel thermocouple which was spot-welded directly to the foil.

RESULTS AND DISCUSSION

1. Titanium

Unprotected titanium metal powder is pyrophoric; that is, a fresh metal surface of titanium can ignite spontaneously in air at room temperature. However, if the metal powder is passivated, e.g., with its native oxide, oxidation rates become negligible so that the powder is stabilized to temperatures in excess of 500°C. Figure 1 illustrates the DTA curves for titanium powder ($TiH_{0.15}$) and for the $TiH_{0.15}$ mixed with $KClO_4$, KIO_4, $KClO_3$, or $RbClO_4$ oxidizers. The exothermic oxidation reactions for these pyrotechnic systems were relatively slow until the temperature exceeded 500° where the reactions became self-sustaining, i.e., ignition occurred. All of the major features in these curves below 500° can be attributed to processes associated with the oxidizers; for example, the strong endothermic peak at 300° in the curve for $TiH_{0.15}/KClO_4$ is due to a rhombic to cubic phase transition in the $KClO_4$. Thus, the DTA thermal data establish that thermal ignition of titanium based pyrotechnics is controlled by processes associated with the fuel and is relatively independent of the oxidizer.

Auger electron spectroscopy (AES) is a well-documented surface characterization technique capable of probing the top nanometers of material. AES surface scans were recorded for a passivated titanium foil sample as a function of temperature and the ratio of the intensity of the L-MM 418 eV line of titanium to the K-LL 509 eV line of oxygen was calculated. This ratio is shown as a function of temperature in Figure 2. The increase in the Ti/O ratio beginning just below 300°C is characteristic of the dissolution of the oxides of titanium into the metal substrate. This is indicative of an increase in surface reactivity due to increased availability of unoxidized titanium metal.

While AES clearly indicates the dissolution process, it cannot provide direct evidence for changes in the oxidation state of titanium which would be expected to accompany this process. It has previously been shown that it is possible to detect lower oxidation states of titanium such as TiO, Ti_2O_3, and Ti_3O_5 within the passive TiO_2 film by using XPS (Ref. 12). Therefore, the O 1s and Ti 2p spectra were recorded at eight different temperatures in order to study changes in the surface chemistry during dissolution. Peak deconvolutions were carried out using a DuPont 310 Curve Resolver under the assumption that titanium was bound as Ti^o, Ti^{+4}, or Ti^{+n} where $o<n<4$. The total counts-per-second under each titanium peak was then ratioed to the total counts-per-second under the O^{-2} portion of the O 1s spectrum and plotted as a function of temperature. This plot, shown in Figure 3, shows that the Ti^o/O^{-2} ratio begins to increase at ∿350° which is in good agreement with the AES data. The Ti^{+4}/O^{-2} ratio begins to decline at ∿300°C coincident with the increase in Ti^o/O^{-2} and Ti^{+n}/O^{-2} ratios. Interestingly, the Ti^{+n}/O^{-2} ratio does not peak until a temperature of 450° is attained. Thus, we conclude from the XPS data that the dissolution process proceeds through the formation of lower titanium oxides.

It should be noted that ultra high vacuums were used in generating the AES and XPS data. In normal oxidizing environments such as those used in generating the thermoanalytical data and in pyrotechnic blends, the replacement of the native oxide is sufficiently rapid between 300° and 500° to keep the active titanium surface concentration very low. This reoxidation of the surface is indicated by DSC as a weak exotherm which we have superimposed on the Auger data in Figure 2.

These data then provide a basis for understanding the chemical processes associated with the thermal ignition of titanium based pyrotechnics. The rapid oxidation reaction necessary to generate sufficient heat for self-sustained reaction is controlled by the availability of reactive titanium at the surface of the fuel particles. At temperatures below 500°, the dissolution reaction that generates the active specie at the surface was relatively slow so that there was insufficient fuel available for sustained oxidation in the DTA sample configuration. At temperatures in excess of 500°, the dissolution became rapid enough that the oxidation reaction which mirrors it generated sufficient heat for ignition. Thus, the ignition process seems to be kinetically controlled by the dissolution of the titanium oxides with the concomitant production of reactive titanium on the surface. The diffusion controlled reaction with oxygen gas at the inner titanium-titanium oxide boundary also occurs but has been shown to be slow as compared to the surface oxidation process (Ref. 2).

2. Aluminum

Aluminum, like titanium, has an oxide coating which stabilizes the very reactive metal against further oxidation until relatively high temperatures. The oxidation process is again controlled by the availability of reactive metal on the surface. When the unoxidized aluminum is exposed to even trace quantities of oxygen, it rapidly reacts as shown by the thermogravimetric curves in Figure 4. A gain in mass is shown for the spherical aluminum powder beginning at about 600° regardless of the atmosphere surrounding the sample; the high affinity of the free metal for oxygen removes trace contaminates of oxygen from the "inert" atmospheres. For the spherical aluminum which has a nominal particle size of 10 μm, the increase in oxide thickness represented by the weight gain shown in Figure 4 is of the order of 4000 Å.

The oxidation of aluminum powder at about 600°C is also shown by the DTA curves in Figure 5. Again, the exotherm is relatively independent of the atmosphere surrounding the sample. The endotherm corresponding to the fusion of aluminum at 660° is very weak or completely absent due to the coincident oxidation process which is much more energetic. However, after the powder has once been heated through this region, the increased oxide layer slows the oxidation process so that the exotherm disappears and the fusion endotherm is well resolved. It should also be noted that the oxide coating appears to remain intact through heating cycles to temperatures of 1000°C; the powder remains unchanged in appearance after heating whereas other metal powders such as the titanium flow together upon melting.

The oxidation process occurring at about 600° that is indicated by the thermoanalytical techniques corresponds to an increase in the concentration of unreacted aluminum at the surface of the particles. This increase in concentration is shown directly by the increase in the Al/O ratio versus temperature plot presented in Figure 6 which was obtained by AES. Since the oxide coatings remain intact, this increase must be due to diffusion of the metal to the surface rather than an oxide dissolution process as observed for the titanium. The continued increase in oxide thickness opposes the increase in the diffusion rate as the temperature increases. Therefore, this type of process is less likely to kinetically control thermal ignition than a dissolution process.

When aluminum was mixed with Cu_2O to form the thermite blend, thermal reactions for the fine powder were relatively easy to control as indicated by the DTA curve shown in Figure 7. Two strong exotherms are evident but the powder did not ignite. However, when the thermite was consolidated, ignition occurred at 545°. While heat flow differences could produce this behavior, there also seems to be a subtle change in the chemistry for the two conditions. The strong endotherm just prior to ignition of the consolidated material is not present in the powdered form and is an indication of a change in the material due to the hot pressing. The nature of this endotherm is indicated by the DSC of aluminum powder in copper pans as shown in Figure 8; an aluminum-copper alloy forms upon heating the two metals together. The endotherm at 540° is characteristic of a phase change associated with this Al-Cu alloy. Thus, the presence of the endotherm in the DTA curve for consolidated thermite indicates that the Al-Cu alloy was formed during the consolidation process.

Ignition of the thermite powder seems to depend on heat generated by aluminum diffusing to the surface of particles for reaction. However, if the thermite has been consolidated, the high pressures in a nitrogen blanket exclude air while the elevated temperatures generate free aluminum at the particle surface. This aluminum can then alloy with copper from the Cu_2O. Ignition can occur due to heat generated by the oxidation of the alloy rather than aluminum. The phase change at 540° apparently makes the alloy oxidation reaction favorable which can generate the heat to achieve ignition of the thermite reaction which is thought to occur at higher temperatures (perhaps the second exotherm in the DTA of the powder).

SUMMARY

The surface chemistry of fuels has been shown to play a key role in the ignition of pyrotechnic materials. Since these fuels are usually easily oxidized, the surface must provide protection from undesirable oxidation processes such as pyrophoricity while permitting the desirable pyrotechnic reactions. For both titanium and aluminum, these criteria are met by metal oxide coatings which control the accessibility of the fuel to the oxidizer. However, we have shown that the mechanisms through which this control is exerted are substantially different. The ignition of titanium based pyrotechnics seems to be kinetically controlled by the dissolution of the titanium oxide coating to generate a reactive surface for the pyrotechnic reaction. Reactions of aluminum seem to depend on diffusion of aluminum (or oxygen at higher temperatures) through its oxide coating. It was also shown that the accessibility of aluminum can be improved by alloying.

REFERENCES

1. W. E. Moddeman and W. D. Pardieck, "Surface Chemical Analysis, Surface Integrity of Starting Materials for Pyrotechnic Applications," Technical Report, University of Dayton, VDRI-TR-75-16, May (1975).

2. L. W. Collins, "Thermal Ignition of Titanium Based Pyrotechnics", submitted to Combust. Flame

3. A. Rengan and W. E. Moddeman,"ESCA Studies on the Thermite Mixture of Aluminum and Cuprous Oxide Using Si Kα X-Radiation", Technical Report, University of Dayton, UDRI-TR-77-30, June (1977).

4. A. Rengan and W. E. Moddeman, "X-Ray Photoelectron Studies on the Thermite Mixture of Al and Cu$_2$O. II. Thickness Measurements of Carbon and of Aluminum Oxide on Aluminum, and Changes in Copper Chemistry", University of Dayton, UDRI-TR-78-22, December (1978).

5. A. Rengan, W. E. Moddeman, P. S. Wang and L. D. Haws, Proceedings, 10th Symposium on Explosives and Pyrotechnics, February 14-16, 1979, San Francisco, California.

6. P. S. Wang, L. D. Haws, W. E. Moddeman and A. Rengan, "Aluminum Particle Surface Studies in Al/Cu$_2$O by Electron Spectroscopy for Analysis and Auger Electron Spectroscopy", MLM-2264, November (1979).

7. P. S. Wang, L. D. Haws and W. E. Moddeman, "Surface Analysis of Consolidated Al/Cu$_2$O Mixture by Scanning Auger Microscopy", to be published.

8. L. W. Collins, L. D. Haws and A. Gibson, "The Electrostatic Ignition of Non-Dispersed Pyrotechnics", accepted in Combust. and Flame.

9. L. W. Collins, "The Role of Potassium Perchlorate in the Desensitization of Titanium Powder to Electrostatic Ignition", to be published.

10. L. D. Haws, M. D. Kelly and J. H. Mohler, "Consolidated Al/Cu$_2$O Thermites", Monsanto Research Laboratory, Mound Laboratory Report, MLM-2531, Miamisburg, Ohio 45342.

11. C. G. Pontano and T. N. Wittberg, Appl Surf Sci (in press).

12. T. Porte, M. Demosthenous and T. M. Duc, J Less Common Metals, 56, 183 (1977).

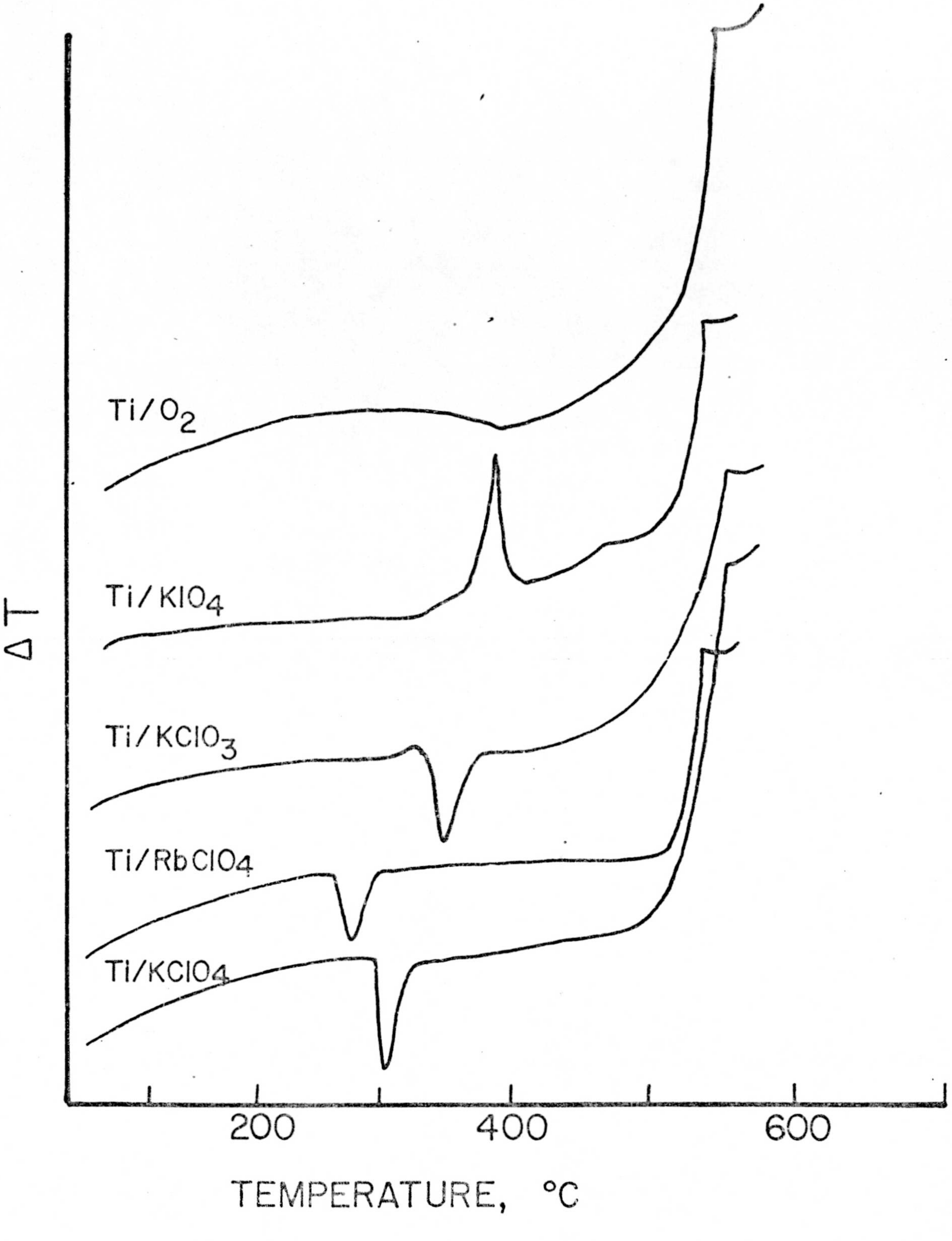

FIGURE 1. DTA curves for $TiH_{0.15}$ powder and $TiH_{0.15}$/oxidizer pyrotechnic blends.

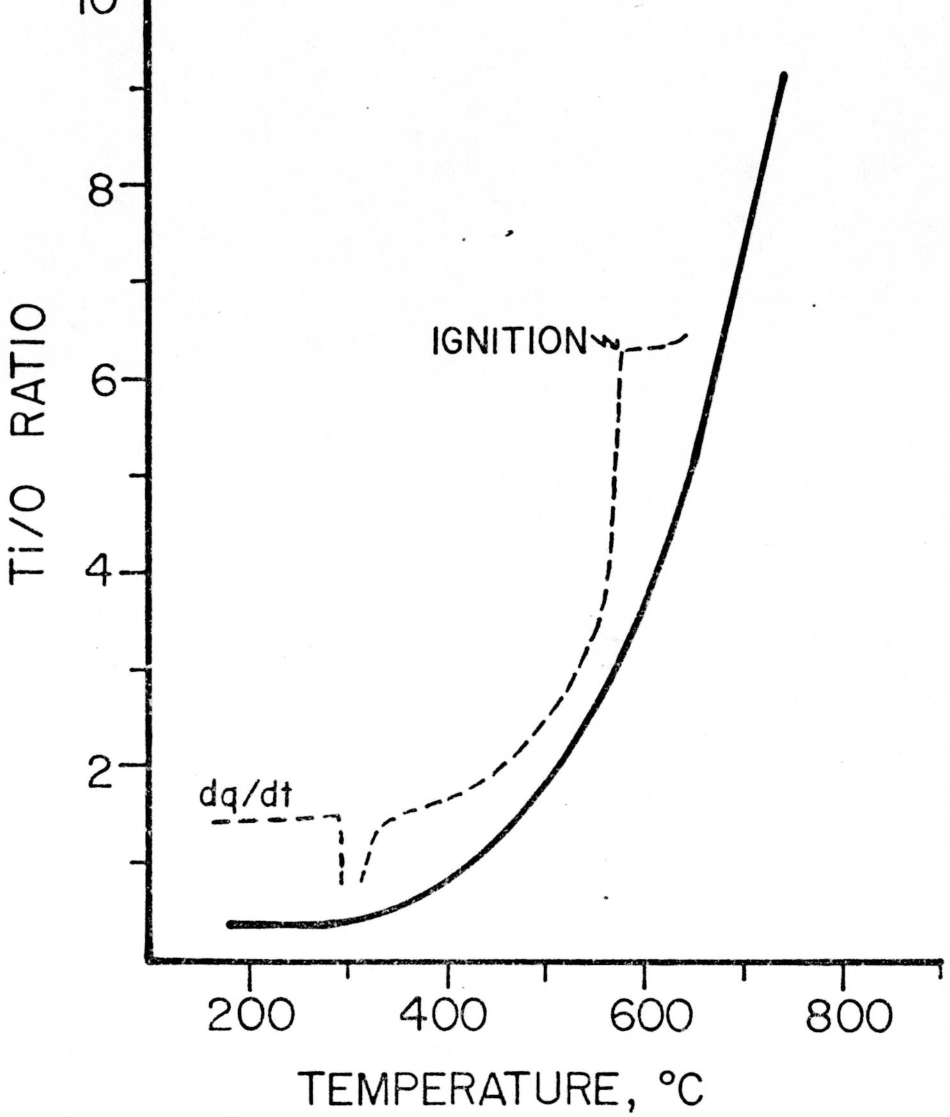

FIGURE 2. Ratio of Ti L-MM Auger (418 eV) line to O K-LL (510 eV) line as a function of temperature.

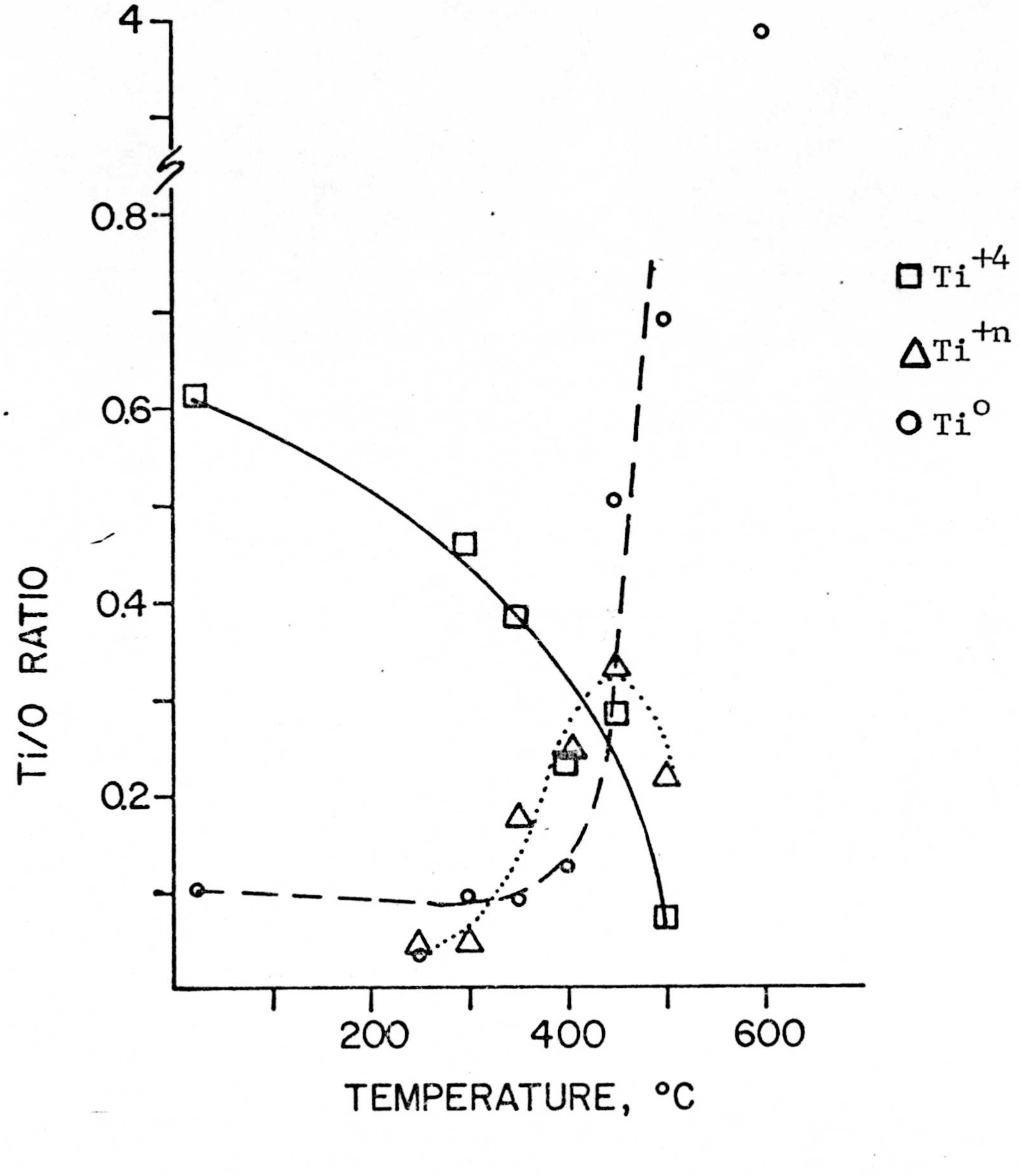

FIGURE 3. Ratio of the titanium $2p_{3/2}$ line to the oxygen 1s line for O^{-2} as a function of temperature.

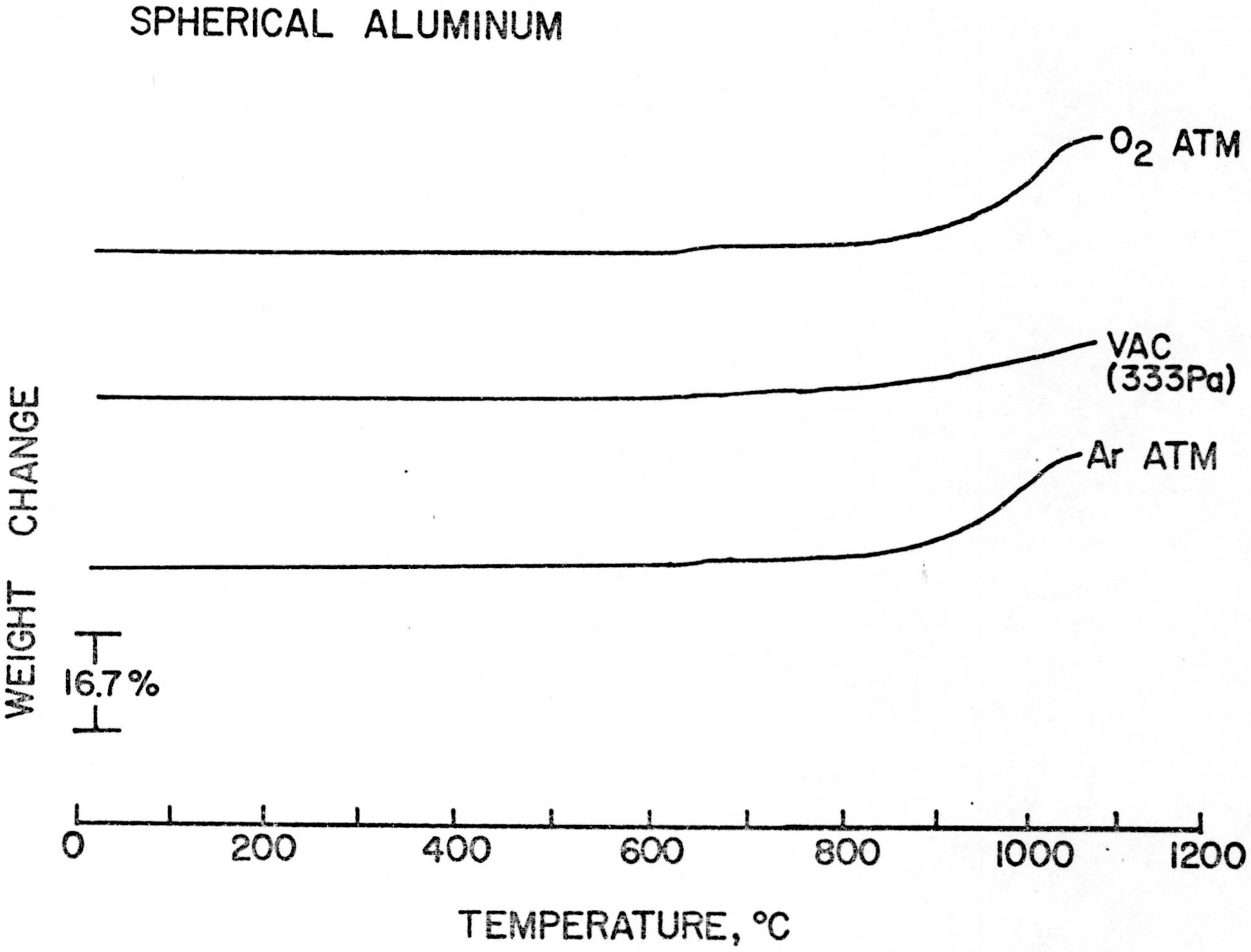

FIGURE 4. Thermogravimetric curves for spherical aluminum powder obtained in different atmospheres at a heating rate of 20°/min.

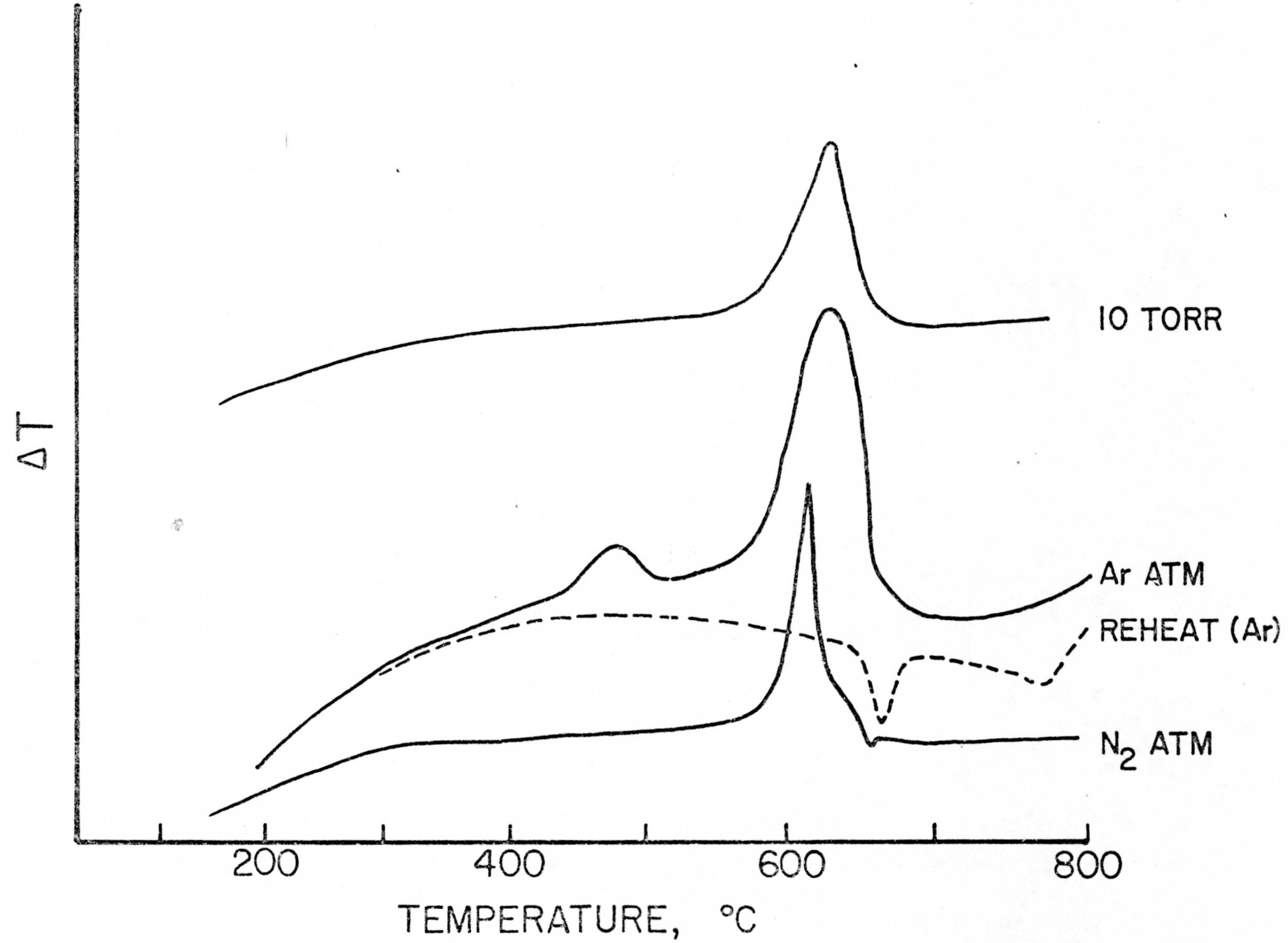

FIGURE 5. DTA curves for spherical aluminum powder.

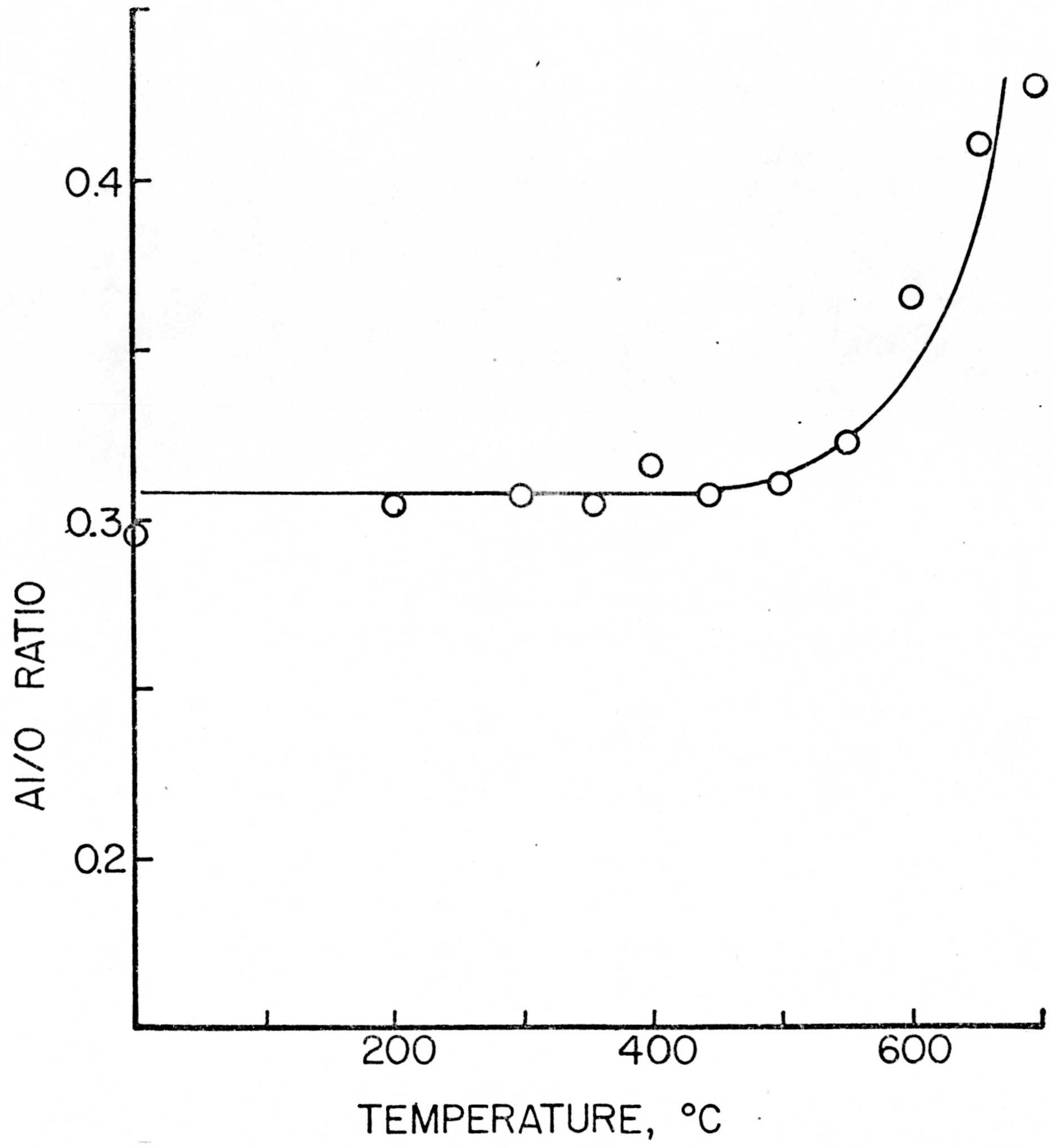

FIGURE 6. Ratio of Al K-LL Auger line to O K-LL line as a function of temperature.

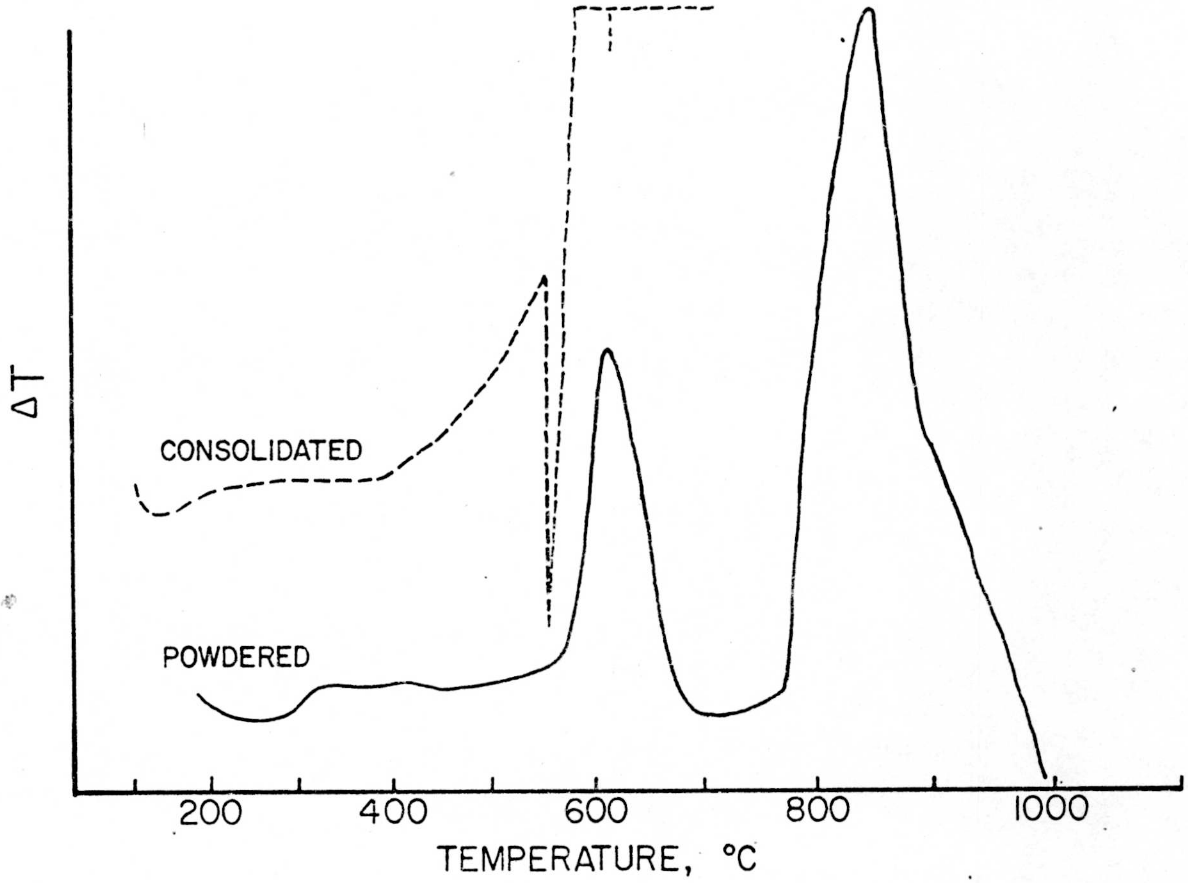

FIGURE 7. DTA curves for Al/Cu_2O thermite powder and consolidated thermite.

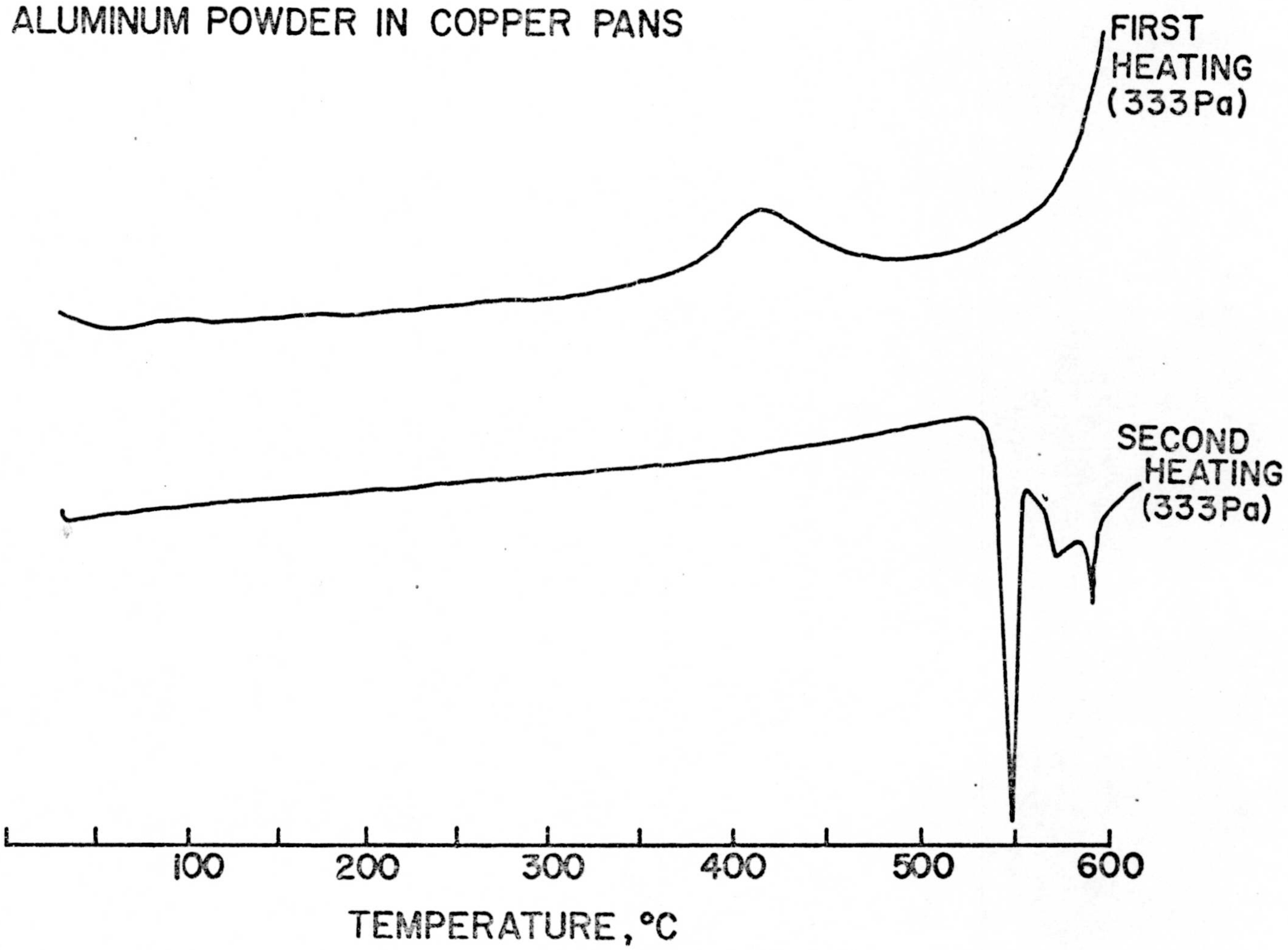

FIGURE 8. DSC curves of spherical aluminum powder in copper pans.