Thermochimica Acta, 192 (1991) 65–71
Elsevier Science Publishers B.V., Amsterdam

Observations on using thermogravimetry as a tool to monitor binder burnout in ceramics [α]

D. Robert Hammond and Sandra H.W. Hankin[1]

GTE Laboratories Inc., 40 Sylvan Road, Waltham, MA 02254 (USA)

(Received 21 December 1990)

Abstract

Thermogravimetry experiments were run for samples of $YBa_2Cu_3O_7$ and WC/Co, both with organic binder. Weight percent gains were observed from 400–800 °C. These weight gains appeared to be the result of insufficient purging but subsequent experiments using a different balance system pointed to an internal oxidation source as a possible contributing factor to the observed increase in weight. Sample shape and stacking density on the furnace pan also affected this weight gain, as well as the extent of an apparent runaway reaction in the $YBa_2Cu_3O_7$ samples.

INTRODUCTION

One of the fundamental uses of the thermogravimetry (TG) method of analysis is to imitate on a small scale what may be happening in a large furnace. This method provides information regarding the temperature ranges where mass losses occur, thus aiding the determination of temperature settings for large furnace conditions. When the results of TG differ markedly from those expected, problems arise in the interpretation of weight percent loss curves. The observation of a mass gain when only losses are expected is such a situation. Finding the source of such a gain is imperative before the TG experimental results can be successfully used to predict scale-up conditions.

The setting of furnace temperatures for the dewaxing of ceramic materials prior to sintering is one such use of thermal analysis instrumentation [1–5]. Organic binders consisting of paraffin and/or ester waxes in combination with either the 1–2–3 superconducting oxide $YBa_2Cu_3O_7$ or WC/Co were analyzed by TG for percent residue under inert gas purge. In the process of

---

[α] Presented at the 19th Annual NATAS conference, Boston, MA, 23–26 September 1990.

[1] Author to whom correspondence should be addressed.

running these experiments two phenomena were noted. The first was the observation of a weight gain for the materials from 400–800 ° C. Such gains have been observed for $YBa_2Cu_3O_7$ and tungsten carbide heated in air or oxygen atmospheres but were unexpected for these materials under inert gas purges. A second, separate observation was that some of the 1–2–3 oxide experiments appeared to show a runaway reaction between 300 ° C and 400 ° C.

EXPERIMENTAL

Samples were first run on a Du Pont 951 balance module and subsequently on a Du Pont 2950 with a 2100 controller. The $YBa_2Cu_3O_7$ samples were run at 10 ° min^{-1} under an argon atmosphere at 100 ml min^{-1} with a 60/40 (furnace/balance) gas inlet split. WC/Co samples were run at 5 ° min^{-1} using nitrogen and argon purging in separate experiments (same split as before). These purge gases originate from liquid boil-off from large storage tanks. The furnace was programmed from room temperature to 900 ° C and sample masses ranged from 30 to 100 mg. These would be considered normal "survey" conditions in the laboratory.

RESULTS

Figures 1 and 2 illustrate the percentage changes in weight observed for the 1–2–3 oxide and WC/Co respectively, between 400 ° C and 800 ° C.

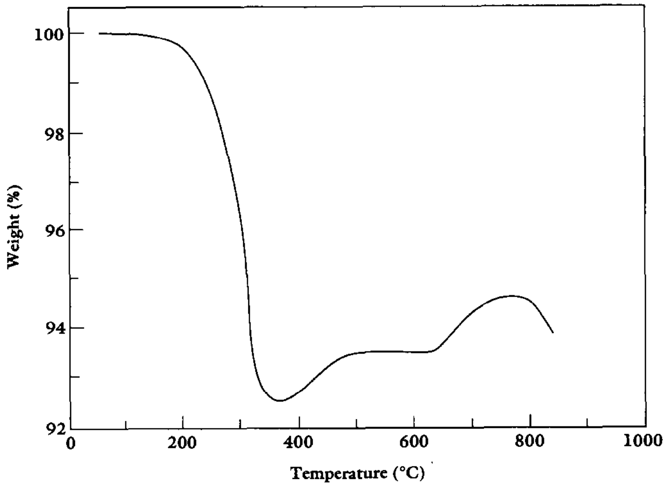

Fig. 1. TG curve of $YBa_2Cu_3O_7$ with organic binder sample showing weight percent gain between 400 ° C and 800 ° C under a nitrogen purge.

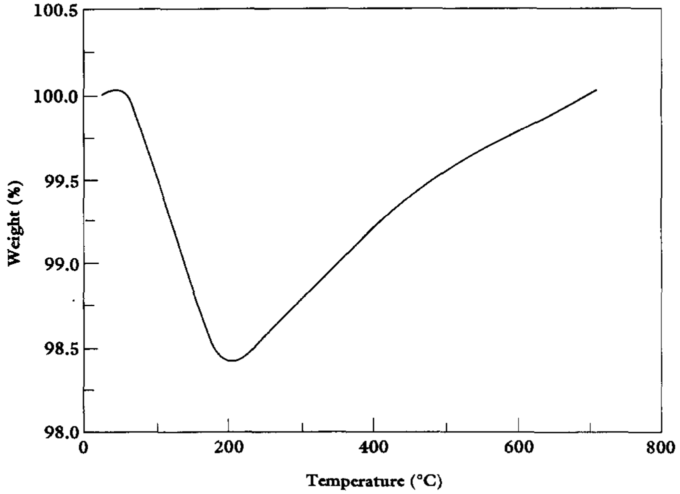

Fig. 2. TG curve of WC/Co with binder sample showing weight percent gain under a nitrogen purge.

Figure 3 demonstrates the observed runaway reaction of a densely packed 1-2-3 oxide sample under an air atmosphere.

After these initial observations of weight gain under nitrogen purge, gas samples were taken from the exit port of the TG module for analysis. Mass spectrometry showed that the nitrogen purge exiting from the 951 balance contained ≈ 600 ppm of oxygen, which was assumed to account for all of the weight gain in the initial experiments. A nitrogen gas sample taken directly from the house nitrogen source gave an oxygen level of 3 ppm.

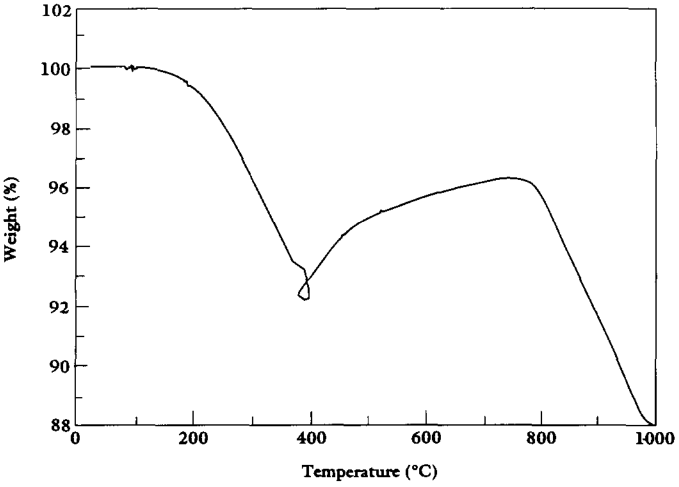

Fig. 3. TG curve in air for a mixture of $YBa_2Cu_3O_7$ and organic binder which was densely packed on the furnace pan. This curve clearly shows a thermal runaway.

Longer equilibrium times of up to 1 h and oxygen scrubbers for the nitrogen and argon gas lines were added in an effort to correct this problem. Purge pressures were adjusted such that the flow meter still registered 100 ml min^{-1} at the balance exhaust. It was at this point that the Du Pont 951 balance module was replaced by a Du Pont 2950 module. After switching balance modules, the problem still occurred to a small extent, necessitating the need to look further for a source of the oxygen contamination.

Figure 4 contains TG curves for the WC/Co with binder mixtures. The upper curve is the result of a run on the 951 balance before the oxygen contamination was discovered in the nitrogen purge. The other two samples, which were run on the 2950 balance under an argon purge differed in mass and physical form. The lighter, crushed, 30 mg sample sustained a greater gain than the heavier, chunk, 100 mg sample. These curves therefore demonstrate a relationship between surface area increase and percentage weight gain.

A surface color change from black to yellow was noted when the samples were examined following the experiments. This color change most likely indicated the formation to tungsten oxide. The 2950 balance system was thoroughly checked for sources of gas leakage, and equilibrium times were extended to 1 h. The rubber gasket at the top of the furnace was replaced with a Viton O-ring as a precaution against any out-gassing contamination from the elastomer.

In an effort to isolate further this oxidation problem, a material that would easily show oxidation effects and another that would not react with

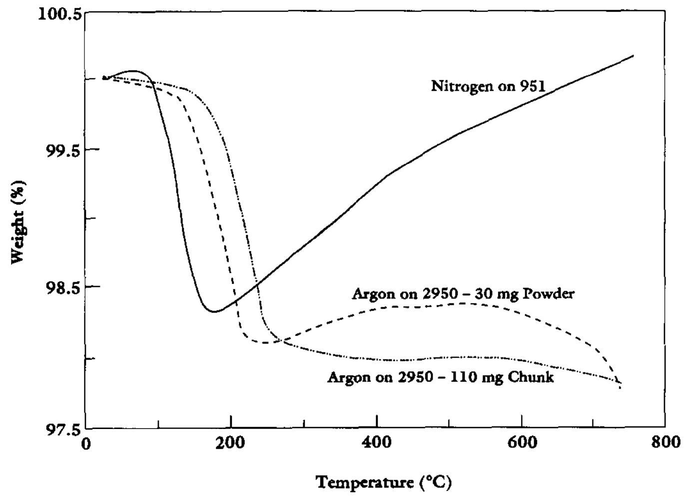

Fig. 4. TG curves for mixtures of WC/Co and organic binder. The top curve was from a run on the Du Pont 951 balance under nitrogen and the other two curves were from samples run on the Du Pont 2950 balance under argon.

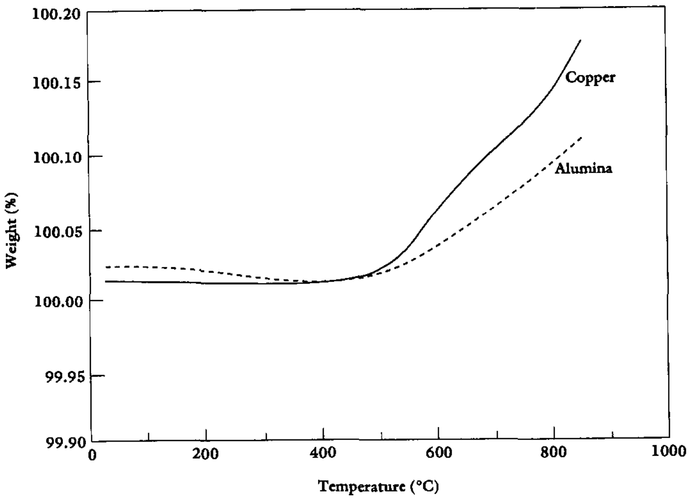

Fig. 5. TG curves for clean copper shot and prefired alumina. The surface of the copper shot was gray after the run.

oxygen at all were chosen for TG runs. Clean copper shot was chosen for the former and prefired alumina for the latter. Figure 5 contains the thermograms for these two materials run on the same instrument under identical conditions. The copper clearly shows a percentage weight gain above that observed for the alumina. The latter apparent weight gain is attributed to "buoyancy" effects (see, for example ref. 6). The surface of the copper shot appeared gray after the TG run. This weight gain is consistent with the

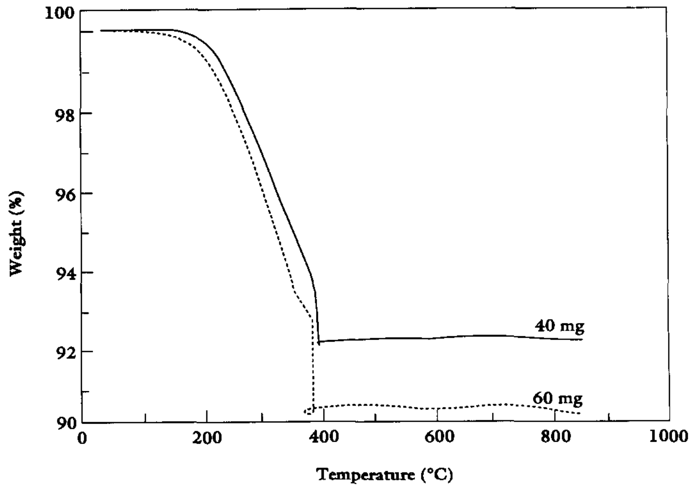

Fig. 6. Two TG curves for $YBa_2Cu_3O_7$ and binder samples initially weighing 40 mg and 60 mg. The sample temperature ran away from that of the balance near 400 °C.

formation of copper oxide in the outer 10 Å of the pellets, and may be the result of very low ppm levels of oxygen passing over the sample during the experiment.

The other observed phenomenon, the runaway decomposition of the 1–2–3 oxide with binder samples, appears to be related to the size of the sample on the furnace pan. The greater the initial sample weight and the more dense the sample, the greater the size of the temperature runaway. This runaway, which is due to the mixing of oxygen in air with the organic binder, is a function of the diffusion of the melted binder material from the cooler center of the sample pile to the surface, where the temperature is high enough to cause exothermic decomposition. Figure 6 shows a comparison for two samples run in air, one of 40 mg and one of 60 mg. The negative temperature indicated by the small circle near 400 °C is related to the amount of excess heat produced during the runaway reaction. If extrapolated to larger samples, these results indicate that the heating program of the furnace must be adjusted to allow for complete dewaxing of the material at temperatures below the decomposition point of the binders.

CONCLUSIONS

The ceramic materials used in these experiments are apparently excellent oxygen scrubbers at elevated temperatures. Even very small amounts of oxygen in the purge gas and, perhaps, volatilized carboxy components of the dewaxed binder are capable of oxidizing the surface of these inorganic materials under inert atmospheres. In the case of the superconducting oxide, if the temperature is taken to about 850 °C, the material loses most of the added weight. The weight loss above 850 °C is not as pronounced for the WC/Co mixtures.

Instrumental problems, such as those described in this report, make it very difficult to extrapolate experimental runs to fully scaled-up conditions. Whenever possible, it is important to be aware of the expected sample behavior so that such instrumental problems will not negatively affect the data interpretation. With the increased need for thermal analysis instrumentation in new materials technology, such problems as those encountered in this report must be recognized and eliminated.

ACKNOWLEDGMENTS

We thank Steve Bennett of GTE Valenite for the WC/Co samples, and Helmut Lingertat, Sophia Su and Donald Dugger of GTE Laboratories for standard materials, 1–2–3 oxide samples, and mass spectrometry analyses and review of the manuscript respectively.

REFERENCES

1 B.O. Haglund, Thermochim. Acta, 85 (1985) 323.
2 W. Schiller and C.-H. Horte, Thermochim. Acta, 93 (1985) 581.
3 S. Masai, P. Calvert, W. Rhine and H. Bowen, J. Mater. Sci., (1989) 1907.
4 C. Dong and H.K. Bowen, J. Am. Ceram. Soc., 72 (1989) 1082.
5 M. Cima, J. Lewis and A. Devoe, J. Am. Ceram. Soc., 72 (1989) 1192.
6 W.W. Wendlandt, Thermal Methods of Analysis, Wiley, New York, 3rd edn., 1986, p. 18ff.