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**FABRICATION OF FLEXIBLE HIGH TEMPERATURE CERAMIC
SUPERCONDUCTING THIN FILMS BY CHEMICAL VAPOR DEPOSITION**

Final Project Report

for the period

15 September 1987 - 28 February 1989

by

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1 May 1989

SUMMARY

The goal of this research program was to develop a chemical vapor deposition (CVD) process which would be suitable for applying coatings of the high- T_c superconducting compound $YBa_2Cu_3O_x$ onto filamentary substrates. Eventually, this process will be extended to coat continuous tows of filaments and to encapsulate these tows with a conductive metal or alloy. The encapsulation would provide back-up electrical conduction, thermal stability, mechanical strength, and protection from atmospheric corrosion. The scope of this initial program, however, was limited to the selection, acquisition, and characterization of the reagents, re-design of the Georgia Tech CVD reactor to accommodate these reagents, and selection and acquisition of promising substrate materials. Each reagent is evaporated by an external vaporizer and is carried into the CVD reactor by a stream of argon controlled by a mass flow meter. Each reagent-argon mixture advances through heated, stainless-steel tubing on the way to the reaction chamber. The mixtures are combined with heated argon and oxygen just before reaching the furnace. Heterogeneous nucleation of all three metal-vapor species has been accomplished; and films several micrometers thick, containing all three of the desired metal cations, have been grown on a variety of substrates. The metal beta-diketonates (TMHD) appear to be the most promising reagents, giving the highest vapor pressures and the best long-term stability.

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FABRICATION OF FLEXIBLE HIGH TEMPERATURE CERAMIC SUPERCONDUCTING THIN FILMS BY CHEMICAL VAPOR DEPOSITION

INTRODUCTION

The goal of this research program was to develop a chemical vapor deposition (CVD) process which would be suitable for applying coatings of the high- T_c superconducting compound $YBa_2Cu_3O_x$ onto filamentary substrates. Eventually, this process will be extended to coat continuous tows of filaments and to encapsulate these tows with a conductive metal or alloy. The encapsulation would provide back-up electrical conduction, thermal stability, mechanical strength, and protection from atmospheric corrosion. The scope of this initial program, however, was limited to the selection, acquisition, and characterization of the reagents, redesign of the Georgia Tech CVD reactor to accommodate these reagents, and selection and acquisition of promising substrate materials. Although we have concentrated on deposition of the $YBa_2Cu_3O_x$ (123) compound, the process is sufficiently flexible to permit the controllable deposition of other superconducting compounds including the bismuth- and thallium-based materials.

EXPERIMENTAL

Reagents. Selection of potential reagents was an extremely important aspect of this project. To this end, vapor pressure data for a number of compounds were evaluated. Reagents with significant vapor pressures at reasonably low temperatures, i.e., $\approx 200^\circ \text{C}$, simplify equipment requirements and permit a more versatile CVD process. In order to obtain vapor pressure data, focused computerized literature searches were performed, resulting in the location of several applicable papers. [1-15] References 1-7 and 9 provide curve-fitted equations for various organometallics. References 8, 10 and 11 contain general information on metal organic vapor pressures and on vapor pressure trends. References 12 and 13 include information on the stability of various organometallics. Finally, references 14 and 15 contain helpful information on using metal-tetramethylheptanedionates (often abbreviated as tmhd or thd) as CVD reagents.

Table I lists the reagents which we chose to evaluate, some of their physical properties, and their price and availability as well. The reagents are all organometallics, the ligands of which were found to produce unusually high volatility in comparison with the more conventional inorganic CVD reagents for these metals.

Thermal stability and sensitivity to air and water were also important to evaporator design and handling procedures, respectively. Note that most of the reagents listed are air stable. The literature seems to indicate that, while organometallics are thermally stable, prolonged exposure to high temperatures (such as in a

Table I. Potential Reagents for Chemical Vapor Deposition of $YBa_2Cu_3O_x$.

Compound & Formula	Color & Form	Stability	Melting Point	Sublimation Temperature*	Vapor Pressure	Source	Price**
Yttrium Isopropoxide $Y(OCH(CH_3)_2)_3$	White Solid	Air sensitive Reacts with water				Strem Chemicals, Inc. (617)462-3191	\$10.64 per gram
Yttrium tmhd $Y(C_{11}H_{19}O_2)_3$	White Powder	Air stable	176-180°C		Thermal Analysis -9 torr @ 200°C	Strem Chemicals, Inc.	\$17.60 per gram
Yttrium hfa $Y(C_5H_9F_6)_3$						Strem Chemicals, Inc.	\$10.00 per gram
Yttrium tfa $Y(C_5H_4O_2F_3)_3$						Research Organic Inorganic Chemical Corp. (714)771-2205	\$33.75 per gram
Barium hfa $Ba(C_5H_9F_6)_2$					Stable up to about 250°C from TGA	Strem Chemicals, Inc.	\$5 per gram
Barium tmhd $Ba(C_{11}H_{19}O_2)_2$	White Powder	Air stable	165°C	105°C (0.05mm)	Significant weight loss at 200°C from TGA	Strem Chemicals, Inc.	\$12 per gram
Copper hfa $Cu(C_5H_9F_6)_2$	Green Crystals	Air stable	85-89°C	100°C (0.1mm)	Soviet Prog. in Chem. -31 torr @ 125°C	Strem Chemicals, Inc.	\$4.50 per gram
Copper tfa $Cu(C_5H_4O_2F_3)_2$	Purple Powder	Air stable	190°C	60°C (0.05mm)	Soviet Prog. in Chem. -72 torr @ 190°C	Strem Chemicals, Inc.	\$2.00 per gram
Copper tmhd $Cu(C_{11}H_{19}O_2)_2$	Blue Crystals	Air stable	191-193°C	88°C		Strem Chemicals, Inc.	\$12.00 per gram

tmhd 2,2,6,6-tetramethyl-3,5-heptanedione
tfa trifluoroacetylacetone
hfa hexafluoroacetylacetone

* - Qualitative data from Strem Chemicals
** - Chemicals purchased in 5, 10, and 25g bottles

vaporizer) will produce some compound degradation. Thus, a balance between vapor pressure requirements and thermal stability will likely be necessary.

As mentioned earlier, the tmhd's, acetylacetonates, and fluorinated acetylacetonates are surprisingly volatile. In fact, the literature indicates that volatility increases steadily with fluorine content. [1] This was the motive for choosing the fluorinated acetylacetonates. Figures 1-3 contain vapor pressure curves for three promising reagents: copper trifluoroacetylacetonate (Cu-tfa), copper hexafluoroacetylacetonate (Cu-hfa), and yttrium tmhd. All the curves indicate that vaporizer temperatures of around 200°C or less should be adequate to obtain reasonable vapor pressures. There was a notable discrepancy in the literature with regard to the vapor pressure of copper trifluoroacetylacetonate. For example, at 170°C reference 2 predicts a vapor pressure of 28 torr, while reference 3 predicts a vapor pressure of only 7.3 torr. However, both references indicate that the vapor pressure of copper tfa is sufficient for use as a CVD reagent in our system. All three curves were generated from least squares-fitted equations of Clausius-Clapeyron plots. No references were found for the vapor pressures of barium compounds in our literature search.

The results of thermogravimetric analyses (TGA) of several potential reagents are presented in Figures 4-8. Figures 4 and 5 give weight loss as a function of temperature for Ba-hfa and Ba-tmhd. Note that Ba-hfa showed no significant weight loss until the temperature reached 250° C. The sample weight then dropped sharply

VAPOR PRESSURE CU(TFA)2

SOVIET PROGRESS IN CHEMISTRY

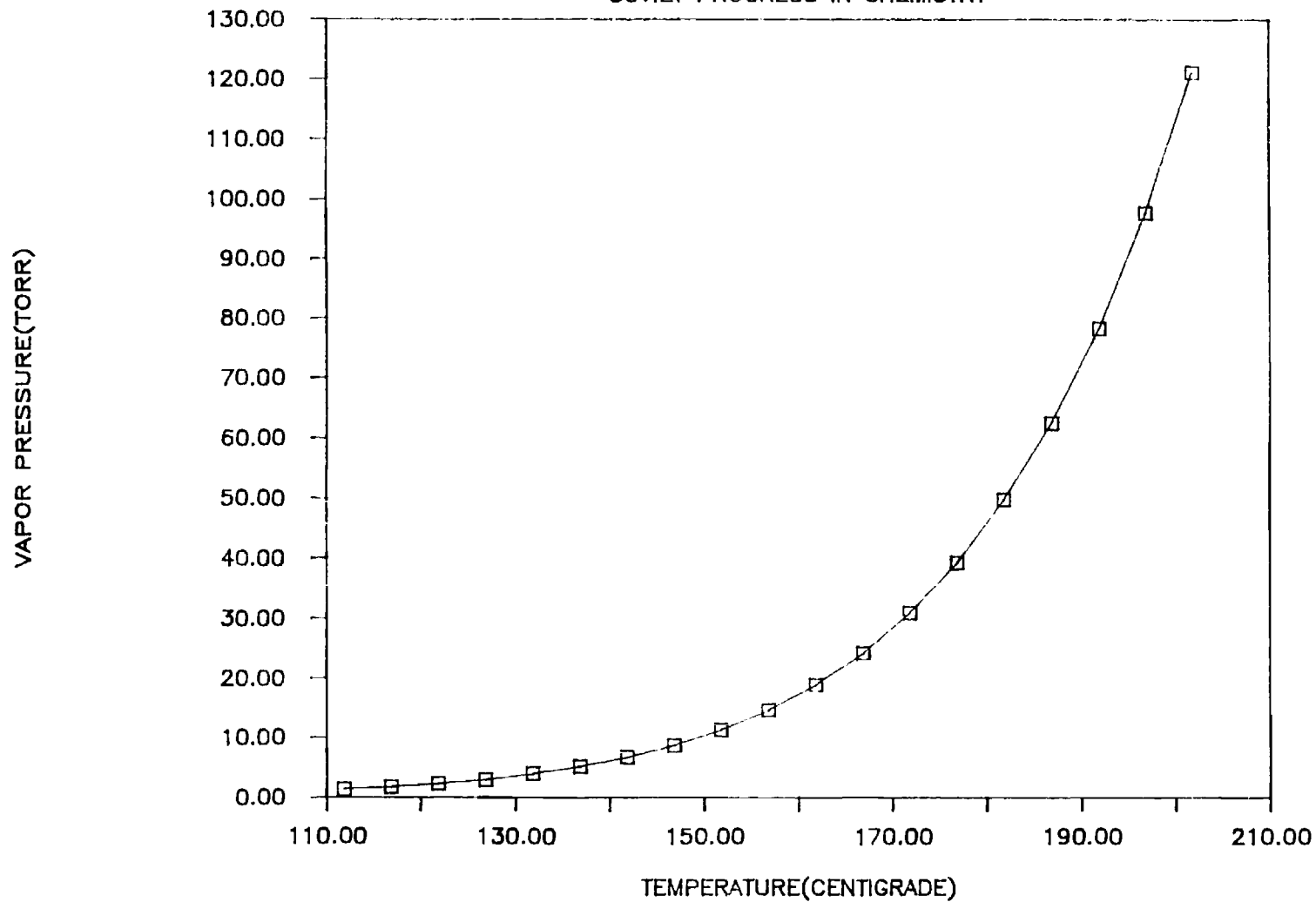


Figure 1. Vapor Pressure Curve for Copper Trifluoroacetylacetonate.

VAPOR PRESSURE CU(HFA)2

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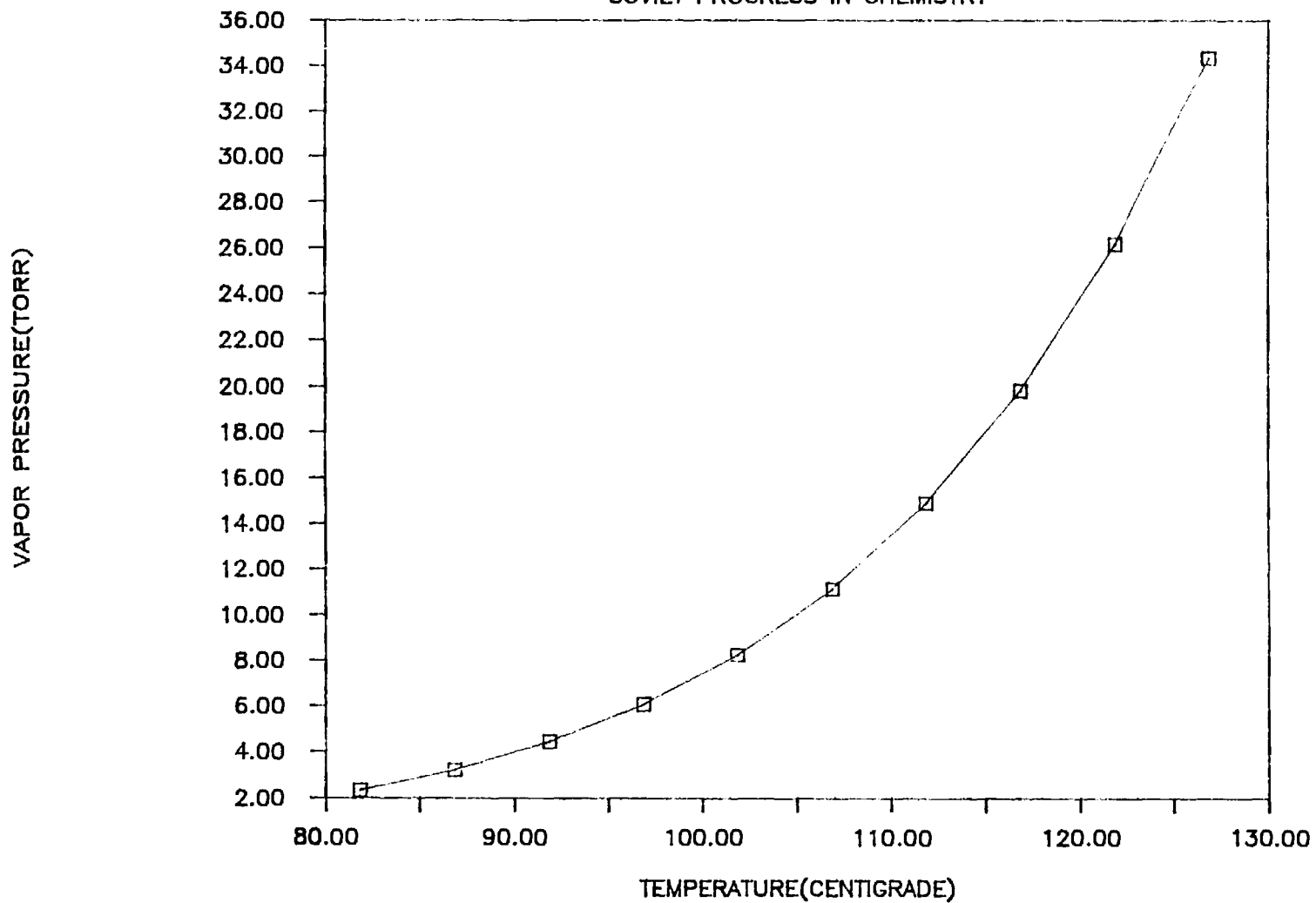


Figure 2. Vapor Pressure Curve for Copper Hexafluoroacetylacetonate.

VAPOR PRESSURE Y(THD)3

THERMAL ANALYSIS

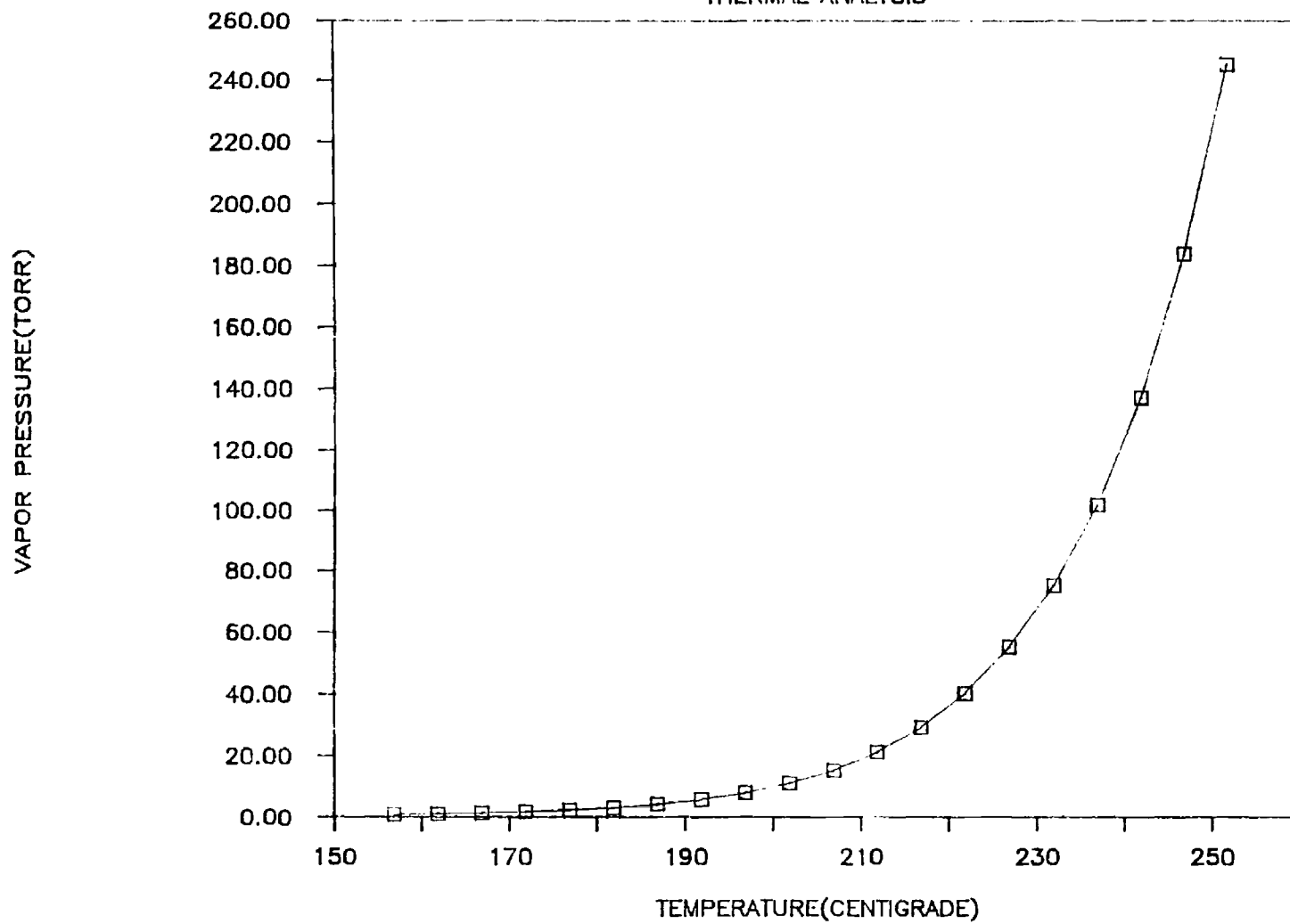


Figure 3. Vapor Pressure Curve for Yttrium Tetramethylheptanedionate.

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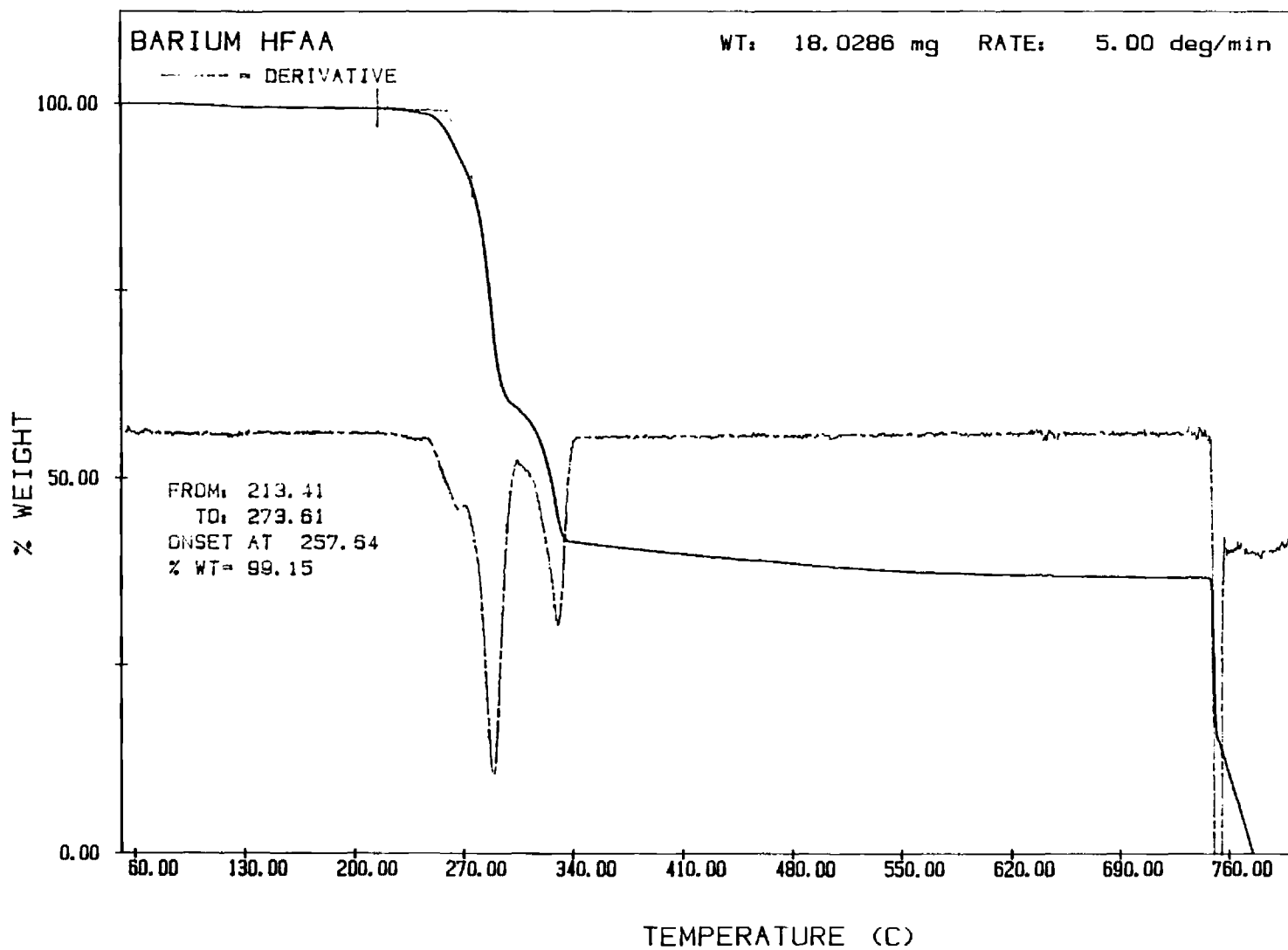


Figure 4. Weight Loss as a Function of Temperature for Barium Hexafluoroacetylacetonate.

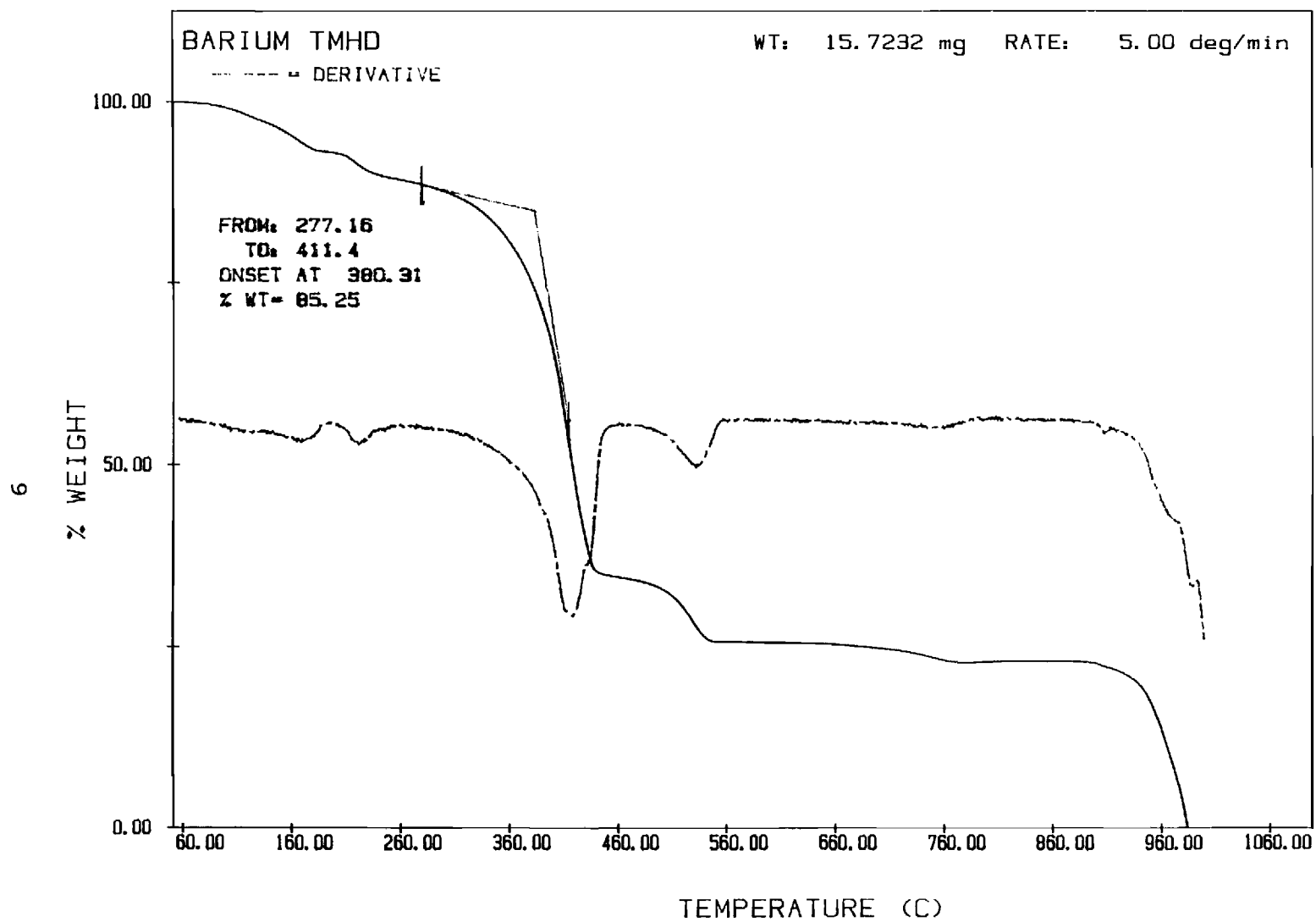


Figure 5. Weight Loss as a Function of Temperature for Barium Tetramethylheptanedionate.

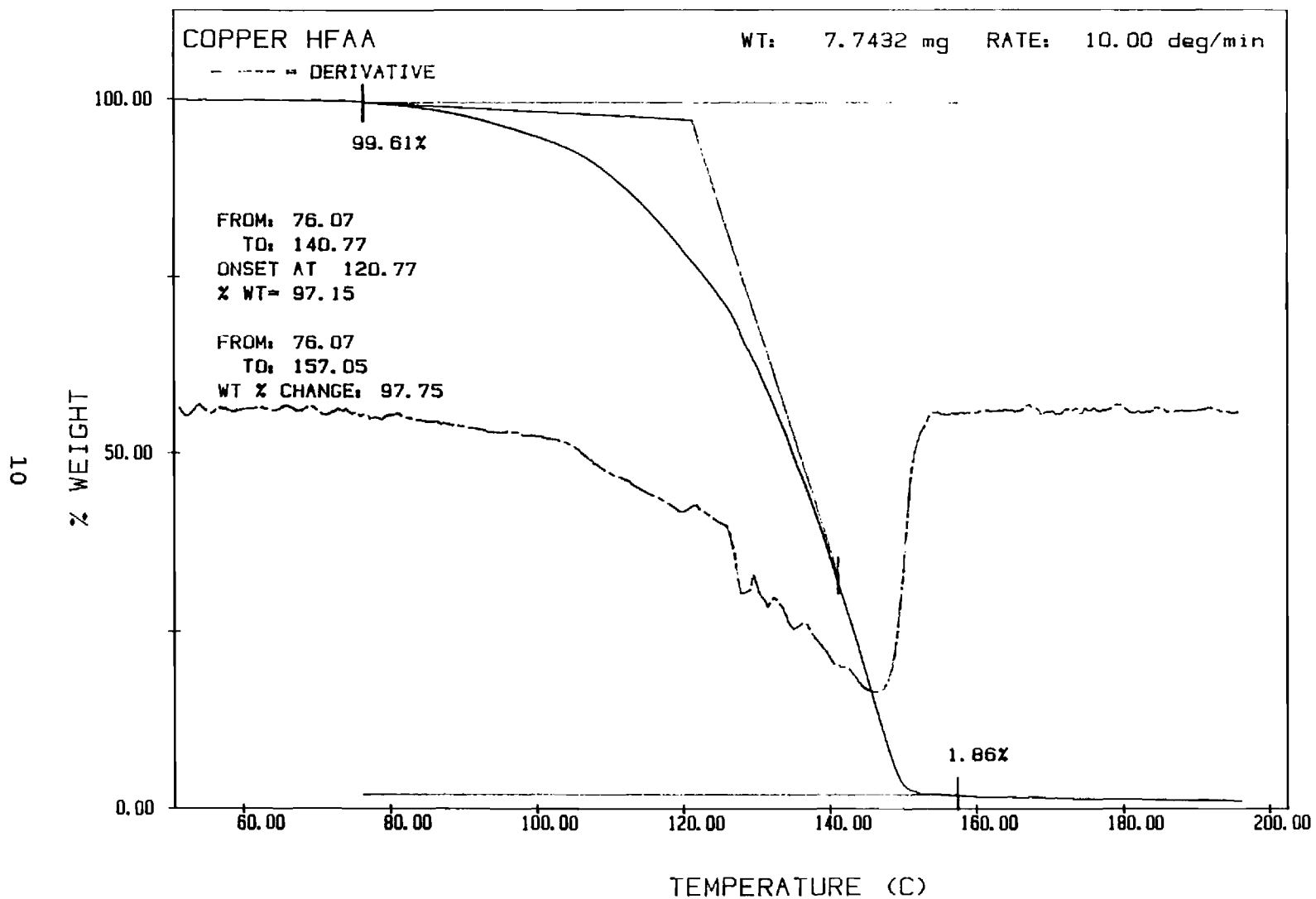


Figure 6. Weight Loss as a Function of Temperature for Copper Hexafluoroacetylacetonate.

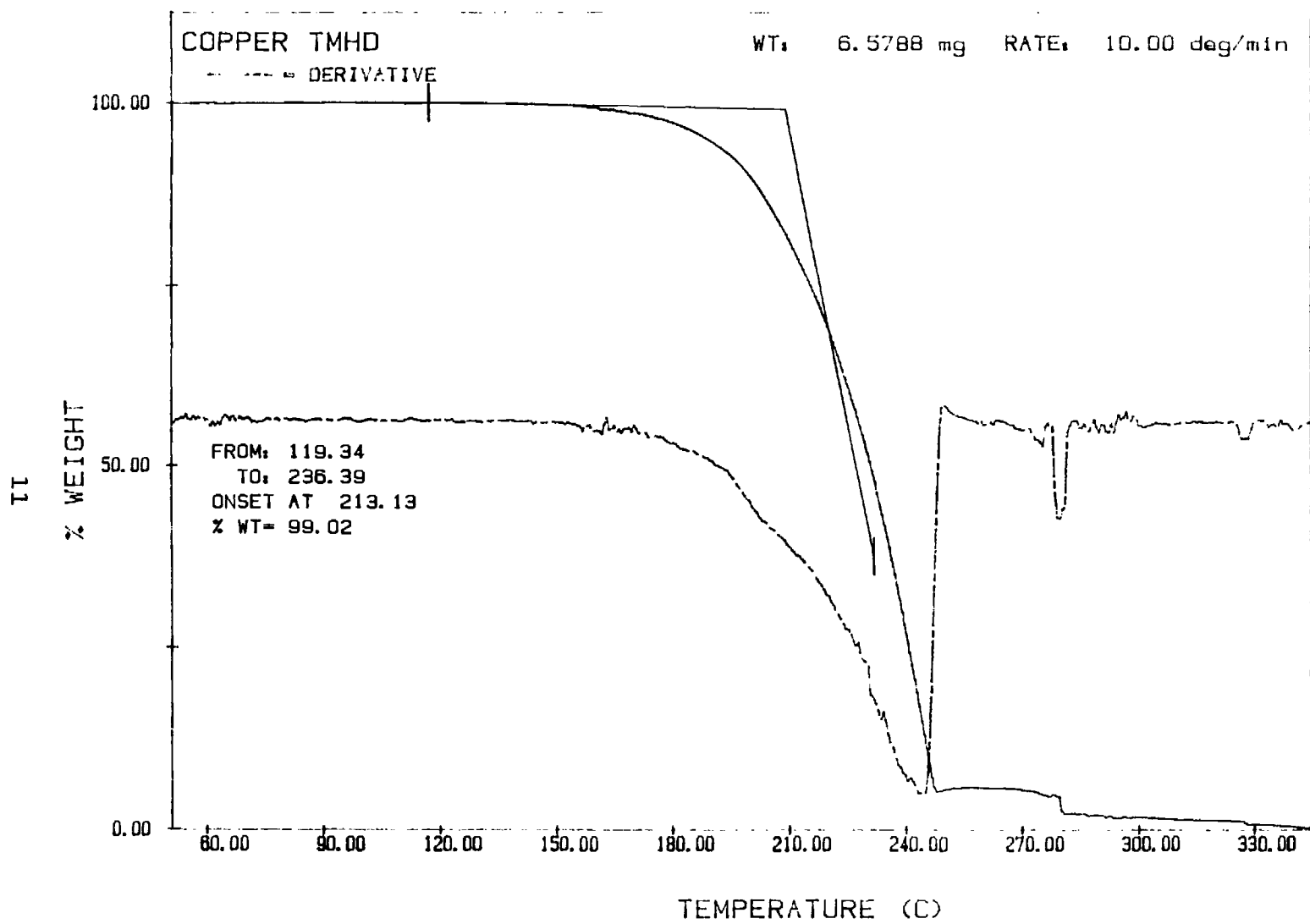


Figure 7. Weight Loss as a Function of Temperature for Copper Tetramethylheptanedionate.

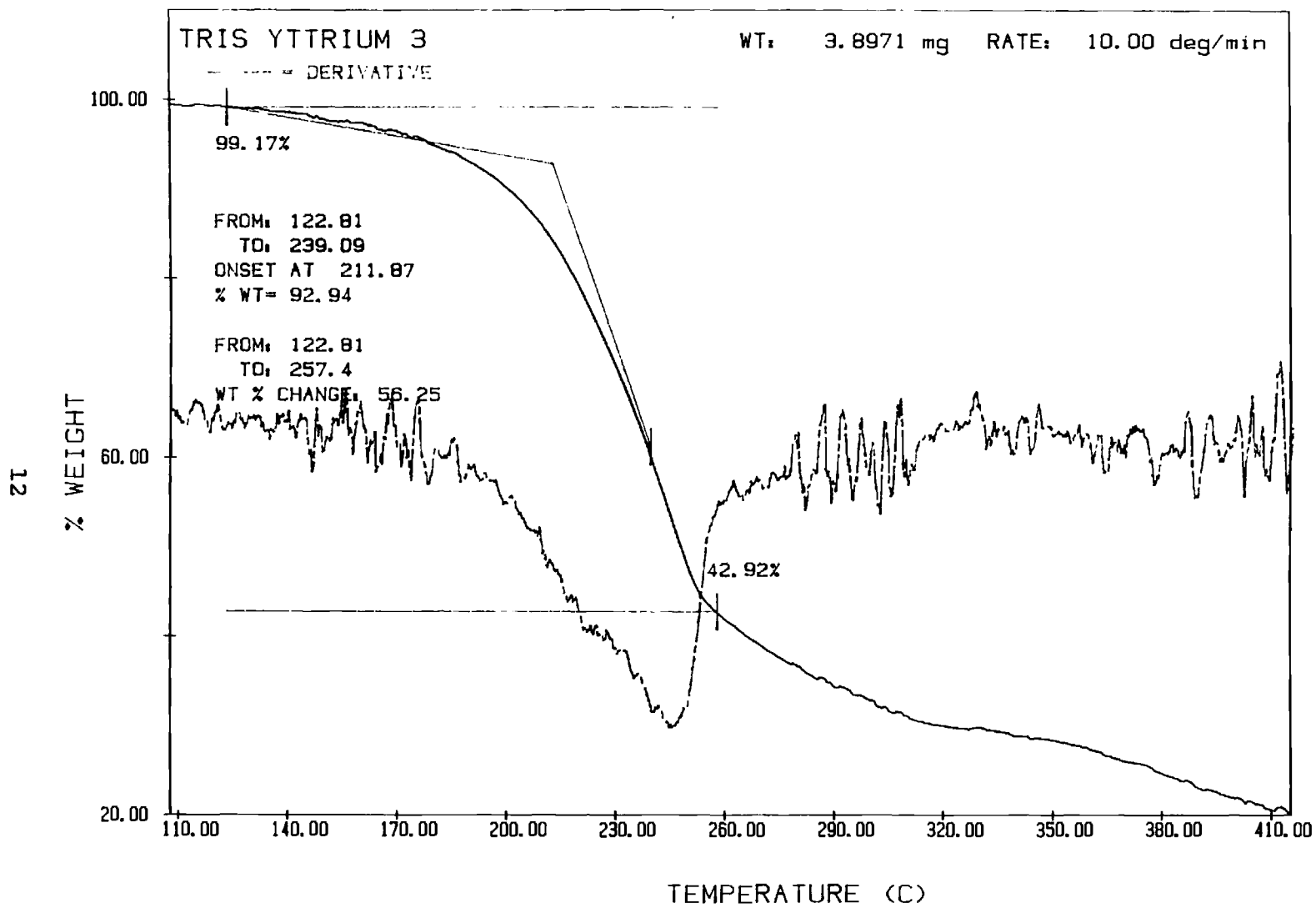


Figure 8. Weight Loss as a Function of Temperature for Yttrium Tetramethylheptanedionate.

and became rather constant, indicating a composition change. The results for barium tmhd were more promising. It showed significant weight loss at 200° C, indicating sufficiently high vapor pressure for use as a reagent. Figures 6 and 7 show the TGA results for Cu-hfa and Cu-tmhd respectively. The Cu-hfa begins to evaporate at 80° C, and has lost $\approx 25\%$ of its weight at 120° C; this corresponds to a vapor pressure of ≈ 26 torr in Figure 2. The trace of Cu-tmhd, on the other hand, shows it to be considerably less volatile, requiring a temperature of $\approx 210^\circ$ C to achieve an equivalent weight loss. However, this is still within the operating range of the CVD reactor. The TGA trace for yttrium tmhd (Figure 8) shows a 20 % weight loss at 220° C, which corresponds to a vapor pressure of ≈ 35 torr in Figure 3. The agreement between the TGA and vapor pressure data has given us more confidence in the use of TGA curves as an indicator of the volatility of those compounds for which no vapor pressure data are available.

Scientists at NRL [16] presented results that indicate the CVD approach can indeed produce superconducting coatings. Using reagents similar to those under study here, they reported coatings of the 123 compound that showed resistance drops beginning ≈ 70 K, although the resistance did not drop to zero until the temperature reached 20 K. Professor Toshio Hirai [17] of the Institute for Metals, Tohoku University, Japan, also reported depositing HTSC 123 coatings by CVD. He did not, however, reveal the reagents that were used.

Substrates. Several materials were procured and received for use as substrates. These included copper and silver wire and foil, single crystal wafers of SrTiO_3 , sapphire, MgO , and cubic zirconia (ZrO_2); polycrystalline discs of Al_2O_3 and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$); and the following fibers: SiC (three sources), Al_2O_3 (two sources), carbon, SiO_2 , and ZrO_2 .

CVD System. The Georgia Tech CVD system was reconfigured to permit deposition of $\text{YBa}_2\text{Cu}_3\text{O}_x$. A schematic diagram of the system is shown in Figure 9, with the CVD furnace itself shown in detail in Figure 10. The system can operate over a pressure range of 1 to 760 torr and a temperature range of 20° to 1800° C. Each reagent is evaporated by an external vaporizer and is carried into the CVD reactor by a stream of argon controlled by a mass flow meter. Each reagent-argon mixture advances through heated, stainless-steel tubing on the way to the reaction chamber. The mixtures are combined with heated argon and oxygen just before reaching the furnace. The CVD system variables include reagent type, flow rates, vaporizer temperatures, gas temperatures, reactor temperature, and system pressure.

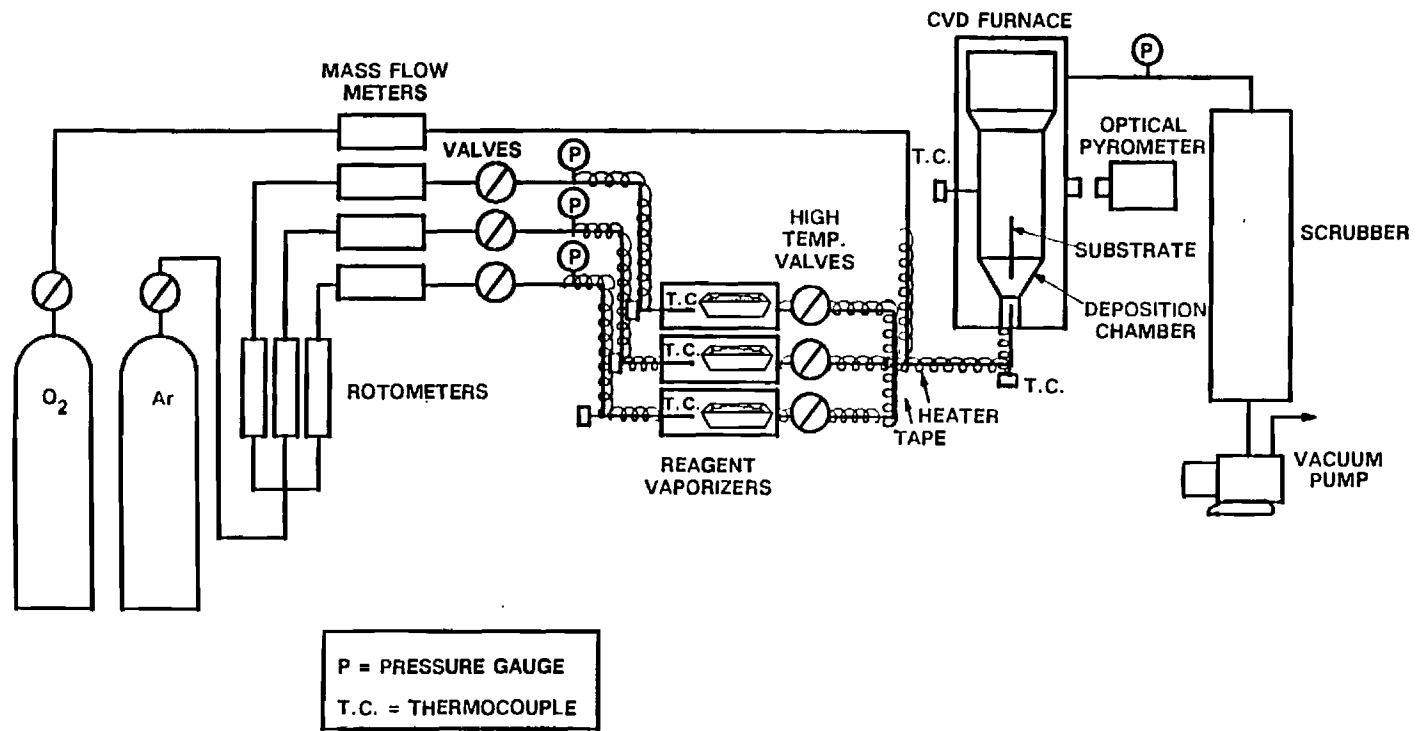


Figure 9. Schematic of CVD System.

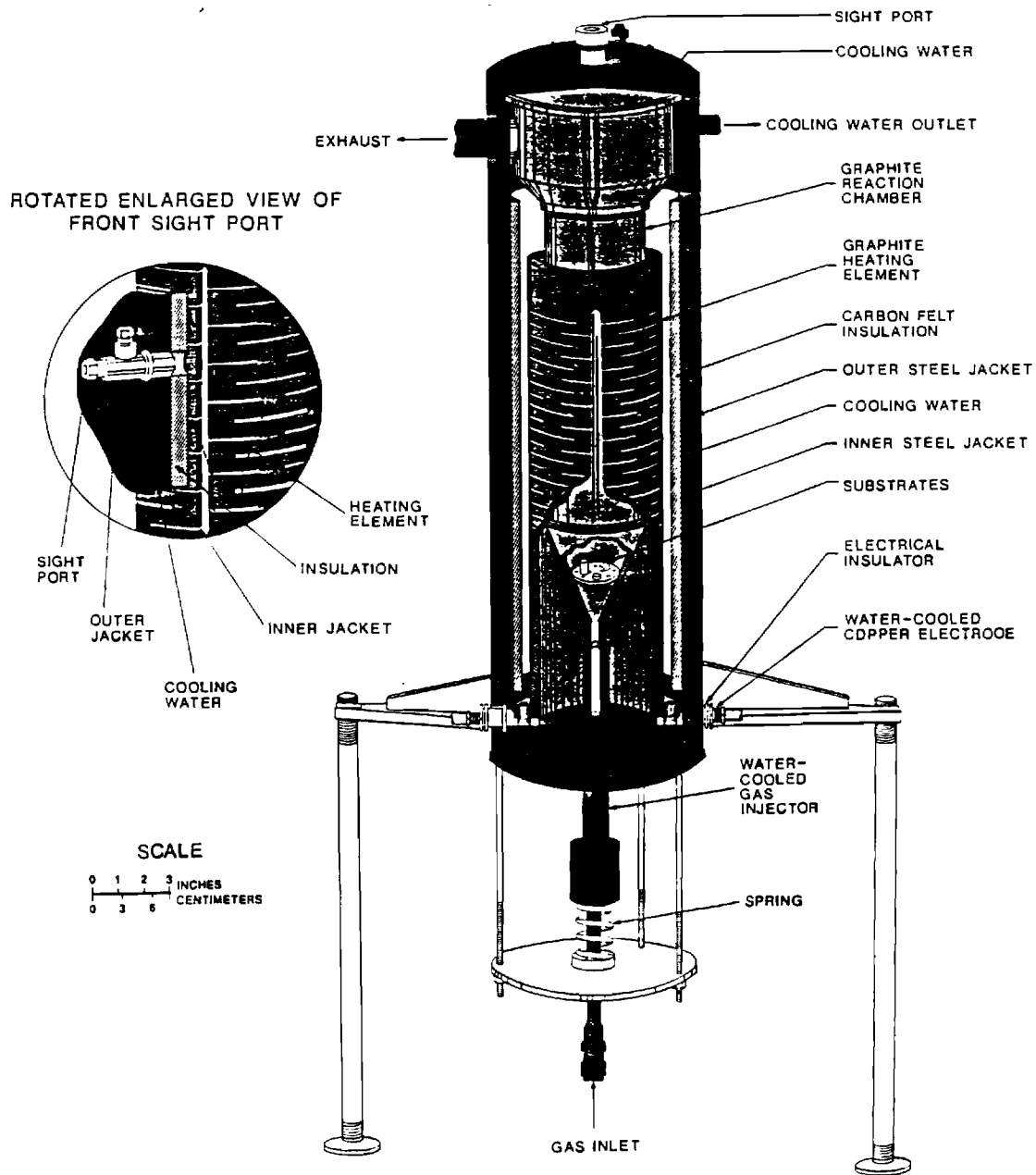


Figure 10. Detail of CVD Reactor.

RESULTS AND DISCUSSION

The Georgia Tech CVD system was used to perform a total of seventeen coating experiments during the course of the investigation. These initial runs focussed on reagent selection, vaporizer temperatures, and reaction chamber pressure and temperature. Reagents tested included Y(TMHD), Ba(TMHD), Y(HFA), Ba(HFA), and Cu(HFA). Experimental conditions, as well as elements detected in the deposits, are shown in Table II.

Compositional analyses were performed on the coatings with energy-dispersive x-ray spectroscopy (EDX) and x-ray photoelectron spectroscopy (XPS). EDX spectra of most of the early CVD runs indicated primarily copper and yttrium in the coatings (Figure 11), although small amounts of barium were detected by XPS on substrates from some of the runs. However, both EDX and XPS analysis of coatings from the last two experiments, SP17 and SP18, clearly showed that all three elements were present in the coating (Figures 12 and 13). The barium content was still not high enough to produce the 123 structure, but the coatings were much closer to the correct stoichiometry than the early runs.

Examination of the coatings in the SEM showed most to be relatively coarse-grained and columnar in appearance, typical of the morphology of many CVD coatings. Efforts to improve the coating morphology will be initiated as soon as the stoichiometry problems are solved. A four-point resistance probe was available, but unfortunately none of the coatings produced to this point have shown sufficient promise to warrant resistance-temperature measurements.

Table II. Summary of Reagents, Process Parameters, and Results of Initial CVD Experiments.

Run #	Furnace Temp. (°C)	Furnace Pressure (torr)	Reagents & Temps. (°C)	Reagent Flows (cc/min)	Detected Elements
S1	900	760	Cu (HFA) 109 Ba (TMHD) 168 Y (TMHD) 170	100 100 100	Cu
S2	900	60	Cu (HFA) 99 Ba (TMHD) 163 Y (TMHD) 155	50 50 50	Cu
S3	900	65	Cu (HFA) 95 Ba (TMHD) 161 Y (TMHD) 180	50 50 50	Cu, Y
S6	850	50	Cu (HFA) 95 Ba (TMHD) 190 Y (TMHD) 170	50 50 50	Cu
S8	500	50	Cu (HFA) 100 Ba (TMHD) 194 Y (TMHD) 172	50 50 50	Cu, Y
S9	850	50	Cu (HFA) 93 Ba (TMHD) 193 Y (TMHD) 172	50 50 50	Cu
S11	500	760	Cu (HFA) 95 Ba (TMHD) 194 Y (TMHD) 175	50 50 50	Cu, Y
S12	500	50	Cu (HFA) 95 Ba (TMHD) 210 Y (HFA) 188	50 50 50	Cu, Y
S13	500	50	Cu (HFA) 103 Ba (HFA) 200 Y (HFA) 190	50 50 50	Cu, Y
S15	500	50	Cu (HFA) 95 Ba (HFA) 135 Y (HFA) 125	50 50 50	Cu, Y
SP16	500	160	Cu (HFA) Ba (TMHD) Y (TMHD)		Cu, Ba, Y
SP17	850	160	Cu (HFA) Ba (TMHD) Y (TMHD)		Cu, Ba, Y

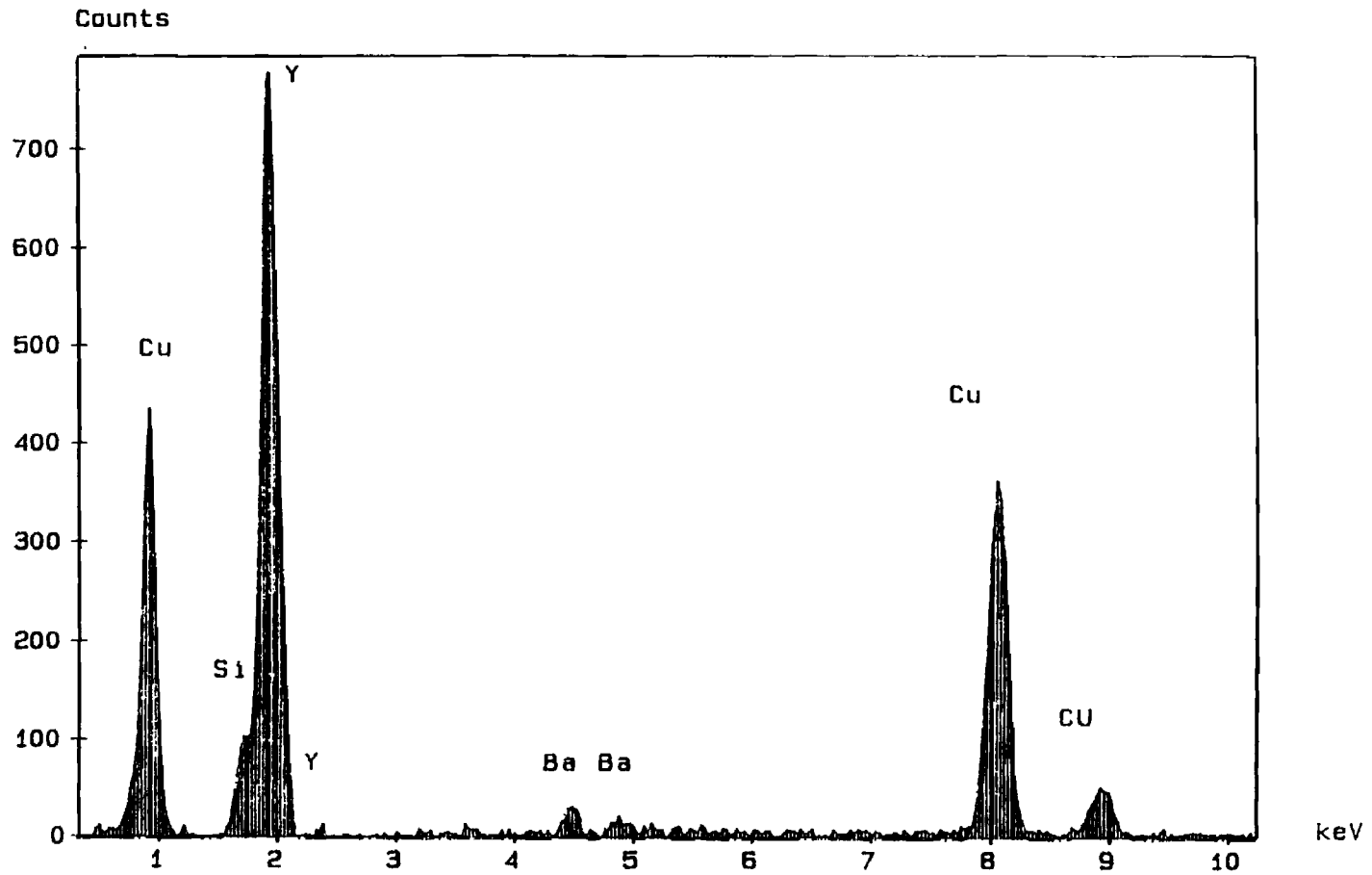


Figure 11. Energy Dispersive X-ray Analysis Trace Obtained from Coating of Sample S12.

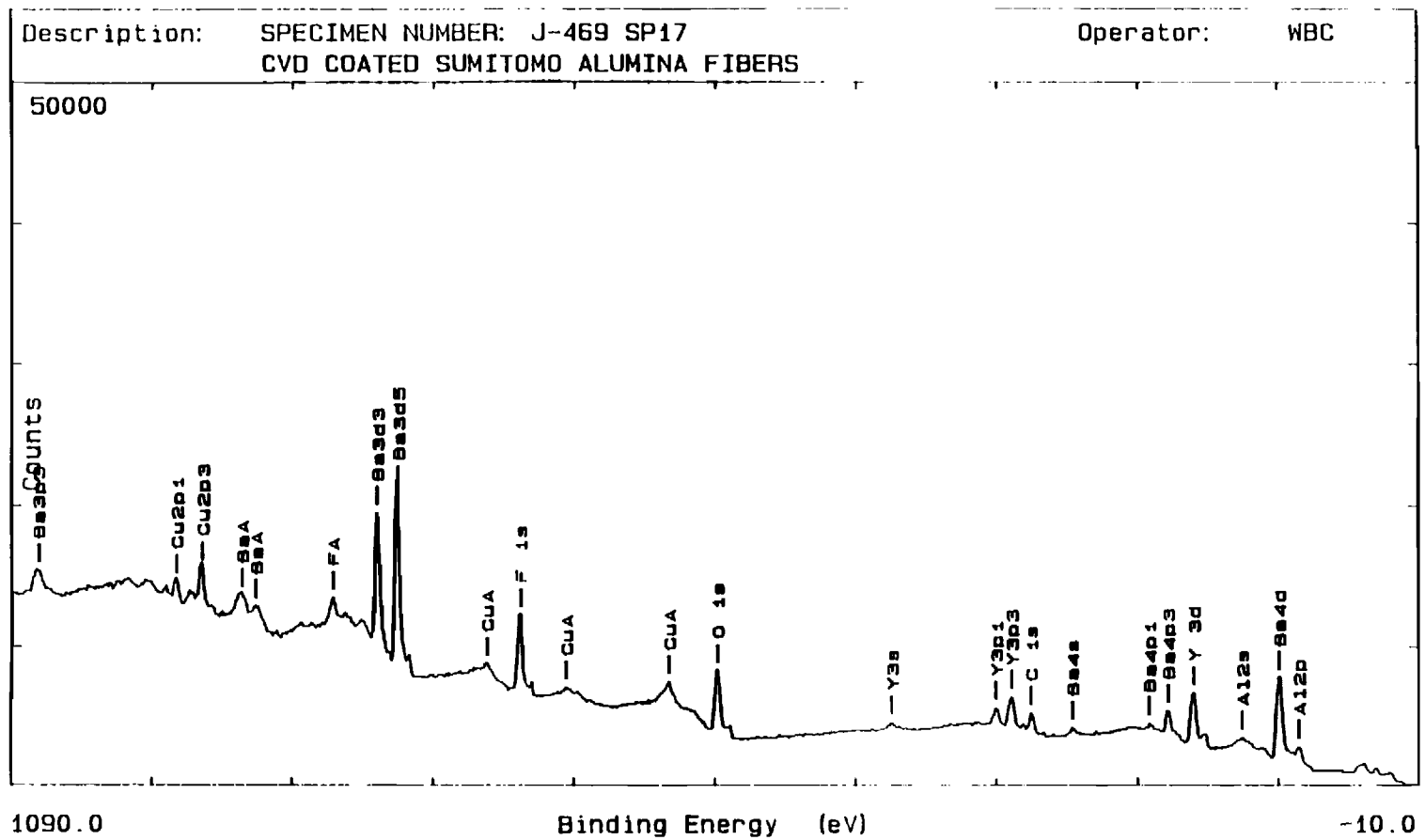


Figure 12. X-ray Photoelectron Spectroscopy Trace Obtained from the Coating on Sample SP17.

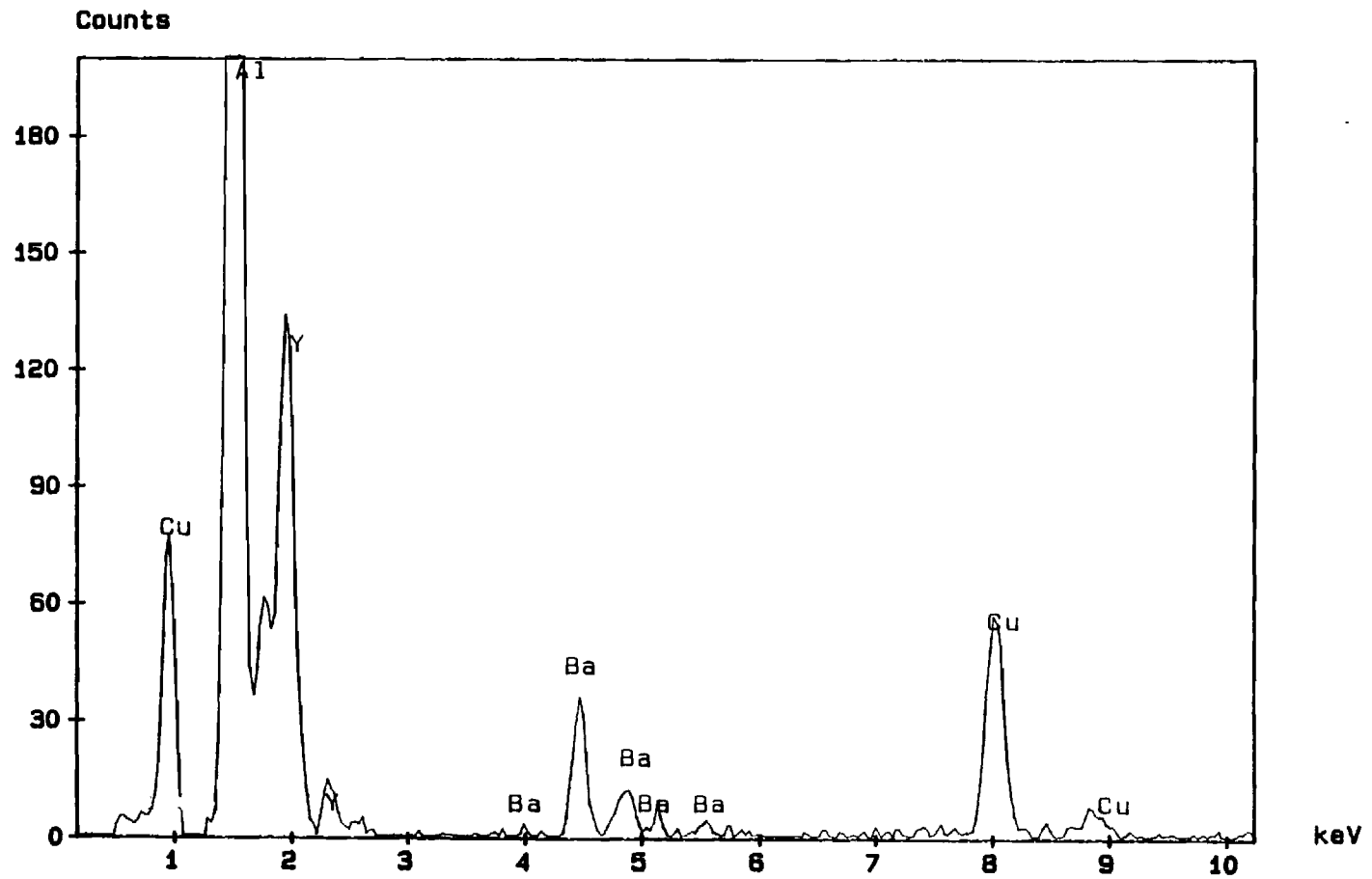


Figure 13. Energy Dispersive X-ray Analysis Trace Obtained from Coating of Sample SP12.

CONCLUSIONS

Although CVD coatings of $\text{YBa}_2\text{Cu}_3\text{O}_x$, containing the proper oxygen stoichiometry to give the superconducting orthorhombic crystal structure have not yet been successfully deposited, heterogeneous nucleation of all three metal-vapor species has been accomplished. Films several micrometers thick, containing the three desired metal cations, have been grown on a variety of substrates; and it should only be a matter of time until the ratios of yttrium, barium, and copper vapor necessary to produce the 123 compound are determined. The metal beta-diketonates (TMHD) appear to be the most promising reagents, giving the highest vapor pressures and the best long-term stability. Stability of the reagents at the vaporization temperature is still a serious problem, however, and this characteristic must be further investigated.

FURTHER DEVELOPMENTS

As was stated at the beginning of this report, this program was designed to initiate studies of the feasibility of applying CVD coatings of HTSC compounds to filamentary substrates. It is now clear, both from this work and from other published studies, that CVD is a viable process for coating a variety of shapes with yttrium-barium-cuprate compounds. This program has been continued under the auspices of DARPA, which has agreed to provide support for the work over the next three years as part of their high- T_c superconductor program. As of this time, highly c-axis oriented 123 films, having critical temperatures of more than 80 K, have been deposited on MgO single crystals. Work is now progressing on a continuous coating reactor designed to coat filamentary substrates.

REFERENCES

1. Robert E. Sievers and Jean E. Sadlowski, "Volatile Metal Complexes," Science, vol. 201, no. 4352, pp. 217-223, 21 July 1978.
2. Zh. N. Bublik, E. A. Mazurenko, and S. V. Volkov, "A Chromatographic Method for Determination of the Vapor Pressure of Metal Coordination Compounds," Soviet Progress in Chemistry, vol. 44, no. 7, pp. 94-96, (Eng. transl.), 1978.
3. Norio Matsubara and Tooru Kuwamoto, "Vapor Pressures and Enthalpies of Sublimation and Evaporation of Trifluoroacetylacetonates in Helium and Helium Containing the Ligand Vapor," Inorganic Chemistry, vol. 24, no. 17, pp. 2697-2701, August 14, 1985.
4. Ryohei Amano, Akiko Sato, and Shin Suzuki, "Sublimation Behavior of Tris (2,2,6,6-tetramethyl-3,5-heptanedionato) lanthanoid (III)," Bulletin of the Chemical Society of Japan, vol. 54, no. 5, pp. 1368-1374, 1981.
5. H. R. Brunner and B. J. Curtis, "The Vapour Pressures of Several Metal-2,2,6,6-tetramethyl-3,5-heptanedione Complexes Measure by a Knudsen Effusion Method," Thermal Analysis, vol. 5, pp. 111-115, 1973.
6. G. V. Trembovetskii, S. S. Berdonosov, I. A. Murav'eva, and L. I. Martynenko, "The Saturated Vapour Pressure of Yttrium and Zirconium Acetylacetonates," Russian Journal of Inorganic Chemistry, vol. 29, no. 8, pp. 1234-1235 (Eng. transl.), 1984.
7. A. S. Alikhanyan, I. P. Malkerova, Ya. Kh. Grinberg, V. B. Lazarev, V. A. Bogdanov, V. I. Gosgoraki, and V. A. Shreider, "Thermodynamics of the Sublimation Acetylacetonates of Al, Cr, Y, Zr," Doklady Physical Chemistry, vol. 292, no. 2, pp. 43-46 (Eng. transl.), July 1987.
8. Kent J. Eisentraut and Robert E. Sievers, "Thermogravimetric Studies of Metal Beta-Diketonates," Journal of Inorganic and Nuclear Chemistry, vol. 29, no. 8, pp. 1931-1936, August 1967.
9. J. E. Siere, J. T. Dubois, K. J. Eisentraut, and R. E. Sievers, "Volatile Lanthanide Chelates II. Vapor Pressures, Heats of Vaporization, and Heats of Sublimation," Journal of the American Chemical Society, vol. 91, no. 13, pp. 3476-3480, 18 June 1969.
10. Eugene W. Berg and J. Jaine Chiang Acosta, "Fractional Sublimation of the Beta-Diketone Chelates of the Lanthanide and

Related Elements," Analytica Chimica Acta, vol. 40, pp. 101-113, 1968.

11. Eugene W. Berg and Nicolas M. Herrera, "Fractional Sublimation of Various Metal Chelates of Dipivaloylmethane," Analytica chimica Acta, vol. 60, pp. 117-125, 1972.
12. A. A. Zholdakov and N. K. Davidenko, "Stability of Complexes of the Rare-earth Elements with Acetylacetone, Dibenzoylmethane, and Salicylaldehyde," Russian Journal of Inorganic Chemistry, vol. 13, no. 12, pp. 1662-1664, 1968.
13. G. V. Trembovetskii, L. I. Martynenko, N. A. Murav'eva, and Academician V. I. Spitsyn, "Synthesis and Study of Volatile Acetylacetonates of the Rare Earth Elements," Doklady Chemistry, vol. 277, no. 6, pp. 273-276, August 1984.
14. John Pickett Dismukes and James Kane, "Chemical Vapor Deposition of Luminescent Films," United States Patent No. 3,894,164, July 8, 1975.
15. Ross W. Moshier, Robert E. Sievers, Lyle B. Spendlove, "Vapor-Plating Metals from Fluorocarbon Keto Metal Compounds," United States Patent No. 3,356,527, December 5, 1967.
16. A. D. Berry, D. K. Gaskill, R. T. Hohn, E. J. Cukauskas, R. Kaplan, and R. L. Henry, "Formation of High T_c Superconducting Films by Organometallic Chemical Vapor Deposition", to be published, Appl. Phys. Lett., May 30, 1988.
17. T. Hirai, et al., Institute for Metals, Tohoku University, referenced in Superconductor Week, March 21, 1988.