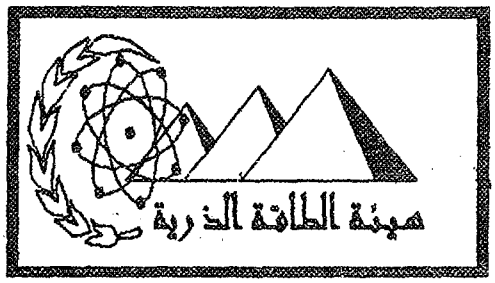
AREAEA/ Rep.No.342



ARAB REPUBLIC OF EGYPT
ATOMIC ENERGY AUTHORITY
METALLURGY DEPARTMENT

INVESTIGATION OF SOME CHARACTERISTICS FOR NICKEL FERRITE PREPARED BY AEROSOLIZATION

BY
M.A.A. EL-MASRY, E.M.H. KHATER
& A. GABER

1997
INFORMATION CENTER
ATOMIC ENERGY POST OFFICE
CAIRO, EGYPT

AREAEA./Rep.No.342

ARAB REPUBLIC OF EGYPT
ATOMIC ENERGY AUTHORITY
METALLURGY DEPARTMENT

INVESTIGATION OF SOME CHARACTERISTICS FOR NICKEL FERRITE PREPARED BY AEROSOLIZATION

BY
M.A.A. EL-Masry, E.M.H. Khater
& A.Gaber

1997
INFORMATION CENTER
ATOMIC ENERGY POST OFFICE
CAIRO, EGYPT

CONTENTS

ABSTRACT

In this report some characteristics of nickel ferrite powder prepared through the aerosolization technique by atomization were investigated. It was found that both concentration of the solution and temperature affect the powder characteristics. The increase of the pyrolysis temperature increases both the degree of crystallinity and particle size but decreases the specific surface area. Lowering the concentration of the solution, raises the decomposition efficiency and produces lower yield with smaller particle size.

INTRODUCTION

The increasing demand for ceramics with sbetter quality and high performance (e.g. high reliability and reproducibility) led stringently to the requirements for greater homogeneity and less imperfection in ceramic structure. Traditional approaches, such as the grinding of powders, are reaching the limits of their utility for microstrucural control

To achieve better control of the quality of advanced ceramic powders several novel processes are under investigation and development these processes exploit liquid-phase or vapor-phase as well as aerosolization. The pupose of these novel processes is to overcome the disadvantages of the traditional methods to achieve better control of homogeneity, purity, morphology particle size distribution of produced particles. In this report traditional and some novel techniques for fabricating ferrite powders are reviewed and some experimental results are given

1.1. Conventional Ferrites Proessing

In this technique the starting materials, are mixed in the appropriate ratio (1). Both dry and wet mixing are in use. In dry mixing, demixing can happen due to the differences in density or particle size (2-4). In wet mixing sedimentation or selective fitration can give rise to composition changes. Then firing is introduced to heat up the mixed powders between 800 and 1300°C to form the ferrite. The fired constituents are then milled to reduce the particle size and increase the homogeneity to achieve the powder characteristics stawted by Williams (5). The miling is followed by shaping green bodies, sintering, and firing.

1-2 Non Conventional Ferrites Processing:

2-1- Precipitation or coprecipitation:

The distinction between precipitation and coprecipitation is based on the character of the precipitate. If two or more cations are existing in the precipitate, the process is referred to as coprecipitation.

A large amount of papers related to this technique have been published (6-16). Although, this technique is superior to the conventional processes, a number of factors (e.g. pH, concentration, stiring rates, precipitating rates of components, etc.) (6-8), govern the characteristics of resultant products and may cause difficulty in precisely controling the formation of the desired products.

2.2 Sol Gel Technique

In this technique, metal alkoxides, which have the general formula $M(OR)_n$ where M is metal with valencey n and R is an alkyl $C_x H_{2k+1}$ are commonly used as starting materials. The alkoxides are dissolved in and appropriate alcoholic solvent and addition of water causes the hydrolysis and the formation of corresponding hydrous oxides (17,18). Carefully controlled conditions can be used to prepare ceramic powders which have betteer homogeneity, higher purity, much smaller particle size, higher rectivity, and lower sintering temperature than the ones prepared from the conventiaonal process. The average degree of polymerization of the hydrolysis products depends on the degree of hydrolysis (19)

Some single metal oxides have been prepared by the sol-gel technique (20-24). Some researchers have successfully applied this technology to the fabrication of multi-metal oxides (25-27).

Although the sol-gel technique offers some advantages, for the preparation of ceramic powders, some problems still remain and need to be solved. The problems include the need to better control shrinkage to avoid cracking and to better control processing to produce final ceramic products with the required degree of crystallinity and porosity.

2-3. Aerosol techniques

The powder synthesis procedures that involve the aerosolization of a solution into a chamber of controlled temperature and atmosphere to accomplish solvent evaporation and chemical reaction to obtain the required phase or phases are referred to as aerosol techniques. Sproson and Messing (28) classified this kind of procedures as the thermal reaction of atomized solutions processes (TRAS). The chemical reactions occurring in these procedures may be classified as decomposition, hydrolysis, and pyrolysis.

Aerosol technique can be used for preparing simple phases produced from one starting material, such as simple oxides, or phases containing oxides of more than one metal produced from more than one raw material. The major atribute of aerosol techniques is that one or more salts can be dissolved in a suitable solvent to form a homogenous solution which then can be sprayed to fine droplets having the reuired amount of reactant . Each droplet acts as separate reactor containing the constituents mixed in the atomic scale with no chemical segregation chemical segregation which is due to the solubility product differences in multicomponent systems ocurs in precipitation process.

The most widely used raw materials for aerosol process are metal salts including nitrates, acetates, chlorides, and sulfates. These salts are used because they can be converted to the corresponding oxides on decomposition. The latter point is significant to ensure complete reaction within the short residence time that typifies aerosol process.

Aerosols can be generated by one of the following to methods: the evaporation condensation method or the atomization method. The evaporation condensation method was used to obtain submicron metal oxides and the mixed metal oxides, with modal diameters below 1 micron (29-31). Evaporation condensation technique can be controlled to produce narrow size distribution of droplets, but this technique cannot be applied to materials which decompose below their boiling point. Aso, the nonvolatile liquids cannot be used to generate the required aerosol, However, atomization technique can be applied to all solutions (volatille or nonvolatile).

The mophologies of resulting particles depend on the physical and chemical properties of the solution and the operating conditions of process. During the process the solvent initially evaporates from the droplet surface, resulting in localized solute super-saturated. Consequently, the salt precipitates at the droplet surface to form dried surface layer of salt particles. The different particle morphologies which can develop during the drying of salt solution droplet were qualitatively classified by Charlesworth and Marshal (32), in terms of the physical nature of the dried surface and relative drying temperature Nitrate derived powders generally consisted of hollow, shell like aggregates, and sulfats result in flakes or hollow shells(28).

A kinetic study of hydrolysis of metal alkoxide aerosol droplet in the presence of water vapor was conducted by Ingebrethen and Matijevic (33). Pratsinis et al. (34), studied the design of laminar flow condensers (used for condensation of some stable alkoxide vapor) for production of monodispersed aerosols and reported the effects of process parameters and condenser configuration on product aerosol characteristics.

Kodas et al. (35), applied the aerosol techniques to the fabrication of a superconducting ceramic, $Y_1\ Ba_2\ Cu_3\ O_7$. They used nebulizers to generate required aerosol droplets. They synthesized fine $Y_1\ Ba_2\ Cu_3\ O_7$ powders by atomizing solution of the nitrate salts of Y Ba Cu in a 1:2:3 ratio.

2- EQUIPMENT AND EXPERIMENTAL TECHNIQUES

2-1- Equipment

A schematic diagram of the equipment used in this study is shown graphically in Fig. 1. The components of this equipment are:

a- Aerosol generator:

A six jet atomizer, Model 9306m thermal system inc., was used to accomplish the generation of required aerosols. From one to six jets can be used to offer a broad range of control over both the droplet number concentration and the total droplet output. A pressure regulator and gauge are ounted on the atomizer, The regulator that ranges from 0 to 3.4 atmospheres governs the input pressure of the atomizer and the pressure is displayed on the gauge.

b- Aerosolization gas system:

An air compressor, model GH-505, was used to supply the required compressed air, which was then filtred using an air filtr, model 3074, Thermal System Inc. The filter is followed by a pressure regulator and a silica gel desiccant drier to remove the moisture from the gas. Finaly the compressed gas passes through a high efficiency filter to remove fines before entering the atomizer

c- Tube furnace and temperature control system:

A tube furnace 50 mm inner diameter 91 Cm length was used to evaporate the solvent and allow for decomposition and solid state reactions. The temperature was controlled using an Omega, Model 4001-KC, temperature controller. To avoid the condensation of aerosol before introducing to the tube furnace, a 60 Cm long fiexible electric heating tabe was used as a preheater.

2-2 Preparation of mixed nitrate solution and aerosolization:

An aqueous solution of frric nitrate and nickel nitrate was prepared from the corresponding salts in the ratio to give nickel ferrite after aerosolization. The aqueous solution was mixed thoroughly. The solution was then loaded into the atomizer container. The furnace was turned on to reach the specified temperature. The air compressor was turned on and the pressure was adjusted. The resultant particdles in the exiting aerosol flow were collected on the nucleopore filter and transferred to glass vials.

2-3- Product characterization:

The effect of operating conditions on the characteristics of the product were investigated by X-ray diffraction, SEM-BET, particle size analysis, and thermal analysis.

The X-ray diffraction and thermal analysis provide means of determing the degree of crystallinity and the efficiency of decomposition. Scanning electron microscopy (SEM) can be used to show the morphology of the product. BET surface area provides the information of surface area. Also, from the particle size measurment the size analysis and distribution can be obtained.

3- EXPERIMENTAL RESULTS AND DISCUSSION

3-1- Operating conditions inside the tube reactor:

All the operating conditions for the process, except the processing temperature and dilution of the starting solution, were kept constant during this study. One jet of the atomizer was used and the input pressure was set at 2.04 atm., (gauge pressure), to generate the required aerosol droplets. This situation correspons to about 7.45L.min aersol output (as assessed by the manufacturrer) and consequentully, Reynolds Number

inside the tubular reactor is estimated to be 396 at 20 °C and 34 at 1000 °C assuming that the flow is mainly air. These operating coditions gave a residence time of the aerosol inside the tube furnace about 3.71 S. As the walltemperatures were adjusted to 500,600,700,800, and 900 °C (in the hotest zone), this corresponded to 480,570,660,740, and 810 °C when using an aerosol produced by applying the prementioned operating conditions. The average temperature at the hottest zone will be used to represent the pyrolysis temperature.

3-2- Charactracterization of aerosolization product using 5 w% $Fe(NO_3)_3$ mixed nitrate solution:

Using the operating conditions mentioned earlier in 3.1., the effect of pyrolysis temperature on the aerosol products for a mixed nitrate solution containing 5w% $Fe(NO_3)_3$ was investigated. The study was carried out using X-ray diffaction analysis, thermal analysis, density measurement, particle size distribution, scanning electron microscopy and BET surface area measurement.

The X-ray diffraction patterns for the aerosol products obtained by using the 5 w% $Fe(NO_3)_3$ as a starting material are shown in Figures 2 and 3 . From these figures it is clear that pyolysis at 570 °C and below yields non crystalline materials. The increase in the processing temperature, 660 °C and above Fig.3, increases the degree of crystallinity and crystal growth (the sharpnes of the peaks).

The thermogram curves, using a heating rate 5 °C/min up to 1500 °C for the aerosolization product are shown in Fig. 4. For the product at 570°C and above lower loss in wight is obtained while for those collected at 480°C and below, higher wieght loss is obtained . This indicates the existence of residual hydrated salts. As the TGA curves indicate the efficiency of pyrolysis and removal of volatile components. Using this assumption, and TGA curves, the efficiency of decomposition

was calculated for the temperature used in this investigation which are 450,480,570,660,740, and 810°C and was found to be74,76,88,91,94, and 96 respectively.

The SEM photomicrographs for the products indicated that the particles are hollow spheres, as it is shown in Fig.5, this agree with the results of Sproson and Messing (28)

The results obtained for particle size distribution showed that the powders formed at high pyrolysis remperatures have a broad size distriubtion as it is clear form Figures 6 and 7 . It is also clear that as the aerrosolization temperature increases the powder so obtained has more than one modal of distribtion i.e. One modally distributed powder at 480 °C and six modally distributed at 810 °C

The specific surface area as measured by BET method is given in Table 1. High values of specific surface area are obtained at low pyrolysis temperature and as the pyrolysis temperature increases the specific surface area decreases. The smaller particles obtained at low temperatures explain the reason for the high specific surface area.

The magnetization of the powder way examined and the results are given in Table.1. It is clear that as the processing temperature increase the magnetization becomes sensible.

3-3- Characterization of aerosolization product using mixed nitrate solution, [1.5 wt% Fe $(NO_3)_3$]

A dilute mixed nitrate solution containing 1.5 wt% $Fe(NO_3)_3$, with a composition to produce $NiFe_2O_4$ after processing. The solution was aerosolized at 480,740, and 810°C . The thermogram curves for the

aerosolization products are shown in Fig.8. It is obvious that the efficiency of forming nickel ferrite for these products is higher than those

prepared using a solution with a higher concentration, aerosolized at the same temperature, Fig. 4.

The X-ray patterns, Fig. 9, reveal that the particles obtained at 480 °C are not well crystalline materials, but those obtained at 740 and 810 °C consist of well crystalline $NIFe_2O_4$.

The SEM for products, obtained from the low concentration solution at the same conditions using the higher concentration solution showed that the particles are smaller in size and more unkform than those obtained using a higher concentration solution. With low concentration the content of the salt in each droplet is less and after evaporating more liquid a smaller spherical crust is formed . Although low concentration produced smaller active particles, the yield is much smaller

4-CONCLUSION

1- The aersosolization products derived by using nickel nitrate, ferric nitrate solution in the ratio form $NiFe_2O_4$ consist of hollow spheres.

2- The aerosolization products very from noncrystalline to crystalline materials

3- The increase of the pyrolysis temperature increaes the decomposition efficiency, the crystallinity, the average size of the resulting particles and the particle size distribution rnage but, decreases the specific surface area and the average bulk density.

4- As the decomposition temperature increases more than one mode of distribution of the product powder is obtained.

5- Decreasing the concentration of the starting solution, raises the decomposition efficiency and produces lower yield with smaller size.

REFFERENCES

1- D.Swallow and A.K. Jordan, Proc. Brit Ceram. Soc., [2] 1-17 (1964).

2- M.B. Donald and B.Roseman, Brit., Chem. Engr., 7[10]749-53 (1962).

3- B.Roseman and M.B.Donald, Brit. Chem. Engr., 7[11]823 (1962).

4- M.B. Donald and B.Roseman, Brit. Chem. Engr., 7[12]922-923(1962)

5- I.J. Mccolm and M.J. Clark, "Forming ,shaping, and working of High- performance Ceraics", pp.84-87,Blackie and osn Ltd., New York,(1988).

6- D.W.Johnoson, Jr. and P.K.Gallagher, "eactive powders from Solution" pp.125-39 in Ceramic Processing Before Firing,. Edited by G.Y. Onoda, Jr.and L.I. Hench, Wiley and sons,NewYork, (1978).

7- P.E.D.Morgan, "Chemical Processing for Ceramics and Polymers"pp.67-76 in Processing of Crystalline Ceramics Edited by H.Palmour ill, R.F., Davis, and T.M. Hare plemum, New York, 1977.

8- D.W.Johnson, Jr., Am.Ceram.Soc.Bull., 60[2]221-224(1981)

9- W.J.Schuele, J.Phys.Chem., 6383-86 (1959).

10- D.G.Klisurski, J.Subrt, V.N.Blaskov, J.Lipka, P.Hanousek, and K.Bchine, J.Materials Sci., 19,183-188 (1984).

11- D.G.Chamare and E.D.Grave, Phys. Chem. Minerals, 12, 176-84 (1985).

12- J.M.Fernandez Rodriguez, J.Morales, and J.L. Tirado, J.Material Sci, 21, 3668-71 (1986).

13- M.I. Mendeison, J.Am. Ceram. Soc. 59[5-6]219-21(1976).

14- M.Kiyama, Bull. Chem.Soc., Jap., 51[1] 134-38(1978)

15- National Bureau of standards, "Nickel Ferrite (Trevorite), $NiFe_2O_4$ (Cubic)", NBS circular 539,Microtext Dept., Texas A&M University, 10,44(1960).

16- B.E. Yolds, J.Am.Ceram. Soc., 65[3]387-93(1982).

17- PH Colmban, "Sol-Gel mSynthesis and Densification of Nasicon Powders", pp.139-54 in Ceramic powder Science, Edited by G.L. Messing,K.S. Mazdiyasni, J.W.McCauley, and R.A. Haber, The Am. Ceram. Soc.,Inc., Westerville, ohio, 1986. 1(1969).

18- J.W.Lorimer and D.E.G. Jones,Can.J.Chem., 47[22]4101-11(1969).

19- D.LL. Catone and E.Matijevic, J.Colloid Interface Sci, 48[2] 291- 301(1974).

20- B.Fegley, Jr., P.white, and H.k. Bowe Am.Ceram.Soc.Bull.,64[8]1115-20(1985).

21- Y.Suwa M.Inagaki, and S.Nake,Am.Ceram.Soc.Bull.55[11]1005- 06 (1979)

22- O.Yamaguchi and k. Shimizu,"Crystallization and Transformaion of Alkoxy-Derived GeO" pp.163-68 in ceramic Powder Science, Edited by G.L. Messing, K.S.Mazdiyasni, J.W.McCauley, and R.A. Haber, The aAm. Ceram.Soc.Westerville, ohio, 1986.

23- K.C.Chen, Tsuchiya, and J.D. Mackenzie, J.Non-Cryst. Solids,81 227-37(1986).

24- J.S.Smith ll, R.T.Dolloff, and Mazdiyasni, J.Am.Ceram. Soc 53[2]91-95(1970).

25- H.Murayama and K.Meguro,Kolloid-Z.U.Z. Polymere, 248 963- 67(1971).

26- K.Takahashi, T.Yoshio, K.Oda, and F.Kanamaru,J.Non-Cryst. Solids, 42 157064(1980).

27- D.W. Sproson and G.L. Messing, "Ceramic powder Synthesis by Thermal Reaction of Atomized solutions",pp.99-108 in Ceramic Powder Science, Edited by G.L. messig,K.S. Mazdiyasni, j.w. Mccauley,and R.A. Haber, The Am.Ceram soc.,Inc., Westerville,ohio,(1986).

28- M.Visca and E.Matijevic,J.Cooloidal Interface Sci., 68[2]308- 19(1979).

29- B.J. Ingebrethsen and E.Matijevic, J.Aerosol Sci., 11 271-80 (1989).

30- B.J.Intgebrethsen, E.Matijevic, and R.E. Partch, J.Colloidal Interfacea Sci.,95(1)228-39 (1983).

31- D.H. Charlesworth and W.R. Marshall,Jr.,J.Am. Inst.Chem. Engr., 6[1]9-23(1960).

32- B.J. Ingebrethsen and E.Matijevic, J.Colloid. Interface Sci.,100[1]1- 16(1984).

33- S.E. Pratsinis, T.Kodas, and A.Sood, Ind.Eng.Chem.Res., 27[12] 105-11(1988).

34- T.T.Kodas, E.M.Endler, V.Y.Lee,R.Jacowitz, T.H. Baum, K.Roche and S.S.P.Parkin, Appl.Phys.Lett.,52[19] 1622-24(1988).

Table.1
Characteristics of the Aerosol Products
Using Mixed Nitrat Solution

Pyrolysis Temperature (deg.C)	Magnetic Character	Average powder Density (g/cm)	Particle Size [Median] (micron)	Specific Surface Areay by BET (m/g)	Crystalliza tion
480	none	3.55	0.57	112	non-cryst
570	none	3.49	0.62	106	non-cryst
660	exist	3.15	0.85	87	slightly cryst
740	exist	3.02	0.91	14	slighly cryst.
810	exist	2.28	1.07	11	slighly cryst.

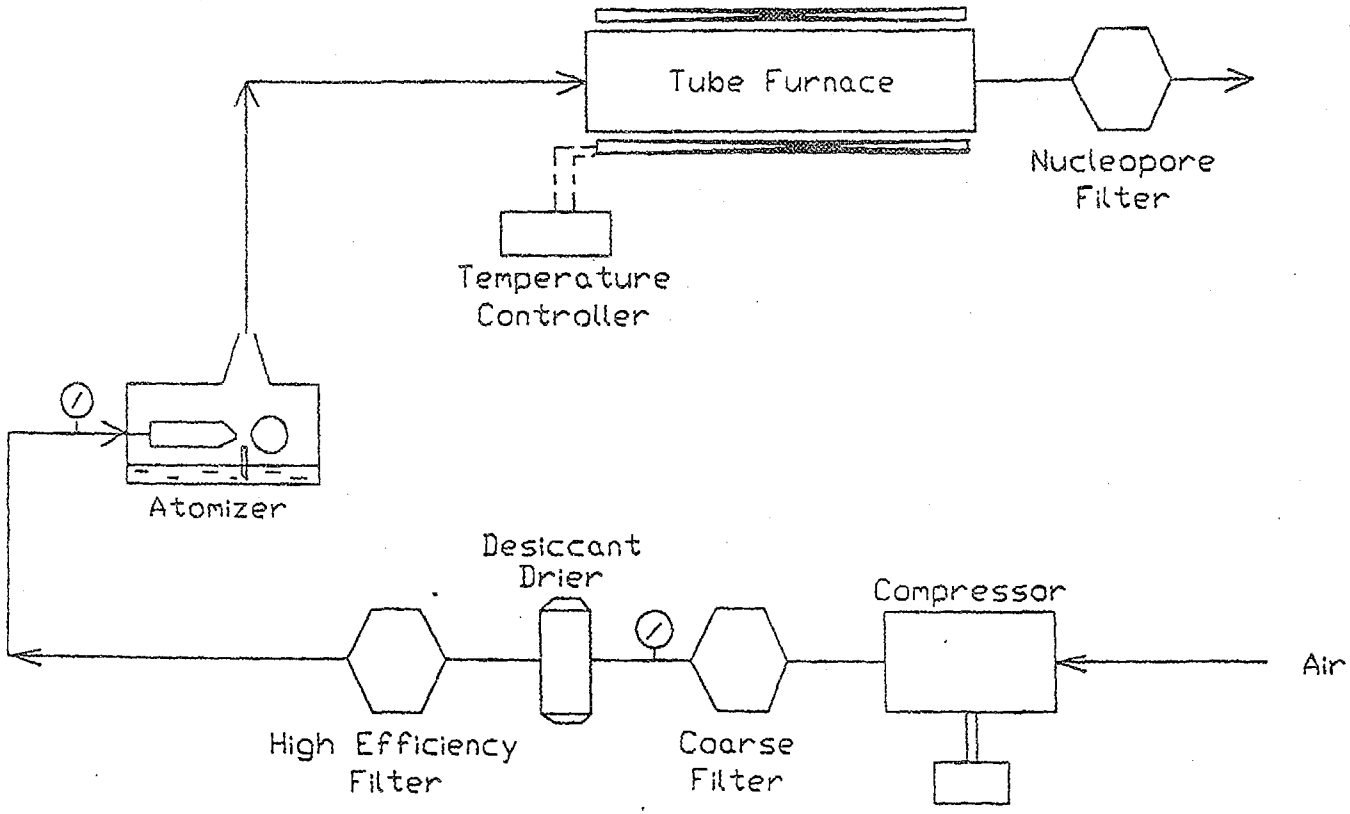


Figure 1. Flow diagram of the aerosolization process

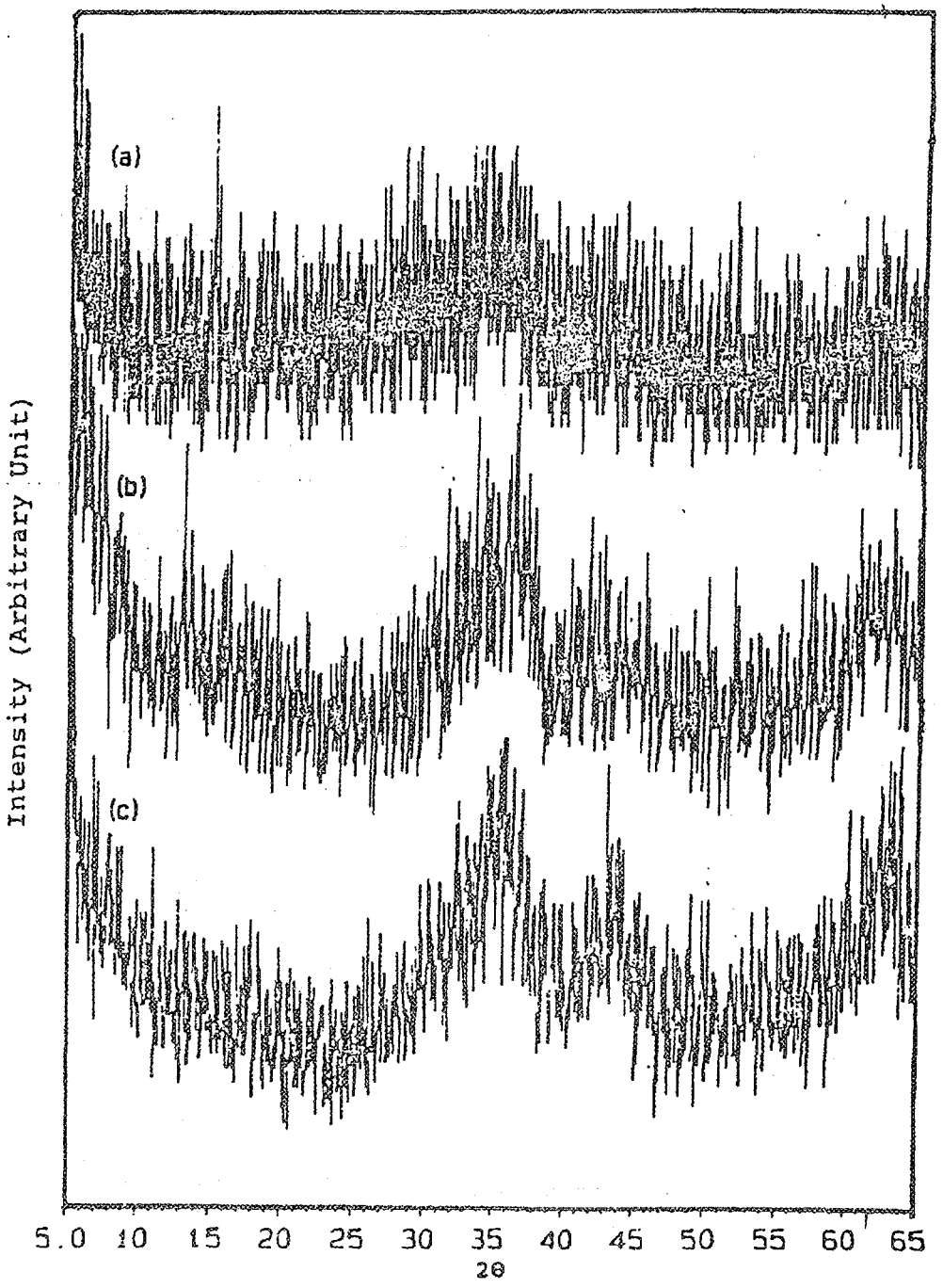


Figure 2 . X-ray patterns for the aerosol products using mixed nitrate solution, (a) 450°C, (b) 480°C, and (c) 570°C

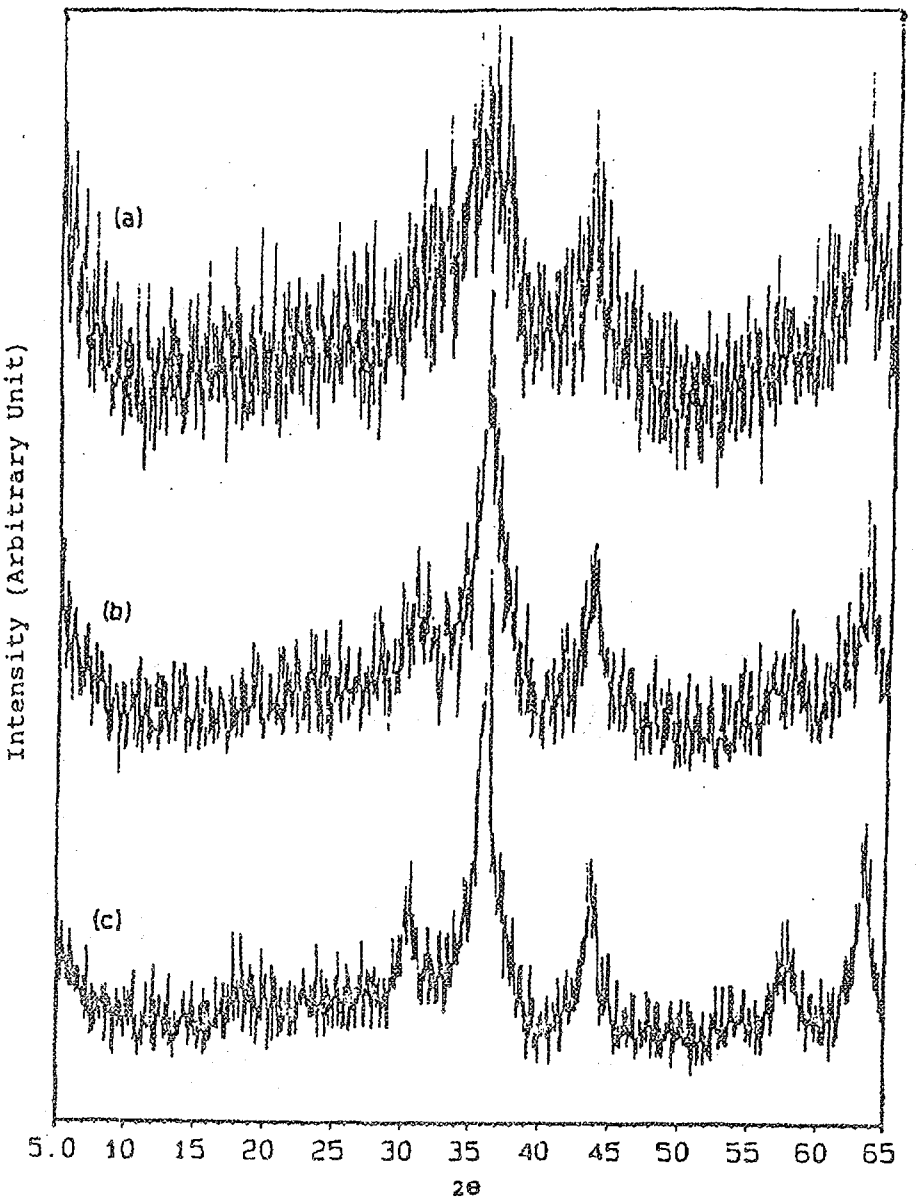


Figure 3. X-ray patterns for the aerosol products using mixed nitrate solution, (a) 660°C, (b) 740°C, and (c) 810°C

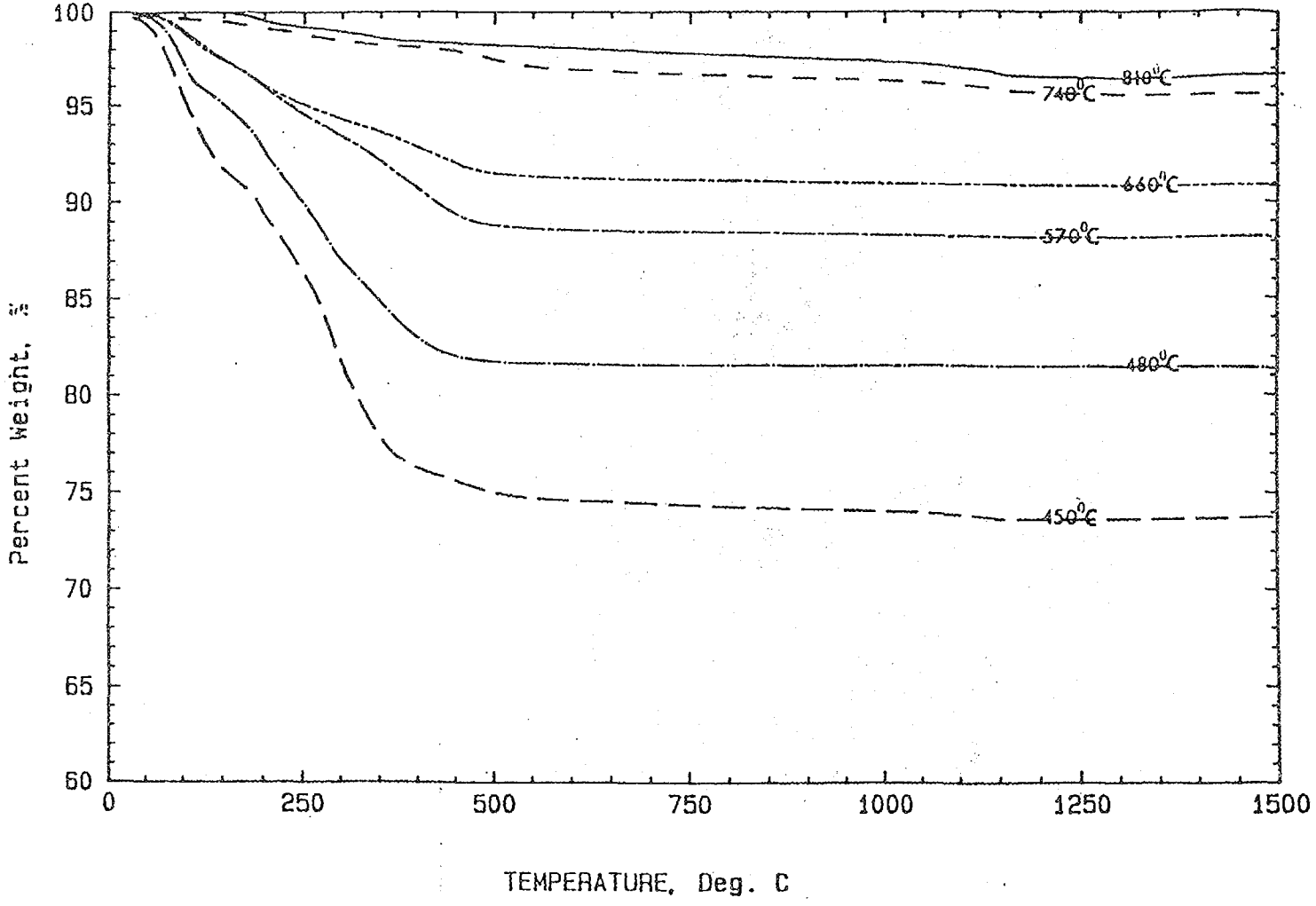


Figure 4. TG curves of the aerosol products using mixed nitrate solution

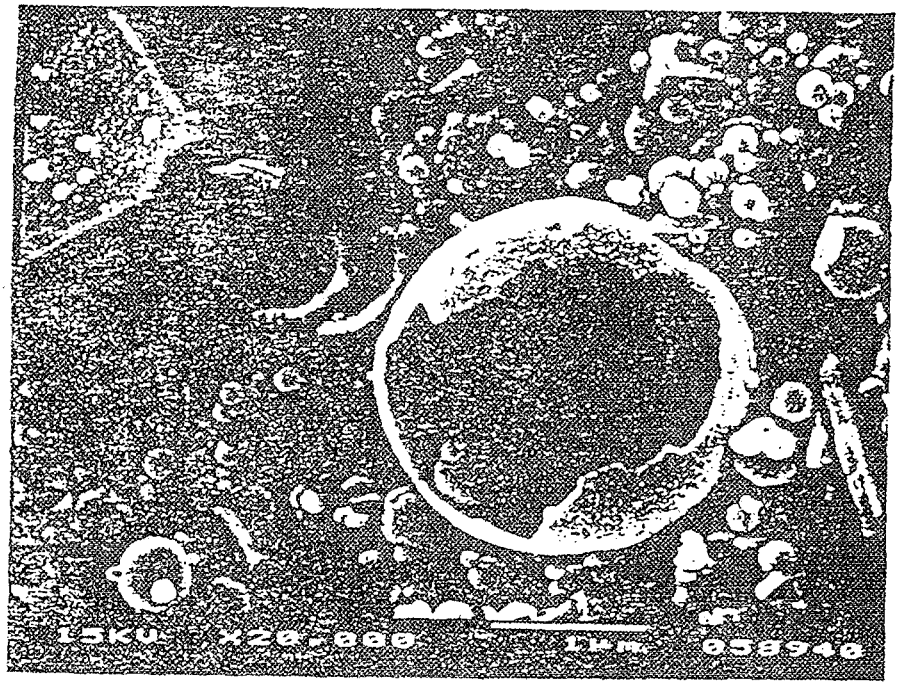


Figure 5. SEM photomicrograph - Aerosol product using mixed nitrate solution, 740°C
(high magnification)

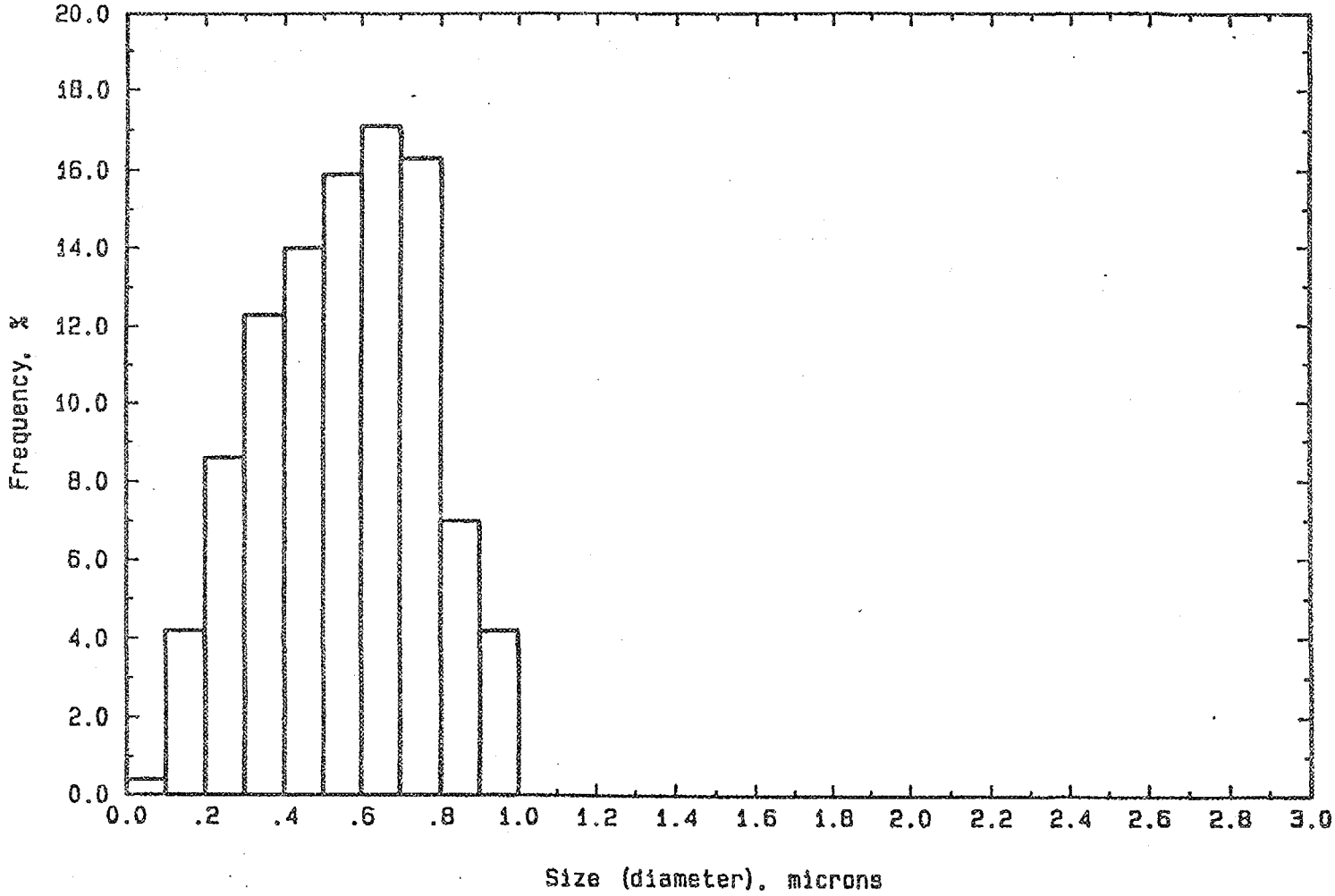


Figure 6 . Size distribution - Aerosol product using mixed nitrate solution, 480 °C

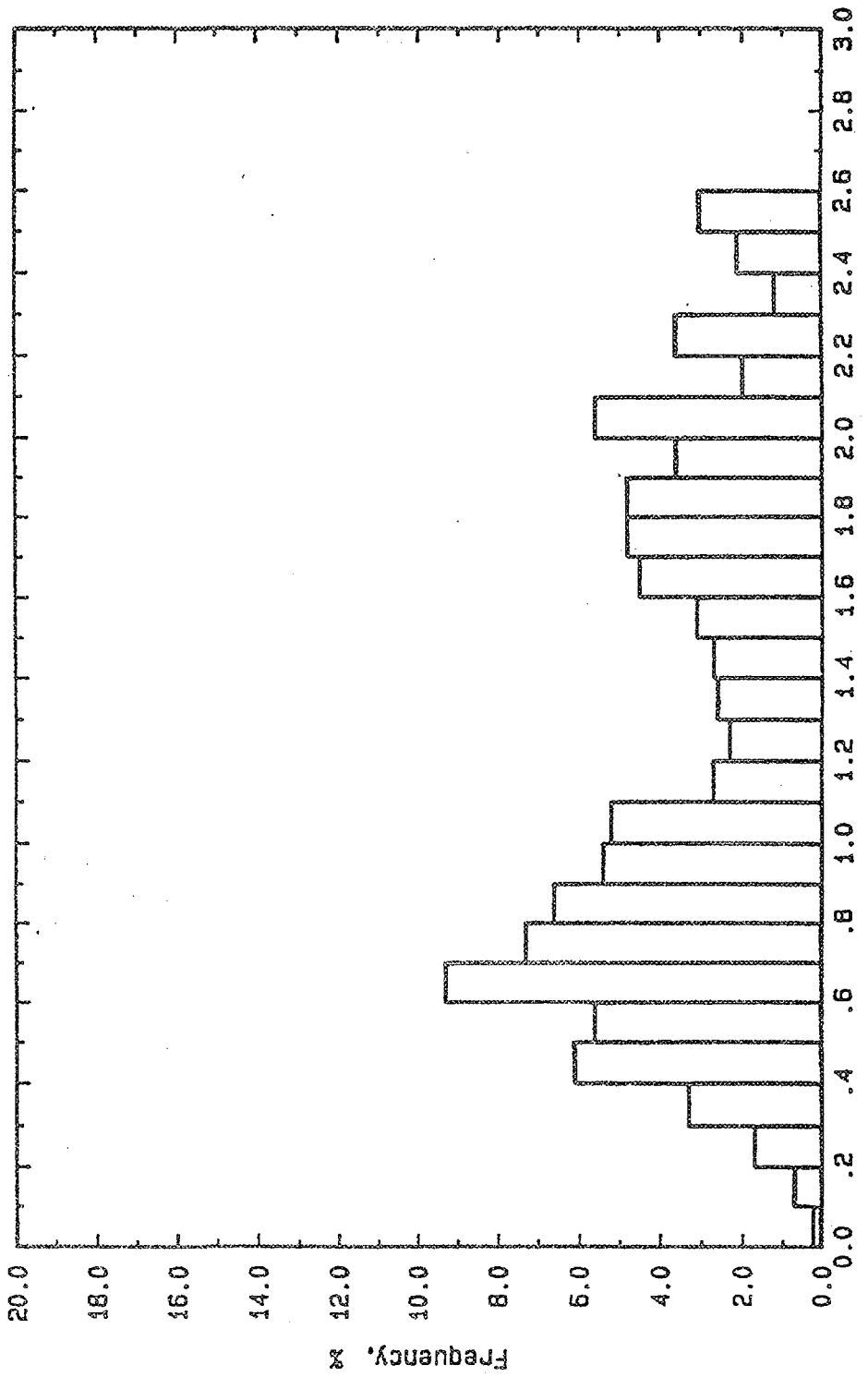


Figure 7 . Size distribution - Aerosol product using mixed nitrate solution, 810 °C

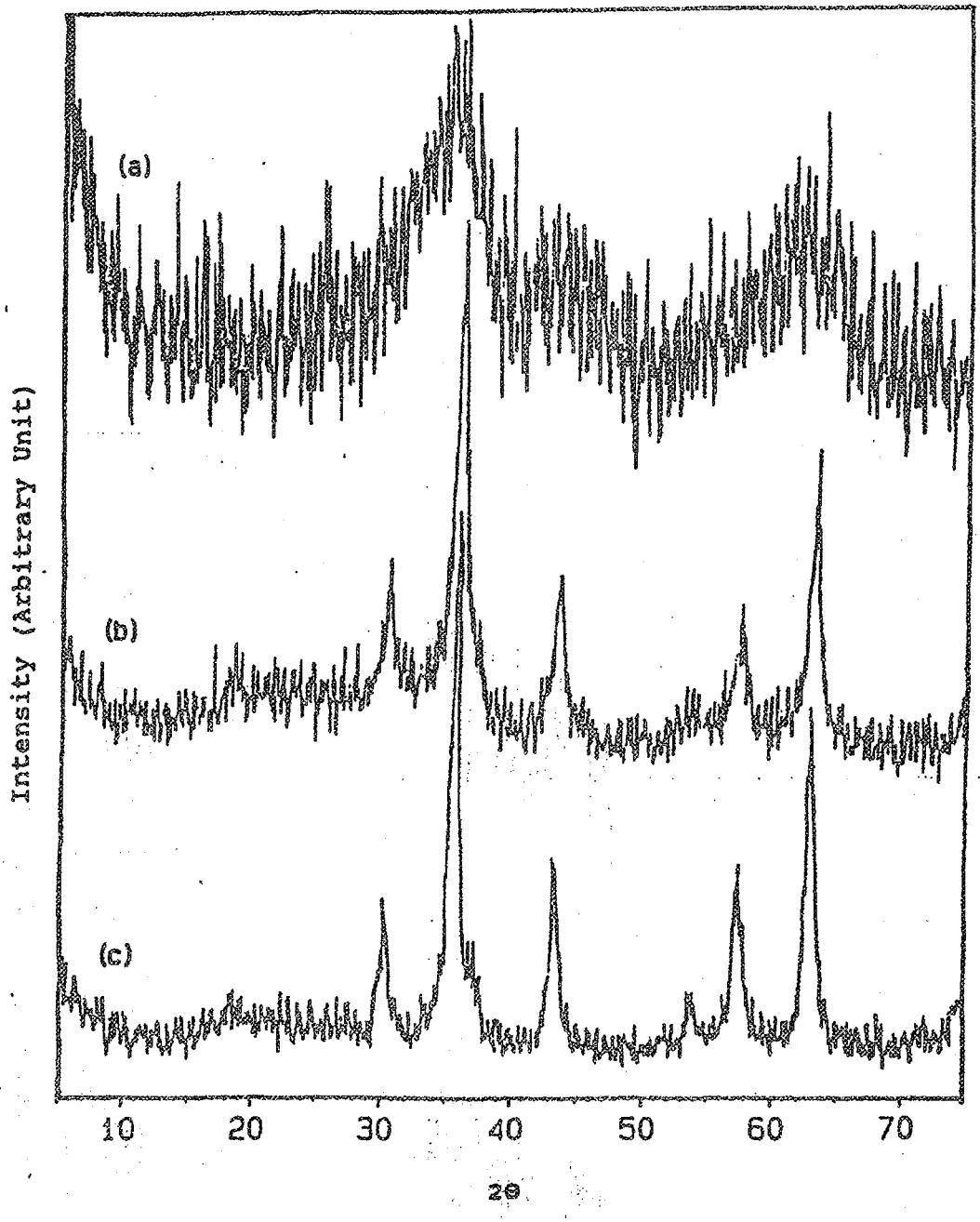


Figure 9. X-ray patterns for the aerosol products using dilute mixed nitrate solution, (a) 480°C, (b) 740°C, and (c) 810°C

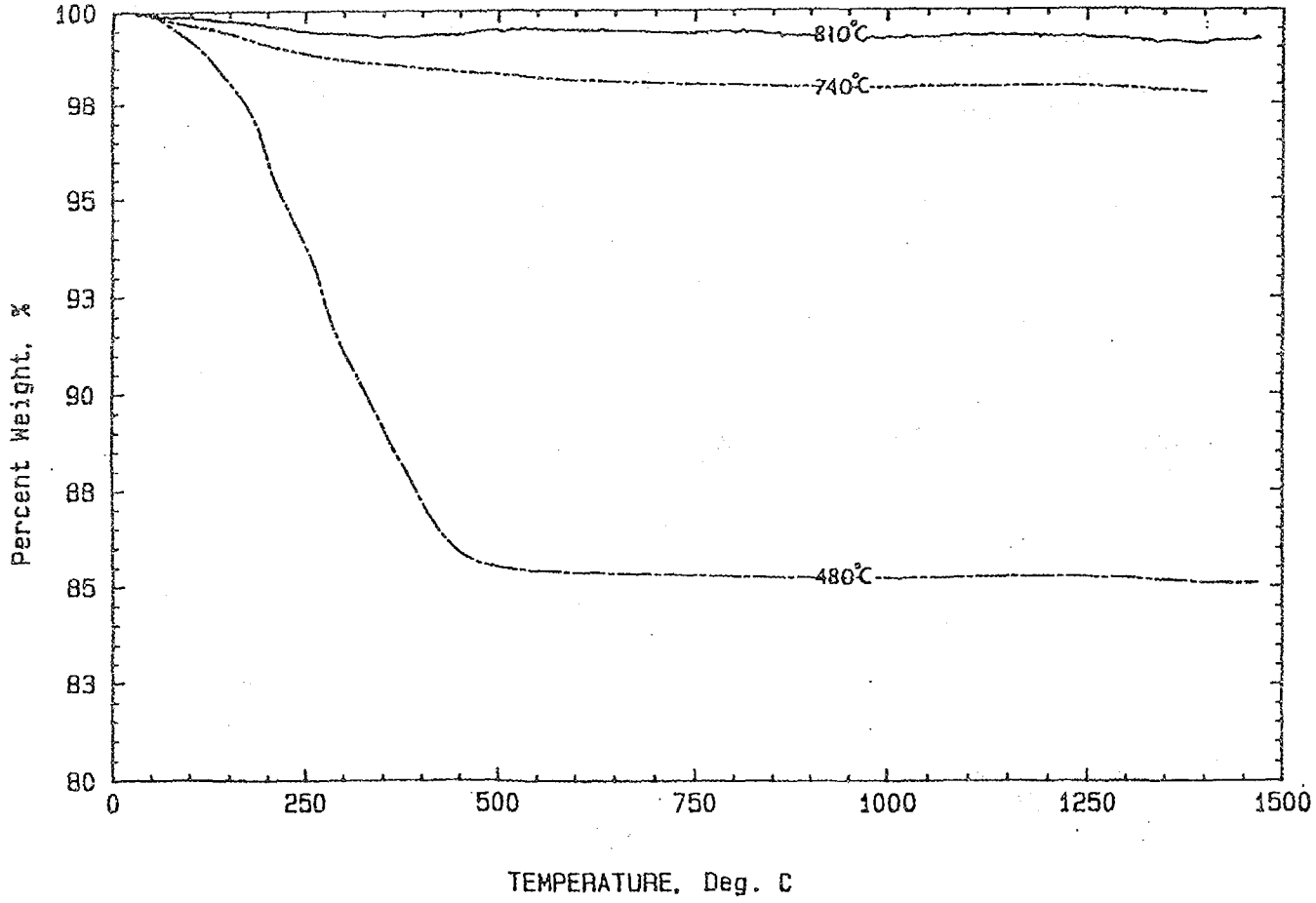


Figure 8. TG curves of the aerosol products using dilute mixed nitrate solution