Mines Branch Technical Bulletin TB 29

FERRITES: GENERAL DESCRIPTION AND FABRICATION OF TOROIDS

by

A.G. Sadler*

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SYNOPSIS

The use of ferrites in electronic and magnetic devices is expanding rapidly. This report gives an account of the work concerning these materials which was carried out in the Ceramic Section of the Mineral Processing Division during the year 1958-59.

A general description of the structure, magnetic properties, uses, methods of preparation and ceramic aspects of ferrites is given. A technique for the fabrication of ceramic toroidal shapes is described. Specimens of nickel ferrite, with and without additions of cobalt oxide, were fired under various experimental conditions. Density and shrinkage measurements are reported.

The construction, development and operation of an atmosphere-controlled, propane-gas-fired furnace are described in an appendix.

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Direction des mines

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FERRITES: DESCRIPTION GÉNÉRALE ET FAÇONNAGE DE BOBINES TOROIDALES

par

A.G. Sadler*

RÉSUMÉ

L'emploi des ferrites dans les dispositifs électroniques et magnétiques prend rapidement de l'importance. Le présent rapport donne une idée des travaux exécutés à l'aide de ces matériaux à la Section de la céramique de la Division du traitement des minéraux au cours de l'année 1958-1959.

L'auteur donne une description générale de la structure, des propriétés magnétiques, des emplois, des procédés de préparation de même que des aspects céramiques des ferrites. Il y décrit un procédé d'élaboration de pièces toroidales de nature céramique. On a soumis à l'action du feu, dans diverses conditions expérimentales, des échantillons de ferrite au nickel avec et sans oxyde de cobalt. Les mesures relatives à la densité et au retrait sont indiquées.

La construction, la mise au point et le fonctionnement d'un four alimenté au gaz propane, à atmosphère contrôlée, sont décrits en annexe.

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INTRODUCTION

The use of ferrite (1) materials in electronic devices (2) operating at high frequencies is one of the most recent developments in ceramics. The principal advantage in using these compounds lies in their comparatively high electrical resistivities, which range from 10 to 10^9 ohm-cm. The high resistivity tends to suppress eddy currents and, therefore, eliminate eddy current losses, which cause heating effects in the presence of high frequency alternating electric fields. Another advantage arises from the high coercivities which are obtainable; thus ferrite permanent magnets resist demagnetizing influences better than the metallic type. The disadvantages of these materials originate in the low saturation magnetization and permeability values.

A bibliography on the literature concerning ferrites has been prepared by Blum, Zlotnick and Zneimer (3).

STRUCTURE AND MAGNETIC PROPERTIES

Structure

In general, ferrites can be described as being composed of the oxides of certain divalent metals combined with iron oxides, and as possessing an atomic structure similar to that of spinel ($MgO.Al_2O_3$). The ferrite may be non-magnetic, as in the "normal" spinel structure, or magnetic, as in the "inverse" spinel structure.

For the normal spinel structure, the divalent metal atoms are surrounded tetrahedrally by four oxygen atoms, and the iron atoms are surrounded octahedrally by six oxygen atoms. The oxygen atoms are built up into a cubic close-packed lattice with 32 to the unit cell. The structural formula is:

$$(Me_8^{2+})^{IV}\ (Fe_{16}^{3+})^{VIII}\ 0_{32}$$

where Me = Zn, Cd.

For a completely inverse magnetic spinel structure, the divalent metal atoms and half the iron atoms are in octahedral co-ordination with the oxygen atoms, and the remaining iron atoms are in tetrahedral co-ordination. The structural formula is:

$$(Fe_8^{3+})^{IV}\ (Me_8^{2+}\ Fe_8^{3+})^{VIII}\ 0_{32}$$

where Me = Mg, Mn, Cu, Fe^{2+}, Co, Ni.

The completely normal and inverse spinels represent extreme cases, and intermediate structures do occur. For example, the degree of inversion in magnesium ferrite and copper ferrite can be controlled by quenching samples from various temperatures.

The "hard" ferrites, which are permanent magnetic materials and contain as the principal cation constituents lead, barium, strontium and iron, do not have the spinel structure. They crystallize in the hexagonal system and are structurally similar to magneto-plumbite, $Pb0.6\ Fe_20_3$.

Magnetic Properties

Magnetism arises from the motion of electrons. An electron carries an electric charge; therefore a moving electron constitutes an electric current which consequently has associated with it a magnetic field.

An electron moving round a nucleus has two types of motion, each of which gives rise to a magnetic field. First there is the orbital movement, and second the spin. In the second case, the total spin contribution to the atomic magnetic moment is the vector sum of the moments caused by the individual spins of all the electrons in a particular atom.

The total atomic magnetic moment is the vector sum of the electronic orbital moments and spin moments. In ferromagnetic materials the magnetic moment due to electron orbital motion is only about 10 per cent of the total moment, and, therefore, a predominant part of the effect is due to electron spin.

The state of an electron is determined by the orbit in which it moves and the direction in which it spins, and according to the Pauli principle no two electrons in an atomic system can be in the same state of motion. In most atoms, the occupancy of each electron orbit is associated with a definite amount of energy, and any one of these orbits can be occupied by a maximum of two electrons possessing spins in opposite directions. Because of these requirements, most elements have either no or only one electron with an uncompensated spin associated with each atom. The Pauli principle holds for all elements, but, in the case of the iron series of transition metals, the five orbits in the M shell (3d) require equal energy for occupancy. In addition, it appears to be more advantageous for electrons to be present in the 3d orbits with parallel spins.

Therefore, only when all five of the orbits are occupied by single electrons with uncompensated spins do electrons of opposite spin begin to occupy the 3d positions. For this transition series, the theoretical maximum magnetic moment per atom or ion is 5 Bohr magnetons (one Bohr magneton per uncompensated spin). This occurs in Mn^{++} and Fe^{+++}, where each ion possesses five single electrons, one in each of the five 3d orbitals.

For the theoretical explanation of diamagnetic and paramagnetic effects, it must be assumed that the direction of the atomic magnetic moment associated with a particular atom is not dependent upon the direction of the moments of neighbouring atoms. However, in some crystalline solids, atomic interactions have a great deal of influence in determining the ultimate magnetic character and behaviour of these substances. Such materials are said to exhibit "ordered" magnetism.

The two initial assumptions required to describe ordered magnetism are:

1. The material is crystalline, and consequently the atoms are distributed regularly over a periodic space lattice.
2. There is a magnetic moment associated with each atom and these moments exist together as an ordered array in the space lattice.

Three important cases of ordered magnetism are:

(a) Ferromagnetism, when the atomic magnetic moments of the metal ions reinforce each other in a parallel array, e.g., iron, cobalt, nickel, and their alloys.

(b) Antiferromagnetism, when the atomic moments of the metal ions are equal and are aligned in an antiparallel array and the resultant magnetic moment is zero, e.g., ferrous oxide and nickel oxide.

(c) Ferrimagnetism, when the magnetic moments of alternate metal ions are aligned in an antiparallel manner, but where each particular type of metal ion has a definite magnetic moment associated with it and the antiparallel moments do not cancel each other out but give rise to a net magnetic moment. The ferrite materials are good examples of this class of magnetic materials.

In an unmagnetized sample of ferromagnetic or ferrimagnetic material, and at temperatures below the Curie point, small regions exist over which the atomic moments are aligned parallel to one another. These regions are known as magnetic "domains", and each is magnetically saturated and possesses a net magnetic moment. The direction of magnetization may differ from domain to domain, so that in the absence of an external magnetic field the net magnetization of a material containing many of these small regions will be equal to zero. The assumption that the atomic moments in a single magnetic domain are aligned parallel can only be true at the absolute zero of temperature. Above this point some disorder in the parallel alignment must exist as a result of thermal agitation. Therefore, as the temperature increases so does the amount of disorder, and the saturation magnetization correspondingly decreases. At a critical temperature called the Curie point the magnetization in a domain disappears, and if the temperature is raised further the substance becomes paramagnetic.

The presence of a domain structure is thought to be related to minimum energy conditions, where the size and configuration of the actual domains are such that the lowest energy possible is promoted under the existing conditions. Three types of energy have been defined in dealing with domain formation:

1. Magnetostatic energy, which is connected with magnetic flux passing through the air from one surface to another.
2. Domain wall energy, which is associated with the formation of domain boundaries.
3. Magnetoelastic energy, which is related to the strain arising from non-perfect alignment of the domains.

The equilibrium domain structure in an actual sample is governed by the requirement that the sum of all these energies be at a minimum. It has been proved that when this condition prevails the domains are present as small regions with the magnetic moments of each aligned in such directions as to produce a net magnetization of zero.

When a magnetic field is applied to a magnetic material the direction of magnetization and the size of domains are changed. This behaviour can be illustrated by consideration of the hysteresis loop, which may be obtained by subjecting the material to an alternating magnetic field. The curve is a plot of the applied magnetic field (H) against the resulting magnetic induction (B). A typical hysteresis curve is shown in Figure 1, and the important stages during the application of the first cycle of alternating magnetic field can be described as follows:

i. When the magnetic field is applied, the initial step, as the strength builds up, is usually a reversible domain boundary displacement. There is a gradual growth in the size of the domains having orientations more closely parallel to the applied field. In this region the ratio of magnetic induction to the strength of the applied field is termed the initial permeability (μ_1).

ii. As the applied magnetic field becomes stronger the magnetic induction increases at a faster rate. The domain boundaries are able to move across obstacles such as inclusions, crystal imperfections and crystal boundaries. Such movements are known as "Barkhausen jumps" and cause an irreversible change in the nature of the magnetic domains. In this region the ratio of the magnetic induction to the applied field is referred to as the maximum permeability (μ_m).

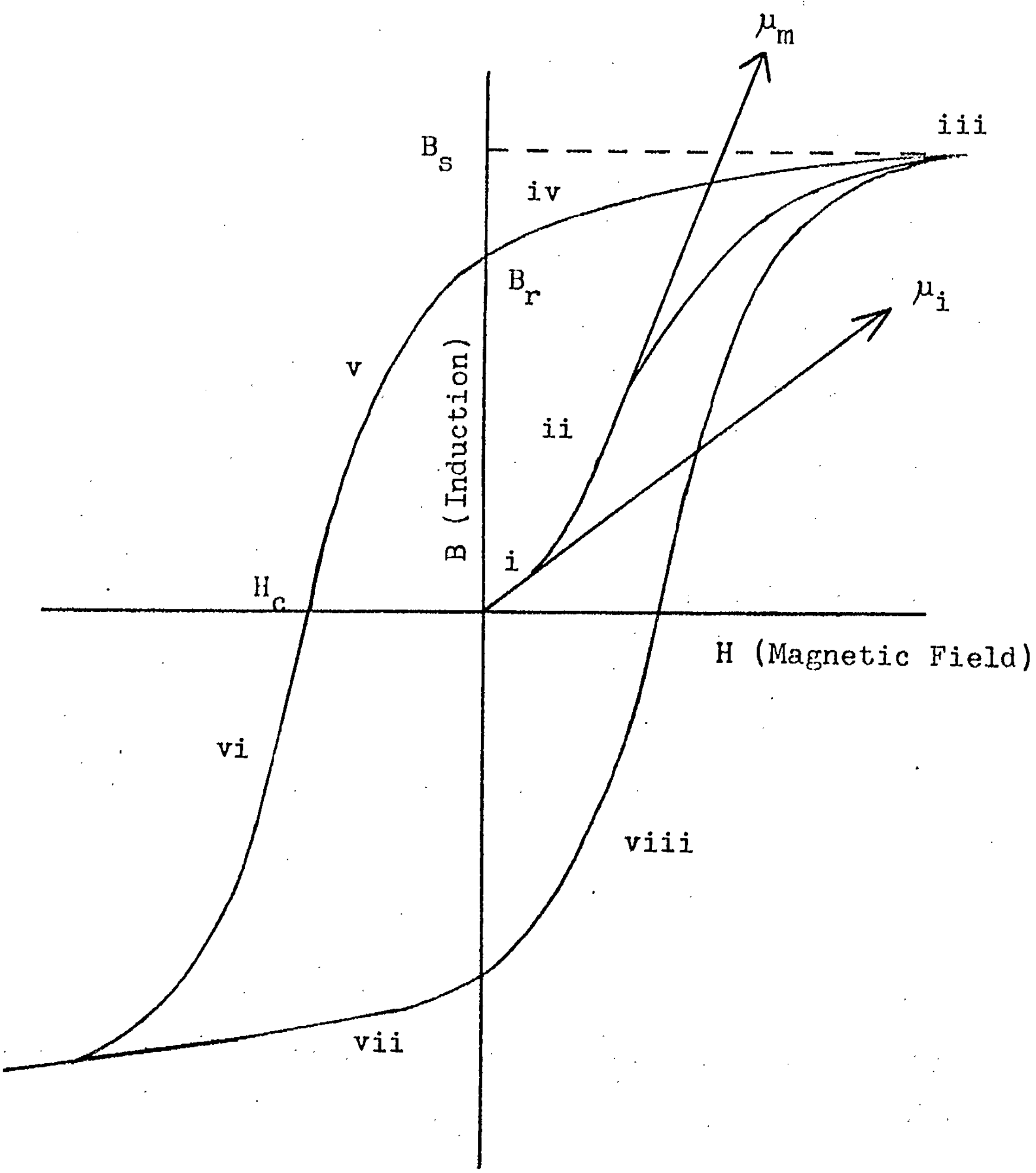

Figure 1. Hysteresis curve for ferrite material.

iii. Following stage (ii), the relative increase of magnetic induction with higher applied field decreases. Domain boundary movement becomes less, and the gradual overall parallel alignment of the resultant magnetic moments of the separate domains becomes the dominant mechanism. At extremely high fields the induced magnetization tends towards a maximum value known as the saturation magnetic induction (B_s). In cases where the magnetic material is subjected to an alternating magnetic field, the strength of which is never sufficient to induce saturation magnetization, the resultant magnetic induction at maximum applied field is termed the maximum magnetic induction (B_m).

iv. Removal of the applied field at the point of maximum induction allows the domain magnetic moments to move from an oriented position. However, because of the irreversible nature of the previous domain wall motion in the form of Barkhausen jumps, the original magnetization sequence is not simply reversed. A partial alignment of domain magnetic moments remains, leaving a residual or remanent magnetic induction (B_r) when the applied field is removed.

v. As the applied field is reversed, the magnetic induction decreases to zero. The value of the applied magnetic field required to reduce the value of the residual magnetic induction (B_r) to nil is known as the coercive force (H_c). The coercive force provides the energy required for the domain walls to perform Barkhausen jumps and traverse the strain inhomogeneities, impurities and imperfections in the crystals.

vi. The increasing reversed applied field induces a reversed maximum magnetic induction in the sample.

vii. Removal of the field leaves the specimen again in a condition of remanent magnetization but the induction is reversed.

viii. As the field increases again a coercive force is required to reduce the induction to zero, and finally the cycle is completed when maximum magnetic induction is once more attained in the forward direction.

The permeability, the remanent magnetic induction, and the coercive force are strongly dependent on the microstructure of the specimen. The values are greatly affected by the presence of impurities, voids, strains, and other imperfections. The saturation magnetic induction is related to the microstructure only in the fact that it is proportional to the amount of magnetic material per unit volume, i.e., the density or purity of the sample.

CLASSIFICATION AND USES

The most convenient system of classification is based upon the magnetic characteristics of the different types of ferrite materials. Five classes can be differentiated:

i. Soft Ferrites

These materials are useful for their initial magnetic properties in both the initial permeability and maximum permeability ranges.

The principal characteristics required are low coercive force, high initial permeability, low remanent magnetization and a high quality factor (Q). Almost all of the soft ferrites contain zinc as one of the bivalent constituents.

The two most important subgroups are manganese-zinc ferrites and nickel-zinc ferrites. The former are used in the lower range of high frequencies (1 kc to 500 kc); the latter are used up to 200 Mc. Materials with initial permeabilities of more than 6000 gauss/oersted are made commercially. Resistivities as high as 10^8 ohm-cm have been reported; this property is an important factor in the Q value. The room temperature saturation magnetic induction (about 5000 gauss) is still considerably lower than that of metals (above 15,000 gauss), limiting the use of these ferrites to high frequencies.

The majority of ferromagnetic materials used today consist of soft ferrites. The principal applications include:

Mn, Zn ferrites - Flyback transformer cores for television sets; filter coils; and components in telephone circuits and intermediate frequency transformers.

Mg, Zn ferrites, containing a small amount of copper, dense fired, high permeability - Recording heads, pulse transformers, wide band transformers, tuning slugs for width control.

Mg, Zn ferrites, porous, low permeability, lower loss, high-temperature stability - Antenna material in broadcast receivers; cup cores in intermediate frequency transformers; transistor receivers in the commercial broadcasting frequency range.

Ni, Zn ferrites - Uses in the high-frequency range.

ii. Hard Ferrites

Hard ferrites are ceramic permanent magnets.

The properties desired in these materials are: high energy product $(BH)_{max}$ on the demagnetizing cycle of the hysteresis loop, high remanent magnetic induction, high coercivity, and rectangular loop characteristics.

The first permanent magnetic ferrite material patented was cobalt ferrite. This has now been superseded by compounds widely referred to as ferrites, but which are derivatives of magneto-plumbite ($Pb0.6FE_2 0_3$). Barium or strontium are used as substitutions for lead in the hexagonal lattice.

Two types of product are available. In the isotropic material the crystals are in a state of homogeneous random dispersion; energy products of over 10^6 gauss-oersteds are attainable. To produce the anisotropic type, the hexagonal crystals are oriented in a definite plane; the hysteresis loops are extremely rectangular and energy products of over 3.5×10^6 gauss-oersteds have been attained.

Typical uses for hard ferrite materials include: mechanical holding appliances; electrical-mechanical devices (relays, magnetos, rotors, small generators, dc motor fields); electronic and polarizing uses (magnetic focussing or deflection in cathode ray tubes, high-frequency alternators, ion traps, sonar devices, transducers, loudspeakers); lightning arrestors and snuffers; and temperature-sensitive devices. Other applications include magnetostriction devices, rotation of polarization planes, focussing of electron beams.

The principal advantages claimed for this type of material include:

(a) High resistance to demagnetization (high coercive force, about 1700 oersteds); property is a significant factor when two or more magnets must be used in close proximity. The ceramic magnets can be placed safely in the direct path of an alternating field. With all other magnetic materials, care must be taken to avoid exposing them to the demagnetizing effects of air gaps greater than will be used in the final assembly. This is not the case with ceramic magnets, and maximum design freedom can be exercised where it is not practical to magnetize the ferrite shapes after assembly in the equipment in which they are to be used.

(b) High electrical resistivity of about 10^9 ohm-cm at 25°C; the ceramic magnets may be used in positions where metallic magnets would cause unwanted current flows resulting in short circuits and high energy losses. Such applications are in high-voltage and high-frequency circuits.

(c) Chemical Inertness; the materials may be used in sealed magnetic drives where magnets have to operate in corrosive atmospheres or even immersed in liquids.

(d) Linear energy variation and retrace with temperature changes, up to the Curie point; these characteristics offer interesting possibilities in temperature controls and temperature sensitive devices.

(e) Maximum flexibility in size and shape; the shapes may be machined by wet grinding after magnetization without affecting the magnetic properties.

(f) Low specific gravity of about 4.9

iii. Square Loop Ferrites

This type is so described because of the nature of the hysteresis loop, which displays high remanence points and possesses a distinct rectangular shape.

The three principal cations involved in the production of this type of material are manganese, magnesium, and iron. Nickel, copper, zinc, calcium and lead may be present in moderate quantities to modify the general properties. Some lithium-nickel ferrites also possess the property of loop rectangularity. The presence of cobalt as a cation in bodies of certain other systems induces rectangular loops; however, as opposed to the magnesium-manganese ferrites, these loops may be destroyed if the material is subjected to certain conditions.

The principal applications of the square-loop ferrites are in magnetic computer memory devices, magnetic switching devices, and magnetic amplifiers. The three most important characteristics required in these materials are:

a. Maximum squareness ratio

b. Minimum switching time

c. Low "noise" voltage

When an alternating magnetic field is applied to a square-loop ferrite toroid, certain definite values of the maximum magnetic induction and the remanent magnetism result. The squareness ratio (R_s) of any hysteresis loop is defined as the ratio of the magnetic induction at half the applied negative magnetic field ($B_{-H/2}$) to the magnetic induction at the maximum applied positive magnetic field (B_H):

$$R_s = B_{-H/2} : B_H$$

For a series of applied alternating magnetic fields of varying amplitude, the squareness ratio reaches a maximum (R_{sm}). Therefore, plotting the squareness ratio against the applied magnetic field indicates the field required to utilize the highest loop rectangularity for a particular specimen.

Switching time is the speed at which a ferrite toroid responds to an applied magnetic pulse. Speeds of better than 10^{-6} second have been achieved.

The low "noise" voltage is necessary for a low signal-to-noise ratio, which is the ratio of the voltage generated by the ferrite switch to the voltage generated by the applied magnetic pulses at the time when the former has reached a maximum.

In magnetic switching devices the primary requirements are a high remanent magnetism, a high ratio of remanent magnetism to maximum magnetic induction ($B_r : B_m$), and a low coercivity.

Magnetic amplifiers using ferrite materials have not as yet found widespread application.

iv. Microwave Ferrites

This group of materials finds use in the field of microwaves where the frequency range is from 500 to 300,000 Mc. These frequencies are normally used in radar and missile applications where the ferrite devices are used to regulate the flow of energy.

Two characteristics of prime importance in these ferrites are the Faraday rotation effect and the ferromagnetic resonance absorption.

The Faraday effect is the resulting rotation of a microwave beam when it passes through a magnetized body. The degree of rotation is dependent on the chemical and structural composition of the magnetic material, the thickness of the component, and the strength of the applied magnetic field. Microwave ferrites are the first materials to have been developed which can be used as non-reciprocal propagation devices in communications. Such components include gyrators, isolators, circulators, and phase shifters.

Ferromagnetic resonance absorption in the microwave range is associated with high magnetic losses and is, therefore, a limiting factor in the application of ferrites.

Other desirable properties of ferrites for microwave applications include: high electrical resistivity; low dielectric loss; high saturation magnetization (consistent with the application); high Curie temperature; high permittivity; and low temperature coefficients of saturation magnetization, permeability, permittivity, and resistivity.

Low to medium microwave frequency applications utilize magnesium-manganese ferrites, and nickel ferrites with various additives are useful for the higher levels.

v. Magnetostrictive Ferrites

If a magnetized ferromagnetic substance is subjected to an external magnetic field, the constituent atoms rearrange themselves slightly according to the direction of the field and there is a resultant change in the dimensions of the crystal unit cell. The application of an alternating field results in a mechanical vibration. The phenomenon is referred to as dynamic magnetostriction.

Present-day magnetostrictive transducers are almost exclusively metallic types; however, the magnetostrictive properties of the ferrites offer great promise for this type of application. Significant coupling coefficients (a measure of the efficiency with which a material converts energy from one form to another) have been reported for nickel ferrite compositions with and without various additives. Wide Curie temperature ranges are also available in certain materials, and these promise to relax substantially the service limitations currently imposed on transducers.

PREPARATION OF FERRITE RAW MATERIALS

There are several methods which have become standard practice. The aim in all these techniques is to achieve as intimate a mixing as possible of the chemical compounds, in order to produce a homogeneous ferrite material on sintering.

i. Mechanical Mixture of the Oxides

Intimate mixing and comminution can be effected by wet milling for long periods. For a high degree of homogeneity it is essential to sinter and regrind a number of times. The rate of ferrite formation will depend upon such factors as particle size of the reactants, temperature of firing, soaking period, activation energies, and crystal structures.

ii. Thermal Decomposition

Carbonates, nitrates, and in some cases sulphates, are milled together in the required proportions, heated to the maximum decomposition temperature, and milled again.

iii. Chemical Precipitation

The mixed cations are precipitated out of solution by a strong base, using the solubility products to determine the favourable pH for complete precipitation. Careful calcination of the precipitates results in a ferrite with a very small average particle size.

iv. Atomization

Dissolved cations (e.g., nitrates in alcohol) are injected into an atomizer and ignited. The result is a ferrite product made up of extremely fine particles.

COMMERCIAL PRODUCTION OF FERRITES

There are two commercial methods in current use for the preparation of ferrite products, and the two techniques differ only in the initial step of preparing the mixed compounds prior to the preliminary calcination. In the "Dry" process, the raw materials are blended together in the dry state; in the "Wet" process, the components are mixed wet, and the resultant slurry is filtered, dried, and pulverized.

After the components are mixed, both techniques employ a preliminary low-temperature calcination at 500 to 600°C. The product, which is composed of the partially reacted oxides, is divided into two parts. One part is wet-ball-milled and dried, the other portion is subjected to further calcination at 1000°C, then wet-ball-milled. The two portions are reunited in predetermined correct proportions, mixed thoroughly with binders and lubricants, pressed into the desired shape, and sintered.

For metals that have various valency states--e.g. Fe, Mn, Cu, Co--a correct partial pressure of oxygen must be maintained during the complete firing cycle, in order to preserve the stoichiometry of the compound.

Of the two techniques the wet method gives the finer-grained and more uniform product, but the dry method is the more economical.

CERAMIC RESEARCH ASPECTS OF FERRITES

In the study of ferrites there are several connected fields in which research may be carried out.

The strictly fundamental approach is that of the theoretical physicist who deals with the phenomenon of magnetism itself. He seeks an explanation of observed facts in terms of modern electromagnetic theory and the atomic structure. Information for such considerations must come mainly from results of the study of single crystals of pure materials.

In cases where suitable single crystals are difficult to obtain, a study of the polycrystalline state can be very profitable, for conclusions may be drawn, by direct analysis, as to the probable fundamental properties of the materials. The ceramist is most active in this latter field.

The ferrites used in commercial applications are for the most part polycrystalline aggregates which have been formed and sintered according to strictly ceramic techniques. The products suffer from all the disadvantages and variations in properties that are prevalent in the more conventional ceramic bodies. However, in the case of magnetic and electrical ceramics, such wide variations of properties as are allowed in conventional ceramics cannot be tolerated. To obtain maximum reproducibility, extreme care must be exercised in the standardization of such factors as: quality of raw materials; initial particle size; grinding; mixing; addition of binders, lubricants and plasticizers; processing; drying; and sintering.

There are several general fields of investigation open to the ceramist, amongst which are:

i. A detailed examination of compounds, and tabulation of the properties for future reference.

ii. A study of the effect of added atoms to materials of known properties.

The examination of the magnetic and electrical properties of single ferrites and mixtures of ferrites in known proportions is by no means complete. Two important discoveries in this field were (a) the so-called "zinc effect" and (b) certain ferrite materials exhibiting a square hysteresis loop. The "zinc effect" is obtained by using zinc as one of the bivalent atoms in a ferrite lattice to induce low coercive force, high initial permeability, and a low Q factor. The existence of square hysteresis loop characteristics was first observed in the system $MgO-MnO-Fe_2O_3$, and these materials are still the principal constituents of many ferrites manufactured for use in memory devices.

iii. An examination of the effect of the purity of the materials.

Inclusions, which may be taken to include air bubbles, greatly affect the magnetic behaviour of a ferrite by altering the energy requirements of the domain structure and domain wall movement. The presence of impurities, therefore, can have a large effect on the characteristics of the hysteresis loop, as the relative positions of the reversible and irreversible domain boundary displacements are changed.

Under certain conditions, where there exists atomic substitution or an oxygen deficiency in the ferrite lattice, the electrical resistance may be lowered considerably. This results in larger power losses when the ferrites are used in high-frequency fields.

iv. An examination of the microstructure of ferrite materials, and correlation of the results with the magnetic and electrical behaviour.

A high coercivity is necessary for permanent magnetic materials, and this is obtained when the energy required to alter the domain structure is high. Such is the case in single domain structures in which domain rotation is the principal factor. For multi-domain structures the force required for change is lower because less energy is required to activate domain wall movement than domain rotation. Therefore, the highest coercivity in a polycrystalline magnetic material is obtained when the size of each crystallite corresponds to the size of a single domain and the structure is relatively loosely packed.

Ceramic fabrication techniques have a bearing on all the fields of investigation mentioned. Some of the principal considerations are:

i. The initial treatment of the raw materials.

The different methods of obtaining the raw materials give rise to products differing in particle size and shape, in amount of reaction, and in degree of mixing. In many cases these products must be ball-milled several times and impurities are thus introduced.

ii. Fabrication of the ferrite bodies.

As in all ceramics, the types of binders and lubricants, and the forming pressures used, affect the final state of the material. In some cases a certain amount of crystal orientation may take place, or be caused to take place, prior to or during the pressing action. Anisotropic magnetic properties are the result of such orientation, and the technique is used commercially in the preparation of ceramic permanent magnets.

iii. The firing cycle.

The rate of heating, the soaking temperature and time, and the rate of cooling control the ultimate crystal size, the density of the product, and the degree of reaction which takes place between the initial constituents.

If the material is underfired a porous structure results. To a certain extent, the voids in the body obstruct magnetic domain wall movements, so that domain rotation becomes the predominant factor during magnetization. A porous product is desirable in the case of manganese-zinc ferrites when it is necessary to have low loss characteristics, low permeability, and good magnetic stability at high temperatures.

With more dense materials, there is a decrease in the number of voids and imperfections and an increase in the amount of material per unit volume. The former permits easier movement of domain walls through the crystallites and results in an increase in the initial permeability and a decrease in the coercive force; the latter results in an increase in the maximum magnetic induction.

iv. Furnace atmosphere

This is especially important where the constituent atoms are able to exist in different valency states. Reducing or vacuum conditions may cause an oxygen deficiency in the lattice, which may in turn greatly increase the electrical conductivity. On the other hand, manganese ferrite is easily over-oxidized and must be fired in a neutral atmosphere.

APPARATUS AND PRELIMINARY INVESTIGATIONS

Certain apparatus available in the Ceramic Section was adaptable to the ferrite program:

(i) A Mettler Gram-atic scale for reasonably accurate batch weighing of the compounds. Maximum, 4000 g ± 0.01 g.

(ii) Small micropulverizer.

(iii) Steel ball mills and steel grinding balls.

(iv) 30-ton hydraulic press.

(v) Steel dies for the production of disk specimens.

(vi) Drying ovens.

(vii) Gas-fired and electric furnaces of several types and sizes.

Additional apparatus designed and built specifically for the ferrite program includes:

(i) A cyclone Atomizer for fine-particle ferrite powder preparation.

(ii) Equipment for the adaptation of the Remmey natural-gas-fired furnace to atmosphere control in the firing chamber.

(iii) Steel die for dry-pressing toroid shapes.

(iv) Propane-gas-fired tube furnace with atmosphere control.

(v) 40% rhodium-60% platinum wire wound tube furnace for high-temperature investigations, including Differential Thermal Analysis (DTA).

Preliminary experiments were carried out by I. F. Wright of the Ceramic Section. Attempts were made to produce a pure, fine-particle-sized, nickel ferrite powder by means of atomization of an alcoholic solution of nickel and ferric nitrates (4). The apparatus is shown in Figure 2. Nickel and ferric nitrates were dissolved in ethyl alcohol in the proportions required to give equimolar fractions of nickel oxide and ferric oxide. The solution was forced through an atomizer and burned in the tube A. The products of combustion and the resultant ferrite powder were separated by cyclone action in the cone-shaped tube B.

Specimens prepared with this equipment proved to be of fine particle size, and X-ray examination revealed only the presence of nickel ferrite. However, the process was slow, difficult to control, and required large quantities of alcohol for a low yield. Disks dry-pressed from this material were difficult to sinter, and over a range of firing temperatures and soaking periods the maximum density attained was only 90 per cent of the theoretical value.

Further experiments carried out by the author involved the rapid thermal dissociation of mixtures of the nitrates. The melting points of nickel and ferric nitrates are 35°C and 56.7°C respectively. The two compounds were melted together in a beaker and the liquid was forced through a small atomizer, from which it emerged in the form of a fine spray. The spray was directed into a steel container heated in a small gas furnace to above 600°C; in this container the nitrates rapidly decomposed. In the first

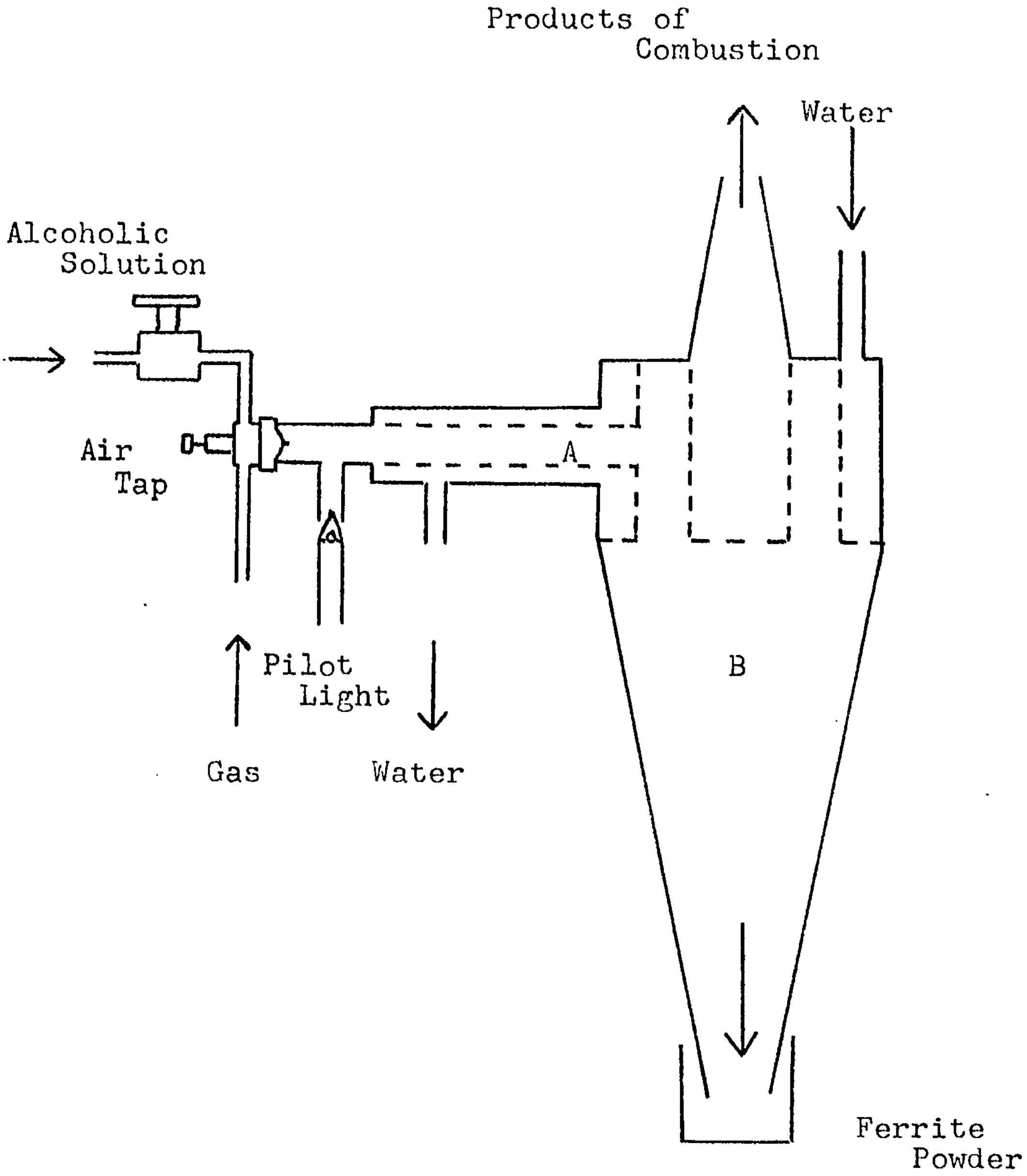

Figure 2. Cyclone atomizer for ferrite powder production.

experiments the nitrates were mixed together in the theoretical proportions to yield equal weights of nickel and iron oxides. A chemical analysis of the combustion product revealed 46.9 per cent by weight nickel oxide, 47.8 per cent ferric oxide, and 4.61 per cent loss on ignition. The partially reacted oxides were ground to pass through a 100-mesh sieve and then dry pressed at 5 tons pressure into disks 1.130 in. in diameter and approximately 0.2 in. in height. Ten per cent by weight of a 10 per cent solution of polyvinyl alcohol (PVA) was used as binder and lubricant. The specimens were fired at various temperatures for various soaking periods, and density and shrinkage measurements were taken.

The tests were carried out in different furnaces according to the facilities available. The conditions in each unit were not the same, and in a small Hevi-Duty globar kiln a temperature difference of 50°C over a distance of 1 1/2 in. was observed. Another variable was the amount of reaction undergone by the nitrate mixture during the thermal dissociation treatment. Strict control of the temperature during the decomposition was impossible and each sample of material produced differed in the percentage of unreacted oxides and nickel ferrite. These variables were sufficient to account for incongruities observed in the results from density and shrinkage measurements.

It was decided that a furnace was required which would have a firing chamber with uniform temperature conditions and which could be reserved solely for firing ferrite specimens. Consequently, experiments were carried out to adapt a large Remmey gas-fired furnace. Figure 3 shows the final result. This simple arrangement could be used for firing samples either in a vacuum or in a specified atmosphere. Disks fired under vacuum conditions required lower sintering temperatures than did those fired in air, and the specimens had higher densities. However, the dc resistances of the samples were very low (about 100 ohm-cm), which indicated that some reduction of the oxides had occurred.

Heavy laboratory demand for the use of the Remmey furnace interfered drastically with the ferrite program. For this reason a propane-gas-fired tube furnace with atmosphere control was designed and built. The unit is described in Appendix I.

In order to minimize the variations in material compositions, oxides and carbonates were adopted as the initial compounds for the preparation of the ferrite specimens.

A steel die for the fabrication of toroid shapes was designed and made.

PVA addition to the raw materials provided good dry strength and sufficient lubrication for good pressing characteristics using a total pressure of 5 tons. Experiments showed that 10 per cent by weight of a 5 per cent PVA solution was required if formation of pressure cracks was to be avoided.

The use of oxides as the raw materials necessitated the adoption of a controlled firing cycle during sintering, to prevent the specimens from breaking due to thermal shock.

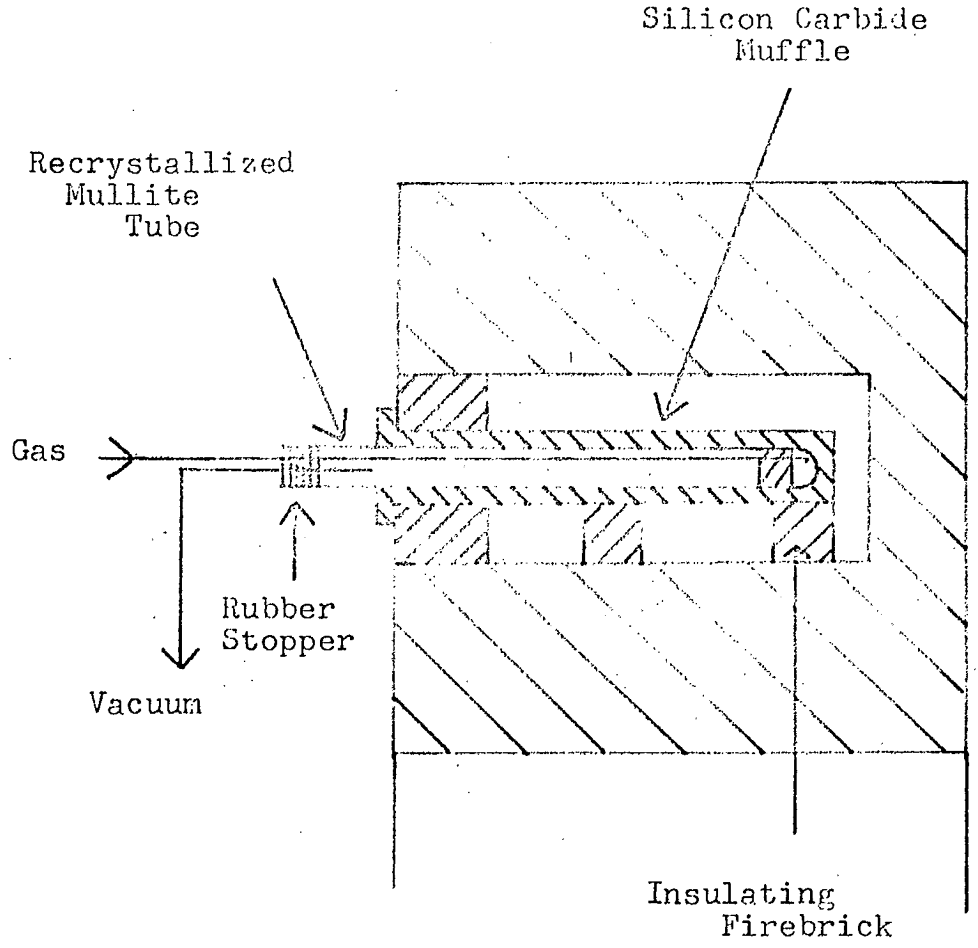

Figure 3. Adaptation of Remmey gas furnace.

FABRICATION AND PHYSICAL TESTING OF FERRITE TOROIDS

Technique

The oxides and carbonates were carefully weighed in the proportions required, and placed in a steel ball mill with steel balls and a sufficient amount of distilled water to give a thick slurry. The mixture was milled for 18 hr, vacuum filtered, dried at 105°C, and micropulverized to a minus-100-mesh powder. The material was mixed thoroughly with 10 per cent by weight of a 5 per cent solution of PVA, and again micropulverized. Samples weighing 35 g were dry-pressed in the toroid die at a pressure of 5 tons and then allowed to air-dry overnight at room temperature.

The toroids were fired in the propane-gas-fired tube furnace to the required temperature. To prevent the toroids from breaking due to thermal shock, the heating rate had to be limited to 900°C in the first hour and 100°C per hour thereafter to top temperature. The cooling rate had to be limited to the natural cooling rate of the furnace. A typical firing cycle is illustrated in Figure 4.

Apparent density and linear shrinkage measurements were made on all samples.

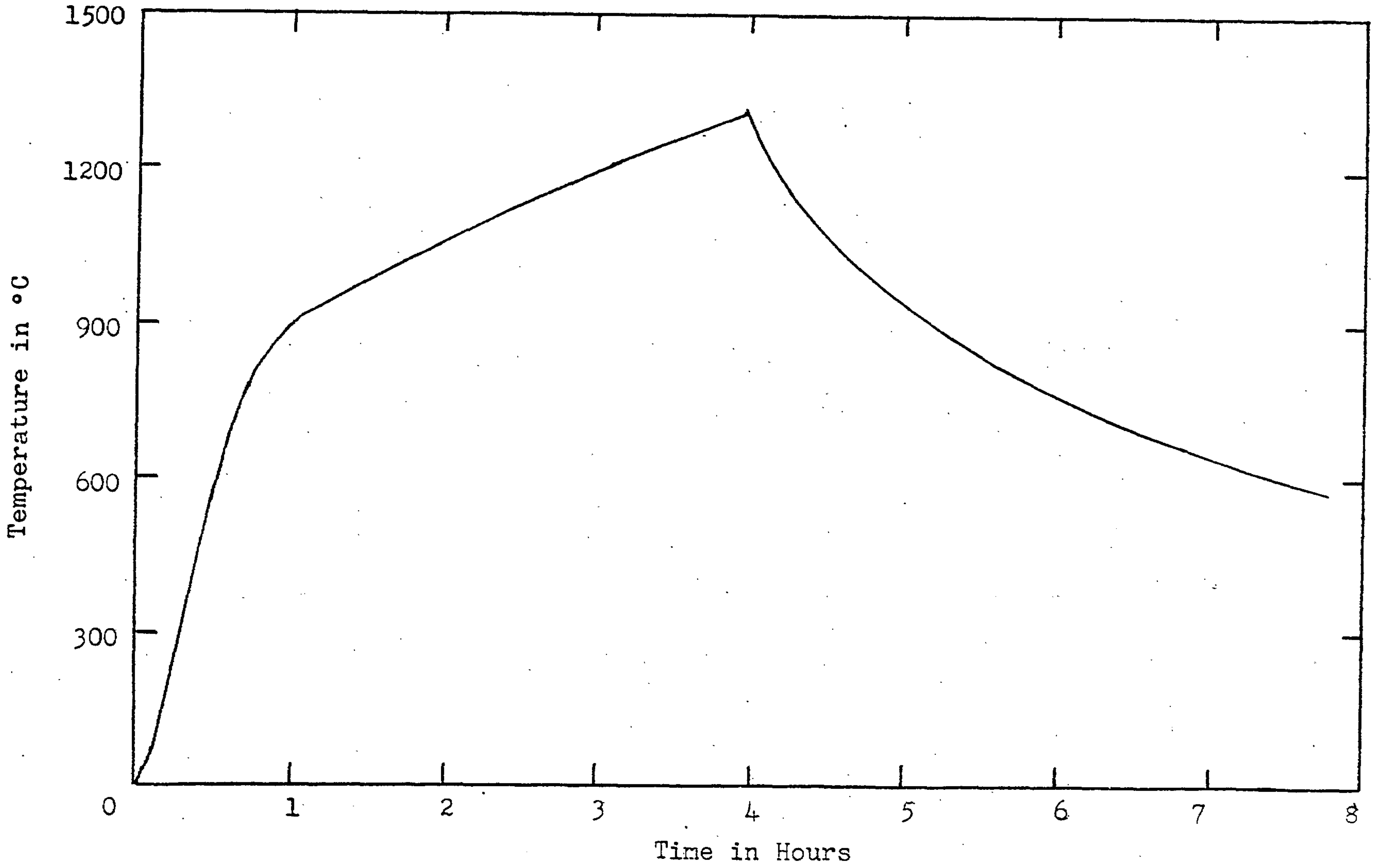

Figure 4. Typical firing cycle used in sintering ferrite toroids.

Nickel Oxide-Ferric Oxide Series

A series of five nickelous oxide (Baker Analyzed Reagent) - ferric oxide (Fisher Certified Reagent) mixtures was made up in the proportions reported in Table 1.

TABLE 1

Nickel Oxide-Ferric Oxide Series

Series	Moles %		Empirical Formula
	NiO	Fe_2O_3	
A	60	40	1.2 NiO, 0.8 Fe_2O_3
B	55	45	1.1 NiO, 0.9 Fe_2O_3
C	50	50	1.0 NiO, 1.0 Fe_2O_3
D	45	55	0.9 NiO, 1.1 Fe_2O_3
E	40	60	0.8 NiO, 1.2 Fe_2O_3

Toroids were fabricated following the procedures previously described.

The firing characteristics of series C were subjected to the most detailed examination. Seven specimens were fired each time at various temperatures and for soaking periods of 0 hr and 3 hr. Shrinkage and density measurements were made, and the results are given in Table 2.

TABLE 2

Firing Characteristics of Series C

Firing Temperature, °C	Soaking Period, hr	Average of Seven Specimens	
		% Shrinkage	Density *
1270	0	16.55	Porous
1300	0	17.30	Porous
1310	0	17.75	Porous
1335	0	17.90	4.84
1350	0	18.50	4.86
1370	0	18.35	4.83
1400	0	18.10	4.80
1200	3	16.25	4.78
1238	3	-	5.08
1250	3	18.90	4.90
1275	3	18.70	4.84
1300	3	18.00	4.83
1350	3	17.50	4.75

*The theoretical density of nickel ferrite is 5.34.

The highest average density recorded was 5.08 for the specimens fired at 1238°C with a soaking period of 3 hr. This figure represents over 95 per cent theoretical density.

The procedure was repeated for the A series, but using only three specimens for each firing. In the B, D and E series, three specimens were fired at various temperatures for soaking periods of 0 hr only. The results for optimum density conditions are illustrated in Figure 5 and Figure 6. The tests on the A and C series indicated that, by sintering the samples at temperatures 100°C lower for a soaking period of 3 hr, densities equivalent or

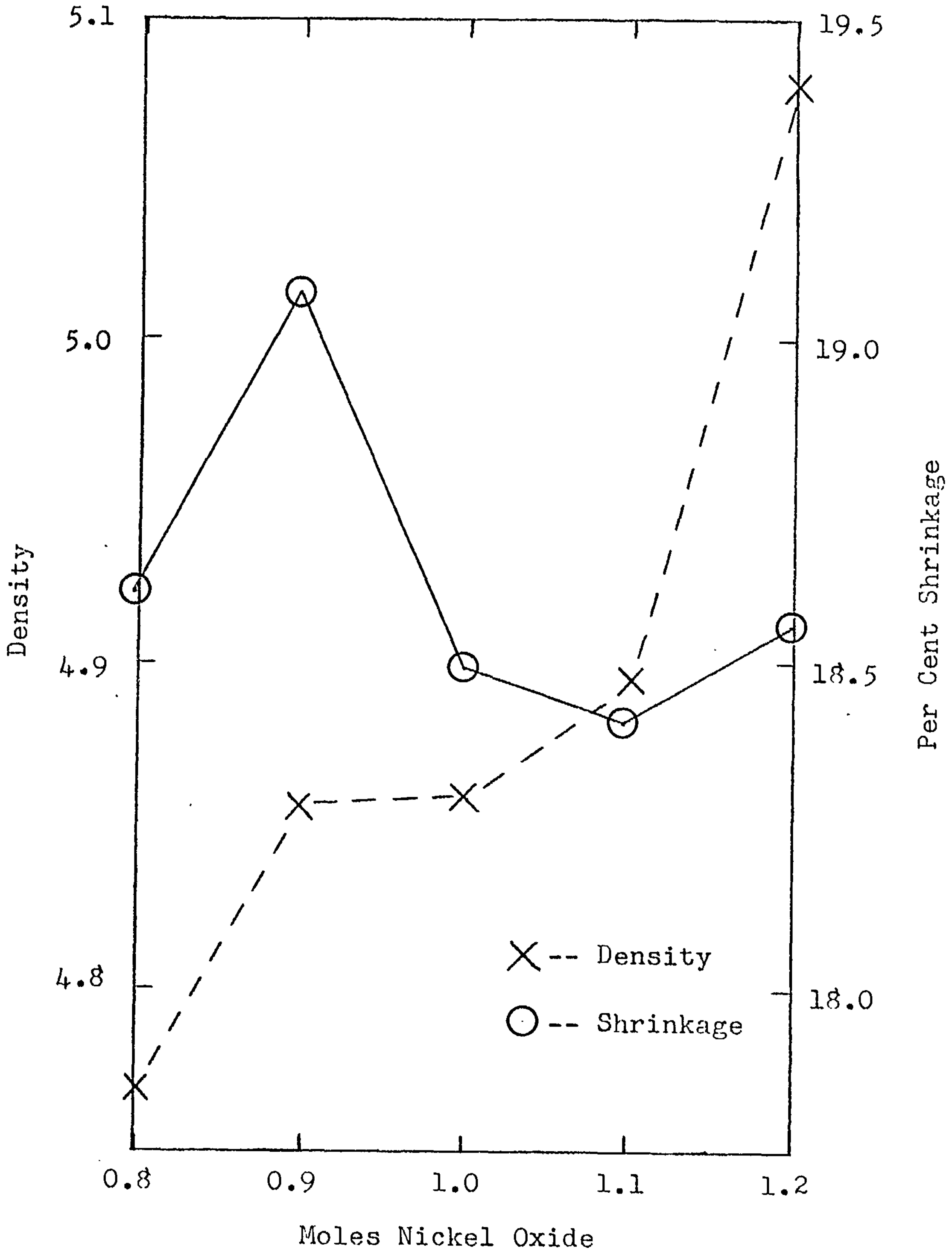

Figure 5. Optimum average density and shrinkage measurements for the nickel oxide-ferric oxide series.

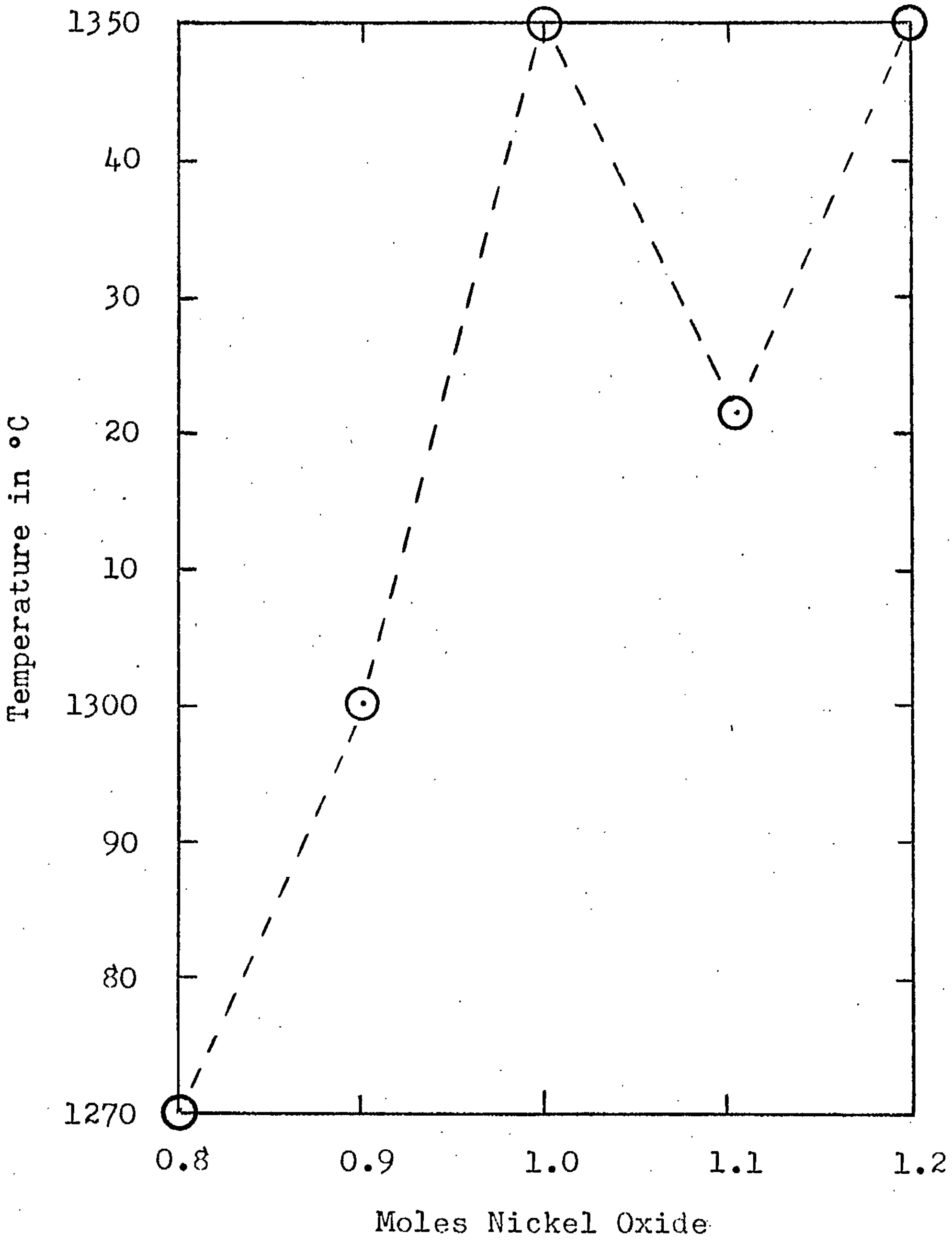

Figure 6. Sintering temperatures for the nickel oxide-ferric oxide series for optimum densities.

superior to those obtained with no soaking period could be achieved.

The sintered nickel-ferrite toroids proved to be machinable, and several specimens were ground to specified dimensions and automatically wire-wound for the purpose of assessing the magnetic properties.

Nickel Oxide-Ferric Oxide-Cobalt Oxide Series

Toroids of this series were fabricated following the procedure established earlier. However, in the material preparation, the vacuum filtering operation was omitted because some loss of the fine constituents had been observed at this stage.

Five mixtures were made. The molar ratios of the constituent oxides are given in Table 3.

TABLE 3

Nickel Oxide-Ferric Oxide-Cobalt Oxide Series

Sample No.	Molar Ratios		
	NiO	Fe_2O_3	CoO
C - 0	1	1	-
C - 0 - 1	1	1	0.031
C - 0 - 2	1	1	0.062
C - 0 - 3	1	1	0.156
C - 0 - 4	1	1	0.324

Toroids of the five mixtures were fired to various temperatures with no soaking period. The results of density measurements (average of two) are given in Table 4.

TABLE 4

Densities of the Toroid Specimens Prepared from the Nickel Oxide-Ferric Oxide-Cobalt Oxide Series Sintered at Various Temperatures with No Soaking Period

Temperature, °C	Density of Samples				
	C-0	C-0-1	C-0-2	C-0-3	C-0-4
1340	4.82	4.84	-	-	-
1350	4.87	4.79	4.86	4.88	4.99
1360	4.71	4.88	4.90	4.95	5.02
1370	-	4.85	4.87	4.88	4.92
1380	-	4.81	4.81	4.86	4.86

REFERENCES

1. J. Smit and H.P.J. Wijn. Ferrites. John Wiley and Sons, Inc., New York, 1959.

2. Harold W. Katz. Solid State Magnetic and Dielectric Devices. John Wiley and Sons, Inc., New York, 1959.

3. S.L. Blum, Herbert Zlotnick and J.E. Zneimer (compilers). "Bibliography on Ferromagnetics and Ferroelectrics." Ceram. Ind. 67 (1) 90-92; (2) 100-101; (3) 116-118; (4) 128, 130; (5) 114-115; (6) 100, 102-103 (1956); 68 (1), 172, 174, 176, 178, 180, 182, 184-187, 190 (1957).

4. George Economos. Magnetic Ceramics: 1, General Methods of Magnetic Ferrite Preparation. Jour. Amer. Ceram. Soc. 38, 243 (1955).

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APPENDIX

CONSTRUCTION AND DEVELOPMENT OF AN ATMOSPHERE-CONTROLLED, PROPANE-GAS-FIRED FURNACE FOR SINTERING SPECIAL CERAMICS

Introduction

Many special ceramics are unstable in oxidizing atmospheres at their sintering temperatures. Such ceramics must consequently be fired under controlled-atmosphere or vacuum conditions. Metal-ceramic combinations, silicides, nitrides, carbides, borides, and most types of ferrites are examples of such unstable compositions. In many cases a particular atmosphere is required during the firing operation as a necessary reactant for the formation of a particular compound in the specimens being fired.

The selection of a propane-gas-fired unit was based on several factors. In this case the most important were: economy; control and flexibility of heating and cooling cycles as compared with a furnace using electrical power; the absence of complications arising from a defective combustion tube; and the availability of a propane gas supply.

General Considerations

It was decided to use:

(a) Propane gas firing.

(b) Low-pressure air-gas proportional mixing.

(c) Tube-type furnace with muffle.

A convenient size for a cylindrical combustion chamber was fixed at 15 in. in length and 12 in. in diameter, giving a volume of about 1700 cu in.

In pressure firing, the volume requirement for the best heating conditions is 17 cu in. per 1000 Btu per hour burned; therefore, a chamber of 1700 cu in. would require 100,000 Btu per hour. Propane gas has a heat capacity of 2500 Btu per cu ft and to provide 100,000 Btu per hour, 40 cu ft per hour of propane would be needed.

The Eclipse Vari-set Proportional Mixer, type V.S.G.B. No. 444, has a gas capacity of 40 cu ft per hour when used with an air blower pressure of 2.5 to 8 oz and a gas that has a heat capacity of 2500 Btu per cu ft (e.g. propane).

In order to allow for the insertion of a silicon carbide muffle tube (4 3/4 in. dia) along the major axis of the combustion chamber, a correction to the dimensions had to be made. The volume occupied by the muffle was $15 \times \pi \times (2\ 3/8)^2$ cu in., approx 266 cu in. This volume was not available for combustion, and therefore the dimensions of the chamber were increased to 15 in. long and 13 in. in diameter.

The furnace was designed to operate with eight burners in order to achieve uniformity of heating in the firing chamber. The total burner area required by the V.S.G.B. No. 444 mixer was marked at 0.15 sq in. minimum to 0.38 sq in. maximum. However, as burner nozzles with plain ends were used having an approximate discharge coefficient of 0.75, the area range was corrected to 0.20 to 0.51 sq in. For eight burners, therefore, the required single burner area was 0.025 to 0.064 sq in., i.e., an inside diameter range of approximately 1/10 in. to 9/32 in.

The recommended flue area for a flue temperature of 2400°F and 100,000 Btu burned per hr is 7 sq in., i.e., approximately 2 1/2 in. in diameter.

Description of Furnace

Diagrammatical sketches of the furnace are shown in Figures 7, 8 and 9, and the essential features are described below:

1. Impervious mullite tube (Morgan Refractories, England) 3 in. OD, 2 1/2 in. ID. Two tubes are available, one 36 in. long and open at both ends, the other 30 in. long and closed at one end. In the latter case, an insulating plug is used to compensate for the shorter length and so prevent excessive heat loss from the furnace.

2. Muffle tube of silicon carbide (Norton 'Crystolon') 4 3/4 in. OD, 4 in. ID, 18 in. long.

3. Combustion chamber walls cast from Alundum 33 I insulating castable (Norton).

4. J.M. 3000 insulating firebricks.

5. J.M. 2-in. Superex insulation block.

6. Transite sheet 30 1/2 x 30 1/2 x 5/16 in.

7. Iron framework 31 x 31 x 31 in. on a 29-in. stand.

8. Burner nozzles, recrystallized alumina tubes (Morgan) 1/4 in. ID, 10 in. long.

9. Flue opening, 2 1/2 in. dia.

10. Passage for Pt - 10% Rh/Pt thermocouple.

The auxiliary equipment is illustrated in Figure 10.

Operation of Furnace

The volume of gas available for the mixer is controlled by Regulating Valve 1. The manometer gives a measure of the gas pressure when the mixer is in use. Valve 2 is present as a safety precaution to control the sudden change in gas flow when the air blower is switched on.

Two thermocouples connected to a multiple recorder are used to aid in controlling the temperature. One is placed in the horizontal mullite tube and held in place by insulating firebrick shapes and a rubber stopper. The arrangement is illustrated in Figure 11. The thermocouple junction is positioned as near as possible to the specimens being fired, and the temperature recorded is taken as the firing temperature. The other thermocouple is led through the top of the furnace, and the junction is situated in the combustion chamber. Manipulation of Regulating Valve 1 governs the volume of gas flowing to the Vari-set Mixer and, therefore, controls the amount of available heat and thus the temperature in the combustion chamber. Any changes in gas-flow result in an immediate change in temperature in the combustion chamber, whereas the

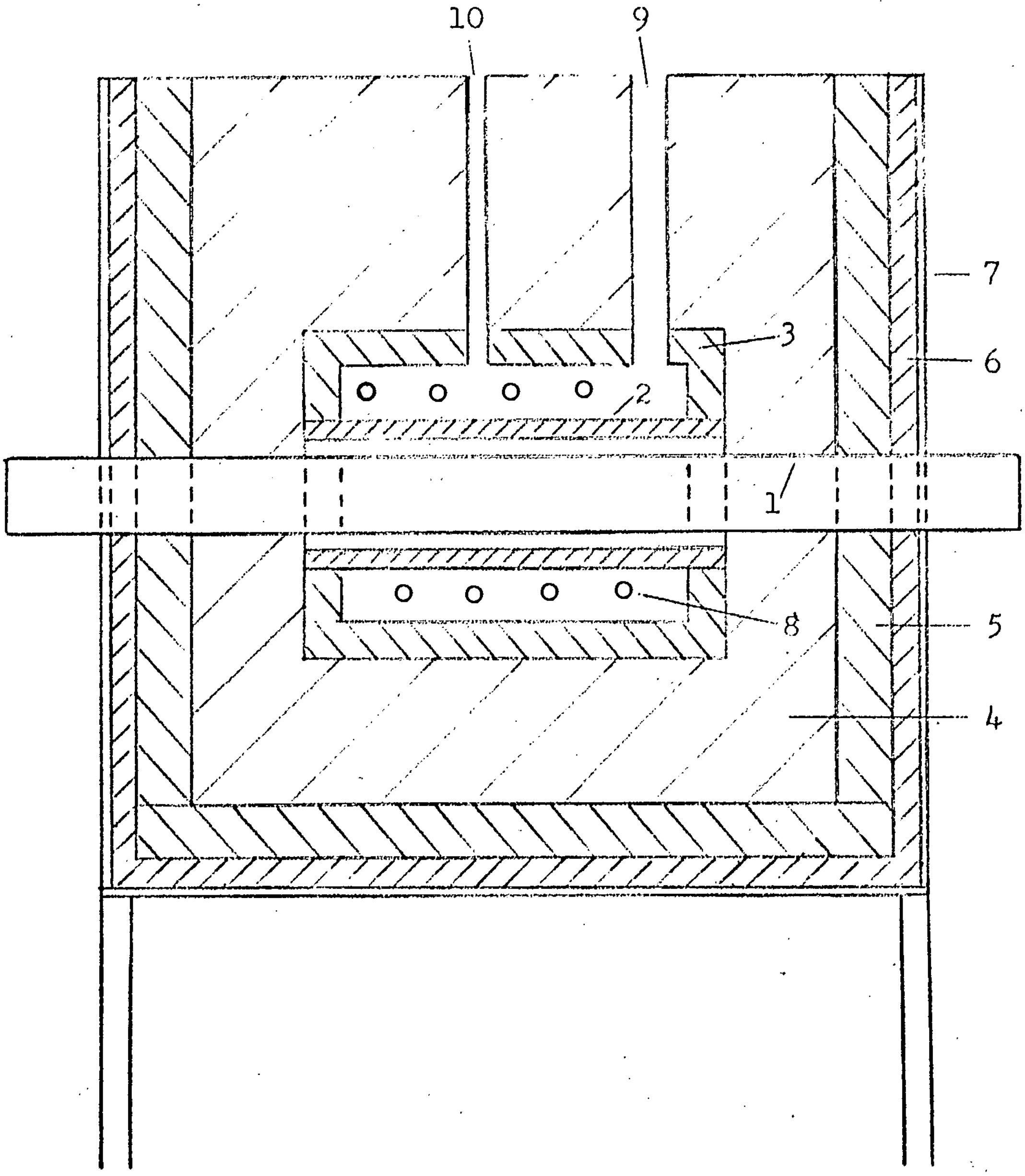

Figure 7. Side view of furnace.

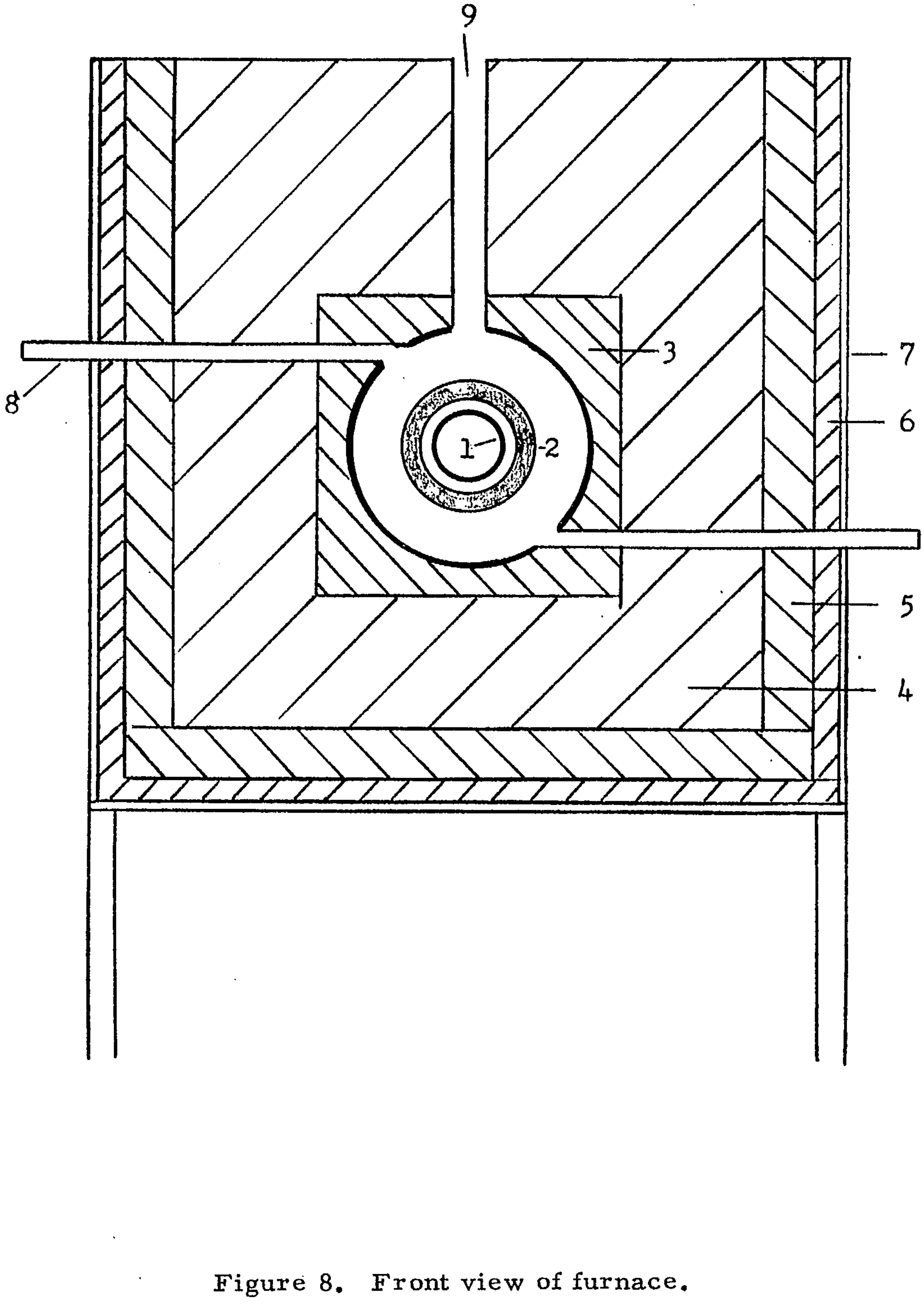

Figure 8. Front view of furnace.

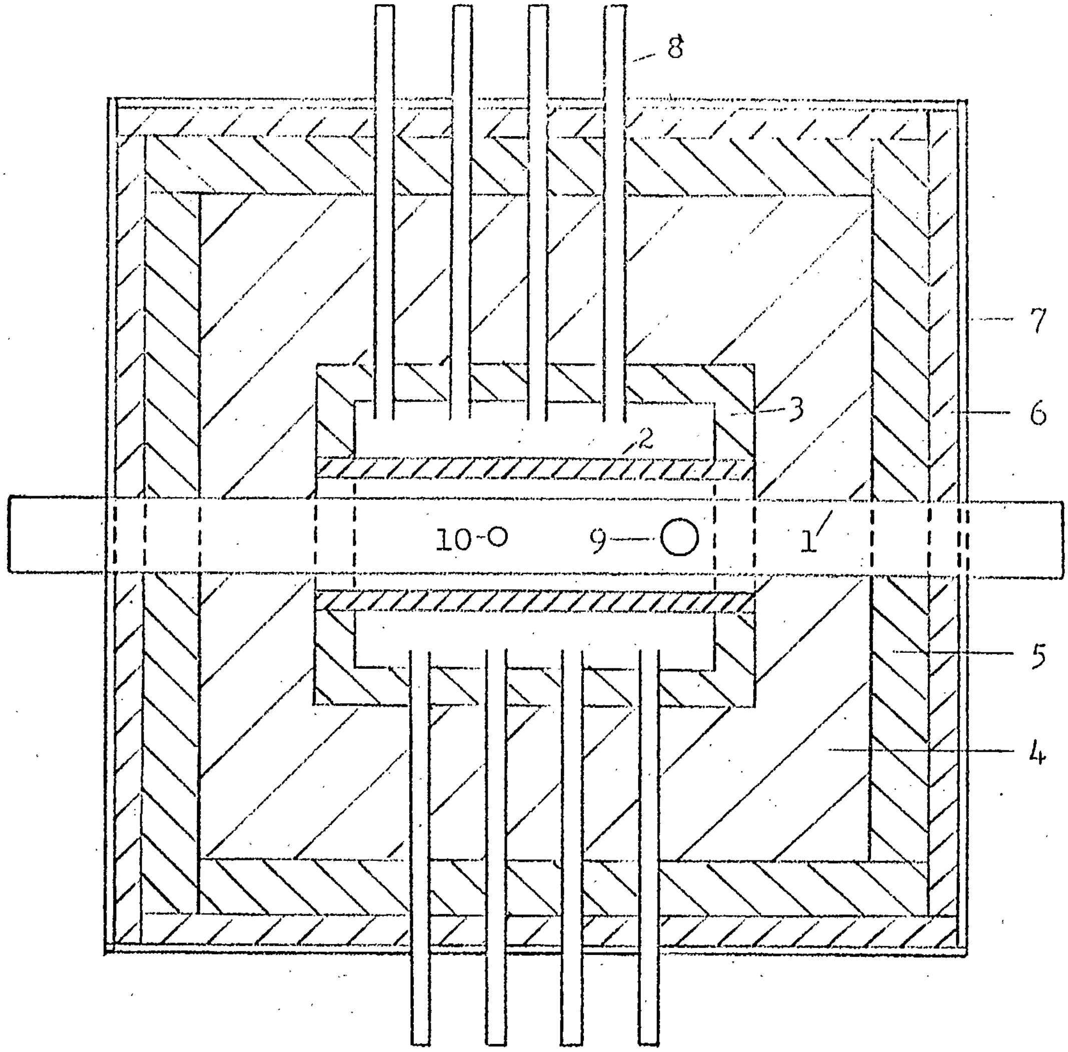

Figure 9. Top view of furnace.

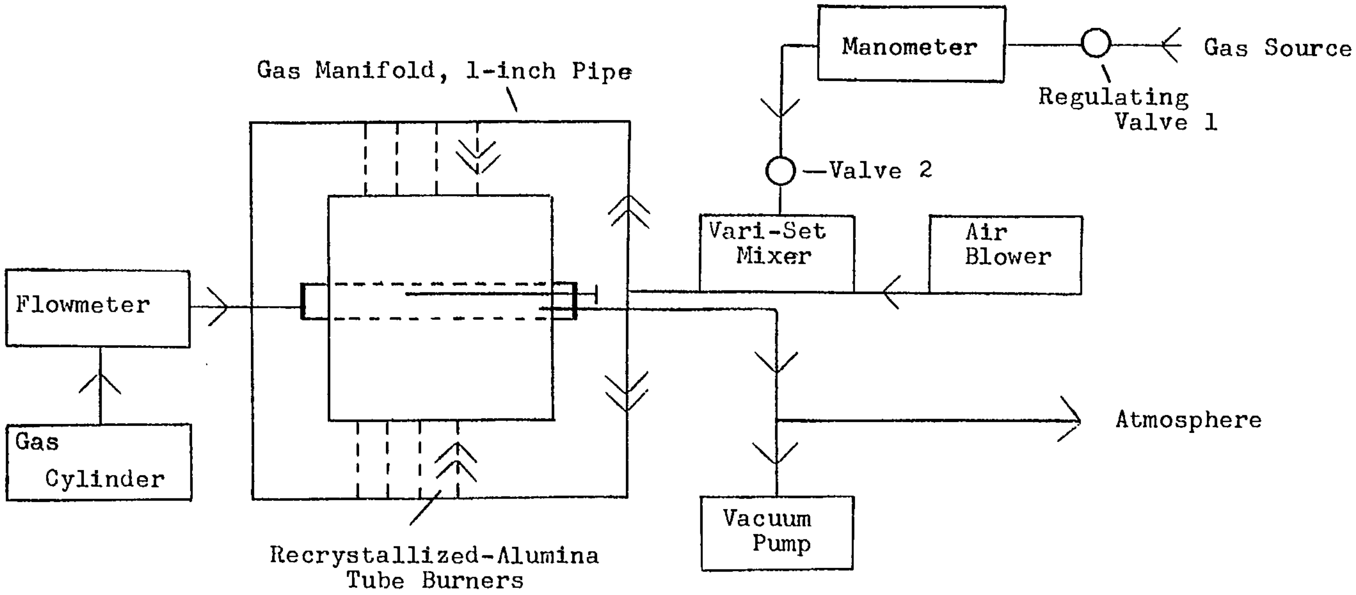

Figure 10. Schematic diagram of auxiliary furnace equipment.

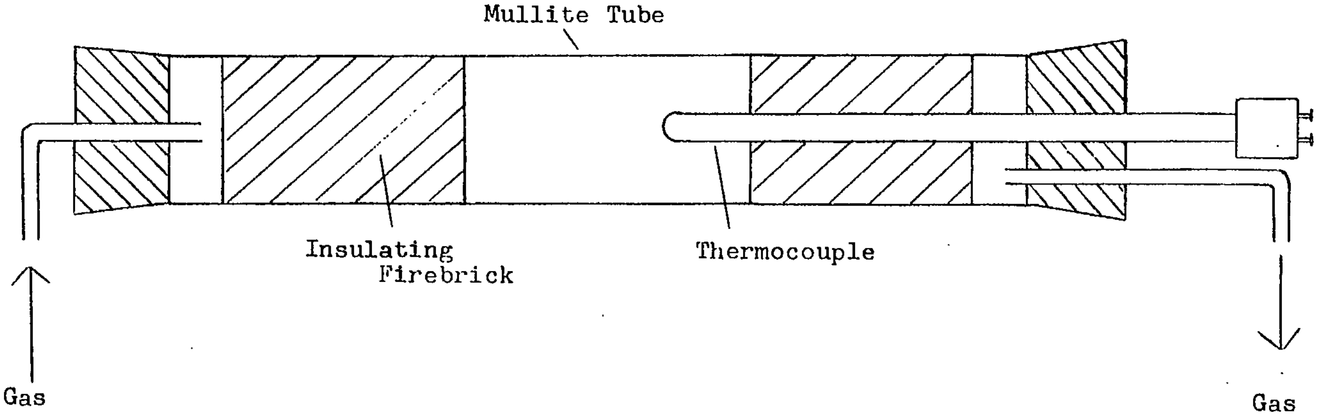

Figure 11. Thermocouple arrangement in specimen firing chamber.

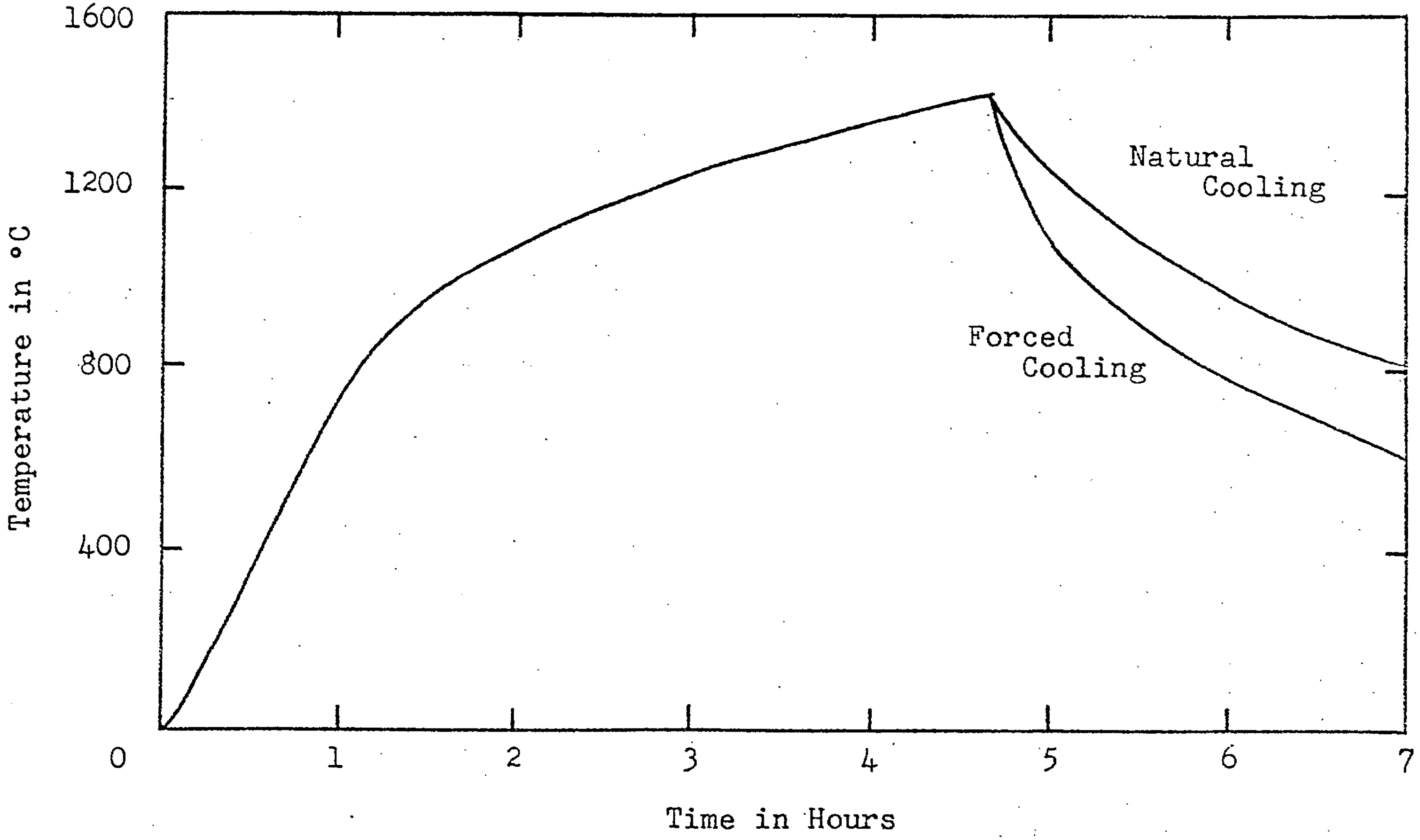

Figure 12. Typical heating and cooling curves for the propane-gas-fired tube furnace.

temperature in the well-muffled mullite tube is affected much more slowly. Therefore, Regulating Valve 1 provides a sensitive means of controlling the temperature of the specimens being fired.

Furnace Characteristics

Typical heating and cooling curves are shown in Figure 12. Fast cooling is achieved by leaving the air blower in action during the cooling cycle. Soaking temperatures can be controlled to within 2°C in a range from 700°C to 1500°C. During special atmosphere tests, the outlet end of the mullite tube must be cooled to prevent the destruction of the rubber stopper. For atmospheric or vacuum firing no precautions are necessary.

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