A LOW DRIVE MATERIAL FOR MONOLITHIC FERRITE MEMORIES

by

C. Wentworth and A. Robbi

RCA Laboratories
Princeton, New Jersey

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I. INTRODUCTION

A monolithic ferrite memory[1,2] consists of an assembly of ferrite sheets containing a matrix of embedded conductors. A memory stack consists of interconnected planes, each with 256 parallel embedded conductors in the short dimension and 100 parallel embedded conductors in the long direction. One such plane mounted in an epoxy frame with interconnecting fingers is shown in Figure 1. The parallel conductors are on 0.010 inch centers. The two sets of conductors are insulated electrically from one another by a thin layer of ferrite, (approximately 0.0005 inches thick) as shown in the sectioned view of Figure 2. Each crossover point is capable of storing a bit of binary information. The memory is organized as a linear select memory. A unique combination of closely packed micro-dimensional storage elements with closed magnetic flux paths fabricated by batch processing is realized by monolithic ferrites. This can be exploited for high-speed low-cost memory systems[1,2] or for low-power low-cost mass memories[3] driven by totally integrated electronics. The materials work described herein is aimed at the latter application.

The specific material properties necessary to make a low-drive monolithic ferrite feasible are low coercive force to permit low drive currents, fine grain size because the storage elements are of micro-dimensions, high electrical resistivity to provide insulation between embedded conductors, and fast switching speed to ensure sufficiently high output signal amplitude. In addition, a degree of temperature stability, depending on the application, is also required. To obtain low coercive force, fine grain size ferrites of the magnesium-manganese-zinc variety have been chosen. As seen below, sufficient resistivity and switching speed are obtainable. The major conflict in properties is to obtain low coercive force, fine grains, and temperature stability.

II. MONOLITHIC FERRITE MEMORY FABRICATION

There are six steps in the fabrication of a laminated ferrite memory plane: (1) ferrite powder preparation; (2) ferrite slurry preparation; (3) ferrite sheet manufacture; (4) conductive line fabrication; (5) laminating; and (6) firing. The technology described here differs from that developed at RCA Needham mainly in the technique used to incorporate embedded conductors.

A. Ferrite Powder Preparation

The composition used for this work is $Zn_{.45}Mg_{.55}Fe_{1.55}Mn_{.45}O_4$ (the reasons for selecting this composition are delineated in Section IV). The formula indicates 15 mol % of Zn, 18.3 mol % of Mg, 15 mol % of Mn, 51.7 mol % Fe. A typical batch contains 244.0 grams of zinc oxide, 309.2 grams of magnesium carbonate (heavy grade), 823.0 grams of iron oxide (Fe_2O_3), and 344.4 grams of manganese carbonate. These materials plus 1900 cm^3 of methyl alcohol are placed in a steel mill of 6-inch I.D., 10.5 inches deep, and charged with 7 kg of 3/4-inch steel balls. This charge is milled for two to three hours at 100 rpm. After milling, the mixture is dried at 150°C, passed through a 4-mesh screen, and placed in fireclay crucibles for calcining. The material is heated to 1900°F in 4 hours, held for 2—1/2 hours and cooled with the kiln. The calcining atmosphere is air in a globar kiln. The calcined powder is placed in the same mill used for mixing, 2000 cm^3 of methyl alcohol are added, and the mixture is milled for 20 hours. After drying as before, the material is ready for use in preparing the blading slurry. The procedure described above is not significantly different from that used to prepare ferrite powder for core pressing.

B. Ferrite Slurry Preparation

A mixture of 640 grams of calcined ferrite, 44 grams of Butvar 76, 20 grams of Flexol D.O. P., 4 grams of tergitol non-ionic TMN, and 480 cm^3 of methyl ethyl ketone are placed in a mill identical to the mill used for mixing and grinding except this mill is lined with Teflon and is milled for 72 to 96 hours. After milling, the slurry is put into a glass jar and rolled at 12 rpm until ready for use. This mixture is then used for doctor blading on silicon rubber. Slurries to be used on glass contain 580 cm^3 of methyl ethyl ketone instead of 480 cm^3. Slurries are passed through a 200-mesh screen as it is loaded in front of the doctor blade. This is necessary to remove undissolved or unmixed clumps.

C. Ferrite Sheet Manufacture

Sheet is made by drawing the doctor blade through a pool of slurry loaded in front of it. The doctor blade is a smooth straightedge which can be set at any desired height above a suitable substrate surface. The height of the blade regulates the thickness of the ferrite slurry applied to the substrate. During drying, the adherence of the slurry to the substrate must be sufficient to prevent lateral shrinkage; all shrinkage should be vertical. Glass and silicone rubber have been found to be the most suitable substrates on which to blade the film.

Highly polished chromium surfaces also are satisfactory, but release of the film is more difficult. Thorough wetting of the dried film with water greatly facilitates release. The vertical shrinkage after drying ranges from 3:1 to 7:1. Thus, to obtain a 3-mil thick sheet, a doctor blade setting of 9 to 21 mils must be used. This ratio depends upon the viscosity of the slurry, the speed of draw of the blade, and also the thickness of the sheet. No definite figures are available for these variables. The specific gravity of the bladed unfired sheet is about 2.8. During drying of the sheet, care must be taken to prevent air currents across the sheet. Drafts cause uneven drying and can cause the film to crack or craze. Drying should be slow enough to allow solvent to escape from the bottom to the top. If the top dries too fast, lateral shrinkage takes place on the surface causing an orange peeling effect and crazing. Sheets thicker than 10 mils are not feasible due to difficulty in obtaining slow uniform drying. Thicker sheets can be made by laminating as many thin sheets as are desired; blocks up to 1 inch thick have been made in this way.

D. Conductive Line Fabrication

There are three methods of putting conductive lines in the ferrite: (1) to embed a solid wire; (2) to squeegee a conductive paste through a mask onto a flat surface and then doctor blade over the conductor pattern; (3) to form grooves in the ferrite and then fill with a conductive paste or powder. The material used for conductors must withstand ferrite firing temperatures and atmospheres. In most cases, this requires that platinum, palladium, rhodium, iridium, or osmium be used. Gold is suitable for ferrite maturing below the melting point of gold.

Solid wires of platinum, palladium, or gold have been used. Shrinkage of the ferrite during firing (about 17 per cent) causes sufficient stress on the ferrite in the vicinity of the solid metal to crack the ferrite, unless the ferrite wall is about ten times as thick as the diameter of the wire. If the ferrite is heavy enough not to crack, the compressive forces on the wires are sufficient to fracture the wire along slip planes in the metal. This has been shown by radiographs of such samples. In the case of gold conductors, the gold melts, then contracts into isolated segments along the line causing an open circuit. Gold-plated platinum, rhodium, and palladium wires have been used successfully. The gold melts, allowing the shrinking ferrite to slide along the wires. However, the mechanical problems involved in stretching many parallel wires seems to make this method impractical.

Pastes have been made of all the suitable metallic powders. Patterns are photoetched in beryllium copper or stainless steel masks. The paste is squeegeed through the masks onto a glass or silicone rubber substrate. Ferrite slurry is bladed over the patterns laid down through the masks. The dried ferrite film is then peeled off including the conductive patterns. This process is limited by the mechanics of the mask. Long, fine, closely spaced conductors are not feasible with the present state of the art, but this technique is employed at RCA Needham to produce conductors about 1 inch long on 15 mil centers.

Grooves in the ferrite sheets are produced by first machining the desired pattern in a lacquer phonograph record master (Figure 3a). RTV60 silicone rubber is then cast over the master producing a male rubber master

(Figure 3b). Ferrite slurry is bladed over the master (Figure 3c). The dried film is peeled off (Figure 3d). The grooves are then filled with conductive powder by coating the sheet with a water mixture of the powder and sugar. After drying, the excess powder is brushed off leaving the grooves filled.

A superior technique is to produce grooves by embossing a plain green ferrite sheet. The embossing punch (Figure 4b) is made by electroplating nickel on a lacquer master (Figure 3a). The nickel master is given a light chromium flash to facilitate removal of the embossed film. Referring to Figure 4, embossing is accomplished by loading the die (g) as follows: bottom punch (a), nickel master (b), plain ferrite sheet (c), aluminum foil (d), rubber pad (e), and top punch (f). The loaded die is heated to 90°C and a pressure of 3000 psi is maintained for about 30 seconds. The die is immediately unloaded and the embossed sheet is removed from the master by soaking in water for 1 to 3 minutes. To facilitate release the master is coated with a 10% solution of Tergitol TMN in water, then dried before using. The grooves are then filled with conductor powder as before.

The embossing technique has certain advantages over the rubber master technique. For one thing, the rubber master tends to swell when the slurry is bladed over it. Furthermore, the ferrite sheet can crack upon drying, particularly if the grooves are rather deep. These problems are circumvented by embossing, but care must be taken in separating the embossed sheet from its punch.

E. Laminating

All laminating is done in essentially the same way. The die (j) in Figure 5 is filled in the following order: bottom punch (a), rubber pressure pad (b), aluminum foil (c), filled word-line sheet (d), blank spacer sheet (e), filled digit-line (f), aluminum foil (g), rubber pressure pad (h), and top punch (i). A pressure of 2000 psi is applied to the punches and the temperature is increased to 90°C. The stack is removed hot.

Figure 6 shows the dies and punches used for laminates: (a), the 256 x 64; (b), the 256 x 100 ; and (c), the 512 x 200.

F. Firing

Firing is done between to flat, ground, doped aluminum oxide setters. One green ferrite plane is placed between a pair of spaced setter plates, as shown in Figure 7. The spacing is about 2 mils greater than the thickness of the ferrite. This limits warping. The firing schedule is to go to 2300°F at 450°F per hour, hold 2 hours, and then cool with the kiln in an air atmosphere. Subsequent nitrogen annealing is required to obtain proper magnetic properties. The annealing schedule is to increase the temperature to 2050°F at the rate of 450°F per hour, hold for 2 hours, and then cool with the kiln.

The fabrication of the doped aluminum oxide setter is important because it determines both the amount of sticking, which causes nonuniform shrinkage, and the degree of setter warping, which determines the flatness of the fired laminate. The powder (10% Fe_2O_3, 10% $MgCO_3$, 40% 220-B Alundum grit, 20% AWIF Electronic Grade Alundum and 20% 1200 AWIF Electronic Grade

Alundum by weight) are thoroughly mixed with sufficient methanol in a steel mill with steel balls to form a stiff slurry. After mixing 2 hours, the slurry is dried. Seven percent by weight of a 7% solution of methyl celulose is thoroughly mixed with the dried powder in a Hobart mixer, then passed through a 30 mesh stainless steel screen. This material is then pressed into plates of the desired size at a molding pressure of 20000 psi. After drying, the plates are fired at 2500°F for 2 hours, then lapped flat on both sides.

In order to facilitate interconnections the finished laminate should have reproducible dimensions within a tight tolerance. For instance, the technique illustrated by Figure 1 (solderweld of a tinned copper finger to an embedded conductor exposed by abrading) requires a tolerance of ±10 mils (better than a 1% tolerance over the 2.5 inches). Measurements have shown that mechanical deviations in the sintering step predominate. In a series of eleven 256 x 64 samples that were air quenched following sintering, only two had dimensions within a ±10 mil tolerance.[3] Using the sintering procedures and setter plates described above approximately 50% of a series of 32 samples were within tolerance.* More careful control of the sintering environment, such as the usage of a tunnel kiln, can lead to further improvements, but the mechanical tolerance required to fully automate interconnections is at the limits of the ceramic art.

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*Preliminary experiments with tin oxide setters show some improvement over these figures -- five of a first group of eight samples within ±6 mils and all eight of a second group were within ± 3.6 mils.

III. EFFECTS OF PROCESSING PARAMETERS

A. Calcining and Grinding

The grinding time and calcining temperature produce changes in magnetic parameters and drastic changes in shape of the hysteresis loop of these materials. Increased grinding time and calcining temperature produce an increase in density, grain growth, and grain size distribution. Material calcined at 1900°F for 2 hours and ground for 17 hours produces a reasonably dense (greater than 90% of theoretical density) ferrite when fired at 2300°F for 2 hours and annealed for 8 hours at 2050°F. The grain size will be between 1 and 6 microns. Lower calcining and shorter grinding times will result in a porous material with 1 to 2 micron grains. Calcining above 1400°F and grinding for 37 hours induces spontaneous grain growth to a size of several hundred microns. These large grains are surrounded by large numbers of 1 to 6 micron grains. This tremendous difference in grain sizes causes extremely jagged nonlinear vertical portions of the hysteresis loop. Small grains are required for a low switching coefficient and uniform grain size is required for a maximum rectangularity in the hysteresis loop. Smaller grains lead to increasing the coercive force; however, this can be maintained at a satisfactory level by compositional adjustment. This adjustment is made at a loss of temperature stability. The resistivity is not noticeably influenced by the processing parameters.

Because of the smaller and more uniform grain size obtained with materials calcined at 1200°F instead of 1900°F, this calcining temperature would be preferred. However, a good workable slurry and sufficiently pliable bladed sheet could not be obtained with these low-calcined powders without excessive use of binders resulting in excessive shrinkage and porosity. Satisfactory workability and pliability can be obtained by calcining at 1800°F to 1900°F for 1 to 3 hours.

B. The Binder System

The binder system performs two important functions: (1) it provides a vehicle in which the calcined ferrite powder is dispersed and by which the powder can be distributed in a uniform layer of controlled thickness over a suitable surface; and (2) it provides a matrix holding the ferrite powder in the form of a flexible, tough sheet that can be cut, formed, embossed, punched, and molded into various shapes, then completely burned out at a low temperature leaving the ferrite particles to sinter and react in a normal manner.

Several binder systems have been tried. Polyvinyl butyral has been found to be the most satisfactory. A workable slurry and bladed sheet can be obtained with as little as 2% Butvar by weight. This small amount of binder results in considerably lower firing shrinkage and fewer burnout problems, particularly, with laminates having thick cross sections.

The solvent, mixing time, and viscositiy are additional important variables. The type of solvent controls the rate of drying of the slurry and the amount of solvent controls the viscosity. Higher viscosities are required for sheets above 6 or 7 mils thick, and lower viscosities are preferred for the thinner sheets. Toluene and methyl ethyl ketone are very suitable for the blading of sheets up to 10 mils thick. Toluene is best for sheets above 5 mils thick and MEK best for the thinner sheets. Sheets between .1 mil and 15 mils have been bladed. Sheets thicker than 6 or 7 mils are best prepared by laminating the required number of thinner sheets.

The degree of mixing is very important as it is the major factor in determing fired density and firing shrinkage. The longer the mixing the better except, if carried too far, the slurry forms a jell which cannot be broken down and hence is useless for blading. The reason for the jelling is not known, but mixing can be increased from 6 hours to 96 hours if a teflon-lined mill, instead of a steel mill, is used. A 50% charge of steel balls is used in both cases. Fired densities can be increased from 3.6 to 4.5 g/cc and linear shrinkage reduced from 20% to 16% by sufficient mixing.

IV. COMPOSITION

Choosing the Composition

The composition was chosen to give the best match with the desired magnetic and electrical parameters. The goals are: coercive force -- $H_c = .5$ Oe; saturation flux density -- $B_s \geq 1000$ gauss; squareness -- $B_r/B_m > .9$; switching coefficient -- $S_w \leq .3$; temperature coefficient a minimum; and electrical resistivity -- $\rho > 10^6$ Ωcm. The system $Z_{n(1-x)}Mg_xFe_{(2-y)}Mn_yO_4$ is known to have many of the desired characteristics; the region between $.55 \leq x \leq .75$ and $.40 \leq y \leq .65$ was chosen for detailed investigation. Basic magnetic data are most conveniently obtained from toroids. The toroids were prepared by cutting from three 4-mil doctor bladed sheets laminated together.

All magnetic data except for S_w, were taken from an hysteresis loop obtained with a drive frequency of 400 Hz on the toroid. The coercive force and B_r/B_m ratio (B_m is measured at approximately 1.5 Hc and is about 1500 gauss in this compositional range) of the samples are shown as a function of composition and firing conditions in Figure 8. A study of these curves shows that maximum B_r/B_m ratios are to be found in compositions having the lower values of both x and y and subjected to more thermal work, (that is, increased firing). The coercive force is seen to be essentially independent of y, but to increase rapidly with x and to decrease somewhat with increase in thermal work.

Since the low drive ferrite is intended for use in a linear-select memory, these materials cannot be compared usefully on the basis of their coincidence current switching time. Rather, their switching time at relatively large overdrive is the quantity of interest. The switching times, with 0.5 microsecond as a maximum, have been measured as a function of mean applied field. The slope of the curve of inverse switching time vs. field, S_w, gives a measure of the relative fast switching performance of the various compositions.

Certain of the compositions have been processed with varying sintering conditions, as seen in Figure 9. Certain toroids from all firing except those involving N_2 anneals at 1800^oF and 1900^oF, which have poor squareness, have been studied. Test cores for switching measurement are cut from green laminated ferrite sheets; all the compositions with $x \doteq .55$ were used. Although S_w ranges from 0.43 ($x = .55$, $y = .40$ at 2100^oF air - 2050^oF N_2 at relatively low drive) to 0.23 ($x = .55$, $y = .55$ at 2300^oF air - 2050^oF N_2 at high drive) the measured S_w's are almost all in the range of 0.30 to 0.35. Similar values have been obtained by Gyorgy[5] for a variety of Mg-Mn-Zn ferrites while Palmer et.al.[4], obtained values ranging from ~1.0 with small amounts of Zn, down to 0.34 with large amounts of Zn. (Palmer's measurements were at quite low driving fields). Exact comparisons are invalid because of differences in measurement technique, but the processing of a particular composition can have a significant influence on the switching properties. Processing for laminated ferrites leads to fine grain materials with generally higher porosity than in pressed cores. Thus, S_w's lower than in pressed cores of similar chemical compositions result.

The percent change in coercive force per degree change in ambient temperature of the more interesting compositions has been found to decrease with increases in x (see Figure 9). This is due to an increase in Curie temperature with decreasing zinc. Higher thermal work lowers the coefficient in compositions with lower values of y. The highest coefficients were found when y = .50 to .55 and in samples having had the greatest thermal work. Generally, compositions with the lowest coercive force also have the poorest temperature stability. The temperature coefficients of the most acceptable compositions run between .3 and 1.3 per cent change in coercive force per degree centigrade over the temperature range of 20°C to 50°C. That is, the coercive force will be 9% to 39% less at 50°C than at 20°C.

In this composition system, the resistivity is roughtly 10^8 Ωcm. at room temperature.

A composition with a value of x = .55, y = .45 has been chosen as providing the best compromise of parameters, and was utilized to develop the fabrication and processing technology described earlier.*

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*A ferrite with considerably better temperature stability has been synthesized by R. Harvey and I. Gordon and produced in laminate form -- $Zn_{.11}Mg_{.83}Fe_{1.65}Mn_{.41}O_4$.[6] Its coercive force is in the 0.7 - 1.1 Oe range.

V. LOW DRIVE MONOLITHIC MEMORY ARRAY OPERATION

The monolithic ferrite memory is operated as a two-wire word-organized (linear select) memory. One of the wires carries the full read and write currents in appropriate time sequence. The other orthogonal set of embedded wires carries the sense signals and digit currents in time sequence. The array is designed to be driven by integrated electronic circuits. Because of the low current values and slow risetimes used, each crossover point of the orthogonal conductors can store an information bit. At very high speeds, two adjacent crossovers are used for one bit so as to cancel common noise voltages.[2]

To store a binary "1", a negative Digit current is applied in time coincidence with the positive Write current; to store a binary "0", a positive Digit current is applied with the Write. The subsequently applied negative Read current erases the flux stored around the digit conductor at the crossover point. This induces a signal voltage on the digit conductor, the polarity of which depends on the stored information — positive for a "1" and negative for a "0". This operation is illustrated in Figure 10. The testing of hundreds of scattered bits in the 256 x 100 planes indicates that uniformity of a signal output can be adequate for memory operation.[3] Still better uniformity is obtained from planes composed of a composition containing less Zn, but requiring a higher drive current.[6]

This sort of low power operation will enable the realization of very low cost random-access mass memories because of the incorporation of batch fabrication techniques for both the magnetic storage medium and the surrounding electronics.

VI. ACKNOWLEDGEMENTS

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VII. REFERENCES

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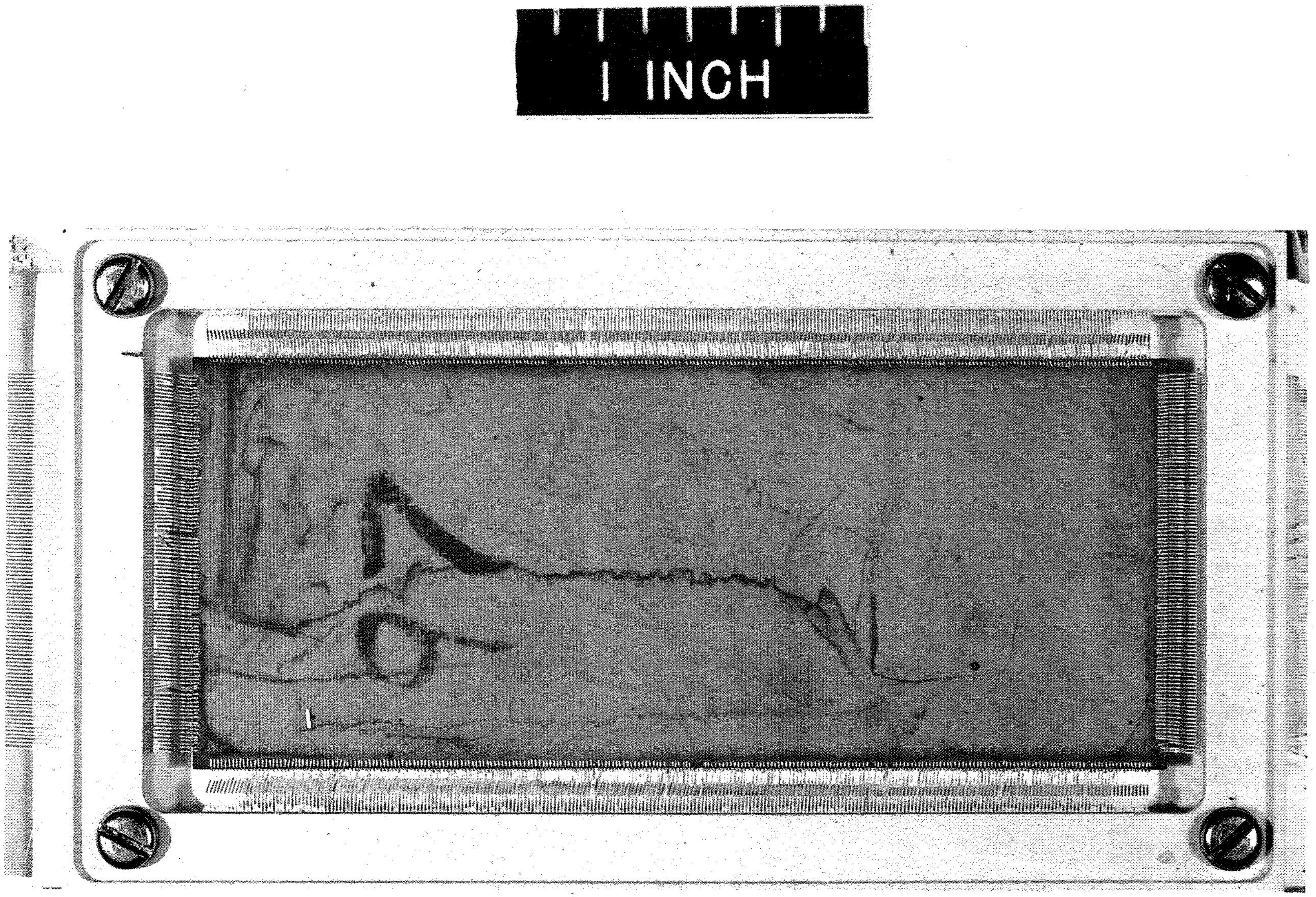
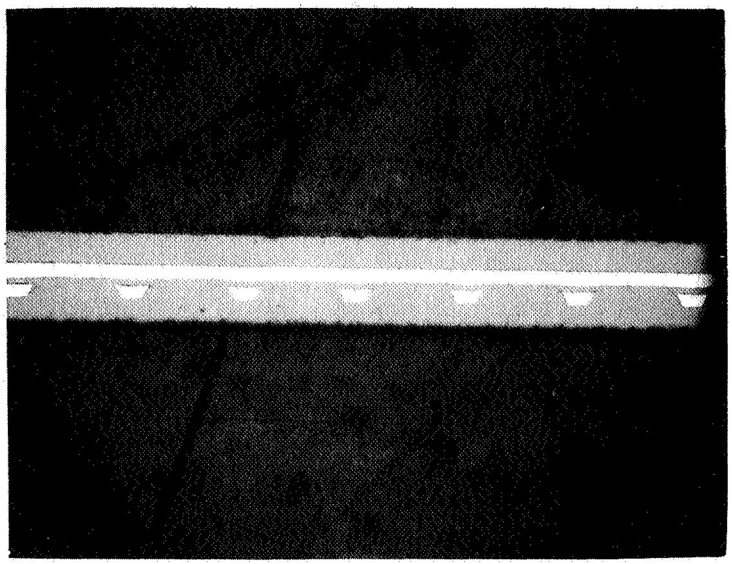
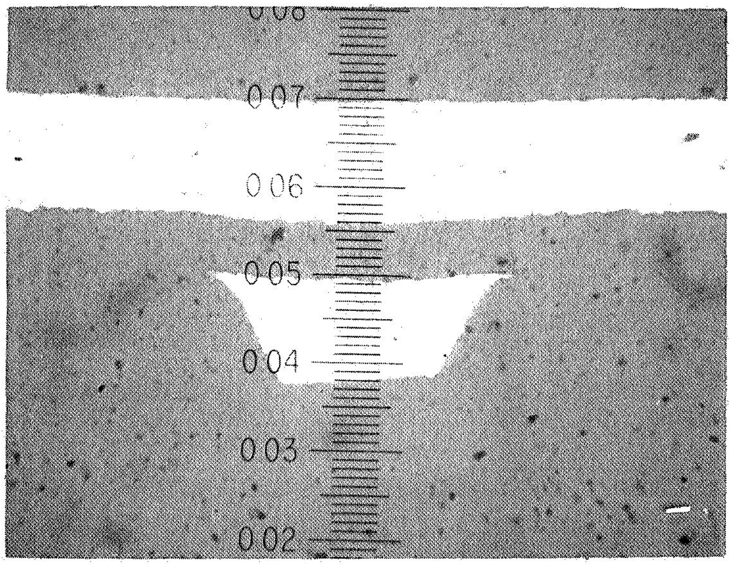


FIG. 1 MOUNTED 256 x 100 LAMINATED FERRITE ARRAY



(a) DIGIT CONDUCTORS ARE ON 10 mil CENTERS



(b) SCALE: 0.0001 INCH PER SMALL DIVISION

FIG. 2 SINTERED LAMINATE SECTIONS

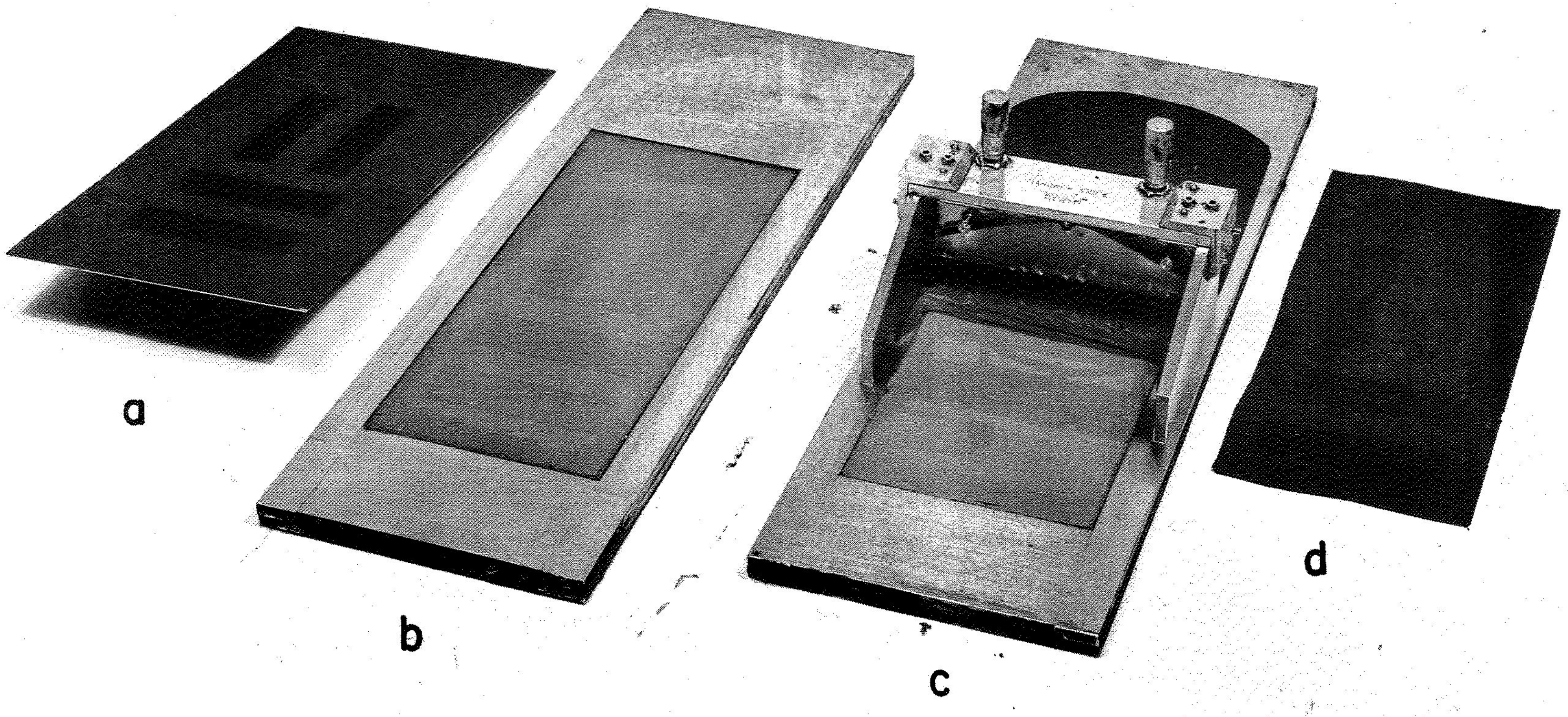


FIG. 3 BLADING FERRITE OVER RUBBER PATTERN MASTER (a) LACQUER MASTER (POSITIVE), (b) RUBBER MASTER (NEGATIVE), (c) BLADING OPERATION, (d) FINISHED GROOVED SHEET

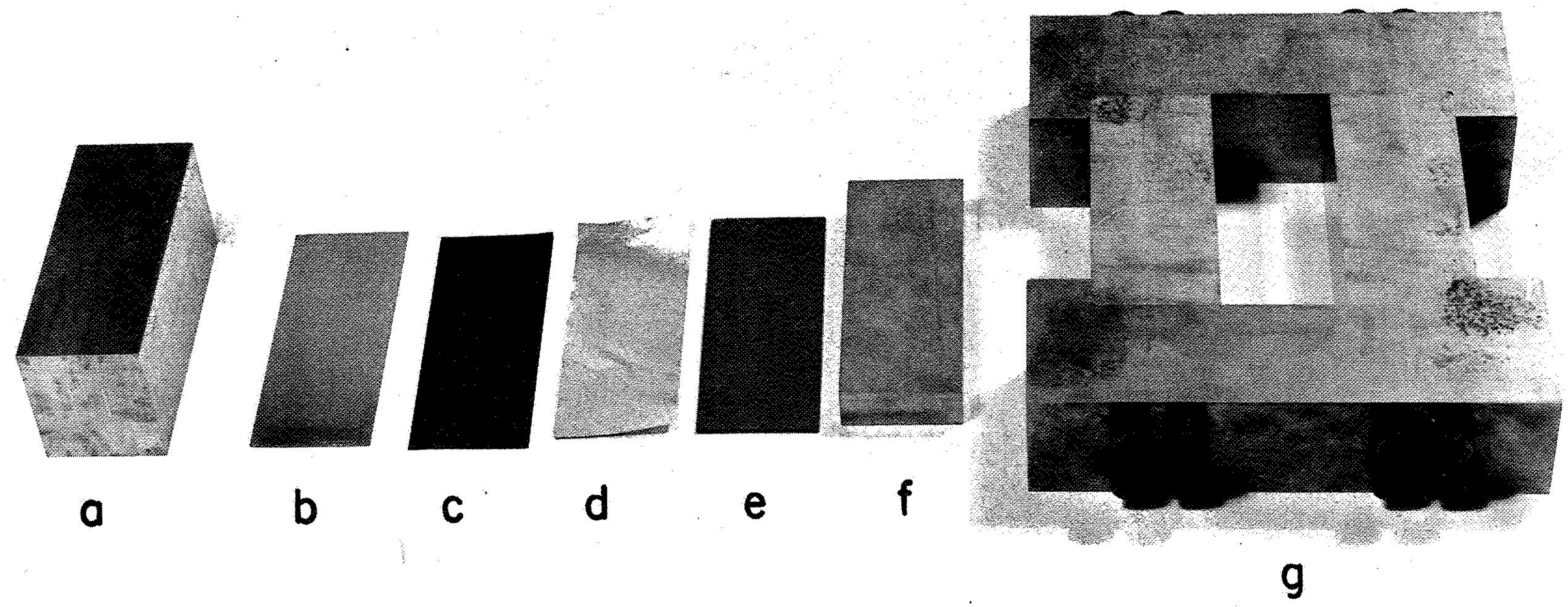


FIG. 4 EMBOSSING MOLD AND FILL (a) PUNCH, (b) PATTERN DIE, (c) FERRITE SHEET, (d) FOIL SPACER, (e) RUBBER PRESSURE PAD, (f) PUNCH, (g) CONFINING MOLD

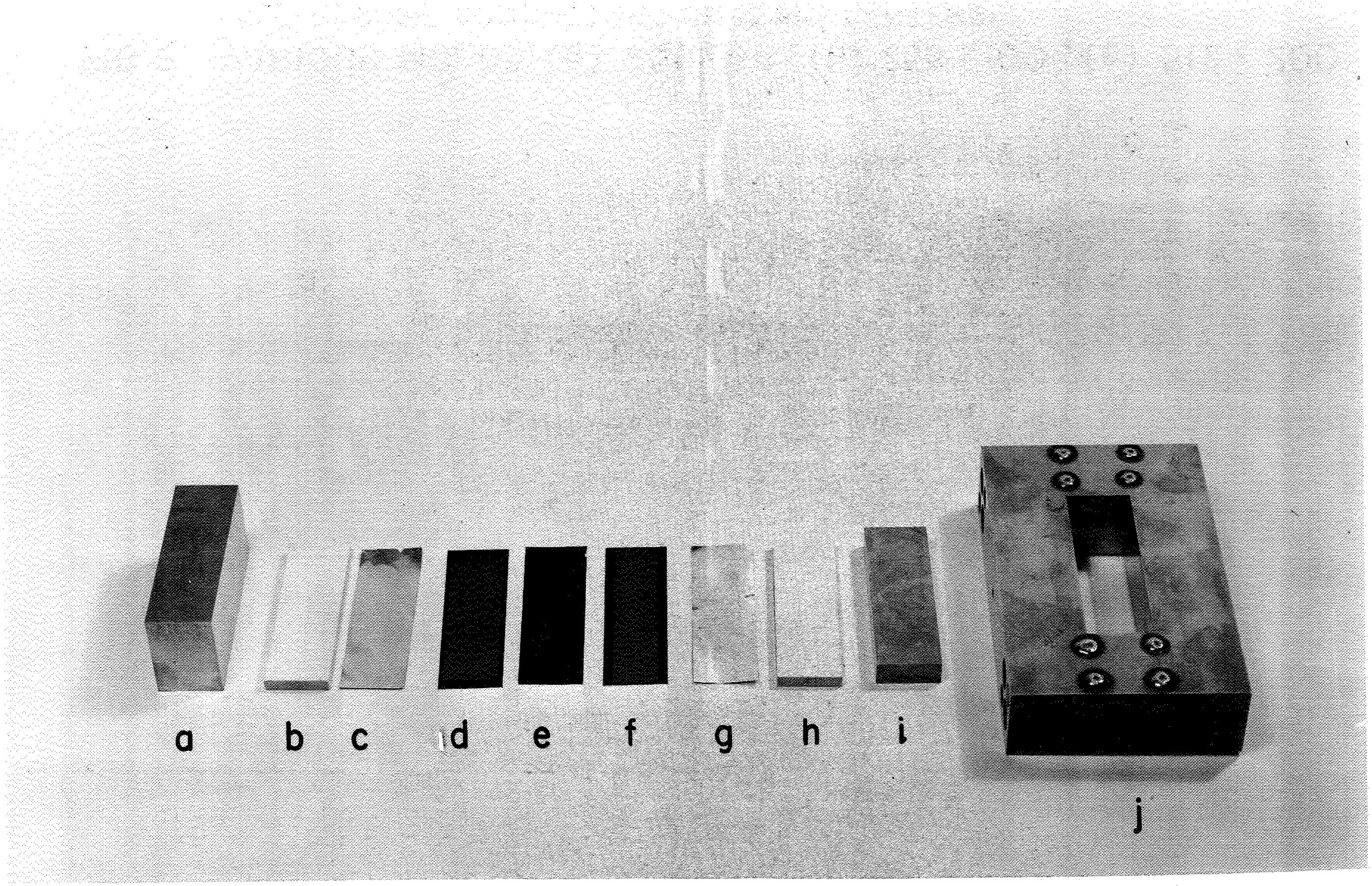


FIG. 5 LAMINATING MOLD AND FILL. (a) PUNCH, (b) RUBBER PRESSURE PAD, (c) FOIL SPACER, (d) FILLED WORD-LINE FERRITE SHEET, (e) FERRITE INSULATING SHEET, (f) FILLED DIGIT-LINE FERRITE SHEET, (g) FOIL SPACER, (h) RUBBER PRESSURE PAD, (i) PUNCH, (j) CONFINING MOLD.

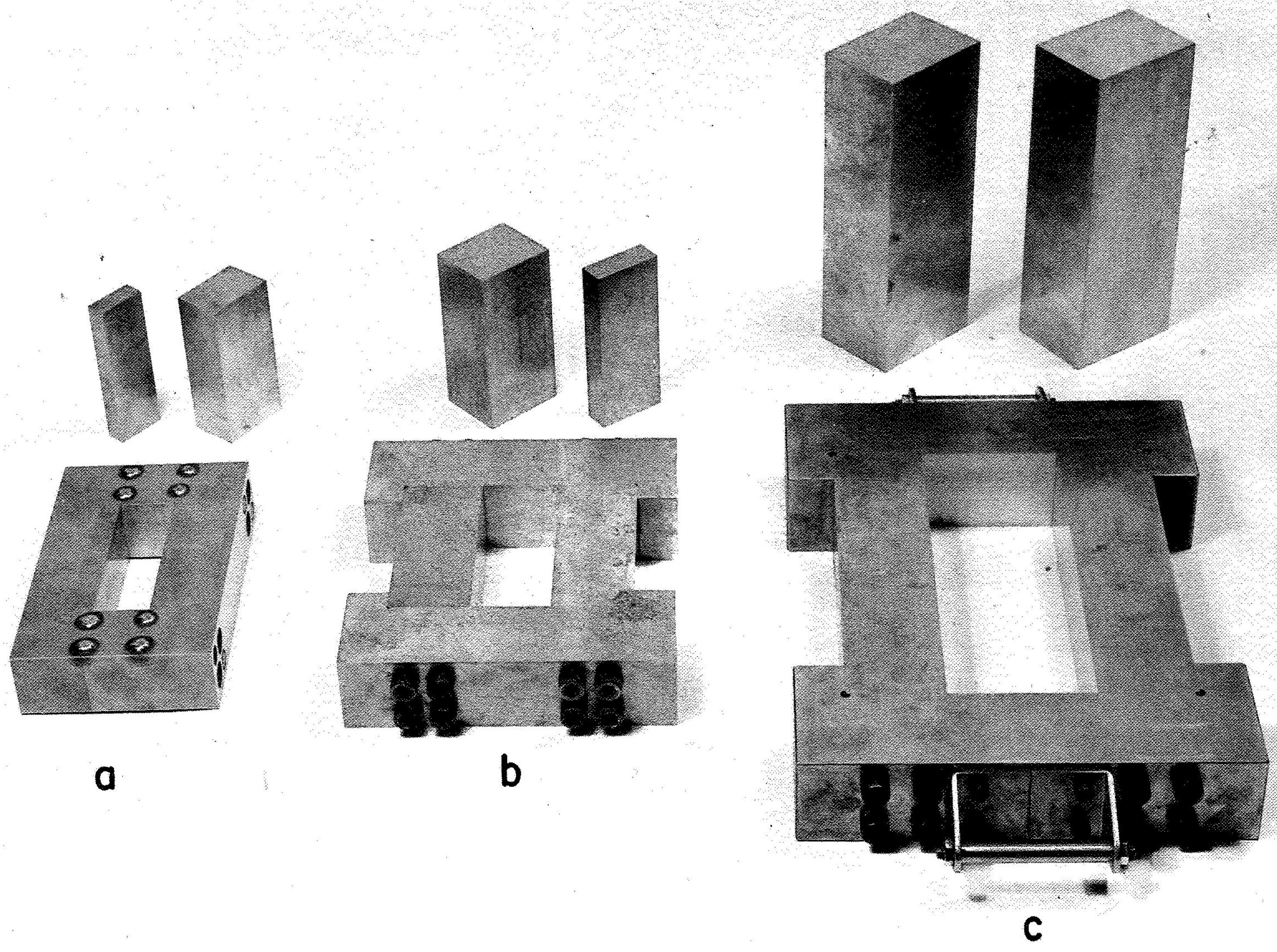


FIG. 6 VARIOUS MOLDS. (a) 256 x 64, (b) 256 x 100, (c) 512 x 200
(ALL ASSUME CONDUCTORS ON 10 mil CENTERS)

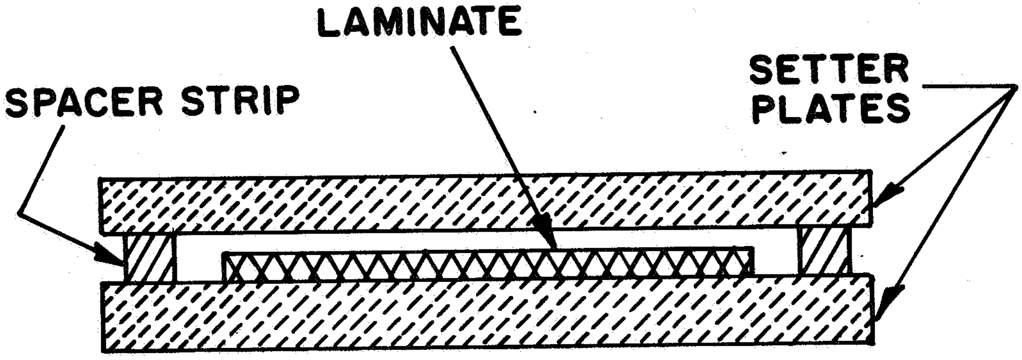


FIG. 7 FIRING ARRANGEMENT—NOT TO SCALE

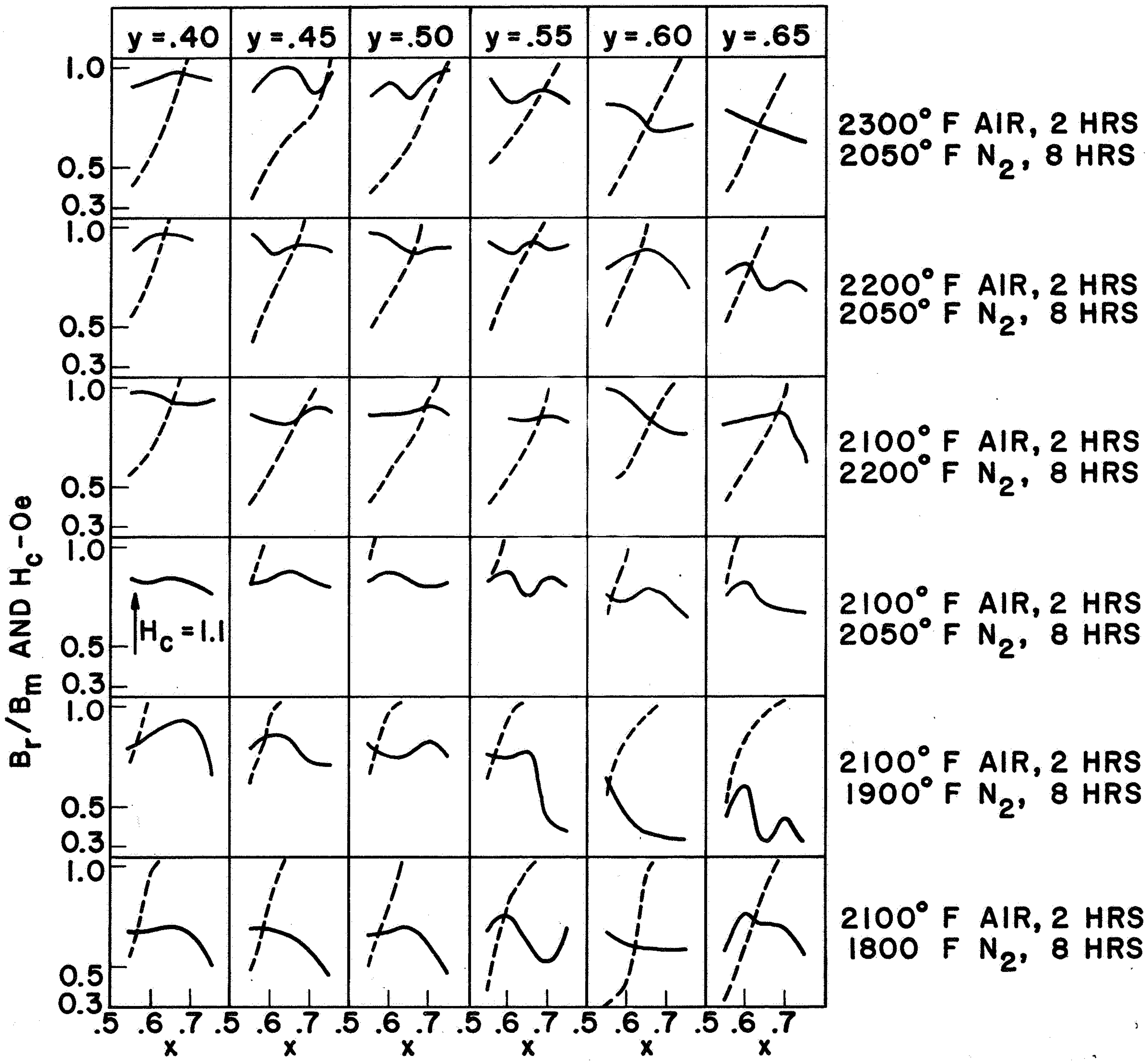


FIG. 8 B_r/B_m AND H_c AS A FUNCTION OF COMPOSITION IN THE SYSTEM $Zn_{(1-x)}Mg_xFe_{(2-y)}Mn_yO_4$

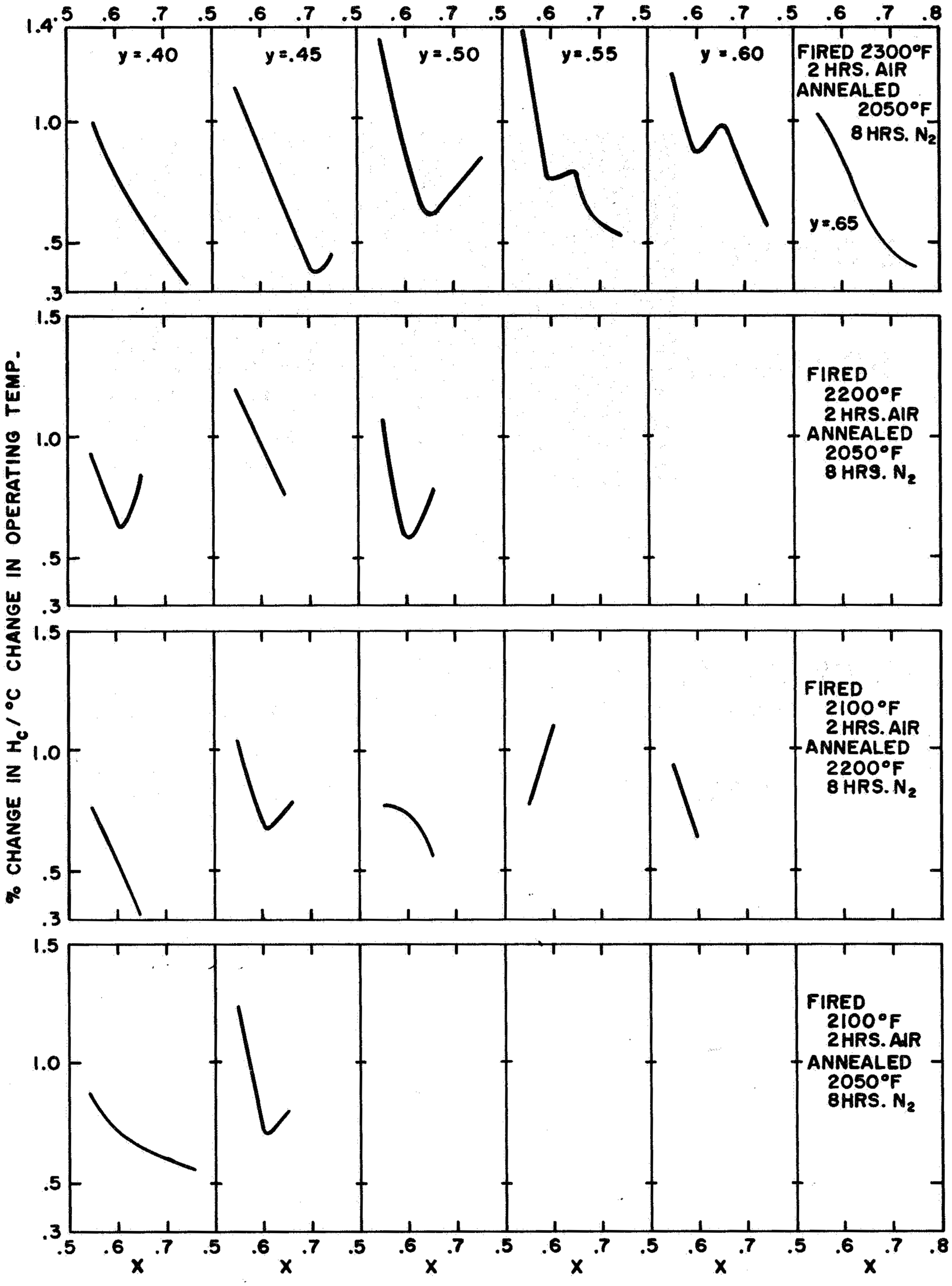
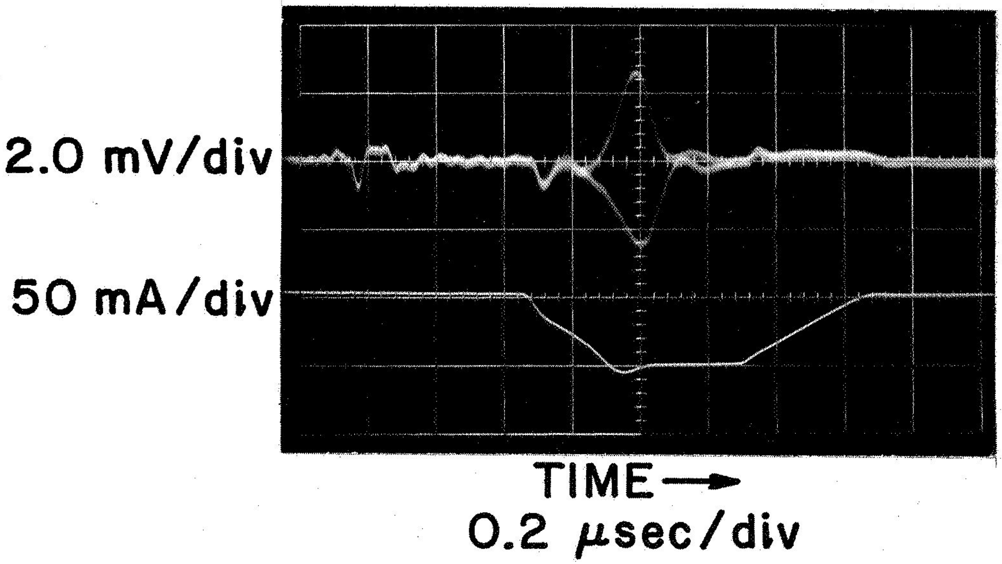


FIG. 9 TEMPERATURE STABILITY AS A FUNCTION OF COMPOSITION IN THE SYSTEM OF FIG. 8



LOW DRIVE WAVEFORMS
(a) UPPER TRACE - SUPERIMPOSED "1" AND "0" SIGNALS
(b) LOWER TRACE-READ CURRENT

FIG. 10