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NAVORD REPORT 2686

BISMANOL PERMANENT MAGNETS, EVALUATION AND PROCESSING

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U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

BISMANOL PERMANENT MAGNETS, EVALUATION AND PROCESSING

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ABSTRACT: Bismanol permanent magnets have been evaluated for stability under various operating conditions. The magnets showed a remarkable flux constancy over a wide temperature range after stabilization at low temperatures. There is some decrease in magnetic flux density at the low temperature; the exact flux loss being dependent on the temperature of stabilization. Because of their high coercive force, the magnets are extremely stable magnetically to shock, vibration, centrifugal force and stray magnetic fields. Except for a tendency to chip, bismanol magnets are sufficiently strong physically for most applications. Unprotected bismanol magnets corrode slightly at ordinary temperatures and humidity, and more rapidly at 95 per cent humidity. Magnets with applied protective coatings remained stable at room temperatures and moderate humidities for the six-month test period.

The processing techniques of bismanol magnets have been improved by eliminating magnetic separation. The new technique consists of the separation of excess bismuth from the melt by hot-pressing prior to pulverization. Since the publication of the previous report, (Navord 2440) bismanol magnets have been made with maximum energy products up to 5.3×10^6 gauss-oersteds. Present maximum value for the coercive force (Hc) is now 3650 oersteds and 4800 gauss for the residual flux density (Br). Various types of pulverizing equipment were also evaluated with respect to the magnetic properties of the resulting compacts. The methods of determining percentage purity (MnBi content), alignment and effective particle size in bismanol magnets are discussed.

U. S. NAVAL ORDNANCE LABORATORY
White Oak, Silver Spring 19, Maryland

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The subject investigation of bismanol permanent magnets was undertaken as part of the broad program of the development of new and improved magnetic materials, Task NOL-Re4a-56-1-53. NAVORD Report 2440 dated May 20, 1952 described previous progress in the preparation of bismanol permanent magnets from powdered manganese bismuthide.

EDWARD L. WOODYARD
Captain, USN
Commander

D. S. MUZZEY, Jr.
By direction

ILLUSTRATIONS

REFERENCES

1. Guillaud, Chas., Thesis, Univ. of Strasbourg (Strasbourg, France) 1943

2. Hoselitz, K., Phil. Mag. 35, 91 (1944).

BISMANOL PERMANENT MAGNETS, EVALUATION AND PROCESSING

INTRODUCTION

1. This report covers six months progress in the development of bismanol permanent magnets since the publication of NavOrd Report 2440, dated May 20, 1952. The first part of this report concerns itself with the evaluation of bismanol magnets under various operating conditions such as, temperature, shock, vibration, centrifugal force, humidity and salt spray. The second part describes continuing progress in the improvement of bismanol processing techniques.

EVALUATION

TEMPERATURE CHARACTERISTICS

2. The dependence of the high intrinsic coercive force (Hci) on a high value of the crystal anisotropy constant (K_1) was first established by Guillaud[1] in his study of powdered manganese bismuthide. He also showed that in MnBi, the value for this anisotropy energy decreased with the lowering of temperature, and at 84°K would be zero. This effect is due to an inversion of the "easy" and "hard" directions of magnetization along the crystal axes of hexagonal MnBi. Because of the decrease in the anisotropy energy, it is apparent that the coercive force value will be less at low temperatures than at room temperature. The effect of low temperature on bismanol magnets in an open circuit is shown in Figure 1a. It should be noted, in this open circuit, that although at -56°C there is a 58 percent loss in flux density, the magnets become quite stabilized over a wide temperature range. However, in a closed circuit there is no loss in induction since the lower temperature reduces only the coercive force. Even at -50°C, as shown in Figure 1b, the coercive force of the magnet is still quite high, i.e., 1600 oersteds. In the use of bismanol permanent magnets, therefore, the circuit should be designed for the flux density available at the operating temperature.

VIBRATION

3. Bismanol magnets were vibrated at frequencies of 50, 100 and 500 cycles per sec. for periods of one-half to an hour

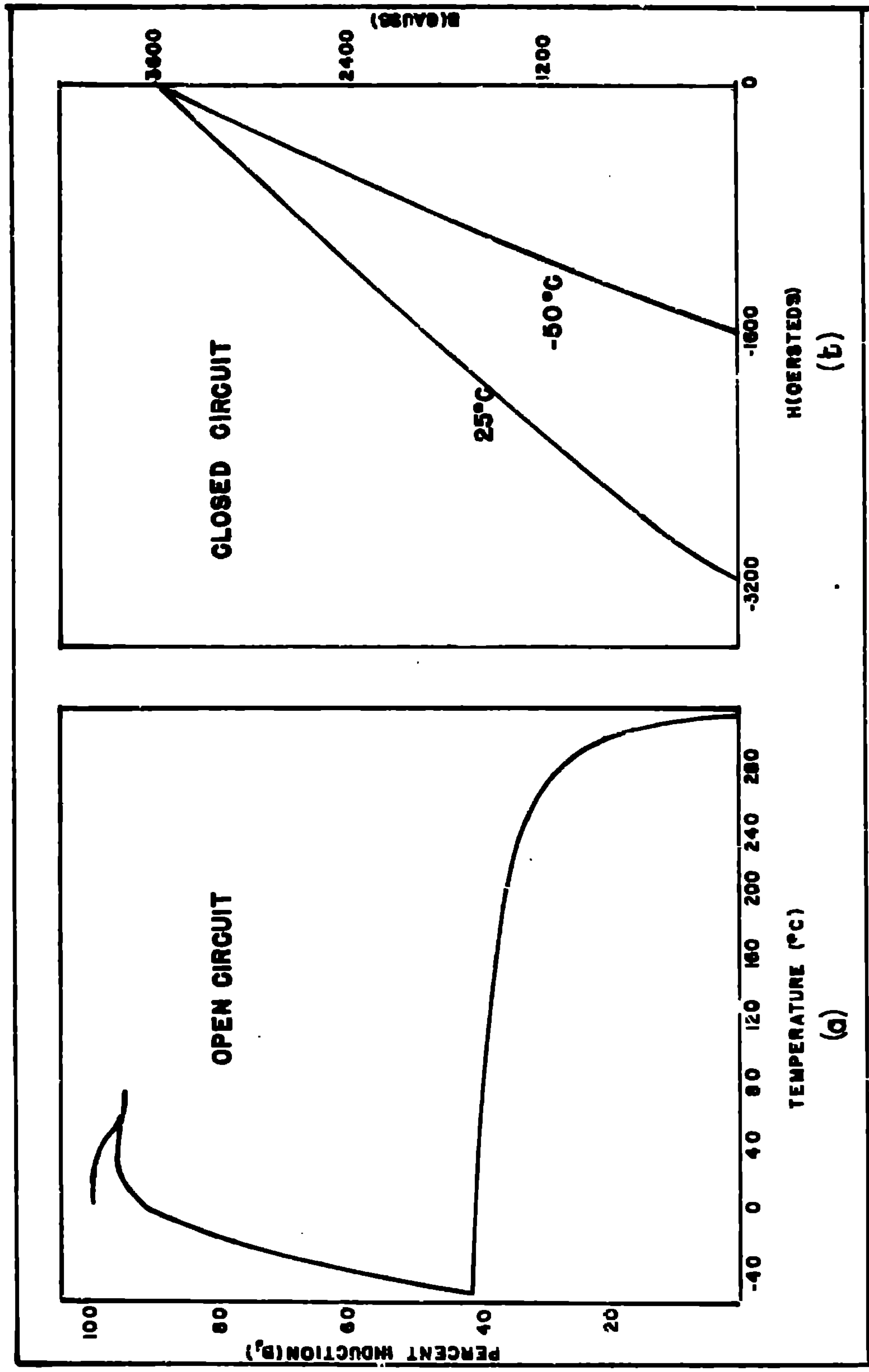


FIG. 1 — TEMPERATURE CHARACTERISTICS OF BISMANOL

at room temperature, 71°C and minus 54°C. No change in magnetic or physical properties was noticed except those due to temperature.

SHOCK

4. The shock tests performed on bismanol magnets were actually drop tests. Table I summarizes the results of these tests. As seen from Table I, the magnetic properties of bismanol magnets are not affected by shock except by actual physical damage to the magnet. This is what one would expect from magnets prepared from high anisotropy materials.

CENTRIFUGE TESTS

5. Bismanol magnets were attached to a shaft with a steel band around their periphery. The whole assembly was rotated until they broke. The calculated maximum acceleration at their outer radius was found to be 143,000 G's at the time of fracture. This severe test suggests their possible use as rotors in generator assemblies.

ROOM STABILITY

6. The magnets have been found to be stable, at room temperature (70° ± 10°F) with a relative humidity not exceeding 70 percent, for the six-month period measured. However, unprotected bismanol magnets which received excessive handling became chipped along the edges and corroded at the exposed portions. This is a result of damage to the thin protective coating of bismuth present after hot-pressing.

HIGH HUMIDITY STABILITY

7. Bismanol magnets exposed to relative humidities of 95 percent or greater tend to corrode rapidly (72 hrs) with some loss in their magnetic properties. Magnets protected by external coatings, such as nickel, cadmium and zinc plating, remain stable for somewhat longer periods (1-4 weeks). This problem has not been satisfactorily solved at this time, but preliminary experiments have shown that acid-dipping puts on a protective coating of a bismuth salt. Evaluation studies of this type of coating are currently incomplete.

SALT SPRAY STABILITY

8. Bismanol magnets subjected to standard ASTM Salt Spray tests for over 100 hours, exhibit only superficial corrosion

TABLE I

RESULTS OF SHOCK TESTS ON BISMANOL MAGNETS

Sample	Feet Dropped	No. of Drops	Approx. G's Max.	Magnetic Change	Physical Change
1. On End	1	3	4000	None	None
1. On Side	1	2	4000	None	None
2. On End	2.17	2	-----*	None	Slight Chipping
2. On Side	2.17	2	-----*	None	Slight Chipping
3. Room ** Temp.	40	1	-----*	None	None
3. Room ** Temp.	40	2	-----*	---	Broke
4. -73°C	40	2	-----*	---	Broke
5. Room Temp.	10	1	15,000	None	None
5. Room Temp.	10	2	15,000	---	Broke

* Not available due to lack of calibration

** Mounted in plastic block; all others magnetically attached, unmounted.

without any loss of their original magnetic properties. Apparently, a stable coating of bismuth oxychloride prevents further corrosion. This phenomenon is now being examined as a possible protective coating for bismanol magnets.

STRAY MAGNETIC FIELDS

9. Because of the high coercive force of bismanol magnets, extremely high accidental fields would be necessary to affect the stability of the magnets. Exposure of the magnets to a General Electric Demagnetizing Coil Unit at its full capacity of approximately 800 oersteds showed no change in their flux density.

PROCESSING TECHNIQUES

ENRICHMENT OF THE ALLOY

10. In order to prepare a magnet with the highest remanence (Br), it is essential to prepare an alloy with the highest percentage of the magnetic phase, manganese bismuthide. Since the amount of MnBi in a melt is limited by its peritectic nature, all attempts to increase the purity were made after the preparation of the melt. The purification was accomplished by one of two methods:

Method (A): This method, previously described in NAVORD Report 2440, consists of the seperation of the magnetic and non-magnetic portion by means of a magnetic separator after pulverization.

Method (B): In this new process, the excess bismuth in the impure melt is squeezed out by hot pressing, before pulverization, at 25 tsi at 350°C in a loose fitting die. Adoption of Method (B) has considerably speeded up the processing of bismanol magnets by eliminating the slower process of magnetic separation.

PULVERIZATION

11. It has been previously shown by Guillaud[1] that by reducing the particle size of MnBi to about 3 microns, one can obtain an intrinsic coercive force (Hci) as high as 12,000 oersteds. In order to increase the coercive force of bismanol magnets, various methods of grinding were evaluated. Table II shows typical magnetic data on bismanol magnets compacted from MnBi powder pulverized by various means.

Table II

GRINDING AND MELT EVALUATION DATA

Grinding Method	Melt No. Type	Mesh Size	Particle Size 1/ BET/μ	Density	Br Gauss	Hc oe	BH (max) X10^{-6}	Effective Particle Size/μ	Percent Alignment	Percent Purity
Mikro-Pulv. 2/	11A	-325	--	8.0	4360	3430	4.3	9	--	--
Mikro-Pulv. Plus Coll. Mill 3/	11A	As Ground	--	8.1	3800	3675	3.9	8	95	61
Mikro-Pulv.	13A	As Ground	1.8	8.3	4775	1190	2.3	46.5	96	72
Mikro-Pulv. Plus Coll. Mill	13B	As Ground	0.7	7.8	3880	3750	3.7	9	78	77
Mikro-Atom. 2/	15B	As Ground	0.5	8.2	3550	3175	3.3	9.5	--	--
Ball-Milled	19 MnBi Cryst.	-20/μ	--	8.7	4700	3250	4.8	9	95	69
Mikro Pulv. 4/	18B	As Ground	--	6.7	4800	3650	5.3	9.5	90	90

1/ As determined by National Bureau of Standards

4/ 1.9 in. dia., all others are .414 in. dia.

2/ Mikropulverizer mfgd
by Pulverizing Machinery Co.
Summit, New Jersey

3/ Colloid Mill mfgd
by Eppenbach Inc.
Long Island City, N.Y.

12. It is apparent from Table II that most bismanol magnets with the highest (Hc) values have a corresponding lower (Br) value. Conversely, magnets with a high (Br) show a lower (Hc) value. Because of the large number of variables involved, conflicting data makes it impossible to determine the exact explanation. However, it is known that finer particles have a larger surface area, increasing their tendency to oxidize, thus decreasing the purity. Small particles are also more difficult to align during pressing because of their lower magnetic moment.

13. Of the various grinding equipment evaluated, a high speed hammer mill of the "Mikropulverizer" type has proven the most satisfactory from a practical standpoint. Wet colloid milling yielded MnBi powder of extremely small particle size, but the decrease in (Br) values reduced the maximum energy product values. (Table II).

14. Powders ground from melts of Method (A) gave higher coercive force values, because the effective particle size is smaller than their apparent size due to the associated bismuth of the particles. Pulverization of Method (B) melts yielded powders requiring no magnetic separation. However, more efficient grinding was usually necessary to reduce the particle size small enough to obtain higher coercive force values.

15. It has been pointed out by Hoselitz[2] that the greatest improvement in (BH) max values for magnets where (Hc) = 0.45 x Br comes from increasing the value for (Br). This is a consequence of the geometry of the demagnetization curve. For magnets where (Hc) $\approx$ (Br), this curve must be a straight line with a slope approaching unity. For a high coercive magnet, such as bismanol, it is impossible to have a fuller demagnetization curve, otherwise the B-H curve would show that the magnetization would rise with a decreasing field. This, of course, is not possible. Figure 2 shows a typical normal and intrinsic hysteresis loop for a bismanol magnet.

PARTICLE SHAPE AND SIZE

16. The quantitative determination of the average particle size and distribution range of MnBi powder has not been made. It would be desirable to have such data but due to the large number of parameters involved, only a qualitative study was made. Figures 3 and 4 are photomicrographs of MnBi powder pulverized by various attrition mills. Except for sample (b), the particle size distribution appears to be unequal, usually

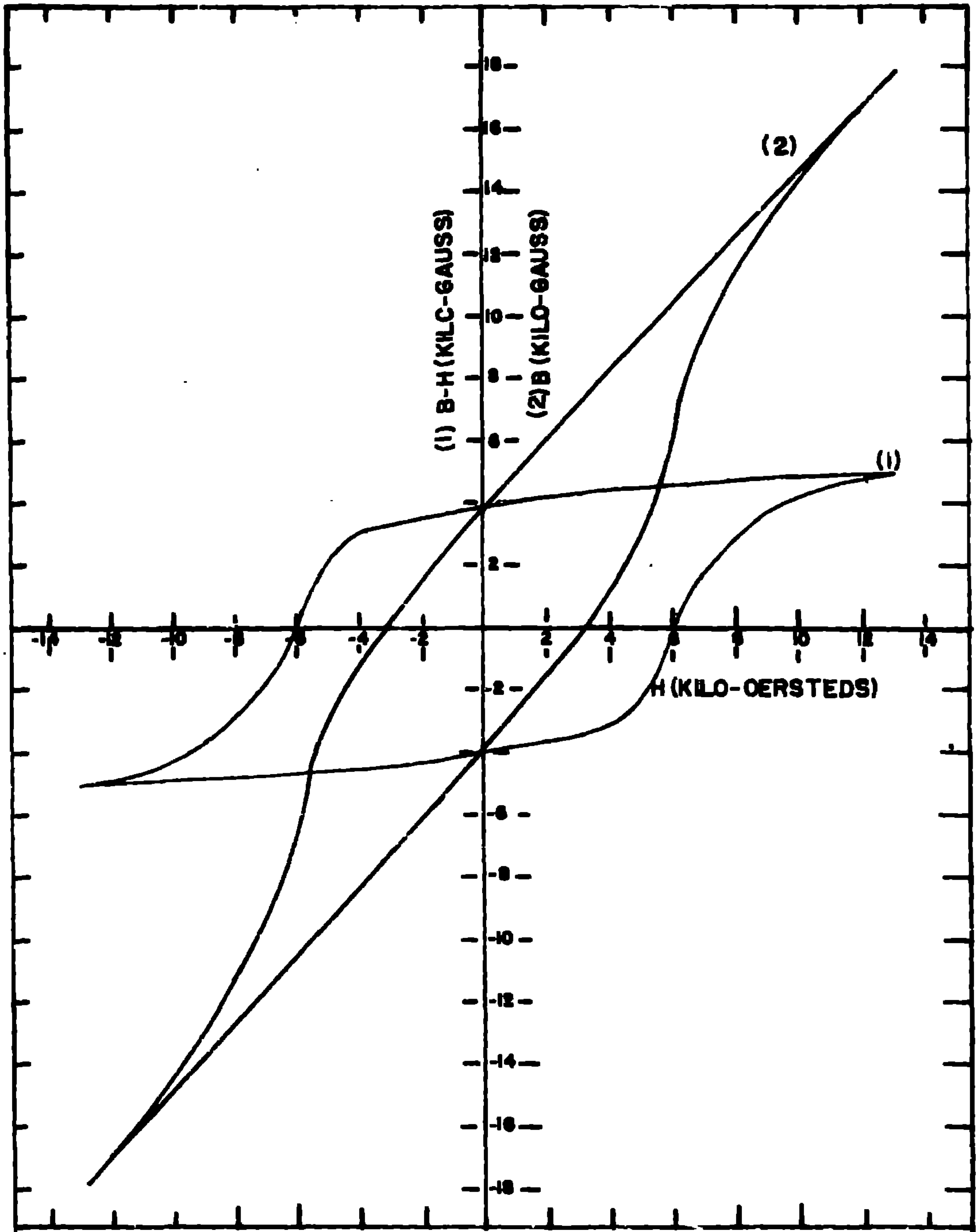


FIG. 2 - NORMAL AND INTRINSIC HYSTESIS LOOPS-BISMANOL

(A)

MIKROPULVERIZED
MAGNETICALLY SEPARATED

(B)

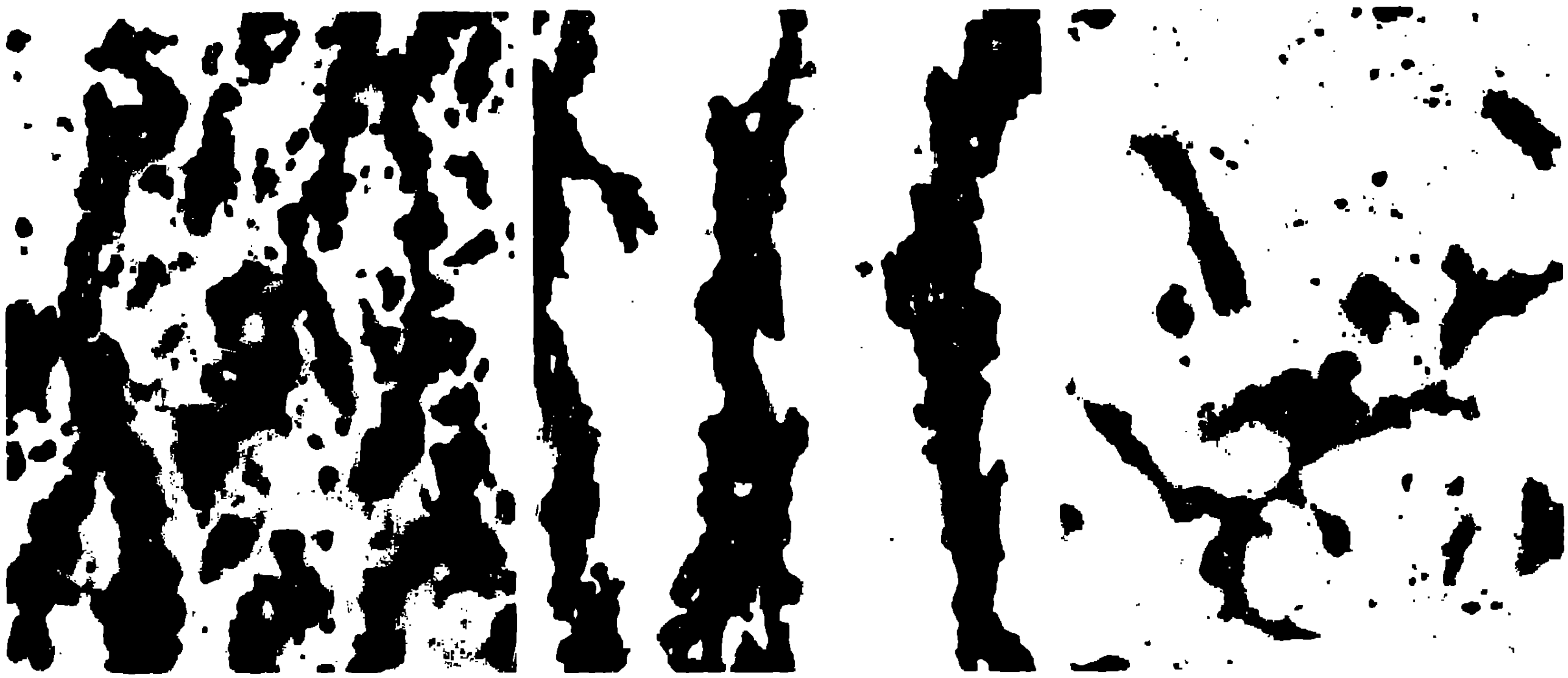
MIKROPULVERIZED PLUS
WET COLLOID-MILLED
AS GROUND

(C)

MIKROPULVERIZED PLUS
WET COLLOID-MILLED
CLUSTERING AFTER BRIEF
EXPOSURE TO MAGNETIC
FIELD

FIG. 3 PHOTOMICROGRAPHS OF MnBi POWDER

10 μ



(D) MIKROATOMIZED AS GROUND

(E) BALL-MILLED CRYSTALS CONTINUOUS ALIGNMENT IN MAGNETIC FIELD

(F) BALL-MILLED CRYSTALS BACKGROUND MATERIAL IN FOCUS

FIG. 4 PHOTOMICROGRAPHS OF MnBi POWDER

10 μ

agglomerated large magnetic particles in a background of extremely fine non-magnetic particles. This background material, shown in focus in sample (f), may be chiefly bismuth or small MnBi particles below domain size or insufficient magnetic mass to agglomerate. A typical alignment of loose MnBi particles into agglomerated chains with equidistant spacing is shown in sample (e).

17. The results of particle size estimations by surface area determinations* made by the BET nitrogen adsorption method are shown in Table II. The values appear much lower than those observed by other methods. This in part may be due to the presence of extremely fine particles in an abnormal particle distribution curve or errors in the BET method dependent on the knowledge of the exact value for the nitrogen adsorption coefficient of MnBi.

18. A semi-quantitative examination of a typical sample of MnBi powder with an electron microscope* shows a few small round particles ranging in size from 0.1 - 0.5 microns and a few cubic twin crystals from 0.2 - 0.3 microns in diameter. The bulk of the powder consists of irregular crystal fragments and clusters ranging in size from 0.1 - 10 microns.

19. Because of the various discrepancies in the particle size determinations, the method finally adopted consisted of directly comparing the intrinsic coercive force of bismanol magnets (compacted under standard conditions) with the curve of particle size versus coercive force as experimentally determined by Guillaud[1]. Assuming that these measurements were correct this gives an approximate value of the effective particle size.

COMPACTION

20. The dependence of the magnetic properties of bismanol magnets on the compacting pressure, temperature and the strength of the aligning field was established early. It was determined that the optimum compacting pressure at 300°C with an aligning field of 10,000 - 12,000 oersteds was 6,000 - 10,000 psi. A lower compacting pressure gives a lower density with slightly higher (Hc) and lower (Br) values. However, as previously shown, for high (Hc) magnets, such as bismanol, a higher (Br) value is more important for a high maximum

* Determined by the National Bureau of Standards

energy product. The temperature of pressing can vary between 300 - 325°C. Higher temperatures tend to sinter the particles thus reducing the (Hc) value. For this reason, such a combination of pressure and temperature was experimentally determined to produce magnets of optimum density, (Br), and (Hc).

21. The die-body material in which the magnets are compacted must be of non-magnetic material. Manganese-bronze, beryllium-copper and austenitic stainless steel alloys were found to be preferable, in the same order. The inside of the die was plated with chromium in order to prevent the adherence of bismuth to the walls. The rams were constructed of chromium-plated hardened carbon steel. Ferro-magnetic rams were used in order to concentrate the aligning field and close the magnetic circuit. This is illustrated in Figure 5. The filling factor for compaction in the die was approximately 5 to 1, varying somewhat with the apparent density of the MnBi powder. Bismanol magnets almost 2 inches in diameter with (BH) max values up to 5.3×10^6 have been compacted using the techniques described. (Table II). Magnets compacted in dies, where the pressing direction is perpendicular to the applied field, did not improve the quality of magnets.

PARTICLE ALIGNMENT, PURITY AND EFFECTIVE PARTICLE SIZE

22. In order to determine the degree of particle alignment and percent purity, it is necessary to know the saturation magnetization $(\sigma)_s$ per gram. This value is obtained by measuring and plotting (B) vs (H) at (H) values from 7,000 to 14,000 oersteds. Then the value of (B-H) is found for each point and (B-H) vs (H) is plotted. The value (B-H)s can then be estimated by estimating the point where this curve is flattening out or by actually subtracting (H_s) from the (B)max value. From the relation $(B = H + 4\pi I)$, (I_s) is equal to $\frac{(B-H)s}{4\pi}$. Since (I_s) is the saturation magnetization per cc, to obtain (σ)s per gram, it is necessary to divide (I_s) by the density; $\sigma s = \frac{Is}{d}$.

23. According to Guillaud[1], pure MnBi should have a magnetic moment per gram $\sigma s = 66$ at room temperature. Therefore, the ratio between the two values determines the fraction of MnBi in bismanol magnets.

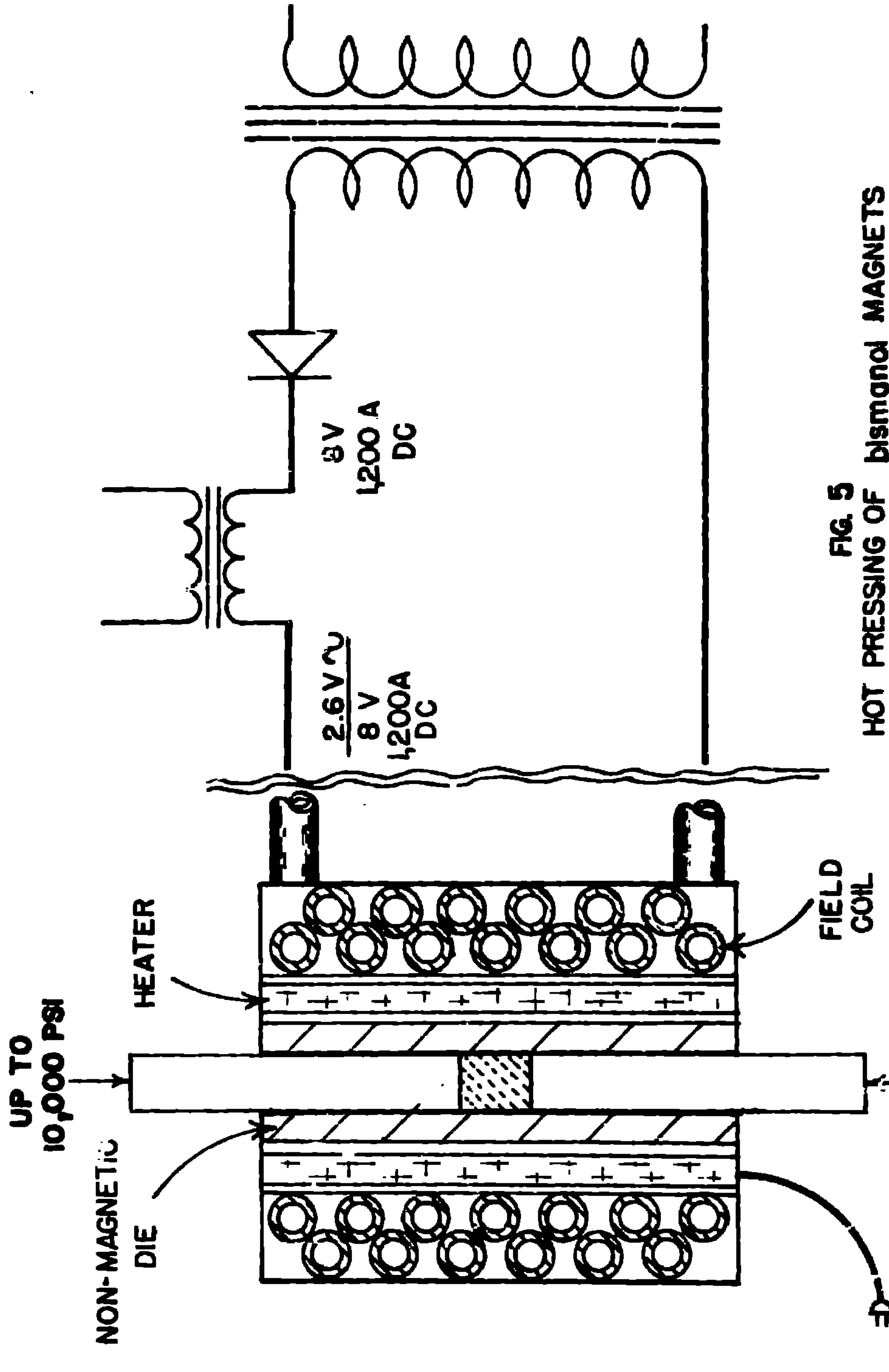


FIG. 5
HOT PRESSING OF bismanol MAGNETS
WITH AN ALIGING FIELD

24. The ratio between (B-H) at (H) = 0 and (B-H)s gives the fraction of the elementary MnBi domains aligned in the preferred direction of magnetization, because for 100 per cent alignment the (B-H) curve would be a straight line from (H) = 0 to (H) = sat.

25. The (B-H) curve is drawn down far enough to intercept the (H) axis giving the intrinsic coercive force (Hci). As previously stated, a comparison of this (Hci) value with the curve showing the dependance of the coercive force on particle size as determined by Guillaud[1] give an approximate value of the effective particle size in the pressed magnets. Table II shows values for alignment, purity and effective particle size on some bismanol magnets.

CONCLUSION

26. Bismanol magnets, after low temperature stabilization, exhibit a magnetic flux constancy over a wide temperature range with some loss in original available energy.

27. The magnets were found to be extremely stable magnetically to shock, vibration, centrifugal force and stray magnetic fields.

28. The application of some protective coating is indicated to prevent corrosion in atmospheres of high relative humidity.

29. By squeezing out excess bismuth from the bismuth-rich melt prior to pulverization, the slower procedure of magnetic separation has been eliminated.

30. A high speed hammer mill of the "Mikropulverizer" type was found to be the most satisfactory of the various types of attrition mills evaluated.

31. Bismanol magnets up to 2 inches in diameter have been compacted with various thicknesses. Such magnets are ideally suited to applications requiring high magnetic flux density, e.g., loudspeakers.

ACKNOWLEDGEMENT

32. Acknowledgement is made to the Technical Evaluation Department, especially J. T. Lamb, for conducting the evaluation studies on bismanol. Work on the improvement of processing techniques was conducted by A. M. Syeles

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