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3,404,026 METHOD OF FORMING MAGNETIC FERRITE FILMS

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ABSTRACT OF THE DISCLOSURE

A substrate is coated with an hexagonally structured magnetic ferrite film by initially mixing a solution of ferric nitrate with a solution of barium nitrate and/or a solution of strontium nitrate using stoichiometric amounts of iron, barium and/or strontium necessary to form the ferrite up to a 40 percent excess of barium and/or strontium. A substrate that is thermally stable up to a temperature of 1100° C. such as alumina or fused quartz is then immersed in the mixed metallic nitrate solution. The coated substrate is then flash fired at 950 to 1100° C. for 30 seconds in a furnace under an air atmosphere. Then, the coated substrate is removed from the furnace and cooled to room temperature in air. The above-mentioned immersion, flash heating, and cooling steps are then repeated until the desired amount of magnetic material is deposited in situ on the substrate.

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment of any royalty thereon.

This invention relates to a method of coating a substrate with a magnetic ferrite film, and in particular, to a method of coating a substrate with an hexagonally structured magnetic ferrite film, and to a substrate coated on its surface with an hexagonally structured magnetic ferrite film.

Heretofore, it has been known to coat the surface of a substrate with a magnetic ferrite film by mixing ferric nitrate or ferric alcoholate solutions with other metallic nitrate or metallic alcoholate solutions, applying the solutions to a substrate, preliminarily heating the coated substrate at 400 to 700° C., recoating to the desired thickness and then firing at 900 to 1100° C. in a controlled atmosphere. The above described method does not work however, where it is desired to coat the surface of a substrate with an hexagonally structured magnetic ferrite film. That is, certain cations such as Sr²⁺ and Ba²⁺ that will enter into the hexagonal ferrite structure are lost due to their volatility at the preliminary heating temperatures of 400 to 700° C.

An object of this invention is to provide a method of coating the surface of a substrate with an hexagonally structured magnetic ferrite film of high compositional purity by a relatively short and simple technique. A further object of this invention is to provide the surface of a substrate with an hexagonally structured magnetic ferrite film suitable for use in resonance isolators at millimeter wavelengths and in millimeter masers as the isolating element.

It has now been found that the foregoing objectives can be attained by initially mixing a solution of ferric nitrate with a solution of barium nitrate and/or a solution of strontium nitrate. The metallic nitrate solutions can be prepared using the stoichiometric amounts of iron, barium and/or strontium necessary to form the ferrite. The metallic nitrate solutions can also be prepared using up to a 40 percent excess of barium and/or strontium. A substrate that is thermally stable up to a temperature of 1100° C. such as alumina or fused quartz is then im-

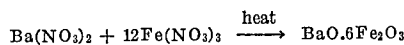
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mersed in the mixed metallic nitrate solution. The coated substrate is then flash fired at 950 to 1100° C. for 30 seconds in a furnace under an air atmosphere. Then, the coated substrate is removed from the furnace and cooled to room temperature in air. The above mentioned immersion, flash heating, and cooling steps are then repeated until the desired amount of magnetic material is deposited in situ on the substrate.

The following examples are illustrative of the invention.

Example 1

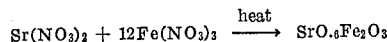
A barium ferrite BaO.6Fe₂O₃ magnetic film of hexagonal structure was prepared in the following manner. A stock solution of barium nitrate is first prepared by dissolving 15.36 grams of Ba(NO₃)₂ in 100 milliliters of distilled water. 135 grams of ferric nitrate Fe(NO₃)₃.9H₂O is then melted to a liquid and 70 milliliters of water added to keep it in a liquid state. The barium nitrate solution analyzed at 0.0800 gram per milliliter of barium, and the ferric nitrate solution analyzed at 0.1408 gram per milliliter of iron. Barium nitrate is then reacted with ferric nitrate in water and in such amounts that 1 mole of barium is present for every 12 moles of iron according to the reaction



Specifically, an aqueous nitrate solution containing a 20 percent excess of barium is prepared from the above-mentioned stock solutions by mixing 20 milliliters of the iron solution containing 2.8160 grams of iron with 8.65 milliliters of barium solution containing 0.6920 gram of barium. A substrate of 96 percent alumina is then used for film deposition. The substrate is dipped in the aqueous nitrate solution allowing the excess to flow back. Alternatively, the substrate can be coated with the nitrate solution by suitable means such as by the use of a medicine dropper. The coated substrate is then placed in a furnace and flash fired at 950 to 1100° C. for 30 seconds under an air atmosphere. The coated substrate is then removed from the furnace and cooled to room temperature in air. During this preliminary heating, nitric oxide fumes evolve causing flaking of material at varied spots upon the surface of the alumina. The flakes are gently removed and the substrate recoated with the solution repeating the above described procedure until an even coat of a desired thickness is obtained. Between 0.5 and 1.0 milligram of material is deposited during each operation. X-ray diffraction of the film shows that the hexagonal structure is obtained. To obtain a better defined crystallographic hexagonal structure, the coated substrate is fired at 950 to 1100° C. for 15 minutes after the desired amount of magnetic material has been deposited in situ on the substrate.

Example 2

A strontium ferrite SrO.6Fe₂O₃ magnetic film of hexagonal structure was prepared in the following manner. A stock solution of strontium nitrate is first prepared by dissolving 40 grams of Sr(NO₃)₂ in 200 milliliters of distilled water. Strontium nitrate is then reacted with ferric nitrate in water and in such amounts that 1 mole of strontium is present for every 12 moles of iron according to the reaction



Specifically, an aqueous nitrate solution containing a 40 percent excess of strontium is prepared from the stock solutions by mixing 20 milliliters of the iron solution (from Example 1) containing 2.8160 grams of iron with 6.16 milliliters of strontium solution containing 0.5100 gram of strontium. The substrate and coating technique is the same as in Example 1. X-ray diffraction studies

show that an hexagonal structure is obtained. Firing the coated substrate at 950 to 1100° C. for 15 minutes after the desired amount of magnetic material has been deposited in situ on the substrate improves the crystallographic hexagonal structure.

In Examples 1 and 2, the thickness of the coated substrate is determined by weighing out prescribed amounts of deposited material on the selected substrate, the selected substrate having a definite specified area. The substrate thickness is measured before and after deposition of the coating with a sensitive instrument such as an electronic micrometer. The calculated film thickness is then correlated with the weight of material deposited on the specified area. Once a correlation is made, only a deposited weight is required over a specified area.

The substrate used is not critical; all that is required is that it be temperature stable up to 1100° C. Alumina or fused quartz have been found to be most useful as the substrate.

A further extension of the invention is the plating or coating of the magnetic film over or on a surface of any geometry required for a specific design application. In such a case, the material plated or coated must be able to withstand the firing temperatures needed to form the magnetic film structure.

What is claimed is:

1. The method of coating a substrate with an hexagonally structured magnetic ferrite film including the steps of

- (1) mixing a solution of ferric nitrate with a solution of at least one nitrate of a metal selected from the group consisting of barium and strontium, using stoichiometric amounts of iron, barium and strontium necessary to form the ferrite up to a 40 percent excess of barium and strontium.
- (2) immersing a substrate that is thermally stable up to 1100° C. in the solution,
- (3) flash firing the coated substrate at 950 to 1100° C. for 30 seconds in a furnace under an air atmosphere,

(4) removing the coated substrate from the furnace and cooling the coated substrate to room temperature in air, and

(5) repeating the immersion, flash firing, and cooling steps until the desired amount of magnetic material is deposited in situ on the surface of the substrate.

2. The method according to claim 1 wherein the coated substrate is fired at 950 to 1100° C. for 15 minutes after the desired amount of magnetic material has been deposited in situ on the surface of the substrate to obtain a well defined crystallographic hexagonal structure.

3. The method according to claim 1 wherein the substrate is fused quartz.

4. The method according to claim 2 wherein the substrate is fused quartz.

5. The method according to claim 1 wherein the substrate is alumina.

6. The method according to claim 2 wherein the substrate is alumina.

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