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To cite this version:

HAL Id: jpa-00217027
https://hal.archives-ouvertes.fr/jpa-00217027
Submitted on 1 Jan 1977

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ADVANTAGES OF THE FLUIDIZED BED TECHNIQUE FOR THE PREPARATION OF HARD FERRITE POWDERS

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Résumé. — On décrit la préparation de poudres de ferrite dur par réaction à l'état solide dans un lit fluidisé. On rapporte les propriétés magnétiques et céramiques de ces poudres, qui ont été préparées à partir d'oxydes de fer pigmentaires, soit régénérés soit naturels. Les résultats démontrent que la technique du lit fluidisé peut être appliquée à la préparation d'aimants frittés et plastiques de hautes performances.

Abstract. — Preparation of hexaferrite powders by means of a solid state reaction in a fluid bed furnace is described. Magnetic and ceramic properties of these compounds, which were prepared starting from pigmentary, regenerated and natural iron oxides are reported. Results show that the fluidized bed technique is suitable for high performance plastically bonded and ceramic magnets.

1. Introduction. — In the production process of both ceramic and plastically bonded permanent magnets, the preparation of hexaferrite powders (firing) is of essential importance for the performance of the final products [1]. Their magnetic properties are in fact determined by the chemical and geometrical properties of the powders as well as by the chemical composition, purity, particle size, size distribution, etc.

In recent years besides conventional methods, a number of wet and dry methods have been proposed for the production of hexaferrite powders [2, 3, 4, 5]. Some of these methods are well suited to prepare fine and homogeneous powders at a laboratory scale, but not for an industrial production.

Of these methods which could be used as alternative to the rotary kiln furnace, the fluidized bed reactor represents a promising substitute, as it allows the continuous production of fine and homogeneous powder at temperatures below those used in conventional furnaces [6].

We report here some results of experiments carried out with the fluidized bed reactor at a laboratory scale for the preparation of hexaferrites starting from different iron oxides, which show the advantages of this technique for the preparation of higher performance hexaferrite powders.

2. Experimental procedures. — The discontinuous laboratory fluid bed reactor we used is schematically shown in figure 1.

It consists of a vertical Pythagoras tube $\varnothing = 38$ mm, flanged at the two extremities and heated by an electrical oven. The gas distributor is a Pt grid.

Experiments were carried out with the following raw materials:

- Pigmentary iron oxides derived from FeSO$_4$.7H$_2$O
  - $a$FeOOH (99.5 %), $S = 0.38$ %, needle
shaped, $S_{\text{BET}} = 13.1 \text{ m}^2/\text{g}$ ($S_{\text{BET}} = \text{specific surface area}$);
- $\alpha Fe_2O_3$ (99.5%), obtained by the calcination of the previous goethite at ca 800°C, $S = 0.3\%$, $S_{\text{BET}} = 3.5 \text{ m}^2/\text{g}$;
- $Fe_3O_4$ (99.2%), $S = 0.40\%$, $S_{\text{BET}} = 3.5 \text{ m}^2/\text{g}$.

- Regenerated Ruthner iron oxide
  - $aFe_2O_3$ (98.0%), ca $0.5\% Fe_3O_4$, $d_a$ taken with a mercury pycnometer, in vacuum, on loose powders after firing. From figure 2 which reports the magnetic values vs temperature, we observe that all samples are fully reacted at 1050°C because the $\sigma_s$ values correspond to the theoretical value. Independently of $\sigma_s$ measurements we carried out X-ray powder diffraction which confirmed the magnetic measurements results. Hexaferrites from $aFe_2O_3$ are nearly reacted even at 1000°C.

When starting with very fine and acicular $\alpha$-FeOOH [7], it has been found that reaction with SrCO$_3$ takes place at a higher temperature (750 vs 600-650°C) which depends apparently on the change of shape [8] of the reacting iron oxide powder. Consequently, the reaction products exhibited very high $H_{ci}$ values, compared to those obtained by reacting pigmentary $aFe_2O_3$. Between 1100 and 1150°C we observed a considerable reduction of $H_{ci}$ values, especially with pigmentary $aFe_2O_3$ and $aFeOOH$, due to the particle size growth.

Figure 3 shows the increase of the densities and the decrease of the specific surface area measurements as a function of the firing temperature. It can be seen that the samples prepared from $\alpha$-FeOOH are the ones that have the greatest specific surface areas, the lowest densities and the highest $H_{ci}$. T. E. M. micrographs of
the hexaferrite powders from $\alpha$Fe$_2$O$_3$ are reported in figure 4 and show the shape, size and agglomeration of the particles as a function of the firing temperature. Up to 1100°C we observe small single magnetic monodomain particles, having an average size of the order of magnitude of the magnetic monodomain. At 1150°C and higher temperatures the particles are agglomerated and grow to sizes bigger than the monodomain particle size. Starting with the other oxides we have obtained almost the same results. Hexaferrites obtained at 1100°C are well shaped, with an average particle size of $d_{10} = 0.4$ μm which strongly adhere to each other due to magnet forces. These powders are not suitable to be magnetically oriented during the pressing process and, moreover, the pressed samples have rather low density (< 50%).

Figure 5 shows S. E. M. micrographs of samples obtained from pigmentary $\alpha$FeOOH, fired at 1150°C and 1200°C, respectively. It is worth noting here the homogeneous and regular hexagonal platelet-like shape of the particles. Due to these properties, samples fired at 1150°C were shown to be suited for oriented plastically bonded and anisotropic ceramic magnets. Crystal size is well known [9, 10] to be dependent not only on the firing temperature but also on the Fe$_2$O$_3$/SrCO$_3$ ratio. At 1250°C, with pigmentary $\alpha$Fe$_2$O$_3$, we have in fact found that by changing the molar ratio from 5.9 to 5.5 the particle size increases remarkably, while from 5.5 to 5.1 it remains almost the same.

To obtain powders which are fully reacted, the reactor soaking time can be shortened when the firing temperature rises. A soaking time of 30 minutes at 1250°C is enough to have strontium hexaferrite powders fully reacted.

The heating rate of the reagent mixture to reach the firing temperature does not greatly affect the microstructure and the size of the hexaferrite powders.
Experiments, performed by heating the reagent mixture (SrCO₃ + 5.7 Fe₂O₃) at 5, 10, 15 °C per minute give nearly the same crystal sizes. The mixing procedure of the reagents was shown not to influence too much the oxides reactivity [12]. Reagent powders, wet and dry mixed, have reacted at the same rate at 1 125 °C.

On pigmentary αFe₂O₃ the hexaferrite powder preparation has been carried out also at a pilot plant size, with a continuous fluidized bed reactor having an internal diameter of 156 mm. Results obtained with this reactor have confirmed laboratory results as far as size and magnetic properties are concerned. With these industrial reactors, to reach the established temperatures, a subsidiary gas burner is needed. In this case some precautions must be taken to have a uniform heat distribution in order to avoid local inter-particle sintering which may cause the sticking of the bed.

4. Conclusion. — The main advantages of the fluidized bed technique are:

I) Magnetic powders can thoroughly reacted at temperatures lower than those necessary with conventional methods. As a result we have submicronic particles (i.e. single magnetic domain), weakly adhering to each other. Size particle can be controlled by varying the temperature. Lower firing temperatures avoid the volatilization of earth alkali oxide [13].

II) The good thermal control of the continuous stirred reagent particles, together with the small micropellet sizes, give homogeneous powders, fully reacted even with slightly reactive reagents. The narrow particle size distribution gives high $H_c$ values with better properties of the final products [14].

III) Magnetic powders obtained in a fluid bed need only a dispersion for plastically bounded magnets and a mild milling for anisotropic ceramic magnet. The short milling time reduces the contamination, as a result we have a more accurate control of the Fe/Sr(Ba) ratio.

As a conclusion, we believe that the fluidized bed technique is very promising and particularly suitable for high performance materials.

References