

Hard ferrite magnets based on La-Co substituted M phase

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I. Introduction

Since their discovery in the 50's, hard ferrite permanent magnets have constantly enjoyed a growing market. As of today, there are the essential components of the automotive auxiliary motors. These applications always require higher magnetic properties, namely remanence (Br) and coercivity (H_{c_j}), in order to increase the power and / or decrease the volume of the motors. These magnets are based on the magneto-plumbite M phase $SrFe_{12}O_{19}$ or $BaFe_{12}O_{19}$.

Research to improve the magnetic properties has been focused on two routes. One way is to precisely control the microstructure through better control of the process parameters. For this purpose some additions were found to be very effective : SiO_2 inhibits the abnormal grain growth at sintering at the benefit of H_{c_j} , while $CaCO_3$ favours a controlled grain growth at the benefit of Br. Another way is to substitute some elements for Sr (or Ba) and/or Fe which modify the intrinsic properties of the M phase, namely its magnetization M_s , thus the Br of the magnet, and its anisotropy field H_a , thus the H_{c_j} of the magnets : compounds such as Al_2O_3 and Cr_2O_3 provide ions such as Al^{3+} and Cr^{3+} which substitute for Fe^{3+} in M phase, which increases H_a , thus H_{c_j} . All these components are used on an industrial basis in order to set Br and H_{c_j} at the right compromise, to fulfil the motor application needs. Nevertheless none of them allows to increase both Br and H_{c_j} properties.

II. Experimental

La^{3+} having the right ionic radius, it might substitute for Sr^{2+} (or Ba^{2+}), but it must be coupled with another ion in order to compensate the electro-neutrality : Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} then substitute for Fe^{3+} . In particular, and as early as 1961 [1], Co^{2+} was demonstrated to be a good candidate : Smolenskii et al, in their study of the substituted $BaFe_{12}O_{19}$ phase, were the first to show that replacing a part of Ba^{2+} by La^{3+} and replacing the same amount of Fe^{3+} by Co^{2+} allows to increase H_{c_j} . A similar result was then obtained in $SrFe_{12}O_{19}$, as suggested by [2], which is not surprising because of the crystallographic and magnetic similarities of $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ and because of the full Ba/Sr continuity in the $Ba_{1-y}Sr_yFe_{12}O_{19}$ system [3-4]. Despite these promising features, the La-Co substituted M phase was not industrially used for permanent magnets because these substitutions affect the microstructure in a way such that it is difficult to use them with the same permanent magnet process than the one used for the La-Co free M phase. In the early 90's, Carbone Lorraine started a development program aiming to adapt the processing conditions allowing to draw all the benefit of these substitutions.

III. Results and discussion

For most of permanent magnets [5], including hard ferrites [6], the intrinsic coercivity is related to the anisotropy field H_a and to the microstructure (α , βMs) with the equation $H_{c_j} = \alpha H_a - \beta Ms$ (1), where βMs is the local demagnetisation field relative to grain shape, and α describes the phenomenological effect of the grain surface. Equation (1) shows that H_{c_j} is increased either by increasing H_a or by increasing the microstructure efficiency (α , βMs).

	$Ba_{1-x}La_xFe_{12-x}Co_xO_{19}$		$Sr_{1-x}La_xFe_{12-x}Co_xO_{19}$	
	H_a (kA/m)	Clinker H_{c_j} (kA/m)	H_a (kA/m)	Clinker H_{c_j} (kA/m)
x = 0	1353	224	1496	302
X = 0.1	1424	220	1607	306
X = 0.2	1496	253	1727	341
X = 0.3	1568	290	1814	374
X = 0.4	1592	321	1838	397

Table 1 : H_a and H_{c_j} measured on the starting clinker both at room temperature in LaCo-M phases with Ba and Sr

		Br (mT)	H_{c_j} (kA/m)	dH_{c_j}/dT (kA/m/°C)
LaCo-M	FXD-11C	450	320	+ 0.7
	FXD-11D	440	360	+ 0.7
	FXD-11E	430	400	+ 0.7
M based	FXD-6D	390	360	+1.0

Table 2 : LaCo-M based grades, and for comparison a LaCo free M based grade.

Table 1 shows the dramatic increase of both H_a and clinker H_{c_j} as a function of the substitution ratio up to $x = 0.4$. In this range, the process is optimised so that the clinker microstructure coefficients remain constant at $\alpha \sim 0.5$ and $\beta Ms \sim 500$ kA/m. It is concluded that the H_{c_j} improvement is essentially due to H_a increase with x . This is one of the particular features of the combined La and Co substitution : whereas Co alone substitutes for Fe in the tetrahedral site in M and decreases H_a [4], the H_a increase with x observed here suggests that Co occupies a different site in the crystal structure.

IV. Conclusion

Using a self developed know-how, we have been able to transform the intrinsic properties here above into permanent magnet properties, adapting the raw materials mixing conditions as well as the calcination conditions. On the basis of a substitution ratio, Carbone Lorraine has launched its new FXD-11 series (Table 2), which combines all the improvements performed during the past five years, and which offers the market several grades at a level of worldwide record.

V. References

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