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THERMAL STABILIZATION TREATMENT AND MAGNETIC PROPERTIES OF CrO_2 POWDERS MODIFIED WITH VARIOUS ADDITIVES

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Résumé - Un traitement thermique a été utilisé pour prévenir la dégradation chimique des poudres de CrO_2 pur et de CrO_2 ayant différentes teneurs d'additifs (Fe, Sb, Te). Ce traitement ne modifie les propriétés magnétiques que dans le cas des poudres ayant une forte teneur en fer. Cet effet est attribué à une migration des atomes de fer de l'intérieur vers la surface des particules.

Abstract - A thermal stabilization treatment which prevents the chemical deterioration of CrO_2 powders is applied to pure CrO_2 and CrO_2 having different contents of additives (Fe, Sb, Te). The treatment changes the magnetic properties only for powders having a high Fe content. The effect is ascribed to a possible migration of Fe atoms from the bulk to the particle surface.

1 - INTRODUCTION

A new process for the stabilization of CrO_2 powders against degradation of magnetic properties has been described in a previous paper [1]. In this method the powders after preparation (stage 1), are heated at 623 K in a N_2 flux for 3 h (stage 2) and then washed in deionized water and dried at 333 K (stage 3). This work analyses the influence of such a stabilization process on the magnetic properties of the powders. Three samples have been prepared according to the following procedure (stage 1). Sample A is obtained by precipitation of hydrated chromic hydroxide from a solution of chromium chloride and heating at 623 K at 300 atm. for 48 h in oxidizing atmosphere [2] without introducing foreign elements into the crystal lattice (pure CrO_2). Samples B and C were prepared by spray-drying of an aqueous solution of $\text{Cr}_2(\text{CrO}_4)_3 \cdot n\text{H}_2\text{O}$ with $n = 10$ or 11 , and subsequent treatment at 623 K and 300 atm. [3]. B was doped with Fe (0.15% by weight) and Te (0.05%), C with Fe (2.5%) and Sb (0.15%). Then, each sample has been subjected to the stabilization process (stages 2 and 3).

2 - EXPERIMENTAL RESULTS AND DISCUSSION

The magnetic measurements were made on diluted aggregates of particles (macroscopic packing fraction = 0.08). The parameters evaluated are the following:

H_{ci} = Intrinsic coercivity	H_r = Remanence coercivity
1-S* = Switching Field Distribution	W_{rmax} = Peak of the rotational loss
R = Rotational hysteresis integral	H_{amax} = Maximum anisotropy field (deduced from the rotational loss W vs. $1/H$)
σ_s = Sat. magnetization per unit mass	

The results are reported in Table I. $H_{\text{ci}\parallel}$ and $H_{\text{ci}\perp}$ are the intrinsic coercivities measured in the parallel and perpendicular direction with respect to the particle alignment. σ_r/σ_s is the squareness ratio.

2.1 Coercivity, anisotropy and S.F.D. - From the values of H_{ci} and H_r measured on random particle aggregates of type A and B, the stabilization treatment is found to produce only weak variations (Table I). However, from the values of $H_{\text{ci}\parallel}$ and $H_{\text{ci}\perp}$ mea

Table I - Magnetic parameters of diluted aggregates of particles.

Sample	random							aligned				
	H_{ci} (Oe)	H_r (Oe)	1-S*	$W_r \text{ max}$ $\frac{\text{erg}}{\text{cm}^3} 10^{-4}$	R	$H_a \text{ max}$ (Oe)	σ_s emu/g	$\frac{\sigma_r}{\sigma_s}$ (σ_s at $H = \infty$)	$H_{ci//}$ (Oe)	$H_{ci\perp}$ (Oe)	$\frac{H_{ci//}}{H_{ci\perp}}$	1-S*
A ₁	440	550	0.568	7.40	1.12	2600	84	0.750	365	410	0.89	0.370
A ₂	470	585	0.638	7.98	1.09	2700	84	0.784	490	400	1.23	0.418
A ₃	440	550	0.615	7.04	1.01	2500	84	0.738	440	330	1.30	0.409
B ₁	600	685	0.466	11.3	1.22	3000	89	0.842	585	610	0.96	0.339
B ₂	565	655	0.495	10.2	1.32	2900	82	0.879	545	415	1.31	0.363
B ₃	580	670	0.483	10.3	1.14	2950	82	0.896	550	390	1.41	0.345
C ₁	705	800	0.470	12.9	1.29	4200	84	0.899	665	550	1.21	0.298
C ₂	310	370	0.580	5.14	1.44	3900	73	0.849	265	210	1.26	0.358
C ₃	460	530	0.540	8.90	1.39	3300	84	0.834	430	330	1.30	0.330

sured on aligned particles aggregates of type A and B, the stabilization treatment is found to produce an increase of the difference between $H_{ci//}$ and $H_{ci\perp}$ and particularly of the ratio $H_{ci//}/H_{ci\perp}$ (Table I and Fig. 1). This effect may be considered as an improvement of the uniaxial anisotropy of the particles, and it is ascribed to the reduction of local anisotropies, at the particles surface, lying not parallel to the long axis. The maximum anisotropy fields (estimated as the fields at which the rotational hysteresis disappears) of samples B are higher than the fields of samples A (Table I). For samples C, having a high dopant content (Fe-2.5%), the thermal treatment drastically reduces H_{ci} , H_r , $H_{ci//}$ and $H_{ci\perp}$ (Table I and Fig. 2), but it produces only a weak reduction of H_{amax} (sample C₂). The successive washing partially restores the values of various coercivities, but reduces H_{amax} (sample C₃). The values of H_{ci} and H_r of sample C₃ are close to those of pure CrO₂. The following explanation accounts for the variations produced by thermal treatment on sample C. According to [4] and [5], the magnetic improvements of the material produced by the Fe dopants are due to the partial substitution of Cr ions by Fe ions (the chemical formulation is reported by [5]) in the CrO₂ matrix where the exchange interactions Cr-Fe are stronger than the Cr-Cr interactions. A migration of some Fe dopants from the bulk

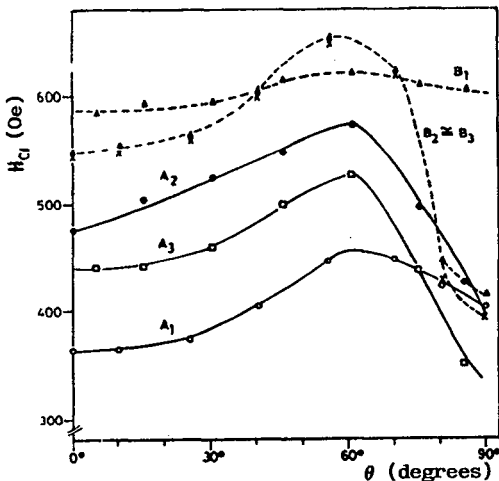


Fig.1-Coercivity vs. angle between alignment and magnetizing field directions.

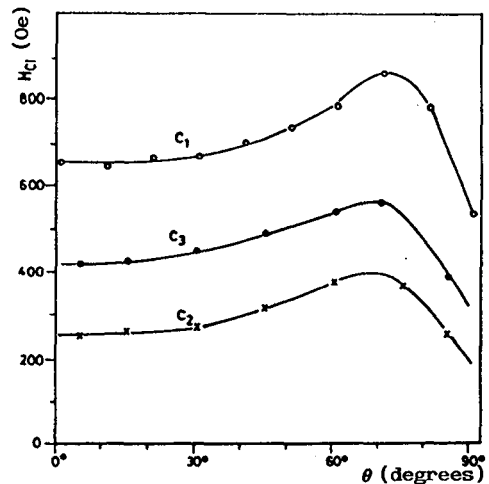


Fig.2-Coercivity vs. angle between alignment and magnetizing field directions.

of the particles to the surface is believed to be caused by the thermal treatment. Probably, part of these atoms gives rise to a non-magnetic phase, therefore σ_s decrease (see σ_s of sample C_2 of Table I) [6]. On the other hand the increase of Fe dopants percentage at particle surface enhances the canted structure [7] and the anisotropy dispersion. The dispersion of the magnetic moments at the particle surface reduces the coercivity because it favours the incoherent magnetization reversal, and increases the switching field distribution which is represented by the parameter $1-S^*$ [8]. The successive washing at 333 K partially restores the Fe dopants in the CrO_2 matrix (Table I).

2.2 Rotational hysteresis and magnetization reversal - For all the samples the values of the rotational hysteresis integral are characteristic of an incoherent rotation of the magnetization (Table I). As regards samples of type A, it is difficult to distinguish between a "fanning" or a "curling" mechanism because the order of magnitude of the reduced coercivity as well as the reduced diameter of the particles lie in the range where the values of R are approximately the same for both models [9]. However, from the behaviour of H_{Ci} vs. θ (Fig. 1) we believe that the prevailing mechanism is the "fanning" one [10]. By increasing the dopant amount (samples B and C) both the peak of the rotational loss and the integral R increase. Particularly, the value of R for aligned particles of type C is very high; they are $R_{C_1} = 1.82$, $R_{C_2} = 2.80$, $R_{C_3} = 2.03$. These values would be typical of a "curling" [9]. Nevertheless, since similar high values of R have been obtained on spheroidal isotropic particles of Co-doped $\gamma-Fe_2O_3$ [11] and it has been assumed that they are due to the multiaxial anisotropy, we believe that also for CrO_2 particles of type C (particularly C_2) the misorientation of the magnetic moments at the particles surface is responsible for the high values of R.

2.3 Magnetic measurements at low temperature and Curie point - Some magnetic parameters are measured at 76 K and compared with the values at room temperature. Table II tabulates the ratio between the coercivity at 76 K and the coercivity at 293 K. The same ratio is also made for the remanence coercivity H_r , and for the saturation magnetization per unit mass σ_s . Generally, the ratios both of the coercivities and of the remanence coercivities are higher than the corresponding ratios of the saturation magnetizations. This fact confirms that the coercivity is not only due to the shape anisotropy, but also to the magnetocrystalline anisotropy (for pure CrO_2 samples too). We found that the relationship of Köster [12]: $H_r = \alpha H_k + \beta M_s$, where H_k is the magnetocrystalline anisotropy field and α and β are constants, is verified in our case by using the experimental values of M_s and the theoretical dependence of H_k from the temperature [13]. This result confirms that for all samples the coer-

Table II - Comparison between some magnetic parameters measured at 76 K and $T_0=293$ K

Isotropic sample	$H_{Ci}(T=76K)/H_{Ci}(T_0)$	$H_r(76K)/H_r(T_0)$	$\sigma_s(76K)/\sigma_s(T_0)$	$H_r/M_s(76K)$	$H_r/M_s(T_0)$
A_1	1.62	1.50	1.30	1.49	1.72
A_2	1.63	1.61	1.34	1.46	1.75
A_3	1.50	1.55	1.26	1.49	1.82
B_1	1.36	1.42	1.36	1.69	1.78
B_2	1.46	1.50	1.28	1.74	2.04
B_3	1.43	1.46	1.24	1.73	2.02
C_1	1.47	1.46	1.27	2.15	2.48
C_2	1.54	1.52	1.34	1.18	1.40
C_3	1.40	1.40	1.30	1.40	1.51

civity depends both on the shape anisotropy [14] and on the magnetocrystalline anisotropy and the variations of the magnetocrystalline contribution with the temperature is approximately the same for all samples. The total contribution of the magnetocrystalline anisotropy to the coercivity increases with dopant contents (see the ratio H_r/M_s of Table II). Sample C_1 shows the highest value of H_r/M_s because it contains the highest percentage of dopants, but our thermal treatment drastically reduces this ratio (see sample C_2) and the successive washing only partially restores the initial value. The reduction of H_r/M_s is a consequence of the reduction of H_r ascribed to Fe migration as described in Section 2.1. Finally, we found that also the Curie temperature T_c of the samples with high Fe percentage decreases by thermal treatment. For samples C_1 , C_2 and C_3 we found respectively $T_c = 152^\circ\text{C}$, $T_c = 125^\circ\text{C}$ and $T_c = 140^\circ\text{C}$. According to [4,15] the Curie temperature of CrO_2 increases with Fe dopants because of the Cr-Fe exchange interactions. Now, the migration of some Fe ions and the corresponding increase of the anisotropy dispersion at the particle surface reduce the contribution due to such interactions and T_c decreases. The washing partially eliminates the Fe ions at the surface, but the particles remains deprived of some Fe dopants so that the Curie temperature does not recover its initial value.

In conclusion, the stabilization process here described generally improves the magnetic parameters, but for samples with high Fe content (samples of type C) it gives rise to a degradation of the magnetic properties and the successive washing partially restores them. We studied a suitable thermal stabilization treatment, for the powders with high Fe content, which produces a satisfactory chemical stabilization without remarkable variations of the magnetic properties. The results concerning this later subject will appear in a next paper.

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