



Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in : <http://oatao.univ-toulouse.fr/> Eprints
ID : 11666

To link to this article : DOI:10.1016/0965-9773(95)00061-5
URL : [http://dx.doi.org/10.1016/0965-9773\(95\)00061-5](http://dx.doi.org/10.1016/0965-9773(95)00061-5)

To cite this version :

Laurent, Christophe and Blaszczyk, Christophe and Brieu, Marc and Rousset, Abel *Elaboration, microstructure and oxidation behavior of metal-alumina and metal-chromia nanocomposite powders.* (1995) Nanostructured Materials, vol. 6 (n° 1-4). pp. 317-320. ISSN 0965-9773

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@listes-diff.inp-toulouse.fr

ELABORATION, MICROSTRUCTURE AND OXIDATION BEHAVIOR OF METAL-ALUMINA AND METAL-CHROMIA NANOCOMPOSITE POWDERS

Ch. Laurent, Ch. Blaszczyk, M. Brieu and A. Rousset
Laboratoire de Chimie des Matériaux Inorganiques, URA CNRS 1311,
Université Paul-Sabatier, 31062 Toulouse cedex, France

Abstract- Metal-Al₂O₃ and metal-Cr₂O₃ nanocomposite powders have been prepared by selective reduction in hydrogen of oxide solid solutions. The metallic phase (either Cr or an (Fe, Cr) alloy) is present in the form of nanometric particles inside and/or at the surface of the oxide matrix grains. The microstructure of the different composites has been compared and their air oxidation behavior has been investigated. The metal particles located in the open porosity of the matrix are totally oxidized at temperatures lower than 600°C, whereas those intragranularly located are stable up to 800°C. The oxidation behavior is generally complex and explanations in relation to the powder microstructure are proposed.

INTRODUCTION

In a previous study (1) on Fe-Al₂O₃ and Fe_{0.8}Cr_{0.2}-Al₂O₃ nanocomposite powders prepared by selective reduction of oxide solid solutions, it was shown that the homogeneity and specific surface area (S_w) of the solid solution had a strong influence on the size and location of the metal particles (MP). Most of the MP are smaller than 10 nm in size and dispersed inside the alumina grains. However, due to the solubility limit of Fe₂O₃ in Al₂O₃ (10 wt%) large MP (≥ 30 nm) may be formed upon reduction. The addition of Cr₂O₃ enhances this solubility, leading to a lesser amount of such MP in the composite powder. A decrease in S_w also leads to a smaller average size of the MP. In this study we have prepared Cr-Al₂O₃ and (Fe, Cr)-Cr₂O₃ nanocomposite powders and investigated their microstructure and oxidation behavior, as well as that of Fe_{0.8}Cr_{0.2}-Al₂O₃ powders.

EXPERIMENTAL

Binary and ternary oxide solid solutions between Al₂O₃, Cr₂O₃ and Fe₂O₃ were elaborated by thermal decomposition and calcination in air of mixed oxalate precursors (1). Calcination at 1100°C allowed to crystallize the solid solutions in the stable α phase and reduce their S_w . Reduction in pure, dry hydrogen at 1050°C (20 h), 1200°C (2 h) and 1300°C (5 h) gave rise to the Fe_{0.8}Cr_{0.2}-Al₂O₃, (Fe, Cr)-Cr₂O₃ and Cr-Al₂O₃ nanocomposite powders respectively. The metal content was 10 wt%, except for the oxidation of the Fe_{0.8}Cr_{0.2}-Al₂O₃ composites in which specimens containing from 2 to 30 wt% of metal were studied. Characterization of the powders was carried out by TEM, XRD (λ Co K α = 0.17902 nm), room temperature ⁵⁷Fe

Mössbauer spectroscopy and thermogravimetric analysis (TGA) in flowing air (heating rate 3°C/mn).

RESULTS AND DISCUSSION

Microstructure

Whatever the composition of the composite, XRD patterns analysis revealed the presence of two phases : the oxide matrix (α -Al₂O₃ or α -Cr₂O₃) and the metallic phase. The metal is in the α (bcc) form as shown by the {110} peak, which is the only one detected. A Mössbauer study (2) of the Fe_{0.8}Cr_{0.2}-Al₂O₃ powders has shown that Fe³⁺ ions were still present in the specimens prepared by reduction at 1050°C and that the real chromium content in the alloy particles varied with the MP size, the smaller ones being chromium-richer. This technique showed that iron in the (Fe, Cr)-Cr₂O₃ specimen is totally in the metallic state and that 1200°C was a high enough temperature to form (Fe, Cr) alloy particles. Chromium content is about 3% in the ferromagnetic particles, and may be higher in the paramagnetic (or superparamagnetic) ones. It was not possible to determine the real metal content in the Cr-Al₂O₃ composite, but its pink-grey colour reveals a rather poor reduction of the oxide solid solution.

TEM observations (Fig. 1) of the Cr-Al₂O₃ and (Fe, Cr)-Cr₂O₃ nanocomposite powders showed that most of the MP are dispersed within the matrix grains and that their size distribution is very narrow. The average size of the MP was calculated from measurements on the TEM micrographs and found to be 8 nm and 11 nm in Cr-Al₂O₃ and (Fe, Cr)-Cr₂O₃ respectively. These microstructures are very homogeneous owing to two reasons : firstly, Al₂O₃ and Cr₂O₃ on the one hand and Cr₂O₃ and Fe₂O₃ on the other hand form complete solid solutions and secondly, calcination at 1100°C decreased the S_w of the α -Al_{1.8}Cr_{0.2}O₃ and α -Cr_{1.8}Fe_{0.2}O₃ solid solutions to small values (2.5 and 0.9 m²/g, respectively).

Oxidation behavior

Fe_{0.8}Cr_{0.2}-Al₂O₃ powders containing from 2 to 30 wt% of metal were heated in air up to 1200°C, kept 2 hours at this temperature and cooled down to room temperature. Oxidation occurs in several steps as shown by the differential thermogravimetric (DTG) curves (Fig. 2a). Five peaks (I-V) corresponding to different phenomena were observed and can be divided in two groups : I-II-III occurring at temperatures lower than 600°C and IV-V occurring at

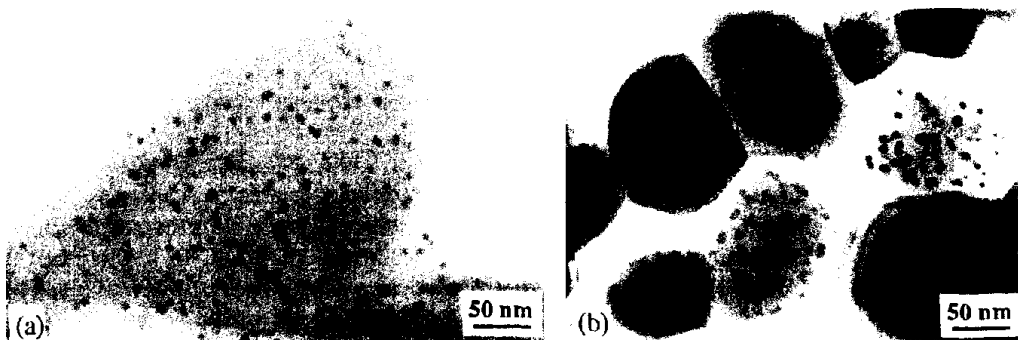


Figure 1. TEM micrographs of the Cr-Al₂O₃ (a) and (Fe, Cr)-Cr₂O₃ powders (b).

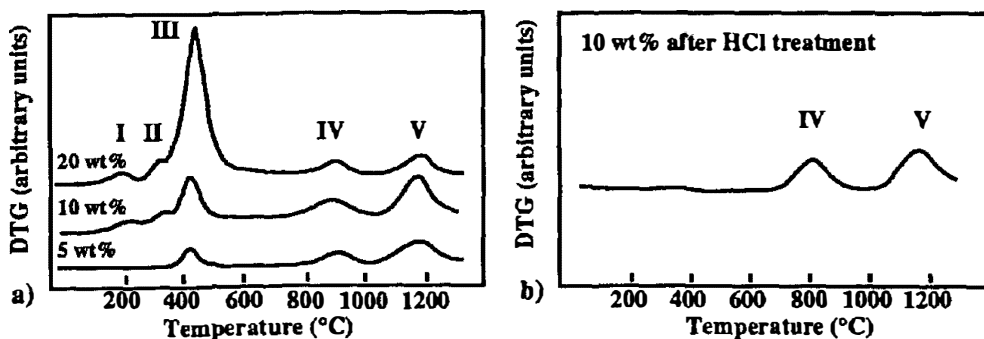


Figure 2. a) DTG curves of 5, 10 and 20 wt% Fe_{0.8}Cr_{0.2}-Al₂O₃ powders; b) DTG curve of 10 wt% Fe_{0.8}Cr_{0.2}-Al₂O₃ after HCl treatment.

temperatures higher than 800°C (Fig. 2a, 3a). Indeed, the relative intensity of peaks I-II-III increases with the increase in metal content, whereas that of peaks IV-V decreases (Fig. 3b). It was supposed that the former ones corresponded to the oxidation of the MP located at the surface and in the open porosity of alumina and the latter ones to that of the intragranular MP. This is evidenced by the DTG curve of a 10 wt% Fe_{0.8}Cr_{0.2}-Al₂O₃ powder which had been treated in HCl (boiling, 1 mol/l) prior to the oxidation run (Fig. 2b) : peaks I-II-III are not present anymore as the corresponding MP were dissolved by the acid. Peaks IV-V remain unchanged because the matrix grains, which were not affected by the acid treatment (3, 4), protected the MP dispersed within. The weight gain measured after the oxidation runs revealed that the metal had not been fully oxidized. This was confirmed by XRD analysis and Mössbauer spectroscopy. Both these techniques as well showed that the oxidation product is based on α -Fe₂O₃. Fe²⁺ ions were not detected by Mössbauer spectroscopy, even in specimens quenched at 300 and 900°C. This is in agreement with the results of Bhide and Date (5), who have shown that iron clusters dispersed in alumina are first converted into α -Fe₂O₃ and finally react with the alumina to give substitutional Fe³⁺ ions in the corundum lattice. However, other studies (6, 7) have shown that FeAl₂O₄-type and FeCr₂O₄-type species can form during the oxidation of iron and iron-chromium alloy nanoparticles. Such species could be present in our specimens, in a

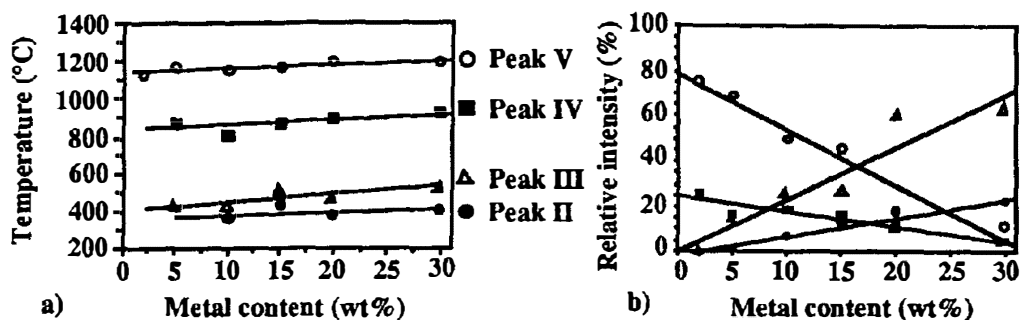


Figure 3. Temperature (a) and relative intensity (b) of the four main oxidation peaks.

certain temperature range, but in a too small amount to be detected by Mössbauer spectroscopy ($\leq 4\%$). Some of the DTG peaks may thus be related to $\text{Fe}^0 \rightarrow \text{Fe}^{2+}$ oxidation phenomena and some others to $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ reactions.

The 10 wt% (Fe, Cr)- Cr_2O_3 powder had a very similar oxidation behavior, with some differences in phenomena temperatures and a stronger preeminence of "high temperature" peaks ($\geq 700^\circ\text{C}$), owing to the higher proportion of intragranular MP. The 10 wt% Cr- Al_2O_3 specimen was expected to have a more simple oxidation behavior since Cr^{2+} ions will not form. However, it proved to be even more complex than the previous ones, six oxidation peaks being detected at 90, 150, 320, 840, 1000 and 1200°C . Unsupported chromium nanoparticles are fully oxidized at 450°C (8). XRD analysis showed that the oxidation product is based on $\alpha\text{-Cr}_2\text{O}_3$. Assuming that the first three peaks are representative of the oxidation of chromium particles located in the open porosity of alumina, their temperature could be related to the diameter of the pores. A possible explanation for the observed high temperature phenomena could be the formation of an oxide "shell", surrounding the metallic "core", which would prevent further oxidation before it is dissolved into the alumina matrix. However, such a "core/shell" microstructure was not observed by TEM investigations. Strains developing at the particle/matrix interface during the oxidation process, which are known to modify the diffusion coefficients of the involved species (9) could as well cause a blocking of the reaction until their relaxation owing to the increase in temperature.

CONCLUSIONS

The size distribution of the metal particles is unimodal (about 10 nm) when the starting oxides form an homogeneous solid solution ($\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$). The nanometric metal particles located in the open porosity of the matrix are totally oxidized at temperatures lower than 600°C , whereas those intragranularly dispersed are stable up to 800°C . The oxidation products are of the $\alpha\text{-Fe}_2\text{O}_3/\alpha\text{-Cr}_2\text{O}_3$ type. The oxidation behavior is surprisingly complex and needs further studies.

REFERENCES

1. X. Devaux, Ch. Laurent and A. Rousset, *Nanostruct. Mater.* **2**, 339 (1993)
2. Ch. Laurent, J.J. Demai, A. Rousset, K.R. Kannan and C.N.R. Rao, *J. Mater. Res.* **9**, 229 (1994)
3. A. Rousset and J. Pâris, *Bull. Soc. Chim. Fr.* **10**, 4009 (1968)
4. A. Rousset and J. Pâris, *Bull. Soc. Chim. Fr.* **10**, 3729 (1972)
5. V.G. Bhide and S.K. Date, *Phys. Rev.* **172**, 345 (1968)
6. C.J. McHargue, P.S. Sklad, C.W. White, G.C. Farlow, A. Perez and G. Marest, *J. Mater. Res.* **6**, 2145 (1991)
7. S.A. Sethi and A.R. Thölen, *Nanostruct. Mater.* **2**, 615 (1993)
8. J. Xu, X.K. Sun, A.Q. He, W.D. Wei and W.X. Chen, *Nanostruct. Mater.* **3**, 253 (1993)
9. B. Domenichini, Doctoral thesis, University of Burgundy, Dijon, France (1993)