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EFFECT OF V_2O_5 ON SPINEL FORMATION

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INTRODUCTION

In the accompanying article, by the term ferrite is meant a compound of trivalent iron and some univalent or divalent metal and accompanying oxygen. The structure is the spinel structure. This material is ferrimagnetic inasmuch as it has a permeability much greater than air, and a nonzero spontaneous magnetic moment. Some of the materials are magnetically "hard" but most are not.

It is suggested that the mechanism of ferrite formation here discussed might be related to the problems involving corrosion of metals, including stainless steel, when subjected to exhaust fumes containing vanadium.

EFFECT OF V_2O_5 ON SPINEL FORMATION

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It is well known that certain substances act as mineralizers or fluxes inasmuch as they promote solid-state reactions. We have found and reported elsewhere* that V_2O_5 has such an effect upon a mixed nickel zinc ferrite. Further, we found that V_2O_5 seemed to be quite unique in this action. We have now extended our investigations to include Fe_2O_3 plus V_2O_5 and the following compounds: NiO, ZnO, Li_2CO_3 , CdO, MnO_2 , $MnCO_3$, Fe_2O_3 , $CoCO_3$, Co_2O_3 , MgO, CuO, BaO and CaO. All materials used were commercially available CP materials.

The mole fraction of materials added were .4925 Fe_2O_3 plus .0075 V_2O_5 plus .5000 RO or equivalent in the case of the higher valent forms and of the carbonates. The amount was also adjusted for the lithium and barium compounds. In each case a control with .5000 Fe_2O_3 plus .5000 RO was made. Each material was pressed into a toroid with a green OD of 25.4 mm. The material was fired four hours at 950°C.

We use as a criterion for reaction completeness the final OD of the sample containing no vanadium minus the final OD of the sample containing vanadium. The results are shown in the table.

*"Effect of V_2O_5 on Nickel Zinc Ferrite Formation," D. M. Grimes, L. Thomassen, C. F. Jefferson, N. C. Kothary. J. Chem. Phys. To be published.

Comparison of Shrinkage Caused by V₂O₅ Addition

Reaction Furthered		Reaction Retarded		Reaction Unaffected	
Material	ΔOD (mm)	Material	ΔOD (mm)	Material	ΔOD (mm)
NiO	2.2	CuO	-0.6	CaO	0.2
ZnO	3.6	Co ₂ O ₃	-0.5	BaO	-0.06
CdO	3.0	MnO ₂	-0.6		
MnCO ₃	3.1				
Li ₂ CO ₃	2.4				
Fe ₂ O ₃	1.0				
CoCO ₃	2.0				
MgO*	0.6				

*Fired at 1100°C.

The difference in strength of attraction to an external magnet, in the case of the inverted spinels, was roughly equivalent to the difference in OD with the exception of the MnCO₃ material, which was not attracted to a magnet.

Previous magnetic measurements on nickel zinc ferrites showed that the difference in magnetic properties obtained using V₂O₅ could be repeated by increasing the firing temperature. It remains to be determined if this is also true for materials such as MgFe₂O₄ which normally require a higher firing temperature.

The mechanism by which V₂O₅ produces these results is uncertain. However, two methods are suggested: (1) The melting temperature of V₂O₅ is 895°C.** It is possible that the vanadium liquifies and dissolves some neighboring oxides. These in turn precipitate out as the spinel. Experimentally it was found that the material at no time underwent appreciable plastic flow. (2) Perhaps the vanadium goes into the spinel lattice as V⁵⁺, thus necessitating cation vacancies on the B sublattices, and thereby promoting diffusion. Method (2) would explain the action of CuO by presuming that in the neighborhood of the V⁵⁺ the copper cation would go from the plus two to the plus one

**Handbook of Physics and Chemistry, Chemical Rubber Publishing Company.

valance state, thereby not only removing the vacancies but also placing blocks of three cations which must diffuse together and would thus block other diffusion. Likewise Co^{3+} and Mn^{4+} would presumably go to Co^{2+} and Mn^{2+} . It is possible that both mechanisms prevail.

Neither Ca^{2+} or Ba^{2+} form an iron spinel.

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