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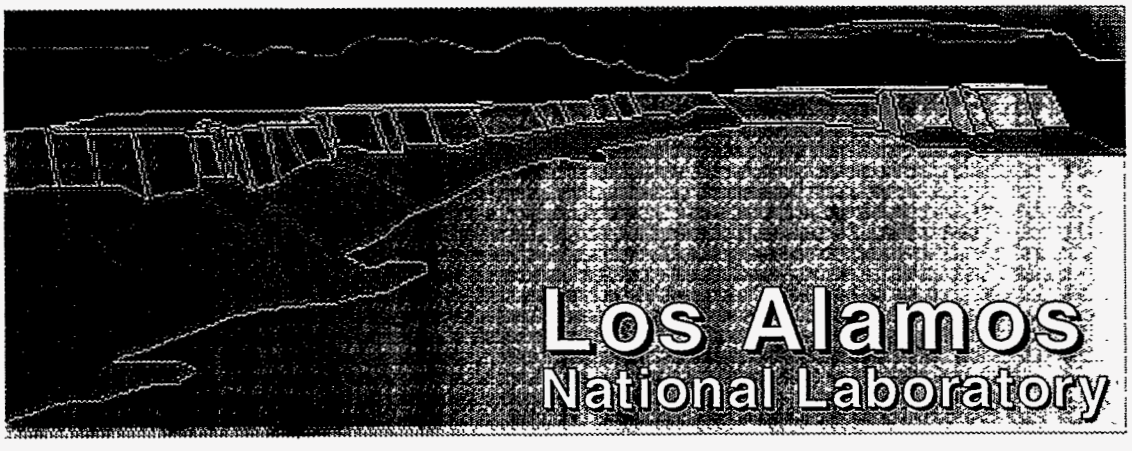

BOROHYDRIDE REDUCTION: A TECHNIQUE TO SYNTHESIZE NANOSIZE TRANSITION METALS, REDUCED TRANSITION METAL OXIDES AND NANOCOMPOSITES

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Introduction

Sodium borohydride was recognized forty years ago as an effective reducing agent for metal ions in aqueous solutions [1]. The reduction of metal ions M^{2+} with borohydrides can be represented as [2]

$$BH_4^- + M^{2+} + 2H_2O = M + BO_2^- + 2H^+ + 3H_2$$

The advantage of the borohydride reduction technique is to synthesize extremely fine (nanosize to amorphous) material at room temperature. The use of borohydrides to generate magnetic metallic particles such as Co, Fe and Ni has been relatively well studied [3-5]. However, use of the borohydride reduction to synthesize transition-metal oxides and nanocomposites is relatively new. Manthiram's group [6-9] was the first to show that borohydrides can be used to reduce oxo-ions $(MO_4)^{n-}$ (M=Mo, W, or V) to obtain reduced transition metal oxides. They also showed [10, 11] that borohydrides can be used to obtain nanocomposites such as Fe-$Al_xB_yO_z$ at ambient temperatures. This paper summarizes some recent studies of using borohydride reduction to synthesize W, transition metal oxides such as WO_2 and MO_2, and Fe-$Al_xB_yO_z$ magnetic nanocomposites.

Transition-Metals Oxides

It is found [6-9] that borohydride-reduction of Na_2WO_4 and Na_2MoO_4 solutions gives at ambient temperature amorphous reduced oxides such as $Na_{0.55}WO_3$, WO_2, and MoO_2. During the reduction, the valence state is reduced from W^{6+} to $W^{5.45+}$ in $Na_{0.55}WO_3$, to W^{4+} in WO_2, and Mo^{6+} to Mo^{4+} in MoO_2. These oxides crystallize around 350-500°C to give nano-crystalline oxides. They also give nanocomposite upon crystallization if several oxide phases are formed during the synthesis process.

The general procedure of borohydride reduction is as follows. The metalates (Na_2W_4, and Na_2MoO_4) were dissolved in distilled water to make the desired metalate solution. NaOH or HCl were added to the solution until the desired reaction pH value is reached. Solid $NaBH_4$ was dissolved in water and its pH value was pre-adjusted to 10 to suppress the evolution of hydrogen. The borohydride solution was added to the metalate solution, which was constantly stirred with a magnetic bar on a stirrer, while adjusting the reaction pH with dilute NaOH or HCl to the desired value. After the reduction, the solid formed was either filtered or centrifuged to remove the unreacted solution. The solid was washed several times with water or dilute $NaBH_4$ solution and then dried in an air oven at 100 °C. The as-obtained powder was then used for further heat treatment in an evacuated sealed quartz tube to form nanocrystalline material.

Shown in Figs. 1 and 2 are X-ray powder diffraction patterns of $WO_2 + W_{18}O_{49}$ and MoO_2 obtained using the above procedure. $WO_2 + W_{18}O_{49}$ was obtained by adding 50 ml of 2.6M $NaBH_4$ to 50 ml of 0.25M Na_2WO_4 at pH=1, while MoO_2 was obtained by adding 50 ml of 2.6M $NaBH_4$ to 50 ml of 0.25M Na_2MoO_4 at pH=1.

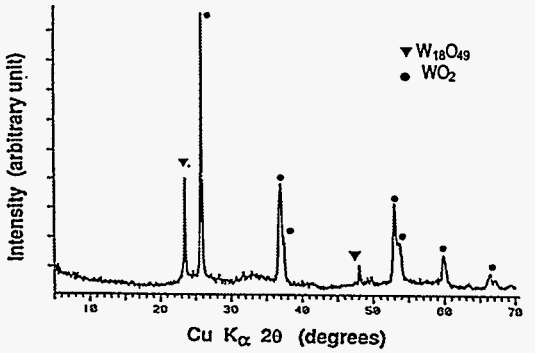

Fig. 1 X-ray powder diffraction pattern of WO_2+$W_{18}O_{49}$ (fired in vacuum at 550°C overnight).

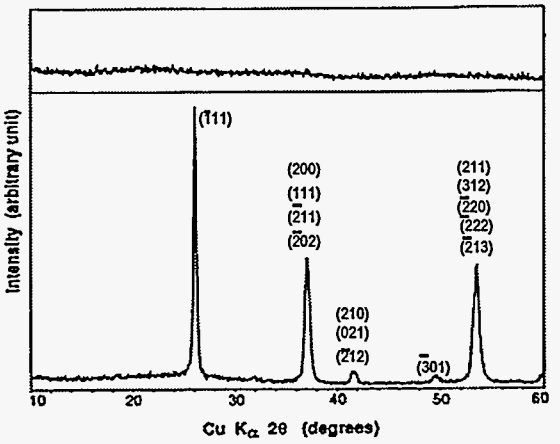

Fig. 2 X-ray diffraction pattern of MoO_2: a) as-prepared; b) after heating in DSC up to 470°C at a heating rate of 10 °C/min.

Metallic Tungsten and an Unknown New Phase

Tungsten metal and an unknown new phase have also been obtained at pH=11 using the procedure mentioned in the last section. The x-ray patterns of these phases are shown in Figs. 3a and 3b [6]. The as-prepared samples are all amorphous; after heating at 900 °C in evacuated sealed quartz tubes overnight, they show strong X-ray reflections.

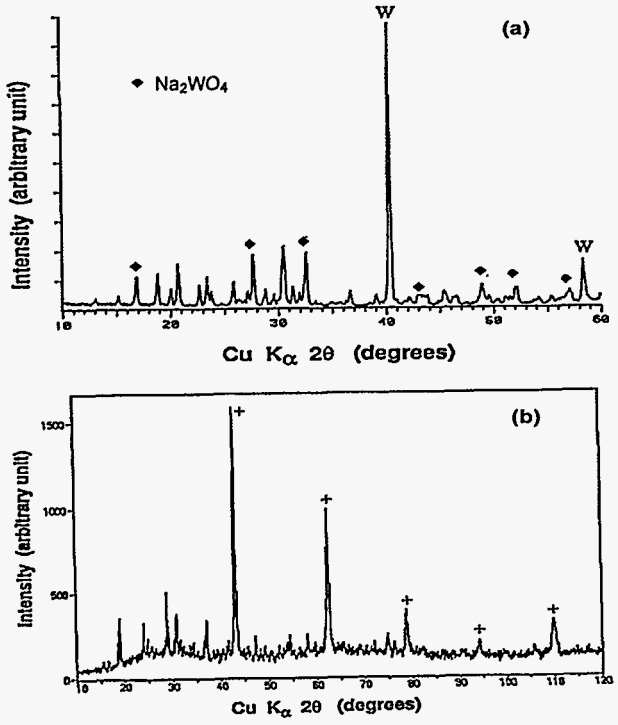

Fig. 3. X-ray diffraction patterns: a) W with some impurity was obtained with 50 ml of 0.25M Na_2WO_4 reduced by 5g of $NaOH_4$ in 50 ml of water; b) A new phase with a cubic structure not corresponding to any known compound was obtained with 50 ml of 0.125M Na_2WO_4 reduced by 20g of $NaOH_4$ in 100 ml of water.

Fe-$Al_xB_yO_z$ Magnetic Nanocomposite

Fe-$Al_xB_yO_z$ magnetic nanocomposite has also been synthesized using borohydride reduction [10, 11]. Fifty ml each of 0.1 M $FeSO_4 \cdot 7H_2O$ and 1 M $NaBH_4$ were prepared in distilled water, and then rapidly added simultaneously to an aluminum tri-sec-butoxide solution diluted with isopropyl alcohol. The black precipitates form in the solution but remain in suspension due to continuous mechanical stirring. The nano-sized precipitates were captured in a filter and rinsed with water and acetone. Shown in Fig. 4 are the X-ray patterns after the precipitate was annealed in H_2 at different temperatures. A weak reflection around $2\theta = 45°$ corresponding to iron from the as-prepared sample indicates that the particle size is very small. Subsequent annealing in H_2 resulted in sharpening of the Fe reflections and a crystallization of aluminum borate at T>800°C.

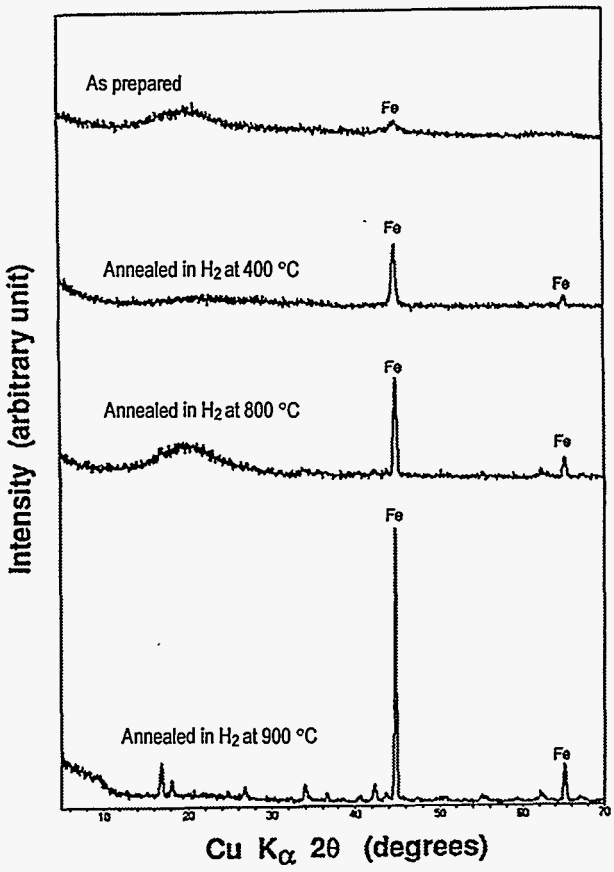

Fig. 4. X-ray diffraction patterns of Fe-$Al_xB_yO_z$ magnetic nanocomposite.

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