the corrosion products found at the electrode interfaces of alkali metal/sulfur cells. Corrosion impedes the development of these cells, and thus any new insight into this problem will be useful in designing suitable electrode materials.

It is evident that this is an exciting new synthetic area and thus far only the surface has been scratched. The bulk of this work and even more interesting chalcogenides are yet to come.

Acknowledgment. I thank three synthetically gifted students, Y. Park, J.-H. Liao, and S.-P. Huang for their dedication and hard work and for making this article possible. I also thank Professor Harry Eick for helpful suggestions and Dr. Robert C. Haushalter, Exxon, for preparing Figure 22 and useful discussions. Financial support from the National Science Foundation for a Presidential Young Investigator Award, CHE-8958451, is gratefully acknowledged.

Articles

Amorphous Metallic Powders Prepared by Chemical Reduction of Metal Ions with Potassium Borohydride in Aqueous Solution

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Amorphous metal–metalloid powders have been prepared by chemical reduction of Fe^{2+}, Co^{2+}, and Ni^{2+} ions with potassium borohydride in aqueous solution. The chemical composition of the samples, TM–B–O, varies with the metal and with the preparation steps. The as-prepared Co–B–O and Ni–B–O samples are definitely amorphous, while the Fe–B–O sample mainly consists of bcc α-Fe. Crystallization of the samples through thermal treatment has been investigated by X-ray diffraction. The Co–B–O sample evolves toward fcc metallic cobalt accompanied first by metastable *o*-Co_3B and, at high temperature, by *t*-Co_2B. The Ni–B–O sample gives rise to fcc metallic Ni and *o*-Ni_3B, which decomposes at higher temperatures. Iron borides are not detected in the thermal treatment of the Fe–B–O sample. No evidence of metal oxides is present in all the samples, thus suggesting the prevalent bonding of oxygen to boron.

Introduction

The science and technology of amorphous alloys is increasing rapidly in view of some excellent physical and mechanical properties of these materials.[1]

Conventional preparation methods by rapid quenching lead to ribbons[1] and thin foils,[2] which to be compacted in a three-dimensional object need to be comminuted. To avoid grinding, which is difficult and expensive because of the high ductility of these materials, methods for preparing amorphous alloy powders are being developed: among these, several atomization techniques,[3] vapor deposition,[4] and mechanical alloying[5] have been reported. All of these methods suffer certain drawbacks that make them impractical for the preparation of significant quantities of homogeneous alloys. Wet chemical synthetic methods offer an alternative to these problems as well as the opportunity to control certain factors in order to meet the needs of the end user.

Reduction of metal salts has been widely reported for the preparation of highly dispersed and reactive metal powders with particular attention to their application in catalytic and stoichiometric chemical synthesis.[6-9] Recently the amorphous structure of metal powders obtained by reduction of metal salts with alkaline borohydrides has been outlined;[10-14] the prepared powders are very complex materials, which have properties strongly dependent upon the metals and some of the preparation steps.

Further investigations carried out on amorphous powder obtained by reduction of Ni^{2+}, Co^{2+}, and Fe^{2+} cations with KBH_4 are reported in this paper.

Experimental Section

Metallic powders containing either Co, Ni, or Fe were prepared according to Schlesinger et al.[15] and Brown and Brown.[6] In a typical preparation 0.2 mol of solid KBH_4 was slowly added, in

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Table I. Composition of the Investigated Samples

sample	Fe	Co	Ni	B	O
	composition, wt %				
Co-B-O		79 (1)		8.6 (2)	12.4
Co-B-O (450 °C)		69 (1)		*b*	*b*
Ni-B-O			84 (1)	7.6 (2)	8.4
Ni-B-O (450 °C)			73 (1)	*b*	*b*
Fe-B-O	89 (1)			5.4 (2)	5.6
Fe-B-O (450 °C)	77 (1)			*b*	*b*

[a] The samples were analyzed by standard methods for Fe, Co, Ni, and B. Oxygen was evaluated by differences. [b] Not determined.

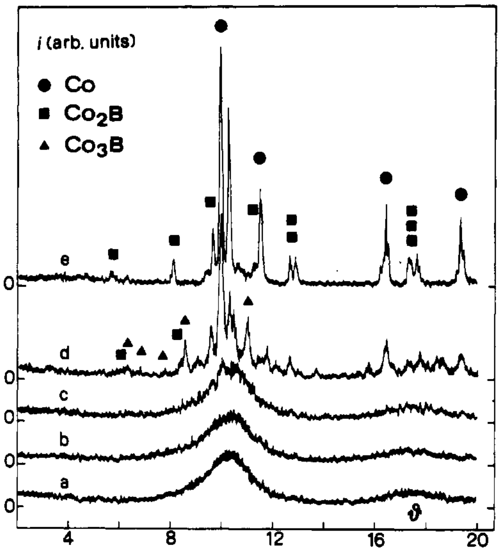

Figure 1. X-ray spectra of the Co–B–O sample as-prepared (a) and after progressive heating at 200, 350, 450, and 600 °C, respectively (b–e).

a hydrogen atmosphere, to 100 mL of 0.5 M aqueous solution of $CoCl_2$, $NiCl_2$, or $FeSO_4$ kept in an ice bath and vigorously stirred.

The resulting powders were washed in a Büchner funnel with water and then with acetone in an argon atmosphere to remove excess reagents. The washing step was found to be influential on the chemical composition of the materials, as described later. Reaction and washing procedures were therefore maintained rigorously constant in the preparation of each investigated sample. The acetone-wet powders can be handled in air; dry powders, like those of extremely fine metals, are highly pyrophoric and must be handled with extreme caution. More stable products are obtained either by slowly drying the wet precipitates in air or by drastically reducing the surface area of dry powders by pressing them into tablets before air exposure. In both cases oxidation is limited to a superficial layer that protects the bulk material.

Metal content in the samples was determined by volumetric analysis and by atomic absorption spectroscopy.[16] Boron was determined by direct current plasma technique with a Spectrometrix Spectropan IV spectrometer.

As shown in Table I the as-prepared powders have a metal content that increases from the cobalt to the iron samples, while the boron content has an opposite trend.

Unlike the recently reported powders prepared by a similar procedure,[10,13,14] the sum of the metal and boron contents is less than 100%. The difference was considered as due to oxygen, which is to a minor extent due to the superficial metal oxide, as also reported by Wells et al.[14] The major part of the oxygen is due to the presence of borates, which form as reaction byproducts;[15] this last fact accounts for the increasing oxygen content with boron.

To investigate the crystallization process, each sample was heated in an argon atmosphere for 2 h at different temperatures up to 600 °C. After each annealing step, X-ray diffraction spectra were recorded with a Seifert GSD ϑ–ϑ diffractometer, equipped with a quartz monochromator, using Mo Kα radiation. Accurate diffraction data at discrete scattering angles were collected on the as-prepared samples in order to obtain radial distribution functions. Details on data collection and treatment have also been described elsewhere.[17]

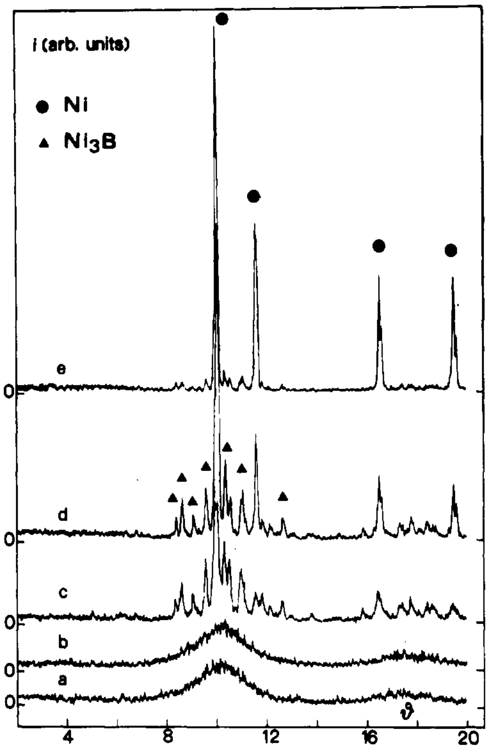

Figure 2. As in Figure 1 but for the Ni–B–O sample.

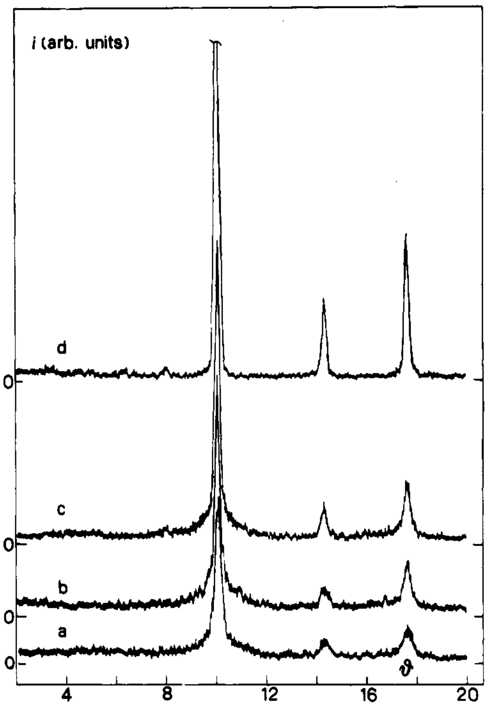

Figure 3. X-ray spectra of the Fe–B–O sample as-prepared (a) and after progressive heating at 200, 350, and 450 °C respectively (b–d).

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Results and Discussion

X-ray diffraction spectra of the as-prepared powders are shown in parts a of Figures 1–3 for Co–B–O, Ni–B–O, and Fe–B–O samples, respectively. Spectra of Co–B–O and Ni–B–O samples exhibit the characteristic pattern of amorphous substances with no evidence of any Bragg peak ascribable to crystalline phases. On the contrary, Bragg peaks that are superimposed on an amorphous halo are clearly evident in the spectrum of the Fe–B–O sample. The presence, on annealing at progressively higher temperatures, of one or more crystalline phases is evident in all samples, as shown in parts b–e of Figures 1–3.

In the Co–B–O samples, the amorphous pattern is still prevalent after the 200 °C thermal treatment (Figure 1b). Bragg peaks begin to emerge after 350 °C, and those characteristic of fcc metallic cobalt[18] and of o-Co_3B[19] are evident after 450 °C. Peaks due to hcp metallic cobalt, which should be present at this temperature,[20] are not discernible. After 600 °C o-Co_3B evolves towards the more stable t-Co_2B,[21] segregating metallic cobalt, while the grains of the fcc phase increase as shown by the higher intensity and sharpness of the pertinent peaks.

An amorphous Co–B–O sample previously prepared in our laboratory, hereafter referred to as Co–B–O(I), showed a significatively different behavior.[12] In fact, after heat treatment, Bragg peaks of the Co fcc phase are clearly evident while peaks ascribable to any of the cobalt borides were not detected. This absence can be related to the hydrolysis of the metal borides in the washing step of the precipitated powders.[22] This possibility was checked by washing some portions coming from the same sample batch with increasing quantities of water. The presence of metal borides decreased on washing and finally disappeared in the portions washed exhaustively. The process is accelerated by washing with warm water.

The diffraction spectra of the Ni–B–O samples are shown in Figure 2. As in the case of Co–B–O, heating to 200 °C does not affect the characteristic amorphous pattern. Bragg peaks due to fcc nickel[23] and o-Ni_3B[24] are evident after annealing at 350 °C, thus confirming the thermal behavior reported for a sample prepared by a very similar procedure.[25] The intensities of fcc Ni peaks increase after annealing at 450 °C, while there is a slight lowering of the Ni_3B ones due to decomposition of this metastable phase. After heating at 600 °C, Ni_3B peaks become barely detectable while those of Ni continue to increase.

The diffraction pattern of the as-prepared Fe–B–O sample shows Bragg peaks due to bcc α-Fe[26] superimposed on the halo due to the presence of an amorphous phase. The general pattern of the spectrum strongly resembles that of a $Fe_{90}B_{10}$ sample prepared by rapid quenching.[27] As for $Fe_{90}B_{10}$ no peaks ascribable to iron borides can be detected by X-ray diffraction after thermal treatment, although their presence cannot be ruled out. On the contrary the presence of t-Fe_3B and t-Fe_2B has been confirmed by X-ray diffraction in the samples with a boron content higher than 10 at. %.[27]

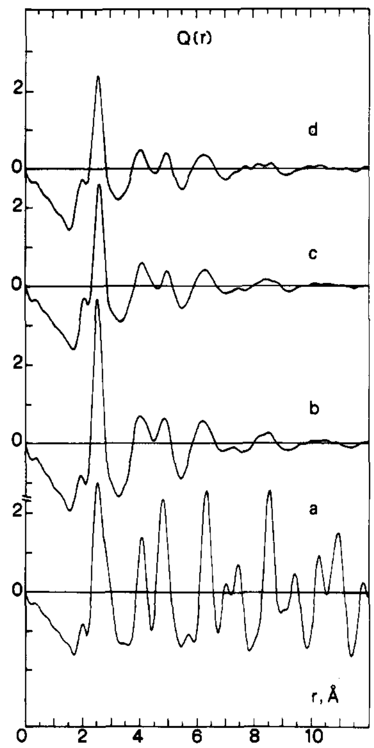

Figure 4. Radial distribution functions of the as-prepared samples: (a) Fe–B–O, (b) Ni–B–O, (c) Co–B–O(I) (see text), (d) Co–B–O.

Peaks due to metal oxides are not present in any of the spectra of the examined samples, not even after thermal treatment, although chemical analysis shows a drop of metal content after 450 °C (Table I). This fact suggests an uptake of oxygen by the samples to give amorphous borates, which appear as a faint diffuse contribution to the diffraction spectra. X-ray photoelectron spectra performed on a sample previously prepared in our laboratory[11] and on samples prepared by the same method by other workers[28] suggested that the oxygen is almost completely bonded to boron; this fact could then explain the absence of metal oxides and would also account for the low content of metal borides in Co–B–O and Ni–B–O samples and their apparent absence in the Fe–B–O sample.

Figure 4 shows the radial distribution functions $Q(r)$ of as-prepared Fe–B–O, Ni–B–O and Co–B–O samples as well as that of the Co–B–O(I) sample. The features of the $Q(r)$'s of the two Co–B–O samples are almost identical and are typical of amorphous substances with short- and medium-range structuring. Since the X-ray scattering powers of boron and oxygen are much lower than those of metals, diffraction data and the derived $Q(r)$'s are dominated by metal–metal contribution; the similarity of the $Q(r)$'s suggests therefore that metal–metal structuring in the two Co–B–O samples is unaffected by the observed significant difference in their chemical composition.

The $Q(r)$ of the Ni–B–O sample shows slightly sharper peaks, in particular the first one, suggesting at least a better defined short-range order. The features of the Co–B–O and Ni–B–O $Q(r)$'s are very similar to those of other amorphous alloys prepared by different methods, so

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that a similar metal–metal structuring can be assumed in all the samples.

The $Q(r)$ of Fe–B–O exhibits sharp peaks up to large r values, thus confirming for this compound a definitely more ordered structure than in the other two, as concluded from the appearance of the diffraction spectrum.

All $Q(r)$'s show a small peak at around 2 Å that is due to metal–metalloid interaction but, as the samples contain both boron and oxygen, a definite assignment cannot be made.

The short- and medium-range order in the as-prepared samples, as inferred by the inspection of pertinent $Q(r)$'s, increases in the sequence Co < Ni < Fe, which is opposite to the reactivity of the cations in the chemical reduction by KBH_4.[15] This suggests that high reaction rates could hinder an ordered structural organization of the products. The amorphous character also seems to be correlated with the boron content of the samples. It is, however, difficult to assess whether this depends only on the boron portion present in the metal bulk, as in the many metal–boron amorphous alloys reported in the literature,[29] or also on the relevant presence of borates; these could in fact play the role of a stabilizing matrix of the materials. The second hypothesis is instead supported in our samples by the low content of boron in the bulk, as shown by the low content or absence of metal borides in the spectra of the heat-treated samples.

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Registry No. KBH_4, 13762-51-1; Co–B–O, 126543-36-0; Ni–B–O, 126543-37-1; Fe–B–O, 126543-38-2; Co_3B, 12006-78-9; CO_2B, 12045-01-1; Ni_3B, 12007-02-2.

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Pressure Dependence of the Raman Spectra of Quasi-One-Dimensional Mixed-Valence Semiconductors and Related Complexes

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The effects of pressure on the resonance Raman spectra of the mixed-valence semiconductors $K_4[Pt_2(P_2O_5H_2)_4X]\cdot 3H_2O$, X = Cl, Br ($Pt_2X$), have been investigated. The related complexes $K_4[Pt_2(P_2O_5H_2)_4X_2]\cdot 2H_2O$, X = Cl, Br ($Pt_2X_2$), and $[(Bu)_4N]_4[Pt_2(P_2O_5H_2)_4]$ (Pt_2) have also been studied so that direct comparisons with the monohalides could be made. Reduction in the intensity of the Pt–Br and a Pt–Pt stretch in the delocalized form of Pt_2Br provide evidence for a pressure-induced structural change from a distorted ground state toward a symmetric structure in which the halogen is centrally located between adjacent Pt dimers. No significant intensity changes were observed in the trapped valence Pt_2Br or in Pt_2Cl, indicating that these complexes remain strongly trapped valence to 5.0 and 10.0 GPa, respectively. Pt_2Br_2 undergoes a pressure-induced phase transition at approximately 2.0 GPa. No transformation was observed in Pt_2Cl_2 to 7.5 GPa. Pressure effects on Raman modes associated with local defect states in Pt_2Cl, Pt_2Cl_2, and delocalized Pt_2Br are also reported. The frequencies of the defect modes shifted toward those of the analogous bulk mode with increasing pressure, suggesting that the defect states become increasingly delocalized with increasing pressure.

Introduction

Quasi-one-dimensional halide-bridged mixed-valence transition-metal complexes MX and MMX have recently received a great deal of attention as model low-dimensional solids exhibiting valence fluctuations and local gap states.[1-12] These complexes are generally in the strongly trapped valence, charge density wave limit with the halogen distorted from the central position between the metal atoms due to a Peierls instability. A new trapped valence form of $K_4[Pt_2(P_2O_5H_2)_4Br]\cdot 3H_2O$ (TV–Pt_2Br) and $K_4[Pt_2(P_2O_5H_2)_4Cl]\cdot 3H_2O$ (Pt_2Cl) are in this limit. However, an increasing number of mixed-valence solids, particularly the delocalized valence form of $K_4[Pt_2(P_2O_5H_2)_4Br]\cdot 3H_2O$ (DV–Pt_2Br), have been found to be much more valence delocalized with small distortion of the halide sublattice.[13-15] A Ni^{III}–XNi^{III} complex with no distortion of the halide has recently been synthesized.[16] An emerging

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