Synthesis and characterization of nano-structured molybdenum-iron intermetallics by gas-solid reaction technique

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Abstract. Ammonium molybdate and ferrous oxalate were used for the synthesis of nano-structured Mo-Fe intermetallics. Co-precipitation technique was applied to produce Mo/Fe precursors containing 58/42, 72/28 and 30/70 mass% respectively. The different phases formed were identified by XRD. The macro- and microstructures were microscopically examined by Reflected Light Microscope (RLM) and Scanning Electron Microscope (SEM) coupled with Electron Dispersion Spectroscopy (EDS). TG-DTA-DSC technique was applied to follow up the behavior of precursors up to 900°C (10K/min.). Endothermic peaks were detected at 97.8, 196.9 and 392.7°C due to the decomposition reactions to produce MoO₃ and Fe₂O₃. The exothermic peak resulted at 427.8°C is due to the solid state reaction between these oxides to form Fe₂(MoO₄)₃. Precursors were isothermally reduced at 600-850°C in a flow of purified H₂ and the O₂-weight loss from the reduction reactions was continuously recorded as a function of time. The isothermal reduction behavior of precursors was investigated. The structures of reduced products and the different phases formed were investigated and correlated with the reduction conditions. At >60% reduction extents, Fe₂(MoO₄)₃ phase was first reduced to Fe₂MoO₃O₈ before the formation of FeMo, while FeMoO₄ and MoO₂ were reduced to FeMo and Mo. In precursors containing higher content of Fe₂O₃, FeMo, Fe₂Mo and Fe phases were produced. The visual observation of reduced samples showed that the volume was gradually shrinking with rise in temperature up to 800°C and beyond which a measurable swelling was observed reaching about 170% at 900°C.

1. Introduction

Gaseous reduction technique is considered a promising method for the synthesis of binary and tertiary metallic alloys powder because the applied reduction temperature is fairly low compared with the traditional thermal processes. Moreover, the phase composition and the morphology of the produced alloys can be controlled by adjusting the reaction parameters such as precursor composition, particle size of reactants, reduction temperature, reducing gas, etc. The production of tailor-made materials by gaseous reduction provides an excellent process which has a positive impact on the environment by applying green energy technology. The wide range of applicability of gas-solid reaction process has not been fully explored toward the synthesis of novel complex materials. Various physical properties of solid reactants play an important role in the manner in which the reduction reactions proceed. About 90% of the world’s ferroalloys production is consumed by the steel industry.
These alloys are essential additives to steel for the inclusion of the alloying elements into the cast or to act as deoxidizers. A great attention is being devoted towards the use of intermetallic alloys as semiconductors, photovoltaic cells, chemical manufacture and special types of ceramics [1,2]. Molybdenum-Iron alloys are used in different industries such as constructional steel, stainless steel, cast iron, tool and high speed steel and super alloys. Morales et al.[3] studied the production of Fe$_2$Mo alloy from the reduction of Fe$_2$MoO$_4$ by H$_2$ in a fluidized bed reactor for the synthesis of Fe-Mo alloys having different Fe/Mo ratios[4]. Molybdenum is essential as an alloying/reinforcement agent and its properties maintain functional reliability under ever increasing temperatures for electronic and aerospace industries [5]. Fe-Mo alloy can be produced by mechanical alloying [6], by electrodeposition [7,8], by hydrogen reduction [3,9] or by ball-milling and subsequent hydrogen-reduction of MoO$_3$ powder[10]. Nanostructured Mo-Fe precursor can be synthesized by chemical co-precipitation, sol-gel, thermal, mechanical processes, etc. On the other hand, co-precipitation technique from the aqueous salts is applied for production of high purity precursors. It has been demonstrated that the co-precipitation method is most suitable compared with other routes due to its low cost in addition to its suitability for mass production. This technique offers considerable advantages, such as better mixing of the starting materials, better control over crystallite size and excellent chemical homogeneity.

The aim of the present work is to study the synthesis of Mo/Fe precursors having different Mo/Fe mole ratios from their aqueous salts using co-precipitation technique. Precursors were then isothermally reduced with H$_2$ at 650-850°C to produce nano-structured Fe-Mo intermetallics. Dry, roasted precursors and Mo/Fe intermetallics were physically and chemically characterized and correlated with the reaction mechanism.

2. Materials and experimental techniques

Wet chemical method was used for producing three Mo/Fe precursors from high purity (>99%) ammonium molybdate [(NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O] and ferrous oxalate (Fe$_2$C$_2$O$_4$.2H$_2$O) hot solutions. The mole ratios in the staff were calculated to synthesize precursors containing 58/42, 72/28 and 30/70% Mo/Fe as illustrated in Fig.1 [11] and named herein after as precursors I, II and III respectively. For a given precursor composition, pre-calculated weights of ammonium molybdate and ferrous oxalate were dissolved in hot distilled water and the aqueous solutions were mixed together, heated up to 80°C for 24hrs. with continuous stirring, then left to dryness. The solid residue was collected and mechanically ground in a ball mill for 5 hrs. The different phases in precursors were identified by X-ray diffraction (XRD). For a given precursor composition, pre-calculated weights of ammonium molybdate and ferrous oxalate were dissolved in hot distilled water and the aqueous solutions were mixed together, heated up to 80°C for 24hrs. with continuous stirring, then left to dryness. The solid residue was collected and mechanically ground in a ball mill for 5hrs. The different phases in precursors were identified by X-ray diffraction (XRD). For a given precursor composition, pre-calculated weights of ammonium molybdate and ferrous oxalate were dissolved in hot distilled water and the aqueous solutions were mixed together, heated up to 80°C for 24hrs. with continuous stirring, then left to dryness. The solid residue was collected and mechanically ground in a ball mill for 5hrs. The different phases in precursors were identified by X-ray diffraction (XRD). For a given precursor composition, pre-calculated weights of ammonium molybdate and ferrous oxalate were dissolved in hot distilled water and the aqueous solutions were mixed together, heated up to 80°C for 24hrs. with continuous stirring, then left to dryness. The solid residue was collected and mechanically ground in a ball mill for 5hrs. The different phases in precursors were identified by X-ray diffraction (XRD). For a given precursor composition, pre-calculated weights of ammonium molybdate and ferrous oxalate were dissolved in hot distilled water and the aqueous solutions were mixed together, heated up to 80°C for 24hrs. with continuous stirring, then left to dryness. The solid residue was collected and mechanically ground in a ball mill for 5hrs. The different phases in precursors were identified by X-ray diffraction (XRD).

![Figure 1. Molybdenum-iron phase diagram [11].](image-url)
The thermal behaviour of dry precursors was examined by DTA-TG-DSC analyzer (Netzsch STA 409, Germany). The magnetic properties were tested at room temperature using a Vibrating Sample Magnetometer (VSM, 9600-1 LDJ, USA) and a maximum applied field of 15 kOe. High pressure mercury pore sizer (Micrometricals Pore-sizer, 9320) was used to measure total porosity, pore size distribution, bulk and apparent densities.

Precursors were isothermally reduced at 600-850°C in a flow of purified H2 gas. The O2-weight loss resulting from the reduction reactions was continuously recorded as a function of time using TG technique. The gas purification system, reduction apparatus and the reduction technique were previously described elsewhere [12]. The reduced products were physically and chemically characterized.

3. Results and Discussion

3.1. Characterization of precursors

The different phases formed in the dry samples were examined by XRD and the patterns obtained showed the formation of less-crystalline materials. In these precursors, iron oxalate, ammonium molybdate, MoO3(H2O)0.5 and FeO(OH) were produced. The extents of these phases (expressed as I/Io) are Mo/Fe mole-ratio dependant. The crystallite size was calculated from the X-ray data using TOPAS.2 software.

Dry precursors were thermally analyzed with TG-DTA-DSC analyzer to follow up their behavior during heating to 900°C (10 K/min.) in air atmosphere. The obtained TG and DSC profiles are shown in Fig. 2 (a), (b) respectively. For a given precursor composition, the TG profile is characterized by the presence of mass loss at 97.8, 196.9 and 392.7°C in Fig. 2 (a), (b) respectively. For a given precursor composition, the TG profile is characterized by the endothermic peak obtained at 427.8°C (Fig.2b) is attributed to the solid state reaction between Fe2O3 (reaction 1) and MoO3 (reaction 4) to produce iron molybdate Fe2(MoO4)3 as follow:

Fe2O3 + 3 MoO3 → Fe2(MoO4)3

The XRD phase analysis obtained from the analysis of roasted precursors shows the presence of iron molybdate [Fe2(MoO4)3] phase in precursor I, while Fe2(MoO4)3 and α-Fe2O3 were detected in precursors II and III. This was the result of the excess iron oxalate in precursors I and III rather than the stoichiometric amount to produce [Fe2(MoO4)3]. Table 1 summarizes the phases formed in roasted precursors, their molar ratios and average crystallite sizes.
Figure 2. Thermal behavior of Mo/Fe dry precursors; (a) TG profile (b) DSC profile

Table 1. XRD phase analysis for precursors roasted at 500°C for 3hrs.

| Prec. | Composition | Phases identified | Mole ratio (%) | Crystallite sizes (μm) |
|-------|-------------|-------------------|----------------|------------------------|
| I     | 58 Mo% 42 Fe% | Fe₂(MoO₄)₃, α-Fe₂O₃ | 72.2 | 3.5 |
| II    | 72 Mo% 28 Fe% | Fe₂(MoO₄)₃, α-Fe₂O₃ | 100 | 5.8 |
| III   | 30 Mo% 70 Fe% | Fe₂(MoO₄)₃, α-Fe₂O₃ | 46.68 | 3.0 |

The internal structure developed in the roasted precursors I, II and III is depicted in Fig. 3 (a), (b) and (c) respectively. Figure 3 (a) shows the presence of relatively small numbers of coarse iron molybdate grains (light gray) embedded in large number of fine hematite grains (gray) and pores (dark gray). The structure formed in precursor II (Fig. 3 b) is characterized by well defined elongated grains having different sizes. Each of these grains are composed of large number of iron molybdate particles coalesced to form aggregates in which large sizes of pores can be distinguished. For precursor III (Fig. 3 c), the structure shows the presence of very fine particles of hematite grains (gray) together with iron molybdate (light gray). It can be noticed that the higher the iron molybdate content in the precursor, the larger the grain structure formed. The grain structure of precursors I, II and III by SEM-EDS is given in Fig. 4 (a), (b) and (c) respectively. Figure 4 (a) shows the presence of well defined iron molybdate grains (345μm) together with small grains of hematite. The structure of precursors II reveals the formation of large grains of iron molybdate (560 μm) connected together forming a relatively dense structure as shown in Fig.4 (b). The structure in precursor III (Fig. 4 c) shows the presence of large number of smaller hematite grains (194 μm) forming aggregates in which the original grains are still identified.

The total porosity and pore size distribution in roasted precursors were measured and the variation between cumulative intrusions (ml/g), incremental intrusions (ml/g) and the corresponding pore diameter (μm) are given in Fig 5 (a) and (b) respectively. The cumulative intrusion values given in Fig 5 (a) are slightly increased with the decrease in pore diameter up to about 8.5 μm then sharply increased to about 3.0 μm followed by a slight increase up to 0.42 μm. It also reveals that precursor III has finer pores than the other precursors. Fig. 5 (b) shows that the incremental pore volume slightly increased with the pore diameter in the range of macropores. In the mesopore range, the incremental value sharply increased with the decrease in pore diameter showing higher increase for precursor II.
Table 2 summarizes the measured values of pore area, average pore diameter, bulk and apparent densities measured in the precursors.

| Prec. No. | Composition | Bulk density (g/ml) | App. density (g/ml) | Pore diameter (μm) | Pore area m²/g | Porosity % |
|-----------|-------------|---------------------|---------------------|-------------------|----------------|------------|
| Ⅰ         | 58 Mo% 42 Fe% | 2.676               | 6.2947              | 0.0259            | 41.01          | 57.49      |
| Ⅱ         | 72 Mo% 28 Fe% | 2.579               | 6.4278              | 0.0223            | 38.19          | 59.87      |
| Ⅲ         | 30 Mo% 70 Fe% | 2.7622              | 5.3525              | 0.0315            | 43.45          | 48.39      |

The influence of Mo/Fe mole ratio on the magnetic properties of precursor was investigated. The M-H magnetic hysteresis loops of the roasted precursors are given in Fig.6. It can be seen that the higher saturation magnetization value (Mₛ = 4.95 emu/g) was obtained in precursor Ⅲ in which free hematite is present (Fe₂O₃ = 53.32%); while the lower value corresponding to precursor Ⅱ (Mₛ = 1.15 emu/g) was recorded.

3.2. Synthesis of Mo/Fe intermetallics

Gaseous reduction technique was applied for the synthesis of Mo/Fe intermetallics at >900°C. The reduction was carried out isothermally at 600-850°C in a flow of purified H₂ gas and the O₂-weight loss resulted from the reduction of Fe₃(MoO₄)₃ and α-Fe₂O₃ was continuously recorded as a function of time using TG technique. The extents of reduction were calculated and plotted against the corresponding reaction time. Fig.7 (a) and (b) shows the isothermal reduction behaviour of precursors containing different Mo/Fe molar ratio at 700 and 800°C respectively. They indicated that the reduction was completed and all O₂-contents in the phases were removed. For each precursor, the rate of reduction increases with rise in temperature.
Figure 5. Pore Size analysis for the roasted precursors (500°C, 3h);
(a) Cumulative intrusion (ml/g)                     (b) incremental intrusion (ml/g)

Figure 6. B-H hysteresis loop of the roasted precursors.

Figure 7. Isothermal reduction behavior of precursors; (a) at 700°C; (b) at 800°C

At a given temperature, the reduction rate of precursors increased in the order III > I > II. This indicated that the reduction rate of Fe₂(MoO₄)₃ is lower than Fe₂O₃ and the rate increases with the increase in α-
Fe$_2$O$_3$ content in precursors. The reduction kinetics and mechanism of precursors will be given and discussed in details elsewhere [13].

3.3 Characteristics of the Mo/Fe intermetallics
Nano-structured Mo/Fe intermetallics were prepared from the reduction of precursors at 600-850°C. The reduction process was carried out isothermally in H$_2$ gas flow using TG technique. The reduced samples were examined by XRD, RLM and SEM-EDS. Figs. 8-10 show the XRD patterns for precursors I, II and III reduced at 700-850°C respectively. In precursor II, where MoO$_3$ and α-Fe$_2$O$_3$ are in the stoichiometric ratio, only FeMo intermetallic was identified. In other precursors, where excess α-Fe$_2$O$_3$ is present, Fe/Mo and Fe$_3$Mo intermetallics were produced. With the increase in α-Fe$_2$O$_3$ mole ratio, metallic iron was detected. The phases identified in the reduced precursors I, II and III in H$_2$ are presented in Table 4.

Table 4. Phases identified in roasted and reduced precursors at 700-850°C.

| Prec. | Composition | Roasted samples | Reduced samples |
|-------|-------------|-----------------|-----------------|
| I     | Mo% Fe%     | Fe$_2$(MoO$_4$)$_3$, α-Fe$_2$O$_3$ | FeMo, Fe$_3$Mo |
| II    | 72 28       | Fe$_2$(MoO$_4$)$_3$ | FeMo, Mo        |
| III   | 30 70       | Fe$_2$(MoO$_4$)$_3$, α-Fe$_2$O$_3$ | FeMo, Fe$_3$Mo, Fe |

Figure 8. Phases identified in precursor I reduced at 700-850°C.

Figure 9. Phases identified in precursor II reduced at 700-850°C.

It can be seen that the Fe/Mo is the main phase identified and Fe$_3$Mo is formed in precursors I and III. The presence of metallic iron in precursor II resulted from the excess mole ratio of Fe$_2$O$_3$. In order to predict the chemical reaction equations, precursors were reduced to different extents and reaction products were analyzed by XRD. Based on the phase analysis, the following chemical reaction equations were given and discussed elsewhere [13].

a- precursor I;  
2 Fe$_2$(MoO$_4$)$_3$ + 3 Fe$_2$O$_3$ + 33 H$_2$ → 4 FeMo + 2 Fe$_3$Mo + 33 H$_2$O  (6)

b- precursor II;  
Fe$_2$(MoO$_4$)$_3$ + 12 H$_2$ → 2 FeMo + Mo + 12 H$_2$O  (7)

c- precursor III;  
Fe$_3$(MoO$_4$)$_3$ + 2 Fe$_2$O$_3$ + 18 H$_2$ → 2 FeMo + Fe$_3$Mo + Fe + 18 H$_2$O  (8)
Figure 10 Phases identified in precursor III reduced at 700-850°C.

The photomicrographs showing the internal structures (RLM) formed in the reduced precursors I, II and III at 800°C in H₂ are shown in Fig.11(a), (b) and (c) respectively. The structure given in Fig.11(a) shows the presence of fine grains of hematite and larger elongated grains of Mo/Fe intermetallics.

The structure shown in Fig.11 (c) for precursor III is characterized by the presence of small amounts of metallic iron (light) and fine grains of intermetallics. The structures of grains in reduced samples I, II and III are shown in Fig.12 (a), (b) and (c) respectively. Unlike in precursors I and III, the grain structure in precursor II is characterized by the formation of large grains in which fibers or needles made from FeMo intermetallics as was defined by EDS analysis. In precursors I and III, small grains composed of Fe₃Mo and larger FeMo grains can be distinguished. The grain structure formed in reduced precursor II at 850 and 900°C is shown in Fig.13 (a) and (b) respectively. The grains structure of the produced Fe/Mo intermetallics were changed from needle form formed at lower temperatures to grain and were composed of large numbers of smaller micrograins which are connected together forming big clusters. It can be seen that relatively smaller micrograins were formed at 850°C and enlarged by the effect of sintering at 900°C.

The visual external shape of compacts made from precursors I, II and III reduced at 650-900°C showed no remarkable changes in the visual shape of compacts from precursors I and III. For
precursor II, the samples showed deformation in shape at ≥ 850°C resulting in an increase in the volume by 175% at 875°C as shown in Fig.14.

![Figure 12. SEM image for samples reduced at 800°C; (a) Prec. I (b) Prec. II (c) prec. III](image)

1. Conclusion

Co-precipitation technique was applied for the preparation of precursors containing 58/42, 72/28 and 30/70 Mo/Fe mole% named as Prec. I, II and III respectively. The thermal behaviour of precursors was carried out up to 900°C (10K/min.) showing the presence of endothermic peaks at 97.8, 196.9 and 392.7°C in addition to an exothermic peak at 427.8°C. The endothermic peaks were due to the moisture content and the thermal dissociation reactions to produce MoO₃ and Fe₂O₃. The exothermic peak was resulted from the solid state reaction between MoO₃ and Fe₂O₃ to develop Fe₂(MoO₄)₃. The precursors were roasted at 500°C for 3hrs and were microscopically examined. In roasted samples, 72.2, 100 and 46.68 mole% of Fe₂(MoO₄)₃ were detected and the balance is being α-Fe₂O₃. Nano-structured Mo/Fe intermetallics were obtained from the isothermal reduction tests at 600-850°C in H₂ gas flow. The reduced products showed the presence of FeMo intermetallic in precursors which were resulting from the reduction of Fe₂(MoO₄)₃. In samples containing excess molar ratios of Fe₂O₃, Fe₃Mo was detected and with the increase of Fe₂O₃, metallic iron was identified. At ≤800°C, the
Mo/Fe is characterized by the formation of clusters that contain well-defined needles structure. At \( \geq 850^\circ \text{C} \), the reduced samples were swelled and the measured \( \Delta V \) values reached to 175% at 900\(^\circ\)C.

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