Hydrogen Reduction Route towards the Production of Nano-Grained Alloys.- Synthesis and Characterization of Fe$_2$Mo Powder.

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DOCTORAL THESIS

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ABSTRACT

With a view to design processes based on gas-solid reaction towards the production of fine-grained novel alloys and intermetallics, studies of the reduction of the mixed oxides of Fe and Mo by hydrogen towards the production of Fe-Mo alloys have been carried out in the present work. The route offers excellent potentials toward the bulk production of nano-grained material of tailored-composition in bulk in a green process path. As a case study, the reduction of the mixed oxides of iron and molybdenum were carried out from the viewpoint of materials processing, chemical reaction kinetics, as well as mechanical and structural properties. The reduction kinetics of thin layer of fine oxide particles of \( \text{Fe}_2\text{MoO}_4 \) was studied using thermogravimetric technique. This technique allowed determining reduction parameters such as temperature of reduction as well as the activation energies for the chemical reaction as the rate-controlling step. The end products were analyzed by X-ray diffraction. The reduction product was found to be reduced to pure, homogeneous \( \text{Fe}_2\text{Mo} \). In order to examine the upscaling of the process, production of the alloy in larger amounts was carried out in a laboratory-scale fluidized reactor and the process parameters were optimized. It was found that, under the conditions of the experiments, the chemical reaction was the rate-controlling step. TEM, SEM and X-ray analyses of the reaction product showed the presence of a monolithic intermetallic with micro- and nanocrystalline structure. The mechanical properties of this alloy were determined. Compositions of microcrystalline Fe-Mo alloys were varied by reducing mixtures of \( \text{Fe}_2\text{MoO}_4 \) with \( \text{MoO}_2 \) or \( \text{FeO} \) with different Fe/Mo ratios. The products after the reduction consisted of two phases, viz. intermetallic \( \text{Fe}_x\text{Mo}_y \) compound and metallic Fe
or Mo. XRD analyses revealed that the former had microcrystalline structure while the latter were in crystalline form.

This work shows that gas-solid reaction method, together with powder metallurgy technique is a promising process route towards the production of novel metallic alloys such as Fe$_2$Mo intermetallic with micro- and nanocrystalline grains.

**Key words:** nanoalloys, intermetallics, iron-molybdenum alloy, hydrogen reduction, thermogravimetry, fluidized bed, mechanical properties, structure
We are all spiritual beings living a human experience…

Deepak Chopra
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I am so honored. I am very proud that I have made more friends; from Mexico, Europe and overseas without their amusement I would be a lesser man.

This work is dedicated to my best friend **Fernando Chapa** from Monterrey who passed away in 1999.

Ricardo Morales Estrella

Stockholm, Sweden
September 2002
SUPPLEMENTS

This thesis is based on the following papers:


Appendix B  Magnetic and Thermal conductivity measurements of Fe$_2$Mo

Parts of this work have been accepted for presentation in the conference:
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1 Introduction

The term nanocrystalline alloy is used to describe those alloys that have a majority of grain size in a range from ~1 to 50 nm. These materials are increasingly gaining importance in modern technological advances due to their unique properties as well as the efforts to miniaturize systems. For example, nanocrystalline materials offer a large surface that could be great importance for magnetic storage media. Chemical and structural variations on a nanoscale are important for determining optimal magnetic properties. The unique microstructures of nanocrystalline materials play an important role on their mechanical properties. In contrast to coarse-grained materials, nanosized grains result in a significant fraction of grain boundaries, which, in turn, act as barriers to dislocation motion; hence, improvements on mechanical properties such as strength and hardness can be achieved. The ability to develop control over microstructure at smaller size scales is expected to have a significant impact on magnetic storage densities as well as optimized mechanical properties.

There has already been much progress in the synthesis, assembly and fabrication of nanomaterials, and, equally important, in the potential applications of these materials in a wide variety of technologies. The explosive growth of nanoscience and technology in the last decade has been due primarily because of the availability of new methods of synthesizing nanomaterials, as well as tools for characterization and manipulation. Because our capability to synthesize, organize and tailor-make materials at the nanoscale is of very recent origin, the next decade is likely to witness major progress in the discovery and commercialization of nanotechnologies and devices. These technologies are bound to have an impact on the chemical, energy, electronics, and space industries. They will also have applications in medicine and health care.

While the demand for this new class of materials with unique properties is receiving a great deal of attention, attempts are also being made to develop processes that could result in the bulk production of these materials. The current processes for manufacturing micro- and nanoscale materials structures are extremely limited with respect to upscaling. The processes normally adopted for nanoscale materials processing are plasma processing, rapid solidification, and deposition techniques where the initial material may be in the
amorphous state and subsequently crystallized. Aquous chemistry and sol-gel technique have also been adopted to produce nanopowders. The various experimental techniques aim to control chemistry and microstructural morphology on increasingly smaller length scales. Towards the production of nanoscale materials, the potentialities of gas-solid reactions have not been seriously looked into so far. In fact, in comparison to the techniques for nanoalloy production being investigated today, the gas-solid reaction route offers an interesting alternative towards the production of these materials in substantial quantities with great scope for quality assurance by the control of process parameters. Establishment of the advantages of this route towards the production of ultra-fine particles is the main scope of the present work.

Gas-solid reaction route is a versatile technique to produce metallic alloys in the form of powder. This technique allows tailor-made materials with large-scale production and rather low energy consumption per ton of product. The gas-solid route towards the production of metallic and composite powder materials has been part of a long-term research in the Division of Metallurgy. By properly choosing the starting material, the end product composition can be suitably tailored. Earlier work in the division has demonstrated the potentialities of this methods in producing transition metal alloys involving tungsten,\(^1\)\(^-\)\(^3\) as well as composite materials of the type Fe-TiO\(_2\),\(^4\) Ni-TiO\(_2\),\(^5\) and Ni-Al\(_2\)O\(_3\).\(^6\) The formation of unique alloys of the type Zn-W,\(^7\) that have not been synthesized earlier by this method has also been demonstrated.

The raw materials used in these studies are often complex oxides with particle sizes of a few microns. In many cases, even natural ores can be used to produce a composite material, which would drastically cut down the number of unit processes and thereby the energy costs. Further, all the investigations carried out in the division were with hydrogen gas as the reductant. This adds a strong environmental component to the advantage of the process. Thus, the gas-solid route adopted in the present work can, in fact, be safely classified as a “green manufacturing process”.

Production of Fe\(_2\)Mo was chosen as a case study in the present work. Structural intermetallics possess unique mechanical properties mainly suitable for high temperature
applications. Today, the commercial viability of the process for synthesizing these materials is normally limited by cost factor. Efforts are centered to make them both technically sound and economically competitive. Thus, the results of the present thesis are expected to have a strong impact on the economic production of industrially important intermetallics with micro- and nanograins.

**The Strategy Adopted in the Present Work:**

The strategy adopted in the present work was to take up a test system and investigate the linking of the properties to the process variables. The material chosen was iron molybdate, a complex oxide. The objective was to adopt this method to complex oxides that occurs in nature. The product, Fe$_2$Mo intermetallic has applications in electronic and aerospace industries. Further, the material is well suited for applications in high technology, where there is a strong need for materials that can withstand high temperatures. This is due to the outstanding refractory properties given by the crystalline structure of the intermetallic itself along with the properties of molybdenum that is attractive for application as an alloying/reinforcement agent as for example, contribution to hardness and toughness of steels and high corrosion resistance.

At the outset, the thermodynamics of the hydrogen reduction of the complex oxide was examined. As a second step, the kinetics of reduction of thin beds of pure molybdenum oxide, MoO$_3$ was studied by thermogravimetry.$^8$ The division has many years of research experience in thermogravimetric studies, which was of great benefit in carrying out the present work. In the present study, thin powder beds were used. Similar studies on the hydrogen reduction of the FeO have been carried out in the division earlier.$^3$

The next step was to study the hydrogen reduction of thin beds of Fe$_2$MoO$_4$ powder. Once again the thermogravimetric technique was used and the activation energy of the reduction reaction was established.$^9$ The product was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. The product was established to be a homogeneous Fe$_2$Mo intermetallic phase; the existence which has been a controversy over the years.
In order to produce the intermetallic phase in bulk, a suitable reactor had to be chosen. Fluidized bed technique was adopted in the present work in view of the obvious advantages.\[10\] In this method, due to excellent contact between the reactant solid and the gas, high reaction efficiencies could be achieved. In view of this, the temperatures of reduction can be low and consequently, the sintering and grain growth in the product phase could be minimized. The reduction experiments were carried out in a fluidized bed reactor and the rate of the reaction was followed by monitoring the rate of evolution of the product gas, viz. water vapor, using a gas chromatograph. The rate of the reduction reaction was found to be controlled by the chemical reaction.

The product was examined by SEM, Transmission Electron Microscope (TEM) and XRD.\[11\] The product was found to be nanograin intermetallic. The mechanical properties were characterized as well. In studies related to the present work, the thermal\[12\] and magnetic\[13\] properties were also studied.

Finally, the potentialities of this method in producing Fe-Mo alloys of varying compositions were established by the investigation of the hydrogen reduction of a series of oxides mixtures with varying Fe/Mo ratios.\[14\] These studies clearly showed that alloy phases of desired composition and structure could easily be produced by this method.

**Intermetallic Phases:**

The problems in the utilization of intermetallics are numerous. One of the serious problems is their brittleness. The brittleness of the intermetallic phases can be attributed mainly to either insufficient number of slip systems or grain boundary weakness. Ductility in intermetallics can be improved by microstructural control, which calls for grain refinement and grain boundary cohesion. In other words, ductility can be enhanced or promoted by grain refinement. On the other hand, the grain size required to produce ductility may be very small (sub-micron order) and is difficult to achieve. In this aspect, the present experimental strategy is of great advantage in controlling the nanosized structures. Thus, the present work is expected to lead to the synthesis and characterization of an entirely new series of materials with industrially interesting properties.
2 Theoretical Aspects of Gas-Solid Reactions

2.1 Kinetics of reaction

Reactions between gases and solids are of great importance in many process metallurgical operations. These reactions can be either of catalytic or noncatalytic type and can happen in packed beds or fluidized bed reactors. Generally, the most common gas-solid reaction practices are: roasting of metal sulfides to metal oxides, reduction of metal oxides to metals and decomposition of metal compounds to metal oxides.\cite{15} The simplest way to describe a gas-solid reaction system is to imagine a single solid sphere which is placed in contact with a reacting gas stream. The reaction can be exemplified as follows:

\[ A(g) + bB(s) = cC(g) + dD(s) \]  \hspace{1cm} [2.1]

Assuming constant temperature in the system, the reaction will take place on the surface of the sphere. Eventually, a sharp reaction interface will form and as time goes on, it will move the core of the particle inwards, leaving behind a product layer. This mechanism is known as topochemical reaction or the so-called shrinking unreacted core. This type of reaction is represented in Figure 2.1.

Figure 2.1 Schematic representation of the endothermic reaction of a single solid sphere with gas.
The heterogeneous reaction shown in Figure 2.1 involves a series of individual steps occurring simultaneously. These steps are associated with a “rate of flow per unit area”, e.g., g-mol cm\(^2\) sec\(^{-1}\). Each step offers resistance for the reaction to progress. It is the slowest step of the series that exerts the greatest resistance and can be said to control the reaction. The rate steps can be generally described as:

1) Mass transfer of the reactant gas from the bulk of the gas stream to the external surface of the solid particle or the product gas from the solid surface to the bulk gas.
2) Diffusion of the gaseous reactant/product through the porous of the product layer.
3) Chemical reaction which consists of adsorption of the reactant gas on the reactant surface and desorption of the product gas from the surface apart from the chemical reaction itself.
4) Heat transport to/from the reaction zones (endothermic/exothermic).

One of the challenges is to determine the impact of the process variables on each of these reaction steps. A sound approach to find the rate-controlling step is by following the conversion and examine how the particle size, gas velocity and temperature affect this conversion. For example, mass transfer control can be easily distinguished from diffusion control by performing experiments at different temperatures, particle sizes and gas flow rates. In addition, chemical reaction is very sensitive to temperature and therefore generally distinguishable by means of the high activation energies.

An investigation of a gas-solid reaction leads to a better understanding of the stoichiometry, the kinetics of the reaction and thereby, the mechanism involved. This leads to improved knowledge regarding the mode and mechanism of such reactions, their relative ease of their occurrence, the physical and energy changes involved, the products obtained from the given materials, and, finally the rate of attainment of these end products.

From a more fundamental point of view, the study of gas-solid reactions provides a tool for gaining insight into the nature of reaction systems, how chemical bonds are made and broken, and for estimating their energies and stability. On the other hand, for a chemical
engineer, the fundamental kinetic data pertaining to the reaction are useful in optimizing the conditions under which the reactors are to be operated.

### 2.2 Modeling of reactions

There are two procedures to analyze experimental kinetic data, the integral and differential methods. In the integral method of analysis one selects a kinetic with corresponding rate equation and, after appropriate integrations and mathematical manipulations, predict that a plot of the concentration against time should yield a straight line. The data are plotted, and if a reasonably good straight line is obtained the mechanism is said to fit the data satisfactorily. In the differential method of analysis, one selects a kinetic model and fits its corresponding rate expression to the data directly. The integral method is easy to use and recommended when testing specific mechanisms, when fitting relatively simple mechanisms, or when data are so scattered that we cannot reliably find the derivatives needed in the differential method. The differential method may be more useful in more complicated situations but requires more accurate or larger amounts of data.

At present, there are models that cover all the kinetics steps involve in a gas-solid reactions for a variety of solid systems, i.e. solid and porous particles, from spherical to cylindrical shape, uniform and non-uniform size, etc. The cases most thoroughly investigated involve nonporous spherical particles of uniform size. If the model corresponds closely to what really takes place, the rate expression derived from the model will closely predict and describe the actual kinetics; if the model widely differs from reality, the derived kinetic expression will be useless.

For engineering design, the theoretical study may be used as a supplementary aid to suggest

1) the temperature sensitivity of a given reaction from a similar type of reaction,

2) the upper limits of the reaction rate, etc.

Final design invariably rests on the experimentally found rates.
3 Experimental Studies

This section will describe relevant details of the experimental techniques and procedures involved in this work. The entire experimental work was carried out within The Department of Materials Science and Technology. The experimental procedures have been grouped in five main subsections. The sequence of these subsections does not represent the order in which this work was conducted.

3.1 Materials and sample preparation for kinetic studies

Table 3.1 shows the starting materials used for the kinetic reduction studies. These studies can be divided into categories: 1) thermogravimetric studies and 2) fluidized bed studies. In the case of thermogravimetric studies several systems were studied, i.e., MoO₃, Fe₂MoO₄ and Fe₂MoO₄-FeO-MoO₂ mixtures. In the case of fluidized bed studies only Fe₂MoO₄ powder was studied. Table 3.2 shows relevant information of the species that were synthesized in the lab.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Purity %</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₃</td>
<td>99.95</td>
<td>Alfa Aesar; Karlsruhe, Germany</td>
</tr>
<tr>
<td>MoO₂</td>
<td>99.95</td>
<td>Alfa Aesar; Karlsruhe, Germany</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>99.8</td>
<td>Alfa Aesar; Karlsruhe, Germany</td>
</tr>
<tr>
<td>Fe</td>
<td>99.95</td>
<td>Merck; Darmstadt, Germany</td>
</tr>
<tr>
<td>Fe</td>
<td>98</td>
<td>Merck; Darmstadt, Germany</td>
</tr>
</tbody>
</table>
Table 3.2 Type of compounds synthesized in the lab.

<table>
<thead>
<tr>
<th>Oxides synthesized</th>
<th>Stoichiometric ratio.</th>
<th>Temp. of heat treatment, K</th>
<th>Phases identified after heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Fe, Fe$_2$O$_3$, MoO$_3$</td>
<td>4:1:3</td>
<td>973, 1273</td>
</tr>
<tr>
<td>B</td>
<td>Fe, Fe$_2$O$_3$</td>
<td>1:1</td>
<td>1273</td>
</tr>
<tr>
<td>C</td>
<td>Fe$_2$MoO$_4$, FeO</td>
<td>1:1</td>
<td>1273</td>
</tr>
<tr>
<td>D</td>
<td>Fe$_2$MoO$_4$, FeO</td>
<td>1:7</td>
<td>1273</td>
</tr>
<tr>
<td>E</td>
<td>Fe$_2$MoO$_4$, MoO$_2$</td>
<td>1:1</td>
<td>1273</td>
</tr>
<tr>
<td>F</td>
<td>Fe$_2$MoO$_4$, MoO$_2$</td>
<td>1:2:25</td>
<td>1273</td>
</tr>
</tbody>
</table>

Solid-state synthesis was used to prepare the starting compounds. The common procedure adopted was as follows: stoichiometric amounts of given powders were mixed thoroughly. The mixture was packed into an iron crucible of 45 mm i.d. The crucible was sealed hermetically by welding an iron lid on its top. Then, the crucible with the powder mixture was heated under argon atmosphere up to a given temperature and kept it at the same for 24 hours. At the end, the crucible was taken out from the hot zone of the furnace and quenched in water. The species thus synthesized were crushed and stored in a desiccator before being used in the reduction experiments. The synthesized powders were subjected to X-ray diffraction analysis (XRD) using a PHILIPS x-pert system. The phases obtained are presented in Table 3.2.

Argon and hydrogen gases (plus grade, maximum 10 ppm impurities) were used in the kinetic experiments. Both gases were supplied by AGA Gas, Stockholm. Argon gas was purified by passing it consecutively through columns of silica gel, ascarite and magnesium perchlorate.

### 3.2 Thermogravimetric studies of thin powder beds

Both isothermal and non-isothermal reductions were carried out using a thermogravimetric unit (SETARAM TGA 92, France) having a detection limit of 1 µg. The schematic diagram of the assembly is shown by Figure 3.1. The balance is controlled by a PC through
a CS 92 controller. An Al$_2$O$_3$ crucible with 8mm i.d. and 1 mm inner height was used to hold powdery compounds.

The crucible containing the sample was suspended from one arm of the balance by Pt suspension wire, long enough to reach the hot zone of the graphite furnace. The crucible was carefully centered to keep it away from the walls of the reactor tube. The temperature of the furnace was controlled by a Pt-10% Rh /Pt (S type) thermocouple placed below the crucible. In an isothermal experiment, the reaction chamber was evacuated after the sample was introduced. Thereafter, the reaction chamber was filled with argon gas and a constant argon flow was maintained. The sample was heated up to the experimental temperature at a heating rate of 25 K/min under argon atmosphere. When the sample temperature was stabilized, the flow of argon was stopped and hydrogen gas was introduced into the reaction chamber to start the reduction. The experiment was terminated by cooling down the furnace at a high cooling rate. Hydrogen flow was maintained until the furnace reached the desired temperature.
room temperature in order to avoid the oxidation of the reduced sample during the cooling of the furnace.

In the case of a non-isothermal experiment, the reaction chamber was initially evacuated after the introduction of the sample into the furnace. The chamber was then filled with hydrogen. A constant flow of H$_2$ gas was then maintained while the sample was heated up at a constant heating rate. The experiments were terminated in a similar fashion as in the case of isothermal reduction.

Preliminary experiments were carried out at different flow rates of hydrogen in order to select a hydrogen flow rate far above the starvation rate for the reaction. Depending upon the system investigated, 10 or 20 mg of sample was used in both isothermal and non-isothermal reductions. In order to examine the aspect of mass transfer through the powder bed on the reduction rate, the height of the bed was changed using two different sample weights for a given isothermal temperature. Moreover, to observe the buoyancy effect of the hydrogen gas velocity on the results of the thermogravimetric experiments, some experiments were performed using alumina powder under similar conditions. Repetition of some selected experiments showed high degree of reproducibility.

### 3.3 Kinetics studies in a fluidized bed

Figure 3.2 shows a schematic diagram of the fluidize bed apparatus used in the experiment. The main reactor was made of quartz of 15 mm i.d. and 1 m long. The gas distributor was a 2-mm thick porous quartz plate (average pore size = 200µm). Flow rates of hydrogen and argon before entering the reactor were controlled by rotameters. The off gases were conducted through a stainless steel pipe of 5 mm i.d. The end of the pipe was coupled to a “T” joint followed by stainless steel ball valves in order to direct the gas stream adequately. The majority of the off-gas was led to a gas chromatograph (Shimadzu GC-9AM with a Thermoconductivity Detector, Kyoto, Japan), abbreviated hence forth as GC. Hydrogen was employed as the carrier gas in the gas chromatograph. The whole stainless
line, including the valves, were wrapped up with a heating tape to prevent the H$_2$O gas phase from condensation before entering the GC.

![Diagram of high temperature fluidized bed experimental set up](image)

**Figure 3.2 High temperature fluidized bed experimental set up (schematic diagram).**

Before starting the actual studies at high temperature, preliminary studies were carried out on a cold model to arrive at some suitable design criteria. In addition, these studies helped to establish conditions of different variables for good fluidization. Thus, the minimum fluidization velocity ($U_{mf}$) was determined experimentally by pressure drop measurements at room temperature. The net pressure drop was calculated from the pressure measured upstream of the gas distributor by subtracting the pressure drop of the gas distributor. Fluidization velocity at a higher temperature was then determined from these calculated values by taking into account the decrease in density and increase in viscosity of H$_2$ due to temperature increase, $^{[16]}$ namely
\[ U_{mf} = U_{mf} \frac{\rho_r \mu_r}{\rho_T \mu_T}, \]  

[3.1]

where \( \rho_r, \mu_r \) and \( \rho_T, \mu_T \) are the density and viscosity of the fluidized gas at room and higher temperature respectively. In the present studies, the factor in Eq. [3.1] equals 1.28 at 1100 K.

The fluidized bed reductions were conducted isothermally. Typically, a charge weight of 2 g was used which gave a static bed of \( H/D \) ratio of about 1. This charge was placed in the even temperature zone of the furnace. A type-S thermocouple was placed at the exterior of the fluidized bed reactor. The reactor was heated electrically using a vertical tube furnace whose temperature was controlled by a temperature controller (Eurotherm-94, Arlöv, Sweden). During the heating ramp, argon was passed through the reactor. When the predetermined reduction temperature was stabilized, argon gas was replaced by hydrogen. GC measurements were carried out on-line. The water phase in the off-gases produced by the reaction of iron molybdate with hydrogen was quantitatively monitored by gas chromatography. When no more traces of water in the system were detected, hydrogen gas was changed by argon gas terminating thus the experiment. It should be noted that the time taken for the product gas to reach the gas chromatograph after the onset of the reaction was about 25 seconds. This elapsed time was evaluated using preliminary experiments. The conversion fraction of the reaction was estimated in the following manner. During the reduction process, the GC measured the relative concentration of water in the system in the form of peaks. The area of these peaks \( (A_P) \) was plotted as a function of time. From this plot, the integration of \( dA_P/dt \) was normalized to 100 pct reduction and the conversion fraction was thus calculated backwards. The degree of reaction is defined as the ratio of the
area under the curve $A_P(t)$ against time at an instant $t$ to the area at the time the reaction ends, namely

$$X = \frac{\int_0^t A_P(t) \, dt}{\int_0^\infty A_P(t) \, dt}$$  \hspace{1cm} [3.2]

The value of the integration of the curve was found to be consistent at every reduction temperature.

Table 3.3 shows the estimated values of gas velocities of hydrogen at different temperatures. The minimum fluidization velocity depends on the physical properties of the gas as well as the diameter and density of the solid particles. The particle size distribution of Fe$_2$MoO$_4$ is given in Figure 3.3.

<table>
<thead>
<tr>
<th>$D_p$ ($\mu$)</th>
<th>$T$ (K)</th>
<th>$U_{mf}$ $^\dagger$ (cm/s)</th>
<th>$U_{mf}$ $^\ddagger$ (cm/s)</th>
<th>$U_f$ $^\ddagger$ (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>297</td>
<td>2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>923</td>
<td></td>
<td>2.47</td>
<td>3.76</td>
<td>258</td>
</tr>
<tr>
<td>973</td>
<td></td>
<td>2.54</td>
<td>3.85</td>
<td>265</td>
</tr>
<tr>
<td>1023</td>
<td></td>
<td>2.59</td>
<td>3.94</td>
<td>271</td>
</tr>
<tr>
<td>1073</td>
<td></td>
<td>2.65</td>
<td>4.03</td>
<td>276</td>
</tr>
<tr>
<td>1123</td>
<td></td>
<td>2.70</td>
<td>4.11</td>
<td>282</td>
</tr>
<tr>
<td>1173</td>
<td></td>
<td>2.75</td>
<td>4.19</td>
<td>287</td>
</tr>
</tbody>
</table>

$^\dagger$ Measure at room temperature

$^\ddagger$ The estimated values at different working temperatures
3.4 Characterization of Microstructure

The microstructure and phases present of the materials processed at high temperature were investigated whenever necessary. The following techniques were used:

*X-ray Diffraction*

The phase composition and nature of the synthesized and processed powders were determined by X-ray diffraction (XRD) using a PHILIPS x-pert system. In some studies, oxide powders partially reduced were also analyzed. For all the analysis, Cu $K_\alpha$ radiation was used at a scanning speed of 2 °/min. In addition, XRD was also used to determine the crystal strain of uniaxially cold pressed powders by measuring the relative changes in the breadth of a particular $(hkl)$ diffraction peak.
**Electron Microscopy**

The morphology, phase distribution and composition of the processed powders were examined using a Jeol microscope (JSM-840) with an electron dispersion spectroscopy (EDS), Link AN-10000, used for determining compositions. The microstructure as well as grain interfaces were examined by transmission electron microscopy (TEM) using a Jeol 200-EX.

### 3.5 Materials and preparation of pellets for mechanical testing

In order to measure the mechanical properties of the Fe$_2$Mo product, pellets had to be prepared. Fe$_2$Mo powder was first produced by reducing Fe$_2$MoO$_4$ at 1173 K under a continuous stream of H$_2$ using a fluidized bed reactor. The powder thus produced was uniaxially pressed using a piston-cylinder die with 11-mm diameter in a hydraulic press, Model M-30 Research and Industrial Instruments Company, England. The amount of powder used for the production of compacts was 1.5 g. The compaction pressures applied were in the range of 50 MPa up to 1300 MPa. The density was estimated from the volume and mass of the compacts and from these, the relative density was calculated by using the theoretical density of Fe$_2$Mo (9.22 g/cm$^3$). The change of relative density of Fe$_2$Mo powder against compaction pressure is shown in Figure 3.4. It can be seen that rather low densification (61 pct) is achieved at the highest pressure applied (1.3 GPa) particularly as compared to densifications around 90 pct obtained for different stainless steels powders under certain comparable conditions.$^{[17]}$ These results imply that Fe$_2$Mo is brittle as expected of intermetallics in general. The SEM photograph of the Fe$_2$Mo powder produced by fluidized bed reduction and was used for unidirectional compaction studies showing the spongy nature of the material is presented in Figure 3.5.
Figure 3.4 Relative density dependence on uniaxial compaction of Fe$_2$Mo powder.

Figure 3.5 SEM micrograph of sponge-like porous Fe$_2$Mo powder particle used for unidirectional compaction.
3.6 Hardness and yield strength measurements

Hardness tests were performed on pellets compacted at different pressures. An Instron instrument (Model 8561) was used adapting a square-base diamond pyramid as an indenter. A load of 10 kg was applied using 20 s loading cycle. At least, a total of 15 indentations were measured for each specimen.

Since the measurements of mechanical properties are limited on particulate materials, a model put forward by Tabor\cite{19} was employed to estimate the yield strength of Fe$_2$Mo. This model is based on an empirical relationship between hardness and yield stress for metals. Tabor demonstrated that hardness measurement by indentation is essentially a measure of elastic limit. Thus, for metals that do not work-harden appreciably, the hardness value $H$ for both the Brinell and the Vickers indenters is approximately three times the yield stress corresponding to 8-pct deformation:

$$H = 3\sigma_y.$$  \[3.3\]

Cahoon, Broughton and Kutzak\cite{20} validated this empirical formula.

The yield strength of Fe$_2$Mo was also estimated by X-ray diffraction. XRD analyses were carried out on the samples compacted at different pressures. The onset of plastic deformation of the grains was followed by measuring the relative changes in the breadth of a particular ($hkl$) diffraction peak. The results were compared with the value obtained from Eq. [3.3].
4 Results and Discussion

4.1 Reduction of MoO$_3$ by hydrogen

Thin powder beds were reduced by hydrogen using a thermogravimetric apparatus. Isothermal and non-isothermal experiments were conducted. It was found that the reduction of MoO$_3$ by hydrogen is likely to proceed in two main steps:

\[
\begin{align*}
\text{MoO}_3 + \text{H}_2 &= \text{MoO}_2 + \text{H}_2\text{O} \quad [4.1] \\
0.5\text{MoO}_2 + \text{H}_2 &= 0.5\text{Mo} + \text{H}_2\text{O} \quad [4.2]
\end{align*}
\]

The weight loss curves for the isothermal reduction of molybdenum oxide by hydrogen at different temperatures are shown in Figure 4.1. Special reduction experiments carried out at 973 K with different initial masses of the samples, viz. 10 and 30 mg instead of the usual 20 mg, showed that below $X \approx 0.25$ the reduction rate is independent of the bed height indicating that mass transfer through the sample could be neglected at the initial stage.

![Figure 4.1 The fractional conversion, X, as function of time during the isothermal reductions of MoO$_3$](image-url)
The derivative of the reduction curves, \( \frac{dX}{dt} \), from both isothermal and non-isothermal experiments indicated that in the case of isothermal experiments Reaction [4.2] could be expected to occur before the completion of Reaction [4.1] particularly at higher temperatures. On the other hand, in the case of non-isothermal experiments, it was found that Reaction [4.2] starts after Reaction [4.1].

Since, in the present work, shallow powder beds, small particle size and high flow rates of \( \text{H}_2 \) at 1 atm were used, the transfer of \( \text{H}_2 \) to the reaction front and the removal of \( \text{H}_2\text{O} \) from there are not likely to be rate controlling steps of the reduction Reaction [4.1]. Furthermore, the results from the experiments with different sample weights at 973 K indicated that mass transfer through the sample could be neglected at the initial stage. Hence, it is logical to assume that the chemical reaction is the rate-controlling mechanism at the beginning of the reduction process.

By taking the maximum reaction rate values at the very early stage from the isothermal experiments at different temperatures, it is possible to calculate the activation energy of the Reaction [4.1] by using Arrhenius equation:

\[
k = k_0 \exp\left(-\frac{Q}{RT}\right)
\]

where \( k \) is the reaction rate constant (\( \text{d}X/\text{d}t \)), \( k_0 \) is the frequency factor, \( Q \) is the activation energy, \( R \) the gas constant, \( T \) is the temperature (K). The Arrhenius plot is shown in Figure 4.2. The plotted points have a good correlation and the corresponding activation energy of the Reaction [4.1] proportional to the slope is 172 kJ/mol.
Figure 4.2 Arrhenius plot for the Reaction [4.1] by isothermal reductions of MoO$_3$.

Figure 4.3 The non-isothermal reduction curves of MoO$_3$ by hydrogen.

Figure 4.3 shows the non-isothermal curves. A model developed by Arvanitidis et al.\cite{21, 22} was used to evaluate the activation energy from the non-isothermal experimental data. This
model was developed on the basis that the chemical reaction controls the overall reaction rate in a topo-chemical manner. Again, assuming that the reduction rate of Reaction [4.1] is controlled by a chemical reaction, a similar model is used to describe the reduction of MoO$_3$ by hydrogen according with Reaction [4.1]. Thus, according to the “shrinking core” model, the reaction rate in the case of chemical reaction can be expressed as

$$
\frac{dX}{dt} = \frac{A_o}{R} \cdot \frac{(1-X)^{2/3}}{T} \cdot k
$$

[4.4]

$X, T, R$ and $k$ in Eq. [4.4] have been defined earlier. $A_o$ is the initial reaction surface area. Insertion of Eq.[4.3] into Eq.[4.4] leads to the following relationship

$$
\frac{dX}{dt} = \frac{A_o}{R} \cdot \frac{(1-X)^{2/3}}{T} \cdot k_o \cdot \exp\left(-\frac{Q}{RT}\right)
$$

[4.5]

By rearranging Eq.[4.5] and taking logarithm on both sides of the equation, Eq.[4.6] is obtained

$$
\ln\left(\frac{dX}{dt}\right) + \ln(T) - \ln(1-X)^{2/3} = \ln B - \frac{Q}{RT}
$$

[4.6]

where $B$ groups the constant terms independent of temperature,

$$
B = \frac{A_o K_o}{R}
$$

[4.7]

The three terms on the left hand side of the Eq. [4.6] can be evaluated using the reaction rate, degree of conversion and temperature obtained from the non-isothermal curves in Figure 4.3. A plot of the value of the left hand side of Eq. [4.6] as a function of $1/T$ is presented in Figure 4.4 with the non-isothermal data corresponding to $X<0.15$. The average value of the activation energy calculated from the different scanning rates leads to
175 ±6 kJ/mol, which is in good agreement with the value obtained by isothermal experiments.

Figure 4.4 Arrhenius plot from the Eq. [4.6] for the Reaction [4.1] by non-isothermal reductions of MoO₃.

The good agreement of the value of $Q$ obtained through the present model with that from isothermal experiments is a further confirmation of the fact that the rate of the initial reduction for the Reaction [4.1] was controlled by the chemical reaction. It also implies that the gas flow used in this work was high enough to let the gas have access to all the small particles and the product gas can leave the site without any hindrance at the initial stage of reduction ($X<0.15$).

### 4.2 Reduction of Fe₂MoO₄ by hydrogen

In this work, the kinetics of reduction of shallow powder beds of Fe₂MoO₄ by hydrogen was studied. Figure 4.5 shows the fractional reduction rate for the isothermal reduction of iron molybdate by hydrogen in the temperature range of 823-1073 K. The reduction curves
showed no discontinuities in their slopes suggesting that reduction of Fe$_2$MoO$_4$ might go through a single step. To verify this aspect, samples partially reduced at 1173 K were examined using XRD. These analyses revealed only two phases, viz. the Fe$_2$MoO$_4$ and Fe$_2$Mo phases, indicating thereby that Fe$_2$MoO$_4$ was reduced to Fe$_2$Mo in a single step.

![Graph showing isothermal reduction curves of Fe$_2$MoO$_4$.](image)

Figure 4.5 Isothermal reduction curves of Fe$_2$MoO$_4$.

Figure 4.6 shows the non-isothermal reduction curves at three different heating rates, viz., 10, 12 and 15 K/min.

XRD and TEM$^{[11]}$ analyses performed in the reduced powder confirmed that Fe$_2$Mo was the only solid product of the reduction. The fact that Fe$_2$Mo was the only solid product found in the partially reduced samples would be an evident confirmation of the mechanism of single step reaction. Hence, the chemical reaction for the reduction of Fe$_2$MoO$_4$ by hydrogen gas can be represented as follow

$$\frac{1}{4}Fe_2MoO_4(s) + H_2(g) = \frac{1}{4}Fe_2Mo(s) + H_2O(g)$$  \[4.8\]
As reasoned in the earlier case, in view of the prevailing experimental conditions such as high reactant gas flow and thin powder beds, it is reasonable to assume that the rate-controlling step for Reaction [4.8] is most likely to be the chemical reaction at the Fe$_2$MoO$_4$/Fe$_2$Mo interface, except probably at the final stage of reduction.

Reaction [4.8] was found to follow the equation that describes a “shrinking unreacted core”\textsuperscript{23}:

$$t = \frac{\rho_{Fe2MoO4} \cdot r_o}{M_{Fe2MoO4} \cdot k \cdot P_{H2}} \left[ 1 - (1 - X)^{1/3} \right]$$ \hspace{1cm} [4.9]

where $r_o$ is the initial radius of the particle, $\rho_{Fe2MoO4}$ and $M_{Fe2MoO4}$ stand for the density and molecular weight of Fe$_2$MoO$_4$ respectively, $k$ is the reaction rate constant, and $P_{H2}$ corresponds to the hydrogen partial pressure. The slopes of the plots of time against $[1-(1-X)^{1/3}]$ give the specific reaction rate constants. With the rate constant values, the activation energy can be calculated by using the Arrhenius equation (Eq. [4.3]). The plot of $\ln k$ against $1/T$ is presented in Figure 4.7. An activation energy of 173.5 kJ/mol is evaluated from the slope of the plot. This value is very close to the activation energy for the
reduction of MoO$_3$ to MoO$_2$ by hydrogen, 172 kJ/mol, estimated earlier in the present laboratory under very similar conditions$^9$

![Image](image.png)

**Figure 4.7 Arrhenius plot for the isothermal reduction of Fe$_2$MoO$_4$.**

In an earlier work, Morales-Estrella et al.$^9$ used the Arrhenius equation that incorporates the “shrinking core” model for non-isothermal experiments, as expressed in Eq. [4.6], to calculate the activation energy for the hydrogen reduction of MoO$_3$ from non-isothermal reduction experimental data. It would be interesting to see if this model could also be applied to the reduction of Fe$_2$MoO$_4$. A plot of the value of the left hand side of Eq. [4.6] as a function of $1/T$ is presented in Figure 4.8. Different symbols represent different heating rates. It is to be noted that the experimental data above $X=0.85$ are not presented in this figure as diffusion step might become important with the increase of the diffusion distance through the product layer of each particle at the later stages of the reduction. The activation energy for Reaction [4.8] is evaluated to be 158.3 kJ/. As shown in Figure 4.8, the heating rate has little effect on the evaluation of the activation energy. The experimental points obtained by using different heating rates suggest small experimental scatter (R=0.99 for the regression).
Figure 4.8 Arrhenius plot for the non-isothermal reduction of Fe₂MoO₄.

The activation energy obtained from the non-isothermal experiments, 158.3 kJ/mol, is found to be in reasonable agreement with the value of 173.5 kJ/mol obtained from the isothermal experiments. In addition, the reduction product was found to be an intermetallic compound, Fe₂Mo, of microcrystalline structure.

4.3 Reduction of Fe₂MoO₄ small particles in a fluidizing reactor

Fe₂MoO₄ was reduced by hydrogen in the temperature range 923 - 1173 K using fluidizing conditions as shown in Table 3.3. Under these conditions, well-mixing of the “emulsion” is expected to occur. The extent of the reaction was followed by gas chromatography (GC). The reduction rate curves at several temperatures are shown in Figure 4.9. It can be seen that, the reaction rate increases significantly above 973 K.
It can be seen that reduction rate increases dramatically with the increase of temperature. While it takes only about 10 minutes for the reduction to finish at 1173 K, the reaction was extremely slow at 923 K. In fact, after nine hours of processing the conversion fraction was estimated to be only 0.91.

Earlier kinetics\[9\] and characterization\[11\] studies have shown that the reduction of Fe$_2$MoO$_4$ by hydrogen occurs in one step according to Reaction [4.8]. Microscopic examination of the product revealed that the reduction process was found to transform a solid reactant particle into multiple-product-particle agglomerate.

In order envisage the production of nanomaterials through the of fluidized bed reduction route, the mechanism of the reduction should be examined. Firstly, the convective mass transfer coefficient $h_m$ was calculated using empirical correlations. The calculated value was found to yield a value of 1162 cm/sec. This extremely high value indicates that external mass transfer is less likely to be the rate controlling-step.
Secondly, the mechanism of diffusion through the product layer as the rate-controlling step was hypothesized and its corresponding rate equation was tested. The experimental data of Figure 4.9 did not fall on a straight line as the predicted by the rate equation. This indicated that the diffusion through the product layer is unlikely to be the controlling step. This argument is further supported by the fact that the particle size is very small, which would lead to very short diffusion distance.

It is seen in Figure 4.9 that the reaction rate strongly depends on temperature. This strong dependence would suggest a chemical-reaction controlling mechanism. From the discussion so far, the gas diffusion through the product layer and external mass transport as rate-controlling steps can be discounted. In view of the fluidization and tiny particle size, even the heat transfer could be assumed less important for the overall kinetics. This strengthens the case for a serious consideration of the chemical reaction as the rate-determining step.

![Figure 4.10 Plots of \(1-(1-X)^{1/3}\) as a function of time for the fluidized reduction of Fe\(_2\)MoO\(_4\) at different temperatures (clockwise 1173, 1123, 1073, 1023, 973 and 923 K). Here time is expressed in seconds to calculate the rate constant \(k\).]
The rate constants of the chemical reaction at different temperatures were obtained from the experimental data using the ‘shrinking unreacted’ core model for the chemical reaction controlling. Thus, using Eq. [4.9], the term \([1-(1-X)^{1/3}]\) shows a linear function against \(t\) as seen in Figure 4.10. This implies that Reaction [4.8] is controlled by the chemical reaction at the interface between product layer and the unreacted core in each particle. The values of the slopes of the plots in Figure 4.10 are plotted against \(1/T\) in Figure 4.11. The value of the activation energy for the obtained from the slope of the plot in Figure 4.11 was 182.9 kJ/mol. This high value suggests again that the chemical reaction is most likely to be the rate-controlling step.

![Figure 4.11 Arrhenius plot for the fluidized reduction of Fe₂MoO₄ by hydrogen.](image)

Although the existence of Fe₂Mo intermetallic phase has been a point of controversy, the present result evidently shows that even bulk production of Fe₂Mo with nanocrystalline structure is possible through the route of gas-solid reduction in a fluidized bed reactor. The reduction of Fe₂MoO₄ renders a uniform distribution of highly reactive Fe and Mo particles as nearest neighbors due to the single step reaction. These particles are then likely
to react with each other by means of surface reaction and grain boundary diffusion leading to uniform composition. This mechanism is favored by the fluidization conditions.

4.4 Mechanical and structural characterization of Fe$_2$Mo powders

Fe$_2$Mo alloy was successfully produced from Fe$_2$MoO$_4$ oxide by the hydrogen gas reduction route. The aim of the present work was to carry out metallographic and mechanical property characterization of the Fe$_2$Mo intermetallic powders produced at 1173 K using a fluidized bed reactor. Another objective was to determine the yield strength of this intermetallic from hardness measurements and to confirm the same with XRD analyses performed on cold-pressed pellets.

Figure 4.12 TEM micrographs of a Fe$_2$Mo pellet pressed at 1 GPa showing: (a) domains of different orientations with perfect coherency at the particle interface, (b) SAD pattern showing microcrystalline structure and (c) SAD pattern showing satellite reflection superimposed on microcrystalline pattern of Fe$_2$Mo.
The results from TEM studies performed on a sample pressed at 1 GPa showed micro- and nanocrystalline grains of different texture orientations and with perfect coherence among themselves. Selected area diffraction patterns did indicate the existence of a hexagonal structure of Laves type Fe$_2$Mo on indexing. The results of microstructural details from TEM studies are presented in Figures 4.12(a)-(c).

Results of uniaxially cold pressing of pellets showed that low degree of densification is achieved (≈60 pct) at the maximum pressure of 1.3 Gpa. This implied that plastic deformation was not the predominant mechanism of compaction. The Fe$_2$Mo intermetallic should have very little ductility leading to a small measure of plasticity before fracture.

The multiple compaction mechanisms were analyzed by Kawakita’s$^{[24]}$ and Balshin’s$^{[25]}$ models. The experimental data of relative density against compaction pressure was found to exhibit fairly good correlation with this the above models. From the regression analysis of Kawakita’s equation, the coefficient of compression $b$ was evaluated to be 0.0096 MPa$^{-1}$. This value gives a good notion of the poor ductility of this material when compared to the value of about 0.25 for stainless steel powders.$^{[18]}$

Vickers Hardness Number (VHN) measurements were performed on both parallel faces of the pellets. The average values along with the standard deviation are plotted in Figure 4.13 as a function of relative density. According to Figure 4.13, hardness seems to follow a linear relationship with respect to relative density. This is reasonable as hardness is inversely proportional to the contact area. As porosity decreases, the resistance of the body to penetration would increase, bringing as a consequence, a reduction of the contact area with higher hardness. Under these circumstances, the extrapolation of the experimental data of Figure 4.13 was considered to be reasonable. Thus, when $\delta_r=1$, one can see that the material under study would arrive at a hardness value of about 343 VHN.
The yield stress ($\sigma_y$) of the intermetallic was obtained by using an empirical relationship between hardness and yield stress for metals. This empirical relationship was put forward by Tabor.\[19\] He demonstrated for metals that do not work-harden appreciably, the hardness value $H$ for both the Brinell and the Vickers indenters is approximately three times the yield stress, $\sigma_y$; i.e., $H=3\sigma_y$. In the case of particulate porous materials, the increase in densification, at latter stages of compaction, is caused by plastic deformation of particles, which can be regarded as mutual particle indentation. Therefore, a relationship would be expected to exist between yield stress and hardness. Thus, taking the extrapolated value of hardness $H=343$ when $\delta=1$, the yield stress has a value of the order of 114.3 kg/mm$^2$ (1121.6 MPa).

The crystal deformation of Fe$_2$Mo pellets compacted at pressures ranging from 1000 to 1300 MPa was followed by measuring the broadening of XRD diffraction lines at angle position of (112), which has an intensity of 100 pct. These results confirmed that plastic

---

Figure 1 The variation of Vickers hardness number with relative density for Fe$_2$Mo pellets uniaxially compacted in the pressure range 500-1000 MPa.
deformation does commence at about 1100 MPa. These reproducible observations are in good agreement with the value estimated from hardness measurements, i.e., 1121.6 MPa and with the fact that Fe₂Mo undergoes a very slight plastic deformation before fracture. Such an easy and reliable determination of yield strength is of utmost importance for the application purposes.

### 4.5 Kinetics of Reduction of FeO-Fe₂MoO₄-MoO₂ Mixtures

The targeted oxide mixtures synthesized for the reduction experiments were all located along the FeO-Fe₂MoO₄-Fe₂Mo₃O₈-MoO₂ join and have been marked in the Fe-Mo-O isothermal (1273 K) ternary phase diagram in Figure 4.14.²⁶

![Fig. 4.14. Isothermal section of the Fe-Mo-O system at 1273 K.][26]
Isothermal reductions were carried out using a thermogravimetric apparatus at four different temperatures, i.e., 873, 923, 973 and 1023 K. Figure 4.15 shows the reduction curves of all the mixtures. As it can be seen, the reaction rates increase with temperature, which is typical of a thermally activated process. Additionally, the rate of reduction for the composition D decreases dramatically at about $X=0.7$. This behavior could be due to the sintering of the iron particles on the Fe$_2$MoO$_4$ as FeO gets reduced.

Fig. 4.15. Isothermal reduction curves for the systems investigated. Experimental temperatures: (1) 873, (2) 923, (3) 973 and (4) 1023 K.

Non-isothermal experiments for each composition were performed at 10 K/min in order to observe the step-wise reduction. From these results clearly showed that the all compositions go through an intermediate step. The Fe-Mo-O ternary phase diagram at
1273 K indicates that the reduction paths through the intermediate three-phase regions which is in conformity with the results the non-isothermal reduction experiments.

From the rates of reaction obtained by isothermal reduction experiments at different temperatures, the activation energies for the two reaction steps could be calculated using Arrhenius equation, Equation [4.3]. For composition F, the activation energy was calculated over the experimental range that encompasses the two reaction steps due to the low transition step (X=0.05). Table 4.1 shows the activation energies for the reduction experiments shown in Figure 4.15. In the case of FeO-Fe$_2$MoO$_4$ mixtures, activation energies for the reduction of both the component oxides were found to be lower than values reported earlier.$^{[3,9]}$ It is not clear if the presence of metallic iron has an impact on the reaction mechanism.

XRD along with SEM analyses indicated that the metallic phase such as iron or molybdenum in the products was of crystalline structure while the intermetallic phase had microcrystalline structure.

<table>
<thead>
<tr>
<th>Table 4.1. Summary of the activation energies for the compositions investigated.</th>
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<td>Range used for calculation</td>
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<td>Composition F</td>
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5 General Discussion

Hydrogen reduction of molybdenum based-oxides was carried out in the temperature range 623-1073 K. These temperatures are essentially half the melting point of iron and far below of the melting point of molybdenum. The activation energies for the reduction of MoO$_3$ to MoO$_2$ and Fe$_2$MoO$_4$ to Fe$_2$Mo are similar. This similarity has also been found in systems involving tungstates. More systems involving molybdates should be investigated in order to see whether or not there is a correlation of the Molybdenum-Oxygen bond energies with respect to the activation energies for the chemical reaction. These observations open future research in the fundamental area. A mathematical model based on the chemical reaction for system displaying the shrinking core model was found to predict the activation energy from non-isothermal experiments. This model was developed earlier in this laboratory. The reduction Fe$_2$MoO$_4$ in a fluidized bed reactor was controlled by the chemical reaction as well despite the bigger particle size used and lower hydrogen flow rate compared to the conditions used in the thermogravimetric experiments. The fluidization conditions led to a solid product consisting of pure Fe$_2$Mo with nano and microcrystalline structure. This finding opens the possibility of producing other nano-crystalline alloys in bulk. The mechanical properties of the Fe$_2$Mo phase were obtained using cold-pressed pellets. The mathematical models used to analyze the mechanisms of compactions were in agreement with fact that Fe$_2$Mo possesses low ductility typical of intermetallics. The measurements of hardness on specimens with different porosities were extrapolated for zero porosity. From these values, the yield stress was calculated using an empirical equation. Although extrapolations are risky and the measurable mechanical properties of porous solid materials are limited, the extrapolation and the empirical equation used were found to be in agreement for the values at the starting of the deformation of crystal due to compaction pressure obtained from XRD technique. XRD results also showed that crystal deformation was very little. This is in agreement with earlier results. This way of measuring mechanical properties is useful when tensile measurements cannot be done. Finally, tailor-made alloys were successfully obtained after reducing adequate mixtures of Fe$_2$MoO$_4$-FeO-MoO$_2$. The activation energies were calculated and the SEM analyses showed that the products obtained consisted of two phases. In all the cases, one of the phases shows microcrystalline structure while the other
is crystalline. This process is successful in producing a variety of compositions with homogeneous phases with different crystalline size.

Thus, this thesis covers fundamental research, practical uses of gas-solid reactions route and mechanical properties of a new microcrystalline phase \( \text{Fe}_2\text{Mo} \).
6 Summary and Conclusions

The present investigation involves the reduction kinetics of molybdenum-based oxides and mechanical and structural characterization of Fe$_2$Mo intermetallic.

Kinetic experiments were carried out using a thermogravimetric equipment as well as a fluidized bed reactor. The experimental temperatures were in the range 823-1073 K. In case of thermogravimetric experiments, the usage thin beds, hydrogen flow rate above the starvation rate and small particle size made possible to obtain the rate of chemical reaction as the rates controlling step. From the rate of the reactions, the activation energies were estimated and compared. It was found that the activation energies for reduction MoO$_3$ to MoO$_2$ and Fe$_2$MoO$_4$ are very close, namely

$$\text{MoO}_3(s) + \text{H}_2(g) = \text{MoO}_2(s) + \text{H}_2\text{O}(g) \quad Q = 172 \text{ kJ/mol} \quad [6.1]$$

$$\frac{1}{4}\text{Fe}_2\text{MoO}_4(s) + \text{H}_2(g) = \frac{1}{4}\text{Fe}_2\text{Mo}(s) + \text{H}_2\text{O}(g) \quad Q = 173.5 \text{ kJ/mol} \quad [6.2]$$

More investigation on other molybdate systems are necessary in order to evaluate any correlation. The activation energy of the reduction of Fe$_2$MoO$_4$ by hydrogen in a fluidized bed reactor was found to be 182.9 kJ/mol. Here the particle size was bigger and the flow rate was lower than in the case of thin beds. The product obtained from the Reaction [6.2] was analyzed by SEM, TEM and XRD. It was found to consist of 100 pct Fe$_2$Mo phase with nano- and micro-crystalline structure. These results led to the possibility of mass production of Fe$_2$Mo intermetallic with microcrystalline structure. This route also opens the possibility to produce other alloys in the nanorange region.

As the existence of Fe$_2$Mo has been a controversy, its bulk properties were not found in the literature. Hence, some mechanical properties were estimated from pellets compacted uniaxially. This was of importance as the mechanical properties on particulated systems are limited. Vicker’s hardness was found to be linear with respect to porosity. Extrapolation of experimental values of pellets with different porosities was performed. The value of Vicker’s hardness when 100 % Fe$_2$Mo solid was found to be 341. This value is twice as high compared to other Fe-Mo alloys with different Mo content. From the
extrapolated hardness vale, the yield stress of Fe₂Mo was estimated using an empirical formula. The yield stress was found to be about 1100 MPa. This value was validated by following the deformation of crystals using XRD technique.

The versatility of using gas-solid reactions was explored to produce a varied range of Fe-Mo alloys from the reduction of oxide mixtures. The mechanism of reduction and final composition are in accordance with the ternary Fe-Mo-O and binary Fe-Mo phase diagrams. The crystalline structure obtained consists of a crystalline phase (either Fe or Mo) and microcrystalline intermetallic FeₓMoᵧ. The kinetics studies showed that the compositions investigated got reduced in tow steps. In the case of Fe₂MoO₄-FeO mixtures, the presence of Fe obtained in the first step of reaction is likely to reduce the activation energy of the second step of reduction.
7 Future work

This work has shown that Fe$_2$Mo and other Fe-Mo alloys with nano- and microcrystalline structure was produced by gas-solid reactions route. The next step will be:

- Synthesis of other intermetallics like Fe$_x$Mo$_y$ will be investigated and also the kinetics of reduction.
- Investigation other systems that are of importance to the industry.
- Introduction of interstitials in the alloys produced by selecting the suitable gas mixtures.
- Producing metal matrix composites with oxides in the matrix.
- Bulk production process of novel materials in the nanoregion will be upscale to a kilogram levels.
8 References

Supplements 1-5

Appendices A, B