SYNOPSIS

This thesis deals with the Mossbauer-effect studies of the thermal decomposition in hydrogen of ferrous oxalate and of homogeneously mixed ferrous-nickel oxalates. Earlier work on the Mossbauer-effect studies of the thermal decomposition of ferrous oxalate in air by Gallagher and Kurkjian in 1966 and by Krauth et al in 1967 indicated that the initial Fe₂O₃ formed is so finely divided that it is superparamagnetic. Halsey et al in 1968 found the presence of Fe₃O₄ during the decomposition of ferrous oxalate in nitrogen. Hang Nan et al in 1973 prepared fine particles of Fe-Ni alloy of 69-31 atomic % by heating the mixed oxalates in a hydrogen atmosphere at 500°C for 2 hours. We report here a systematic study of the thermal decomposition in hydrogen of ferrous oxalate and of mixed ferrous-nickel oxalates of different Fe-Ni ratios. The decomposed samples are studied using Mossbauer-effect techniques.

Ferrous oxalate is obtained by mixing ferrous salt solution and ammonium oxalate solution maintained at low pH to prevent hydroxide precipitation. The solution are heated separately and then mixed together; the precipitation of the ferrous oxalate is carried out in an inert atmosphere so as to prevent oxidation of ferrous
ions. Similarly, the ferrous-nickel oxalates are prepared by mixing ferrous and nickel salt solution of definite iron to nickel atomic ratio and by co-precipitating the ferrous-nickel oxalate as in the case of ferrous oxalate.

The thermogravimetric analysis of ferrous oxalate and of mixed ferrous-nickel oxalates with Fe:Ni ratios of 2:1, 64:36, 1:1, 1:3, 1:10 and 1:19, have been carried out in hydrogen atmosphere. After the dehydration and decomposition regions are well established, a detailed isothermal study is carried out. It has been found that the decomposition rates and the products formed depend on the mounting of the sample in the furnace and on the flow of hydrogen gas. In the experiments done using a vertical type of furnace, hereafter referred to as vertical experiments, the sample is taken in a 5 cm long culture tube with a 0.5 cm diameter mouth at the top. Hydrogen gas is passed over it. In this arrangement the gasses liberated during the reaction are not swept away very fast. In the experiments done using a horizontal type of furnace, hereafter referred to as horizontal experiments, the sample is taken in a 5 cm long porcelain boat of 0.5 cm width and 0.4 cm height. The sample is spread evenly to a thickness of 0.3 cm and hydrogen is passed over the boat; the product
gases could be easily swept away from the reaction zone along with the hydrogen flow. It has been found that the reaction occurs faster in the horizontal experiments. Careful steps are taken to pretreat the samples so as to avoid oxidation during exposure to atmosphere. The ESCA studies confirm that less than 6 layers of oxygen are formed on the surface of the product sample. Mössbauer study is carried out for the samples prepared in both vertical and horizontal experiments.

The Mössbauer experiments are carried out using a 512-channel multi-channel analyser and a $^{57}\text{Co}(\text{Pd})$ Mössbauer source. The decomposed samples are used as Mössbauer absorbers. The 14.4-keV resonance gamma rays are detected by a krypton filled proportional counter. Low temperature and high temperature Mössbauer studies are carried out on some of the absorbers in order to study the superparamagnetic (SPM) phase existing in them. The change in the oxidation state of iron is clearly followed and the products thus identified are confirmed by x-ray diffraction studies. The Mössbauer spectra are least-square fitted by a computer programme in order to extract the Mössbauer parameters.

In the vertical experiments, the ferrous-oxalate sample decomposed in hydrogen at 340°C for 1 hour is found to be super-paramagnetic; low-temperature Mössbauer
experiments confirm the presence of fine particles of Fe₃O₄. The experiments indicate that, when ferrous oxalate is heated at 340°C for 2 hours and 36 minutes or at 360°C for 36 minutes, approximately 160 Å particles of Fe₃O₄ are formed. As the reaction proceeds for longer times and at higher temperatures, Fe₃O₄, Fe₃C and Fe are detected in their magnetic phases. X-ray diffraction studies identify the phases present in the decomposition products. Ultimately only iron is formed indicating that the reaction has occurred to completion.

In the horizontal experiments, it has been found that the fine particles of Fe₃O₄ formed initially reduce quickly to Fe. Some of the iron particles react with the product gases, perhaps with CO, to form Fe₃C. The Mossbauer spectrum of the sample decomposed at 317°C for 1 hour indicates six lines due to Fe₃C which collapse into a single line (SPM state) when the sample is taken to around 160°C. Thus Fe₃C is seen to be produced in fine-particle form; the values for the anisotropy energy estimated from these studies are 5.6 x 10⁻¹⁶ ergs/sec and 7.0 x 10⁻¹⁶ ergs/sec, respectively, for the samples decomposed at 318°C for 1 hour and 2 hours.

A systematic study of the decomposition of mixed ferrous-nickel oxalate with Fe:Ni ratio of 2:1, 1:1 and 1:10 has been carried out in hydrogen atmosphere
in both vertical and horizontal experiments. A few chosen experiments are carried out for the mixed oxalates with Fe:Ni ratio of 64:36, 1:3 and 1:19. The Fe$_3$O$_4$ formed initially is very fine in size and is probably formed on the nickel particles which are also finely divided. The Fe$_3$O$_4$ soon starts reducing to the metallic form. A clue to the presence of Fe$_3$O$_4$, Fe and Fe-Ni fine particles is obtained through low-temperature Mossbauer studies. When the mixed oxalates are heated in hydrogen, simultaneous decomposition and reduction take place. Under favourable conditions, the metallic and the alloy powders can be formed directly without passing through the oxide phase. However, when the product gases accumulate, the oxide and the carbide phases appear. The scanning electron microscope pictures show that, during the initial stages of decomposition, the sample is porous and pyramid-like in shape; the morphological changes are seen as the decomposition progresses and ultimately they agglomerate. The x-ray diffraction studies identify the phases existing in the decomposition products.

In our decomposition studies, it has been found that the Fe-Ni alloy is formed at sufficiently low temperatures such as 300°C. The hyperfine field varies from
Fe-rich side to Ni-rich side as the concentration of nickel in the ferrous-nickel oxalate increases. The Mossbauer line-width of the alloy peak in the spectrum is wide (FWHM = 0.9 mm/sec) indicating that alloys of different compositions are formed. The hyperfine field of the Fe-Ni alloy, formed by decomposing samples in hydrogen at 360°C for 24 hours, is determined for different concentrations of Ni or Fe. The variation of the hyperfine field is found to be similar to that obtained by Johnson et al (1961) and bears similarity to the Slater-Pauling diagram. However, the saturation magnetisation in our case is higher than that of Johnson et al (1961). This is explained by the fact that, in the Fe-Ni alloy formed in our experiment, alloys of different composition are present: the stoichiometry of the alloy formed does not exactly follow that of the mixed oxalate. The formation of alloy takes place at considerably lower temperature and in shorter durations than in other conventional methods.