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Phase Transitions and Deoxidizing Effect in the Thermal Decomposition of Hydrous Ferrous Oxalate

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Powder of hydrous ferrous oxalate is annealed in non-oxidizing atmosphere of Ar, and the solid decomposition products obtained at various temperatures are studied by Mössbauer effect (ME) and X-ray diffraction (XRD). The results indicate that in Ar the initial product which is wüstite changes into magnetite and α -Fe with increasing annealing temperature, at the same time a small amount of Fe₄C appears. Annealing the oxalate at higher temperature, the magnetite in the solid products begins to transform into non-stoichiometric FeO (Fe_{1-x}O or FeO_x), and so an obvious deoxidizing effect of magnetite is indicated. At about 600 °C, the transition from magnetite to Fe_{1-x}O is already completed. Further results show that the deoxidizing effect does not result from the action of Ar and suggest that the deoxidizing effect of oxide is a general phenomenon.

1. Introduction

FeC₂O₄ · 2 H₂O is a typical representative of the decomposable metal-organic compounds which has simple chemical composition and structure, and is used extensively [1 to 5]. The thermal decomposition of FeC₂O₄ · 2 H₂O in oxidizing (air, oxygen) and inert (N₂, Ar, CO₂, vacuum) atmospheres had been studied widely and profoundly with thermal analytical methods by a large number of authors [6]. Although a scheme of decomposition routes can be obtained from the results, the influence of the annealing conditions on the decomposition products of FeC₂O₄ · 2 H₂O is not still clear. In this paper the transitions of the decomposition products of FeC₂O₄ · 2 H₂O in non-oxidizing atmosphere of Ar at various annealing temperatures have been studied by Mössbauer effect (ME) and X-ray diffraction (XRD). The deoxidizing effect of the magnetite in the products with increasing temperature has also been discussed.

2. Experimental

Hydrous ferrous oxalate was prepared by coprecipitating ferrous sulfates and ammonium oxalate at 60 °C. The precipitate was washed with water and then washed with acetone completely, finally dried at about 80 °C. The anealing temperatures were chosen appropriately on the basis of the results of DSC measurements in Ar. The FeC₂O₄ · 2 H₂O powder was placed in a copper crucible and then the crucible was put into a quartz tube through which hydrogen or argon can be passed. The tube was inserted in a furnace. Having kept it

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at the chosen temperature for a constant time, the tube was taken out and quenched in air. Throughout the process the atmosphere was passed through at a constant flow. To prevent it from oxidation, the annealed product was protected by the addition of toluene. The Mössbauer spectra of the annealed products were collected on a MR-351 spectrometer in a sine driving mode at room temperature, the source is 10 mCi $^{57}\mathrm{Co}(\mathrm{Rh})$. The isomer shift is determined relative to $\alpha\text{-Fe}$ at room temperature. The measurement of XRD was carried out on a D/max-RB X-ray diffraction spectrometer with CuK_{\alpha} radiation.

3. Results and Discussion

3.1 Phase transitions in the thermal decomposition of hydrous ferrous oxalate in Ar

In order to investigate the transitions in the decomposition of $FeC_2O_4 \cdot 2 H_2O$ in Ar, the $FeC_2O_4 \cdot 2 H_2O$ powder was annealed at various temperatures chosen on the basis of the measured DSC results of $FeC_2O_4 \cdot 2 H_2O$ in Ar. The Mössbauer spectra of the solid products obtained are shown in Fig. 1 and some fitting results are listed in Table 1, furthermore the XRD scheme of the solid products obtained at 450, 480, and 600 °C are also given in Fig. 2.



Fig. 1. The Mössbauer spectra of the solid product of $FeC_2O_4 \cdot 2 H_2O$ annealed in argon at various temperatures: (a) 350, (b) 390, (c) 450, (d) 480, (e) 540, (f) 600 °C



Fig. 2. The XRD schemes of the solid decomposition products of $FeC_2O_4 \cdot 2H_2O$

Some obvious transitions in the decomposition products are indicated with increasing annealing temperature from Fig. 1. It has been found that the oxalate begins to decompose in Ar at 350 °C and the initial decomposition product is wüstite [6], then the wüstite begins to transform into magnetite and α -Fe with increasing annealing tempera-

treatment temperature, time	$H_{ m hf}\ ({ m T})$	$\begin{array}{c} \mathbf{QS} \\ \mathbf{(mm/s)} \end{array}$	m IS (mm/s)	
450 °C, 1 h	48.8	0.00	0.27	magnetite
	45.8	0.00	0.66	U
	32.8	0.00	0.01	iron
	34.5	-0.06	0.28	Fe_4C
	21.8	0.01	0.28	
	_	_	0.14	defected
	_	_	0.69	magnetite
600 °C, 1 h	32.9	0.01	0.03	iron
	34.9	-0.29	0.39	Fe_4C
	21.5	-0.05	0.34	
	_	0.70	0.82	$Fe_{1-x}O$
	_	0.64	1.01	_ w

Table 1

The solid decomposition products of $FeC_2O_4\cdot 2~H_2O$ and their hyperfine parameters after annealing at various temperatures in argon

ture. Combining the XRD scheme of the product obtained at 450 °C which only indicates the existence of Fe₃O₄, Fe, and a small amount of Fe₄C [7, 8] with the Mössbauer spectrum of the product, two sets of ferromagnetic subspectra except the subspectra of Fe₃O₄ and α -Fe can be attributed to Fe₄C, and the paramagnetic subspectra should be assigned to the defected Fe₃O₄ in which there are some vacancies produced in the transition from wüstite to magnetite.

When the $\text{FeC}_2O_4 \cdot 2 \text{ H}_2O$ powder is annealed at 480 °C the transition from magnetite to non-stoichiometric FeO (Fe_{1-x}O or FeO_x) [8] occurs, and a large fraction of Fe₃O₄ in the product becomes paramagnetic. Increasing the annealing temperature, the transition from Fe₃O₄ to non-stoichiometric FeO (Fe_{1-x}O or FeO_x) is finished at 600 °C, while Fe₄C and α -Fe in the products remain.

So it is clear that, increasing the annealing temperature till 600 °C, two transitions in the decomposition products occur. One is the transformation in which the wüstite is oxidized to magnetite and the other is that in which the magnetite is reduced to $Fe_{1-x}O$ at higher temperature. In these processes the minor products of $FeC_2O_4 \cdot 2 H_2O$ such as α -Fe and Fe₄C remain.

3.2 Deoxidizing effect of the magnetite in products

According to the above results, the transition from magnetite to non-stoichiometric FeO indicates an obvious deoxidizing effect, in other words, there is a tendency that the magnetite is reduced in Ar at high temperature. To clarify the action of Ar in this process, the decomposition product (mainly magnetite) of $FeC_2O_4 \cdot 2 H_2O$ in nitrogen at 450 °C was annealed in vacuum at 600 °C. The Mössbauer spectrum of the product is shown in Fig. 3, curve a and the fitting results are given in Table 2. It shows a similar result so that it could be concluded that the deoxidizing effect is not due to the existence of Ar.

Furthermore we annealed α -Fe₂O₃ in vacuum at 600 °C, which had been obtained by decomposing FeC₂O₄ · 2 H₂O in air at 600 °C, and cooled in vacuum to avoid reoxidizing. The product obtained is magnetite and Fe_{1-x}O, and its Mössbauer spectrum is shown in Fig. 3b, the fitting result is also listed in Table 2, i.e., α -Fe₂O₃ is deoxidized



Fig. 3. The Mössbauer spectra of the solid product of $FeC_2O_4 \cdot 2 H_2O$ annealed in vacuum at 600 °C after annealing in nitrogen at 450 °C, (b) after annealing in air at 600 °C

and reduced to Fe_3O_4 and FeO. From this result it may be suggested that the deoxidizing effect of oxide at high temperature is a general phenomenon. Usually the reoxidization in the cooling process covers up this effect.

4. Conclusion

Table 2

So far the transitions of the solid decomposition products of hydrous ferrous oxalate in argon, which are the changes from wüstite to magnetite at about below 450 °C and from magnetite to $Fe_{1-x}O$ at higher temperature, have been studied by ME and XRD. In the first transition the wüstite is oxidized to magnetite, and in the second transition the magnetite is reduced to $Fe_{1-x}O$. The second transition shows an obvious deoxidizing effect, and further experimental results indicate that the deoxidizing effect of oxide at higher temperature is a general phenomenon. It might be inferred that the oxide is not stable at high temperature.

treatment temperature, time	${H_{ m hf} \over (10^{-1}~{ m T})}$	$\begin{array}{c} { m QS} \ ({ m mm/s}) \end{array}$	m IS m (mm/s)	
600 °C, 1 h	33.1	0.00	0.13	iron
(after annealed in	_	0.69	0.96	${ m Fe}_{1-x}{ m O}$
nitrogen at 450 °C)	_	0.42	0.17	
600 °C, 1 h	48.9	-0.02	0.29	magnetite
(after annealed in	45.0	0.05	0.59	
àir at 600 °C)	_	0.67	0.99	$Fe_{1-x}O$
	_	0.70	0.72	

The solid decomposition products of $\rm FeC_2O_4\cdot 2~H_2O$ and their hyperfine parameters after annealing at 600 °C in vacuum

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