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Study the structure stability of $NiFe_{2-x}Cr_xO_4$ ($x = 0, 0.08$) during H_2/CO_2 cycle reaction

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Abstract H_2/CO_2 cycle reaction activities of spinel structure $NiFe_{2-x}Cr_xO_4$ ($x = 0$, 0.08) prepared by co-precipitation were determined. The results showed that pure $NiFe_2O_4$ had almost lost its CO_2 decomposition activities after 15 cycles, while Cr^{3+} doped $NiFe_2O_4$ still had about 40% of the initial reaction activity value after 50 reaction cycles. The magnetic properties of samples annealed at 350 °C indicated that M_s and M_r decreased from 32.49 to 26.04 emu/g and 9.39 to 7.31 emu/g, respectively, but H_c increased from 230 to 1800 Oe with the increasing of Cr^{3+}content. XRD Rietveld analysis showed that there appeared 23.15% Fe_yNi_{1-y} ($0<y<1$) and no Fe_3C in pure $NiFe_2O_4$ system after the first H_2/CO_2 cycle reaction. With the increasing of cycle times, the phase abundance of $NiFe_2O_4$ decreased rapidly. At the same time, Fe_3C appeared and its content increased fast. After 15 cycles, the phase abundance of $NiFe_2O_4$ is less than 5%wt, but those of Fe_yNi_{1-y} ($0 < y < 1$) and Fe_3C enhanced to 48.15 %wt and 46.92 %wt, respectively. However, the cycle reaction life of $NiFe_{2-x}Cr_xO_4$ ($x = 0.08$) was much longer than $NiFe_2O_4$. The spinel structure stability was improved dramatically because of the existing of Cr^{3+} in the cell of $NiFe_2O_4$. After 50 cycles, the phase abundance of $NiFe_2O_4$ still had 20 %wt.

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Introduction

In the early of 1990, Tamaura [1] reported that CO_2 could reduce to C with an efficiency of nearly 100% at 290 °C on the oxygen-deficient magnetite. Subsequently, some researchers [2–6] found that the oxygen-deficient spinel structure $MFe_2O_{4-\delta}$(M = transition metals, $\delta > 0$) could also decompose CO_2 to C about 300 °C in 100%. No matter what magnetite or other spinel ferrite would form oxygen-deficient structures when they were reduced by H_2 at about 300 °C. Such oxygen-deficient compounds had strong reducing ability. They could capture oxygen not only from CO_2 but also from H_2O or other oxides. Being strong reducing agent, the oxygen-deficient compounds are very difficult to exist under normal conditions, so there are little studies on such compounds. Though there were some reports of oxygen-deficient compounds such as $Fe_3O_{4-\delta}$ and $MFe_2O_{4-\delta}$(M = Fe, Ni, Co, Mn, etc.) about their reaction activities of decomposing CO_2 to C, the structure change of these spinels in H_2/CO_2 cycle reaction is not clear yet. For H_2/CO_2 cycle reaction, the activity life, in the fact the structure stability of the spinel, is very important. But till today we have not found how to improve the structure stability of spinel in cycle reaction.

$NiFe_2O_4$ is a typical AB_2O_4 spinel compound. Its oxygen-deficient structure has good ability to decompose CO_2 to C. In this paper, we studied the activity and structure change of $NiFe_{2-x}Cr_xO_4$ ($x = 0$, 0.08) in H_2/CO_2 cycle reaction. In order to elucidate Cr^{3+} doping effect and the structure stability of $NiFe_{2-x}Cr_xO_4$ during cycle reaction process, we adopted physical property measurement system to determine the magnetite properties of 350 °C annealed samples, and XRD Rietveld analysis method to obtain the phase combination and phase abundance of samples after 15 and 50 times H_2/CO_2 cycle reaction respectively.

Experimental

$Ni(NO_3)_2$, $Fe(NO_3)_3$ and NaOH (A.R.) were used as starting materials. $NiFe_2O_4$ was prepared by mixed ions coprecipitation from $[Ni^{2+}] = 1.0$ M, $[Fe^{3+}] = 1.2$ M, $[NaOH] = 3.0$ M with the molar ratio of Ni^{2+} and Fe^{3+} were 1:2. Before precipitating, two metal ions were mixed sufficiently. Then the mixed metal ions and NaOH precipitated in parallel-current way under 50–70 °C and pH = 11–14 conditions. The suspension was filtered and washed carefully until all NO_3^- was removed. The precipitated was dried at 120–150 °C and calcined at 350 °C for 3 h in air atmosphere. Cr^{3+} doped $NiFe_2O_4$ was prepared using the same method.

The equipment used for H_2/CO_2 cycle reaction was built according to the literature [2]. Sample was heat-treated at 310 °C and 40 mL/min hydrogen follow through a quartz tube treatment. H_2 reduction time was kept 2 h for each reaction. After finishing reduction, the reaction system was pumped to vacuum for 10 min. Then using pure Ar blew 10 min to remove the absorbed H_2. Conducted CO_2 into the reaction system to 0.1 MPa and counted the reaction time immediately. The total decomposition time was 4 h in each cycle reaction. With the increasing of cycle reaction, CO_2 in the system could not decompose completely. Before the next cycle reaction, the remaining gas must be removed. When the cycle reaction finished, the system was cooled down to the room temperature and the sample was taken out for XRD analysis. We chose 1 and 15 H_2/CO_2 cycle reaction times for pure $NiFe_2O_4$ and 1, 15, 35, 50 times for Cr^{3+} doping samples, respectively.

The magnetic properties were investigated by physical property measurement system (USA Quantum Design Corp. PPMS-9T). XRD data for Rietveld analysis were obtained with a Rigaku D/max-3B X-ray powder diffractometer, using CuK_α radiation and a power of 40 kV × 40 mA, a diffracting beam graphic monochrometer over the range $2\theta = 15$–100° with a step interval of $2\theta = 0.02°$ and a count time of 6 s per step. Rietveld refinements were performed on a personal computer using Rietica software [7]. The crystallite size of Fe_yNi_{1-y} $(0 < y < 1)$ was obtained using Scherrer method.

Results and discussion

CO_2 decomposition activity

Figure 1 shows CO_2 decomposition activity curves of $NiFe_{2-x}Cr_xO_4$ ($x = 0, 0.08$) at the 15th and 50th cycle. From Fig. 1 we can find that pure $NiFe_2O_4$ had almost lost CO_2 decomposition activity at the 15th cycle. When doped with Cr^{3+}, $NiFe_2O_4$ still had about 40% of the initial activity value at the 50th cycle.

Magnetite properties

Figure 2 shows 5K hysteresis loops of $NiFe_{2-x}Cr_xO_4$ ($x = 0, 0.08$) after annealing at 350 °C. Table 1 gives the saturation magnetization M_s, remanent magnetization M_r and coercivity H_c calculated from Fig. 2. According to Table 1, it obviously shows that the magnetic properties of samples changed corresponding to the doping content of Cr^{3+}. M_s and M_r decrease as the content of doping Cr^{3+} increases while H_c increases. For nickel ferrite material, the saturation magnetization M_s and remanent magnetization M_r are defined by the molecular magnetic moment. In the spinel structure of $NiFe_2O_4$, Ni^{2+} ions and a half of Fe^{3+} ions located in octahedral A site, another half of Fe^{3+} ions located in tetrahedral B site. It is known that Cr^{3+} ions have strong B-site preference. When Cr^{3+} ions were introduced into the inverse spinel $NiFe_2O_4$, Cr^{3+} ions substituted for some of Fe^{3+} in B-site. Cr^{3+} ions have 3 μ_B, less than 5 μ_B of Fe^{3+} ions. So the introduction of Cr^{3+} ions on octahedral B sites in the inverse spinel nickel ferrite will reduce the saturation magnetization. On the other way, the doping sample has smaller crystallite size than the pure one, the

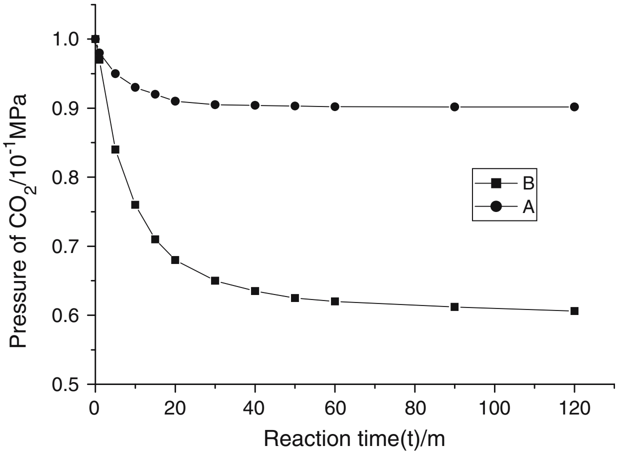

Fig. 1 CO_2 decomposition activity curves of $NiFe_{2-x}Cr_xO_4$ ($x = 0, 0.08$) A: 15th cycle, B: 50th cycle

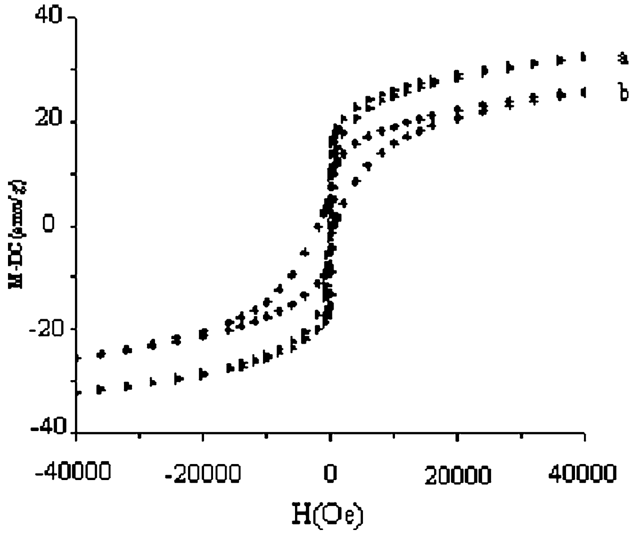

Fig. 2 5K hysteresis loops of $NiFe_{2-x}Cr_xO_4$ after annealing at 350 °C, curves a, b stand for $x = 0, 0.08$

Table 1 Magnetic properties of $NiFe_{2-x}Cr_xO_4$ ($x = 0, 0.08$) annealed at 350 °C

Annealed temperature	$NiFe_{2-x}Cr_xO_4$		
	Magnetic parameters	$x = 0$	$x = 0.08$
350 °C	M_s (emu/g)	32.49	26.04
	M_r (emu/g)	9.39	7.31
	H_c (Oe)	230	1800

atomic distance of the surface get longer, as a result, the saturation magnetization also will reduce while the coercivity H_c increases [8]. This is consistent with the magnetic properties of $NiFe_{2-x}Cr_xO_4$ ($x = 0, 0.08$) on Table 1.

XRD results

Figures 3 and 4 show XRD patterns of $NiFe_{2-x}Cr_xO_4$ ($x = 0, 0.08$) after different times of H_2/CO_2 cycle reaction, respectively. Figure 5 shows XRD Rietveld analysis patterns of $NiFe_{2-x}Cr_xO_4$ ($x = 0, 0.08$) and Table 2 gives the results of XRD Rietveld analysis. According to Figs. 3 and 4 and Table 2, it was obviously found that a new phase Fe_yNi_{1-y} ($0 < y < 1$) appeared after the first cycle reaction in spite of Cr^{3+} doped or not, but the phase abundance of Fe_yNi_{1-y} ($0 < y < 1$) in Cr^{3+} doped $NiFe_2O_4$ system was less than that in pure $NiFe_2O_4$ system. With the increasing of reaction cycles, the phase abundance of $NiFe_2O_4$ decreased, while Fe_3C appeared and its abundance increased quickly. After 15 cycles, the abundance of $NiFe_2O_4$ in pure $NiFe_2O_4$ system just left 5 %wt and the sample had almost lost CO_2 decomposition activity, while the crystallite size of Fe_yNi_{1-y} ($0 < y < 1$) increased from 9.8 to 73.5 nm. However, the abundance of $NiFe_2O_4$ in Cr^{3+} doped $NiFe_2O_4$ system still had about 20 %wt and its CO_2 decomposition activity also had 40 %wt of the initial activity value at the 50th cycle. At the same time, the phase abundance of Fe_yNi_{1-y} and Fe_3C attained 41.23 %wt and 39.02 %wt, respectively. The crystallite size of Fe_yNi_{1-y} ($0 < y < 1$) increased from 9.6 to 85.0 nm gradually. According to the above results, we can find that the existing of Cr^{3+} in the cell of $NiFe_2O_4$ not only delayed the collapsing the spinel structure, but also inhibited the increasing of Fe_yNi_{1-y} ($0 < y < 1$) crystallite size.

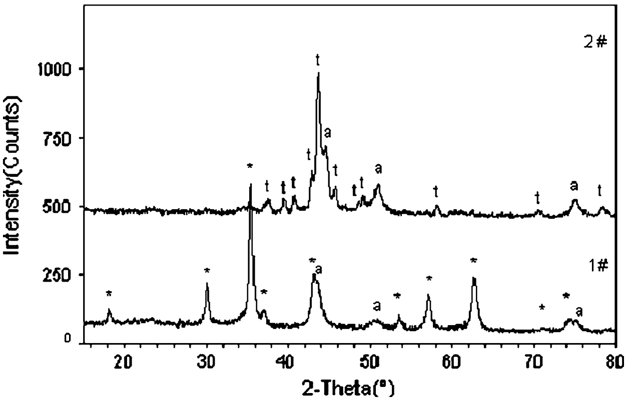

Fig. 3 XRD pattern of $NiFe_2O_4$ after 1, 15 cycles 1#: 1 cycle, 2#: 15 cycles *: $NiFe_2O_4$, a: Fe_yNi_{1-y} ($0 < y < 1$), t: Fe_3C

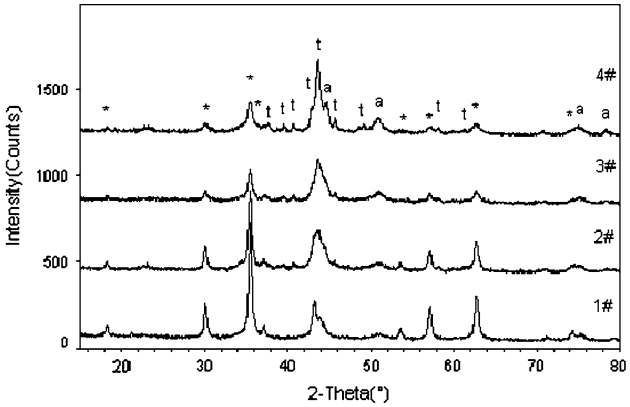

Fig. 4 XRD pattern of $NiFe_{2-x}Cr_xO_4$ ($x = 0.08$) after 1, 15, 35 and 50 cycles 1–4 are 1, 15, 35, and 50 cycles, respectively, *: $NiFe_{2-x}Cr_xO_4$, a: Fe_yNi_{1-y} ($0 < y < 1$), t: Fe_3C

Discussion

Being as AB_2O_4 type of spinel structure, the oxygen closed-packing of $NiFe_2O_4$ is fcc, Ni^{2+} and a half of Fe^{3+} ions located in octahedral sites, other half of Fe^{3+} ions located in tetrahedral sites. During H_2/CO_2 cycle

Fig. 5 XRD Rietveld pattern of $NiFe_{2-x}Cr_xO_4$ (x = 0, 0.08) after reaction cycles

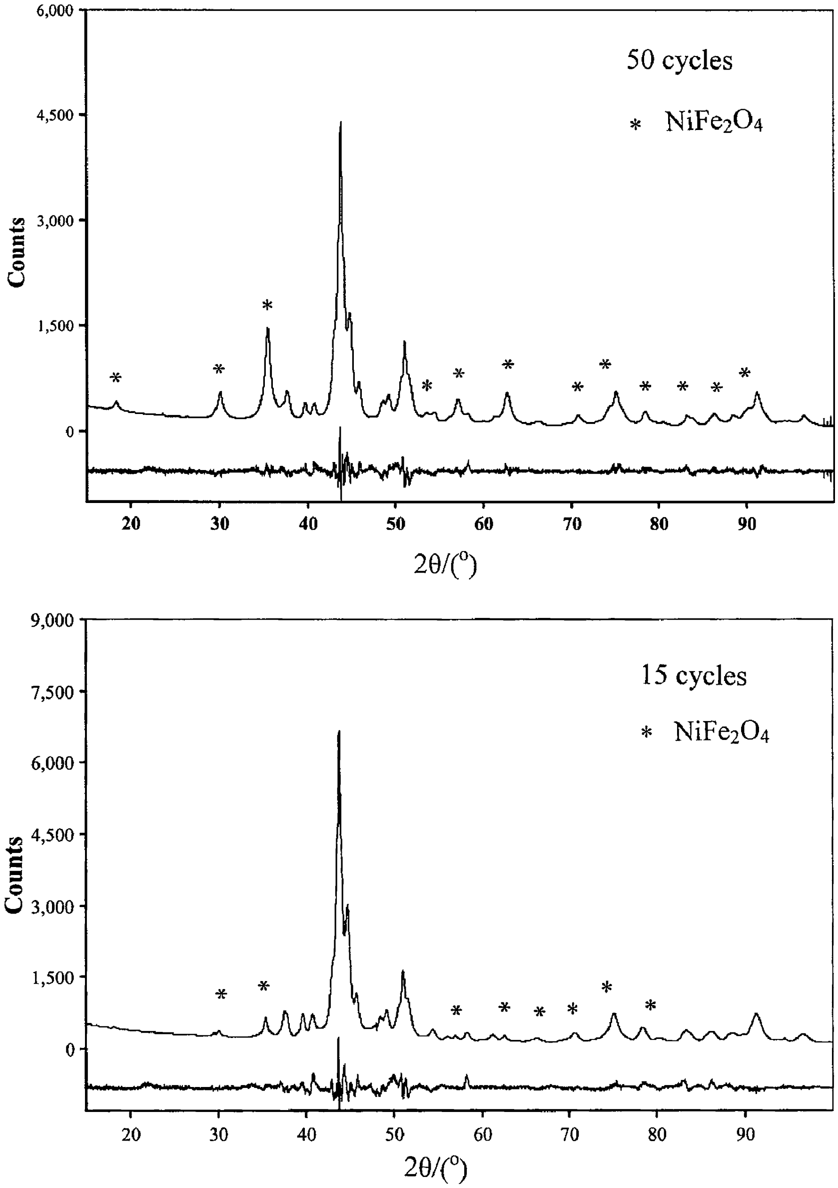

Table 2 Rietveld analysis results of $NiFe_{2-x}Cr_xO_4$ (x = 0, 0.08)Note: R_{wp} = weighted pattern factor, R_p = pattern factor, S = Goodness of fit [9]

	Cycle time			
	x = 0		x = 0.08	
	1	15	1	50
R_{wp}	8.955	9.78	9.32	11.25
R_p	6.78	7.25	6.85	9.24
S	1.71	1.79	1.75	1.91
$NiFe_2O_4$ (%wt)	76.85(1.23)	4.93(0.54)	85.26(1.74)	19.75(0.67)
Fe_yNi_{1-y} (%wt) ($0 < y < 1$)	23.15(0.56)	48.15(1.33)	14.74(0.61)	41.23(1.12)
Fe_3C (%wt)	0	46.72(1.09)	0	39.02(1.30)
The crystallite size of Fe_yNi_{1-y}/nm	9.8(3)	73.5(5)	9.6(4)	85.0(7)

reaction, $NiFe_2O_4$ was reduced by H_2 to form oxygen-deficient structure at first. In the reducing process, O^{2-} migrated from the bulk structure of $NiFe_2O_4$ to the surface and reacted with the absorbed H_2 to form H_2O, the electron remained on the solid surface. Fe^{3+} accepted these electrons reduced to Fe^{2+} in order to preserve the electrical neutrality of compound, as a result, $NiFe_2O_4$ transformed to oxygen-deficient structure. When the oxygen-deficient compound reacted with CO_2, Fe^{2+} oxidized to Fe^{3+}, O^{2-} migrated into the bulk of $NiFe_2O_{4-\delta}$ and the oxygen-deficient structure return to the normal structure too. Because Ni^{2+} is easier to be reduced than Fe^{3+}, Ni appeared at the first step. The reduced product Ni had the behavior of H_2 spill. So the appearance of Ni in the system would enhance the reducing ability of H_2. Under the processing of cycle reaction, some amount of Fe appeared, and such Fe would alloy with Ni to form Fe_yNi_{1-y} $(0 < y < 1)$. Small crystallite Fe_yNi_{1-y} $(0 < y < 1)$ could react with CO_2 to form Fe_3C. When the crystallite size of Fe_yNi_{1-y} $(0 < y < 1)$ grew up, its CO_2 decomposition activity declined. But Fe_3C had no CO_2 decomposition activity. Finally, the spinel structure of $NiFe_2O_4$ collapsed and sample lost its CO_2 decomposition activity.

When $NiFe_2O_4$ was doped with Cr^{3+}, the spinel structure stability raised dramatically. Though the cycle reaction times up to 50, the phase abundance of spinel still had 20 %wt and CO_2 decomposition activity still had 40% the initial reaction activity value for Cr^{3+} doping sample. According to samples' magnetic properties discussed above, we can conclude that Cr^{3+} entered the bulk structure of $NiFe_2O_4$. Based on the ligand field theory, we known that Cr^{3+} located in octahedral site (B site). Cr^{3+} was a stronger acid than Fe^{3+} by virtue of its ability to attract electron pair as the radii of Cr^{3+} and Fe^{3+} were 0.064 and 0.067 nm respectively, thought they all had a valence of three. Furthermore, the strength and stability of Cr–O covalent bond are stronger and better than Fe–O. When doped Cr^{3+} entered the bulk structure of $NiFe_2O_4$ and replaced the same amount of Fe^{3+}, Cr–O bond would distribute equally in B sites of the spinel. Such Cr–O bonds could raise the stability of $NiFe_2O_4$ structure. During the formation process of oxygen-deficient structure under H_2 atmosphere, the collapsing rate of $NiFe_2O_4$ decreased and the cycle reaction life was lasted effectively.

Conclusions

$NiFe_2O_4$ have good H_2/CO_2 reaction activities. But the pure $NiFe_2O_4$ lost its decomposition CO_2 activity just after 15 times H_2/CO_2 cycle reaction. The structure of $NiFe_2O_4$ gradually collapsed to Fe_yNi_{1-y} $(0 < y < 1)$ and Fe_3C during cycle reaction process. When $NiFe_2O_4$ was doped with some amount of Cr^{3+}, the stability of $NiFe_2O_4$ spinel structure was dramatically raised. Though the cycle reaction times up to 50, the phase abundance of spinel still had 20 %wt and CO_2 decomposition activity still had 40% the initial reaction activity value.

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References

1. Tamaura Y, Tabata M (1990) Nature 346:255
2. Kodama T, Tominaga K, Tabata M et al (1992) J Am Ceram Soc 75:1287
3. Tabata M, Nishida Y, Kodama T et al (1993) J Mater Sci 28:971
4. Akanuma K, Nishizawa K, Kodama T et al (1993) J Mater Sci 28:860
5. Zhang CL, Li S, Wang LJ et al (2000) Mater Chem Phys 62:44
6. Zhang CL, Li S, Wang LJ et al (2000) ibid. 62:52
7. Howard CJ, Hunter BA (1997) A computer program for Rietveld analysis of X-ray and neutron powder diffraction patterns. Lucas Heights Research Laboratories, Australia, p 2
8. Lide Z, Jimei M (2002) Nanomaterials and nanostructure. Science Press, p 315
9. Young RA (1993) The Rietveld method. Oxford Science Publication, p 22