Conversion of Concentrated Solar Thermal Energy into Chemical Energy

Yutaka Tamaura

Abstract When a concentrated solar beam is irradiated to the ceramics such as Ni-ferrite, the high-energy flux in the range of 1500–2500 kW/m² is absorbed by an excess Frenkel defect formation. This non-equilibrium state defect is generated not by heating at a low heating-rate (30 K/min), but by irradiating high flux energy of concentrated solar beam rapidly at a high heating rate (200 K/min). The defect can be spontaneously converted to chemical energy of a cation-excess spinel structure (reduced-oxide form) at the temperature around 1773 K. Thus, the O₂ releasing reaction (α -O₂ releasing reaction) proceeds in two-steps; (1) high flux energy of concentrated solar beam absorption by formation of the non-equilibrium Frenkel defect and (2) the O₂ gas formation from the O²⁻ in the Frenkel defect even in air atmosphere. The 2nd step proceeds without the solar radiation. We may say that the 1st step is light reaction, and 2nd step, dark reaction, just like in photosynthesis process.

Keywords Ni-ferrite · Solar hydrogen · Frenkel defect · α -O₂ releasing reaction · Concentrated solar heat

INTRODUCTION

The O₂ releasing reaction is an endothermic process, but is able to absorb the concentrated solar heat by a thermochemical process; the concentrated solar beam energy can be converted to a chemical energy in the thermochemical process. When the O₂ releasing reaction takes place for some metal oxides, solar energy is converted to the reduced form of the oxides. We have reported so far the formation of the cation-excess form of the NiMn-ferrite (reactive ceramics) by O₂ releasing reaction during irradiation of a concentrated solar beam (Tamaura et al. 1995). However, in general, this kind of metal-oxide reduction takes place at a

lower O₂ partial pressure. Therefore, absorption of the high flux of the concentrated solar beam energy seems to be difficult by the endothermic reaction with the metal oxides at such a lower O₂ partial pressure. To solve this problem, we have further studied how the high flux of the concentrated solar energy is absorbed by the O₂ releasing reaction in view of chemical reaction rate and crystalline chemistry. Recently, we have found out that the O₂ gas releasing reaction, which can take place at a high O₂ partial pressure of the air, by irradiating a high flux infrared beam to the Ni-ferrite in air at 1773 K (heating rate = 200 K/min) (Tamaura et al. 2007, 2009; Tamaura and Kaneko 2009). This α -O₂ releasing reaction proceeds in a high O₂ partial pressure.

In this paper, we will describe the energy transferring process of the concentrated solar beam of a high flux intensity into the reduced form of the Ni-ferrite for “the α -O₂ releasing reaction”.

RESULTS AND DISCUSSION

Figure 1 shows O₂ releasing profiles (lower panel; measured by direct gas/mass spectrometer) of Ni-ferrite for the O₂ gas releasing reaction in the air by irradiation of infrared beam from imaging furnace at heating rate of 30 and 200 K/min for the final temperature of 1773 K. At the low heating rate (30 K/min), the broad peak of O₂ releasing reaction appeared (Curves A in upper and lower panels in Fig. 1). However, as can be seen from Curve C in lower panel, a strong peak of O₂ gas evolution appeared (α -O₂ releasing reaction). The O₂ gas releasing reaction immediately stopped (intensity goes down to background level), when the temperature was rapidly lowered after reaching the temperature of 1773 K (Curve C in upper panel). As seen from Curve B, however, after reaching 1773 K

Fig. 1 DMS signal for O₂-releasing reaction in Ar at 30 K/min (A) and 200 K/min (B, C)

(heating rate 200 K/min) and by keeping the temperature constant at 1773 K, the O₂ gas intensity was kept higher over the background level (Curve B in lower panel), indicating that another O₂ gas releasing reaction different from α -O₂ releasing reaction takes place. In the X-ray diffractometry (XRD) measurements for the case of Curve C shown in upper panel of Fig. 2 (C for Fig. 1), only the peaks corresponding to spinel type compound appeared whose lattice constant (0.8348 nm) is higher than that of the starting sample of Ni-ferrite (0.8336 nm). In the case for Curve B, peaks for spinel type compound (0.8336 nm) and wüstite phase appeared. These results suggest that a cation-excess spinel structure of Ni-ferrite is formed immediately

after the α -O₂ releasing reaction, but decomposed into the two compounds (1) a non cation-excess spinel structure of Ni-ferrite and (2) wüstite composed of Ni²⁺ and Fe²⁺. When these reduced oxides (cation-excess spinel structure, wüstite compound) are converted to H₂ gas by the reaction with H₂O, cation-excess spinel structure has a higher reactivity compared than wüstite compound, because the cation-excess spinel compound keeps the spinel structure of the Ni-ferrite, but the wüstite compound has NaCl structure which is different from the Ni-ferrite structure. Therefore, it is preferable using α -O₂ releasing reaction (Curve C in Fig. 1) for conversion of the solar energy into solar hydrogen by the further reaction with H₂O.

Fig. 2 XRD of solid products for curves A and B, and curve C for Fig. 1

Figure 3 shows changes in the lattice constant (Curve a) of the Ni-ferrite (spinel structure) and the O₂ gas volume released (Curve b) during the rapid increase in the reaction temperature (200°C/min) by an irradiation with the high flux infrared beam. The XRD was measured for the samples, after being quenched when the temperature attained at the values given in Fig. 3 (The Ni-ferrite might have melted at $T > 1850$, melting point; 1910 K in air). At $T < 1673$ K, the O₂ gas was little evolved, but the lattice constant was largely increased. This indicates that an excess amount of the Frenkel defect is formed under non-equilibrium state. Some amount of cations moves into the interstitial site, which causes the increase in the lattice constant. Also, this result shows that the O₂ releasing reaction rate (the O₂ gas formation reaction rate of the lattice oxygen (O²⁻)) is lower than the cation mobility to form the Frenkel defects at $T < 1673$ K. Thus, it can be concluded that the high flux beam energy is first absorbed by the Frenkel defect formation in non-equilibrium state. The Frenkel defect is a stoichiometric defect and involves an atom displaced off its lattice site into an interstitial site that is normally empty. In general, a minimum in free energy occurs at a certain defect concentration of the Frenkel defect present in the crystal under conditions of thermodynamic equilibrium at a given temperature (West 1984). In the present study, Frenkel defect is formed in an extra amount in non-equilibrium state by a rapid absorption of the high flux energy of the beam.

This was confirmed by the Mössbauer effect measurement. Table 1 lists the Mössbauer effect parameters measured at $T = 1673$ K. The changes in the intensity ratio

between A site and B site area and those between initial and $T = 1673$ K shows that some of the Fe³⁺ in the B-site moved into the A site during heating at $T = 1673$ K. Because all the normal lattice site of A site is situated with Fe³⁺, some of the Fe³⁺ ions are considered to move to the interstitial A site. At $T > 1773$ K, however, α -O₂ releasing reaction takes place (Curve b in Fig. 3), and the evolved O₂ gas amount increased with an increase in the temperature. The lattice constant also increased with increase in the temperature at >1773 K (Curve a in Fig. 3). This increase in the lattice constant is caused by the formation of the oxygen deficient structure (reduced form) of the Ni-ferrite by the O₂ releasing at >1773 K.

These results mentioned above show that, as a first step, the high flux energy of the concentrated beam is directly absorbed by the Frenkel defect formation in non-equilibrium state at $T > 1673$. The enthalpy change in the Frenkel defect formation of Fe₃O₄ is 754 kJ/mol (Dieckmann et al. 1987). Therefore, the concentrated solar beam could be absorbed at around this enthalpy energy change for the non-equilibrium Frenkel defect formation. And, in the second step, the Frenkel defect, which is excessively formed in non-equilibrium state, is decomposed transferring the absorbed energy to generate the O₂ gas from the lattice O²⁻ (formation of a reduced form of Ni-ferrite), as the temperature reaches near 1773 K. The O₂ formation reaction rate would be higher at the temperature around 1773 K. As a total process, the concentrated solar energy is transferred to the reduction potential of the reduced form of the Ni-ferrite. This would be the energy-transfer process in the α -O₂ releasing phenomenon, which we have reported so

Fig. 3 Change in lattice constant (a) and O₂ gas evolution (b) of Ni-ferrite with reaction temperature

Table 1 Mössbauer effect parameters of Ni-ferrite

Sample	Relative absorption intensity (%)		Isomer shift (mm/s)		Quadrupole splitting (mm/s)		Magnetic hyperfine field (T)	
	A-site	B-site	A-site	B-site	A-site	B-site	A-site	B-site
Initial	54.2	45.8	0.29	0.39	0.00	0.00	49.4	52.7
1623 K	60.3	39.7	0.31	0.40	0.00	0.01	49.4	52.6

far (Tamura et al. 1995, 2007, 2009; Tamura and Kaneko 2009). In the case of ceria-zirconia, an oxygen deficient structure was formed after the α -O₂ releasing reaction in the air atmosphere.

From these findings, it might be concluded that the solar thermochemical process for the reduced ceramics formation by irradiation of the energy flux in the range of 1500–3000 kW/m² proceeds by two steps; (1) The visible light in the high flux of concentrated solar beam is absorbed and the relaxation process of the excited states takes place, generating an excess Frenkel defect structure in non-equilibrium (Light reaction), and (2) The lattice O^{2−} in the crystal with the excess Frenkel defect structure reacts to form O₂ gas (Dark reaction). This O₂ gas formation process (Dark reaction) is the chemical reaction process, and its reaction rate is slower than the relaxation process taking place after the visible-light absorption. Thus, the concentrated solar beam energy with high flux is absorbed (visible-light absorption rate) and transferred to the lattice energy in non-equilibrium (fast relaxation rate), and successively transferred to the activated ceramics by the O₂ gas formation reactions (chemical reaction rate). These energy-transfer steps proceed even at a high oxygen partial pressure such as air atmosphere. Here, the “Light” and “Dark” means that the reactions proceed under solar light (concentrated solar light) (Light) and without solar light (Dark). In the light dependent reactions of the photosynthesis, the absorption of solar photon energy results in the synthesis of two high-energy chemical compounds: ATP and NADPH/NADP. These high-energy compounds react with CO₂ and produce three carbon sugars without light (Calvin cycle in the light-independent or dark reactions) (Blankenship 2002). In a similar concept, the high flux solar energy conversion into chemical energy of the reduced form of the ceramics seems to be divided into Light reaction (Light) and Dark reaction (Dark); the high flux concentrated solar beam energy is absorbed by Frenkel defect formation (generation of a high-energy compound using solar light energy) (Light). The Frenkel defect forms O₂ gas from the lattice O^{2−} without solar light (Dark).

Considering the O₂ gas evolution amount, the concentrated solar beam energy, which can be absorbed by the Frenkel defect formation is estimated to be 317 kJ/mol. This energy would be stored in the lattice structure by the absorption of the high flux of concentrated solar beam. This

absorbed solar energy is considered to be transformed to the chemical energy of the reduced form of the Ni-ferrite with the cation-excess spinel structure (α -O₂ releasing reaction). This accumulated solar energy in the cation-excess spinel structure can be used for water decomposition reaction to generate solar hydrogen, because the cation-excess structure has a reduction potential for water decomposition reaction.

Acknowledgment I would like to express my gratitude to my colleagues in our institute, prof. Hirhoshi Kaneko, Mr. Satoshi Shigeta, Mr. Yousuke Ishikawa, Mr. Chong-il Lee, who made enormous contribution to this paper, and like to appreciate Ministry of Education, Culture, Sports, Science & Technology for the Science Research Grant on this paper (Grant; (A)21246147)).

REFERENCES

- Blankenship, R.E. 2002. *Molecular mechanisms of photosynthesis*. Oxford: Blackwell, ISBN-10: 0632043210.
- Dieckmann, R., M.R. Hilton, and T.O. Mason. 1987. Defects and cation diffusion in magnetite (VIII); migration enthalpies for iron and impurity cations. *Physical Chemistry* 91: 59–66.
- Tamura, Y., and H. Kaneko. 2009. O₂ releasing reactivity of ceramics for rotary-type solar reactor with two-step H₂O splitting. *Proceedings of the 2009 ASME 3rd international conference on energy sustainability*, ES2009-90421.
- Tamura, Y., H. Kaneko, H. Ishihara, S. Taku, Y. Naganuma, and H. Fukuzumi. 2007. The reactive ceramics for solar H₂ production by rotary type solar reactor with two step water splitting. *16th international symposium on the reactivity of solids*.
- Tamura, Y., Y. Naganuma, N. Hasegawa, and H. Kaneko. 2009. Concentrated solar energy conversion into chemical energy(88): α -O₂ releasing reaction of reactive ceramics by rapid heating. *Annual spring meeting of Japan Chemical Society*, 4B5-01.
- Tamura, Y., A. Steinfeld, P. Kuhn, and K. Ehrensberger. 1995. Production of solar hydrogen by a 2-step water-splitting thermochemical cycle. *Energy* 20: 325.
- West, A.R. 1984. *Solid state chemistry and its applications*. New York: Wiley, ISBN 0-471-90377-9.

AUTHOR BIOGRAPHY

Yutaka Tamura (✉) is a Professor of Tokyo Institute of Technology. His research interest includes solar thermochemical energy conversion, solar concentration system (Beam-down), solar hybrid fuel production using concentrated solar energy and fossil fuels of coal and natural gas, solar hydrogen production.
Address: Department of Chemistry, Science and Engineering, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152, Japan.
e-mail: ytamura@chem.titech.ac.jp