Influence of SO_2 Gas on Output of Resistive Oxygen Sensor Using CeO_2 or $Ce_{0.8}Zr_{0.2}O_2$

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It is very important to investigate the influence of corrosion gas in exhaust gas on the resistive oxygen sensor for practical use. In this study, the influence of SO_2 gas on the output of resistive oxygen sensors using CeO_2 or $Ce_{0.8}Zr_{0.2}O_2$ thick film with 200 – 300 nm particle size was investigated. Furthermore, the reason why the influence was larger in the case of CeO_2 thick film was also investigated.

Mist of mixed solution (cerium nitrite and zirconium oxynitrate) was introduced in the furnace at 973 K and pyrolyzed. The particle size of pyrolyzed powder was about 200 – 300 nm. The paste mixed with the powder and organic binder was screen-printed on alumina substrate. The screen-printed thick films were calcined at 773 K and fired at 1473 K in air. Finally, the CeO_2 and $Ce_{0.8}Zr_{0.2}O_2$ thick films were obtained. The average particle size of the films was 200 – 300 nm and no difference between the CeO_2 and $Ce_{0.8}Zr_{0.2}O_2$ thick films was observed. The Pt electrodes with interdigital structure were deposited on the thick films. The sensor was placed in the measurement room where oxygen partial pressure ($P(O_2)$), SO_2 partial pressure ($P(SO_2)$) and temperature (T) were able to be changed. The resistance between two electrodes was measured as an output of sensor.

The output (resistance) change of resistive oxygen sensors based on CeO_2 and $Ce_{0.8}Zr_{0.2}O_2$ thick films in cases where $P(O_2)$ and/or $P(SO_2)$ changed is shown in Figs. 1 and 2. When the gas changed from A to B, $P(O_2)$ decreased from 10^5 to 10^4 Pa. So, the output of oxygen sensor using CeO_2 and $Ce_{0.8}Zr_{0.2}O_2$ changed. This change was normal response of oxygen sensor. Next, the gas changed from B to C or C'. In the case of the sensor using CeO_2, the resistance changed after the gas changed to C or C'. That is to say, the response of the sensor using CeO_2 was influenced by 1 ppm SO_2 and 500 ppm SO_2 at 873 and 1073 K. Especially, it was strongly influenced by the condition except 1 ppm SO_2 at 1073 K. In the case of the sensor using $Ce_{0.8}Zr_{0.2}O_2$, the sensor response was hardly influenced by SO_2 except 500 ppm SO_2 at 873 K. Even under the condition of 500 ppm SO_2 at 873 K, the influence of SO_2 on the response of the sensor using $Ce_{0.8}Zr_{0.2}O_2$ was smaller than CeO_2. Comparing the resistance of CeO_2 to that of $Ce_{0.8}Zr_{0.2}O_2$, the former was 10 times the latter. The structure and electrodes of both sensors were the same. It was, therefore, confirmed that the resistivity of CeO_2 was 10 times larger than that of $Ce_{0.8}Zr_{0.2}O_2$ in this study. And these results were in agreement with ref. (1).

The two possibilities can be considered as the reason why resistance of CeO_2 thick film decreased by introducing SO_2 gas. One is the formation of reaction product between CeO_2 and SO_2. The other is the adsorption of electrical conductive substances such as SO^{3-}. So we examined which possibility is right reason.

When CeO_2 powder was annealed in 500 ppm SO_2 + 10% O_2 + N_2 at 823 and 873 K, the reaction product formed a little. This product was the mixture of $Ce_2(SO_4)_3{\cdot}4H_2O$, $CeOSO_4$ and $Ce(SO_4){\cdot}4H_2O$, and was the same as the sample obtained after annealing $Ce_2(SO_4)_3{\cdot}8H_2O$ at 773 K in air. When CeO_2 powder was annealed at 1073 K in the same atmosphere, the reaction product did not form. The resistivity of the reaction product was 100 times larger than that of CeO_2 at 873 K. Thermodynamic calculation revealed that CeO_2 is more stable than $Ce_2(SO_4)_3$ at 1073 K in 500 ppm SO_2. From these results, it was concluded that the resistance decrease of the sensor using CeO_2 thick films by introduction of SO_2 was unrelated to the formation of reaction product.

After the alumina substrate attached with only electrodes was annealed at 873 K in 500 ppm SO_2 + 10% O_2 + N_2, the resistance between two electrodes at room temperature in air was 70 MΩ. After the surface of the electrodes was wiped using ethanol, the resistance was over range (more than 120 MΩ). These results showed electrical conductive substances were adsorbed on both the surface of the alumina substrate and the electrodes by annealing in 500 ppm SO_2 + 10% O_2 + N_2. So, the reason why the influence of SO_2 on CeO_2 thick film was larger than that on $Ce_{0.8}Zr_{0.2}O_2$ might be that the resistivity of CeO_2 was 10 times that of $Ce_{0.8}Zr_{0.2}O_2$ and larger than that of electrical conductive substances described above.

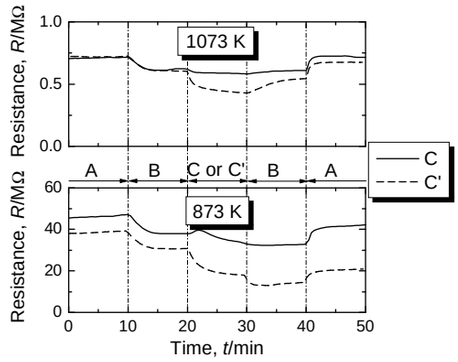

Fig. 1 Output (Resistance) changes of oxygen sensors using CeO_2, when $P(O_2)$ or $P(SO_2)$ changed. A: 100%O_2 ($P(O_2)$ = 10^5 Pa), B: 10%O_2 + N_2 ($P(O_2)$ = 10^4 Pa), C: 1 ppm SO_2 + 10%O_2 + N_2 ($P(O_2)$ = 10^4 Pa, $P(SO_2)$ = 0.1 Pa), C': 500 ppm SO_2 + 10%O_2 + N_2 ($P(O_2)$ = 10^4 Pa, $P(SO_2)$ = 50 Pa).

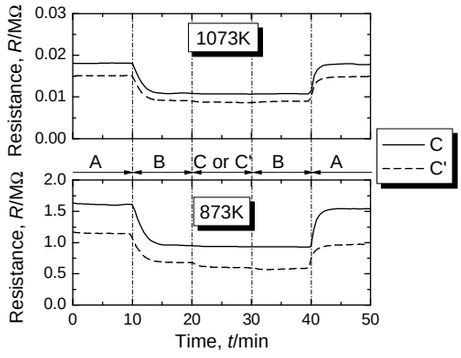

Fig. 2 Output changes of oxygen sensors using $Ce_{0.8}Zr_{0.2}O_2$, when $P(O_2)$ or $P(SO_2)$ changed similarly to Fig. 1.

References

(1)N. Izu, W. Shin, I. Matsubara, N. Murayama, *J. Ceram. Soc. Jpn*. **112**[5] S535 (2004).