Thermochimica Acta, 163 (1990) 303-312
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

THERMAL DECOMPOSITION OF MIXED ZIRCONIUM AND YTTRIUM OXIDE HYDRATE

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SUMMARY

The thermal decomposition of mixed Zr-Y oxide hydrates containing 0-12 mol% Y_2O_3, $(Zr, Y)O_2 \cdot nH_2O$, was examined by means of TG-DTA and TG-DSC, and XRD. When heated, any hydrate is changed into the oxide up to 700°C. DTA curves show one, two or three endothermic peaks and an exothermic peak. The endothermic peaks at temperatures between 100 and 200°C are due to the dehydration, and the exothermic peak is due to the transformation of amorphous to crystalline phase, which has tetragonal and/or cubic crystal structure. The exothermic peak temperature is raised from 420 for ZrO_2 to 500°C for the oxide of 12 mol% Y_2O_3, while the enthalpy of the phase transition is varied between -15 for ZrO_2 and -11 kJ mol^{-1} for the oxide of 12 mol% Y_2O_3.

INTRODUCTION

Zirconium dioxide, ZrO_2, has three modifications: monoclinic, tetragonal and cubic. The monoclinic to tetragonal phase transition occurs at 1170°C, and the tetragonal phase is transformed to the cubic at 2370°C. Both transitions are martensitic. When divalent or trivalent metal oxides such as calcium oxide, CaO, or yttrium oxide, Y_2O_3, is dissolved in ZrO_2, the tetragonal or cubic phase of the mixed oxide is stabilized even at lower temperatures below 1000°C.

Mixed zirconium-yttrium oxide, $(1-x)ZrO_2 \cdot xY_2O_3$ is used as an oxide-ion solid electrolyte, so-called PSZ and YSZ, which contain 3 and 8 mol% Y_2O_3, respectively. The mixed oxide can be prepared from various kinds of compounds as starting materials (refs. 1-5). Of these starting materials, the mixed oxide hydrate prepared by co-precipitation is the most favorable material. Studies on the thermal decomposition of the mixed oxide hydrate, $(Zr, Y)O_2 \cdot nH_2O$, has scarcely carried out, although the mixed oxide has been being examined on the phase relations and physical and ceramic properties by many researchers (refs. 6-7). This will probably come from a reason that the thermal behavior and properties of the mixed oxide produced at lower temperatures is not so important from a view of industrial materials, because the mixed oxide is practically calcined and sintered at temperatures as high as 2000°C. The sinterability, and physicochemical and electronic properties of the mixed oxide, however, are actually

0040-6031/90/$03.50

governed to calcining conditions of the hydrate at lower temperatures.

In the present study, the thermal decomposition of the mixed oxide hydrates is examined using thermogravimetry(TG) and differential thermal analysis(DTA) or differential scanning calorimetry(DSC). Phases of the products are identified by X-ray diffraction(XRD).

EXPERIMENTAL

The mixed oxide hydrates, $(Zr, Y)O_2 \cdot nH_2O$, were prepared by co-precipitation due to adding a mixed nitrate solution into excess ammonia water, where starting nitrates, $ZrO(NO_3)_2$ and $Y(NO_3)_3$ as guaranteed reagent grade were used. Yttrium content in the oxide was varied in the range between 0 and 12 mol% as Y_2O_3. After aged overnight at temperatures between 20 and 40°C, the precipitates were filtered, and dried at about 100°C in vacuum drier for 50h or longer. The water content combined with the oxide, expressed as n in $(Zr, Y)O_2 \cdot nH_2O$, was about 1 or little less and mol number of water was increased up to around 2 for the hydrates of any Y_2O_3 content when the hydrates were left in air for a long time.

Thermal analysis was carried out using both a simultaneous TG-DTA apparatus (TGD-5000, Shinku Riko Co.) and a TG-DSC (Energy-compensation type, Rigaku Denki Co.). For the former apparatus, a powder hydrate of about 50 mg was placed in a Pt sample holder, 8 mm in diameter and 10 mm in height, was used. Experiments were performed at a heating rate of $5^{o}C \cdot min^{-1}$ in a 100 $cm^3 \cdot min^{-1}$ air flow. The latter apparatus was mainly used for measuring enthalpy changes and temperatures of peaks produced during phase changes. A powder of about 10 mg was placed in a Pt vessel, 5 mm in diameter and 2 mm in height. Experiments were carried out at a rate of $5^{o}C \cdot min^{-1}$ till 800°C in a 100 $cm^3 \cdot min^{-1}$ oxygen or argon flow.

X-ray diffraction for powder specimens was performed by a diffractometer (Rigaku Denki Co., type Rad-1A) with CuKα radiation monochromatized with a bent graphite crystal. Some samples were examined by high-temperature XRD.

RESULTS AND DISCUSSION

TG and DTA of the mixed oxide hydrates

Figure 1 shows TG and DTA curves of the zirconium oxide hydrates and the mixed oxide hydrate of 6.45 mol% Y_2O_3 at a heating rate of $5^{o}C \cdot min^{-1}$ in a 100 $cm^3 \cdot min^{-1}$ air flow. In the figure, weight loss is shown in moles of the water combined with the oxide instead of weight percent. The number of moles of the combined water begins to change just after heating, and the dehydration proceeds as if $(Zr, Y)O_2 \cdot H_2O$, i.e. $(Zr, Y)O(OH)_2$, is formed for the hydrate with n of about 2, and $(Zr, Y)O_2 \cdot 0.5H_2O$, i.e. $(Zr, Y)O_{1.5}(OH)$, for the hydrate with n of about 1. For hydrates of other different yttrium contents, similar curves were also obtained. Weight loss was completed till 700°C for any oxide of different yttrium content.

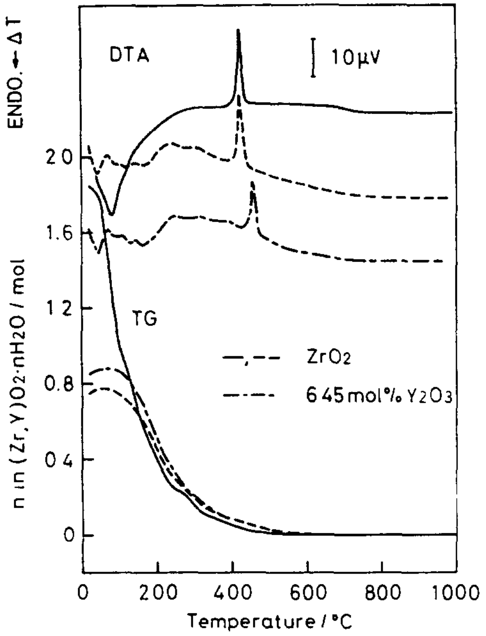

Fig. 1 TG-DTA curves for $ZrO_2\cdot1.85H_2O$, $ZrO_2\cdot0.74H_2O$ and $ZrO_2\cdot6.45mol\%Y_2O_3\cdot0.85H_2O$ at $5^{o}C\cdot min^{-1}$ in a 100 $cm^3\cdot min^{-1}$ air flow.

Every sample yielded endothermic peaks and an exothermic peak. For the hydrates with the combined water of about 2 mol, one large endothermic peak appears at around 100°C, at which bending of TG curves are formed the compound of (Zr, $Y)O_2\cdot H_2O$. This large peak is produced by the loss of water which is loosely combined with the oxide. When the hydrates with the water of about 1 mol were heated, two or three weak peaks yielded instead of one large peak found for (Zr, $Y)O_2\cdot H_2O$. The peak at the highest temperature of these endothermic peaks occurs at about 200°C, and the bend on TG curves corresponds to the composition of (Zr, $Y)O_2\cdot0.5H_2O$. Bends of TG and DTA curves may suggest that the hydrates exist as compounds of (Zr, $Y)O(OH)_2$ and (Zr, $Y)O_{1.5}(OH)$. After the endothermic reactions finish, the exothermic reaction occurs. According to XRD, the exothermic peak is formed by the transformation of amorphous to crystalline state. The peak temperature has a tendency toward to be raised with increase of yttrium content: That is, the temperature obtained by DTA is 420°C for ZrO_2, and it comes up 490°C for the mixed oxide with 12 mol% Y_2O_3.

Thermodynamic functions of the thermal decomposition for $Y(OH)_3$ and $Zr(OH)_4$

The thermal decomposition of metal hydroxides is represented by the general formula

$$1/mM(m)(OH)_m = 1/2mM(m)_2O_m + 1/2H_2O \tag{1}$$

where M(m) is metal of the oxidation state, m. The existence and stability of metal hydroxides can be evaluated using the enthalpy and the Gibbs energy change of decomposition. The thermodynamic properties of common metal hydroxides have been compiled in the NBS Thermodynamic Tables (ref. 8), JANAF Thermochemical Tables (ref. 9) and the thermodynamic data base, MALT (ref. 10). Standard enthalpies and entropies of decomposition for metal hydroxides at 298.15K, calculated using these data sources, are summarized in Table 1. For $Y(OH)_3$, only the Gibbs energy of formation at 298.15K is given as $-1291.1 \cdot kJ\ mol^{-1}$ in the NBS Tables. Thus, the standard enthalpy of the decomposition is obtained as to be $104.5\ kJ \cdot mol^{-1}$ when the average entropy of $72.2\ J \cdot K^{-1}\ (mol\ of\ OH)^{-1}$, which is calculated from the values of all hydrates in Table 1, is used.

As the standard enthalpy of formation for $Zr(OH)_4$ is not determined, the enthalpy of decomposition for $Zr(OH)_4$ was also evaluated. When the standard enthalpies per hydroxide-ion of the decomposition for hydroxides are plotted against oxidation state of constituent metal, the relationship becomes nearly linear. By extrapolating this line to four of the oxidation state, a value in the range between zero and $-10\ kJ \cdot mol^{-1}$ is obtained. This value means that $Zr(OH)_4$ is not stable at room temperature. Therefore, it is suggested that only $ZrO(OH)_2$ and $ZrO_{1.5}(OH)$ might exist, as are seen at bending on DTA curves.

TABLE 1

The standard enthalpies and entropies of the decomposition for metal hydroxides at 298.15K: $1/mM(m)(OH)_m = 1/2mM(m)_2O_m + 1/2H_2O$.
M(m) is metal of the oxidation state, m. The upper numbers are $\Delta H^o_{d298.15}/kJ \cdot (mol\ of\ OH)^{-1}$ and the lower $\Delta S^o_{d298.15}/J \cdot K^{-1} \cdot (mol\ of\ OH)^{-1}$.

Ia group	Li	Na	K	Rb	Cs
	65.05	97.59	123.11	127.78	123.44
	70.40	67.49	62.56		69.14
IIa group		Mg	Ca	Sr	Ba
		42.37	54.59	62.59	74.69
		76.78	72.59	73.06	76.07
III group		Al	Sc	Y	
		25.14	15.49	(35)	
		80.09	73.91		

The average entropy: $72.2\ J \cdot K^{-1} \cdot (mol\ of\ OH)^{-1}$
The standard enthalpy of the decomposition for $Y(OH)_3$ is the estimated.

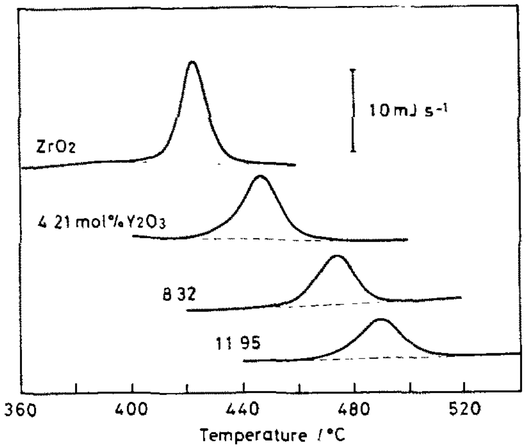

Fig. 2 Exothermic peaks on DSC curves for monohydrates of ZrO_2 and (Zr, Y)O_2 with different Y_2O_3 at $5^oC\cdot min^{-1}$ in a 100 $cm^3\cdot min^{-1}$ oxygen flow.

DSC of the mixed oxide hydrate

Experiments on TG-DSC were carried out for examining thermal changes during the decomposition of the mixed oxide hydrates. DSC curves were similar to DTA curves for all samples. DSC curves gave the information for energy changes due to reactions in details rather than DTA curves. Both initiation and peak temperatures obtained by DSC were slightly lower than those obtained by DTA for any sample. In Fig. 2, only an exothermic peak for the hydrates is shown. The endothermic peaks produced at temperatures below 400°C are not shown in Fig. 2 because DSC measurements with weight loss are not meaningful if any correction is not carried out.

The exothermic peak temperature for the mixed oxides are shown in Fig. 3. The peak temperature has a tendency toward being raised with increase in yttrium content, although the temperatures are scattered. One of reasons why the exothermic peak temperature is scattered comes from the aging temperature of the hydrate precipitates. When the aging temperature went up, it is found that the peak temperature had a tendency to be raised. ZrO_2 and (Zr, Y)O_2 have little quantity of the combined water even at a temperature at which the phase transformation occurs, and are gradually losing furthermore little quantity of the water during the crystallization. The water content in the oxide at the initiation temperature of the exothermic peak was 0.05 mol for ZrO_2 and 0.03 for the oxide with 12 mol% Y_2O_3. Generally, the content of the water combined with the oxide is comparable or slightly decreased with Y_2O_3 content. As shown in Fig. 2, broadness of the exothermic peak is hardly affected with increasing in Y_2O_3 content: The difference between initiation and peak temperature is about 40°C

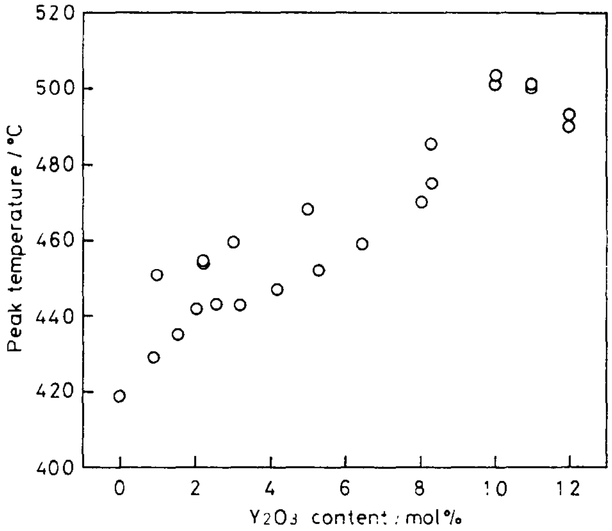

Fig. 3 Relationship between exothermic peak temperature and yttrium content in Y_2O_3 mol% for mixed zirconium-yttrium oxide, $(1-x)ZrO_2 \cdot xY_2O_3$.

for all the mixed oxides regardless of Y_2O_3 content, and the difference between the initial and the final temperature are about 70°C. Figure 3 shows that the exothermic peak temperature increases nearly linear with the yttrium content. This means that the crystallization is hindered by dissolution of yttrium into ZrO_2. It is not known from Fig. 3 whether the phase relations are related with the peak temperature as a function of Y_2O_3 content.

Enthalpy of crystallization

An area obtained by integration of a peak on DSC curve corresponds to an enthalpy change due to the first order phase transformation or any chemical reaction. As the phase transformation in the system ZrO_2-Y_2O_3 occurs after the dehydration almost finishes, the peak area is approximately equal to the heat of crystallization, or the negative value of enthalpy change, due to the crystallization from amorphous state to tetragonal or cubic phase. Rigorously, the enthalpy change of the transformation consists of the apparent enthalpy due to the crystallization, the enthalpy of the thermal, partial decomposition of the mixed oxide hydrate, although the content of combined water is very small, and the enthalpy of the water released out of the system during the crystallization.

Enthalpy change and weight change in each reaction step from dehydration to crystallization is examined to evaluate thermal behavior of the hydrates. Two examples are shown. For the sample of $ZrO_2 \cdot 0.988H_2O$, 11.17mg of the hydrate were used. The exothermic peak occurred at 380°C and finished at 450°C, and the

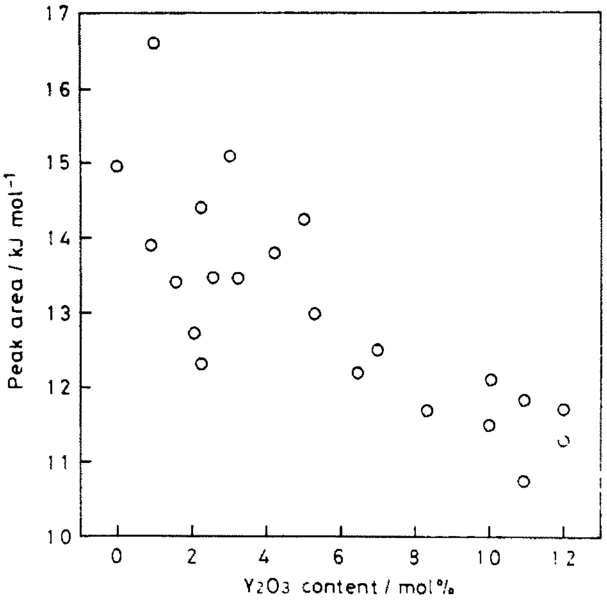

Fig. 4 Relationship between peak area, which is negative enthalpy of crystallization, obtained from exothermic peak and yttrium content in the mixed oxide.

peak temperature was 419°C. The exothermic peak area was 1.49J. During the transformation, 0.02mg of the water was lost, and the enthalpy of the water which was released out of the system became 0.02J. It is thought that this enthalpy change consists of the base line of the DSC curves because weight loss goes on nearly at a constant rate during the exothermic reaction. The enthalpy of decomposition of $ZrO_2 \cdot 2H_2O$ to ZrO_2 may be ignored as already estimated. For $0.9355ZrO_2 \cdot 0.0645Y_2O_3 \cdot 0.856H_2O$ as another example, 12.34 mg of the hydrate were used: The exothermic peak occurred at 417°C and finished at 500°C. The peak temperature was 458°C, and the peak area was 1.17J. During the transition, 0.04 mg of water was lost. This corresponded to the enthalpy of 0.04J. The peak area actually becomes the heat of crystallization, as mentioned above.

The relationship between peak area and yttrium content is shown in Fig. 4. The heat of crystallization decreases nearly linear with increasing in yttrium content, although the results are scattered. Generally, the higher the aging temperature of hydrates after precipitated, the smaller the peak area. When yttrium oxide hydrate is decomposed, amorphous state is not found, and an exothermic peak, therefore, does not appear on DTA or DSC curve. Therefore, it is understood that when Y_2O_3 is dissolved into ZrO_2, the heat of crystallization of amorphous to the crystalline phase decreases, but the yttrium in the crystal lattice of ZrO_2 has an effect of hindering the crystallization.

It is reported that the phase transformation of amorphous to crystalline state is exothermic for aluminum hydroxide (ref. 11). This exothermic phase transformation followed with the decomposition is found for titanium dioxide hydrate (ref. 12). The transformation of amorphous to crystalline state is exothermic in most cases. The enthalpy change, however, has not been quantitatively determined, but only the occurrence of the thermal change has been qualitatively given by DTA. For $Al(OH)_3$, the dehydration occurs endothermic at about 300°C, and then the amorphous state is transformed to the crystalline state at temperatures beyond 800°C, where the weight loss is not observed by TG-DTA. For titanium dioxide hydrate (ref. 12), the phase transformation of amorphous to anatase occurs exothermic at temperatures above 300°C just after the dehydration almost finishes. The transformation behavior of the latter case is similar to that of the mixed oxide in the ZrO_2-Y_2O_3 system.

Consideration on the phase relations

Using the results of thermal analysis and XRD, the phase relations in the system ZrO_2-Y_2O_3 can be evaluated. This system is known to take much time to attain in equilibrium. Thus, it should be noted that the phase relations is not in equilibrium, but in quasi-equilibrium.

The results of thermal analysis and XRD are summarized as: There are three regions in the system ZrO_2 - $0.88ZrO_2 \cdot 0.12Y_2O_3$: Phase I is the region that is less than approximately 2 mol%, phase II of 2 to 8 mol%, and phase III above 8 mol% Y_2O_3. In phase I, the amorphous state is first changed to the tetragonal phase when the hydrate is heated at a constant rate, then the tetragonal phase is being transformed to the monoclinic phase with temperature. In the case that the oxide is kept at 300 or 400°C for time as long as 500h, the tetragonal phase is being gradually transformed to the monoclinic phase. The ZrO_2-rich region in phase I should be and is actually changed to the monoclinic single phase. Phase II consists of two part: Tetragonal phase and two-phase region of tetragonal and cubic. However, it was unable exactly to find the composition of the region that the tetragonal single phase exists. When the hydroxide in phase II is heated, the amorphous phase is changed to two phase mixture of tetragonal and cubic, but the tetragonal to monoclinic phase transition in phase II was not found to proceed. In the phase III region, the amorphous state is directly changed to the cubic phase, but no phase transformation was caused by further heating.

Table 2 shows the relationship among the Y_2O_3 content, the attained phases and heating conditions when the mixed oxide hydrates are heated at 300 and 400°C in air. From this table, it can be deduced that the region between 0 and 2 mol% Y_2O_3, which is named as phase I, consists of monoclinic single phase and two-phase region of monoclinic and tetragonal, the region between 2 and 8 mol% Y_2O_3, phase II, contains tetragonal single phase and two-phase region of tetragonal and cubic, and phase III above 8 mol% Y_2O_3 contains single phase of cubic. Thus, It can be led that the phases are composed of monoclinic, tetragonal and cubic even at temperatures as low as 400°C, although in quasi-equilibrium.

The phase diagram in the system ZrO_2-Y_2O_3 at temperatures below 1000°C is reviewed by Yoshimura(ref. 7). According to the diagram, the monoclinic single phase is in the region between 0 and about 1.5 mol% Y_2O_3, and the cubic phase exists in the region beyond 8 mol% Y_2O_3. The phase between 1.5 and 8 mol% Y_2O_3 will be the two-phase region of tetragonal and cubic. From the phase rule, tetragonal single phase should exist in the phase between monoclinic and cubic. In the present work, the single phase of tetragonal is formed at the composition of approximately 2 mol% Y_2O_3 when heated at 300°C for 500h, or heated at 400°C for 450°C. From XRD patterns of the mixed oxide of 1.5 to 3 mol% Y_2O_3, it is thought that this tetragonal phase is the single phase or the main component of the phase formed at about 2 mol% Y_2O_3.

TABLE 2

Relationship between phases and Y_2O_3 content in the system ZrO_2-Y_2O_3

The mixed oxide hydrates were heated at temperatures and time shown in below.

Y_2O_3 content mol%	Heating conditions				DTA
	300°C		400°C		to 1000°C
	less	500h	less	450h	at 5°C min^{-1}
0 (ZrO_2)	T(<349h)	T+M	T(<16h)	T+M	M
0.89			T(<156h)	T+M	T+M
1.53			T(<250h)	T+M	T+M
2.07		T		T	T+M
2.57				T+C	T+M
3.18				T+C	T
4.21		T+C		T+C	
5.29				T+C	
6.45		T+C		T+C	
8.03		C		C	C
10.12		C		C	C
11.98		C		C	C

M: monoclinic, T: tetragonal and C: cubic.

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