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HIGH PRESSURE INVESTIGATIONS ON Zro, DOPED WITH Cr, Fe AND Nb

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ABSTRACT

High pressure x-ray investigations using a diamond anvil cell at ambient and higher temperatures show that the borderline between the fields of existence of different polymorphs of ZrO_2 in the p-T-diagram is heavily affected by doping zirconia with Cr, Fe or Nb. Furthermore, transformation kinetics are enhanced by the dopant ions, acting as additional nucleation sites for the transition from one polymorph to the other. The observed effects are explained on thermodynamic grounds by different entropy contents of the doped oxides and the pure ZrO_2 in the low and the high pressure modification.

MATERIALS INDEX: zirconium, dioxides, iron, chromium, niobium

INTRODUCTION

The thermal polymorphic transitions of pure and doped ZrO_2 have long been investigated [1] [2], and since the discovery of the mechanisms of transformation toughening [3] there has been a renaissance of interest in the properties of these and related materials. On the other hand, much less is known about the high pressure polymorphs of pure and doped ZrO_2 . Most recent studies were mainly concerned with the behaviour of pure ZrO_2 under high pressure conditions and knowledge about doped oxides is still very small.

Our own interest in the high pressure polymorphism of doped ZrO_2 stems from our investigations on the corrosion behaviour of Zircaloy. It was conjectured [4] that the typical "break away" characteristics of the corrosion may be due to a transition induced by the stresses in the growing oxide scale which are estimated to be in the order of 1-2 GPa, comparable to the pressure where pure ZrO_2 is found to undergo a polymorphic transition.

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EXPERIMENTAL

Preparation of samples

 ZrO_2 was prepared by thermal decomposition of $ZrOCl_2*8$ H₂O (p.a. grade MERCK) at 450°C and subsequent firing for 2d at 1100°C. For the doping experiments Cr_2O_3 was prepared from CrO_3 (p.a. grade MERCK) by thermal decomposition on increasing the temperature slowly to 1100°C. Fe₂O₃ (p.a. grade MERCK) and Nb₂O₅ (purissimum, > 99%, ROTH) were commercially available. Mixtures containing from 0.5 to 10 atomic % of the dopant as oxide were co-milled in a mechanical agate mortar for 1d, they were then pressed to pellets and fired in air at 1500°C for 1d (or additionally at 1300°C for 4d in the case of ZrO_2/Nb_2O_5) and subsequently quenched to room temperature.

The solubility limits of Cr_2O_3 , Fe_2O_3 and Nb_2O_5 in ZrO_2 at 1500, 1500 and 1300°C respectively were established by comparing the xray powder patterns of the parent oxide mixtures with the corresponding one of the fired oxides and found to be 2, 2 and 0.5 atom% respectively.

In the following the doped samples of ZrO_2/Cr_2O_3 (2 atom%), ZrO_2/Fe_2O_3 (2 atom%) and ZrO_2/Nb_2O_5 (0.5 atom%), referring to constitutions $Zr_{0.98}Cr_{0.02}O_{1.99}$, $Zr_{0.98}Fe_{0.02}O_{1.99}$ and $Zr_{0.995}Nb_{0.005}O_{2.0025}$ are designated as ZrCr-2, ZrFe-2, and ZrNb-0.5, the postponed number indicating the atomic percentage of dopant cation.

Crystallites of the undoped and doped oxides were found to be of similar size and in the range of approximately 300 and 200 nm respectively, as determined from the analysis of the x-ray reflection halfwidth applying a modified SCHERRER-equation. Details of our studies of solubilities, crystallographic data and crystallite sizes in the systems $\text{ZrO}_2/\text{Fe}_2\text{O}_3$, $\text{ZrO}_2/\text{Cr}_2\text{O}_3$ and $\text{ZrO}_2/\text{Nb}_2\text{O}_5$ are given elsewhere [2].

<u>High pressure experiments</u>

High pressure experiments on samples of pure ZrO_2 , ZrCr-2, ZrFe-2and ZrNb-0.5 were made in a diamond anvil cell (DAC) of the KELLER - HOLZAPFEL-type [5]. The Inconel gaskets 0.3 μ m thick were prepressed to a thickness of ≈ 0.15 mm. In the indentation region (approximately 0.6 mm in diameter) a hole of 0.3 mm was drilled for the containment of the sample.

NaCl in approximately twice the amount (by volume) of the sample was taken both as pressure transmitting medium and as pressure calibrant, according to the equation of state of DECKER [6]. Heating the DAC to $\approx 300^{\circ}$ C was possible with a radiative heater mounted around the diamond anvils. The temperature was monitored by a NiCr/Ni-micro thermocouple placed near the sample-bearing hole in the gasket. Temperature calibration was done by correlating measured thermo-emf against known temperature transition points of standards recommended by NBS/ICTA which were placed in the gasket holes of the unloaded DAC (Room temperature: T = 23°C, KNO₃: T_t = 128(5)°C, KClO₄: T_t = 299(6)°C). The accuracy of temperature and pressure measurement is estimated to be $\approx \pm 15^{\circ}$ C at 300°C and ± 0.12 GPa at 6.0 GPa.

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RESULTS

<u>p,T-phase diagrams</u>

On loading the DAC the beginning of transformation to the first high pressure phase (named OI in the literature [7] to distinguish it from the orthorhombic cotunnite-type modification OII seen at even higher pressures [8]) could clearly be seen by the appearance of its strongest reflection between the (111) - and $(11\overline{1})$ -reflection of the monoclinic phase at about 3.5 GPa. In the case of single crystal experiments the transformation takes place rather suddenly once the necessary p,T-conditions are reached. However the onset of the transformation depends on the nucleation sites present in the crystal, i.e. on its history. With powder samples as used in this study we observe transformation within a broad range of pressures. Therefore the conditions under which the first traces of the orthorhombic phase could be detected by x-ray diffraction on increasing the pressure were taken to define the fields of stability of the different modifications in p and T. Figs. la-d give the results of these in situ high pressure x-ray investigations in the form of p,T-phase diagrams. From these it is clearly seen that doping ZrO2 heavily affects the transformation from the monoclinic to the OI-Phase. There are little changes in transition pressure p_t at room temperature, however the temperature dependance of p_t is completely different in the doped phases, where the borderlines separating the different fields of existence of the phases in the p,T-diagram have a positive slope in contrast with the negative one for pure ZrO_2 . At higher temperatures the transformation to the high pressure phase takes place at considerably higher pressures (e.g. $p\approx + 1$ GPa at 200°C). The derably higher pressures (e.g. question arises wether this is a thermodynamic effect or a kinetic one, in that doping with Cr or Fe leads to a hindrance in the mechanism of transformation. A first answer can be given by the evaluation of hysteresis effects as seen in pressure cycling experiments.

Hysteresis effects and transformation rates

For a kinetic study the ratio

$$u = \frac{I(111)_{o}}{I(111)_{o} + I(111)_{m}}$$

(I(111) or I(111) is the maximum intensity of the (111) reflection of the orthorhombic or monoclinic phase respectively.)

was taken as a measure for the degree of transformation of the specimens at given p and T conditions. Defects created during a transition may form nucleation centres which make a subsequent transformation easier. However they could as well serve as traps pinning a new transformation front. For our investigations on the effect of doping on the hysteresis of transformation we have star-

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ted with virgin samples on which pressure was increased and decreased in several cycles. The Figs. 2a-d show the degree of conversion - defined by the ratio u - at different pressures and ambient temperatures for pure and doped ZrO_2 . In no instance is conversion complete up to pressures of 5.0 GPa. The amount of conversion, the way it increases with pressure and the area of the hysteresis loop change significantly by doping. Transformation seems especially sluggish in pure ZrO_2 and ZrNb-0.5, is fastest and most complete in ZrFe-2 and shows the strongest change of hysteresis characteristics in subsequent cycles in the Cr doped phase. Figs. 3a,b show the results of similar experiments at a higher temperature on pure ZrO_2 and ZrFe-2. The area of the hysteresis loop is now smaller and there is no longer a difference in behaviour in subsequent cycles. (In all figures triangles give the







p,T-phase diagrams of (a) pure ZrO_2 , (b) ZrCr-2, (c) ZrFe-2 and (d) ZrNb-0.5



FIG. 2

Degree of conversion u vs. pressure at ambient temperatures for (a) pure ZrO₂, (b) ZrCr-2, (c) ZrFe-2 and (d) ZrNb-0.5

data from a first cycle and squares those from a subsequent one. In the case of the sample ZrFe-2 additional crosses correspond to the results of a third cycle after the sample had undergone two cycles at 160°C. The system behaves as before and seems to be "saturated" with respect to defects which affect the transition.)

A certain drawback in our experiments is the fact that NaCl is used as pressure transmitting agent. This may lead to considerable shear stresses especially at low temperatures. (The influence of shearing forces could be seen in our DAC experiments with metastable orthorhombic $2rO_2$ which we have prepared and quenched in a belt-type apparatus. When putting load on the DAC filled with this phase together with NaCl as pressure transmitter, the orthorhombic phase was readily converted at lower pressure to the thermodynamically stable monoclinic one even at room temperature, shear stresses facilitate this back transformation.) The slope of the flanks of a hysteresis loop gives an estimate for the kinetics of the transformation. The rate of conversion of pure ZrO_2 depends



Degree of conversion u vs. pressure at 160°C for (a) pure ZrO_2 and (b) ZrFe-2

strongly on the temperature (viz. figs. 2a and 3a), the increase in hydrostaticity of the solid medium at higher temperatures en-hances conversion. However, it is hardly influenced in the case of ZrFe-2 (figs. 2c and 3b), where the kinetics seem to be governed by the defect structure of the crystallites. The rather broad hysteresis mirrors the particle size distribution of the powder samples. According to DA JORNADA et al. [9] large crystallites will transform more readily in both directions than smaller ones owing to the different number of nucleation centres which initiate the structural rearrangement. In an ealier paper [2] we have shown that the mean crystallite size of these doped phases is even slightly smaller than that of pure ZrO2 prepared by the same procedure. The higher degree of conversion of the phases ZrFe-2 and ZrCr-2 can therefore be attributed to the chemical substitution creating defects which can act as such nucleation centres. The fact that the enhancement by doping is smaller than expected in view of the chemical composition may be taken as an indication that the substitutional defects cluster in the crystal structure thereby reducing the number of potential nucleation centres.

CONCLUSIONS

The results given in the foregoing section show that the kinetics of the high pressure transformation and its hysteresis are affected by doping ZrO_2 . This could mean that the fields of existence of the different polymorphs in the p,T-diagrams given before do not represent a thermodynamic but a kinetic stability. The main difference between the diagrams of the doped and undoped phases is the change in slope of the borderline separating the field of the orthorhombic from that of the monoclinic phase. It was shown that higher temperatures and doping should both accelerate the kinetics of a transformation. Therefore the change of slope from negative to possitive on doping is clearly a thermodynamic effect and inVol. 26, Nos. 2/3

teresting conclusions may now be drawn from the CLAUSIUS-CLAPEYRON equation.

$$\begin{pmatrix} dT \\ dp \end{pmatrix}_{coex} = \frac{\Delta V_t}{\Delta S_t} = \frac{T_t * \Delta V_t}{\Delta H_t}$$

Since $\Delta V < 0$ in all high pressure transformations the negative slope in the case of pure ZrO_2 implies an increase in entropy ($\Delta S > 0$) during the high pressure transformation. The opposite is true for the transformation of the doped phases. When comparing a doped phase with an undoped one, it seems reasonable to expect a higher entropy in the former, and this will hold for the low and the high pressure phase as well. The following scheme gives the entropy content of all phases in comparison



From this scheme it can be seen that the increase in entropy by doping depends strongly on the structure. It seems to increase more in the case of the low pressure modification, or, given in other words, the entropy content of the high pressure phase is much larger from the very beginning, so that doping will add little to it. (The cross-over point in the diagram (*) would give a dopant concentration, where the entropy content of the low pressure form equals that of the one at high pressures ($\Delta S = 0$)).

These findings lead to the conclusion that disorder is incorporated as a structural element in the high pressure phase. KUDOH et al. [10] have reported on a single crystal study of ZrO₂ under high pressure. Their interpretation of the data leads them to a model of an orthorhombic structure very similar to that of monoclinic ZrO₂. However, in this model four oxygen atoms are placed "in two ordered distributions" on the eightfold site of the space group Pbcm, an unsatisfactory solution from a crystallographic point of view. The authors "explain" how different domains, within which such an "ordering" could take place in forms which they call "reverse" and "obverse", could intergrow coherently and give the observed diffraction pattern. This interpretation can surely be questioned, however their study shows that the high pressure phase

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is a highly disordered structure and/or a polydomain system, and this is confirmed by the results of our investigations.

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