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Analysis of Mechanical Loss Spectra in Zirconia Ceramics by Applying the Coupling Model

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Abstract. Mechanical loss spectra (two peaks) observed in ZrO_2 doped with Y_2O_3 (2-10 mol%), are attributed to oxygen vacancy (V)-yttrium (Y) associates (V-Y pairs and V-2Y agglomerates). Both peaks were analysed numerically by applying the coupling model. It has been shown that: i) the activation enthalpy H for both peaks increases with Y_2O_3 content, ii) the values of coupling parameter n are about 0.6 - 0.7, iii) the activation enthalpy H_0 corresponding to the noninteracting system (dilute case) is about 0.4 eV which is considerably smaller than the activation enthalpy for reorientation of isolated dipoles (0.8 - 0.9 eV)

1. INTRODUCTION

It is well-known that interaction among diffusing species (e.g. point defects) in solids manifests itself as a broadening of loss maxima (mechanical or dielectric) compared with ideal Debye peaks for noninteracting systems (dilute case). With increasing defects concentration the experimentally observed broadening is usually accompanied by a shift of the loss maxima towards higher temperatures (or lower frequencies) and by an increase of the activation enthalpy of the relaxation process [1-9].

These interaction effects can be accounted for by the coupling model which describes the dynamics of relaxation processes in strongly correlated systems. According to this model the jump transition rate of the diffusing defects to neighbouring sites is time dependent for sufficient long time. As a consequence the relaxation function (static response function) takes a stretched exponential form, which is also known in literature as a universal response function [1,10,11]. The activation enthalpy of the relaxation process is affected by correlation effects and depends on the concentration of interacting defects. As was shown in [11] the stretched exponential function corresponds to a broad continuous distribution of relaxation times describing the experimentally observed shift and broadening of the loss spectra. Applicability of the coupling model to many interacting systems (like polymers, glasses etc.) has been demonstrated in the past [1]. Recently this model was applied to the Snoek-Köster relaxation by taking into account the interaction between interstitial atoms into the Cottrell atmosphere [12].

In the case of relative weak interactions among diffusing species, as it has been already demonstrated for the Snoek relaxation in bcc metals [13-15], the correlation effects do not play a significant role and the activation enthalpy does not depend on the defects concentration. All features of the observed phenomena (i.e. the shift towards higher temperatures and the broadening of the Snoek peak) are well described by the model with random distribution of interaction energies between elastic dipoles.

The aim of this paper is to test the applicability of the coupling model for the description of the anelastic relaxations in yttria stabilised zirconia oxide. In ZrO_2 doped with Y_2O_3 (2-10 mol%) one oxygen vacancy (V) is formed for every two Y ions for charge compensation. The pair V-Y represents an elastic as well as a dielectric dipole. The vacancy is sited in one of the eight nearest neighbour positions of the dopant ion (see fig.6 in [3]). The defect symmetry is trigonal as the dipole axis lies in $\langle 111 \rangle$ direction [2-6]. Reorientation of the dipole under an external applied field (electric or elastic) may occur by jumping of the vacancy around the dopant ion.

Mechanical loss spectra of yttria stabilised zirconia (3-10 mol% Y_2O_3) consist of two maxima which are attributed to thermally activated reorientation of V-Y pairs (the peak at lower temperatures denoted as I) and complexes of type V-2Y (the peak at higher temperatures denoted as I_2) [3,7,9]. It was shown that

the activation enthalpy for reorientation of V-Y pairs increases with yttria content [7] and also that both peaks are much broader than a single Debye relaxation (2-4 times) [3,9]. These effects are expected for a strong interacting defect system and should be described by the coupling model.

2. EXPERIMENTAL RESULTS

The experimental data were obtained for samples of tetragonal zirconia polycrystals (TZP) with 2 and 3 mol% Y_2O_3 and also for crystals of cubic stabilised zirconia (CSZ) with 10 mol% Y_2O_3 ([110] orientation of the longitudinal axis). Details on sample preparation are described in [6-8] and [3].

Mechanical loss measurements were carried out with two types of apparatus by using the same samples. Low frequency measurements were performed with inverted torsion pendulum with oscillation frequencies ranging from 2-15 Hz. High frequency measurements in the kHz-range were performed by exciting the specimens in eigenvibrations. Fig.1 represents mechanical loss curves obtained with the low frequency torsion pendulum ($f \approx 2$ Hz). For lower Y_2O_3 contents the mechanical spectrum shows one maximum - I. With increasing yttria content this maximum shifts towards higher temperatures and the second peak (I_A) appears at about 500 K. For high frequency measurements the loss spectra exhibit similar variations with yttria content as presented in figure 1.

3. ANALYSIS BY APPLYING THE COUPLING MODEL

The elastic energy loss curve (loss tangent) $Q^{-1}(T)$ according to the coupling model can be written in the form [11]:

$$Q^{-1} = \omega \Delta \int_0^{\infty} \exp[-(t/\tau)^{1-n}] \cos(\omega t) dt \quad (1)$$

where ω is the angular frequency, Δ denotes the relaxation strength, τ the relaxation time corresponding to the interacting system, n the coupling parameter ($0 < n < 1$) describing the degree of correlation of the system. The relaxation time τ obeys an Arrhenius equation of the form:

$$\tau = \tau_{\infty} \exp(H/kT) \quad (2)$$

where τ_{∞} is the preexponential factor, H the activation enthalpy, k the Boltzmann constant. The activation enthalpy H reflects the interaction effects via many body correlations and can be expressed as:

$$H = H_0 / (1 - n) \quad (3)$$

where H_0 is the activation enthalpy describing the noninteracting system which in practice corresponds to a dilute case. If $n=0$ the correlation effects are neglected, $H=H_0$ and eq.(1) takes the form of a single Debye curve. If $n>0$ the correlation effects play a significant role and H increases in relation to H_0 , but the product $H(1-n)$ should be constant.

In order to perform the quantitative analysis of the experimental data by applying the coupling model, the non-linear regression procedure was used [16]. The model function defined by eq.(1) together with eq.(2) for τ , contains four parameters: Δ , H , n and T_p . The peak temperature T_p corresponds to the condition $\omega\tau=1$ (it is convenient to insert T_p as a fitting parameter instead of τ_{∞} from eq.(2)). In the case of two loss maxima the model function is taken as a sum of two independent components given by eq.(2). The correctness of the calculations and the fit quality may be judged by two criteria: i) the activation enthalpy values H obtained from fitting the individual $Q^{-1}(T)$ curve (denoted as H_{ic}) should agree with the value of H_0 calculated from the frequency shift between the fitting parameters T_p for curves measured at different frequencies, ii) the value of the product $H_{ic}(1-n)$ should be independent on yttria content.

As the first attempt it was assumed that $Q^{-1}(T)$ curves obtained for 2Y-TZP and 3Y-TZP consist of one single loss peak (I). Fig.2 shows the experimental data for 2Y-TZP and the theoretical curve calculated according to eq.(1) for one process. From this figure it can be recognised that the quality of the fit is not good enough. This indicates that the second peak (I_A) is already present in samples with lower Y_2O_3 concentrations. According to this result all measured spectra were analysed with the assumption that both

peaks (I and I_A) were present for all Y_2O_3 content. The results of this analysis are listed in Table 1 and presented in Figs.3 and 4.

Fig.1 Experimental data obtained in low frequency range.

Fig.2 Results of the preliminary numerical analysis.

Table 1. Activation enthalpies H_{fit} , H_{fs} , coupling parameter n , values of $H_0=(1-n)H_{\text{fit}}$ obtained by applying the coupling model for peak I and peak I_A for different concentration of Y_2O_3 .

Y_2O_3 [mol%]	f [Hz]	peak I				peak I_A			
		H_{fit} [eV]	H_{fs} [eV]	n	$(1-n)H_{\text{fit}}$	H_{fit} [eV]	H_{fs} [eV]	n	$(1-n)H_{\text{fit}}$
2	2.72	0.89	0.90	0.60	0.36	1.11	1.11	0.56	0.49
	2070	0.92		0.56	0.40	1.14		0.70	0.34
3	2.52	0.92	0.92	0.61	0.36	1.25	1.25	0.76	0.30
	2230	0.91		0.58	0.39	1.25		0.62	0.48
10	1.76	1.21	1.21	0.69	0.38	1.88	1.93	0.72	0.53
	2650	1.21		0.62	0.46	1.88		0.61	0.72

4. DISCUSSION AND CONCLUSIONS

From Table 1 it can be recognised that the two criteria (i) and (ii) of the previous section are well fulfilled. Values of the activation enthalpy H_{fit} and H_{fs} are equal within error limits (0.02-0.03 eV). For both peaks (I and I_A) H_{fit} as well as H_{fs} increase with increasing Y_2O_3 content. In the first approximation this increase is linear and fulfils the relations:

$$\text{peak I: } H [\text{eV}] = 0.81 + 0.04 c [\text{mol\%}]; \quad \text{peak } I_A: \quad H [\text{eV}] = 0.93 + 0.1 c [\text{mol\%}] \quad (4)$$

The values of $H_0=(1-n)H_{\text{fit}}$ are also approximately constant. This criterion is much better fulfilled for peak I. The mean values of H_0 are 0.40 ± 0.03 eV and 0.5 ± 0.1 eV for peak I and I_A , respectively.

According to the coupling model H_0 is the activation enthalpy of the relaxation process for $n=0$, corresponding to the dilute case where the correlation effects do not play any role. In the case of the stabilised ZrO_2 the dilute case does not exist since the doping is required for stabilisation. Independent of that one can compare the obtained value of H_0 with the value of the activation enthalpy determined from eq.(4) for $c=0$ which is $H = 0.8-0.9$ eV. Evidently the obtained H_0 values are about two times smaller than the expected values from eq.(4).

Fig.3 Results of the numerical analysis for 2Y-TZP.

Fig.4 Results of the numerical analysis for 10Y-CSZ.

This disagreement is difficult to explain in the frame of the coupling model. The parameter n describing the broadening of the loss maxima has to be high enough because the measured spectra are 2-4 times broader than a single Debye peak. According to eq.(3) the high values of n (0.6-0.7) correspond to small values of H_0 . In our opinion it could be explained by assuming that additionally the activation enthalpy for thermal reorientation of the V-Y pairs (and also V-2Y) is distributed itself. As a consequence, the values of the parameter n obtained in this paper are overestimated and the value of H_0 has no physical meaning. The verification of this hypothesis requires however additional examinations.

The main results from the analysis of mechanical loss spectra in zirconia ceramics made by applying the coupling model are the following: i) the activation enthalpy for both peaks I and II increases with Y_2O_3 content, ii) the values of the coupling parameter n are about 0.6-0.7, iii) the activation enthalpy H_0 corresponding to the noninteracting system (dilute case) is about 0.4 eV. This value is about two times smaller than the activation enthalpy for reorientation of dipoles in dilute $ZrO_2 - Y_2O_3$ (0.8 - 0.9 eV).

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