The approach for intended thermomechanical properties adjustment via the solid solution formation: doped-MgO oxide layers on metal substrates

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The system of MgO film on nickel base metallic substrate is studied in relation to its thermophysical properties. It is observed that the thermal expansion coefficient (TEC) of the material can be varied on purpose via proper doping. Thus, the mismatch of more than 20% for Ni/MgO system can be reduced to below 4% for $Mg_{0.75}Zn_{0.25}O$/Ni5at.%W system. The usefullness of the empirical rule stating that TEC increases with the decrease of the melting temperature of the compound is outlined.

1. Introduction

The mismatch of thermal expansion coefficients (TEC) of different materials in layered structures often leads to destruction of system integrity [1]. This poses a serious problem in technology of solid oxide fuel cells, thermal barrier coatings and other important material classes. The problem appears also in emerging field of superconducting oxide coatings on long flexible textured nickel alloy tapes, since such tapes undergo a sequence of deposition processes at temperature higher than 600°C followed by their operation at 77 K or below [2]. MgO is often used as a buffer layer between the metal substrate and superconducting coating [3]. Its TEC is approx. 20 % lower than that of a metal tape. We have chosen this system as a model one to study the possibilities of the adjustment of TECs of the oxide scale and the metal substrate. To increase the TEC of MgO, it was doped by CuO, ZnO and NiO with the formation of the cubic solid solutions. The choice of substituents is based on empirical relation between TEC and the melting point: TEC value increases as the melting point decreases [4]. This rule can be very helpful in the search for the material with particular thermophysical properties, since melting of substances is known better and typically with much higher accuracy than their thermal expansion behaviour. According to the phase diagrams, the substitution of MgO by ZnO, CuO or NiO leads to the lowering of the temperature at which liquid phases appear, hence one could expect the increase of TEC caused by such a doping. Additionally, thermal expansion of nickel and three nickel base alloys were evaluated to find out which substitutions can lead to the lowering of the nickel TEC value.

2. Experimental

The solid solution ceramic samples of MgO-ZnO, MgO-CuO and MgO-NiO systems have been prepared by "paper synthesis" starting from acetates of corresponding metals. Ashless filters were impregnated with the acetate solution, dried and burnt, the powder formed was pressed to pellets and sintered at about 1000°C for 24 hours. This synthetic route takes advantage of a chemical homogenization resulting in significantly lower temperature and time required for the preparation of equilibrated and well-sintered sample. The samples were routinely analysed by XRD and SEM with EDX. From these measurements the lattice constants and phase composition have been determined. To measure the thermal expansion coefficient, the sample was placed in a quartz dilatometer, heated up to 850°C with the rate of 2°/min, held at high temperature for 1 hour and cooled with a rate of 2°/min down to room temperature. The sample dimensions were typically 3*3*12 mm³, the position sensor provided the accuracy of ± 1 μm. The accuracy of the TEC value determination was calculated to be of about ± 2% of its value, the largest error being produced by the measurement of the initial sample length (accuracy ± 0.1 mm, corresponding to ± 1% of TEC). TEC was also measured for metallic nickel and three nickel base alloys (at.%): Ni 88.8 - W 1.8 - Cr 9.4; Ni 88.9 - W 2.4 - Cr 8.7; Ni 95.3 - W 4.7. The sample dimensions and measurement conditions were the same as for the ceramic samples.

3. Results and discussion

The XRD study has shown that the stability limit of MgO-based solid solutions at 1000°C lays about $x(lim) = 0.25$ for $Mg_{1-x}Zn_xO$ and $y(lim) = 0.15$ for $Mg_{1-y}Cu_yO$. This is in a good agreement with the data known from literature [5,6]. The samples with the dopant content larger than these limiting values were two-phase mixtures: ZnO(MgO) solid solution with wurtzite structure and $MgCu_2O_3$ were observed as secondary phases. The solubility of NiO in MgO is not limited. In accordance with this, the $Mg_{1-z}Ni_zO$ samples were single phase for the whole range studied $0 \leq z \leq 0.75$. The lattice constant of the rock-salt solid solution increased linearly with the Zn or Cu doping and decreased with the Ni doping. The dependencies were in a good agreement with the data reported previously for $Mg_{1-x}Zn_xO$ [7], $Mg_{1-y}Cu_yO$ [6] and $Mg_{1-z}Ni_zO$ [8].

Table 1. TEC of MgO-based solid solutions in 25-850°C interval.

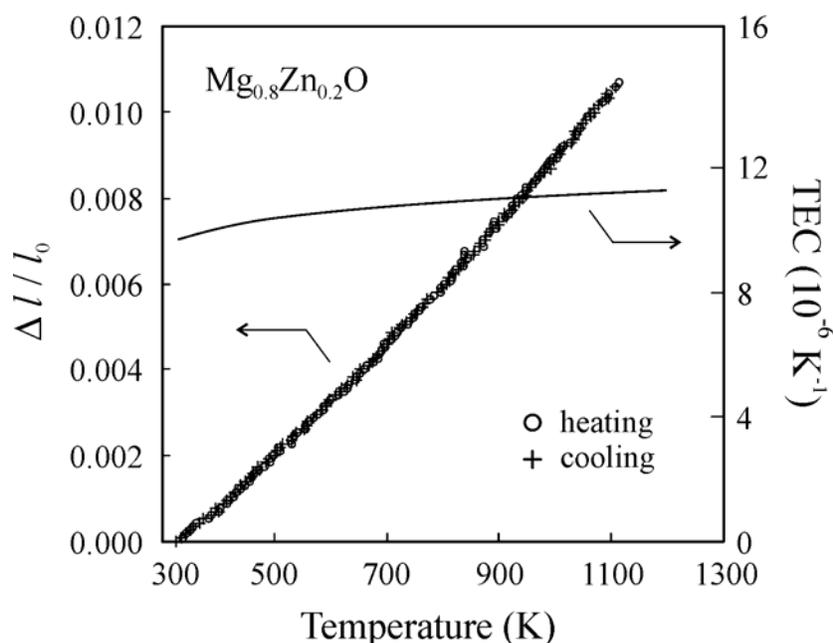| Substitute content	TEC (25-850), 10^{-6}/K		
	ZnO	CuO	NiO
0.00	13.0	13.0	13.0
0.05	13.4	13.1	
0.10	13.3	13.4	
0.15	14.0	13.2	
0.20	13.7		
0.25	14.0		13.0
0.50			13.3
0.75			13.4

Fig. 1. The typical dilation of the sample on heating and cooling and TEC determined from these data.

The typical temperature dependence of the dilation of the sample on heating and cooling is given in Fig. 1. The thermal expansion coefficients found for the 25-850 °C temperature interval are summarized in Table 1. It can be seen from the data that the substitution of Mg by Zn, Cu and Ni leads to the gradual increase of the TEC. This behaviour is discussed in some details below.

The thermal expansion is a measure of the bond strength in the solid. This fact is reflected in the empirical relation between TEC and melting point: for compounds with a similar bond type, the average value of TEC in the range from 0 K to the melting point is approximately inversely proportional to the melting point of the compound [4].

The melting behaviour of solid solutions can be found on phase diagrams of corresponding systems reported in [5] (MgO-ZnO), [6] (MgO-CuO) and [9] (MgO-NiO). According to the data of Segnit et al., the MgO-ZnO system has an eutectic at about 1830°C. The maximum solubility of ZnO in MgO at this temperature is about 40 mol.%. MgO-NiO system is a typical system with unlimited solubility without eutectic. Unfortunately, there exist no

detailed study of the MgO-CuO phase diagram at high temperature because of increasing complexity of this system due to the reduction of copper oxide. However, it is rather evident that copper substitution also lowers the melting point of MgO. The increase of the TEC value is thus in accordance with phase diagrams (Fig.2). It would be interesting to draw parallels with the known inverse relation between melting point and TEC [4], but the analogy between solid solutions and individual compounds is not straight-forward. First of all, the melting of the solid solution is not a congruent process, therefore it is not clear which temperature (solidus or liquidus one) should be taken into consideration. Second aspect is that the measured value of TEC in 25-850°C interval is not equal to the average value of TEC in the range from 0 K to the melting point.
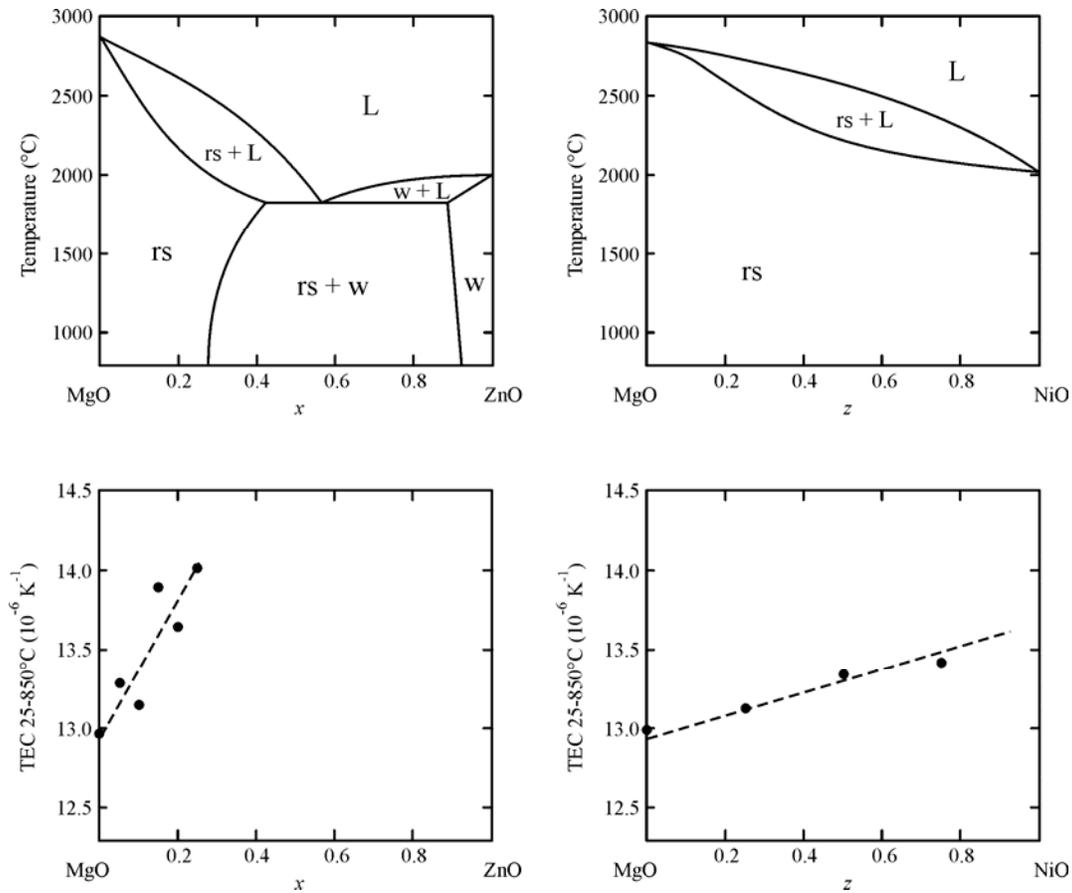

Fig. 2. The phase diagrams after Segnit et al. [5] (MgO-ZnO) and Jacobsson et al. [9] (MgO-NiO) in comparison with the variation of the TEC value of solid solutions with the rock-salt structure.

The measured TEC values for nickel and its alloys are given in Table 2. From these data it can be supposed that a remarkable decrease of the TEC value is caused by W substitution, however more data are necessary to make definite conclusion. Similar observation was reported by Simak et al. [10]. These authors have calculated TEC of Ni-W alloys from first principles and observed that TEC value decreases by approx. 15-20% on substitution of 5 at. % of Ni by W.

Table 2. TEC of nickel and its alloys in 25-850°C interval.

Sample	TEC (25-850), 10^{-6}/K
Ni	16.3
Ni 88.8 - W 1.8 - Cr 9.4	15.4
Ni 88.9 - W 2.4 - Cr 8.7	15.6
Ni 95.3 - W 4.7	14.5

By comparison of the data from Tables 1 and 2 it can be concluded that the thermal expansion mismatch between the oxide layer and metal substrate can be reduced by proper substitution with solid solution formation. Thus, the initial mismatch of TEC of more than 20% for Ni/MgO couple is reduced to below 4% for e.g., $Mg_{0.75}Zn_{0.25}O/Ni5at.\%W$ system.

It would be also important to find out the effect of such substitution on other technologically important properties of oxide solid solutions. These are for example Young modulus, strength, oxygen diffusion coefficient, chemical compatibility with high T_c superconductor. Futher work is necessary to prove if these solid solutions can be effectively used as buffer layers on metal substrates.

4. Conclusions

The solid solution formation is a viable route to modification the thermophysical properties of functional materials. We have demonstrated that the TEC mismatch in the MgO/Ni system can be significantly reduced by doping of MgO by ZnO, CuO or NiO and Ni by W. The behaviour observed, even though its nature could be more complex, fits into the empirical model of inverse proportionality of TEC and the melting point.

Acknowledgments

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