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ScienceDirect
Materials Chemistry and Physics 105 (2007) 278–285
MATERIALS CHEMISTRY AND PHYSICS
www.elsevier.com/locate/matchemphys

Influence of yttrium on the interface valence electron density of thermal barrier coatings

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Received 16 September 2006; received in revised form 23 April 2007; accepted 26 April 2007

Abstract

Most of the bonding layers of thermal barrier coatings contain some yttrium to improve the physical consistency of the substrate and the ceramics layer. But the reason of the improvement and the proper yttrium content are not clear. In this paper, the valence electron densities ρ_{hkl} and ρ_{uvw} of the two sides and their difference $\Delta\rho_{\min}$ of the bonding layer/ceramic layer interface of thermal barrier coatings are calculated with the empirical electron theory in solids and molecules at various bonding layer yttrium content. The results show the following. The addition of yttrium has beneficial effect on the decrease of the interface stress because it decreases the $\Delta\rho_{\min}$. The addition of yttrium can also increase the valence electron density ρ_{hkl} or ρ_{uvw} of the interface and so increase the interface cohesion force. The most effective yttrium content is at 0.4 wt% or so. The deductions accord with the actual coating, so the method can be applied to design the composition of the bonding layer of thermal barrier coatings. Furthermore, the calculation and the analysis methods of the interface valence electron densities can also be extended to other crystal coatings or composites with special orientation relationship, no matter the interface is a alloy/alloy one, a ceramics/alloy one or a ceramics/ceramics one.

Keywords: Alloys; Coatings; Interfaces; Computer modelling and simulation

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1. Introduction

Thermal barrier coatings (TBC) are mainly used for heat insulation in aviation engine parts working at high temperature today, so that the high-temperature alloy parts can resist higher temperature under the service condition of thermal cycling, oxidation, etc. Most TBC applied nowadays have the double layer structure of substrate + bonding layer + ceramics thermal barrier layer. Namely, depositing a *M*CrAlY (*M* = Ni, Co, Ni + Co) alloy bonding layer on the nickel base high temperature alloy, then depositing a zirconia ceramic thermal barrier layer on the surface. The main function of *M*CrAlY alloy is to improve the physical consistency between the ceramic coating and the high temperature alloy substrate, so that it has transition effects in thermal expansion coefficient, mechanical properties, and interface conjunction, etc. [1–4]. It is a development direction of bonding layer composition optimization to consider the mechanical properties of the bonding layer synthetically [4].

To promote the mechanical properties of the TBCs, one of the important methods is to optimize the composition of the bonding layer so that it has good interface conjunction with both the substrate and the ceramic layer [5]. Of the two interfaces of the bonding layer, the interface between ceramic layer/bonding layer is critical for its poor physical consistency. Therefore, the crisis to optimize the bonding layer composition is to improve the ceramic layer/bonding layer interface conjunction. Nowadays there is no systemic research on the relationship between the composition of the bonding layer of TBC and its properties and service life because the lack of the report of the actual applied bonding layer composition. To ascertain this relationship, large amount of alloys with various composition have to be prepared, coated and tested with various methods. Those are fearful amount of tasks. Therefore, it is significant to predict the effect of composition on properties theoretically.

Most recent bonding layers of TBC contain less than 1-wt% yttrium to promote the cohesion force between the substrate alloy and the Al_2O_3 film formed during the service [5,6]. But, the reason for yttrium to improve the cohesion is not clear. And the suitable content of the yttrium is also to be researched. Although yttrium does not belong to the lanthanide series in the period

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doi:10.1016/j.matchemphys.2007.04.062

table, it is commonly considered being a rare earth element. Because, the electron structures of rare earth elements are complex, they have some strange properties, which are difficult to be explained with the existing theories.

With the rapid development of computers, many numerical methods, such as *ab initio* simulation, molecular dynamics (MD) simulation, and Monte Carlo simulation become more and more popular in the calculation prediction of the properties of materials. Although *ab initio* simulation is convincing for its safe basis of quantum theory, it is only suitable for the systems with small clusters [7,8]. MD method is more effective. It is believed that the calculations involving millions of atoms are now feasible with the advent of massively parallel computers [9]. However, those methods still cannot treat the electron structure of actual industry materials with huge amount of atoms. In this aspect, empirical theory has special superiority.

The empirical electron theory of solid and molecule (EET) was established by Yu Ruihuang [10]. The theory is based on L. Pauling's electron theory and quantum theory. The fundamental hypotheses and the main ideas of EET can be easily found in Ref. [11–13]. With the bond length difference (BLD) method in that theory [11–13], the covalent electron pair numbers of all bonds in a crystal with known lattice constant can be calculated out. The calculated covalent electron distribution on every bond and the corresponding atom state was called the valence electron structure of the solid or molecule. Since its publication, many researchers have been engaging in its theoretical research and applications. More than 10 branches were formed, including mechanics, thermodynamics (such as melting point, boiling point, coefficient of linear expansion, cohesive energy of elements, alloys and compounds, thermal conductivity, crystal growth), electromagnetics (such as electron conductivity, magnetic moment, high temperature superconductivity, etc.), binary alloys phase diagrams and phase transformations, high compression phase transformations, etc. [14–19].

Analyzing the calculation results with EET, Liu et al. first noticed that the valence electron density on the biphase interface between the martensite (1 1 0) crystal plane and the austenite (1 1 1) crystal plane [*K–S* orientation relationship, $(1\,1\,1)_A//(1\,1\,0)_M$] is almost equal under the first order of approximation [20]. This fact just accords with the deduction in the improved Thomas–Fermi–Dirac theory that the boundary condition between atoms in solids is just the electron density being equal [21]. On this foundation, Sun et al. advanced the calculation method of the valence electron density of the biphase interface with the orientation relationship of $A_{hkl}//B_{uvw}$ in alloys [22]. Large amount of calculation results verified that the larger the electron density ρ_{hkl} and ρ_{uvw} of the two sides of the interface are, the stronger the interface conjunction is; the smaller the minimal electron density difference $\Delta\rho_{\min}$ is, the smaller the interface stress is [23,24]. On the basis of large amount of calculations of the valence electron densities of the interfaces among the alloy phases of austenite, martensite, cementite, special carbides and nitrides in steels, Liu et al. successfully discovered the nature of phase transformation toughening, deformation hardening, dispersion hardening, surface modification, recrystallization refining. So, they advanced an alloy composition design method on the basis of valence electron density calculation, and successfully design some industry alloys with the method [24].

Although the calculation method was advanced in alloys, it can also be expended to ceramics for EET being suitable for all crystals. Therefore, the mechanics properties of TBC interface may be predicted with the calculation result of its electron density. On these bases, the effect of yttrium content on the valence electron density of the ceramic thermal barrier layer/bonding layer interface is calculated in this paper.

2. Calculation of the valence electron densities of the ceramics layer/bonding layer interface

For simplicity, suppose the ceramics layer of the TBC being t-ZrO_2 and the bonding layer being nickel base (γ phase with fcc structure) yttrium solid solution. Although there is no constant orientation relationship between the coating and the substrate, the formation of coating texture under various technique conditions is a common phenomenon [11,25]. If the fewer the total number of the electrons on the surface suspending bonds, the lower the surface energy, then researches show that the texture of the (1 1 0) crystal plane paralleling to the surface for t-ZrO_2 coating is easy to form. If the textures of crystal planes with low indices are easy to form for the bonding layer, then those planes with the preferred orientation tend to parallel to the (1 1 0) plane of the ceramic layer. Therefore, the valence electron density calculation is based on the (1 1 0) plane of t-ZrO_2 paralleling to the (1 0 0), (1 1 1), (1 1 0) plane of the nickel–yttrium solid solution, respectively.

The head and tail hybridization states in EET of zirconium, oxygen and yttrium are given in the appendix. Those of nickel were given in the Appendix II of Ref. [11]. Substitute those parameters into the *k* formula, the hybridization table of these elements can be calculated out. The calculation results show that both the A type and B type hybridizations of zirconium have 18 hybrid levels. The hybrid level numbers of yttrium and oxygen are 10 and 4, respectively. The covalent electron numbers n_c and the single bond radius $R(1)$ of the atoms at every hybrid level can be listed in the hybridization table.

2.1. Valence electron structure of the ceramic layer and the valence electron density of its (1 1 0) crystal plane

2.1.1. Valence electron structure of t-ZrO_2

The crystal structure of t-ZrO_2 belongs to tetragonal system. It belongs to D_{4h}^{15}-$P4_2/nmc$ space group. The atom positions are similar to those in CaF_2. Its lattice constants are $a = 0.512$ nm, $c = 0.525$ nm. Then its crystal cell is shown in Fig. 1. The coordinates of the atoms are as follows [26]:

- Zr : 0, 0, 0; 0, 0.5, 0.5; 0.5, 0, 0.5; 0.5, 0.5, 0
- O : 0.25, 0.25, z; 0.25, 0.75, $\bar{z}$; 0.75, 0.25, $\bar{z}$; 0.75, 0.75, z; 0.25, 0.25, $0.5 + z$; 0.25, 0.75, $0.5 - z$; 0.75, 0.25, $0.5 - z$; 0.75, 0.75, $0.5 + z$