NEW MATERIALS AND IDEAS TO BE USED IN ADIABATIC ENGINES

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Abstract

This note concerns several topics. Firstly, a review of some less-known topics regarding the contemporary knowledge on TBC and piston caps is given. Then, it turns out that almost unknown New Periodic System of Elements can be of assistance to predict several properties of new TBC materials. Theoretically, there exist a possibility to join Si-Al.-piston alloy with yttria-stabilised zirconia (and the like) by means of feldspars (plagioclase). The latter do not attain to melting temperature and can be arrested within the alloy. A shortened integral optical equation in the manner of inverse problem was used to compute the temperature drop accros the piston cap's layers. The YSZ layer operating in this hypothetical engine gave 517.5 ° K drop, whereas the feldspar gave about 100-50ºK temperature drop per nm. This arrangement would give minimised radiation and more or less 'cold' engine(piston). Perhaps, oxides of the thalium-sesquioxide-type structure would be better to stick to metal than the commonly used ones.

Keywords: feldspar, absorption coefficient, radiative transfer, coatings, piston cap, temperature drop, thermal conductivity, pyrochlore, PSZ, YSZ, BC, TBC

1. Introduction

In spite of vast literature on coatings and the high-temperature-protective shields, e.g. piston caps, several items have not been addressed; likewise the definite data. Nor will this note, unfortunately, cover the necessary , e.g. spectroscopical data. This paper is aimed at commenting on the definite works, pointing ways of joining ceramics to aluminium cast (piston) alloys, and, presenting a hypothetical joined assemblage (shield + join + substrate) and its temperature performance. The other solutions are mentioned as well. All that when observing rules of mineralogy and crystal chemistry.

It should be stated that coatings are totally other then ceramic slabs, and even the same formula of the sprayed compound can result in a different crystal structure (than customarily deemed to be!), giving an other compound (Klechkovskaya et al. 1980). Spraying, as seen by crystallography, is rather detrimental for the ongoing performance of the engine, i.e. as regards durability of the respective coating. There is the problem of nucleation , chill and negative diffusion, i.e. the substrate should be heated and the coating-to-be side chilling! Such methods using arc density of current in substrate when electroplating ceramics already exists (Chigrinova, 2001). There are some novelties within the thermal barrier coating (TBC) topic, e.g. Dietrich et al.(2002) described a metal-glass TBC transforming to monticellite (on MCrAlY) with very good thermal shock resistance. Bast and Schumann (2002) searched for prospective materials ,e.g. of perovskite, spinel and pyrochlore structure, the latter being not resistant to reciprocating (cyclic) temperature stress, but perovskite has avoided spallation even at 1350º C. The latter authors claim high thermal expansion of perovskites which, according to the present authors' opinion is questionable even mid in the solid solution series. It is, however, possible that a definite perovskite solid solution series is regarded there (details

not given). YSZ as a whole has a poor performance as regards thermal shock resistance and, partly, langevity. But the-still talking on transformations, the engineered porosity and the like appears immaterial in part, since the piston cap and the other elements with eminent performance has been fabricated, i.e. Al.- bearing 6YSZ (Ivanova et al., 1991). Mirkovich (1979) tried to enhace the YSZ shock performance by Ba-brittle mica, but it led to higher heat conductivity (surely due to mica transparency perpendicularly to sheet, polarised and an additional heating due to mica).The more specific items of the topic will be addressed below.

Recently, the diverse fluorite- or pyrochlore-structure derived materials has been launched, e.g. Wu et al.(2002), Zhu and Miller (2002) or Schelling et al. (2004). They display very low heat conductivity of 1.5 $Wm^{-1}deg^{-1}$, or as a coating even 0.6. It is known that only a few common compounds stick relatively tightly to metals. Interestingly, Y_2O_3 (Ia3, Tl_2O_3 group) bonds very tightly to W-Ni-Fe alloy (Skaggs, 1979). Two points should be stressed. Firstly, there is an knowledge on sticking properties, but it concerns base metals, mainly. The same methods are used to aluminium piston alloys. Secondly, there is no simple ,and general relation between tight jojning and reactivity, e.g. ceria sticks to many and without testing we know nothing.

2. Psz , Pyrochlore And The Akin-Structure-Confined Problems

It is beyond the scope and purpose of this paper to analyse all the notions and results regarding any kind of stabilised zirconia, but is worth mention how is it and why.There are, contrary to the notions, many compounds with highly anisotropic coefficient of thermal expansion (CTE).Zirconia, after many years, is only down-stabilised, i.e. we cannot prolonge the existence of monoclinic zirconia to high temperatures, except by using hafnia (Karaulov and Zoz, 1991), but it enhance the heat conduction. It is abnormal that a simple oxide at high temperature aquire coordination number (7 and 8 instead of 6), and , consequently, behaves as framework silicate in expansion which is not. It appears as if it were from high temperatures but low pressures, cf. Filatov (1985) and the literature therein. Surely, the short bond length in some polymorphs are cause of instability of zirconia, cf. McCullogh and Trueblood (1959). Pyrochlore-structure increment may or may not occur in diverse PSZ, depending on the ion added. The XRD methods of detecting pyrochlore in PSZ's are poor , and should be replaced by modern intensity methods, or more sensitive ones (low angle, Auger or optical). Finally, the new Periodic System (Marakushev, 1984) should be used to predict the properties of the outcome mixed oxides, e.g. with lanthanides. By using that system , the authors should know that a definite couple of lanthanides in fluorite-related, PSZ or pyrochlore structure will give a definite efect on the heat conductivity, whereas the other couple will not! There are definite groups of lanthanides,e.g. EuYb (II), LaGdLu (III) and CeTb(IV), or, theoretically, with non-lanthanides PrDy & Ta (V), CeTbHf (IV) and the like.Assuming all the lanthanides 3+ ions or, seldom, 4+ , is a serious error. Consequently, there can be diverse clathrates, sybotaxics and shear compounds (and not!!! clusters), clusters of which create a definite anionic pattern which do lower conductivity and enhance CTE. By using the strong-field ions in the above compounds they become more high-pressure ones. Pr-bearing ZrO_2 is extremely stable, cf. Schneider et al. (1979). Likewise, practically, the shape of all the graphs of Schieling et al. (2004) can be predicted by using the above-System and polarizability of cations. The unique position of Sn pyrochlores there is also to predict when one recognize the extreme thermal shock resistance of SnO_2. According to one of the present authors, the compound has a striking elliptic polarisation which might have bearing on the radiative transfer, due to coordination milieu of Sn, and, thence, lower the conductivity (a conjecture). Moreover, we are not talking on stannates (cf. ibidem), but on pyrochlore, a double oxide with or without F, $A_2B_2O_7$ or $A_2B_2O_6F$.

3. Ysz-Alsi-Alloy Join By Plagioclase Bond Coat

One of the authors (Krzyżak, 2003) has claimed that 'glassy structures' as PSZ with their low melting enthropy and poor crystallisation force are relatively poor insulators at high temperatures. One of the solutions would be to place a material with high crystallisation force, high melting enthropy, rigid and roomy structure and increasing CTE. One of the candidates will be feldspars (plagioclase) – by the way of example. There can be other ,e.g. some niobates. Plagioclases are framework silicates group creating the series $NaAlSi_3O_8$ (albite) – $CaAl_2Si_2O_8$ (anorthite). They are generally triclinic with no well-defined cleavage, albeit the Na-rich members are not interesting here due to interfingering of sub-members and cleavage along ,e.g.(-801). They are no refractories , but their melting temperatures are enough to be the bond coat.There is a vast literature on feldspar diagnostics, but it cannot be given here. Plagioclases are build up of domains which change and regenerate upon temperature.Likewise twinning can go back and forth ,e.g. in anorthite.They can be ordered or disordered with two militating governing ordering systems, even anorthite can be disordered (Smetannikova et al., 1987). Short- and long-range order do project as fading reflections on XRD patterns. We will be interested in Ca-rich members. CTE is highly anisotropic, negative in part (Willaime et al., 1974) and similar to monoclinic zirconia and hafnia,being not far from that of TSZ, 13 ppm/K for anorthite at 300°C and up to e.g. 28 for some mid members.They display the same as PSZ or zirconia 'framework silicate way' of CTE, resulting, however ,also due to loss of long-range order in a climax of CTE at definite temperature, and pointing on the II-type transformation on temperature , so-called λ (of Münster). They are better insulators than PSZ, and the E modulus , 74.9-87.0 GPa being comparable with that of 2 times PSZ sprayed coating or galena (83.3). In spite of the hardness of feldspar they are 'rubber' in character. Finally, feldspars rather easily sinter with metals.There is no similarity to zirconia structure (whatever) except, perhaps, 7-coordinated metals,and very faint similarity of pattern of oxides. Nor, classically, the unit-cell twinning is possible.

The idea of joining is as follow. A good kind of YSZ or other will be prepared, followed by a delicate sintering of rather oriented feldspar at about 1000°C and casting the Si-Al. Alloy on that. There are also other prospects, e.g. in-situ synthesis of anorthite from kaolinite and calcium chloride. We should ,at any rate, avoid reaction,

$$3\ CaAl_2Si_2O_8 + 8Al. = 3\ Ca(AlO_2)_2 + 4\ Al_2O_3 + 6\ Si(\downarrow)$$
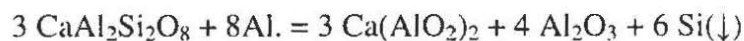
or related , which would go at that temperature. If they were to go, the product would generally not be soluble in water (the information upon request). Simply the feldspars have prospects to be arrested in the alloy due to their partly negative CTE and the temperature hysteresis thereof. Theoretically, there can be a problem with shield(zirconia,YSZ)–feldspar CTE alignment, but it is to cope with. There are chances for 'accepting' more incompatible compounds (rigid) than PSZ or pyrochlore. Refraining from the discussion on the up and down temperature performance of the described triplet (PSZ + feldspar + the alloy), it will be made an object of the ongoing study. But see below.

4. The Temperature Drop Along The 7ysz-Feldspar Sandwich

The shortened form of the nonlinear integral equation of Men' and Sergeev (1971, 1972), i.e. that of Men' (1973) for flat slab has been used to compute temperature drop along the 7YSZ-feldspar couple. This approach is practically inverse with only one input temperature ,from the hot side. The thickness of YSZ of 6 mm (dense!) was adopted, whereas feldspars thickness was diverse, mainly to obtain the lowest temperature. There are immense

difficulties in obtaining proper high-temperature spectra of the above materials, i.e. to use the full-form of the equation, but all that is in progress. Due to definite shape of (part) of spectra feldspar and YSZ can be assumed gray. A short Fortran 95 programme , using 7-point Gauss quadrature has been written by one of the authors to solve the above equation. The programme was tested against a few substances in literature, and the results were rather excellent. But see below. The final used equation was:

$$\Delta T = Q\tau/k\lambda - \{8n^2\sigma T^3/k\lambda\}F_3\varepsilon_2\Delta T \quad \text{where,}$$

$$F_3(\tau) = {}_0\!\int^{\pi/2}\cos^2\varphi\sin\varphi\{R_1\exp((-\tau_0 + \tau)/\cos\varphi) + \exp((-\tau_0 - \tau)/\cos\varphi) - R_1\exp(-\tau_0/\cos\varphi) -$$

$$\exp(-\tau_0/\cos\varphi)\}[1 - R_1R_2\exp(-2\tau_0/\cos\varphi)]^{-1} \quad \text{where,}$$

$$\tau_0 = kH \quad \text{and} \quad \tau_0 = \tau$$

ΔT being the temperature drop, Q – heat flux, τ_0 – optical density, λ – heat conductivity coefficient, k – absorption coefficient, n – refractive index, σ – the Stefan-Boltzmann constant, T – the hotter side temperature, F_3 – the function above, ε_2 – emissivity of the second, colder wall, φ – the angle, H –thickness of the layer (slab), τ – optical depth , and, R_1 and R_2 – the reflectivity of the hotter and colder wall.

The computation were performed as if it regarded a real uncooled adiabatic engine.The average working temperature was assumed of 1473.15°K, whereas that of gas of 1794.15° K. The input temperatures of the piston were taken from Woods et al. (1985) or assumed,i.e. from the bowl centre to the rim: 989.15, 1023.15, 1073.15, 1198.15, 1273.15 and 1173.15°K. The fluxes were computed using Bloch (1962) and Jaskólski (2001). Heat conductivity for YSZ was taken from Wu et al.(2002), whereas that of feldspar computed for labrador(or rather andesine, a mid member) from diffusivities of Magnickij et al. (1971). 2.70 for refractive index of YSZ was adopted – which is too high, but the lower ones do not practically change the output (7.3 °K difference) and 1.5572 for feldspar. The temperature-dependent absorption coefficients were computed using the method of Chekhovskoj et al.(1971) which contradicts the Genzel's law, but it turned out that even a $\ln(\sigma T^3/\lambda_{photon})$ is not a stright line vs. temperature. The stright are only sections.There are three of them for feldspar and four for YSZ. The kink at 1000°K on the feldspar curve can tentatively be interpreted as order-disorder event or that one(a set) of crystallographic planes become opaque. Nothing can be said on YSZ. Within the operating temperature range we used the following absorption coefficients for feldspar

$k(700-800°K) = 70586.6771\exp(-5.8763\cdot10^{-3}\,T)n^2,$
$k(800-1000°K) = 327.5027\exp(+8.1785\cdot10^{-4}\,T)n^2$ and
$k(1000-1200°K) = 4034.0260\exp(-1.6482\cdot10^{-3}T)n^2$ and for YSZ
$k(973-1273°K) = 14107.0994\exp(-1.6536\cdot10^{-4}\,T)$ for n =2.7.

Owing to the partial translucency of YSZ and the feldspar (which otherwise is difficult to estimate in this case), the emissivity used was that reduced. It gave at once correct reflectivity at the YSZ/feldspar boundary.Emissivities there were computed from optical principle (Hervé, 1979) while using extinction values from the above absorption curves, but there is no difference in (also hemisphaerical) emissivity, nor is especial difference in the outcome. i. e. in the temperature drop. The problem of the emissivity at the feldspar/ the alloy boundary was immense due to lack of emissivity of the piston alloy (12%wt. Si). Nor it was possible to compute emissivity (or reflectivity) back ,i.e. from spectral values since the

wavelength in the authors' disposal are diverse for Si and Al.; no mention on admixtures of the alloy. Finally, the emissivity was computed from reflectivity of a similar alloy (12%wt. Si), assuming the latter constant beyond the red light (the curve is abnormal and the alloy is a blend!). Such the approach will surely cover the difference in emissivity if it were computed from the exact formulae (Lingart and Stipel'man, 1981); the alloy namely reflect into feldspar and not into vacuum or air. Summing up we have obtained likely temperature drop accross the YSZ and the feldspar layer, but see below about credibility of the result. See the Tab.1.

Table 1. The temperature drop accross the layers of the piston cap [°K]

Point	1	2	3	4	5	6
INPUT TEMP	989.15	1023.15	1073.15	1198.15	1273.15	1173.15
YSZ, 6mm	517.5571	491.5218	447.8555	327.5796	247.1811	352.9479
Feldspar,1mm	103.4623	102.7935	99.9733	68.4073	51.2102	74.4444
Feldspar,2mm	206.9041	205.5578	199.8994	–	–	–
Feldspar,4mm	–	–	–	272.5590	203.8438	296.6414

It can be seen that the results are quite promissing, but let us make an appraisal of the credibility of the drops. The rules of credibility given by Men'(1973) are beyond the point in part, but the solution should not differ from the exact one more than a few degree. The experimental or semi-experimental values of Woods et al. (1985) gave on more conducting TTZ 421, 455,675 and 135 degree [°C] for the points 1,3,4 and 5, respectively, but the setup of that piston is other and it was on cast steel. Taking into account that we do have fairly good values for absorption and that the drop for a freestanding coating of 7YSZ is about 500° C (Bast and Schumann, 2002), we have to asses that ours drops are quite likely, or fairly good, but tentative in character. The experiment is needed. It turns out that using the above arrangement of the cap (we can economize on it) we do not transmit much radiation and even enhance the drop – contrary to Eldridge et al. (2002). If one wishes, emissivity of the top coat (YSZ) can be varied, or, several shields given, but mechanically it can be detrimental (for engine!!!). The thickness can also be surely reduced. One can see that such the hypothetical engine would be quite cold at the feldspar/piston boundary.

5. The other solutions

It is nothing strange that pyrochlore on metal does not withstand the temperature cycling (see before). Its structure is incompatible to many metals. There, only octahedra can distort, and surely not the scalenohedra (8). The alumina as TGO is not much better, though a FGM to Ia3 type (see before) should, perhaps, alleviate the problem. Scandia should also stick (?), and ceria do react with Al. The mechanical performance of such a couple is unknown, but the 'fuel elements', i.e. urania + Al. (the same) will display high CTE. Our interests concerning pyrochlore should rather be confined to how 'derive' pyrochlore structure from e.g. fluorite-like one to merge into thalium sesquioxide structure which stick. There is a vast area of hypothetical mineralogical solutions, but all these without experiment (especially) are beyond the scope and purpose of this paper. Silicides as BC and the other problems of crystal chemistry cannot be addressed here due to shortage of place.

6. Conclusions

The above conclusions militating with the literature will not be repeated here. The offered way of thinking, YSZ-feldspar-alloy triplet, or alike one can be of interest since we can avoid brazing, 4 layers or (we hope) demage. It also quench radiation! Thermophysical data for minerals are almost non-existing. The same is valid for definite (also optical)

properties of the definite aluminium alloys. Feldspars and ,sensulato, alike ones can also accept diverse rigid structures, and the problems of emerging porosity (upon sintering) can be menaged using orientation of grain and the preparation methods.

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