

SOME NOVEL MATERIALS FOR COMBUSTION ENGINES

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Abstract

A review of a few ceramic materials and mainly minerals, being hypothetically prospective materials for bond coat (BC) and, partly, the thermal barrier coating, TBC of the engine parts is given. It turns out that several framework silicates can be prospective materials as BC for Al.- alloys, whereas sorosilicates should match properties of the alloyed steel. The joining prospects of some materials as feldspars, yttria, pyrochlore and perovskite were partly addressed in the earlier author(s)' papers, and are mentioned. Apart from mechanical properties, coefficient of thermal expansion as well as crystallisation force of the phases under consideration, rules of epitaxy as well as symmetry-energy problems are addressed. Finally, several synthetic phases are mentioned and their prospective character as BC – indicated.

1. Introduction

This paper is no review of the contemporary achievements in joining metal to ceramics, nor is a scavenging of information from the 'older' literature. The paper rather presents a personal view (considerations) of the authors on the problem of joining materials from the mineralogical-chemical-mechanical point of view while presenting only a few prospective materials or more or less hypothetical regularities. The joining prospects of some materials as feldspars, yttria, pyrochlore and perovskite were partly addressed in the earlier author(s)' papers, and will be mentioned if needed. We are talking on a material which joins ceramics to metal; unfortunately, to this end one can also count coatings – per se which otherwise do join their self. The joining material does not have to be a refractory one, but has to withstand definite temperatures (or 0.7 thereof) and pressures as well as shocks in a definite location, e.g. in piston. One of the main problems of diverse coatings and ceramic caps is TGO layer, and the MCrAlY bond coat (BC) is not reliable as regards longevity and service. The same is valid at diverse brazed materials, but neither some aluminides with moderate coefficient of thermal expansion (CTE) nor low-expanding new piston alloys do really alleviate 'the joining

problem'. There is no simple relation between tight joining, reactivity, crystallochemical similarity and good thermal shock (cycling) resistance. There are some epitaxial 'tricks' like rotation of crystallographical directions to match not necessarily most densely populated directions of the substrate, but to match alternately atom and hole (or anion) directions (Kosevich et al., 1980). Surprisingly enough, the strength of the metal-ceramic join is sympathetic with the melting temperature of the metal substrate (Szymański, 1997). It is well known that phosphates, e.g., berlinite, AlPO_4 , do penetrate the deposit (coating) as silicates and the deposit as well as the join itself benefit in their mechanical aspect. The problems of interactions on interface are not always well known, but e.g. talc can improve all the mechanical properties of Al_2O_3 ceramics. The joining material must also display a high crystallisation force not to transmit much radiation into metal parts (cf. Krzyżak, 2003). The Young modulus, E , will generally decrease with increasing temperature, but it depends on the form of the grain, crystallographic direction, and, surprisingly, according to the authors' opinion, not only on bond strength, but more or less 'homodesmic' directions can have E as high as the real 'rigid' directions, e.g. $\langle 010 \rangle$ in feldspars; $\langle 001 \rangle$ being rigid. Joining of metal to ceramics via a metal interlayer needs not be successful, e.g. Au can catalyse the formation of oxides on Al. (Kosevich et al., 1980), thence uncontrolled TGO results. Likewise, Cl supports formation of oxides on the other metals. The oxidation of an integral part of alloys create a protecting oxide layer which apparently stick well, e.g. the Al_2O_3 layer on MCrAlY or Cu-Al. alloys (Chen and Lou, 1999; Saunders and Pryor, 1968). One is tempting to use such layer to deposit the other ceramics thereon. To enhance the temperature drop on every ceramic layer, the low emissivity of the 'colder' wall (here metal boundary) is necessary. Emissivity frequently increase with temperature, whereas reflectivity does, e.g. with pressure. There are several mineralogical phenomena which apparently are not exploited in materials science up to date, e.g. Mo may replace S in some structures, whereas Mn replaces W instead of Ca in Mn-bearing schelite, CaWO_4 (Sherbina et al., 1971). This, at once (MnF_4 isomorphic with WO_4) will supposedly lower thermal conductivity of the compound. Also the rules of organics epitaxy on hard materials are interesting to introduce metals (e.g. oxides). The Reader should notice that the just-mentioned idea is different from decomposition of metal alcoxides. Several other statements on epitaxy one can find in the literature (Jaskólski and Krzyżak, 2005). It is important that not only the main metal of the alloy, but also the minor (elements) ones may play a role in joining/epitaxy, e.g. Si in steel will disintegrate PSZ. Finally, it is hypothetically conceivable to build up a functionally graded material (FGM) capped with ceramics, or, to cap the metal with composite.

2. The framework silicates

Some framework silicates are interesting due to their expansion mode; firstly they rotate polyhedra to a definite temperature, then they expand less (not fully, or even stop for a while) with increasing temperature (Taylor, 1972). Their CTE being high, frequently $10\text{-}28 \cdot 10^{-6} \text{ K}^{-1}$, with anisotropy, and comparable to those of many metals. The mechanical properties, E , G , K , ν (Aleksandrov et al., 1966) of such minerals as plagioclase (also, feldspars, $\text{NaAlSi}_3\text{O}_8\text{-CaAl}_2\text{Si}_2\text{O}_8$), rather Rb-type nepheline ($(\text{Rb},\text{Na},\text{K})\text{AlSiO}_4$), hauyne ($(\text{Na},\text{Ca})_4\text{-}_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)_{1-2}$) or scapolites (carbonate, Cl-bearing framework silicates of Na and Ca rather exactly match those of Al.-piston alloys and of a part of cast irons. The low crystallisation force is the problem at nepheline, whereas good epitaxy of Al. on sodalite, a Cl-analogon of hauyne, is known (Palatnik and Papirova, 1964). Having in mind the similar bond length and structures in the above-minerals, one can try to join them to such metals as Pt, Pt-Rh, Al. and ...($\text{Fm}3\text{m}$). At the first glance, the a and c of Ca-feldspar can be surely matched to $\langle 100 \rangle$ and $\langle 311 \rangle$ of Al. (Pt), but even more probable would be the $\langle 110 \rangle$ and

<110> matching on (111) metal and (001) feldspar, respectively, with a bit rotation, perhaps, and might, supposedly, give a highly populated joining plane of the alternating atom-hole type and with Volmer-Weber mode of deposition. Owing to the diverse causes, matching to 'PSZ' is conceivable since the HgI_2 grows on feldspar (Palatnik and Papirov, 1964), the former being of the TZP type. The feldspar being rather thermal cycling resistant, but the cycling performance of the join metal-feldspar-PSZ is unknown. The temperature map beneath such ceramics, i.e. in the metal is somewhat promising (Jaskólski and Krzyżak, 2005).

3. Sorosilicates

Mechanical aspect of forsterite, Mg_2SiO_4 , and its CTE of $11 \cdot 10^{-6} \text{ K}^{-1}$ on average (Krzyszhanovskiy and Shtern, 1973), will surely match the mechanical demands of some alloyed steels, e.g. of the valve of Diesel engine. Coatings of this mineral were investigated by Russians (upon request) on carbon rich steel with CTE of $14.7 \cdot 10^{-1} \text{ K}^{-1}$ and NiCr plating, and the mechanical performance of the join (sticking, cycling) was rather excellent. The other 'popular' sorosilicates do not match the properties of the 'popular' engine materials (metals). Albeit, there is no hindering to analyse the less-known ones and there exist some ideas, the thermophysical and mechanical data pertaining to them hardly exist. Monticellite, MgCaSiO_4 , formed as a recrystallisation product of the metal-glass composite on metal (Dietrich et al. 2002).

4. Chain silicates

Albeit jadeite, $\text{NaAl}[\text{Si}_2\text{O}_6]$, or an aggregate thereof can display mechanical properties as cast iron, the low CTE of it, 5.5 and 8.8 of CTE-above units and $\mu = 9$ (monoclinic) (Filatov, 1985) can be detrimental to the join. Using it as a part of composite or FGM is not precluded, either.

5. The other materials

There is a vast area of diverse compounds in mineralogy which, surely, after some tests, can be regarded as a prospective BC or even TBC-component. MoSi_2 is well known with its affinity to PSZ and hafnium, but up to the authors' knowledge only on Mo, W and Mg-Ti alloys as the substrate. The non-using of ceramics of otherwise excellent properties as dysprosium-based one or scandia is not well understood. The latter might surely stick to metals. Of course, one can try to build up a FGM structure, the top of which can be covered by another TBC material, the filler being joining agent. It would create some problems, e.g. in piston, but going further a fit pressing of a composite to the bowl is possible. If so, the materials of e.g. wurtzite structure might be good locus of co-crystallisation for PSZ, (the material being filler in metal) since TSZ-type is the centre for crystallisation of the wurtzite one, e.g. ice, cf. (Palatnik and Papirov, 1964). Several sulphides may well stick to metals or be produced in them, having sometimes relatively or extremely high temperature of decomposition. They can be e.g. BC, but it demands the other philosophy behind the TBC problem than that hitherto used, i.e. with the avoidance of S diffusion. A very interesting compound is MoO_3 with its unique CTE with kinks (Toloukian et al., 1977) and high crystallisation force might easily be arrested by metal and work as BC. Surprisingly, it easily grows on ZnS (Palatnik and Papirov, 1964), but taking into account a huge difference in CTE of the two the usage of the two together can only be speculated over (tested).

6. Conclusion

There are still prospects to use (the) minerals or their aggregates as BC; framework silicates for Al.-alloys and soro-ones for steels. There are also other possibilities. From the existence of the phenomenon of spallation and cracks of materials on MCrAlY and/or low thermal resistivity of ceria and PSZ on steel, one can derive a purely geochemical conclusion that Fe, Mg, Al. and Si affiliate (go for) with Ni and Cr and not with Ce and Zr. Thence, what should be the BC for refractory material, PSZ and the like – surely some minerals, also artificial ones, e.g. with Ca and Fe (ferrites as well), but not most of the spinals. These minerals (materials) should have affinity to substrate (Al, steel) and it would be best to inter finger with it (fabrics). The minor elements esp. of the substrate should also be taken into account. Finally, definite planes of the material should have (attain to) definite (low) surface energy or high crystallisation force to not to need to use the interfacial compound. The crack phenomena and tight up ceramics can namely be managed by using the-high-crystallisation-force material and low diameter of the grains, e.g. sphere, CaTiOSiO_4 , the synthetics of which are knowable for their (high) thermal resistance in ceramical sciences. At last, one facing the problem of joining material or epitaxy should, in general case, abandon the ideas of statistical orientation of grains and, thence, iso (ortho) tropic millieu of ceramics. The rules of the peculiar symmetries will govern also multi plicate ones which leads to definite fabrics (texture, Engl.: structure) and the pattern ‘perched’ with inhomogenities (whatever the description is) should be used instead of customary approach since such is the nature, i.e. direction- and the-scale- sensitive, of materials.

6. References

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