Mechanism of hardening for the surface phosphates under external high pressure

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Abstract

Mechanism by which Zn/Fe methaphosphate material is transformed to glassy meta-phosphate is partially understood. The two decades of intensive study demonstrates that Zn and Fe ions participate to cross-link network under friction, hardening the phosphate.

In the present work we consider our (in progress) spectroscopy study of zinc and iron phosphates under the influence external high pressure to determine Zn ion change coordination from tetrahedral to octahedral (or hexahedral) structure. The standard equipment is the optical high pressure cell with diamond (DAC). The DAC is assembled and then vibrational or electronic spectra are collected by mounting the cell in an infrared, Raman, EXAFS or UV-visible spectrometer.

Transition metal atoms with d orbital have flexible coordination numbers, for example zinc acts as a cross-linking agent increasing hardness, by changing coordination from tetrahedral to octahedral. Perhaps the external pressure effect on the $[Zn–(O-P-)_4]$ complex causes a transformation to an $[Zn –(O-P-)_6]$ grouping

High pressure spectroscopy has been extensively applied for the investigation of 3d transition metal ions in solids. When studying pressure effects on coordination compounds structure, we can expect changes in ground electronic state (spin-crossovers), electronic spectra due to structural distortions (piezochromism), and changes in the ligand field causing shifts in the electronic transitions.

Keywords: antiwear additive; hardness; external pressure; transition metals; flexible coordination number; spectroscopy

1. Introduction

Wear is a critical factor limiting the usable lifetime of engines. To counter wear, lubricant formulations include zinc dialkyldithiophosphates (ZDDPs) as anti-wear (AW) additives. The mechanism by which this material is transformed to glassy polymeta-phosphate is partially understood. Two decades of intensive study demonstrate that Zn and Fe ions participate in cross-link network under friction, hardening the phosphate [1-6].

Zinc dialkyldithiophosphates are lubricating oil additives, providing the important functions of wear and oxidation inhibition. Experiments clearly indicate [1, 3, 6], that zinc dithiophosphates (ZDDP) tribofilm was characterized as short-chain meta-phosphate layer attached to the steel surface, and covered by a long-chain meta-polyphosphates. However, the molecular-level mechanism by which this material hardening occur due to chemical changes is not well understood [7, 8].

Recently, molecular-level theory based on the concept that the transformation of zinc phosphates shown increased hardness under high-pressures was introduced by Mosey, Muser and Woo [9]. It was further proposed that tribochemical reaction products act as solid layer and have calculated induced shear modulus values 140 GPa for zinc phosphates. The calculated the bulk modulus transformation of zinc phosphates has not been proven experimentally. Their conclusions can be extended to other d-orbital metals; the purpose of this work is to explore experimental data in literature to support the idea that pressure is required for transformation of the coordination and hardness. The modification of the bond length, of the bond angles and of the coordination number under pressure is responsible for this transformation [10].

2. Tribofilm formation on iron surfaces

Experiments clearly indicate that ZDDPs decompose in lubricating oil to form zinc meta-phosphate, and then during friction is transformed to glassy Zn/Fe poly-meta phosphate layer. It has also been shown first in 1986 by Martin's research school [4,5] and later by others [1] that wear decrease mechanism is associated with the build-up of an amorphous interfacial tribofilm (see Fig.1A).

Special attention has been paid to the state of iron (III) in the amorphous wear materials. Results indicate the presence of Fe (III) of the octahedral symmetry, and Fe (III) ions act as network modifiers of the zinc phosphate network formed during triboreaction. In recent work [6] using three analytical techniques (AES, XPS and XANES) a clear characterization of each layer in tribofilm was shown. Also, a tribochemical reaction between the zinc polyphosphate and iron oxides species was proposed on the basis of the Hard and Soft Acids and Bases (HSAB) principles [11].

$$5 \, Zn \, (PO_3)_2 \; + \; Fe_2O_3 \;\; = \;\; Fe_2 \, Zn_3 P_{10} \, O_{31} \; + \; 2 \, ZnO \qquad\qquad (1)$$
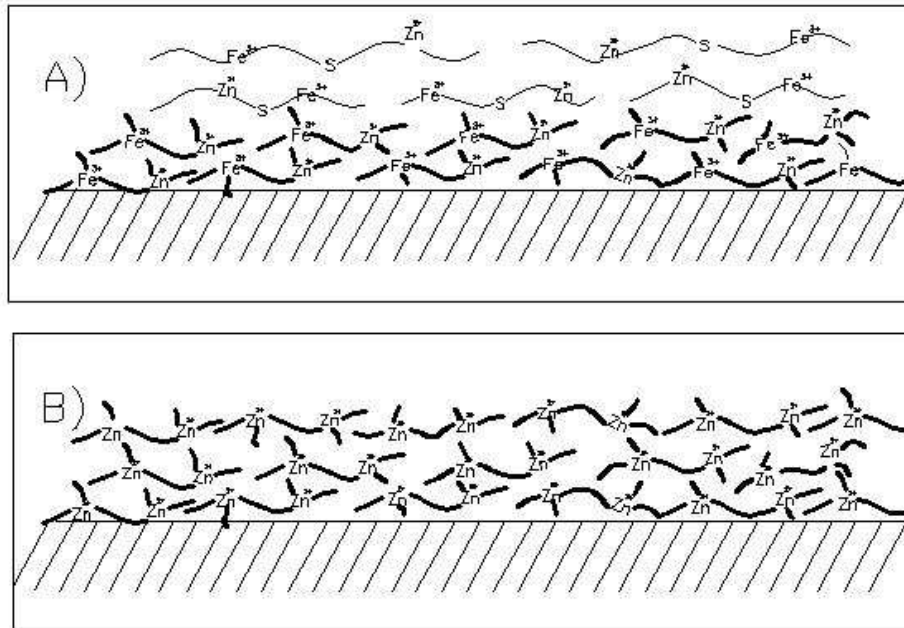
Fig.1. Schematic structure of tribofilm layers. (A) Zn/Fe long-chain poly(thio)-phosphate (top), and Fe/Zn short chain polyphosphate (bottom) Martin model. (B) Zn polyphosphate cross-link network layer - Mosey-Muser-Woo model

Despite of this development of research on ZDDP tribofilm formation, the molecular structure theory and hence the functionality of the antiwear tribofilm has not been determined [9].

Currently, the computer molecular level theory simulation suggests that formation, functionality, and fractional properties of zinc phosphate are due to pressure-induced changes in the bonding of zinc phosphate chain, into a chemically cross-linked system [9]. At a pressure of 6 GPa, tetracoordinate bonding arrangements are irreversibly altered, so that cross-linking leads to a chemically connected networks structure. This leads to formation of new Zn-O bonds. When pressure exceeded 17 GPa zinc phosphate structure exhibit-cross-linked in all three directions (3D) in which Zn atoms adapted hexacoordinate arrangement through the formation of two additional Zn-O bonds. The pressure induced hardening of zinc phosphates, and calculated the block modulus of the system to 140 GPa [9]. In Mosey-Muser-Woo model Fe (III) ions do not participate in process of tribofilm formation directly., see Fig.1B. In Martin tribofilm model iron ions are most important as network modifier-formers in the hardening process. High pressures induce cross-linking through the central atoms, increasing the hardness of the material [5, 6].
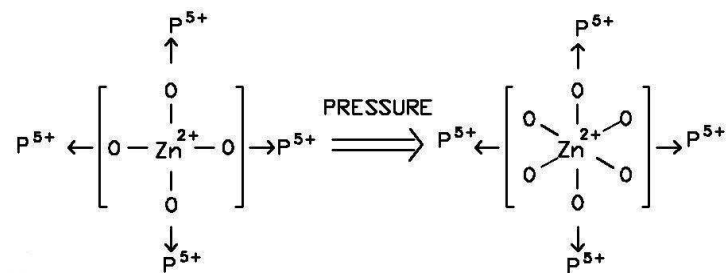

Fig.2. Schematic of the coordination change of Zn (II) phosphate under external pressure from tetrahedral to hexahedral

The zinc ion Zn^{2+} with a d^{10} orbital is particularly suited for the formation of coordination polymers and cross-linking. The spherical d^{10} orbital configuration is associated with a flexible coordination environment. The versatile coordination of Zn complexes can vary from tetrahedral through trigonal bi-pyramidal, square pyramidal, octahedral, hexahedral and the ideal polyhedron easy occur [12, see Fig. 2. Due to the general lability of Zn complexes the formation of coordination bonds is reversible which enables metal ions and ligands to rearrange during the process of polymerization to give highly ordered network structures. Consequently, zinc can readily accommodate all kind of dimensions 1D, 2D and 3D architecture [12, 13].

To correctly assess the test conditions of investigated tribosystems, the calculated value of 'friction power intensity, (FPI)', (eq.2) for antiwear additives is good for comparison results with other investigators [14].

$$FPI = \text{friction coefficient } (\mu) \cdot \text{pressure } (p) \cdot \text{sliding velocity } (v) \; [MW/m^2] \qquad (2)$$

The authors [14] performed ball-on-disk and four-ball tests. The results for the FPI were calculated for two tribosystems: (a) for the ball-on-disk, FPI = 51 [MW/m^2], (low friction conditions); low FPI, decomposition of ZDDP was not observed on surface, and (b) for the four-ball test method, FPI = 435 [MW/m^2] (severe friction or extreme pressure (EP); high FPI, the Zn-S and P-S bonds are cleaved, and on the surface–layer presence of S, P, Zn, and Fe were detected by Auger electron spectroscopy.

3. Effect of external pressure on transition metal systems

The physical structure changes in phosphates compounds under external pressure have found many applications in technology. Compression of a material results in the interaction between transition metal and the surrounding ligands. High pressure spectroscopy has been extensively applied for the investigation of 3d transition metal ions in solids [15, 16, 17, 18]. When studying pressure effects on coordination compounds structure, we can expect changes in ground electronic state (spin-crossovers), electronic spectra due to structural distortions (piezochromism), and changes in the ligand field causing shifts in the electronic transitions [10]. It is not completely certain how the pressure induces hardening of zinc phosphates in antiwear tribofilm, as suggested by [9] based on parameter free Car-Parrinello ab initio molecular dynamics computer simulations (AIMD). It is necessary to look at the coordination systems under pressure with the broader look in studied compounds, which hardening was steadily increased by chemical modification. The standard equipment is the optical high pressure cell with diamond (DAC).

The four possible changes that can occur when external pressure is applied to the sample of coordination compounds [19, 20] are as follows: changes in space group and shifts in band energy, piezoelectronism, spin crossover, and spin-crossover with drastic changes in spectra. The spin-crossovers are the result of rearrangement of the molecular geometries which is expressed in changes in spin-state.

Specially interesting are materials when compound is spiked with different ions, eg., lead phosphate or zinc phosphate with contribution (doped) of iron ions. Under pressure, iron ion Fe (II) acts as a network modifier, or network former Fe (III) [5, 21]. In the case of iron oxide containing diborate glasses it could be shown that with increasing Fe (II)/Fe (III) ratio, Fe (II) is predominantly octahedral coordinated and acts as a strong network modifier, Fe (III) is tetrahedral coordinated and acts as a network former [22, 23].

3.1. Effect of pressure on zinc-iron phosphates

The physical and chemical properties of zinc phosphate glasses with the addition of Fe (III) or other metal ions have been receiving increasing attention for their chemical durability and mechanical strength [24, 25, 26]. The environment of Fe(III) in lead phosphate glasses demonstrates that Fe and Pb serve to cross-link network by lead atoms, and iron atoms the latter forming "knots' in the percolation pathways which will inhibit diffusion and increase durability dramatically [27, 28].

The structure of a phosphate glass is based on corner-sharing PO$_4$ tetrahedral, which form chains, rings or isolated PO$_4$ groups. With the addition of Fe (III) to a phosphate glass, the P-O-P bonds are replaced by more chemically durable P-O-Fe (II), and/or P-O-Fe (III) bonds [29, 30]. In the structure of iron phosphate glass, the Fe (II) and Fe (III) ions are believed to be bonded in FeO$_6$ groups which form (Fe$_3$O$_{12}$)$_{16}^-$ clusters that are interconnected via (P$_2$O$_7$)$_4^-$ group through the network. All the properties measured for zinc-iron phosphorus-oxygen network become stronger with increasing Fe$_2$O$_3$ content [31].

Many coordination compounds, silica, and phosphate glasses undergo interesting transformations under high pressure. The structure of material is transforming from eg., tetrahedral coordination (T) at low pressure to octahedral coordination (O) of ions at high pressure. The transformation from T $\rightarrow$ O in silica glass occurs at pressures above 8 GPa at room temperature [32], and also in melts silica [33, 34]. The formation of new ionic structures markedly improves the material properties such mechanical strength and elasticity, clarity, moldability as compared with started material.

3.2. Temperature effect on some coordination systems

The fact is that, in contrast to layer hardness by transition metal ions, the phosphates layer becomes hardened only after a subsequent pressure process. Indeed, it has been shown that the hardness of phosphates is caused the pressure values. It is known from ligand field theory that even small changes in the ligand field may cause enormous changes not only in the absorption behaviour (colour) but also to hardness. To illustrate some applications of temperature effect on silicate and phosphate glasses of coordination compounds, some examples will be presented here that demonstrate interesting changes in their coordination numbers upon melting process [35].

(a) for silicate glasses a transition from tetrahedral (Fe^{III}O$_4$) to octahedral (Fe^{III}O$_6$) complexes is observed with increasing metal concentrations, (b) the coordination number change from 6 to 4 of cobalt (II) borate glasses from (Co^{II}O$_6$) to (Co^{II}O$_4$) in presence of Na$_2$O at a concentration > 25 % mol, (c) coordination number change in cobalt (II) phosphates and silicates acidic base glasses for Co^2, for a phosphate glass (Co^{II}O$_6$) and silicate glass(Co^{II}O$_4$) complexes. In the case of phosphate, P^{5+} ions counter-polarize the Co-O coordination sphere to the extent of a loosening of the coordination from 4 to 6.

Phosphate glasses have been known for a very long time and their hardness mechanism has been the subject of numerous studies [36]. The interaction Fe-O in the octahedral ($Fe^{II}O_6$) phosphate complex is weakened significantly by the stronger counter-polarizing effect of the P^{5+} ion, see Fig. 3. The ($Fe^{II}O_6$) complex is much more loosened in a phosphate glass than in a silicate glass.
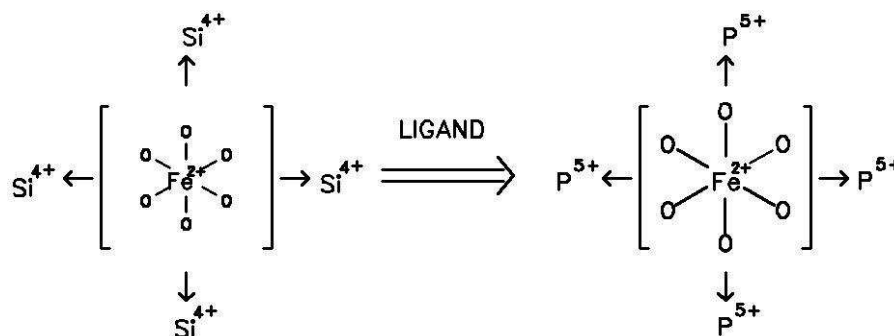

Fig.3. Schematic of the interaction Fe-O in the octahedral ($Fe^{II}O_6$) phosphate complex is weakened significantly by the stronger counter-polarizing effect of the P^{5+} ion

Paper [37] has reported that a rapidly cooled $ZnCl_2$ melt solidifies to a glass. Although $(ZnCl_6)^{4-}$ as well $(ZnCl_4)^{2-}$ groupings are present in crystalline modification, it is believed that primarily a 3-dimential network of $(ZnCl_4)^{2-}$, analogues to that of $(BeF_2)^{2-}$, is responsible for glass formation.

The process of strengthening by tempering of flat glass materials is in use for motor vehicles and aircraft. A fairly thick-walled glass object is heated above the glass-transition temperature, and quenched by cold air or by cold metal plates. The surface glass solidifies rapidly while the inner layers continue to contract. In this way the surface ends up in compression, while the interior is in tension, compensating for the surface compression. Fissures in the surface are compressed and, under load, resist their opening and the introduction of the fracture process. The strength achieved in this manner by a controlled surface crystallization following ion exchange is from 90 MPa (initial glass) to about 600 MPa [38, 39].

Iron exists in two oxidation states Fe (II) and Fe (III), in reduced state silicate glasses Fe (II) generally occupies fairly regular octahedral sites, evidently behaving as a modifier [41]. In oxidized silicate glasses, Fe (III) adapts tetrahedral symmetry and contributes to the network. The structural role of Fe (III) in phosphate glasses is quite different from its behaviour in silicate glasses [42].

When 5 to 10 wt % iron oxide (III), is added to lead metaphosphate glass, the chemical resistance to aqueous attack improves dramatically [43]. The environment of ferric iron in lead methaphosphate glasses has been examined using EXAFS spectroscopy [44]. Lead-iron-phosphate glasses are comprised of long phosphate chains which shorten in length as iron is added. Iron is found to be octahedral coordinated with a mean Fe-O bond length 1.95A, and lead has a coordination number of 8 and a mean Pb-O bond length 2.49A. Lead-iron phosphate glasses are comprised of long phosphate chains which shorten in length as iron is added. The EXAFS results demonstrate that Fe and Pb serve to cross-link network, and in this context Fe and Pb ions will migrate along the channels between the polyphosphate chains, where iron will create 'knots' in glass structure which will inhibit diffusion.

Using Mossbauer spectroscopy (ME), distinction between Fe (II) and Fe (III) in a silicate glasses is possible to establish, eg., the ratio of Fe (II)/Fe (total) or to find a change of Fe (II) to Fe (III) with an external applied pressure. For low Fe (III) concentration in a silicate glasses tetrahedral coordination is fevered an increased amount Fe (III) goes into octahedral coordination [45].

4. Conclusion

Pressure induced transformations in zinc poly-meta-phosphates glass in presence of iron cations was investigated. The structural role of Fe (III) is important for the chemical and mechanical hardness. Iron-zinc phosphate glasses are comprised of long polyphosphate chains which shorten in length as iron is added during friction process. The results demonstrate that Fe and Zn serve to cross-link the phosphate ions, and in this context Fe and Zn staying connected between phosphate chains. Taken together there is no doubt that the local structure of zinc is affected by the presence of iron and vice versa. Iron (III) in phosphates is found to be octahedral coordinated with a mean Fe-O bond, and zinc coordination should be determined.

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