



STRUCTURAL INTEGRITY AND MATERIALS AGING

Fracture Mechanics and Applications

Editors: G.C. Sih, S.T. Tu and Z.D. Wang

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STRUCTURAL INTEGRITY AND MATERIALS AGING



Fracture Mechanics 2003

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Preface

This book contains the *Proceedings of the Fracture Mechanics Symposium 2003*. The Symposium was held at East China University of Science and Technology in Shanghai, China, August 19-22, 2003.

The symposium is the first one of Fracture Mechanics symposium series in China, and was motivated by the increasing need for structural integrity assessment and development of use-specific materials. It is intended to be a group effort and to call attention to the engineers designing a new bridge or building, to the official administrators considering new specifications to reduce the incidence of mechanical failures. Although there has been an explosive growth of applying fracture mechanics technology since the 60s, structural failures remain a risky factor to the community at large. A great need for failure prevention has been identified in the developing countries. This is because of the lack and/or out-dated design codes and regulation rules. Oversimplified codes and standards used in the advanced countries may be equally vulnerable if they are not up-dated by more advanced theory and accumulated experience. This calls for an integration of science and engineering such that the industry could benefit by developing codes and standards based on more advanced theory. Special topics such as dissimilar materials, ageing of materials, degradation of nano-materials, etc., require a concerted effort of the academicians from universities, professional engineers from societies and industries to interact, exchange ideas and make recommendations on failure prevention and design improvement.

The symposium is co-organized by Chinese Pressure Vessel Institution, East China University of Science and Technology, Zhejiang University, Nanjing University of Technology, Zhejiang University of Technology, and co-sponsored by Ministry of Science and Technology of China, National Natural Science Foundation of China, Chinese Society of Theoretical and Applied Mechanics, Chinese Mechanical Engineering Society, and General Administration of Quality Supervision, Inspection and Quarantine of China.

I would like to take this opportunity to thank the above organizations for making this symposium possible. I also wish to thank the other members of the program committee for their advice and for reviewing the papers. The Symposium is made possible only through the support of Professor George C Sih. His personal involvement helped to set the tone for the Symposium. Special thanks are due to the support of the key research program "Inspection and safety assessment of In-Service Pressure Vessels at High Temperature" (2001BA803B03) of China Ministry of Science and Technology and support from the China National Natural Science Foundation.

Shan-Tung Tu, Symposium Chairman
East China University of Science and Technology and
Nanjing University of Technology
August 2003

From the Editors

Industrialization is a double edge sword. It can be beneficial and detrimental to the community at large. The development needs to be fostered to minimize the undesirable consequences. Mechanical failures stand out as a pervasive fact of life in our society. Failure of small items can be annoying while failure of large structures can cause loss of life or serious injury to people in addition to financial loss. Need-the-less to say, the Government would ultimately be charged with the responsibility to look after the well being of the public. However, it has not been clear where does this process start? Past histories of the developed countries could serve as a guide line. This may involve failures associated with structural components in chemical and nuclear power plants or aircraft transports and high speed trains. The disastrous failure of the Comet jet after Second World War II is a warning to short cut research and development work. The loss of the Aloha airliner in 1975 is another lesson where the wrong repair was made in accordance with out-dated rules and regulations. Certification by federal air aviation or government agencies is necessary but it is not sufficient to guarantee air travel safety.

Professional societies have equal responsibility to update and modify codes and standards by implementing the latest findings in research and development. The intention should not be focused exclusively on providing specific solutions but rather to understand and find out whether certain codes and standards are still applicable. Modifications should be regarded as advancement in science and technology. This symposium was organized following the spirit of ICF (International Congress of Fracture) that was founded in 1965 by Professor Takeo Yokobori. He had the vision to foster research in fracture mechanics, a discipline that has since been developed into a technology to guard against premature and unexpected failure. It is only appropriate that he should lead the fracture mechanics community into the 21st century by delivering a key-note lecture on "Fracture Mechanics in Retrospect" to which he graciously accepted the invitation. Professor Alberto Carpinteri the Chairman of ICF 11 has also agreed to attend this symposium in an effort to further enhance the fracture mechanics activities at the international level. Their absence from this symposium was largely due to the SARS episode less than a couple of month ago that made them to change their commitments. The organizers of FM 2003 wish to offer their sincere apologies to the participants. They also wish to express their gratitude to those key-note speakers who had the faith to keep their commitments.

When science and technology reach a new horizon, new challenges in research must be met. Devices have shrunk in size to nano-scales while structures are being thought to enclose an entire city to ensure a clean habitat owing to worsening of the environment. There are definite needs to up-date codes and standards of yesteryears and to provide new ones, particularly in areas where operating temperatures have been elevated to increase efficiency and faster time of operation is the norm for miniature size machine rather than the exception. The process of globalization is exerting relentless pressure on the

undeveloped countries to leapfrog to the frontier of research and development. This transition is being experienced before a well defined mission could be found for the developed as well as the under-developed countries. In the meantime, diversified opinions will prevail. This can be evidenced from the variety of subjects covered by the technical papers in the proceedings. The topics range from processing techniques, weldments, corrossions, life assessments and material characterization methods to those on the cutting edge of research such as aging of polymers, laser beam welding, high temperature effects, failure behavior of multifunction materials, etc. One obvious trend is that all disciplines such as physics, chemistry, mechanics, engineering and others seem to converge. More than ever, timely dissemination of scientific and technological information becomes critical. This is a process that the organizing institutions are committed to continue on a yearly basis. They include the East China University of Science and Technology in Shanghai, Nanjing University of Technology in Nanjing, Zhejiang University and Zhejiang University of Technology in Hangzhou, and General Machinery Research Institute in Hefei. Special efforts were made to include scientists and engineers from Europe and North America such that the latest findings from abroad would be made available at FM 2003.

Editorial changes have been made in some of the papers with the objective of enhancing the readability and avoiding possible misinterpretations. Sincere apologies are due to those situations where the changes may have caused misrepresentations.

The editors and local organizers wish to take this opportunity to express their gratitude to the representatives of the organizing institutions. Their collaborative efforts and ideas have contributed to the success of this conference. Even more important is their continuing support and participation in the future. This conference could not have made possible without the leadership and encouragement of Prof. P. N. Li. His technical knowledge in the field of pipeline and pressure vessels is invaluable to those in academic research and industrial application. Thanks are also due to those who assisted in typing manuscripts, operating projectors, taking care of local transportation and numerous tasks behind the scene that are often overlooked by the organizers. Last but not the least, acknowledgements are due to Ren Huifang and Liang Lining for making the ladies feel at home while their husbands attended the technical sessions.

Shanghai, China
August, 2003

G. C. Sih
S. T. Tu
Z. D. Wang

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Why, where and when it becomes necessary to consider chemical reaction effect in mechanics

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Abstract

As more and more use specific materials are being made by combining different microscopic constituents, new ways of failure unknown previously are being discovered. This is not unexpected because the size and time scales have been altered from large to very small and from slow to very fast (or very slow). One area of particular concern has been the long term effect of aging of strategic materials such as solid rocket propellants or the alike and short term effects of detonation or combustion. The effects of chemical reactions have been clearly identified to affect the macroscopic behavior of materials while the geometry and size of macrospecimens could alter the end results of chemical decomposition by significant amounts. Although microchemistry and macromechanics have been regarded as separate subjects, their similarities and dissimilarities should be made aware with the hope that they would merge into a third discipline referred to as Chemechanics.

Mathematical formulation and the underlying physics should overlap at the microscopic and macroscopic scale. The activation energy for assessing the rate of chemical reactions for instance should have a counterpart at the macroscopic scale and the same should hold for macrostress and macrostrain. This calls for a reconciliation of the continuum and discrete view for modeling matter. Modeling of continuum models should always entail a defect such as a crack in order to distinguish local and global considerations. For a macrospecimen (centimeters), the global (macroscopic) and local (microscopic) effects could therefore be reflected. A consistent model should also be constructed for the microspecimen (microns) where the microscopic effects would be global while the atomic scale effects now become local. The same applies to the atomic and subatomic scale. To this end, the concept of electronic imperfections may be introduced to involve phonons that produce atomic displacements similar to dislocations. Except that phonon is associated with quanta of thermal energy absorbed or emitted by a crystal. The energy of a phonon is much smaller than an electron and it may be regarded as the unavailable (or dissipated) energy in a process of particle collision that produce resistance to conductivity. This is analogous to plastic flow holding back the fracture process as phonons retard conductivity.

It is apparent that energy would be the preferred quantity to use over that of stress or strain. Recognition of size scale would further require reference be made to a unit area and/or unit volume of matter. The transient character of particle interactions could not avoid the time variable. On fundamental grounds, the power density function should be adopted for describing the evolution of energy redistribution in matter as manifested by the transient-like character of photons, dislocations and cracks. It appears that dual scale models could be advanced to include energy used in particle interaction and hence chemical reaction. The objective would be to focus attention on developing physical models that could accommodate the inclusion of chemical effects known to degrade the mechanical properties of materials.

Keywords: chemical reactions; mechanics; microscopic; macroscopic; global and local; electrons; phonons.

1. Introduction

The present day understanding of material properties rests on classifying the different arrangement of atoms with a repetitious pattern. Groups are formed owing to the bonding forces. They may contain hundreds or several thousands atoms. The bonding forces could be strong or weak. They are referred to, respectively, as the inter-atomic and van der Waal forces. These dif-

ferent groups and their corresponding constituents would interact depending on their numbers within a unit volume, the temperature and pressure, similar to the macroscopic material behavior where reference is made to specimen geometry, environment temperature and applied loading or stress. Quantitative assessment of their behavior in terms of force and displacement would invariably lead to the concept of energy. Again, the macroscopic counterparts would be stress and strain while energy or force makes no reference to size scale unless it is specified in terms of a unit volume. This makes the energy density func-

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tion sensitive to change in size scale, barring the effect of time that would be discussed in the work to follow [1-3].

Because of the variety of interactions that could result for the different arrangement of atoms under different conditions, names and classifications are assigned to distinguish the separate disciplines. For many engineering problems, only a knowledge of the macroscopic material behavior would suffice. There is no need to consider the events at the microscopic level, even less at the atomic level. Corrosion reaction, however, is probably the most significant chemical reaction connected with behavioral change of engineering materials. It entails the deterioration and loss of materials due to chemical reactions that could initiate from mechanical and/or electrical inhomogeneities at the atomic level. The separation of a metallic ion from the metal proper could cause the removal of valence electrons from the outer shell of atom.

Strong solvents could lead to chemical reactions when they come into contact with material such as salt and metal. Even water could affect the mechanical strength of metals, particularly when defects are present on the surface. The fatigue life of wet aluminum sheet could be decreased by an order of magnitude when compared to that in a dry environment. These effects were not known until the 1950s when aluminum sheets were used in large quantities to build jumbo jet transports. It is therefore important to identify the underlying mechanisms. The creation of a potential between electrodes or electrolytes could trigger the process of current flow. This could arise from dirt accumulated on a metal surface, moisture trapped in crevices, stress gradients along grain boundaries, defective surface coating, dissimilar material interfaces and a multitude of similar situations where imperfections tend to promote the establishment of an anode that produces electrons and a cathode that consumes electrons. The slight difference between the properties of two neighboring grains may be sufficient to create an anode at the grain boundaries where the atoms have a higher potential. The grain boundary region could be considered to be strained since the atoms are not at their positions of minimum energy. The neighboring grains serve as the cathode. A fine-grained metal with more anode area would therefore tend to corrode faster

than a coarse-grained metal.

On a more refined scale, the situation that creates corrosion is somewhat paradoxical. While localized oxidation accentuates corrosion but it occurs at locations where oxygen concentration is lower. A surface scratch or crack restricts the access of oxygen; this promotes still greater accumulation of oxygen or electrons to be removed from the nearby surface serving as the cathode. It so happens the oxygen-deficient areas are actually the loci of corrosion. They correspond to cracks, crevices and scratches serving as the anode. It has also been apparent that unless the cause of corrosion at the microscopic scale is quantified in terms of parameters that could be related to those at the macroscopic scale, corrosion prevention would remain as a technology based on empirical means.

This work makes an effort to point out the areas where chemical reactions may have a dominant influence on the macroscopic behavior of solids, particularly when the temperature, time and size scales are outside the normal range of operation. A good example would be the chemical reaction kinetics and physical processes related to the thermal decomposition of solid rocket propellant and explosive ingredients such as RDX and HMX [4,5]. Understanding of the reaction mechanisms and reaction kinetics of these materials has been limited to lower temperatures and on longer time scales in comparison with those of combustion. For conditions ranging from normal storage to combustion, the time scale could range from years (10^9 sec) for aging to 10^{-9} sec for detonations. To identify the intermediate products, small size measurement of the gas phase reaction requires accuracy of the order of $100\mu\text{m}$ and smaller. Only in recent times that realistic chemical reaction experiments have been made at the Sandia National Laboratories after sampling the data of more than 500 tests. Thermal decomposition of RDX and HMX has been shown to be sample size, pressure and time dependent, a situation that is well known in mechanics. Loading and specimen size effects are being addressed in chemistry and more surprisingly in terms of surface area to volume ratio [6]. It is not surprising that different and often conflicting results have been reported in the past. The interaction of size and time effects must be observed when analyzing processes where both microscopic and mac-

roscopic quantities come into play. The interest here lies in translating the knowledge gained in the decomposition RDX and HMX into the mechanics formulation. This would bring chemistry directly into the design of solid fuel rockets. It would aid to identifying potential problems related to the aging and detonation of solid propellants.

Deficiencies in the development of the continuum mechanics theories are also responsible for holding back the progress in connecting chemistry with mechanics. They are inherently limited to equilibrium processes. It is implicit in classical mechanics that all events are homogenized and addressed only in an average sense, statistically or otherwise. That is for each time step a period is required for the system to reach equilibrium before proceeding to the next step although this requirement is seldom observed in tests or numerical calculations. One immediate example is the bonding of two similar or dissimilar materials where the traditional approach is not able to account for the energy transfer across the interface. That is the interaction of the surface with volume. Stated more precisely is that the length parameter dV/dA has been assumed to vanish. This parameter represents the rate change of volume with surface and is equivalent to the mean free path of the atoms. It essentially deprives mechanics from determining two phase systems.

For nonequilibrium systems, the local material behavior changes with time and the size of the local region under consideration. In an open thermodynamic system, the surface energy density $(dW/dA)_j$ ($j=x,y,z$) is related to $(dV/dA)_j$ via the volume energy density function dW/dV , a scalar. To reiterate, dV/dA no longer vanishes and hence dW/dA and dW/dV becomes dependent. This is in fact the Gibb's law of homogeneous crystal nucleation that determines the size of a crystal grain from the rate of exchange of the surface and volume energy density. No wonder the state of affairs at the interface between the propellant and rocket casing (at the liner) remain a mystery to the rocket designer. Unexpected explosion can still occur for no obvious reason. The plausible explanation is that the stored energy density in a solid propellant, say dW/dV in the bulk increase with time up to the point of detonation or even beyond. The quantities $(dV/dA)_j$ in all directions rise even more rapidly with time, espe-

cially at combustion when the solid changes to gas. At this instance, dV/dA can increase 100 to 1000 times and more. What this does is to convert all of the stored energy into surface energy. That is trapping the energy at the interface of the propellant and its surrounding. This can lead to an explosion globally because the mechanical integrity of the interface was not designed to account for such a condition. What has been emphasized is the nonequilibrium character of phase transformation where solids change to gases. This is manifested by the quick release of energy within a small time interval causing an explosion. Here, the chemical reactions at the microscopic scale can directly influence the macroscopic material behavior. On the other hand, corrosion mentioned earlier or material aging involve long term chemical reactions also can severe the material's ability to carry load and they can be equally damaging.

Microscopic and macroscopic material damage models have traditionally been treated separately with the understanding that they would somehow be connected in time. Such a preconceived notion has no fundamental bearings and may have hindered progress in this field. The desire is to identify the situations where microscopic entities bear a direct influence on the macroscopic material behavior with due considerations given to the size, time and temperature^[7,8]. Their coupling effects may pave the way to interlace chemistry and mechanics. Hence, the acronym Chemechanics has been dubbed to describe those situations where the time, size and temperature are such that the disciplines of chemistry and mechanics must be linked together for quantifying the physical phenomenon. Furthermore, the discussion would be confined to the damage of metallic or polymeric materials under special conditions. Even within these limitations, their common ground will be microscopic in scale. Therefore, mechanics that was developed without consideration given to size effects must be refined to cover at least the effects of two scales, say the micro and macro.

2. Microchemistry and macromechanics

Chemistry begins with a study of the basic elements and their atomic weights while mechanics delves into the motion of particles or rigid bodies. Technological development in mate-

rial science has benefited by using both disciplines whenever possible although their direct connection is by no means obvious. Effective use of them could perhaps be further enhanced by adopting the same fundamental quantities that could describe chemical reactions and stress and strain behaviors, if this is possible without being entangled in semantics. At the very start, the distinction of micro and macro scale has not followed any strict rules. What can be seen by the unaided eye without the help of a microscope is normally referred to as the macroscopic scale. This may involve only a factor of ten where microscopic scale may be inferred. Taking the premise that materials are made of atoms bonded together in different arrangements, the breaking of these bonds would lead to fracture. Since the definition for an atom itself is a vague concept, it does not have a definite size, say radius. However, to quantify events, it is useful to speak of an atomic radius, the size of which can be used as a reference to distinguish its behavior from that of the ion and molecule. The different behaviors of ionic and covalent bonds follow in addition to the van der Waal forces. Metals are made of well arranged atomic structure and they fracture by breaking the covalent or primary bonds in contrast to many polymers that may fail by breaking the relatively weak van der Waals bonds or the secondary bonds. The situation in general is very complex because there are different shades of primary and secondary bonds while the bond strength may be affected by the thermodynamic conditions. Nevertheless, it is not difficult to agree that the energy required to break the bonds would not be meaningful unless it is qualified with the number of bonds broken, say in a unit volume. That is the energy density, dW/dV .

2.1. Consideration of defects and chemistry

The fabrication of metal alloys starts with different chemical compositions processed under different conditions until the desired macroscopic material behavior is achieved by performing uniaxial tests. Chemical properties and their differences between elements are decided by the number of valence electrons. Moreover, all chemical reactions involve the formation and the disruption of bonds. Fig. 1 shows the relative size of an atom, ion and molecule. The ion is smaller since electrons have been removed from the atom. The

molecular bond length is of course larger as it may consist many atoms. The basic structure applies to polymeric materials except that they have a chain-like structure. These chains are aligned parallel or cross-linked. Ideally, the structure would consist of a perfectly periodic array of atoms whose arrangement conforms to certain geometric symmetry that could be described mathematically by space groups. Deviations from a periodic arrangement, however, are found to be inherent in all materials, metals or polymers. The ideal theoretical strength in contrast to the actual strength differs by several orders of magnitudes. The latter would include the effects of line defects involving edge and screw dislocations or of plane defects that involve misalignment of grain boundaries or stacking faults. The discrepancy between the idealized and measured data for strength has been the subject of investigations for many decades and is still not completely understood. Large scale computational models using molecular dynamics schemes have further expanded the horizon of research to three dimensions. Ledges in dislocation loops produce results that have no resemblance to those in two dimensions. In order to bring chemistry into the mechanics of crystal lattices and molecular groups, it is believed that the emphases should be placed on the interaction of defects with chemical reactions rather than complicating the geometry of the physical model based on unrealistic assumptions. It is not unrealistic to assume that chemical reactions might not be one hundred percent complete because of the presence of atomic and molecular defects. That is not all of energy will be available to complete a particular reaction.

In principle, the energy associated with the formation and disruption of bonds in a chemical reaction can be calculated. It is another matter in practice whether the interatomic force model could predict macroscopic material behavior. Two body interatomic force potential such as that of Lennard-Jones could formally give an estimate for the Young's modulus E assuming that the size^[9] and time scale factors going from micro to macro scale can be ignored. The relation $\sigma_{\text{theo}} = E/10$ in the text books would presumably give an estimate of the atomic bond strength which is contained in the derivation of E and assumed to be equivalent to the uniaxial tensile strength σ_{theo} for the macrospecimen. Obviously, the matter is

not that simple. Even for a body centered cubic lattice, a realistic representation of the interatomic force potential should involve the interaction of nine atoms^[10,11]. The physical mechanisms associated with bond breaking and fracture of a macrospecimen may differ fundamentally from those associated with breaking atomic or molecular bonds. Microstrength and macrostrength are obviously not the same. The critical applied stress that breaks a uniaxial specimen has been known to depend on the volume to surface ratio of the specimen. The Weibull statistical approach^[12] has been used to correlate data for specimens of different sizes by assuming that the probability would depend only on the ratio of the initial to the deformed volume. Inclusion of the corresponding surface area ratio is also essential for ductile fracture^[13] in addition to the inclusion of defects in a unit volume of material.

The so called size effect is not limited to the geometrical proportion of lineal dimensions. It is more complex since energy dissipation comes into play. Past works related to the fracture of polymethyl-methacrylate (PMMA)^[14] and cross-linked rubbers^[15] have shown that the energy required to cause crack growth is greater than twice the surface free-energy or $2\gamma = 0.07 \text{ J/m}^2$ which reflects only the rupture of the secondary bonds. That is to overcome only the van der Waal forces. Fracture of PMMA and rupture of cross-linked rubber requires the breaking of covalent bonds which are much stronger. The critical energy per unit area were measure to be 0.5 J/m^2 for PMMA^[14] and 40 J/m^2 for rubber^[15]. They are several orders of magnitude greater than 2γ . The energy dissipated in a macrospecimen can involve viscoplastic and/or plastic energy dissipative processes that are away from the path of crack growth. Refer to the definition of ASTM fracture toughness^[16]. Recent works on the aging and yielding behavior of polycarbonate^[17] have also illustrated the need to consider the portion of the total energy that is not available to drive the crack. It was referred to as the non-essential work in contrast to the essential work for driving the crack.

2.2. Size and time dependency of disruption in atomic packings

Prior to considering the chemistry of bond breaking, there is the need to know the mode of

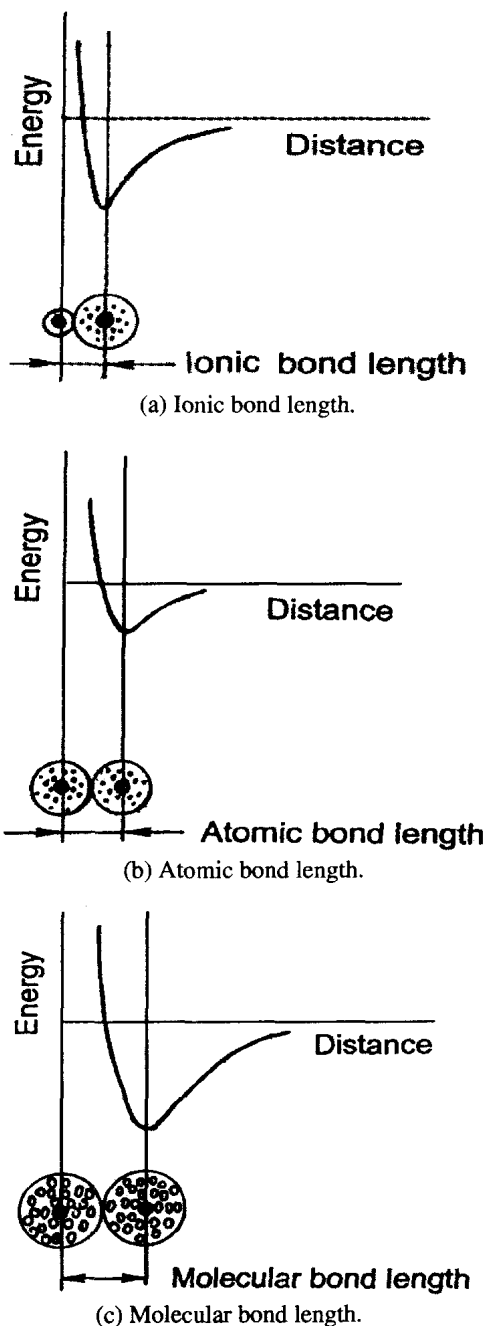


Fig. 1. Bond length for atoms and molecules.

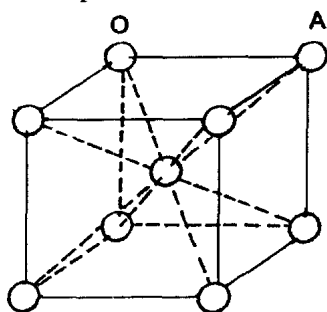
disruption of atomic packings. The conditions that would favor the breaking of a single bond between two atoms in contrast to the separation of two clusters of atoms or molecules should be determined, not by empirical means which should be used only as a check. Analytical models could be constructed according to the rate of energy density per unit area and unit volume distributed over a region that consists of array of atoms or mole-

cules. The time dependent stationary values of the energy densities would provide information on the size of the local regions and time at which failure is likely to occur according to the critical values of the energy densities. Single bond model would suffice if the critical region size corresponds to the distance between two atoms. Larger distance may favor the breaking of molecular bonds. Fig. 2(a) shows a single body-centered-cubic (BCC) cell while Fig. 2(b) shows an array of BCC cells. The bond strength between any pair of atoms OA may be calculated.

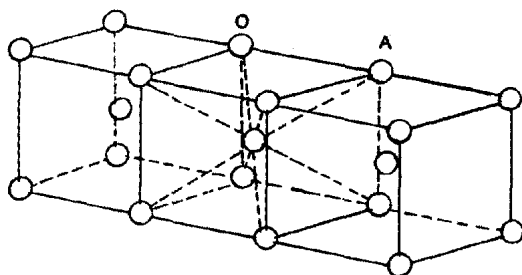
The structure of molecule chains may also be taken as an example. Take a single SiO_4 tetrahedron as shown in Fig. 3(a) that belongs to a chain. The side and top of the chain in Fig. 3(b) receive electrons from adjacent positive ions. In ceramics, the adjacent chains are commonly held together by ionic bonds in Fig. 4(a) between chains. The ionic bonds are not as strong as the covalent Si-O bonds within the chain. Detachment is therefore expected to occur parallel to the chain. Fig. 4(b) shows the Si-O structure used to estimate the number of ionic bonds. The distance between silicons is approximately three Angstrom units or 3\AA where one \AA is equal to 10^{-8} cm or 10^{-4} microns . The angle is about 120° and hence the distance x equals to $(\sqrt{3}/2)(3\text{\AA}) = 2.6\text{\AA}$. There are two ionic bonds per silicon as a result of the two

unsatisfied oxygen with each silicone. The number of bonds per micron is estimated to be 2 bonds divided by $2.6\text{\AA} = 7700$. The energy required to break these bonds can thus be calculated for a unit area and unit volume. The line model can be extended to a plane. Hence, sheet structures of silicon and oxygen could be constructed and held together by secondary bonds. Foreign chemical elements to alter the interface bond structure could also be assessed quantitatively in terms of surface energy density and volume energy density. In this way, provision can be made in a mechanical model for corrosion cracking where the influence of chemistry could be related directly to the degradation of not only the mechanical properties but also of loading and geometry.

The interplay of surface and volume energy densities via the rate change of volume with surface has been used in the isoenergy density theory^[1,2] for solving non-equilibrium thermomechanics problems where phase transformations take place.

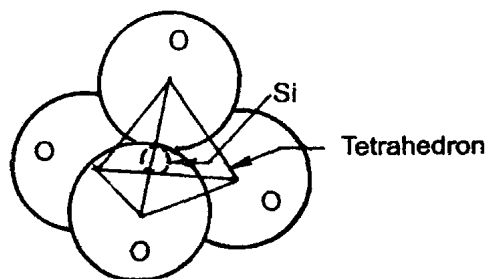


(a) Body center cube (BCC).

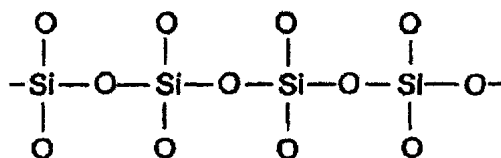


(b) Array of BCC cells.

Fig. 2. Single and multiple cell(s) for BCC.

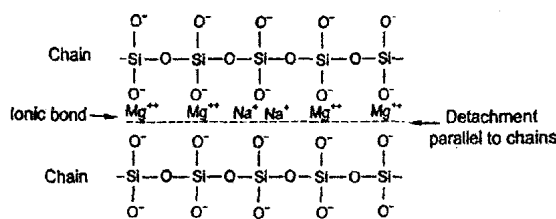


(a) Tetrahedron structure.



(b) Single chain of SiO_4 .

Fig. 3. SiO_4 structure.



(a) Weaker ionic bonds.

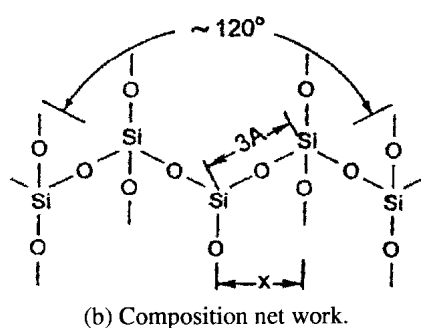


Fig. 4. Molecular chains and ionic bonding.

2.3. Chemical reaction kinetics and overload behavior

Chemical equilibrium refers to a macroscopic portion of material whose composition remains unchanged with time under specified conditions of pressure and temperature. That is opposing chemical reactions take place at equal rates as in the case of equal and opposite forces applied to a uniaxial specimen. Keep in mind that chemical equilibrium does not imply thermodynamic equilibrium. Differences in chemical potential can cause matter to flow from one region to another in the same way as pressure and/or temperature. At certain threshold controlled by the chemical rate kinetics, bond breaking could occur. Accumulated bond breakage could lead to macrofracture of the body.

The term “activation energy” applies to the energetics of the process. It refers to the energy that must be acquired by an atom or molecular system to enable a particular process to occur. Similar to the necessity of an overload for distinguishing the metastable stress-strain state in contrast to that in the region of failure, this can be illustrated by the energy released by a falling ball that sits in a bowl at A in Fig. 5. The ball is in a metastable state as it will return to its equilibrium position if it is disturbed only slightly without getting over the edge. The energy released in the reaction is from A to B. A greater energy, however, must be supplied from the external source to move the ball over the edge. This additional amount is the activation energy. By analogy, the presence of an alloying element requires a greater supply of energy to nucleate before the transformation would take place.

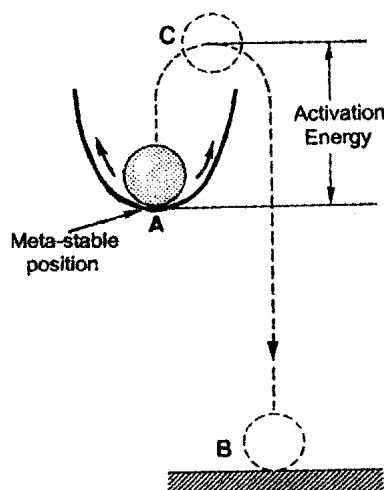


Fig. 5. Analogy for activation energy.

Suppose that a cracked specimen is subjected to a slowly rising tensile stress up to the critical state and then kept constant thereafter by following the path OABD. If this process were monitored on the stress and strain diagram in Fig. 6, it is necessary to have a failure curve. The loci of this curve would represent the critical states of stress and strain^[18]. They are the metastable states. An overload in stress and strain would be required to push the point A on the curve into the failure region at C. Once in C, the stress could reduce to that at A and kept constant thereafter while failure continues. The additional energy is the small triangle ABC which is equivalent to the activation energy in Fig. 5. The area of ABC depends on the specimen size, material and loading rate. The same applies to the activation energy for a chemical system at the atomic or molecular scale. It could represent the moving of a lattice defect to a neighboring site or annealing in crystalline materials.

The normalization factor associated with the activation energy U is the thermal energy kT of the electrons in a solid, gas or plasma. Since the electrons are not in equilibrium with the surroundings and only approximately with themselves, the process is kinetic in character. Note that k is the Boltzmann's constant and T is the absolute temperature in degree Kelvin or K. A rate equation of the form

$$\phi = \phi_0 e^{-\frac{U}{kT}} \quad (1)$$