Nature and Properties of Materials Professor Bishak Bhattacharya Department of Mechanical Engineering Indian Institute of Technology Kanpur Lecture 35 Thermal properties

In the last lecture, I have talked about it are properties and particularly we have shown it for an optical fibre how this is manifested. Now our focus is on the thermal properties of mechanical system because even more than optical property, thermal property is very-very important for any mechanical system as there is always relative velocity in the mechanical system and that means there will be fiction and that means there will be heat that will be generated in the system.

(Refer Slide Time: 01:23)



Not only that, in order to drive a mechanical system also you need to many a times go for systems like internal combustion engine, so hence there will be some heat which will be generated and the heat is the temperature is to be kept within a particular level in order to safeguard many of your systems and hence thermal properties become important. So in this particular lecture, we will go through the heat capacity, the thermal expansion, conductivity, thermal stress and thermal shock, the things which most commonly occurs in most of the materials for engineering applications.

(Refer Slide Time: 01:38)



Now, over all thermal properties describe the response of a material to the application of heat. As a solid absorbs energy in the form of heat, its temperature rises and its dimensions change. The important thermal properties related to these are the heat capacity, the amount of heat that it is able to absorb per unit volume, thermal expansion and thermal conductivity.

(Refer Slide Time: 02:15)

| Represents the amount of energy required to | produce a unit temperature |
|--|--|
| rise. | produce a diffe temperature |
| ✓ Indicative of a material's ability to absorb heat | t from the external surrounding |
| ✓ Mathematically, | |
| Energy Change (gain or loss) | dQ |
| $C = \frac{1}{\text{Resulting temperature change}}$ | $= \frac{dT}{dT}$ Unit : Joule/mole-Kelvin |
| Specific heat (c): Heat capacity per unit mass. | |
| Unit : Joule/kg-K | |
| ✓ Two ways to measure heat capacity: | |
| C _p : Heat capacity at constant pressure. | |
| C _v : Heat capacity at constant volume. | |
| \checkmark C _p > C _v , as more heat to be supplied for unit de | egree rise in temperature while |
| the system expands. | |
| • | |
| Sinari Materiala Structures and Syste Laboratory | enai |
| C 8 | |

So, heat capacity represents the amount of energy required to produce a unit temperature rise. Now, this is indicative of a material's ability to absorb heat from external surroundings because from the same unit temperature increase, if you can absorb more energy that means you have a higher heat capacity and that is sometimes good because you can actually in a small change of temperature by changing this or creating a small change of temperature, you can actually absorb much more energy inside the system.

So mathematically, this heat capacity C is defined as energy change that is gain or loss that is dQ over the resulting temperature change dT okay, so it unit is joule per mole Kelvin. Now, along with this there is a specific heat which is heat capacity per unit mass and its unit is joule per KG Kelvin. There are 2 ways to measure the heat capacity, one is the heat capacity at constant pressure C p and another is heat capacity at constant volume C v. C p is greater than C v as more heat to be supplied for unit degree rise in temperature while the system expands. So these are some of the basic things that are required in relation to the heat capacity of a system.

(Refer Slide Time: 04:10)



Now, how the heat capacity changes with respect to temperature? 1st point is that it increases with temperature and for solid however, it reaches a limiting value of 3R, where R is the gas constant 8.31 joule per mole K. Now, the way it behaves is that as the temperature is gradually increased, there will be actually the atomic vibrations that will take place. Now with respect to the increase of temperature, the average energy of atomic vibration will increase.

However, atoms are restricted in a particular region, so hence there is a maximum level because of up to which it can actually exhibit this energy increase because beyond that the bond of strain would not allow it to go here and there and as a result what you will see is that initially there is a sharp jump because the atoms are getting excited more and more, but as you are reaching the 3R value, there is a maximum that is permitted so it is coming down to a saturation, so that is how this particular thing happens in the case of any material.

And there is a temperature which is called the Debye temperature and which is usually less than the room temperature in which you will see that this saturation is happening to the system and various materials will show various Debye temperature. Now if I compare various materials with respect to the specific heat that is heat capacity per unit mass, then we have 3 groups of materials; polymers, ceramics and metals.

(Refer Slide Time: 06:27)



What you will be very interesting is that polymers have much higher heat capacity, polypropylene, polyethylene, polystyrene, Teflon; they have much higher heat capacity. Next are the ceramics and below that are actually the metals. Among the metals of course some metals have higher heat capacity than the others. One important point is that there are covalent bonds in polymers that do not let the atoms to exchange electronic like the metallic bonds because metals have free electrons and hence it can exchange the electron, so this also increases the temperature at a faster rate.

And as heat capacity actually is inversely proportional to the increase of temperature, so the less there will be change of temperature the better it is from the heat capacity point of view. I think you remember that C is dQ dT right, so for metals because of the presence of free electrons, this dT is going to be more as a result, their heat capacity is less in comparison to the polymers.

(Refer Slide Time: 07:50)



Now, there is a way in which we actual describe this entire phenomena in solids. Atoms in solid materials are constantly vibrating at a very high frequency and with relatively small amplitudes. These vibrations are coordinated in such a way that lattice waves are produced which propagate through the crystal at the velocity of sound because this is I am not on like your photons or not like your electron magnetic waves, this is actually longitudinally wave, so it moves at the velocity of sound. A single quantum of vibrational energy is called a Phonon here, which is analogous to the quantum of electromagnetic radiation which is Photon.

Now, these elastic waves also participate in the transport of energy during the thermal conduction. So here we have shown that there is a lattice wave that is generating in a crystal and then you can see that the Phonons are actually getting displaced and thus with respect to this direction, you can see that the yellow lines are the normal lattice position and blue line are positioned due to the vibration, so there is this continuous this change that is happening and that wave is passing through the system.

(Refer Slide Time: 09:27)



Now there are some important thermal properties which also can be explained from the point of view of atomic bonding, the most important of them being the melting temperature T m. Now, if you remember the curves that we have drawn earlier for the bond energy, we have shown that there exists a particular position in the bond energy, where the energy is the minimum and hence the bond becomes very-very stable. Now what happens is that, those materials which has actually larger melting point, you will see invariably that they have modulus of elasticity which is also large.

And modulus of elasticity if you remember actual talks about inter atomic bonding, so that bonding force is actually much more okay in the in the materials which has actually larger melting point. Or in other words, if the bonding force is more than you need more energy to generate the force and hence T m is larger for this type of a system. So for a typical energy curve for a material with larger T m will show actually more drop in the system in comparison to the material with the smaller T m.

(Refer Slide Time: 11:07)



Now from the bonding point of view, the elastic property is very important and you can also see it in this way that suppose you have considered a particular strip which is un-deformed of length L 0 okay and cross-sectional area is A 0. Now, you are applying force F and then it is deformed and then there is a change of length, which is Delta L. So, what is the stress that is generated in the system, that is F over A 0 and how it is related to the strength that is E that is generalised, there is the Hooke's law E times change of length over the original length, which is nothing but the Epsilon, so Sigma equals to E Epsilon, E is thus similar to a spring constant.

And then if you look at that E is the curvature at r 0 then you can say that those materials which are having the larger elastic modulus at r 0, they have a sharp curve the curvature is higher. So modulus of elasticity is actually larger if the curvature is larger. On the other hand, modulus of elasticity is smaller if the curvature is small as is shown in this particular case. So thus from the curvature point of view also by looking at the bond energy, you may say that between the 2 material which one is possessing higher modulus of elasticity.

(Refer Slide Time: 13:08)



Next we talk about thermal expansion and as w that temperature of solid is also measure of its potential energy in some sense. Now most solid materials expand upon heating and contract on cooling. There are exceptions we have seen for example, shape memory alloy which actually upon heating will show sharp contraction due to the phase shift. But normally, solid materials will expand upon heating and contract on cooling. Heating to successively high-temperature raises the vibrational energy thus, as the vibrational energy increases the inter atomic separation increases, so from r 0 you are going gradually to r 1, r 2, r 3, r 4, r 5 up to a particular distance.

So the greater the atomic bonding energy the deeper and narrower this potential energy trough will be. And thus, the increase in inter-atomic separation with a given rise in temperature will be actually lower because we already told you that in comparison to thing with smaller bond energy, these are actual sharper here as you can see in comparison to the one with smaller bond energy. So since it is sharper, so the increase in interatomic separation with a given rise in temperature will be lower in this particular case.

(Refer Slide Time: 15:14)

| $\left(\frac{t_f - t_i}{t_i}\right) = \alpha_l (T_f - T_i)$ | - | ℓ initial |
|---|--|---|
| or $\frac{\Delta l}{l_i} = \alpha_l \Delta T$ where, l_i a temperatu $\alpha_i = \frac{\sqrt[4]{l}}{\Delta J}$ where, l_i a temperatu | nd l_f are initial an re increases from in coefficient of them | ℓ_{final} d final length after iitial T_i to final T_f , mal expansion (°C ⁻¹) |
| | A REAL PROPERTY AND A REAL | W. Maluse manage (90-1) |
| and the second | Material | al values range (C) |
| | Material Metals | 5 - 25 x 10 ⁻⁶ |
| | Material Metals Ceramics | 5 - 25 x 10 ⁻⁶ 0.5 - 15 x 10 ⁻⁶ |

So as a result, the thermal expansion coefficient will be actually lower. If we try to see that in terms of the thermal expansion coefficient definition first, which says that the relationship between change of length over original length and the change of temperature, so essentially Alpha you can write it as Alpha is Delta L over L over Delta T. So L i and L f are the initial and final length after temperature increases from initial T i to final T f and Alpha is the linear coefficient of thermal expansion.

Following this definition, metals have thermal expansion coefficient, which is like 5 to 25 into 10 to the power minus 6 per degrees centigrade. Ceramics 0.5 to 15 lower than the metal and polymers it is very-very high 50 to 400, significantly higher than the metals. And you can see it here that with respect to a unit change of temperature you would actually see in polymers more change in length in comparison to the metals and that is because the polymers offer because of their less bond energy they are actually offering much more change.

(Refer Slide Time: 16:41)



Now, the heating and cooling affects not only in one dimension but it affects all the 3 dimensions hence the volume change as well. So, similar to Alpha in one direction you can also define Alpha v, which is like Delta V over V 0, so Alpha v is Delta V over V over Delta T. So Alpha v in general for isotropic thermal expansion it is about 3 times of Alpha 1. But some cases some materials Alpha v is anisotropic that means the material expands at a different rate in different directions.

For example, crystallographic direction or for example if you consider a fibre reinforced composite, then along the direction of the fibre it has one coefficient and across the direction, so in these 2 directions it has 2 different thermal expansion coefficients, so these are anisotropic cases. Otherwise, for isotropic cases Alpha v is approximately 3 times the Alpha L.

(Refer Slide Time: 17:58)



Again, we can explain the thermal expansion coefficient from the properties of bonding. As, we have earlier shown you that the same expansion of the unheated and the heated beam if you consider and suppose the change in length is Delta L okay. So for the same change in temperature what you will see is that in some material this Delta L will be much more. And Alpha is actually your Delta L over L 0 over Delta T, so if Delta L over L 0 increases more in comparison to Delta T then you are going to get a higher value of Alpha.

So Alpha is larger if E 0 is smaller and many are symmetric, why because for a softer material for the same change in temperature you may see that it allows more change in interatomic distance because the bond energy is less in comparison to the other material, so as a result Alpha A is larger if E is smaller because for this material E is smaller, so E is smaller and in comparison to this particular material, so in this case E is higher. Higher the E, narrower will be this curve and smaller will be Alpha. Lower the E, larger will be this curve and higher will be the value of the Alpha that is the point we have to keep in our mind.

(Refer Slide Time: 20:02)



Next if I compare the thermal expansion coefficient, we will see that this is indeed getting reflected. You get a large thermal expansion coefficient for all the polymers, metals it come down, ceramics it also comes down further. Now polymers have larger Alpha L values because of the weak secondary bonds, it allows it to move farther. In fact, linear and branched polymers expand more because the secondary intermolecular bonds are very weak and there is minimum cross-linking. Lower coefficients are found in thermosetting network polymers in which the bonding is almost entirely covalent. Now in comparison to the polymers, bond energy is much higher in metals and ceramics and as a result, Alpha L is much-much longer these cases.

(Refer Slide Time: 20:59)



Next is the thermal conductivity. Thermal conduction is the phenomenon by which heat is transported from high to low temperature regions of a substance. And there is a particular law which is known as Fourier's law that states that for steady-state the heat flux is directly proportional to the temperature gradient, so the relationship is something like this that q over A is minus k dT over dX. And the negative sign here indicates that heat flows in the direction of decreasing temperature, so from high temperature towards the low temperature the heat is flowing, that is the Fourier's law which actually brings this thermal conductivity k into picture for us which is measured in terms of many units are there, but one common is watt per meter Kelvin.

(Refer Slide Time: 22:07)



Now, if you look at it how the heat conduction takes place in materials, then you will see that there are 2 ways in which it happens; one is through the lattice vibration way so to say through the phonons and other one is through the free electrons, so thus the total conductivity is partly due to phonons and partly due to the free electrons. Now metals are extremely good conductor of heat why because it has relatively large number of free electrons, so that takes care of the conduction.

The purest form of metal also will have high conductivity in comparison to the alloys like if you compare iron which has thermal conductivity of 80 in comparison to that steel has 52 only because whenever you are alloying, then you have less availability of free electrons and as a result the heat conduction comes down. The alloy in the alloy, different atoms will have different electron affinity thus the movement of excited electrons becomes hard in this case. And there are some materials where the phonon is more than the free electrons for example,

ceramics materials, the free electrons availability is very-very less because mostly it is electoral in bonding, so there the phonons actually dominate in terms of heat conduction.

(Refer Slide Time: 23:41)

| | I Since free electrons are responsible for both thermal and electrical conduction in pure metals, the two conductivities are related by Wiedemann–Franz law as | | |
|----------|--|--|--|
| | $L = \frac{k}{\sigma T}$ $L = \text{Lorentz Constant (2.45 \times 10^{\circ} \text{ Ohm-Watt/K}^2)}$ $k = \text{Thermal conductivity (W/m-K)}$ $\sigma = \text{electrical conductivity (Ampere/Volt-meter),}$ $T = \text{absolute temperature (K),}$ | | |
| <u>c</u> | <u>eramics</u> | | |
| • | They are thermal insulators as they lack large numbers of free electrons. | | |
| • | Thus, the phonons are primarily responsible for thermal conduction ($k_e < k_i$). | | |
| • | Also, the phonons are not as effective as free electrons in the transport of heat energ due to phonon scattering by lattice imperfections . | | |
| • | The room-temperature thermal conductivities range between approximately 2 - 50 W/m-K. | | |
| • | Amorphous ceramics have lower conductivities than crystalline ceramics as atomi structure is highly disordered and irregular. | | |
| • | Higher porosity also reduces conductivity due to presence of still air (k = 0.02 W/mk in pores. | | |
| 10 | Baranofakiry BT Kanpus | | |

So in the case of pure metals, the 2 conductivities are related by a law which is called Wiedemann-Franz law, where the thermal conductivity and electrical conductivity are related together and this is defined by a Lorentz constant L, where k is our thermal conductivity, Sigma is the electrical conductivity and T is the absolute temperature. Now in ceramics, they are thermal insulators as they lack large number of free electrons okay, so free electron based transfer does not take place, only the phonons are primarily responsible for the thermal conduction?

Also, the phonons are not as effective as free electrons in the transport of heat energy due to the phonon's scattering by the lattice imperfections, so as a result the overall thermal conductivity comes down for the ceramics. The room temperature thermal conductivity is range in ceramics between 2 to 50 watt per meter Kelvin. Now, amorphous ceramics have even lower conductivities in comparison to the crystalline one okay, because crystalline ones a have regular ordered structure, where as amorphous are highly disordered and irregular, so the phonon-phonon excitation is much lower, the damping is more.

Higher porosity also because in ceramics they have high porosity that also reduces the conductivity due to the presence of still air because still air has only a conductivity up to 0.02 watts per meter Kelvin, so that is important part of the ceramics.

(Refer Slide Time: 25:38)



Now in the case of polymers, there are 2 types of heat conduction possible, one is the vibration mode and another is the rotation of the chain molecules. And for the polymers the conductivity is generally of the order of 0.3 watt per meter Kelvin. The magnitude of thermal conductivity in the polymer also it depends on the degree of crystallinity; higher crystalline and ordered structure means effective coordinated vibration and higher thermal conductivity. So those polymers which are highly crystalline like linear polymers or branched polymers, they have higher thermal conductivity in comparison to the amorphous polymeric systems.

(Refer Slide Time: 26:29)



Now let us look at the thermal conductivity summary. Metals, they have thermal conductivity due to free electrons highest, then there comes the ceramics and here the mode of conduction atomic vibrations, and polymers it is the lowest, here it is atomic vibration or rotation of chain molecules either of them creates this thermal conductivity.

(Refer Slide Time: 26:58)



Next we come to thermal stress; thermal stresses are stresses which are induced in a body due to changes in temperature when the deformation is hindered. For example, if you consider the thermal stress due to change of temperature change of T 0 minus T f, then the expression comes like E Alpha Delta T. That means thermal stress is a function of modulus of elasticity, thermal expansion coefficient and the change of temperature. In a constrained body, this will be of compressive nature if it is heated and when you release the heat, then it will become like a tensile stress. This you will see actually comes in many practical cases.

(Refer Slide Time: 27:48)

| fracture of brittle mate | nges in a material are not uniform, that may lead rials like ceramics. It is known as thermal shock. |
|--|--|
| The capacity of a mater shock resistance, TRS. | rial to withstand thermal shock is defined as Therm $TSR \cong \frac{\sigma_{f}k}{E\alpha_{I}}$ |
| Thus for high Thermal shock re A low value of thermal exp A high value of Thermal co | esistance pansion coefficient(α_l) and Elastic modulus (E) is desired. prductivity (k) and fracture strength (σ_f) is desired; |
| | vented by |
| Thermal shock may be prev Reducing cooling or heat Minimizing thermal grad | ting rates. fient across the body. |

The other thing, which happens mostly for ceramic material is actually called thermal shock. In ceramic materials, if the dimensional changes in a material are not uniform then that would lead to fracture of the brittle materials okay. Now, the capacity of the material to withstand the thermal shock is defined as thermal shock resistance, so thermal shock resistance is defined in terms of this particular relationship Sigma f k over E Alpha 1. Thus, for high thermal shock resistance and a low value of thermal expansion coefficient and elastic modulus E is required okay.

So if thermal expansion coefficient is low and E is low, then you will get high thermal shock resistance or a high value of thermal conductivity k and picture strength is desired if you want to increase the thermal shock resistance. So that means, it may be reduced by otherwise reducing cooling or heating rates or minimising the thermal gradient across the body. And it is not a problem in metals because it has sufficient ductility to permit deformation rather than fracture and thermal stress in ceramics and glass are usually removed by annealing heat treatment. So this is where we are coming to an end of this lecture, in the next lecture will talk about numerical problems based on thermal property using Ashby approach, thank you.