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Lecture – 29 Introduction to High Temperature Materials (Contd.)

Welcome to NPTEL, myself Doctor Jayanta Das from Department of Metallurgical and Materials Engineering, IIT, Kharagpur, I will be teaching you Advanced Materials and Processes.

Last couple of classes, we were discussing about the high temperature materials and we have discussed or classified various types of alloys or other materials which can be used or which has been used as high temperature materials.

Now, if you look at some of the steels that we have discussed containing ferritic microstructure like δ-ferrite or let us say the austenite or maybe martensitic steels; all these microstructures are somewhat stable up to at a range of 600 °C. So, the idea has been developed that we may need to explore some new kind of alloys or compounds which can be used at such a high temperature much higher than 650 °C.

In a common metallurgical sense, if you look at any of the phase diagrams, then the intermetallics has the highest melting temperatures which are somewhat like a or may be higher than the pure metals whereas the intermetallics majority of them has a ordered structure at low temperature. So, this ordered structure has some beneficial effect that we will be discussing today.

Let us have a look at some of the very common intermetallics that has been explored for high temperature application.

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So, here I show you the common physical and mechanical properties of some important intermetallics. If you have a look, so far, a large number of these intermetallics are aluminides, these aluminides means that aluminium containing compounds which may has a very low solubility limit or a little wider range somewhat like 2 at. %. Here, this is titanium aluminide and these are nickel aluminide or these are iron aluminide. From the table itself, it is clear that these as a stoichiometric compound.

Now, very interesting feature of titanium aluminides that they have a very low density because the principle elements aluminium and titanium both has very low density, whereas they have a crystal structure which are ordered at room temperature and Young's modulus in the range of 120 GPa to 250 GPa

On the other hand, the thermal expansion coefficient is also important because if we need to explore these aluminides, then we have to see how it really matches with the neighbouring component and without any failure. The tensile yield strength which are also in a quiet good range, but the most important that these intermetallics has a much higher melting temperature, so, it can reach up to 1680 in case of titanium aluminide.

Now, in case of nickel aluminide also, it may have a relatively higher density than titanium aluminide; however, we can have a larger or higher melting temperature. Now interestingly, if we think about iron aluminide, they also have an ordered structured like this D_{03} or B2 compounds, they have the highest tensile yield stress and this is something very much interesting and higher melting temperature. You may find in the table, I have also some of the compound containing silicon; this is called as silicides and you can have a look that the silicides has the highest melting temperatures, here also some nickel containing silicides.

We will come to discussion regarding silicide later on, but let us first try to understand; what we can use out of a intermetallic, they have a metallic bonding because they contain aluminium and along with some other refractory metals or let us say nickel and these aluminides we can also deposit on a surface so that we can use as a coating and the question all time comes why aluminide, why not other type of compound? That is a major purpose aluminium react with oxygen it form alumina.

So, far we have understood that there are 2 very important element that gives us a surface protection, one is chromium another one is aluminium; chromium producers chromia Cr_2O_3 and aluminium produces Al_2O_3 .

Now, chromia has a problem at a temperature at an elevated temperature because it simply vaporises; however, alumina is very stable up to its own melting temperature. So, aluminides could be a good candidate for high temperature materials.

Now, let us talk about each and every aluminide and try to look at what we can learn out of this.

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So, here I show you one table that shows different aluminides, let us say nickel aluminide which has a L12 structure which is a basically a ordered FCC structure and this nickel aluminide use as a precipitate in a superalloy that is very common and a like I have a γ nickel matrix inside there are Ni₃Al and this Ni₃Al helps in this is a γ ' phase, prime is basically, it is a ordered phase L12 type of structure and these Ni3Al has a fracture toughness of around 20.

In case of steel, maybe it is somewhat like 40,50 or even sometimes, it goes to 100. So, they are not like typical ceramic, ceramic has a fracture toughness of 2. So, ceramic is good to use at higher temperature, but at least intermetallics in some way are relatively better because they has a higher toughness values.

Now, let us have a look at some titanium aluminide here, this is the same type like $L1_0$ structure and D0²² structures. These are again a kind of ordered structure and this titanium aluminides has also a toughness which is somewhat in the range of 10 to 20 MPa√m and the interesting point here are the antiphase boundary energies. You must have a known about antiphase boundary because when there is a ordered structure if we simply move one of the top layer or atomic layer means the dislocation when it passes through its gliding plane, it produces 1 vector set which basically means that the ordering sequence of let us say ABAB type of sequence that basically changes and we produces a antiphase, which basically means just the opposite of the phase. That was initially, until another dislocation pass, then the again the initial structure could be recovered. So, after passing a dislocation, it left behind an antiphase and increases the local energy and this is actually the antiphase boundary energy because the antiphase associate some energy with it.

So, let us say I have an atom here. So, these are the two type of atom which is a marked by 1 is basically the field bubble and another one is unfiled. Here, this is another one and if we pass a dislocation through it then they basically just shifted and we have a boundary where we there exist an antiphase another one is phase. So, until and unless we pass another dislocation, the antiphase actually never recovered. So, the antiphase boundary always appear to lie in the range of a stacking fault energy; however, these antiphase boundary energies required to a bit higher. So, they provide a higher strength at the elevated temperature because of the super dislocation that required to pass.

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Now, the iron aluminides are also, one of the very good candidate as I have shown you that they exhibit the highest tensile strength at higher temperature, they also have a higher antiphase boundary energy. On the other hand, these iron aluminides; they have a toughness in the range of something like 10 to 40 which is comparable. Now if you compared with the silicides; the silicides has the lowest toughness value because of that bonding characteristics.

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Now let us see the titanium and aluminium phase diagram. So, here this is aluminium, aluminium has a lower melting temperature of 660 °C and we have basically titanium in the right hand side and at higher temperature titanium has a β phase which is stable at low temperature which is a hexagonal phase actually like somewhat close that α and this is the BCC one. However, Ti₃Al is has a quite high melting temperature in the range of 1460 °C, so, in that range of here.

So, we are taking about this intermetallic and this titanium aluminide. So, they have a quite higher melting temperature and that very low density. So, to improve the properties of aluminide means titanium aluminide, we need to choose proper alloying elements, means further, we can add some other alloying elements to improve its properties. What kind of properties we are talking about? Because, if it is intermetallic, then they are non heat treatable, a non heat treatable means that even though whatever heat treatment procedure which you we can neither change its microstructure nor the properties.

So, the heat treated response can only be achieved when we can have some microstructure which contain Ti₃Al plus β. Such kind of microstructure may improves the properties so, like $α$ -β alloys.

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So, in that case, we need further alloy addition to this intermetallic and people have already discovered this α_2 alloy where 15% aluminium and niobium vanadium and molybdenum can be added. You can see the niobium vanadium and molybdenum, these are all BCC elements and basically stabilizes the β phase in the microstructure. So, instead of Ti₃Al, we take advantage of another solid solution phase which are heat treatable in order to improve the properties of this Ti₃Al.

Now, there are some other elements intermetallic in the same system like the 50-50 composition with titanium aluminium.

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So, here we call it as γ alloy. So, the γ alloy are based on titanium aluminium which has a slight range of solubility, it also exhibits very low density that I told you in the range of 3 to 4 and here, we add basically some niobium and chromium because the basic composition is near 50-50 and we take advantage of this niobium and chromium. What is the purpose of that? Because we can get a larger room temperature elongation up to 4 % and we improve the fracture toughness. So, this is a secondary addition or alloy addition that improves the properties of the basic intermetallic.

The processing of this intermetallic; you can understand that we can start from the liquid here and we get an ingot out of that or maybe a cast object. However, sometimes, it is more preferred to control the grain sizes. In that case we may start with powder and we can go for some a densification at higher temperature by hot isostatic pressing which is often called as HIP or let us say some of the powder metallurgical route thus that are very much common because if we need to produce a near net shaped component and intermetallics are quite a bit brittle, then it is more preferable to go for a powder metallurgy route.

Now, what are the use of these titanium aluminides? We produces turbine blades turbochargers where we have the maximum use of this titanium aluminides and automobile exhaust compressor blade or some vanes. So, these are the important areas where titanium aluminides are used.

Now, as I said that the intrinsically aluminides has a good oxidation resistance. So, uncoated this gamma aluminides has an inadequate oxidation resistance above 800 °C. So, the scale protection alumina that basically dominate at less than 750 °C, because we have both titanium and aluminium in the material; so, if I oxidize, both will be oxidized, titanium will form titanium dioxide and aluminium will form aluminium oxide and here, the titanium dioxide basically dominate above 750 °C and the problem with titania is that it basically provide a short circuit diffusion path and allow ingress of oxygen or nitrogen which further embrittle material.

So, like an internal oxidation or let us say dissolution in the solution itself, those are the problem of the diffusion. So, then we need to think about further some protection by some overlay coating. However, we can use these intermetallic titanium aluminides at up to 800 °C without any problem.

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Now the second category of aluminides are nickel aluminides where two of the compounds are very interesting and important. One is Ni3Al, another one is NiAl, you can see a quite a large solubility range exist and these Ni₃Al has a γ ' phase which is used for strengthening nickel superalloy. This is like a strengthening by using an intermetallic that we discussed and we will also discuss the nickel based superalloy in the next week in detail.

So, the melting temperatures of these intermetallic are quite a bit high and the density is also comparable with nickel. So, since these are intermetallic as I said that is each has the inherent brittleness. So, like a polycrystalline Ni3Al if we think about since it is also an ordered phase. So, we purposely add some alloy like molybdenum, zirconium, hafnium or boron where we intentionally produce some disordered Ni3Al along with the ordered phase and those has been observed to overcome some of the intrinsic brittleness and increases its toughness value and this is a very common used in a diesel engine material.

Now, if you think about nickel aluminium, where aluminium content is higher it is around 50 % compared to Ni3Al and therefore, it always has a lower density and the lower density and better oxidation resistance we can achieve compared to Ni3Al, where the major problem of nickel aluminium again the brittleness and low strength at elevated temperature. So, throughout the discussion for this aluminides, even though the aluminides has the highest melting temperatures and can give us good protection due to the formation of aluminium scale; however, there are always some intrinsic problem with the inherent brittleness at room temperature.

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So, the third type of the intermetallics, we are interested for was the iron aluminide and initially I told among all the different aluminides iron aluminides has the highest strength level compared to the other aluminides. So, here to the iron aluminide provide a good corrosion and oxidation resistance and the comparison of iron aluminides are always done with the ferritic steels that the heat resistant steel. This are used for some of the commercial purposes and the attack rate or rate of degradation is very slow in case of iron aluminides.

So, here there is a large range of solubility limit for iron aluminides whereas Fe₃Al is dominating in this place. So, these aluminides offer a much lower cost because of the presence of iron and aluminium is also cheaper than nickel aluminides or titanium.

However, further improvement of iron aluminides has done by the alloying addition even though the aluminium must be present, but addition of some chromium, niobium, and molybdenum or let us say, zirconium and boron has been done which further increases the tensile elongation at ambient temperature in the air.

However, in an aggressive environment like a reducing environment iron aluminides survive much better in a coal gasification system. Let us say where carbon monoxide is present and where nickel aluminides we cannot use due to insufficient corrosion resistance.

So, these are the very common summary of the understanding of these intermetallic that we look for that even though this intermetallic we think about that they have limited range of solubility of the alloying elements, but intermetallics, we can take advantage of addition of further elements which can improve some of their properties.

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Now, the second type of intermetallics are the silicides and the silicide has the highest melting temperature compared to other aluminides; however, they have the very low toughness values; however, there are some application areas where silicide can never be replaced with other materials like the heating elements, we often use some of the silicon carbide heating elements.

However, for 1600-1700 °C, the molybdenum silicide or M_0 Si₂ are the best for using as a heating element. The purpose here as I said that silicon produces silicon dioxide which produce a glassy layer on the top of the surface of the material and provides the best oxidation resistance because it decreases the oxygen diffusivity through the layer.

So, this silicides are for the heating element or the best material or best candidate and you can see the melting temperature is highest and density is quite comparable Young's modulus and let us say, there is a brittle to ductile transition temperature around room temperature, toughness value is relatively low; however, the oxidation resistance is highly reliable in the range of 700 °C to 1700 °C. Why I talked about this 700 and 1700 °C; there must be a reason, that what about below 700 °C; silicon dioxide when it forms a glassy layer that occur around a temperature above let us say; 900 °C to 1000 °C, but below that the silicon dioxide is non protective.

So, if we take a polycrystalline molybdenum di-silicide and $=$ some silicon oxide may form, but they are not continuous and as the oxygen level increases, the oxygen goes inside through the grain boundaries because at lower temperature grain boundary provide a short circuit of the diffusion path and the oxygen forms some oxide and there is a volume expansion and due to the volume expansion of these oxide, it provides some stresses and it produces simply powders. So, this is a phenomena called as the Pesting.

And this Pesting phenomena to avoid we need to find a solution so that the melting temperature of the glassy silica should reduce and you know that borosilicate has a lower melting temperature, than the silicate. So, if we add boron into the molybdenum silicide, then the pesting reaction will never happen and it will decrease.

So, this is one of the purpose of addition of boron and improve the properties of the silicides; however, the melting temperature and the density all are given in this table and you please have a look at some of the very important silicides including 5-1-2 phase which is called often called as T2 phase, even though the melting temperature is quiet higher, density is slightly higher than the molybdenum silicide.

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However, oxidation resistance is very good and we have some single crystal where the brittle to ductile transition temperature is quite high and Young's modulus is also quite high and means basically the stiffness is higher.

However, people try to improve the oxidation resistance by adding some aluminium instead of silicon, we replace with some of these aluminium. So, here also we can get a quiet wide range of the oxidation resistance.

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So, these are some of the very common silicides and there are also some other refractory metal based silicides like tungsten suicide or titanium silicide, niobium silicide or chromium silicides and these are the silicide material, these days are thinking to go beyond the nickel based superalloy limit.

However, due to the poor toughness values, we cannot use and we do not get a much higher toughness or produces by simple alloy addition to the intermetallic phase and therefore, people think about that producing some composite means taking advantage of some of the solid solution phases, means intermetallics matrix maybe there, but we can produce some composite incooperating some ductile phases.

So, therefore, the idea came of multiphase silicide alloys.

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So, along that direction; we can have a look at some of the phase diagram containing a molybdenum, here is the silicon and here is the boron.

So, this is a area where we get basically molybdenum as a as a solid solution phase or MoSS that is the solid solution and T 2 phase provides a better oxidation resistance because of the presence of the boron and that boron form boron oxide which again join with the silica and reduces the melting temperature of silica and form a glassy layer.

So, this is one of the advantage where the molybdenum Mo3Si or Mo2B that intermetallics phase form along with the solid solution phases. So, these are some of the common composition that has been discovered recently where the flexural strength which has been measured by some Bend test and with an improved fracture toughness values you can see around 10, 14, 13 and 7 to 4. So, these are quite multiphase composite that gives us a better toughness values and commonly, they can be produced from arc melting to hot pressing and they are very common technique.

So, we can get such an interesting microstructure with composite.

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So, the usual microstructure actually contain the molybdenum solid solution phase and the intermetallic phases. So, here these dark grey colour are the 5-1-2 phase, this is that 5-1-2 phase and the light colour are the Mo₃Si phase.

So, usually these phrases are the intermetallic phases, but the problem with molybdenum that it evaporates at a temperature greater than 704 °C as molybdenum trioxide and there is no protection and the protection can only be achieve by the glassy layer which will cover this. So, this is a half way oxidized surface, you can see the top layer where you can see this molybdenum phase which has been evaporated and produces some cavities and the A15 phase which is the 3 1 phase or 5 1 2 phase they basically assist on covering this using Borosilica layer and this is a Borosilica layer on the top of a alloy scale. So, this is one of the interesting protection mechanism that people have discovered in case of silicides and these silicide matrix composite could be one of the good alternative for future application. We will continue with the discussion in the next class.

Thank you.