ELEVATED TEMPERATURE CHARACTERISTICS OF ENGINEERING MATERIALS

- High temperature alloys broadly refer to materials that provide strength, environmental resistance, and stability within the 260 to 1200^{o}C temperature range.

- They have generally been used in the presence of combustion from heat source such as turbine engines, reciprocating engines, power plants, furnaces.

- In order to retain strength under these conditions, it is imperative that their microstructures remain stable at high operating temperatures.

- During the last few decades, a better understanding of alloying effects, advances in melting technology, and the development of controlled thermo-mechanical processing have led to new and improved high temperature alloys.

- Most such alloys have sufficient amounts of chromium (with or without additions of aluminum or silicon) to form chromia (Cr_2O_3), alumina (Al_2O_3), and/or silica (Si_2O) protective oxide scales, which provide resistance to environmental degradation.

- However, oxides cannot protect against failure creep, mechanical of thermal fatigue, thermal shock, or embrittlement.

- In actual service, failure of a component/material is typically caused by a combination of two or more attack modes, which synergistically accelerate degradation.

CAST IRON AND STEELS:

- **Heat-Resistant Cast Irons** are basically alloys of iron, carbon, and silicon having high temperature properties markedly improved by the addition of certain alloying elements, singly or in combination, principally chromium, nickel, molybdenum, aluminum, and silicon in excess of 3%.

- Silicon and chromium increase resistance to heavy scaling by forming a light surface oxide that is impervious to oxidizing atmospheres. Both elements reduce the toughness and thermal shock resistance of the metal.

- Although nickel does not appreciably affect oxidation resistance, it increases strength and toughness at elevated temperature by promoting an austenitic structure that is significantly stronger than ferritic structures above 540^oC.

- Molybdenum increases high temperature strength in both ferritic and austenitic iron alloys.

- Aluminum additions are very potent in raising the equilibrium temperature (A_1) and in reducing both growth and scaling, but they adversely affect mechanical properties at room temperature.

- Alloy cast irons that have successfully been used for low stress elevated temperature applications include:

  - High silicon irons (4 to 6% Si), with or without molybdenum additions (0.2 to 2.5%), used at temperature up to 900^oC.

  - Austenitic nickel alloyed irons (18 to 34% Ni with 0.5 to 5.5% Cr), used at temperature up to 815^oC.

  - High Chromium white irons (12 to 39%), used at temperatures up to 1040^oC.

- Application for these alloys include cylinder liners, exhaust manifolds, valve guides, gas turbine housings, turbocharger housings, nozzles rings, water pump bodies, and piston rings in aluminum pistons.

- **Carbon Steel** the most widely used steel is suitable where corrosion or oxidation is relatively mild. It is used for applications in condenser, heat exchangers, boilers, super heaters.

- The widespread usage reflects its relatively low cost, generally good service performance, and good weld-ability. The basic low carbon grade contains nominally 0.15%C and is used in various tubing applications.

- Medium carbon grades contain 0.35%C (max) with manganese contents ranging from 0.3 to 1.06%. These grades are used for tubing, pipe, forging, and castings.

- For low stress applications, plain carbon steels can be used at temperatures $\leq 425\,^{o}$C. Temperatures up to about 540^{o}C can be withstood for only short periods.

- **Carbon Molybdenum Steels** contains 0.5% Mo with a carbon content of about 0.2%.

- These steels are used in the same kind of equipment as carbon steels, but they can be more highly stressed because the Molybdenum addition increases short time tensile strength and reduces the creep rate for a given stress and temperature.

- If graphitization under service conditions is possible, the maximum service temperature for carbon molybdenum steels is about 450^{o}C.

- **Chromium-Molybdenum Steels** Creep resistant low alloy steels usually contain 0.5 to 1 % Mo for enhanced creep strength, along with chromium contents between 0.5 to 9% for improved corrosion resistance, rupture ductility, and resistance against graphitization.

- Small additions of carbide formers such as vanadium, niobium, and titanium may also be added for precipitation strengthening and /or grain refinement. The effects of alloy elements on transformation hardening and weldability are, of course, additional factors.

- The three general types of creep-resistant low alloys steels are:

    - Plain chromium molybdenum steels include the 1Cr-0.5Mo and 1.25Cr-0.5Mo alloys used at temperature up to 510^{o}C; 2.25C–1Mo steel, the most widely employed grade, used at temperatures up to 620^{o}C, and the 7Cr-0.5Mo and 9Cr-1Mo alloys, used at temperatures up to 650^{o}C.

    - The chromium-molybdenum-vanadium steels provide higher creep strengths and are used in application where allowable design stresses may require deformations less that 1% over the life of components operating at temperatures up to 540^{o}C. The most common contains 1 % Cr, 1% Mo and 0.25%Mo.

- Modified chromium-molybdenum steels contain various micro alloying elements such as vanadium, niobium, titanium, and boron and are used for thick section components in hydrogen containing environments. Depending on the grade, these modified grades can be used at temperature up to 455 to 600^{o}C.

- Chromium-molybdenum steels are widely used for pressure vessels and piping in the oil and gas industries and in fossil fuel and nuclear power plants, product forms include forgings, tubing, piping, castings, and plate. Figures 1 to 3 compare the properties of chromium-molybdenum steels with those of other systems.

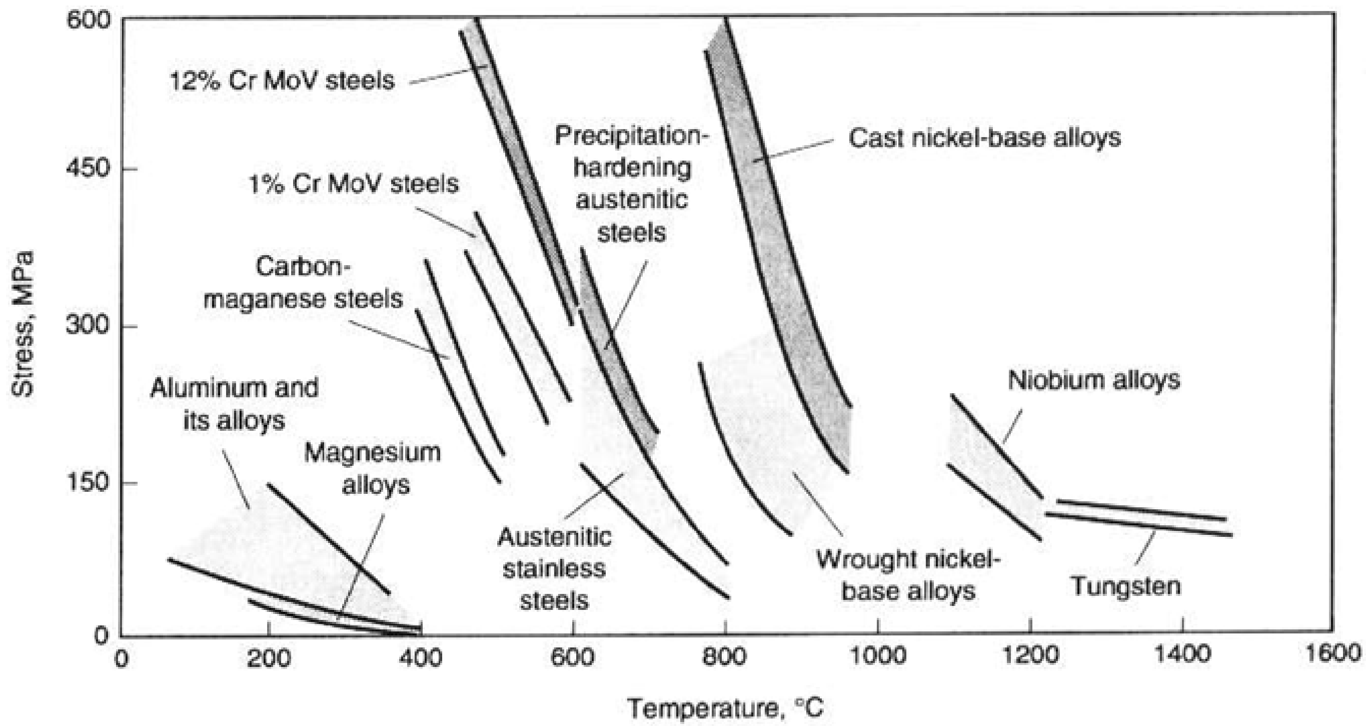

Fig. 1 Stress to produce rupture in 100h for various alloys

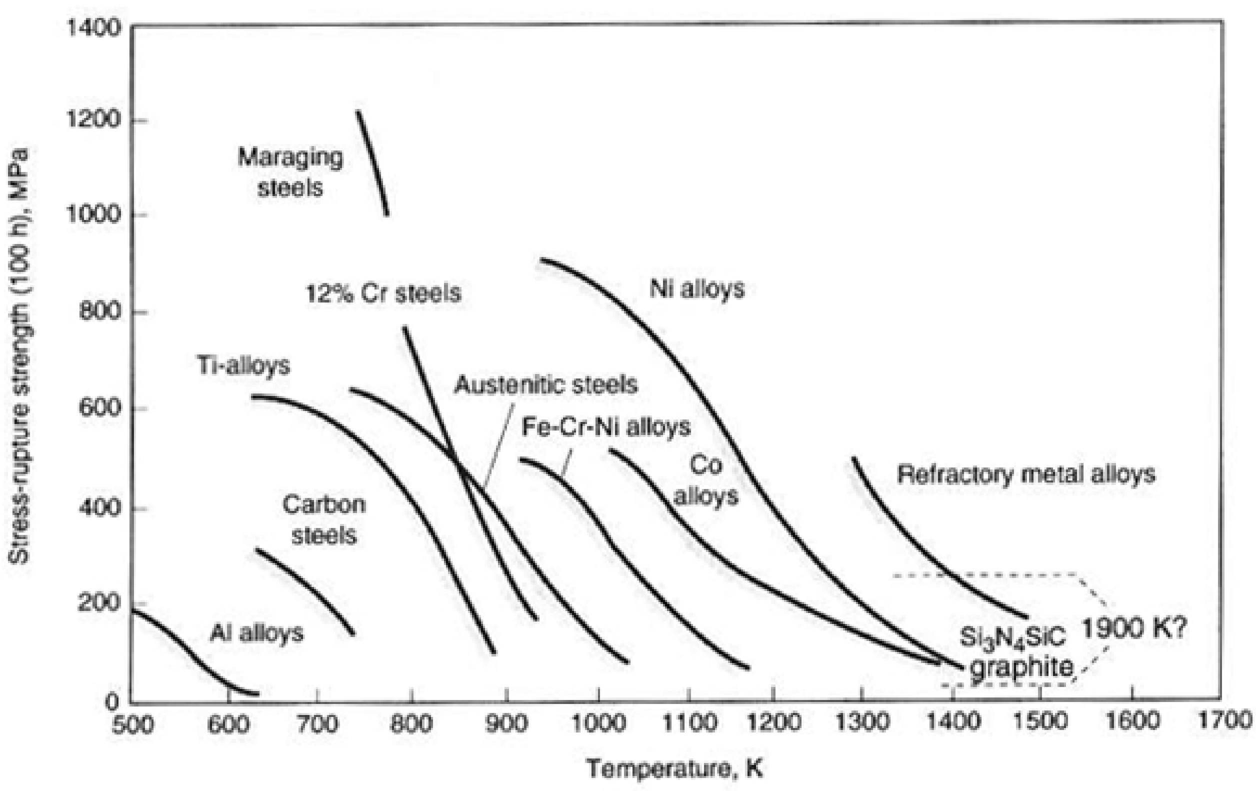

Fig. 2 Maximum service temperatures of various creep-resistant materials

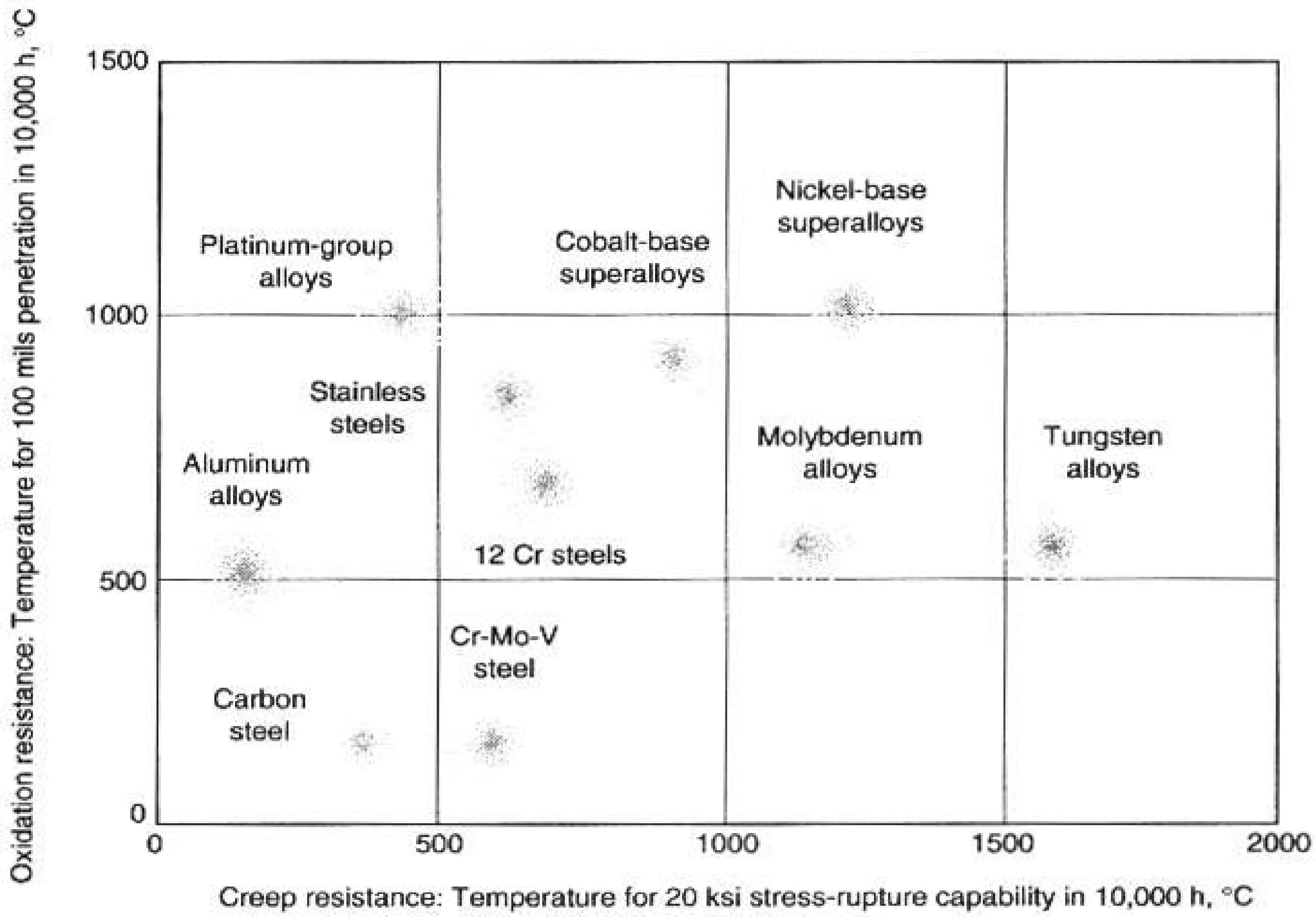

Fig. 3 Relative Oxidation/stress-rupture capability of various alloy systems

- **Chromium hot-work die steels** have good resistance to thermal softening (high hot hardness) up to 500°C because of their medium chromium content (5%) and the addition of carbide forming elements such as molybdenum, tungsten, and vanadium. An increase in silicon content (up to 1.20%) improves oxidation resistance at temperature up to 800°C.

STAINLESS STEELS AND SUPERALLOYS:

- When the severity of the service environments precludes the use of cast irons, carbon steels, or low alloys steels, more highly alloyed materials such as stainless steels and superalloys must be considered.

- Generally, however, stainless steels can be differentiated by their lower alloying content. For example, compare the analysis of type 304 stainless with Waspaloy alloy, a precipitation hardening nickel base high temperature alloy. Type 304 includes carbon, manganese, silicon, chromium, and nickel. Waspaloy alloy, in addition to these elements, includes molybdenum, cobalt, titanium, aluminum, zirconium and boron. These additional elements in the right combination give Waspaloy alloy its consideration strength and corrosion resistance at temperatures up to 870^{o}C.

Stainless Steels

- Stainless steels for elevated temperature applications include ferritic, martensitic, austenitic grades and precipitation hardening.

- Next to the superalloys, the stainless steels provide the best combination of high temperature corrosion resistance and high temperature mechanical strength of any alloy group.

- **The ferritic grades**, which have good resistance to oxidation at elevated temperature, are not known for their mechanical strength at high temperature. Instead, these alloys are primarily used in corrosion resistant applications.

- The 17% Cr stainless steel, Type 430, is used in applications that require oxidation and corrosion resistance up to 815^{o}C. Where elevated temperature strength is a requirement, the use of this composition is limited because of its relatively low creep strength. Although it is ductile between about 400 and 590^{o}C, this steel will be brittle when it is cooled to ambient temperature after prolonged heating in this range. The brittleness may be eliminated by reheating to about 760^{o}C.

- The 27% Cr stainless steel, type 446, which has relatively low elevated temperature strength, is used between 870 and 1095^{o}C in applications where the most severe oxidation is encountered. It is also subject to the same embrittling phenomena as type 430 steel. The major application of type 446 steel is in such as furnace parts and thermocouple protection tubes, where low stresses are relatively low.

- **The martensitic stainless steels** most commonly used for elevated temperature applications are the so called "Super 12 Chrome" steels that contain molybdenum (up to 3%) and/or tungsten (up to 3.5%) for greater strength at elevated temperatures. Other elements, such as vanadium, niobium, and nitrogen may be added in small amount for additional strengthening.

- The 12% Cr martensitic with the aforementioned alloying additions can be used at temperatures up to 650^{o}C, but they provide only moderate strength above 540^{o}C. Straight (unalloyed) martensitic grade can only be used at temperature up to 400^{o}C.

- **The austenitic stainless steels** are essentially alloys of iron, chromium, and nickel. These steel as a class are the strongest steel for services above about 540^{o}C.

- Type 304 is the most common grade of austenitic chromium-nickel steels which as a group are used for handling many corrosive materials or resisting severe oxidation. Type 304 steel has excellent resistance to corrosion and oxidation has high creep strength and is frequently used at temperature up to 815^{o}C. Type 304 is steel being used successfully and economically in high temperature service in such application as high pressure steam pipes and boilers tubes, radiant super-heaters, and oil-refinery process industry equipment.

- Types 321 and 347 stainless steel are similar to type 304 except that titanium and niobium respectively have been added to these steels. The titanium and niobium addition combine with carbon and minimize intergranular corrosion that may occur in certain media after welding. However, the use of niobium (or titanium) does not ensure complete immunity to sensitization and subsequent intergranular attack when the steel is exposed for long time in the sensitization range of 425 to 815^{o}C. However, types 321 and 347 stainless steels are widely used for service in this temperature range.

- Type 316 stainless steel, which contains molybdenum, is used for high-strength service up to about 815^{o}C, and it will resist oxidation up to about 900^{o}C. However above this temperature, in still air, the molybdenum will form an oxide that will volatilize and result in rapid oxidation of the steel.

- For service above about 870^{o}C, types 309 and 310 stainless steels, which contain about 23 to 25% Cr, are used. These steels have the best high temperature strength of the austenitic stainless steels at these temperature, and because of their chromium contents, they can be used in application where extreme corrosion or oxidation is encountered.

- The highest service limits for oxidation resistance of stainless steels is achieved by the highly alloyed type 330 grade. This alloy, which contain 19%Cr, 25%Ni and 1.0%Si, is suitable for continuous service at temperature as high as 1150^{o}C.

- **Precipitation-hardening stainless steels** have the highest room-temperature strengths of all the stainless steels .They fill an important gap between the chromium-free 18% Ni maraging steels and the 12% Cr quenched and tempered martensitic grades. One grade, the austenitic A-286, has moderate strength and long-term service capability up to 620^{o}C.

- **Valve steels** are austenitic nitrogen-strengthened steels that have been used extensively in automotive /internal combustion engine valve application .Examples of such alloys include 21-2N (21Cr, 8Mn, 2Ni +N), 21-4N (21Cr, 9Mn, 4Ni+N), 21-12N (21Cr, 12Ni, 1.25Mn+N), and 23-8N (21Cr, 8Ni, 3.5Mn +N). The nitrogen contents in these alloys range from 0.20 to 0.50%.These engine valve grades are used at temperature up to 760^{o}C, but they provide fairly low strength at the upper end of their temperature capability.

- **Cast heat-resistant alloys** are primarily used in application where service temperatures exceed 650^{o}C and may reach extreme as high as 1315^{o}C .Many of the cast heat-resistant alloys are compositionally related to the wrought stainless steels and to the cast corrosion-resistant alloys. The major difference between these materials is their carbon content. With only a few exceptions, carbon in the cast heat-resistant alloys falls in arrange from 0.3 to 0.6 compared with the 0.01 to 0.25% C that is normally associated with the wrought and cast corrosion-resistant grades.

- The standard cast heat-resistant grades have high creep strength and generally good oxidation resistance, show better carburization behavior than the corresponding wrought alloy, and are available in product forms such as tubes retorts and hangers at relatively low cost for the alloy content.

Superalloys

- Superalloys are Nickel, Iron-Nickel, and Cobalt-Base alloys generally used at temperatures above about 540°C.

- The iron-nickel base superalloys are an extension of stainless steel technology and generally are wrought, whereas cobalt and nickel-base superalloys may be wrought or cast, depending on the application/composition involved.

- Appropriate compositions of all superalloys base metals can be forged, rolled to sheet, or otherwise formed into a variety of shapes. The more highly alloyed composition normally are processed as castings. Properties can be controlled by adjustment in composition and by processing (including heat treatment), and excellent elevated-temperature strengths are available in finished product.

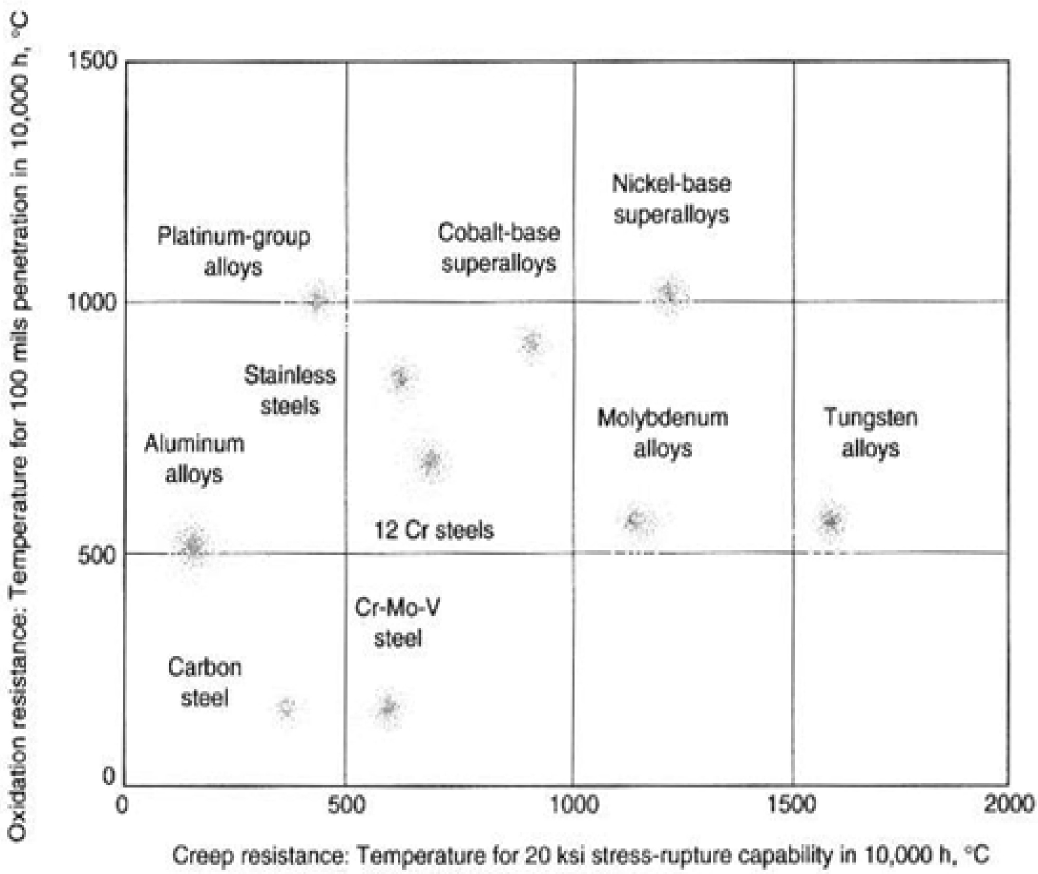

Fig. 4 Relative oxidation/stress rupture capabilities of various alloys systems

- As indicated in Fig.4, no other alloy system has a better combination of high-temperature corrosion resistance and stress-rupture strength.

- Some superalloys, particularly nickel-base casting alloys, can be used at temperatures that are approximately 85% of their incipient melting point. Such alloys exhibit outstanding creep and stress-rupture properties at temperature in excess of 1040^{o}C.

- The oxidation resistance of most superalloys is excellent at moderate temperature about 870^{o}C and below. Some alloys can be used at temperature up to 1200^{o}C. Coatings can further enhance high temperature corrosion resistance.

LOW DENSITY METALS:

- Density is very important in the design of aircraft because excess weight in engine and structural components decreases load carrying capacity. As a result, materials with a high strength to weight ratio are in ever increasing demand.

- Low density alloys, which are commonly referred to as light metals, include magnesium-, aluminum-, and titanium-base alloys.

- **Magnesium alloys** have the lowest densities (~1.8 g/cm^3) of any structural alloy. Magnesium alloys for elevated-temperature application usually contain thorium (up to 3 wt%).

- The magnesium-thorium-zirconium cast alloys HK31A (Mg-3.3Th-0.7Zr) and HZ32A (Mg-3.3Th-2.IZn-0.7Zr) are intended primarily for use at temperature of 200^{o}C and higher.

- At 260^{o}C and slightly higher, HZ32A is equal to or better than HK31A in short time and long-time creep strength at all extensions. The HK31A alloy has higher tensile, yield and short time creep strength up to 370^{o}C.

- Another cast alloys, QH2IA (Mg-2.5Ag-1.0 Th0.7Zr) retain a high yield strength up to 300^{o}C. This alloy is relatively expensive due to its silver content.

- Rare earth (RE) additions also contribute to improved elevated temperature performance. Alloys WE54 (Mg-5.2Y-3.0RE-0.7Zr) and WE43 (Mg-4.0Y-3.4RE-0.7Zr) have high tensile strengths and yield strengths, and they exhibits good properties at temperature for up to 1000hrs, whereas WE43 retains its properties at high temperature in excess of 5000hrs.

- Thorium alloyed wrought alloys are also used at elevated temperatures. Alloy HM31A (Mg-3Th-0.6Mn), produced in extruded forms, is of moderate strength. It is suitable for use in applications requiring good strength and creep resistance at temperatures in the range of 150 to 425^{o}C.

- Alloy HM21A (Mg-0.2Th-0.6Mn), produced as forgings, is useful at temperatures up to 370 to 425^{o}C for applications in which good creep resistance is needed.

- HK31A and HM21A alloys, produced in sheet and plat forms, are suitable for use at temperatures up to 315 and 345^{o}C, respectively. However, HM21A has superior strength and creep resistance, as shown the following table:

Alloy	Stress for 0.1 % creep in 100 hrs	
	MPa	Ksi
At 205^{o}C		
HM21A	86.2	12.5
HK31A	41	6.0
At 260^{o}C		
HM21A	72.4	10.5
HK31A	28	4.0
At 315^{o}C		
HM21A	52	7.5
HK31A	14	2.0

- **Aluminum Alloys** have higher densities (~2.8g/cm^3) and higher room temperature strengths than magnesium alloys. Some cast aluminum alloys are used in applications at moderately elevated temperature (e.g., pistons in internal combustion engines).

- One commonly employed alloy is permanent mold cast alloy 242 (Al-4Cu-2Ni2.5Mg). As shown in fig. 5 this alloy retains its strength at temperature as high as ~150^{o}C. Some other cast aluminum alloys can be used at slightly higher temperatures 175^{o}C.

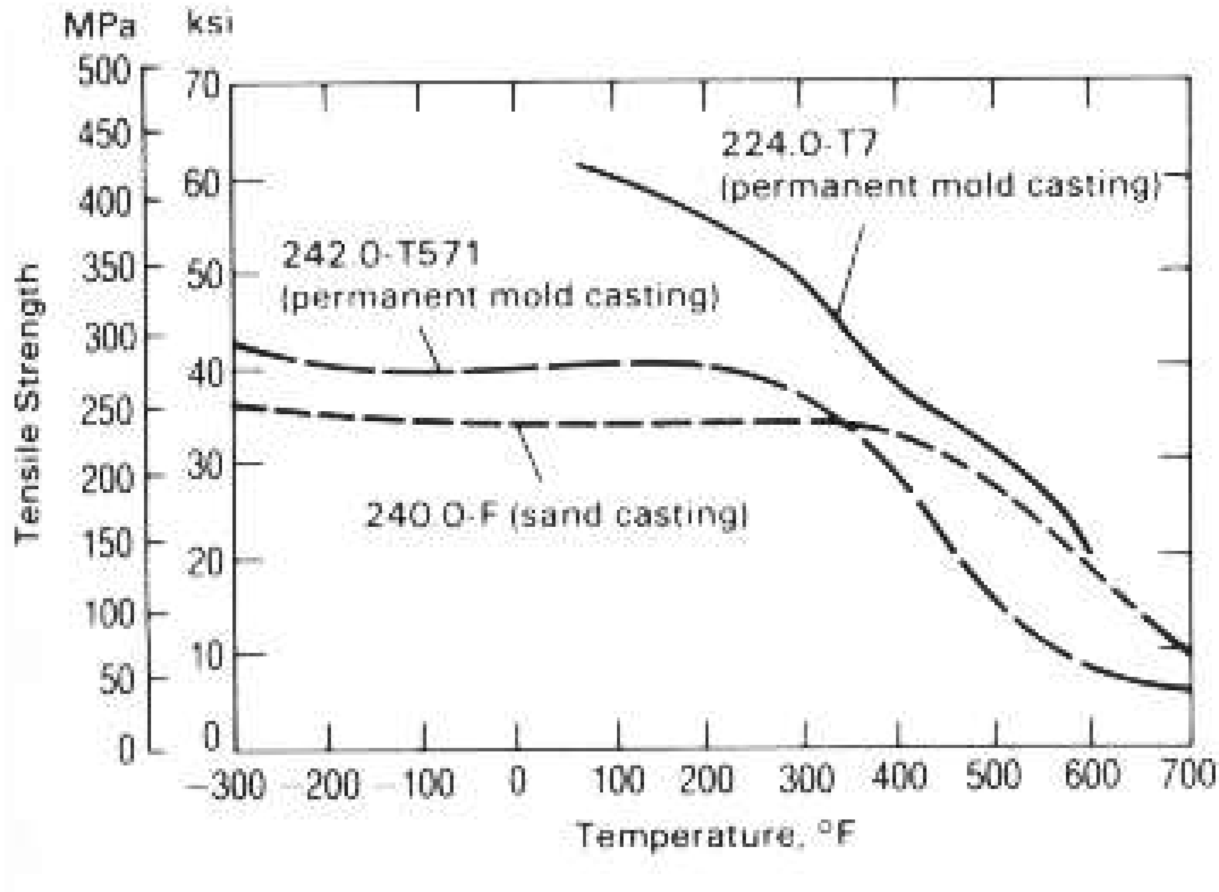

Fig. 5 Tensile strengths of aluminum alloys
240.0-F, 224.0-T7, and 242.0-T571 as function of temperature

s

- The 7xxx series of wrought age-hardenable alloys that are based on the Al-Zn-Mg-Cu system develop the highest room temperature tensile properties of any aluminum alloys produced from conventionally cast ingots.

- However, the strength of these alloys declines rapidly if they are exposed to elevated temperatures as shown in fig.6, due mainly to coarsening of the fine precipitates on which the alloys depends for their strength.

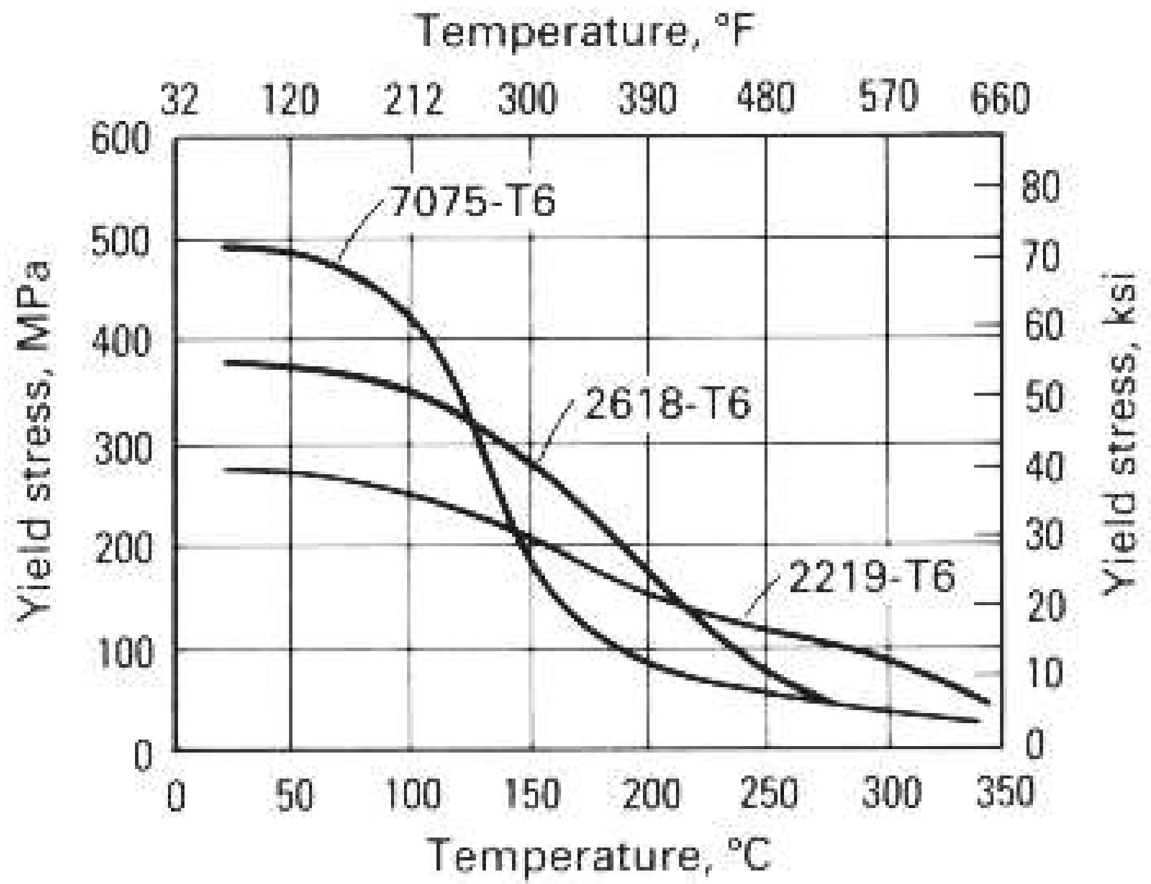

Fig. 6 Values of 0.2% yield stress of aluminum alloys after exposure for 1000h at temperatures between 0 and 350°C

- Alloys of the 2xxx series, such as 2014 and 2024, perform better above these temperatures but are not normally used for elevated temperature application.

- Strength at temperatures above about 100 to 200°C is improved mainly by solid solution strengthening or second phase hardening.

- Another approach to improve the elevated temperature performance of aluminum alloys has been the use of rapid solidification technology to produced powders containing high super-saturations of elements such as iron or chromium that diffuse slowly in solid aluminum.

- **Titanium Alloys** provide an outstanding combination of low density (~4.5g/cm^3) and high strength (up to 1100 MPa, or 160 Ksi, yield strength).

- Alloys have been developed that have useful strength and resist oxidation at temperatures as high as 595°C. The improved elevated temperature characteristics of these alloys, combined with their high strength-to-weight ratios, make them an attractive alternative to nickel base superalloys for certain gas turbine components.

- Most of the titanium alloys for elevated temperature applications are based on the Ti-Al-Sn-Zr system. Important alloying elements are molybdenum, silicon, and niobium. Molybdenum enhances hardenability and enhances short time high temperature strength or improves strength at lower temperatures.

- Minor silicon additions improve creep strength, while niobium is added primarily for oxidation resistance at elevated temperature. Examples are Ti-1100 (Ti-6AI-2.75Sn-4Zr-0.4Mo-0.45Si) and IMI-834 (Ti-5.5AI-4Sn-4Zr-0.3MO-INb-0.5Si).

REFRACTORY METAL ALLOYS

- Refractory metals include tungsten, molybdenum, niobium, tantalum, and rhenium. These metals and their alloys have melting points in excess of 2200^oC, which is substantially higher than those of stainless steels or superalloys. As indicated in fig 1 to 3.

- The creep strength of some refractory metals (tungsten and niobium) exceeds that of superalloys. There are, however, a number of deficiencies of refractory metals and alloys that have precluded their being viable alternatives to superalloys in gas turbine engine applications.

- The body-centered cubic structure (precluding high creep resistance relative to the melting point), lack of low-temperature ductility in the VI A metals (tungsten and molybdenum), severe lack of oxidation resistance for all, and significantly higher density than superalloys for all except niobium.

STRUCTURAL INTERMETALLICS:

- An intermetallic compound can be defined as an ordered alloy phase formed between two metallic elements. The ordered structure exhibits superior elevated-temperature properties because of the long-range ordered super-lattice, which reduces dislocation mobility and diffusion processes at elevated temperatures.

- Intermetallic compounds are generally brittle and high melting. They often offer a compromise between ceramic and metallic properties when hardness and/or resistance to high temperatures is important enough to sacrifice some toughness and ease of processing.

- They can also display desirable magnetic, superconducting and chemical properties, due to their strong internal order and mixed (metallic and covalent/ionic) bonding, respectively.

- Intermetallics have given rise to various novel materials developments. Some examples include Nickel aluminides based on Ni_3AI and NiAI, Titanium aluminides based on Ti_3AI and TiAI have also attracted interest for turbine blade applications and Iron aluminides based on Fe_3AI and FeAI.

- These aluminides possess many attributes that make them attractive for high-temperature structural applications. They contain enough aluminides to form, in oxidizing environments, thin films of aluminides oxides that often are compact and protective. They have low densities, relatively high melting points, and good high-temperature strength properties.

- Nickel, iron, and titanium aluminides, like other ordered intermetallics, exhibit brittle fracture and low ductility at ambient temperatures. Poor fracture resistance and limited fabricability restrict the use of aluminides as engineering materials in most cases. Nevertheless, these materials appear the most likely to replace superalloys in high-performance applications.

- **Nickel Aluminides** based on NiAl has a melting point of 1638^{o}C, compared with a solidus temperature of about 1300^{o}C for most superalloys.

- NiAl has excellent cyclic-oxidation resistance to 1300^{o}C, low density, and, through minor alloy addition, can provide creep strength superior to that of superalloys.

- Has good ductility in single-crystal form.

- Ni_3AI compound which has a lower melting point than NiAl but still offers strength and density advantages over current superalloys.

- Boron additions significantly enhance ductility over a wide temperature range up to its melting point.

- Ni_3AI ingots produced using conventional electroslag remelt (ESR) and vacuum induction melting (VIM) techniques.

- Advantages claimed for nickel aluminides over conventional nickel-base superalloys include:

    - Lower densities due to the higher aluminum content of the aluminides
    - Much simpler chemical compositions than many superalloys
    - Single-phase structure
    - Strength derived from their ordered structure not from precipitates of second phase; thus, no special heat treatments, such as aging, are required
    - Yield strength that increase with increasing temperatures (as high as 650 to 750^{o}C)

- Very good oxidation resistance to 1100^{o}C due to their high aluminum content
- Potential lower cost than many superalloys when full-scale production is achieved.

- Nickel aluminides use in applications such as hot-forming dies, turbochargers, permanent molds, and advanced pistons.
- **Iron and Titanium aluminides**, unlike the nickel-aluminum compound, do not offer the same creep strength at very high temperatures.
- They do, however, have unique specific properties that should ensure their use of some rotating components. FeAl, for example, has good strength to 700^{o}C, while its high melting point 1340^{o}C and good oxidation resistance may well lead to its use as a matrix material in metal-matrix composites.
- Both Ti_3Al and TiAl have good specific strength at temperatures to 1100^{o}C. However, compared with superalloys, they each have limitations, such as inferior oxidation resistance (Ti_3AI) and ductility (TiAl).

NONMETALLIC MATERIALS

- **Polymer-Matrix Composites.** Generally, polymers or polymer-matrix composites are not considered heat-resistant materials. Most organic polymers soften or melt below 205^{o}C. As a result, most polymeric materials are used at or just above ambient temperature (less then 100^{o}C).
- The most successful high-temperature polymeric material developed to date is a polyimide resin reinforced with graphic fibers.
- Graphite reinforced polyimide composites have been reported to be suitable for use in air at 288^{o}C for at least 5000hrs. At 316^{o}C, the useful life of these composites is in the range of 1200 to 1400hrs.
- **Ceramics**, both in monolithic and composite forms, offer the prospect of useful heat resistance, possibly to temperatures near 1650^{o}C, coupled with low density and in some cases excellent oxidation and corrosion resistance.
- Unfortunately, these ceramics also are brittle, prone to thermal shock, and less thermally conductive than heat-resistance metals, leading to severe deficiencies under

tensile loading. These are inherent properties determined by the nature of the inter-atomic bonds.

- Mechanical properties also are highly variable, depending sensitive on preparation technique, impurities, and surface finish; in ceramics the process basically determines the properties. Processing of ceramics is also quite costly.

- Nevertheless, the toughness and thermal shock resistance of silicon nitride (Si_3N_4) and its ability to form protective SiO_2 layers makes it a candidate for turbine or diesel applications. Silicon carbide (SiC) has similar properties. Other applications include heat exchangers and furnace components.

- Oxides, such as alumina (Al_2O_3) and zirconia (ZrO_2), are also used for high-temperature applications. Zirconia has been in service as a thermal barrier coating in aircraft combustors on superalloys for many years.

- The oxide-type ceramics tend to be less desirable mechanically than are carbide-nitride ceramics, although they are very stable in oxidizing atmospheres.

- Ceramics-matrix composites also show great potential.

- The excellent high-temperature strength, oxidation resistance, and thermal shock resistance of Si_3N_4 has led to the development of SiC_w reinforced Si_3N_4. The major phase, Si_3N_4, offers many favorable properties, and the SiC whiskers provide significant improvement in fracture toughness. Whisker-reinforced Si_3N_4 is a leading candidate material for hot-section ceramics-engine components.

- **Carbon-Carbon Composites.** The highest temperature capability of any material considered for high-temperature use is exhibited by carbon-carbon composites, graphite fibers in a carbon-graphite matrix.

- Carbon-carbon composites are now used for one-time service in rocket-nozzle and missile exit core structures and in turbine aircraft brake shoes; SiC-coated carbon-carbon parts are being used as the nose cap and heating edges of the shuttle.

- Carbon-carbon composites retain their tensile strength at extreme temperatures. Carbon-carbon composites provide unmatched specific stiffness and strength at temperatures from 1200 to 2200^{o}C. At temperatures below 1000^{o}C, carbon-carbon composites exhibited specific strength equivalent to that of the most advanced superalloys.

- Carbon-carbon composites also have superior thermal shock, toughness, ablation, and high-speed friction properties. Another outstanding feature is the low density (~1.6g/cm^3) of carbon- carbon composites.

- Because carbon-carbon is not stable in oxidizing environment at temperatures above about 425^oC, coatings are essential. Refractory carbides such as SiC are applied by various processes.