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Materials Development for Indian Nuclear Power Programme: an Industry Perspective

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Abstract

Materials play very crucial role for a safe, reliable and economic operation of nuclear power plants. Materials used in nuclear reactors encounter hostile environment and aggressive media during service, and are expected to retain their structural and metallurgical integrity over a long period of use. The major challenges are the effect of radiation on embrittlement, creep, erosion, corrosion, radiation induced growth, swelling, stress corrosion cracking, hydrogen embrittlement and radioactivity build up. In order to realize a high degree of reliability and at the same time meet the imposing challenges, material specification and acceptance criteria are extremely stringent and the products have to undergo a detailed testing and characterization prior to their use. To ensure the conformance to the specification, processes need to be developed which involves melting the alloy with stringent chemistry control, optimizing thermo-mechanical treatment and modifying heat treatment schedule suitably to achieve mechanical properties.

A typical nuclear power plant makes use of nuclear fuel materials such as uranium, structural materials such as zirconium alloys, stainless steels, nickel base alloys as well as low alloy and carbon steels. The paper outlines processing methodologies and gives an overview of some of the structural materials.

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Key words: Reactor materials; structural materials; stainless steels; zirconium alloys; nickel base alloys

1. Introduction

A wide spectrum of engineering materials ranging from metals and alloys to highly advanced ceramics, polymers and composites find application in strategic sector. The designer working in these industries goes through an elaborate evaluation of various characteristics of materials, while making his choice for intended application. Among the important criteria the designer adopts for material selection are – high strength to weight ratio, functional and environmental stability as well as high degree of reliability. Adequate knowledge of service requirements and detailed information regarding material capabilities are absolutely essential for the designer to make right choice of materials.

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Nuclear materials can be broadly be categorized into nuclear fuels and structural materials. There has been historical increase in fuel burnup with improved performance of material used in reactor fuels, reactor core components, and reactor vessels. Structural materials play vital role in the economics of the nuclear power plant.

Materials for structures need to be such that they give long life to the nuclear reactors where it encounters hostile environment and aggressive media during service. The requirements for the materials are low thermal neutron absorption cross-section, adequate strength, ductility and toughness at reactor operating temperatures, good corrosion resistance, low hydrogen absorption, long term dimensional stability under irradiation conditions, resistance to fracture and good thermal conductivity. Material specification and acceptance criteria are extremely stringent and the products have to undergo a detailed testing and characterization prior to their use.

There is continuous effort in developing and producing radiation resistant material that can withstand harsher irradiation environment and higher temperatures to ultimately support higher burnups. In this direction Indira Gandhi Centre for Atomic Research (IGCAR) - Kalpakkam and Bhabha Atomic Research Centre (BARC) - Mumbai on one hand and Mishra Dhatu Nigam Limited (MIDHANI) - Hyderabad on the other have worked together. New materials for core (D9I, variants of 9Cr1Mo, etc.) have been designed by IGCAR and manufactured at Midhani. With BARC, MIDHANI has developed new steels such as Maraging 400, modified 430 SS etc.

The most essential part for manufacture of any strategic material include clean melting techniques, tight control of alloy chemistry, appropriate forging techniques to ensure homogeneity and soundness and the analytical capability to characterize the product.

MIDHANI produces a number of specialty steels, stainless steels, maraging steels, titanium and its alloys and nickel, cobalt and iron based superalloys. Primary melting of ferrous alloys are carried out in Electric Arc Furnace or Air Induction Furnace or Vacuum Induction Refining Furnace or Vacuum Induction Melting Furnace depending upon the specification requirements. The secondary melting is carried out in either Vacuum Arc Remelting (VAR) or Electro Slag Remelting (ESR). However, titanium and its alloys are manufactured by compacting the sponge and alloy additions. The compacts are welded to give a single unit called electrodes, which are then remelted in Vacuum Arc Remelting Furnace. Higher purity titanium alloys are manufactured by repeated remelting in VAR. These are then known as double or triple melted grades. Nickel, cobalt and iron base superalloys are generally melted in Vacuum Induction Melting furnace using virgin raw materials and remelted either in Vacuum Arc Refining or Electro Slag Remelting Furnace.

2. Manufacturing process

Material specifications for advanced alloys have several restrictions imposed with respect to individual as well as total levels of residual and trace impurities. At the same time, the specifications call for restrictions in gas levels and non-metallic impurities in the product. Apart from these restrictions the desired range of different alloying elements are required to be maintained within narrow limits to satisfy the microstructural and mechanical properties requirement.

To meet these formidable challenges the first step is to identify suitable sources of different raw material having very low impurity level. Most of the critical raw materials need to be sourced from reputed manufacturers and traders from all parts of the world.

An array of special melting and remelting facilities, such as Vacuum Induction Melting (VIM), Electron Beam Melting (EBM), Vacuum Arc Remelting (VAR) and Electro Slag Remelting (ESR) having different melting and remelting capacities are ideally suited for carrying out developmental work as well as commercial production.

The choice of melting facilities and processing route to be adopted is primarily dictated by the specification needs. Alloys for very critical requirements are often processed through double vacuum melting (VIM + VAR) route, which ensures material with very low gas levels and high degree of oxide cleanliness. Alloys having high levels of titanium are preferably processed by VAR route to avoid titanium loss during air melting. Similarly alloys requiring very low levels of sulphur and at the same time are required to maintain nitrogen within the specific range are processed through Electro Slag Remelting. Most of the nickel-based superalloys are processed through double vacuum melting route (VIM + VAR). In this case special care is taken to retain required level of magnesium that is very volatile and is easily lost during vacuum melting. Magnesium retention around 100 ppm is very important for proper hot workability of superalloys. Titanium alloys are processed by mixing titanium sponge and suitable alloying elements, compacting them to briquettes, making a electrode by plasma welding and subsequently melting it in a water cooled copper crucible in VAR. These are essential steps in titanium processing in view of its high reactivity with oxygen, hydrogen and refractory material. Apart from melting, due attention is also given to hot working process in order to realise uniform microstructure and properties in the material. Repeated heating without adequate reduction gives non-uniform coarse-grained structure, often resulting in inadequate tensile and impact properties. Higher than optimum forging reduction ratio (2 to 3:1) leads to non isotropic mechanical properties i.e. ductility and impact toughness is higher in longitudinal direction (along the fibre) than in transverse (across the fibre) direction. Therefore, there is need for optimising the thermo-mechanical processing to obtain the best out of the material.

3. Materials for Fast Breeder Reactor

The melt route to be adopted will depend on the product specification of the customer. Depending on the product specification, same grade may be processed by different melt route and sometimes the aimed composition needs to varied within the specified range. Some of the critical grades manufactured are discussed.

MIDHANI is currently engaged in the manufacture of frontline austenitic stainless steel for Fast Breeder Reactor such as Ti modified 316 SS (D9), 304L -(N) SS and 316L -(N) SS. Controlling volatile elements like manganese in D9 alloy within narrow limits while double vacuum melting and manufacturing the product to stringent ultrasonic standards are some of the challenges, which have been successfully overcome during material processing. MDN316Ti modified (D9) finds extensive use in reactor core application for clad and wrapper tubes. The specification calls for narrow range of chemical composition, low gas levels, stringent ultrasonic requirement (1mm FBH) and fine grains. Ensuring high quality raw material during primary melting, double vacuum melting (VIM + VAR), adequate forging reduction and homogenization of material fulfills the requirement. Based on the study under taken by IGCAR an optimized version D9I with alloy additions such as phosphorus, silicon and boron that improve resistance to void swelling has been developed.

Austenitic stainless steel 316L -(N) and 304L -(N) has been chosen as major structural material for Fast Breeder Reactor because of the high temperature mechanical properties, compatibility with liquid sodium coolant, good weldability, availability of design data and a vast experience. The material has been selected for critical components like main vessel, grid plate, primary sodium pumps, intermediate heat exchangers and piping of the sodium conduit. These critical components of the reactor have stringent requirements such as good high temperature strength, toughness as well as controlled microstructure of the component.

MDN304L -(N) and MDN316L -(N) are low carbon grades of austenitic stainless steels. All the elements have been narrowed down and nitrogen limits is specified, essentially to minimize the scatter in mechanical properties, improve strength and weldablity. These steels are manufactured through electric arc furnace to provide pure iron with low sulphur and phosphorus. The hot liquid metal is transferred to Vacuum Induction Refining furnace where major alloying elements are added and final aimed composition is obtained. The cast electrode is then remelted in ESR and subsequently processed by forging, hot rolling into bars, flats, plates or sheets.

Steel containing 9 -12% Cr have been developed with the objective of extending the operating range of creep resistant ferritic steels to temperature upto 600°C and higher. These steels have favourable physical properties such as higher thermal conductivity and lower coefficient of thermal expansion coupled with higher resistance to thermal shock and hence offers advantages over austenitic steels in several applications. Since steam generators of the Fast Breeder Reactor are designed with a wall separating the water/steam from the sodium coolant, the very high reactivity of sodium with water makes the steam generators one of the most critical components governing the safe and efficient running of the plant. Modified 9Cr -1Mo is the choice material based on the superior creep resistance and high temperature strength of the steel due to the presence of Nb and V in it. Extensive developmental work on improving the mechanical properties of the steel further has been carried out by IGCAR.

MIDHANI has manufactured a number of heavy forging of modified 9Cr -1Mo steel for PFBR applications. PFBR material specifications have been exclusively formulated and are stringent compared to ASME requirements. Some of the components such as tube sheet material required control of sulphur to be maintained within a specific range for wettability during autogenous welding. Nitrogen to aluminum ratio greater than 2 is also one of the requirements so that ample supply of free nitrogen is available to form creep strengthening intragranular carbonitrides precipitates. The piping material also required sulphur, nitrogen and carbon in a narrower range for weld consideration. These problems have been addressed by modifying the slag composition and carefully controlling deoxidation during ESR.

4. Materials for Pressurised Heavy Water Reactor

MDN403 is a low carbon martensitic stainless steel that finds applications as end fitting in Pressurized Heavy Water Reactor due to its high strength and impact toughness, adequate resistance to corrosion, wear, erosion and oxidation resistance; and of the thermal expansion coefficient close to zirconium alloy pressure tube. The steel for end fitting specifies a limit of cobalt of 0.025 wt.% and copper 0.06 wt.%. The product after heat treatment is expected to have high strength and toughness. This steel is produced in MIDHANI through Electric Arc Furnace, in which pure iron of low sulphur and phosphorus and also cobalt and copper requirement is achieved. The hot liquid metal is then transferred to Vacuum Induction Refining furnace for obtaining low gas levels. The secondary melting is carried out in ESR. The outcome is a material that has low trace element such as sulphur, phosphorus, oxygen, hydrogen, cobalt and copper and a sound and dense material. Thermo-mechanical working and adequate forging reduction ensures a fine-grained, homogenous material. These forgings are then heat treated in calibrated furnace to obtain optimum strength and toughness.

A variety of precipitation hardening stainless steels such as 17 -4PH and 13 -8 Mo have been supplied for the manufacture of critical peripheral structural components and fuel handling assembly. Composition controls within specific range and modification to heat treatment procedure have been carried out after careful laboratory trials in order to realise the required toughness at high strength levels in a consistent manner.

MDN 174 is widely used for components in nuclear power generation. A limit of 0.04 wt. % cobalt is specified. This grade is difficult to process and is crack prone. Primary melting is carried out in electric arc furnace. Qualified raw materials are taken to ensure low cobalt and phosphorus. The electrode is then remelted in ESR to improve the cleanliness by reduction of oxygen, sulphur and aluminium. An optimum thermo-mechanical treatment and forging reduction ensures a uniform and fine-grained structure. The chemical composition of this grade is such that some amount of delta ferrite forms. This affects the transverse impact toughness.

MDN138 and MDN155 are the improvement over Type 174. Higher nickel and lower chromium content reduces or eliminates the formation of delta ferrite. MDN138 is widely used for ball screw manufacturing. Lower delta ferrite ensures a homogenous material that in turn ensures isotropic properties. The alloy finds applications where a combination of stress corrosion cracking and high strength is required. The specification for ball screw calls for minimum impact toughness of 2.8 Kg.m in H1000 condition with hardness of 40 HRc minimum. None of the international specification specifies impact toughness as a requirement. MIDHANI took up the challenge and manufactured the material to the satisfaction of the customer. The material is double vacuum melted (VIM+VAR) to obtain a material that is clean, low in gas content, sound and homogenous. This material is forged and hot rolled in a controlled temperature range to result in a fine-grained structure. Solution annealing and ageing cycle are carried out in well-calibrated furnace. After initial setback, MIDHANI's MDN138 is consistently meeting the required specificational requirement.

MDN138 PH was developed specifically for use in large cross section parts, which required yield strength upto, about 1500 MPa and good ductility properties irrespective of grain orientation. Toughness in the transverse direction is obtained by composition balance designed to prevent formation of delta ferrite in the structure, lower carbon content to minimize grain boundary carbide precipitation and double vacuum melting to reduce alloy segregation. Studies show that low carbon, phosphorus, sulphur, silicon, manganese, nitrogen and titanium have beneficial effect on the toughness of the steel. Control of these critical elements is achieved by careful selection of raw materials and processing.

5. Materials for other nuclear applications

MIDHANI developed a special variant of 430 SS by introducing small and controlled amounts of nickel and nitrogen to meet specific needs of BARC. These additions rendered the steel heat treatable resulting in a two-phase ferrite and martensite duplex microstructure. The resultant steel MDN 430 modified had superior strength and toughness as compared to the parent 430 SS ferritic steel.

Manufacturing a variety of high quality maraging steels in different mill forms has been one of the significant contributions of MIDHANI in the last three decades. Maraging steels are a family of ultra high strength steel coupled with excellent fracture toughness. These steels are characterized by very low carbon contents and the use of substitution elements to produce age hardening in iron nickel martensite which can be further strengthened by subsequent precipitation of intermetallic compounds during age hardening. These steels have good hot and cold workability, fabricability, and machinability and are easily heat treated without problems of distortion and cracking. In addition, these steels possess very high specific strength comparable to titanium alloys. Supplies of maraging 300 and 350 to very stringent acceptance standards for the Indian nuclear programme have been a feather in the cap for MIDHANI. These development called for careful balancing of chemical compositions as well as control over hot working and heat treatment parameters to achieve uniform fine grained structure free from harmful titanium carbide precipitation and thereby obtain exceptionally high fracture toughness at ultrahigh strength levels. Maraging 400 with an ultimate tensile strength of close to 3000 MPa is under development.

Another important steel is MDN440C, which is a very high carbon martensitic stainless steel that is capable of developing extremely high level of hardness (over R_c 60) and wear resistance. This steel maintains excellent dimensional stability after heat treatment and finds application as critical valve parts and control systems in aerospace and also as bearing component in nuclear sector. MIDHANI manufactured this grade of steel for bearing application. One of the main requirements is that the microstructure should not have any coarse primary carbide that forms banded structure. The primary melting is carried out in air induction furnace and subsequently remelted in ESR. The ingot size is maintained small to minimize segregation because this alloy is highly segregation prone as the carbon content is in excess of 1 wt. %. The ingot is forged, hot rolled to bars. These hot rolled bars are then cut to required lengths, upset and rolled in the forms of rings with adequate reduction so that the carbide network, if any, will be broken. The result is a fine distribution of carbides in the matrix of ferrite.

The main material of construction for component in the nuclear waste management plant is austenitic stainless steel 304L SS particularly 304L -(N). These components are exposed in service to nitric acid of varying concentration at different temperatures. The corrosion behavior of 304L SS NAG (Nitric Acid Grade) in nitric acid is a strong function of materials parameters such as composition, microstructure, sensitization, segregation, cold work etc.

MDN304 NAG (Nitric Acid Grade) specifies a corrosion rate of 5 mils per year (mpy) maximum. This steel is processed in vacuum induction refining furnace to ensure low sulphur and phosphorus. Carbon is lowered below 0.015 wt. % by carbon boil with addition of nickel oxide or iron oxide. In order to eliminate delta ferrite that increases corrosion, austenitic stabilizer such as nickel, manganese etc are kept on the higher end and ferritic stabilizer such as chromium, silicon etc are kept on the lower end of the specified limits. The material is then remelted in ESR to further lower sulphur, silicon and oxygen. The material is then forged and hot rolled to sheets and solution annealed. In this case the corrosion rate directly depends mainly on the carbon content. Material so processed met the corrosion rate specified.

MIDHANI has successfully developed and commercially manufactured several other special steels and catered to specific needs of nuclear sector. Notable among them is the austenitic stainless steel MDN 321. Heavy and hollow cylindrical forgings have been manufactured with close control over grain size and meeting of high temperature tensile property. This called for very close control over hot working parameters. The specification requirement is varied with some application specifying delta ferrite below 2% and others between a range of 4 – 10 %.

Though the specified composition is same, the manufacturer has to aim the chemistry in the specified range in such a way that the final product meets the specification.

6. Materials for fusion applications

Ferritic martensitic steel has been chosen as the main structural material of the breeding blanket modules for DEMO that will be used in the test blanket modules (TBM's). These steels have excellent dimensional stability under irradiation (swelling resistance), better thermo physical and thermo mechanical properties. The objective of development of 'low activation' or 'reduced activation' ferritic steels is the induced radioactivity delay is more rapid that will allow the steels to be disposed of after service by shallow land burial rather than more expensive deep geological storage.

RAFMS steels are similar to modified 9Cr -1Mo ferritic martensitic steel and are obtained mainly by exchanging high activation elements such as molybdenum and niobium with low activation elements such as tungsten and tantalum respectively. High activation tramp elements such as Mo, Nb, Co etc are eliminated or reduced below a very low limit. Strengthening is achieved by means of MX carbonitrides such as vanadium nitride or tantalum nitride, which stabilize the dislocation network, coupled with tungsten to provide solid solution strengthening.

Melting is usually carried out by double vacuum process. This ensures a clean, homogeneous, segregation free and sound input. Hot working is carried out in a controlled range to obtain fine-grained structure. Heat treatment at close temperature ensures less scatter in mechanical properties.

MIDHANI has also taken developmental heats of 304B4 SS (~1 wt. % boron) and 304B7 SS (~2% boron) that is used for neutron shielding and processed them to plates and sheets. Despite the highly reactive nature of the boron (it has a high affinity for oxygen, carbon and nitrogen), steel making practices have been developed to ensure boron contents are within 0.1 wt. % of aim composition. It is virtually insoluble in the solid state, forming a chromium rich boride, a eutectic reaction on solidification. In order to optimize the microstructure, including the boron distribution, the steel is cast into small ingots. Rapid solidification is thus obtained. The presence of a high volume fraction of boride particles in the austenite matrix produces a large reduction in hot ductility. The effective hot working range is 950 – 1150 ^{0}C. During hot working, the eutectic structure of the ingot product is gradually broken down to form a uniform distribution of fine boride particles within the austenite matrix. After hot working it is necessary to restore the ductility by a solution annealing heat treatment.

7. **Conclusion**

Material development is a continuous process. There is need to develop radiation resistant materials that make it possible to increase the burnup and thereby improve the economics of nuclear power. This is possible only when both research institutes and industry work together. Closer interactions in the past has resulted in development of several variants of D9 and modified 9Cr1Mo and identifying the key areas for further R&D works that can be undertaken. In this context MIDHANI is currently developing frontline advanced materials for test blanket module for futuristic fusion reactor.

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