ANALYSIS OF OXIDATION BEHAVIOUR OF SUPER CRITICAL FOSSIL FUEL POWER PLANT MATERIAL INCONEL718 AT TEMPERATURES OF 650°C AND 700°C

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ABSTRACT

Nowadays there is scarcity for electricity in the world so we are in position to increase the performance of the power plant. Around eighty percent of the electricity depends on the coal fired steam power plant. The performance of the power plant is affected mainly by four important factors. One of the important factor is high temperature oxidation which always happen inner and outer tube of steam path. The main objective of this work is to evaluate the oxidation behavior of super heater material which is used in the High temperature application such as super critical boiler. High temperature application operates at elevated temperature range above 650˚C and 700˚C. At elevated temperature, oxidation occurs surface of metal which leads to failure of material. This turns the metal to corrode which interrupts and decrease its functionality of plant. Hence, the selective super heater material (Inconel 718) is selected for this wok. High temperature oxidation behavior is to be analyzed by testing the material in tubular furnace in CO_2 and O_2 environment at 650˚C and 700˚C .The material is to be tested in the furnace by three methods. First one is without coating of metal surface of specimen and second one is with Al_2O_3coating of metal surface of specimen and third one is Cr_2O_3 coating of metal surface of specimen. After the test specimens are to be taken for analyze by SEM and EDX. From that results suitability of the metal for high temperature application in power plant is will be discussed.

I. INTRODUCTION

A. Review on Industrial Practice for Power Generation – Steam Plants:

The initially developed reciprocating steam engine has been used to produce mechanical power since the 18th Century, with notable improvements being made by James Watt. When the first commercially developed central electrical power stations were established in 1882 at Pearl Street Station in New York and Holborn Viaduct power station in London, reciprocating steam engines were used. The development of the steam turbine in 1884 provided larger and more efficient machine designs for central generating stations. By 1892 the turbine was considered a better alternative to reciprocating engines; turbines offered higher speeds, more compact machinery, and stable speed regulation allowing for parallel synchronous operation of generators on a common bus. After about 1905, turbines entirely replaced reciprocating engines in large central power stations. The largest reciprocating engine-generator sets ever built were completed in 1901 for the Manhattan Elevated Railway. Each of seventeen units weighed about 500 tons and was rated 6000 kilowatts; a contemporary turbine set of similar rating would have weighed about 20% as much.

B. Working and Components:

Components of a coal-fired thermal power station:

1. High Pressure Steam Turbine	10. Steam Control Valve	19.Super Heater
2. Cooling Water Pump	11. Cooling Tower	20.Combustion Air Intake
3. Transmission Line (3-Phase)	12. Reheater	21.Economizer
4. Step-Up Transformer (3-Phase)	13. Feed Water Heater	22.Air Preheater
5. Electrical Generator (3-Phase)	14. Coal Conveyor	23.Precipitator
6. Low Pressure Steam Turbine	15. Coal Hopper	24.Draught (Draft) Fan
7. Condensate Pump	16. Coal Pulverizer	25.Flue-Gas Stack
8. Surface Condenser	17. Boiler Steam Drums	16.Bottom Ash Hopper
9. Intermediate Pressure Steam Turbine		

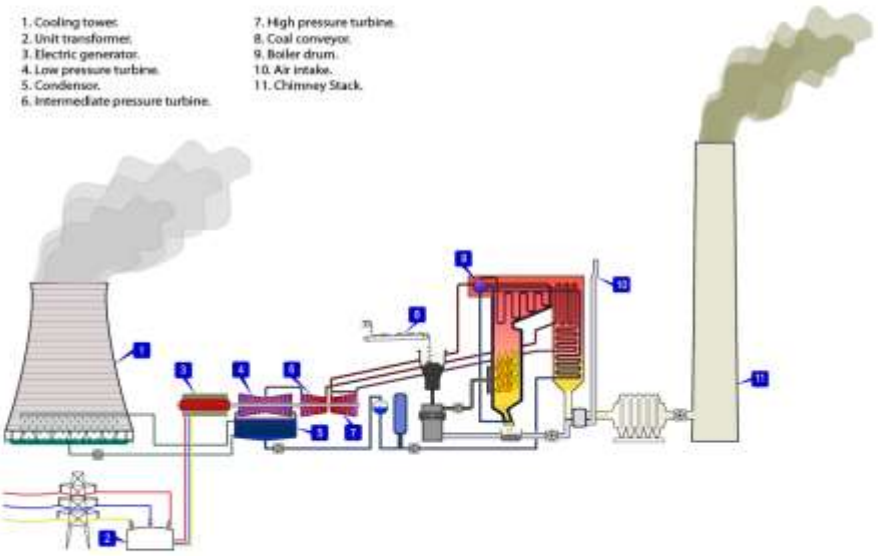

Fig 1: Thermal Power Plant Layout

A thermal power station is a power plant in which heat energy is converted to electric power. In most of the world the prime mover is steam driven. Water is heated, turns into steam and spins a steam turbine which drives an electrical generator. After it passes through the turbine, the steam is condensed in a condenser and recycled to where it was heated; this is known as a Rankine cycle. The greatest variation in the design of thermal power stations is due to the different heat sources, fossil fuel dominates here, although nuclear heat energy and solar heat energy are also used. Some prefer to use the term energy center because such facilities convert forms of heat energy into electrical energy.[1] Certain thermal power plants also are designed to produce heat energy for industrial purposes of district heating, or desalination of water, in addition to generating electrical power. Globally, fossil-fuel power stations produce a large part of man-made CO2 emissions to the atmosphere, and efforts to reduce these are varied and widespread. For units over about 200 MW capacity, redundancy of key components is provided by installing duplicates of the forced and induced draft fans, air preheaters, and fly ash collectors. On some units of about 60 MW, two boilers per unit may instead be provided. The list of coal power stations has the 200 largest power stations ranging in size from 2,000MW to 5,500MW.

Increasing the efficiency of energy production is one method to reduce the carbon dioxide emissions generated, and thus contain the global climate change. Increased level of CO2 in atmosphere derives mostly from combustion of fossil fuels. Since fossil fuels will most probably remain as an important source of energy in the coming decades, increasing the efficiency of energy production will have direct and crucial impact to the greenhouse gas emissions generated. Another method to reduce greenhouse gas emissions generated in combustion of fossil fuels is carbon capture and storage (CCS), which involves capturing the carbon dioxide from the fuel and pumping it to storage where it is not released to the atmosphere. Steam power plants equipped with CCS require considerably more auxiliary power than conventional boilers, so increasing the efficiency is an important step in making CCS economically feasible technology. Two crucial factors affecting on the efficiency of condensing power plant are the temperature and pressure levels of live steam. With improved steam parameters, higher efficiency is achieved. The maximum operating temperatures of structural alloys limit the achievable steam temperature. The final super heaters are exposed to highest temperatures, so proper material selection for those components is crucial in order to achieve high plant efficiency and availability. The materials must have sufficient mechanical high-temperature strength and adequate resistance against corrosion in both inner and outer tube surface. High-temperature strength and corrosion rate depend on the temperature level.

Additionally, corrosion rate is greatly affected by the exposure atmosphere, which in turn is derived from combustion method and fuel on the outer tube surface, and from the water/steam properties on the inner tube surface. This thesis work focuses on the oxidation process taking place on the inner tube surface, which is also known as steam-side oxidation. Other material degradation mechanisms in steam boilers are discussed superficially in order to introduce the challenges in material selection to the reader. The theory section introduces the theory of high-temperature oxidation and factors affecting the oxidation mechanisms in sub- critical and supercritical steam as they appear in public literature.

II. STEAM BOILER TECHNOLOGY

Steam boilers, or steam generators, are an important source of electrical and thermal energy. Steam boiler may be considered to be a heat exchanger which transfers the thermal energy generated by combusting selected fuel in the furnace to the working fluid circulating in the system. The thermal energy carried by the working fluid may be utilized in heating and production of electrical energy. The electrical energy is produced by evaporating the working fluid (water) and using the steam in driving a steam turbine, which in turn drives the electric generator. Majority of electrical energy in the world is produced with this method; see Table 2.1, where sources of electrical energy in the world are listed. Basically, all sources of electricity listed in the table are utilized with steam boilers, except hydroelectric power, wind power and solar power produced with photovoltaic method. Gas and oil may be used in driving a gas turbine, or in a combustion engine which drives electric generator, but also as a fuel in steam boiler.

A. Coal fired power plant

To fully comprehend the solutions to power plant corrosion, lets first review the basic operating conditions and components of a typical coal-fired power facility. The fossil fuel working in a steam turbine plant can be pulverized coal (pc), oil, or natural gas. Here, water is first preheated to a relatively low temperature in feed water heaters and pumped into tubes contained in a boiler. The water is heated to steam by the heat of combustion of pulverized coal in the boiler and then superheated.

B. Thermal power plants

Super critical fossil fuel power plants with efficiencies of 45% have much lower emissions then subcritical plants for a given output .steam temperature is a key factor, which controls the plant efficiency and the emission gas. Increasing the steam operating temperature and the pressure will proportionally increase the plant efficiency with reduction in the emission gas. Materials used in the power plant should withstand against creep and steam oxidation, with increase in the steam operating temperature. The most modern fossil fuel power plant now in operation, reaches efficiencies of around 42% with steam temperature of 600^0 c and pressures of 250 to 300 bar. The next generation of steam power plant should be capable of operating with steam temperatures at 625 to 650 ^{0}c.

Super heaters and re heaters are exposed to highest temperature and pressure levels in boiler steam circulation systems. Therefore the proper material selection is very crucial. The most important criteria for material selection are high-temperature, mechanical strength and creep resistance as well as corrosion and erosion resistance of material. Because of relatively high steam-side heat transfer coefficient, the metal temperature in superheater loops is close to the steam temperature, and less dependent on the furnace temperature.

C. Sub critical power plant.

Energy is an important ingredient of development in economic aspect for the countries. The growth of economic development is directly or indirectly related to production and consumption of energy. Power plants using conventional fossil fuels are supplying more than 70% of the total World's electricity production. Economic growth as well as standard of living increases due to the higher energy demand. Currently, demand for all global energy is increasing at an average rate of approximately 2% per annum. Most of the electrical power used worldwide is produced by the use of Rankine cycle which may be driven by various kinds of heat sources (coal, gas, oil, nuclear, solar) and uses steam as the chief working fluid. World electricity generation is expected to double over next20-25 years, and correspondingly, coal-fired power plants that produce 41% of the total world electricity are projected to generate 44% of the total in 2030.The study of thermodynamic cycles applied to power generation is of great importance due to the increasing consumption of energy and widely opened electricity markets. Steam is the most common working fluid used in vapor power cycles because of its many desirable characteristics, such as low cost, availability, and high enthalpy of vaporization.

Supercritical steam cycle technology has been used in the2recent years and is becoming the system of best choice for new coal-fired plants in many countries, because of the high performance, to compare to sub-critical coal-fired power plants. Hence, the efforts to develop high temperature steam supercritical power plants have become more important. Fossil fuel (coal, oil and natural gas) power plants can be built almost anywhere so long as one can get large quantities of fuel to it.

Coal is still the key fuel for power generation from the view of “best-mix energy policy”. World has abundant proven reserves of coal and thus coal based thermal power plants dominate almost everywhere. Energy, in general, and electricity in particular, plays a vital role in improving the standard of life everywhere.

India is the 6th largest energy consumer in the world. Nearly 70% of electricity produced in India is by thermal power plants, where coal is used as a fossil fuel. It is predicted that, coal will be available in India for at least 119 years more.

III. METHODOLOGY

A. Procedure For Specimen Material Preparation

1. Cutting

When cutting a specimen from a larger piece of material, care must be taken to ensure that it is representative of the features found in the larger sample, or that it contains all the information required to investigate a feature of interest. One problem is that preparation of the specimen may change the microstructure of the material, for example through heating, chemical attack, or mechanical damage. The amount of damage depends on the method by which the specimen is cut and the material itself. Cutting with abrasives may cause a high amount of damage, while the use of a low-speed diamond saw can lessen the problems. There are many different cutting methods, although some are used only for specific specimen types. MTI provides the SYJ-150 low speed diamond saw for cutting OM (optical microscope), SEM (scanning electron microscope), and even TEM (transmission electron microscope) specimen.

2. Lapping

The lapping process is an alternative to grinding, in which the abrasive particles are not firmly fixed to paper. Instead a paste and lubricant is applied to the surface of a disc. Surface roughness from coarser preparation steps is removed by the micro-impact of rolling abrasive particles.

3. Grinding

Surface layers damaged by cutting must be removed by grinding. Mounted specimens are ground with rotating discs of abrasive paper, for example wet silicon carbide paper. The coarseness of the paper is indicated by a number: the number of grains of silicon carbide per square inch. So, for example, 180 grit paper is coarser than 1200 grit. The grinding procedure involves several stages, using a finer paper (higher number) each time. Each grinding stage removes the scratches from the previous coarser paper. This can be easily achieved by orienting the specimen perpendicular to the previous scratches.

4. Polishing

Polishing discs are covered with soft cloth impregnated with abrasive diamond particles and an oily lubricant or water lubricant. Particles of two different grades are used a coarser polish - typically with diamond particles 6 microns in diameter which should remove the scratches produced from the finest grinding stage, and a finer polish typically with diamond particles 1 micron in diameter, to produce a smooth surface. Before using a finer polishing wheel the specimen should be washed thoroughly with warm soapy water followed by alcohol to prevent contamination of the disc. The drying can be made quicker using a hot air drier. Mechanical polishing will always leave a layer of disturbed material on the surface of the specimen. Electro polishing or chemical polishing can be used to remove this, leaving an undisturbed surface.

5. Preparation of material-alloy 718

The samples were manually polished on silicon carbide (SiC) papers with a fine roughness of 600-1000 grit and also machinery polished (Disc polishing). After polished the material to be washed and subsequently cleaned in Acetone. Above the processes should be finished then the material is cutting in the size of 10 x 10 mm by using WIRE CUTTING machine. The thickness of the specimen is 5mm. After the cutting process the specimen should be coated by high temperature oxidation coating. We choose the two coating name is Nickel – Chromium (both are mixed equally) and Inconel coating. Thickness of the coating is 0.1mm.

Thermal conductivity (K) in W/mk for

- Aluminum oxide (Al2O3)
- Chromium oxide (Cr2O3)
- Inconel

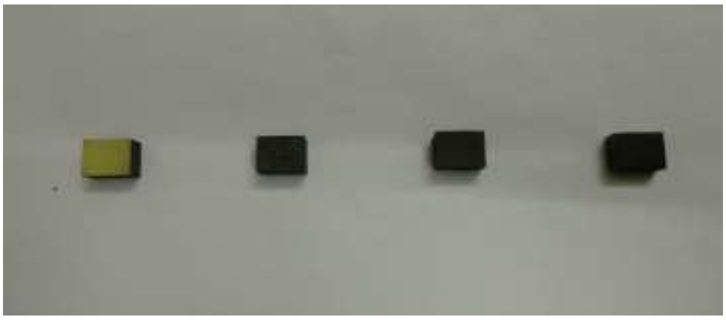

Fig 2: Inconel Material

6. Thermal spraying

Thermal spraying is one of the most versatile hard facing techniques available for the application of coating materials used to protect components from abrasive wear, adhesive wear, erosive wear or surface fatigue and corrosion. Generally, any material which does not decompose, vaporize, sublimate, or dissociate on heating, can be thermally sprayed. Consequently a large class of metallic and nonmetallic materials (metals, alloys, ceramics, cermets, and polymers) can be deposited by thermal spraying.

(1) Flame spraying with a powder or wire,

(2) Electric arc wire spraying,

(3) Plasma spraying,

(4) Spray and fuse,

(5) High Velocity Oxy-fuel (HVOF) spraying,

(6) Detonation Gun.

The technique of thermal spraying has developed at a fast pace due to progress in the advancement of materials and modern coating technology. Plasma-sprayed ceramic coatings are used to protect metallic structural components from corrosion, wear and erosion, and to provide lubrication and thermal insulation [33]. In particular, coatings made of Al2O3 containing 13 wt% TiO2 (Al2O3-13 wt% TiO2) are commonly used to improve the wear-corrosion and erosion resistance of steel. In conventional plasma-spray processing of Al2O3-13 wt% TiO2 coatings, powder particles are injected into a plasma jet, causing them to melt into droplets that are propelled towards the substrate .Solidification of the droplets stream onto the substrate as "splats" results into the buildup of the coating, typically 100-300μm thick.

7. Oxidation kinetics

Whether the oxidation takes place on the scale-gas interface or metal-scale interface, ion diffusion through the oxide scale is a very important rate controlling factor. If the oxide layer acts as a diffusion barrier for oxygen or metal ions or as an insulating layer, the rate of oxidation slows down when the oxide scale becomes thicker. That is, of course, if the oxide layer is presumed to be compact and adherent. In this case, the oxidation rate can be described by a *parabolic* relationship,

Oxidation were taken into account, a constant, off-setting parameter should be usually the effect of transient oxidation is ignored for simplicity because it has only little practical purpose.

This leads to fact that the calculated oxide scale thicknesses or mass gains have always slightly lower values than actual values. If the oxide scale does not prevent diffusion, the oxidation rate follows *linear* relationship

$$w^2 = 2k_p t$$

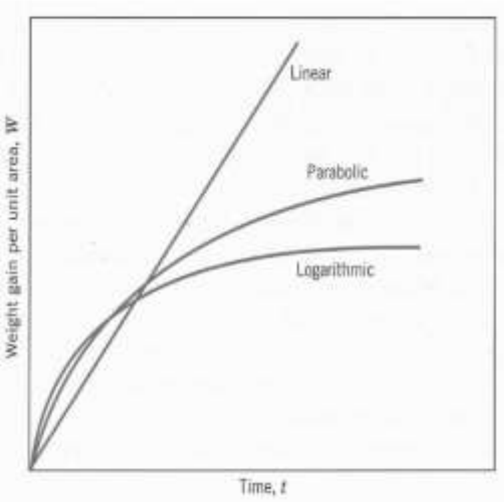

Fig 3: Oxidation behavior

Where *W* is weight gain per unit area, *t* is time and kp_r is the parabolic rate constant, which is a time-independent constant at a given temperature. An idealized case, because the protective scale is assumed to grow by parabolic rate from the beginning of the exposure. In practice, when a "fresh" metal surface is exposed to oxygen atmosphere, there is always an initial stage where the overall oxidation rate is usually much faster. This initial oxidation stage is also called transient oxidation stage.

8. Material description:

Inconel 718, Alloy 718, UNS N07718

Table:1 Chemical Composition

Composition of the alloy [% weight]						
Ni+Co	**Cr**	**Mo**	**Nb+Ta**	**Ti**	**Al**	**Fe**
Investigated Inconel 718 alloy						
53,7	17,9	2,9	5,22	1,0	0,49	Bal.

Table:2 Technical Specification of furnace

Quantity Supplied	1
Operating Voltage	230 VAC, 1-Phase, 50 Hz
Power Consumption	4 KW
Inner Chamber	310 S.S tube (60mm ID x 400mm hot zone)
Maximum Temperature	1000 ^{0}C
Skin Temperature	Not more than 75 ^{0}C
Temperature control	Digital Programmable - Temperature indicator & Controller
Thermocouple	K type

Initially the material which is to be tested should be selected after that high temperature oxidation environment to be created by tubular furnace at the temperature of around 1000°**C** with CO_2 and O_2 cylinder. And then specimen to be prepared for required specification. The prepared specimen surface is to be modified by Nano- coating of metal oxides. After that it is to be tasted in the experimental setup. Next to testing the specimens are to be analyzed by SEM and EDX Machines. Finally the results may be discussed to find the suitability of material for application of supercritical power plant. For the same work, the equipment is designed to carry out the desired project. Initially, the equipment is designed to withstand 1000°C which can be operated at normal alternating current supply. The manual switches are ON/OFF for main supply and furnace, Voltage indicator, PID controller for programming. Since, the experiment is designed to run programming. From the furnace equipment, PID is the heart of the furnace, which controls the entire operation. It is made of Stainless Steel of 310 series having 60mm inner diameter and 750mm running length. From the length 350mm is the uniform hot zone.

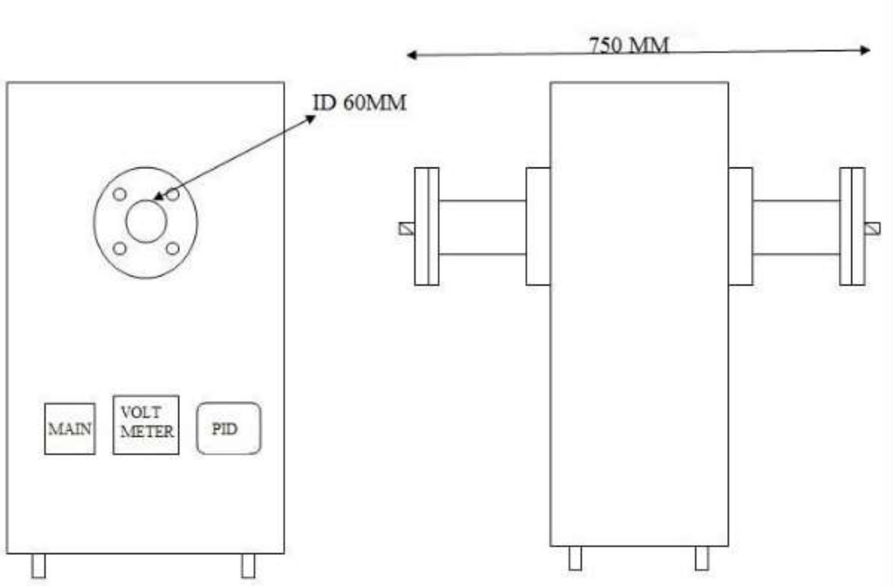

Fig 4: Furnace

PID controls the whole operation, so that the operations are programmed to segments. Each segment provides individual timings for furnace operations. Totally it consists of 2 patterns of 16 segments. PID holds various unique features such as Auto tuning, combined operating pattern, Alarm etc.PID controls the whole operation, so that the operations are programmed to segments. Each segment provides individual timings for furnace operations. Totally it consists of 2 patterns of 16 segments. PID holds various unique features such as Auto tuning, combined operating pattern, Alarm etc.

Fig 4: Furnace

Fig 5: Furnace with Co_2 and O_2 cylinder arrangement

The construction setup consists of

- Furnace
- Regulator
- Flow meter
- Co_2 and O_2 cylinder

The initial weight of specimens is measured by weighing balance. The furnace is ON to insert our testing specimen. Our testing materials are three different coated material such as Un-Coated, Aluminum and chromium. Before performing the oxidation experiment we check the surface area of samples were measured with a digimatic caliper and weighed on a precision balance. After finish the above procedure to insert the specimen in the furnace with the help of boat. The Temperature of the Furnace will be programmed at 650°c and 700˚c. The Temperature will reach 650°c and 700˚c then the steam and O2 gases are passes through the Furnace. Every 10hours the Specimen will Kept from the Furnace and the Weight of specimen should be measured. The weight should be change due to hot flow gases. The Same Procedure is Repeated for every 10 hours. Totally, 100hours the reading will be noted and graphed.

9. Scanning Electron Microscopy:

It is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image.

SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, in wet conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures. The most common mode of detection is by secondary electrons emitted by atoms excited by the electron beam.

10. Energy-dispersive X-ray:

Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum.

To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons (see PIXE), or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray.

The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS allows the elemental composition of the specimen to be measured.

CONCLUSION

To analyze the high temperature oxidation behavior of super heater material (Inconel-718), the material was cut into small pieces and then polished with emery sheet and disk polishing and it was cleaned with acetone. The cleaned specimens were coated with Nano particle of Aluminum oxide and Chromium oxide and to analyze the coated specimens these are to be kept inside the furnace at temperature of 650ºC and 700ºC upto100hours in CO_2 and O_2 environment. Based on the results from the experimental test and the test specimens are to be taken for analyze by SEM and EDX. From this results super heater material (Inconel-718) is suitable of the high temperature application in power plant is proven.

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