

CORRELATION BETWEEN ULTRASONIC PARAMETERS, MECHANICAL PROPERTIES AND MICROSTRUCTURES OF MOD T91 FERRITIC –MARTENSITIC STEEL (PFBR)

Ramachandran.K¹, Arun.M², Vaidehi Ganesan³ & Sivaraja.M⁴

¹ Assistant Professor, Dept. of Mech Engg., N.S.N. College of Engg. & Tech, Karur, India, Mail ID: ramachandrakmech@gmail.com

² Assistant Professor, Dept. of Mech Engg., N.S.N. College of Engg. & Tech, Karur, India, Mail ID: mparun87@gmail.com

³ Materials & Metallurgy division, Indira Gandhi Centre for Atomic Research, Kalpakkam, India, Mail ID: vaidehi.ganesan@gmail.com

⁴ Principal, N.S.N. College of Engg. & Tech, Karur, India, Mail ID: m.shivaraj2006@gmail.com

ABSTRACT:

Mod T91 ferritic martensitic steel is used as steam generator material in Prototype fast Breeder Reactor (PFBR). The objective is to determine the long term aging characteristics of modified T91 (Steam generator material). In general, steam inlet temperature is 525°C & outlet temperature is 490°C in PFBR. Results of low temperature aging (around 400°C) for higher durations and high temperature (650°C) aging for lower durations are expected to be comparable. This is an accelerated test to check the stability of the material after high temperature and long durations. This is an out of pile experimental study to check the stability of the material at various conditions (650°C - 5000, 10000, 20000hrs).

The research allowed the identification of micro structural changes that take place during long term aging and their influence on mechanical properties of ferritic-martensitic Mod T91. The microstructures were characterized for the aged Mod T91 material using light metallography, Scanning Electron Microscopy and Transmission electron microscopy.

The Light Microscopic results reveal the lath type martensitic structures in the as received specimen (1050°C Solution Annealing in 2 Hrs & 650°C Tempering in Few Hrs) and tempered martensitic structures and phases formation are confirmed in the long term aged specimen. The phase composition of the steam generator material and the chemical composition of the MC, M₂₃C₆ type phases and silicides/silicates phases formed after long-term aging were determined using SEM-EDAX results. The SEM results reveal the presence of carbonitrides (bigger & smaller in size) and

metallic silicides/silicates. Presence of small size carbonitrides improve the mechanical properties of the material in the initial aging conditions and bigger size carbonitrides will decrease the mechanical properties of the material in the long term aged conditions. Presence of higher silicon content & its segregation also confirmed from the SEM- EDAX analysis in the higher aged specimens. The TEM results reveal the presence of fine scale martensitic structure in the as received specimen and globular carbonitrides in 20000hrs aged specimen. Metallic silicides are also present in 10000 & 20000hrs aged specimens. Presence of these metallic silicides/silicates will decrease the creep strength and toughness of the materials.

The mechanical properties of Mod T91 ferritic-martensitic steel are studied by hardness measurement and elastic modulus determinations. Ultrasonic attenuation and velocity were determined and reported. Elastic modulus was determined using velocity data. Reduction in hardness values in 10000 & 20000hrs are due to the presence of silicides/silicates & tempered martensite structures. Lower attenuation and lower modulus values in 10000hrs aged specimen are also due to the presence of silicides. These results were correlated with micro structures. The present work is helpful to understand the material degradations due to long term aging conditions and to further improve the alloy for future applications. The results and analysis are discussed in detail in the paper.

INTRODUCTION

A modified 9Cr-1Mo steel (T91) has been chosen as the material for the steam generator of the 500 MW (e) fast breeder reactor

under construction at Kalpakkam, India. Plates of various thicknesses were developed indigenously by Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, in collaboration with the Indian Steel Industry. The modified 9Cr–1Mo steel is being used extensively as structural material for steam generator components of liquid metal cooled fast breeder reactor and fossil fired power plants. The selection of this material is primarily based on a good combination of mechanical properties, high thermal conductivity, low thermal expansion coefficient and good resistance to stress corrosion cracking in water–steam systems compared to austenitic stainless steels and better monotonic tensile and creep strengths at elevated temperatures compared to plain 9Cr–1Mo steel. The alloy also exhibits good weldability and micro structural stability over very long periods of exposure to high temperature service conditions [1].

The 9–12%Cr–Mo ferritic/martensitic steels are some of the candidates being considered for the new-generation reactor parts such as reactor vessels, pipes or spallation target [2, 4]. The good mechanical properties of these steels are due to their complex microstructure [3]. The martensitic microstructure improves the creep resistance thanks to its high dislocation density. The high chromium content ensures a high resistance to both corrosion and oxidation, and the addition of 1% of molybdenum increases the austenization temperature and the solution hardening. These elements form $M_{23}C_6$ carbides and Nb(C, N) carbo-nitrides, which increase the creep resistance by precipitation hardening. This alloy also presents a low-swelling character and a low expansion coefficient

An understanding of the micro structural and micro chemical changes during thermal exposure is necessary to assess the stability and performance of the steel for an industrial application. A detailed study on micro structural evolution in modified 9Cr–1Mo steel at different temperatures and time durations has been carried out. Based on these studies, an attempt is being made to obtain a correlation between ultrasonic

parameters, mechanical properties and microstructures of mod T91 ferritic steel are discussed [5-9].

2. EXPERIMENTAL WORKS

The chemical composition of the as-received (Mod T91) material is given in Table 1. The objective is to determine the long term aging characteristics of modified T91 (Steam generator material). In general, steam inlet temperature is 525°C & outlet temperature is 490°C in PFBR [10]. Results of low temperature aging (around 400°C) for higher durations and high temperature (650°C) aging for lower durations are expected to be comparable. As received specimen were subjected to a 1050°C Solution Annealing in 2 Hrs and 650°C Tempering in Few Hrs. In order to verify the Long Term stability of the Mod T91, thermal aging at 650°C has been carried out in different specimens for durations of 5000hrs, 10000hrs, and 20000hrs.

The heat treated specimens were prepared metallographically by standard preparation procedures. Mod T91 ferritic steels are widely used for high-temperature structural applications in the power generating industries. When these steels are exposed to high temperatures for a long period of time, however, they generally undergo a softening of the matrix, because of the coarsening of secondary phases and the recovery of dislocations [11]. Therefore, in order to assess the lifetimes of the components made of this type of steel, it is essential to quantitatively evaluate its microstructure.

To monitor the micro structural degradation of structural steels, various techniques have been employed such as Optical Microscopy, Scanning Electron Microscopy and Transmission Electron Microscopy. The mechanical properties have been evaluated from conducting experiments like Hardness measurement & Elastic Moduli determination using ultrasonic technique.

C	Cr	Mo	Mn	Ni	P	Si	V	Co	Nb	Cu	N	Fe
0.1	9.0	1.00	0.07	0.12	0.02	0.43	0.22	0.02	0.12	0.07	0.03	bal

Table 1 The chemical composition of the As-received (Mod T91) material

2.1 CHARACTERIZATION

The heat treated specimens were prepared metallographically by standard preparation procedures. Mod T91 ferritic steel was chemically etched by Vilella's reagent for both Optical and SEM analysis. It contains 1gm of picric acid and 5 ml of HCL in 100ml Ethanol. The chemical compositions of segregations which were present in the material were analyzed in the SEM with an energy dispersive X-ray spectrometer (EDAX). The technique was used in order to identify the precipitates of metallic carbides and its composition on the aged specimen. Surface morphology was studied by Scanning Electron Microscopy with Energy Dispersive Spectroscopy. The SEM & EDAX (PHILIPS) available at IGCAR, Kalpakkam.

The changes in lath and dislocation density inside the lath structure with aging were determined by TEM. Analytical Transmission Electron Microscopy (TEM) was carried out on thin foils to study the structure and chemical analysis [12]. Thin foil for transmission microscopy was prepared by window thinning method using 10% perchloric acid in methanol as electrolyte. The prepared thin foils of less than 100µm were analyzed in JEOL HRTEM, available in PSG Institute for advanced studies at Coimbatore. A detailed analysis of carbide precipitates was made in terms of their observed morphology and distribution, and their composition confirmed by the EDS and electron diffraction analysis.

2.2 MECHANICAL PROPERTIES

2.2.1 Hardness Measurement

Vicker's hardness (HV) measurements have been carried out on the samples at room temperature using micro hardness tester. A sharp diamond indenter, a three sided pyramid with the same area to depth ratio was used as an indenter. An indentation made at a selected position on the polished surface of the sample. For each sample, at least five indentations were made by applying a load of 500gms for 15 sec duration. The average values are also presented.

2.2.2 Density Measurement

Density of the sample was measured at room temperature, employing Archimedes's principle. Therefore, the density of the samples measured at room temperature was used for the determination of the elastic moduli at various durations at 650°C. All the weight measurements were made using the model Mettler-Toledo SAG 285 balance.

2.3 ULTRASONIC PARAMETERS

Ultrasonic testing uses sound waves of short wavelength and high frequency to detect surface and subsurface flaws and measure thickness of material. Using this average measured thickness values and Transit time of respected specimens to calculate longitudinal velocity of the material. Pulse Echo Testing technique and longitudinal type of probe is used for ultrasonic testing. Equipment ESM 2M with probe frequency 5MHz and 30mm probe diameter available at IGCAR, Kalpakkam is used for Ultrasonic testing. Sound velocity testing is one method for characterization of physical

properties of materials. These measurements allow rapid and reliable determination of the elastic moduli like young's modulus, bulk modulus, shear modulus and transverse velocity of the material.

3. RESULTS & DISCUSSION

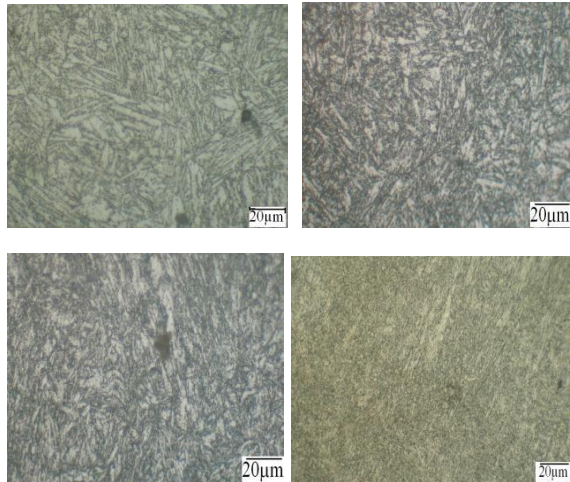


Fig.1. Optical Microscopy Image (A).As received (B) 5000Hrs
 (C) 10000Hrs (D) 20000Hrs

The microstructures taken from the different heat treated specimens are shown in Figures.1. (A) to 1. (D). These images are obtained at the magnification of 500X. The Optical microscopy image shows the presence of plat or lath type martensite structures in Mod T91 (as received) Specimen. Microstructure shows that Mod T91 (as received) specimen is not 100% martensites material. There is Ferrite & metallic carbonitrides are observed in the initial material. The martensites get tempered with aging treatment and plate size is increasing with aging time.

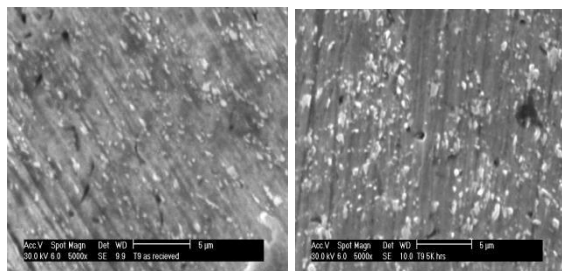
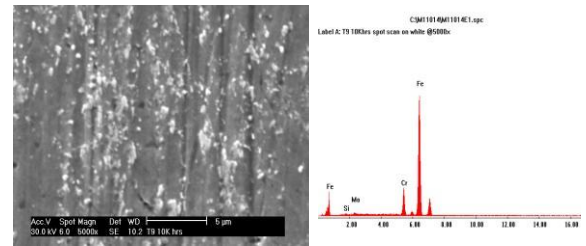
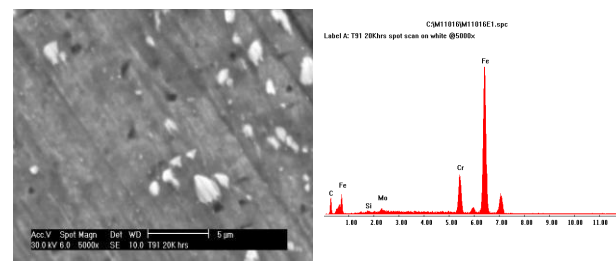


Fig.2.SEM Images (A)As Received (B) 5000 Hrs Aged



Element	Wt %	At %	K-Ratio	Z	A	F
SiK	1.36	2.68	0.0032	1.1046	0.2103	1.0026
MoL	2.86	1.65	0.016	0.9328	0.5982	1.0013
CrK	10.78	11.47	0.1234	0.9964	0.9496	1.2096
FeK	85	84.21	0.7886	1.0008	0.927	1
Total	100	100				

Fig.3.SEM & EDAX Image of 10000Hrs



Element	Wt %	At %	K-Ratio	Z	A	F
C K	41.07	76.29	0.1105	1.0845	0.2481	1.0003
SiK	0.36	0.29	0.0011	1.0312	0.3059	1.0019
MoL	1.32	0.31	0.0099	0.8713	0.8579	1.0013
CrK	8.06	3.46	0.0891	0.925	1.021	1.1717
FeK	49.2	19.66	0.4504	0.9289	0.9856	1
Total	100	100				

Fig.4.SEM & EDAX Image of 20000Hrs

The SEM Microstructures & EDAX (Energy Dispersive Analysis of X-rays) taken from the different aging time (hrs) at 650°C are shown in Figure 2 to 4, these images are obtained at the magnification of 5000X. Microstructure shows that grain size is increasing with aging time. Carbon peak is present in figure 4 EDAX results. It indicates carbonitrides, since Mod T91 contain nitrogen. Both Figure 2(B) and 3 shows the metallic silicides (White). It will decrease the mechanical properties of the material. Figure 2 (A&B) shows the smaller size carbonitrides. Smaller size carbonitrides to increase the mechanical properties. Figure 4 (20000Hrs Aged) shows the bigger size carbonitrides. It decreases the mechanical properties of the material.

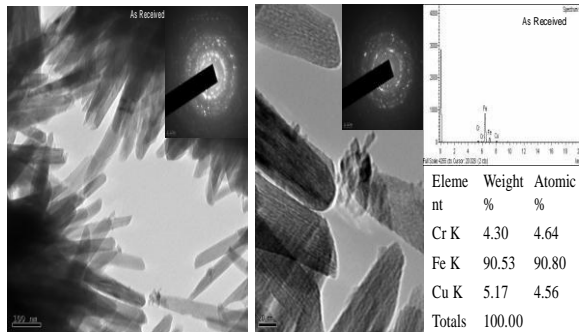


Fig.5 TEM, SAED & EDAX Image of As Received

Figure 5 shows the TEM image, SAED and EDAX analysis result of As Received Mod T91 material. TEM image shows the very fine nano size martensites rod. In this region, EDAX results shows decrease in percentage of Cr & increased percentage of Fe.

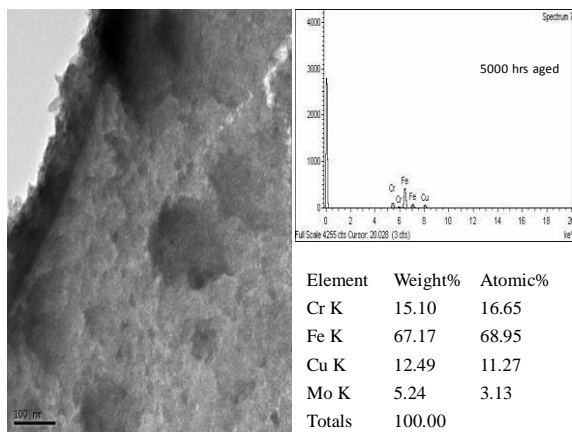


Fig 6 TEM & EDAX Image of 5000Hrs

Fig 6 shows the composition analysis using EDAX on the black spot region. It shows the higher content of chromium and lower percentage of Iron present. This black spot region is confirmed as carbonitrides.

Figure 7&8 shows the TEM image, SAED and EDAX analysis result of 10000Hrs Aged Mod T91 material. It shows the presents of metallic silicides and carbonitrides.

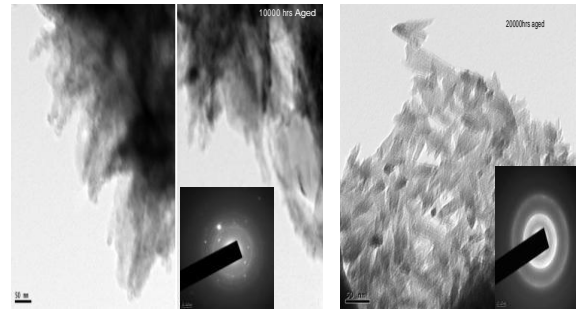


Fig.7 TEM & SAED Images of 10000Hrs

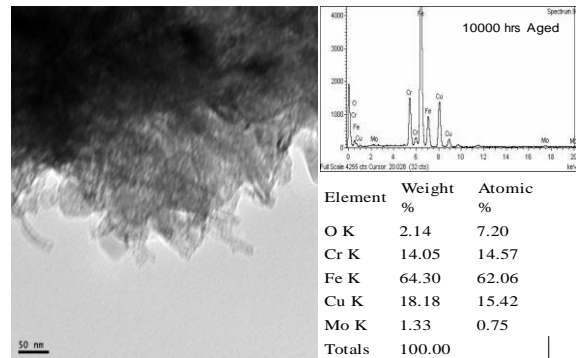


Fig.8 TEM, SAED & EDAX Images of 10000Hrs

Figure 9 shows the TEM image & EDAX analysis result of 20000Hrs Aged Mod T91 material. It shows the presents of martensites and globular carbonitrides. There is

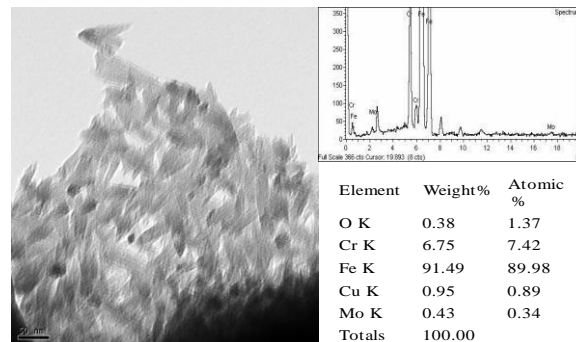


Fig.9 TEM & EDAX Images of 20000Hrs

Fig 10 shows the TEM & SAED images of 20000Hrs Aged specimen. It shows the tempered martensites and carbonitrides. Micro crack present in this TEM image during sample preparation. This is due to condition of the material.

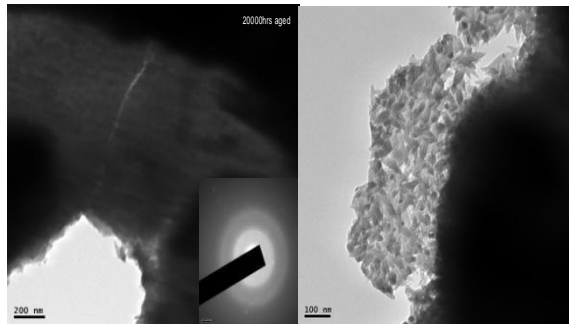


Fig.10 TEM & SAED Images of 20000Hrs

Hardness & Density Measurement

The table 2 shows the hardness values measured from the different heat treated specimen. Increase in hardness aging at 5000hrs (7646kg/m³ 228HV) due to smaller size carbonitrides (Fig 2 A&B). The slight decrease in hardness at 10000hrs and appreciable decrease in hardness at 20000hrs due to segregation of Si, which reduce mechanical strength.

Aging time (hrs) at 650°C	Micro Hardness (HV)					
	Location 1	Location 2	Location 3	Location 4	Location 5	Average
As-received	225	226	228	224	226	226
5000	234	227	223	232	223	228
10000	219	220	217	223	220	220
20000	183	181	183	184	174	181

Table 2. Hardness values of different heat treated specimen

The table 3 shows the density and impedance values measured from the different heat treated specimen. Decrease in density and impedance values at 10000hrs due to tempered martensites and silicides formations. Ultrasonic impedance is resistance offered to ultrasonic wave propagation. Decreases in impedance indicate reduction in strength.

Aging time (hrs) at 650°C	Sample 1	Sample 2	Density(ρ) Kg/m ³	Ultrasonic Impedance(Z) (kg/m ² .s)x10 ⁶
As-received	7.588	7.650	7.619	46.29
5000	7.671	7.621	7.646	48.27
10000	7.580	7.633	7.606	42.60
20000	7.614	7.619	7.616	45.49

Table 3 Density & Impedance values of different heat treated Mod T91

Ultrasonic Velocity

Table 4 shows the ultrasonic velocity of different duration of aging specimens. It shows the decrease in velocity values during 10000hrs aging time due to silicides formation (refer 10000hrs SEM Image). During 20000hrs aging time, there is also reduction in velocity (as observed in Fig 4) due to tempered martensites and carbonitrides.

Aging time (hrs) at 650°C	Longitudinal velocity (m/s)				Transverse velocity (m/s)
	Location 1	Location 2	Location 3	Average	
As-received	6075.77	-	-	6075.77	3247.67
5000	6332.50	6298.82	6312.31	6314	3385.35
10000	5600.27	2269.12	5639.71	5602	3003.51
20000	6009.00	5964.23	5946.50	5973	3202.21

Table 4 ultrasonic velocity of different heat treated Mod T91

Elastic Modulus Calculation

Elastic Modulus of young's modulus; shear modulus and Bulk modulus at different heat treated are shown in table 5. It shows the decrease in elastic modulus values during 10000hrs aging time. This is due to silicides formation (refer 10000hrs SEM Image). This silicides formation, decrease the mechanical properties of the material.

Aging time(hrs) at 650°C	Young's modulus (Gpa)	Bulk modulus (Gpa)	Shear modulus (Gpa)
As-received	208.93	167.41	80.35
5000	226.43	181.43	87.62
10000	177.30	142.06	68.61
20000	201.84	161.69	78.09

Table 4 Elastic Modulus values of different heat treated ModT91

CONCLUSIONS

Aged Mod T91 material was characterized using Optical microscopy, SEM and TEM. The lath structure is stable in certain regions even after 10000hrs of aging at high temperatures.

Ultrasonic technique was used to determine impedance, attenuation, velocity & elastic modulus and it is reported.

Carbides in modified 9Cr-1Mo steel grow with aging time and temperature. The coarsening of V (Nb) carbides was negligible compared to $M_{23}C_6$ carbides [13]. The 'Z' phase normally forms in 9-12% Cr- Mo.T91 is modified with 'N' addition (not stabilized). Steel containing more than 10.5% Cr strongly accelerates Z phase precipitation which leads to reduction in mechanical properties. Steels not formed in this Mod T91 material have Z phase after aging at 20000hrs (650°C). The 'Z' phase formation reduces the creep strength. In this work possibility of Z phase formation is low due to aging at 20000 hrs [14].

Silicides formations and segregations decrease the mechanical properties. Its is better to have very low impurity elements (Si, S, P, etc.) in the alloys for better service. These impurity elements have tendency to segregate on grain boundaries during long term aging at high temperature.

Results of this work will be very useful for the in-service inspection of PFBR components, in order to evaluate the microstructure and mechanical properties using ultrasonic parameters. Health of various components is assessed during the service life of the plant to ensure that no failure results in the actual service condition of the component.

This laboratory experiments and data generation will be useful for quality Control of the material during pre-service and in- service inspection of engineering components.

REFERENCES

- [1] A. Nagesha, M. Valsan, R. Kannan, K. Bhanu Sankara Rao , S.L. Mannan Materials Development Group, Indira Gandhi Center for Atomic Research, Kalpakkam 603 102, Tamil Nadu, India, 15 March 2002
- [2] R. Klueh, A. Nelson, J. Nucl. Mater. 371 (2007) 37–52.
- [3] F. Abe, Sci. Technol. Adv. Mater. 9 (2008) 1–15.
- [4] J. Henry, T. Auger, Y. Die, Materials Issues for Generation IV Systems Status, Open Questions and Challenges, NATO Science for Peace and Security Series, 2008, pp. 575-584
- [5] W.B. Jones, C.R. Hills, D.H. Polonis, Metall. Trans. 22A (1991)427.
- [6] R. Kishore, T.K. Sinha, Metall. Mater. Trans. 27A (1996) 3340.
- [7] V.S. Dwivedi, B.K. Jha, Mater. Sci. Eng. A301 (2001) 221.
- [8] A.P. Greeff, C.W. Louw, H.C. Swart, Corros. Sci. 42 (2000) 1725.
- [9] V. Moorthy, S. Vaidyanathan, B. Raj, Metall. Mater. Trans. 31A (2000) 1053.
- [10] Indira Gandhi Centre for Atomic Research, Kalpakkam, India-1998_Blue Brochure
- [11] Evaluation of quasistatic fracture toughness of a modified 9Cr-1Mo (T91) steel G. Sasikala, S.K. Ray Materials Technology Division, Indira Gandhi Center for Atomic Research, Kalpakkam 603102, India ,11 June 2007
- [12] The Preparation of Thin Foils of Metal Surfaces for Transmission Electron Microscopy D. J. Duquette Anij L. P. Lemaire Advanced Materials Research and Development Laboratory Pratt and Whitney Aircraft, Middletown, Connecticut.
- [13] Micro structural stability of modified 9Cr-1Mo steel during long term exposures at elevated temperatures V. Thomas Paul, S. Saroja *, M. Vijayalakshmi.
- [14] HimlarK. Danielsen and John Hald "Influence of Z phase on long term creep stability of martensitic 9-12% Cr steels. VGB power tech 5(2009)68-73.