Clean Steel: Superclean Steel

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Proceedings of a Conference organised by
The Institute of Materials
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The Electric Power Research Institute, California, USA

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THE INSTITUTE OF MATERIALS

Book 635
Published 1996 by
The Institute of Materials
1 Carlton House Terrace
London SW1Y 5DB

ISBN 0 901716 90 1

British Library Cataloguing-in-Publication Data
A catalogue record of this book
is available from The British Library

Cover picture courtesy of
Y. Ikeda, H. Yoshida, Y. Tanaka and T. Fukuda (see p.80)

Typeset by
Fakenham Photosetting Ltd
Fakenham, UK

Printed and bound at
The University Press
Cambridge, UK

Preface

The improved understanding of the factors leading to the long term in-service embrittlement of L.P. rotors which developed from basic research carried out in the 1970s enabled the late Bob Jaffee to formulate his ideas for the production of superclean steels. A history of the progress from experimental studies to actual rotors has been recorded in the proceedings of four previous workshops organised by the Electric Power Research Institute of Palo Alto, California, U.S.A.

The proceedings of the Fifth Workshop are recorded in the present volume which appears some three years after that of the Fourth Workshop.

The progress during the intervening period, as outlined in the twenty one papers presented, has been extensive. Not only have the properties of superclean 3.5Ni–Cr–Mo–V steels been thoroughly established, the economies of their production has been assessed and the extent of their use in the power generation industry has been recorded.

The concepts involved with the already developed superclean steels are applicable to a wider range of steels than the conventional 3.5Ni–Cr–Mo–V varieties. Already some progress is now being made with the development of single shaft HP–LP rotor steels to a superclean specification and the same comment applies to the more highly alloyed 9–12% Cr steel, where, once again, low residual contents are found to alleviate the long-term embrittlement problems.

It is also clear that the superclean steels can be used for other than conventional power generation equipment. The use of these improved materials for general pressure vessels, nuclear components and the petro-chemical industry's pressure vessels is now becoming more widespread, where the requirement is to minimise in-service embrittlement at elevated temperatures. But, superclean steels also have excellent fracture toughness, at around ambient temperatures, with good stress corrosion resistance and these characteristics have led to the application in off-shore structures.

It is not surprising, therefore, that there is considerable interest in the future development and applications of superclean steels. Many views were expressed on these topics at a round table discussion, a summary of which is given in the proceedings.

The Editors of the proceedings are grateful to the other members of the organising committee for their unstinted help and to Miss Lisa Davies of The Institute of Materials, for her assistance as General Organiser of the Conference. Many others helped, but in particular, our thanks are due to Monsieur André Coulon, for his continued interest and advice.

We hope that the present volume will be looked upon as a further fitting tribute to the memory of the late Bob Jaffee.

J. Nutting and R. Viswanathan.

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Application of Clean Steel/Superclean Steel Technology in the Electric Power Industry – Overview of EPRI Research and Products

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1. INTRODUCTION

The adverse effects of impurity elements phosphorus (P), antimony (Sb), tin (Sn), arsenic (As), sulphur (S), oxygen (O), and deoxidants aluminum (Al) and silicon (Si) on the mechanical properties of steels have been known for many decades. P, Sb, Sn and As interactively with Si and Mn cause temper embrittlement and lead to reduction in the fracture toughness (K_{IC}) and increase in the ductile–brittle transition temperature (FATT). Presence of sulphide inclusions, and nonmetallic inclusions containing Al and Si can facilitate cavity nucleation at the grain boundaries and in the grains, thus facilitating creep fracture at high temperatures and ductile fractures in the upper shelf region. These changes result in reduced creep ductility at high temperatures and reduced fracture toughness at lower temperatures. Advancements in the steel making technology during the last two decades have enabled reduction of these impurities and deoxidants to levels as low as 20 ppm leading to what might be called 'clean steels'. Further realisation that in view of the low sulphur levels achievable, even Mn is no longer necessary to 'fix' the sulphur and can, therefore, be reduced to levels as low as 0.01 to 0.02% has resulted in 'superclean steels'.

The development that has made 'clean' and 'superclean' steels possible was secondary steel refining via ladle furnaces in conjunction with vacuum degassing in the ladle and during casting. Ladle treatment of molten steel for the purpose of desulphurisation and vacuum carbon deoxidation were developed only in 1975. These techniques provided a production means of manufacturing high purity steels that previously could only be made in the laboratory as a control for temper embrittlement research studies. Thus, the practical solution to the problem in alloy steels was to refine the steels from Mn, Si, P, Sn, As, and Sb during steel making operations. Manganese, silicon, and phosphorus are easily removed during the oxidising stage of steel making, because they oxidise preferentially to iron, and enter the oxidising slag. This generally is done in the electric arc furnace. Tin, arsenic, and antimony are controlled by scrap selection, with basic oxygen furnace steel scrap used as the starting material for electric arc furnace melting if possible. After separation of the oxidised steel from the oxidising slag, it is transferred to a reducing slag in a ladle refining furnace, which removes the sulphur. Vacuum treatment of the desulphurised steel in the ladle furnace accompanied by argon bubbling provides a means for deoxidation via the vacuum carbon deoxidation (VCD) process. This leaves no oxide particles dispersed in the steel as would occur if deoxidation were done with silicon. The alloying elements are added at this stage. Casting into molds contained in a vacuum chamber, called vacuum stream degassing (VSD) completes the double degassing treatment. The extensive degassing combined with argon bubbling removes nitrogen and hydrogen as well as oxygen. The result is a superclean steel free to the maximum extent possible of grain boundary segregates and of nonmetallic oxides and sulphides. Alternate routes to produce clean/superclean steels also include use of Al deoxidation in lieu of VCD and conventional pouring in air with argon shrouding.

The primary driver in cleaning up steels has been the desire to achieve improved fracture toughness, although benefits in other properties such as resistance to creep, stress corrosion, etc. have accrued incidentally and serendipitously, making cleanliness even more desirable. In general, any modifications to alloy content or heat treatment to improve toughness of the steels have an opposite effect on the creep strength. Getting rid of the impurities (tweaking) provides one of the few viable ways of achieving the best results with respect to all the mechanical properties.

Good fracture toughness and freedom from impurity induced temper embrittlement are crucial requirements for rotors and discs. Regardless of the operating temperature, the final failure scenario for all catastrophic rotor/disc bursts involves either failure due to peak thermal stresses during a start-up/shut-down transient, during overspeed testing or during steady operation at low temperatures. Hence FATT and fracture toughness considerations at low/intermediate temperatures are important.[1,2]

Reduced fracture toughness of rotors and discs arising either inherently due to sulphides and inclusions or due to impurity-induced embrittlement results in a decrease of the component life under base load and cyclic operation due to increased risk of brittle fracture, and is one of the major causes of early component retirement. Embrittlement can also have a major constraining effect on the operating procedure. To keep transient stresses low, stringent controls have to be exercised with respect to the start–stop cycles. For instance, during each cold start, the rotors may need to be pre-warmed to a temperature above the ductile–to–brittle fracture appearance transition temperature (FATT) over a period of several hours prior to imposition of full load. These requirements lead to increased operational costs for the plant and decreased flexibility and availability. Reduced toughness also increases inspection costs due to the more frequent inspections required. In the case of low-pressure (LP) rotors, the LP cross-over temperature in fossil plant turbines is kept below about 370°C (700°F) to avoid embrittlement, even at the risk of reduced efficiency. Increase of the LP cross-over temperature to 400 to 427°C (750–800°F) would result in major efficiency gains. Improving the toughness of LP rotor steels also means that the increasing of the strength such as the tensile strength and the proof strength can be obtained along with maintaining the conventional toughness level by the modification of the tempering condition. Accordingly, the length of the last stage blading can be increased to improve the turbine thermal efficiency. Toughness of steels thus has a significant effect on the reliability, availability, cycling ability, efficiency and operating and maintenance costs (O&M) of turbines.

Table 1 shows the principal 'driver' requiring advancements in the different types of turbine rotors. For a more complete summary of rotor developments the reader is referred to Ref. 3. In the case of HP/IP rotors operating at elevated temperatures, improved creep strength permitting operating at higher temperatures and providing greater efficiency and improved toughness providing greater reliability, longevity and cycling ability have been the drivers. For LP rotors, increasing the LP cross-over temperature from 370°C (700°F) to 400°C (750°F) without the risk of temper embrittlement has been the principal driver since such a change would increase the turbine efficiency substantially. Increased longevity under stress corrosion conditions has also been an incidental benefit. For HP/LP combined rotors, reduced installed cost/kwh by housing the entire rotor inside a single casing has been the driver. This becomes possible if the creep strength requirements in the high temperature end and toughness requirements in the low temperature end can both be satisfied in a single forging. In all cases, improved reliability of the rotor leads to decreased inspection costs since the inspection intervals can be extended. An order of magnitude estimate the cost impact of various improvements is provided in Appendix 1, strictly for illustration purposes.

EPRI has been active in sponsoring and catalysing research pertaining to improved HP, LP and HP/LP rotor steels primarily through improvements in cleanliness since the mid 70s. Although the deleterious effects of impurities were known prior to that, there were no systematic studies of the synergistic effects of impurities. Although it was known that Mn contributed to embrittlement, high Mn levels were routinely maintained although no longer required in view of the steady decrease in the S content of steels.[3b] In order to make clean steels a reality, the steel makers, especially in the U.S. needed to be convinced of three things:

1) That impurity elements do in fact adversely affect the toughness, creep ductility, stress corrosion and key properties of steel.

2) That clean steel components in the sizes needed can be successfully made with available technologies, without driving up the costs to unrealistic levels.

Table 1 Principal Drivers for Development of Cleaner Rotor Steels

Rotor	Primary Requirement	Current Material	Advanced Material	Advantages	Principal Drivers
HP and IP <538°C (<1000°F)	Creep strength with adequate toughness	1Cr 1 Mo 0.25V	Clean 1Cr 1 Mo 0.25V	• Improved toughness • Incidental improvement in creep strength ductility	• Reliability • Longevity • Cycling ability
HP and IP <565°C (<1050°F)	Creep strength with adequate toughness	12CrMoV 11CrMoVNbN 11CrMoVTaN	Further modifications with • Nb, W, Ta • Cleanliness • High N	• Improved creep strength	• Efficiency gain due to operability up to 620°C (1150°F) in USC plants. • Cycling ability.
LP <370°C (<700°F)	Toughness	3.5%NiCrMoV	Superclean 3–3.5%NiCrMoV	• Improved toughness (freedom from embrittlement). • Incidental improvements in SCC resistance. • Incidental improvements in creep strength/ ductility	• Efficiency gain due to increased LP cross-over temperature to 400°C (750°F) in USC plants. • SCC resistance
HP/LP single shaft	Creep strength in HP end and toughness in LP end	• 1Cr1Mo0.25V differentially heat treated. • 1Cr1Mo0.25V and 3.5NiCrMoV bolted. • 2CrMoNiWV	• Superclean 2.5NiCrMov • Clean 2CrMoNiWV • Clean 2CrNiMoVNbW • Clean 2Cr1Mo2Mn 1.5NiV • Clean 1.8NiCrMoV	Improved toughness maintaining the creep strength of CrMoV at HP and maintaining the toughness of 3.5NiCrMoV at the LP.	• Reduction in installed cost. • Cycling ability.
Combustion turbine discs	Creep strength with adequate toughness	1Cr1Mo0.25V 1%CrNiMoV	Superclean 11%CrNiMoV	• Improved toughness • Freedom from embrittlement	Efficiency gain due to higher temperature capabilities.

3) That superclean steels with a very low Mn could be made and forged into product shape.
All of these concerns were systematically addressed through a series of research and development and demonstration projects. A summary of these projects, the principal outcome of each project leading to the next step and the EPRI product relating to each of these developments is provided in Table 2. The objective of this paper is to review the various EPRI-sponsored developments relating to clean/superclean steel technology.

2. HP AND IP ROTORS

These rotors typically operate at a maximum temperature of either 540°C (1000°F) or 565°C (1050°F) at the steam inlet end with temperature falling to about 345°C (650°F) at the steam exit end of the high pressure (HP) or the Intermediate Pressure (IP) turbines. For temperature up to 540°C (1000°F), a 1CrlMo 1/4V steel is generally used and for temperatures up to 565°C (1050°F) variations of a 12%Cr martensitic steel are used.

Figure 1 shows the reduction in the concentration of impurity elements in 1Cr1Mo 1/4V steels over the last few decades, due to advancements in steel making and refining technologies.

Numerous improvements have been made since the late 1940s in terms of rotor compositions, fabrication practices and cleanliness, as illustrated in Fig. 2 for high temperature forgings, based on the extrapolation of results cited in Refs 4 and 5. The toughness and rupture ductility have seen corresponding improvements as shown in Fig. 2.[4,5] The key events in this evolution include:
1) Switching to higher creep strength CrMoV rotors from the NiMoV rotors in 1948.
2) Introduction of D-grade rotors austenitised at 954°C (1750°F) in place of the earlier C-grade rotors austenitised at 1010°C (1850°F) to eliminate notch sensitivity and low ductility problems around 1953.
3) Use of electric furnace melting and vacuum pouring introduced around 1958 to reduce bore segregation of nonmetallic inclusions and sulphide streaks.
4) Introduction of 12 percent Cr rotors for 1050°C service in 1960.
5) Application of vacuum arc remelting process in 1970.
6) Demonstration of clean steel CrMoV rotors about 1984.
7) Demonstration of higher creep strength in modified 12 percent Cr rotor compositions about 1987.
The integrity of rotors has also been improved by advances in welding procedures for the initial fabrication or repair incorporating smaller forgings of higher quality.

The first EPRI project dealing with clean steels, RP1343 was started in the

Table 2 EPRI Resources Pertaining to Clean/Superclean Steels

Project	Performed By	Outcome	Product
RP559	University of Pennsylvania	Embrittling effects of impurities and synergisms in pressure vessel and rotor steels were demonstrated and the need for steel cleanliness was established.	EPRI Report NP-1501, September 1980.
TPS82–628	Engineering Materials and Processes	A survey of advanced steel making processes was completed.	EPRI RD3336, December 1983.
RP2741–1	University of Leeds	Demonstrated that low Mn superclean steels could be forged.	Report on RP2741-01, 1987.
RP1343	Westinghouse Electric	Improved toughness due to reduced S content was demonstrated in three trial HP rotors of 1Cr1MoV composition using VCD, VSD and low S steel making.	EPRI CS-4516, May 1986.
RP2060–1,-2	Japan Steel Works/ Bethlehem Steel Company	Four structural steels were evaluated in high purity form with low levels of Si and Mn. The basis for superclean 3.5NiCrMoV LP rotor development was established. In 1CrMoV HP rotors, the need for compensating for loss of bainitic hardenability due to removal of Mn by adding Ni and the impossibility of developing superclean versions based on straight 1Cr1Mo1/4V were identified.	EPRI NP-5399, September 19897.
RP1403–8	Vereinigte Edelstahlwerke	A trial rotor (VEW1) of superclean LP 3.5%NiCrMoV was made and improved mechanical properties were demonstrated.	Paper in Ironmaking Steelmaking, Vol. 13, p 322, 1986.

Table 2 *(continued)* EPRI Resources Pertaining to Clean/Superclean Steels

Project	Performed By	Outcome	Product
RP2741–3	Vereinigte Edelstahlwerke	A superclean LP 3.5NiCrMoV rotor (VEW2) with relaxed specification was evaluated. Concluded that the more stringent specs of VEW1 were needed.	RP2741–3 Final Report, unpublished.
RP1403–15	Toshiba/JSW/GE	A superclean LP 3.5NiCrMoV trial rotor was evaluated. Concluded that the steel was superior to conventional steel.	Draft EPRI Report RP1403–15, December 1991.
RP1403–18	ASEA Brown Boveri	Stress corrosion evaluations were completed on superclean 3.5NiCrMoV LP material from VEW1. Superiority in crack initiation was demonstrated.	EPRI GS-6907, 1990.
RP1403– 32	Daedalus Associates	All developments on superclean 3.5NiCrMoV LP rotor steels were summarised and reviewed.	EPRI GS-6610, December 1989.
RP1403–32	Daedalus Associates	Developments on superclean 3.5NiCrMoV LP rotors were reviewed and a concise guide for utility use including chemistry specification was prepared.	EPRI GS-6612, December 1989.
RP2426–4, 2741–4	Bethlehem Steel Corporation	Following up on the work in RP2060–1,-2, a superclean version of 1Cr1MoV HP rotor in which loss of Mn was compensated by adding 2.5%Ni and Nb was developed based on evaluation of lab heats. It was found the alloy could match the creep strength of 1CrMoV HP and the toughness of 3.5NiCrMoV LP. This paved the way for evaluation of 2.5NiCrMoV for HP/LP single shaft application.	EPRI ER-6887, July 1990.

Table 2 *(continued)* EPRI Resources Pertaining to Clean/Superclean Steels

Project	Performed By	Outcome	Product
RP1403–55	General Electric/Toshiba Corp./Japan Steel Works	A trial rotor of 2.5NiCrMoV for HP/LP was made and evaluated. The alloy had FATT below room temperature and creep strength comparable to CrMoV, but was found to be notch weak in creep.	EPRI TR-103689, February 1994.
RP1403–21	KWU-Siemens Corp. Saarstahl. Asea Brown Boveri. MAN Energie Inc. GEC Alsthom Inc. Parsons Inc.	Laboratory heats of a 2%CrMoNiWV European alloy was evaluated. A trial rotor of the optimised chemistry was made. This material is currently under evaluation.	Reference 29.
RP1403–7	Engineering Materials and Processes	A survey of open literature provided information on the capabilities of current 12Cr steels up to 565°C (1050°F) and modified 12Cr steels up to 593°C (1100°F).	EPRI CS-5277, July 1987.

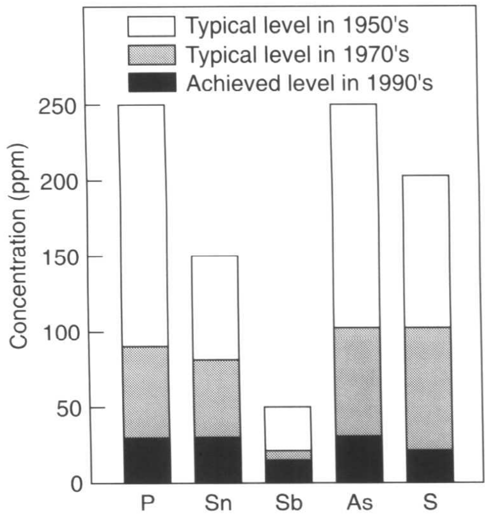


Fig. 1 Trends in impurity levels in Cr–Mo–V rotor steels

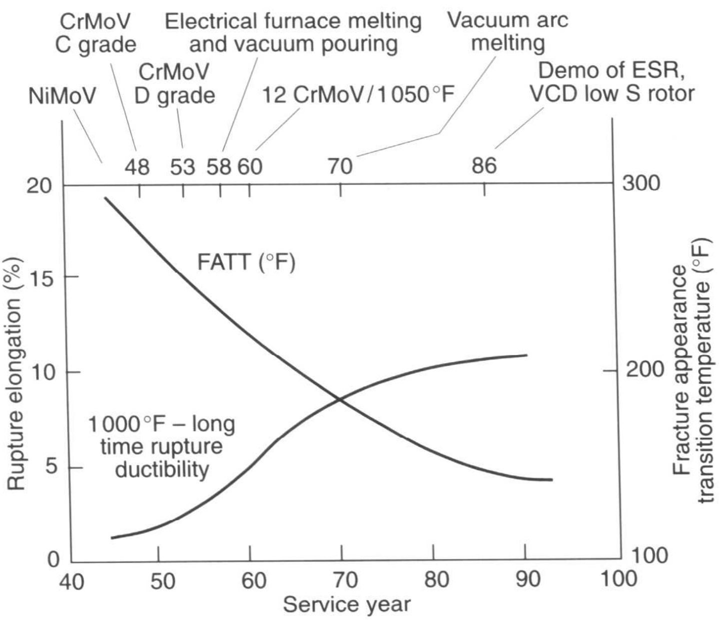


Fig. 2 Evolution of HP rotor properties in relation to changes in steel making technology

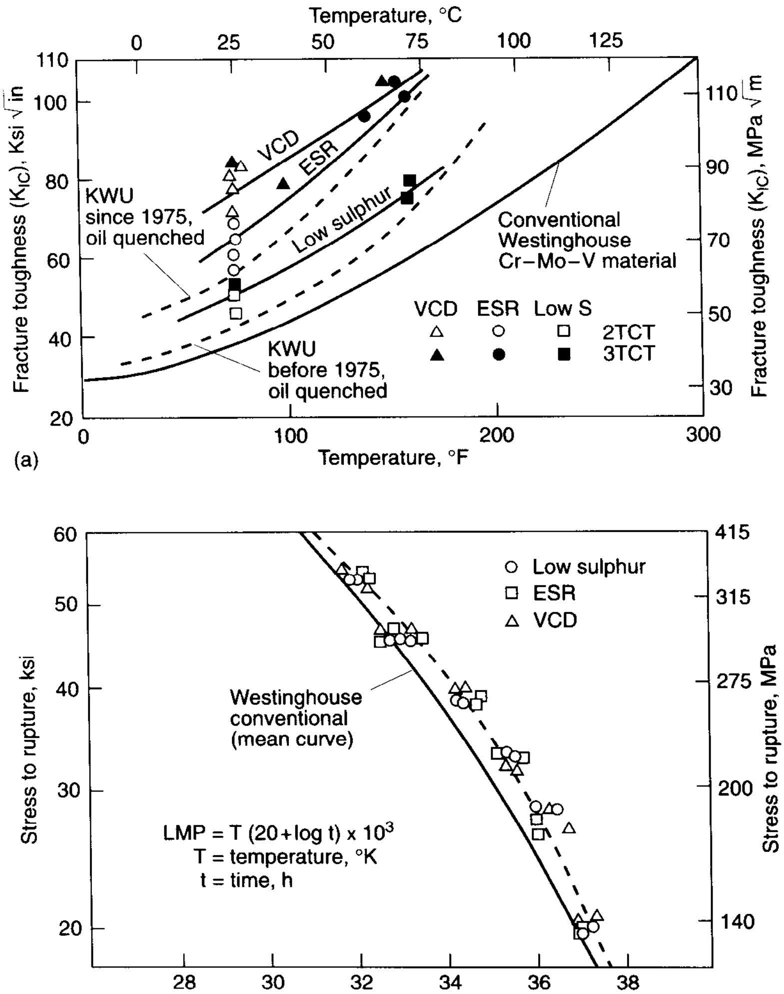
wake of the catastrophic failure of the Gallatin HP/IP rotor, wherein presence of sulphide stringers at the bore had been implicated in a major way.[6] To reduce the sulphur level in HP/IP 1Cr1Mo 1/4V type (ASTM A470 – Class 8) rotors, Swaminathan and Jaffee demonstrated the effectiveness of three advanced steel making technologies.[7,8] Three full-size 30 ton Cr–Mo–V rotor forgings were produced from 100 ton ingots each by vacuum carbon deoxidation (VCD), electroslag remelting and low sulphur vacuum silicon deoxidation (low S) processes. Ladle refining was applied to the liquid metal in the low S and VCD processes, whereas in the ESR process refining of the steel was achieved during electroslag remelting. All the processes reduced sulphur to very low levels in the range 10–20 ppm resulting in excellent bore quality and cleanliness. In addition, the VCD process also resulted in low P (30 ppm) and low Si levels. Table 3 provides a comparison of the composition of the advanced rotors with the conventional rotors. The centreline cleanliness of the rotors were appreciably better than conventional rotors.

Table 3. Chemical Compositions of Advanced Technology and Conventional 1CrMoV Forgings Evaluated by Jaffee and Swaminathan[7,8]

Element	Low S	VCD Low S	ESR[2]	Conventional[3]	ASTM A470, Class 8
Carbon	0.31	0.28	0.31	0.32	0.25–0.35
Manganese	0.78	0.76	0.78	0.83	1.0 max
Phosphorus	0.007	0.004	0.009	0.009	0.015 max
Sulphur	<0.001	0.001	0.002	0.009	0.018 max
Silicon	0.23	0.05	0.19	0.27	0.15–0.35
Nickel	0.33	0.40	0.27	0.23	0.75 max
Chromium	1.13	1.18	1.18	1.07	0.9–1.5
Molybdenum	1.15	1.21	1.18	1.17	1.0–1.5
Vanadium	0.23	0.26	0.26	0.25	0.2–0.3
Tin	0.002	0.010	0.003	0.006	–
Antimony	0.0012	0.0015	0.001	0.001	–
Copper	0.04	0.04	0.04	0.09	–
Aluminum	0.004	0.005	0.009	0.003	–
Arsenic	0.003	0.006	0.011	0.010	–
Nitrogen[4]	84	96	105	–	–
Hydrogen	1.5	0.37	1.6	–	–
Oxygen	16	38	33	–	–

1. Elements in wt%, gases in ppm. 2. Average of top and bottom analyses. 3. Mean value of 29 Westinghouse conventional rotors (1971–77). 4. Gas analysis from hot top.

Compared with conventional forgings, the fracture toughness, creep–rupture strength, rupture ductility, and LCF strength were found to be superior, as shown in Fig. 3. Considering the fact that, in general, improvements in rupture strength and ductility and in rupture strength and fracture



Figs 3a and **b** Improved mechanical properties achieved by advanced melting technologies and oil quenching compared with air-cooled conventional Cr–Mo–V steel rotor forgings

toughness are mutually opposed, the simultaneous improvements achieved with respect to all of these properties must be considered a major milestone in rotor technology. The three trial rotors made in this project were installed at three operating plants in the U.S. rated at 520 MW each. Rotors with low levels of Si produced by the VCD process have been used in several commercial plants recently.[9] In Germany, on the other hand, fracture toughnesses comparable to the low sulphur steels have been achieved since 1973 even in commercial cleanliness CrMoV steels by oil quenching, in contrast to the practice of air quenching in the U.S.[9a] However, the extreme reduction of