

# Ferritic/martensitic steels for next-generation reactors

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## Abstract

Concepts for the next generation of nuclear power reactors designed to meet increasing world-wide demand for energy include water-cooled, gas-cooled, and liquid-metal-cooled reactors. Reactor conditions for several designs offer challenges for engineers and designers concerning which structural and cladding materials to use. Depending on operating conditions, some of the designs favor the use of elevated-temperature ferritic/martensitic steels for in-core and out-of core applications. This class of commercial steels has been investigated in previous work on international fast reactor and fusion reactor research programs. More recently, international fusion reactor research programs have developed and tested elevated-temperature reduced-activation steels. Steels from these fission and fusion programs will provide reference materials for future fission applications. In addition, new elevated-temperature steels have been developed in recent years for conventional power systems that also need to be considered for the next generation of nuclear reactors.

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## 1. Introduction

The dramatic increase in world-wide demand for energy expected in the 21st century has spurred international cooperation to consider ways to meet future energy needs while maintaining and improving the environment. This has led naturally to nuclear energy, since large amounts of power can be produced with nuclear reactors without the adverse environmental effects that accompany the use of coal or petroleum products. Although renewable energy sources offer a similar possibility, concerns exist on economic efficiency and reliability when used for base-load power generation. The technology and economic reliability of nuclear

energy have been demonstrated by the reactors operating throughout the world today.

Rather than rely on the present fission reactors, an international collaboration has been organized to develop a new generation (Generation IV) of reactors that will produce abundant, reliable, inexpensive energy in safe and proliferation-resistant reactors [1]. The proposed next-generation reactor concepts include thermal and fast water-cooled (super critical water reactor – SCWR-Th and SCWR-F), gas-cooled (very high-temperature reactor – VHTR, gas fast reactor – GFR), and liquid-metal-cooled (sodium and lead fast reactors – Na-LMR and Pb-LMR) designs. Operating conditions are often quite demanding, such as the elevated temperatures of the VHTR and the liquid sodium and lead/bismuth coolants of Na-LMR and Pb-LMR, respectively, which combined with extended exposures to neutron and gamma

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irradiation offer challenges for engineers and designers on structural and cladding materials selection [1].

In the current generation of light-water reactors (LWRs), the pressure vessels are constructed of low-alloy ferritic steels, such as SA-533 grade B (nominally Fe–0.25C–0.25Si–0.6Ni–1.2Mn–0.5Mo) and SA-508 class 2 (nominally Fe–0.25C–0.3Cr–0.3Si–0.75Ni–0.75Mn–0.6Mo) [2]. Most are fabricated with 200–300 mm thick plates using axial and circumferential welds. Operating temperatures and pressures of most of the next generation of reactors are expected to be higher than the typical operating temperatures ( $\approx 288^\circ\text{C}$ ) and pressures (about 7 MPa for boiling-water reactors and 15 MPa for pressurized-water reactors) of current LWRs [2].

For several proposed Gen IV reactor concepts (VHTR, GFR, SCWR-Th, SCWR-F, Na-LMR, and Pb-LMR), elevated-temperature ferritic and martensitic steels are contemplated as in-core (cladding, wrappers, and ducts) and out-of-core (pressure vessel, piping, etc.) applications [1]. This paper will discuss briefly irradiation effects data obtained for such steels when they were first considered for fast and fusion reactors in the 1970s and for the steels developed in the fusion program in the 1980s. In addition to steels considered in the past for nuclear applications, advances in steel technology have been made in recent years for non-nuclear power-generation systems [3–5], and these steels will be examined for applicability to the new reactor designs.

Because of the high temperatures envisioned in the designs of Generation IV reactors (up to  $650^\circ\text{C}$  and higher) where ferritic and martensitic steels are considered for application, the primary emphasis is on the high-chromium (9–12%Cr) steels. However, in some designs, the out-of-core components (e.g., pressure vessel, piping, etc.) will operate at lower temperatures, thus providing an opportunity to use a lower-alloy steel, although probably not the low-alloy steels used in present-day LWRs.

To limit the length of this paper, tensile, creep, and impact properties of the steels and the effect of irradiation and elevated-temperature exposure on those properties will be emphasized, although it is recognized other mechanical properties (e.g., fatigue, fracture toughness, etc.) are also important. Although it is recognized that the use of the steels can be restricted or eliminated from consideration based on corrosion by the coolant, corrosion will not be considered. Since the choice of the structural

material has economic consequences, a brief discussion on the economic implications that arise from the choice of structural materials will be presented.

## 2. Ferritic/martensitic steels for nuclear reactors – past history

### 2.1. Fission reactor studies

Until the 1970s, the primary material for fast-reactor structures and fuel cladding were austenitic stainless steels. The appeal of the 9–12%Cr–Mo steels for in-core applications (cladding, wrappers, and ducts) for fast reactors was their higher thermal conductivities and lower expansion coefficients than those of austenitic stainless steels. In addition, the steels have excellent irradiation resistance to void swelling compared to austenitic stainless steels (Fig. 1). Void swelling limits the use of the high-swelling austenitic steels for fuel cladding and other in-core applications.

In the US fast reactor program, Sandvik HT9 steel was the chosen candidate (see Table 1 for nominal composition of all steels discussed in the paper). Similar steels to Sandvik HT9 with maximum operating temperature in conventional fossil-fired power plants of  $\approx 550^\circ\text{C}$  were chosen in Europe and Japan: EM-12, FV448, DIN 1.4914, and JFMS were chosen in France, United Kingdom, Germany, and Japan, respectively (Table 1). For comparison purposes in this discussion, Sandvik HT9 will be used as representative of these steels. Sandvik HT9

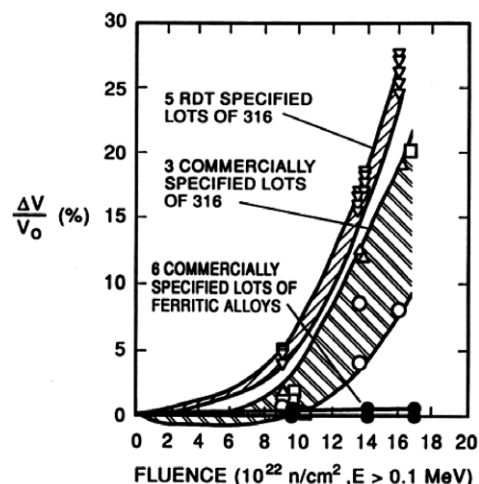


Fig. 1. Comparison of swelling behavior of commercial ferritic/martensitic steels with commercial type 316 stainless steel at  $420^\circ\text{C}$  (D.S. Gelles, unpublished research).

Table 1  
Nominal composition of commercial and experimental steels (wt%)

Steel	C	Si	Mn	Cr	Ni	Mo	W	V	Nb	B	N	Other
A533 Grade B	0.25	0.20	1.30		0.60	0.50						
A508 Class 2	0.25	0.30	0.75	0.30	0.75	0.60						
2.25Cr–1Mo (T22)	0.15	0.3	0.45	2.25		1.0						
2.25Cr–1.6WVNb (T23)	0.06	0.2	0.45	2.25		0.10		0.25	0.06	0.003		
2.25Cr–1MoVTi (T24)	0.08	0.3	0.50	2.25		1.0		0.25	0.08	0.004	0.03	0.07 Ti
3Cr–3WV	0.10	0.14	0.50	3.0			3.0	0.25				
3Cr–3WVTa	0.10	0.14	0.50	3.0			3.0	0.25				0.10 Ta
9Cr–1Mo (T9)	0.12	0.6	0.45	9.0	0.20	1.0						
Mod 9Cr–1Mo (T91)	0.10	0.4	0.40	9.0	0.10	1.0		0.20	0.08		0.05	
E911	0.11	0.4	0.40	9.0	0.20	1.0	1.0	0.20	0.08		0.07	
NF616 (T92)	0.07	0.06	0.45	9.0	0.25	0.50	1.8	0.20	0.05	0.004	0.06	
F82H	0.10	0.2	0.50	8.0			2.0	0.2		0.003		0.04 Ta
EUROFER	0.11	0.05	0.50	8.5			1.0	0.25		0.005		0.08 Ta
ORNL 9Cr–2WVTa	0.10	0.30	0.40	9.0			2.0	0.25			0.025	0.07 Ta
12Cr–1MoWV (HT9)	0.20	0.4	0.60	12.0	0.50	1.0	0.50	0.25				
HCM12A (T122)	0.11	0.1	0.60	12.0	0.30	0.40	2.0	0.25	0.05	0.003	0.06	1.0 Cu

steel was developed in Europe in the 1960s for the power-generation industry. Likewise, most of the steels considered in the other international programs were also developed for this industry.

Because of the large amount of information generated on HT9 for the Clinch River Breeder Reactor (CRBR) Project in the US during the 1970s, the logical first choice of material for in-core applications for the US program on next-generation reactors was HT9. Data were obtained on the properties of HT9 before and after irradiation. In addition to obtaining the raw data for a wide range of mechanical and physical properties, the data were analyzed, and equations were produced and compiled in the *Nuclear Systems Materials Handbook* for use by the reactor designers, safety analysts, and materials engineers.

Besides data for HT9, the handbook also contains data for modified 9Cr–1Mo and 2.25Cr–1Mo steels. By far, the most data for ferritic/martensitic steels were obtained for the latter steel – even more than for HT9. No data for irradiated material are given for 2.25Cr–1Mo and modified 9Cr–1Mo, since these steels were candidate structural materials for the steam generator of the CRBR. As such, they were not going to be exposed to irradiation. There is less data for the modified 9Cr–1Mo steel than 2.25Cr–1Mo in the handbook because it was developed during the program specifically for the steam-generator application. However, considerable data were generated for the modified 9Cr–1Mo following the demise of the CRBR because of its ultimate choice for applications in conventional power-generation systems. Furthermore, prior to

the ending of the FBR program, a program was begun to obtain post-irradiation mechanical-property data for modified 9Cr–1Mo and 2.25Cr–1Mo steels, although most of the properties evaluation of the irradiated steels was carried out in the US Fusion Materials Program after the fast reactor program was terminated.

## 2.2. Fusion reactor studies

Sandvik HT9 was the first ferritic/martensitic steel considered in the US Fusion Materials Program when it was decided to investigate these steels as structural materials for the first wall and blanket structures of fusion reactors [6,7]. Similarly, the first such steels in the programs in Europe and Japan were the steels previously considered in their fast reactor programs (i.e., EM-12, FV448, DIN 1.4914, and JFMS) [6,8].

In the mid-1980s, the concept of low-activation materials was introduced into the international fusion programs [9–17]. The objective was to build reactors from materials that would either not activate when irradiated by neutrons or, if activated, develop low-level radioactivity levels that would decay quickly, allowing for improved safety of operation as well as hands-on maintenance [9,10]. Truly ‘low-activation’ steels proved impossible, because the steels are limited by the decay of radioactive products from transmutation of the iron atoms. ‘Reduced-activation’ materials were considered possible, and in the mid-1980s and early 1990s, fusion reactor materials research programs in Japan, Europe, and the United States

developed reduced-activation ferritic/martensitic steels [10–28]. For reduced-activation steels, activity decays in a relatively short time, thus allowing for shallow land burial as opposed to deep geological storage for disposal of decommissioned plant components. Based on nuclear calculations, the typical steel alloying elements Mo, Nb, Ni, Cu, and N needed to be eliminated or minimized, and the development of reduced-activation ferritic/martensitic steels involved the replacement of molybdenum in conventional Cr–Mo steels by tungsten [12,14–18] and/or vanadium [14–18] and the replacement of niobium by tantalum [12].

Steels with 7–9%Cr were favored over those with 12%Cr because of the difficulty of eliminating  $\delta$ -ferrite in a 12%Cr steel without increasing carbon or manganese for austenite stabilization. Delta-ferrite can lower toughness, and manganese promotes chi-phase precipitation during irradiation, which can cause embrittlement [18]. Low-chromium (2.25%Cr) steels were considered [11,12,18,20,21], but in the end, 7–9%Cr steels were chosen for further study and development.

Eventually, the Japanese program settled on an Fe–7.5Cr–2.0W–0.2V–0.04Ta–0.10C (F82H) [15,22,23] steel. In Europe, an Fe–8.5Cr–1.0W–0.05Mn–0.25V–0.08Ta–0.05N–0.005B–0.10C (EUROFER) was the endpoint of the development program [19,26,28]. The steel with the best properties in the US was an Fe–9Cr–2W–0.25V–0.07Ta–0.10C (ORNL 9Cr–2WVTA) steel [12,17,21,27]. Nominal compositions of the steels are given in Table 1.

### 3. Irradiation effects on ferritic/martensitic steels

#### 3.1. Microstructure

The Cr–Mo and Cr–W elevated-temperature steels are used in the normalized-and-tempered condition. Normalizing consists of austenitizing by annealing above  $A_1$ , the equilibrium temperature where ferrite (body-centered-cubic structure) transforms to austenite (face-centered-cubic structure), after which it is air cooled. For steels with about 5–12%Cr, this produces martensite (body-centered-tetragonal structure) (Fig. 2). In steels with  $\lesssim$ 5%Cr, bainite (ferrite containing a high dislocation density and carbides), polygonal ferrite, or a combination of these two constituents form, depending on the section size and hardenability. Since there is more information on the irradiation effects on the 7–12%Cr steels, they will be discussed

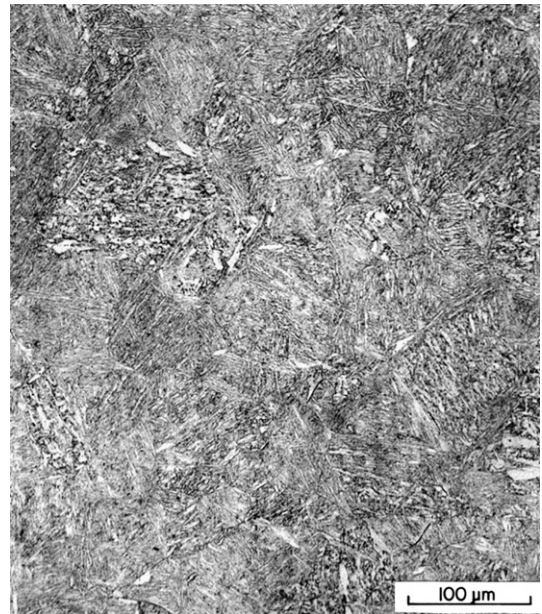


Fig. 2. Optical photomicrograph of tempered martensite microstructure of Sandvik HT9 [6].

in some detail, followed by a brief description of the effects on the lower-chromium steels.

As normalized, 7–12%Cr steels contain a high number density of dislocations (Fig. 3(a)). To increase toughness and ductility, normalized steel is tempered. During tempering,  $M_{23}C_6$  (M is primarily Cr, Fe, and Mo) and MX (M is primarily vanadium and niobium, and X is carbon and nitrogen) precipitate (Fig. 3(b)), resulting in a ferrite matrix with the large (60–200 nm)  $M_{23}C_6$  particles on lath and prior-austenite grain boundaries and smaller (20–80 nm) MX particles in the matrix. In addition, the high number density of dislocations in the untempered martensite is reduced.

High-energy neutron irradiation in a fast reactor displaces atoms from their normal matrix positions to form vacancies and interstitials. It is the disposition of the ‘displacement damage’, measured as displacements per atom (dpa) that affects the mechanical properties. The progressive change in microstructure with irradiation dose and temperature involves the agglomeration of vacancies and interstitials into voids and dislocation loops that lead to swelling. Irradiation-induced segregation and precipitation also occurs. Loops form below 400–450 °C with the loop size increasing and number density decreasing with increasing temperature. With increasing temperature, loops evolve into a dislocation network [29–33]. Above 400–450 °C,

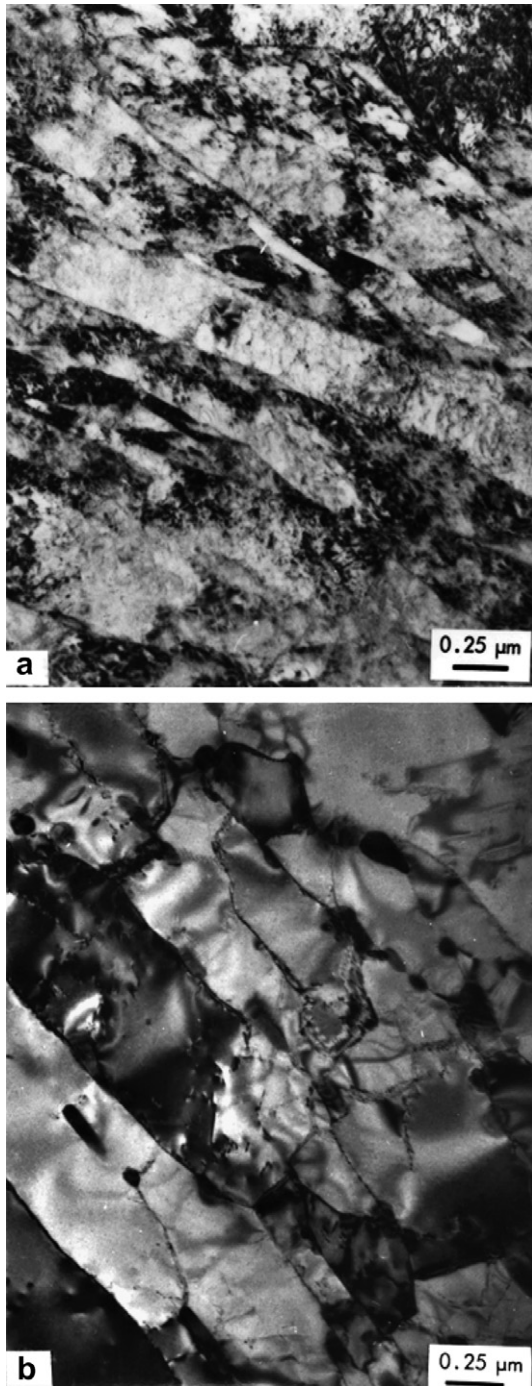


Fig. 3. Transmission electron microscopy photomicrograph of Sandvik HT9 in the (a) normalized and (b) normalized-and-tempered conditions [6].

more rapid diffusion allows the irradiation-induced defects to anneal out and precipitates to coarsen. Agglomeration of vacancies can lead to void swelling up to about 500 °C.

The low-swelling character of 5–9%Cr ferritic/martensitic steels has been demonstrated in irradiations of HT9 and modified 9Cr–1Mo (T91) in the Experimental Breeder Reactor (EBR-II) (Fig. 1) and the Fast Flux Test Facility (FFTF) [32,34]. Irradiation in EBR-II and FFTF to over 200 dpa at 400–420 °C, which is near the maximum swelling temperature for the steels, produced swelling of <3% for irradiation in EBR-II and <2% in FFTF. Slightly more swelling occurred in modified 9Cr–1Mo than HT9, and an effect of heat treatment was observed for HT9 [32]. In irradiation creep studies, it was found that high stress levels accelerated swelling [34].

Recently, concern was expressed that the ferritic/martensitic steels may have steady-state swelling rates closer to those of austenitic stainless steels, and the observed difference in swelling amounts was attributed to a much longer cavity incubation time for ferritic steels [35]. This conclusion was based primarily on swelling experiments on binary Fe–Cr alloys irradiated in EBR-II [36] and FFTF [37]. It must be remembered, however, that these binary and ternary alloys are essentially solid-solution alloys with microstructures significantly different from the tempered martensite of HT9 and modified 9Cr–1Mo that showed 2–3% swelling after >200 dpa.

Radiation-induced segregation and irradiation-induced precipitation can also affect properties [29–33,38]. Precipitates observed in the 9–12%Cr steels during irradiation include  $\alpha'$  [31,38], G-phase [38],  $M_6C$  [30,33] and chi-phase [31,38]. For most of the 9–12%Cr Cr–Mo steels investigated, Laves phase, which forms during thermal aging and irradiation at  $\approx 400$ –600 °C [29,31,33,38,39], can cause embrittlement [39]; it does not form if irradiation is above  $\approx 600$  °C [29,31,38,39]. In addition to the formation of new precipitates and their possible effect on mechanical properties, the  $M_{23}C_6$  and MX coarsen during elevated-temperature irradiation, similar to what happens when the steels are exposed to elevated temperatures in the absence of irradiation. The only difference is that irradiation can accelerate coarsening.

Displacement damage produced by the neutron irradiation will lead to transmutation reactions of neutrons with metal atoms to produce a new atom (usually another metal atom with a smaller atomic number) and a gas atom – helium or hydrogen. This effect is of major importance for the neutron energies in a fusion reactor. However, for the energy

spectrum of fast reactors, relatively little helium will form. The helium:dpa ratio for ferritic/martensitic steels in most fission reactors is about two orders-of-magnitude lower than in a fusion reactor, and it is expected to have minimal effect on swelling or mechanical properties.

The limited information available on irradiation effects on the microstructure of lower-chromium (2–5%) bainitic/ferritic-type steels was obtained during the development of the reduced-activation steels [18,20,21]. Although these steels were abandoned relatively early, the limited data collected indicated that the irradiation effects on microstructure were qualitatively similar to those observed on the high-chromium steels.

### 3.2. Mechanical properties

The effect of irradiation on the tensile behavior of the 5–12%Cr ferritic/martensitic steels depends on temperature [40–44]. Yield strength increases (hardening) (Fig. 4) and ductility decreases (Fig. 5) caused by the irradiation-induced microstructural changes discussed above were observed for modified 9Cr–1Mo [41] and HT9 [42] irradiated to 9–12 dpa at 390 °C. There was essentially no change in the amount of hardening observed when the steels were irradiated at 390 °C to  $\approx 23$  dpa, indicating that hardening saturated with increasing fluence [43]. For irradiation at around 400 °C, saturation occurs by 10 dpa [43], but higher fluences are required at lower temperatures [44]. For irradiation above 425–450 °C, properties are generally unchanged

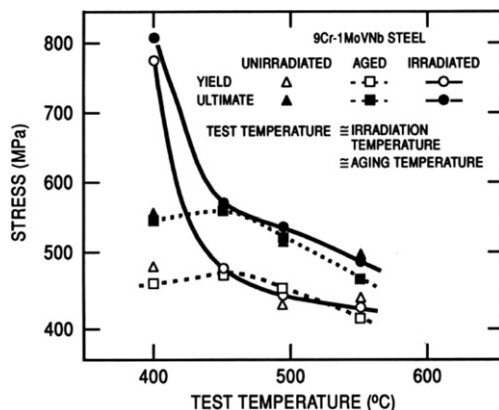


Fig. 4. Yield stress and ultimate tensile strength of modified 9Cr–1Mo (9Cr–1MoVNb) steel in the unirradiated, thermally aged, and irradiated conditions. Irradiation was at 390, 450, 500, and 550 °C in EBR-II to  $\approx 12$  dpa [41].

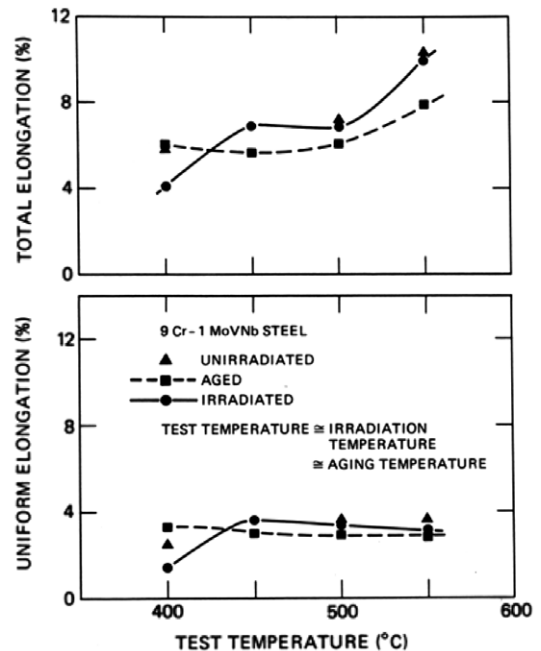


Fig. 5. Uniform and total elongations of modified 9Cr–1Mo (9Cr–1MoVNb) steel in the unirradiated, thermally aged, and irradiated conditions. Irradiation was at 390, 450, 500, and 550 °C in EBR-II to  $\approx 12$  dpa [41].

compared to unirradiated and thermally aged samples (Figs. 4 and 5), although there may be enhanced softening, depending on fluence and temperature [41–43].

Irradiation hardening affects other properties, such as fatigue and toughness. The latter is of major concern and has received considerable attention in the development of steels for fusion and in studies of the pressure-vessel steels used in light-water reactors. The effect of irradiation hardening on toughness is observed qualitatively in a Charpy impact test as a shift of the Charpy curve to higher temperatures, which results in an increase in the ductile–brittle transition temperature (DBTT) and a decrease in upper-shelf energy (USE) [45–50]. For HT9 irradiated in FFTF at 365 °C (Fig. 6) [45], the increase in DBTT ( $\Delta$ DBTT) saturates with fluence (the shift is the same after 10 and 17 dpa) in the same way as the yield stress saturates [43]. The magnitude of the shift varies inversely with irradiation temperature, similar to the variation in hardening.

For similar strengths, the impact toughness of HT9 is less than that of modified 9Cr–1Mo in both the unirradiated and irradiated conditions (Fig. 7) [46]. The  $\Delta$ DBTT variation with temperature after irradiation at 390, 450, 500, and 550 °C for modified

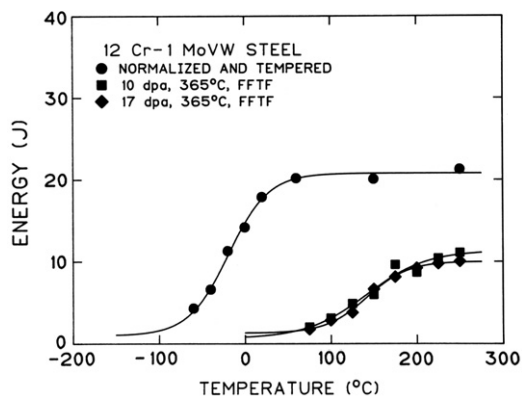


Fig. 6. Charpy impact curves for Sandvik HT9 (12Cr-1MoVW) in the unirradiated condition and after irradiation to 10 and 17 dpa at 365 °C in FFTF [45].

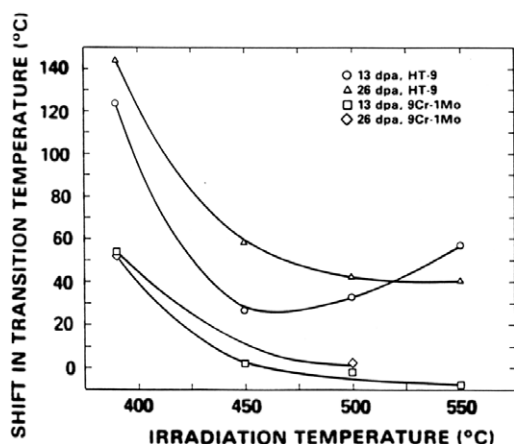


Fig. 7. Shift in ductile-brittle transition temperature of Sandvik HT9 and modified 9Cr-1Mo steels irradiated at 390, 450, 500, and 550 °C to 13 and 26 dpa in EBR-II [46].

9Cr-1Mo reflects the increase in strength at 390 °C and no change at the three higher temperatures (Fig. 4). The reason the  $\Delta$ DBTT does not disappear for HT9 at 450, 500, and 550 °C (Fig. 7) even though there is no change in yield stress [42,43] has been attributed to the higher carbon concentration of HT9 (0.2% vs. 0.1% for modified 9Cr-1Mo), which induces the formation of more and larger  $M_{23}C_6$  particles during irradiation and elevated-temperature exposure [6,47].

Although all 2–12%Cr conventional and reduced-activation steels irradiated to relatively high displacement damage (>10 dpa) below 425–450 °C exhibit this effect on toughness, there are differences among the different steels. This is demonstrated in Fig. 7, where modified 9Cr-1Mo is

compared with HT9, and in Fig. 8, where Charpy curves before and after irradiation at 365 °C in FFTF for HT9 and ORNL 9Cr-2WVTa are compared [6,47,48]. The reduced-activation steel showed a much smaller shift (about 32 °C vs. 125 °C for HT9). Part of this difference was attributed to the larger carbon concentration in the HT9 (0.2%) than the 9Cr-2WVTa (0.1%); the tantalum in the 9Cr-2WVTa has also been shown to have a favorable effect on the impact properties [6,48]. Although modified 9Cr-1Mo (T91) has a  $\Delta$ DBTT about half as large as HT9 at 365–420 °C for similar test conditions [47], it is still more than twice that for the 9Cr-2WVTa [48] for these irradiation conditions. In addition, the DBTT for the 9Cr-2WVTa in the unirradiated condition is at least 25 °C less than that for modified 9Cr-1Mo.

The effect of irradiation on the shift can be affected by the normalizing-and-tempering treatment [47,49] and by the processing used on the steel during manufacture [50]. It has been demonstrated that part of the reduction in USE on 10%Cr steel can be recovered by annealing 0.5 h at 535 °C [49]. Such an anneal would dissolve irradiation-induced defects (tiny clusters and dislocation loops) that lead to hardening.

Just as there was little information available on the irradiation effects on microstructures of low-chromium (2–5%) steels, there is also little information on the effect of irradiation on mechanical properties. The 2.25Cr-1Mo steel (T22) [51,52] and several reduced-activation steels [18,20,21, 25,48] were irradiated in fast reactors. The low-chromium steels appeared to be more prone to

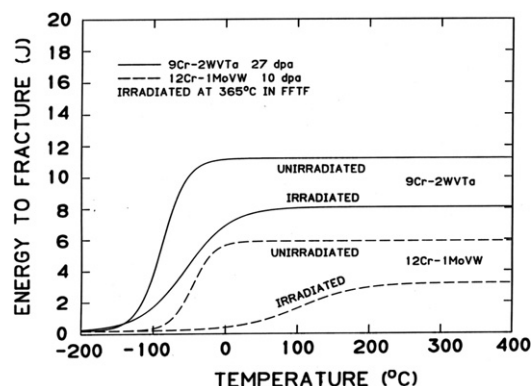


Fig. 8. Comparison of Charpy impact curves for Sandvik HT9 (12Cr-1MoVW) and reduced-activation steel ORNL 9Cr-2WVTa in the unirradiated condition and after irradiation in FFTF at 365 °C [6].

hardening and embrittlement than 9Cr steels for similar irradiation doses. Because of their elevated-temperature strength and corrosion limitations, these steels can only be considered for pressure-boundary applications in the next-generation fission reactors. For this application, they may still prove adequate for appropriate temperatures, because pressure-boundary structures would probably not experience high neutron fluences.

The above discussion on embrittlement concerned 2–12%Cr steels and irradiations to high displacement damage ( $>1$  dpa). In the low-alloy pressure-vessel steels of the light-water reactors (i.e., A508 and A533B) operating today, hardening and embrittlement are observed for irradiations to much lower doses ( $\ll 1$  dpa) [2], where there is little effect on the high-alloy steels.

As measured by a shift in DBTT in Charpy tests, there are indications that transmutation helium may cause an increase in embrittlement of the steels in a fusion neutron environment after irradiation in the hardening range (below  $\approx 425$  °C) [53]. However, because of the much lower helium concentrations formed in fission light-water and fast reactors, helium should not be a significant factor for future fission reactors at temperatures where hardening occurs, and the effects will not be discussed.

Intergranular low-ductility tensile fractures attributed to small amounts of helium are observed in austenitic stainless steels irradiated and tested at  $T_i \gtrsim 0.5T_m$ , where  $T_m$  is the melting temperature of the steel (in Kelvin). Such elevated-temperature helium embrittlement in austenitic stainless steels at temperatures above where irradiation hardening occurs can appear with as little as 1 appm He or less, depending on the composition, thermomechanical processing, irradiation conditions and test conditions (temperature, strain rate, etc.). All indications are that the ferritic/martensitic steels are relatively immune to this type of embrittlement [6].

#### 4. Evolution of elevated-temperature steels

The ferritic/martensitic steels considered for fast reactors in the 1970s and for fusion reactors in the 1980s were developed by the steel industry for use in conventional power-generation systems and in the petrochemical industry. Since then, steel technology has advanced, and it is of interest to examine the evolution of the elevated-temperature steels for use in those industries since the 1980s.

Development of elevated-temperature ferritic/martensitic steels began in the 1920s with the introduction of Cr–Mo steels for conventional power-generation applications. The 2.25Cr–1Mo (concentration in Table 1) steel, designated by ASTM as Grade 22\*,<sup>1</sup> was introduced in the 1940s and is still widely used today. Along with Grade 22, 9Cr–1Mo (Grade 9), an Fe–9.0Cr–1.0Mo–0.6Si–0.45Mn–0.12C composition, was an early development, the additional chromium being added for corrosion resistance. Since then, there has been a continual push for increased operating temperatures in the power-generation and petrochemical industries.

Following the introduction of 2.25Cr–1Mo (T22) and 9Cr–1Mo (T9) steels, three ‘generations’ of elevated-temperature steels were introduced [3]. The T22 and T9, termed the ‘zeroth’ generation, had 100 000 h creep-rupture strengths at 600 °C of about 40 MPa with a maximum operating temperature of  $\approx 538$  °C (Table 2). These properties were improved in each of the following generations, with the third generation of steels that include NF616 (Grade 92) with 9%Cr and HCM12A (Grade 122) with 10.5–12%Cr. The steels have operating conditions dictated by the  $10^5$  h creep-rupture strengths at 600 °C of 140 MPa and maximum operating temperature  $\approx 620$  °C. A goal for the fourth generation now in development is  $10^5$  h rupture strengths at 600 °C of about 180 MPa and a maximum operating temperature of 650 °C (Table 2).

The next generation of nuclear reactors will, in many cases, have operating conditions well beyond those of earlier designs. As with most new technologies or technological advances, success often hinges on materials available to meet the new operating conditions. When materials are considered for the new nuclear reactor systems, it is natural to revert to materials for which data, especially data on irradiated materials, are available. Even if those materials are adequate for the new designs, new materials may offer advantages and should be considered. This applies to results from work on the steels considered for applications in fast reactors

<sup>1</sup> Grade 22 and the other commercial steels discussed here (Table 1) are given designations by ASTM (e.g., Grade 9 is 9Cr–1Mo and Grade 91 is modified 9Cr–1Mo). The steels are further distinguished as T22 or T91 for tubing, P22 and P91 for piping, F22 and F91 for forgings, etc. The ‘T’ designation will mainly be used in this paper, since many of the steels were developed for boiler tubing, although they are also used as other product forms.



Table 2  
Evolution of ferritic/martensitic steels for power-generation industry

Generation	Years	Steel modification	$10^5$ h Rupture strength, 600 °C (MPa)	Steels	Max use temperature (°C)
0	1940–1960		40	T22, T9	520–538
1	1960–1970	Addition of Mo, Nb, V to simple Cr–Mo steels	60	EM12, HCM9M, HT9, HT91	565
2	1970–1985	Optimization of C, Nb, V, N	100	HCM12, T91, HCM2S	593
3	1985–1995	Partial substitution of W for Mo and add Cu, B	140	NF616, E911, HCM12A	620
4	Future	Increase W and add Co	180	NF12, SAVE12	650

in the 1970s international programs. Therefore, to determine the best steels available for the next generation of reactors, mechanical properties of the steels considered for previous fission applications need to be compared with newer elevated-temperature steels developed since those programs were discontinued. This will be done in the next section, where the objective is to determine which steels offer the best chance for the new reactor designs to efficiently and economically achieve their specified goals.

## 5. Ferritic/martensitic steels for nuclear reactors – the future

### 5.1. High-chromium steels

First-generation steels, such as HT9 that were developed for conventional power plants, had a maximum use temperature of 565 °C in such plants (Table 2). The maximum design temperature in a fossil-fired power plant is determined by the creep strength, which is affected by the operating environment. When used as fuel cladding in a fast reactor, the use temperature is expected to approach 650–700 °C, and helium gas produced by transmutation of fissioning fuel will be the source of stress on the cladding. For HT9 to be used at this temperature, design stresses would need to be reduced, meaning either the wall thickness has to be increased or the gas plenum for reducing the stress on the cladding due to helium will need to be enlarged [54].

The need for higher operating temperatures in conventional power plants led to the development of new steels with higher creep strengths. A significant increase in creep strength was achieved in going from first-generation steels to second-generation compositions. This involved the addition of the strong carbide-forming element niobium and the addition of nitrogen, which increased the maximum

use temperature to 593 °C and increased the  $10^5$  h rupture life at 600 °C to 100 MPa from 60 MPa for the first-generation steels. Second-generation steels include modified 9Cr–1Mo (Table 2). At 650 °C, the difference in creep-rupture properties of the first-generation HT9 and second-generation 9Cr–1Mo is quite large at long rupture times-low stresses (Fig. 9).

As shown above, the impact toughness of the ORNL 9Cr–2WVTa steel is much improved over that of HT9 before and after irradiation. It is also somewhat better than modified 9Cr–1Mo, but there are no long-time creep-rupture properties available for this reduced-activation steel. However, properties are available for the reduced-activation steels EUROFER and F82H, and when compared to HT9 and modified 9Cr–1Mo steels, the modified 9Cr–1Mo steel has the advantage (Fig. 10). Based on creep-rupture properties, which is the method used to qualify the ‘generation’, the reduced-activation steels could be classified as generation 1.5. This is logical, for although the reduced-activation steel compositions contain the strong carbide former tantalum, which is analogous to niobium in modified

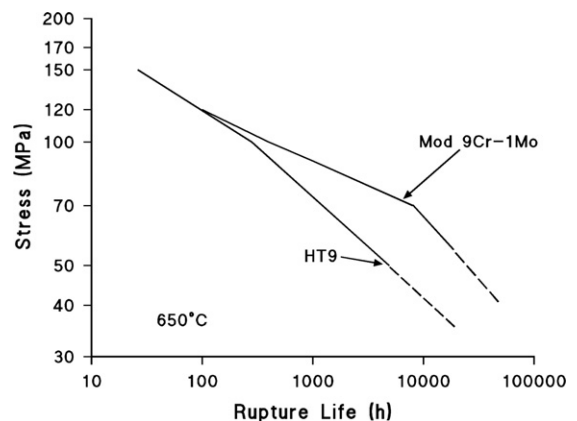


Fig. 9. Comparison of creep-rupture curves for Sandvik HT9 and modified 9Cr–1Mo steels tested at 650 °C.

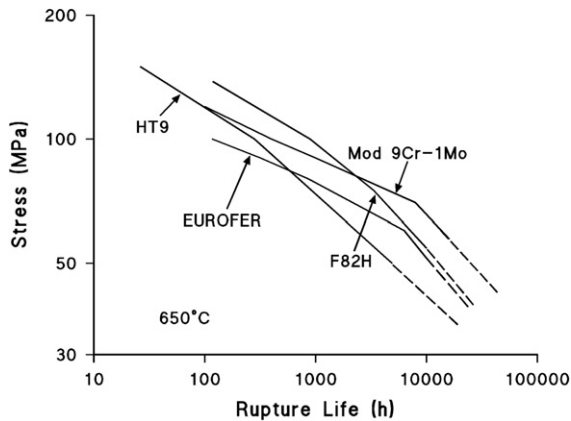


Fig. 10. Comparison of the creep-rupture curves for tests at 650 °C for commercial steels Sandvik HT9 and modified 9Cr–1Mo with the two reduced-activation steels F82H and EUROFER.

9Cr–1Mo, the nitrogen present in second-generation steels is missing.

Generation 3 steels were modifications of generation 2 obtained by substituting tungsten for some or all of the molybdenum and the addition of boron. The generation 3 steel that shows the most promise is NF616 (T92)\*,<sup>2</sup> which like modified 9Cr–1Mo has received ASME code approval for pressure-boundary applications. Creep-rupture properties of NF616 are a significant improvement over those for HT9, modified 9Cr–1Mo, and the reduced-activation steels (Fig. 11). This strength advantage is evident when 10<sup>5</sup> h rupture stresses are compared for the five steels at 550, 600, and 650 °C (Fig. 12). Note that HT9 has a slight strength advantage over all but NF616 at 550 °C, but for the two higher temperatures, modified 9Cr–1Mo is the second strongest steel.

Based on elevated-temperature creep-rupture strength and impact toughness, HT9 is the least favored material of those considered. Although elevated-temperature mechanical properties favor NF616, data are lacking for this steel after neutron irradiation. In addition to the toughness advantage after irradiation of modified 9Cr–1Mo steel over HT9, modified 9Cr–1Mo has also been shown to be more resistant to irradiation creep [34,55].

In essence, NF616 is a variation of modified 9Cr–1Mo in which most of the molybdenum was

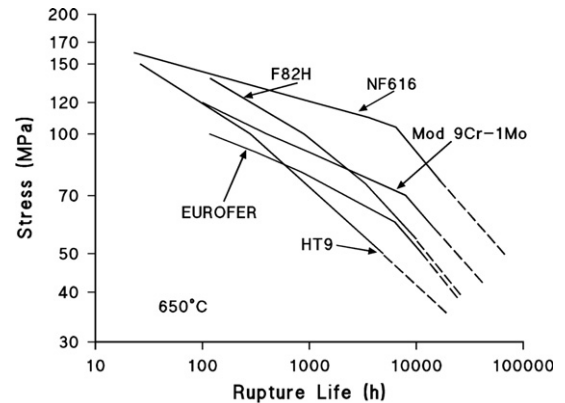


Fig. 11. Comparison of the creep-rupture curves for tests at 650 °C for commercial steels Sandvik HT9, modified 9Cr–1Mo, NF616, F82H, and EUROFER.

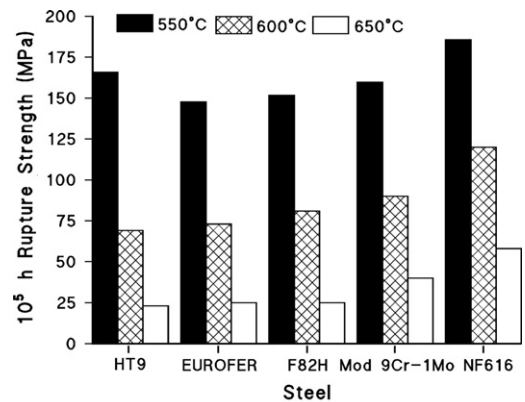


Fig. 12. A comparison of the 100000 h rupture strengths for Sandvik HT9, EUROFER, F82H, modified 9Cr–1Mo, and NF616 at 550, 600, and 650 °C.

replaced by tungsten and boron was added. Development of the reduced-activation steels proceeded by replacing all molybdenum by tungsten, and there was no indicated negative effect of the tungsten during irradiation. Then the difference in the two steels involves the presence of boron in NF616. It has been concluded that boron stabilizes M<sub>23</sub>C<sub>6</sub>, which in turn stabilizes the subgrain structure that is partly responsible for the improved creep strength of NF616 [56].

A problem with boron in steel for nuclear applications is that natural boron contains ≈20% <sup>10</sup>B and 80% <sup>11</sup>B, and when irradiated, the <sup>10</sup>B undergoes an (n,α) reaction to produce helium and lithium in the steel, both of which could influence the mechanical properties [6]. For a steel containing 0.005% natural boron, ≈50 appm He will form. This could be

<sup>2</sup> The HCM12A (Grade 122) is also a possibility for the application, but there have been questions about the stability of this steel; therefore, only the NF616 will be discussed here.

avoided by alloying with  $^{11}\text{B}$  instead of natural boron;  $^{11}\text{B}$  is relatively inexpensive. With the addition of 0.003–0.005% B and  $\approx 0.05\%$  N to the best reduced-activation steel, ORNL 9Cr–2WVTa, properties should be similar to those of NF616. Alternatively, NF616 could be produced using  $^{11}\text{B}$  instead of natural boron.

### 5.2. Low-chromium steels

With the increased operating temperatures of the next-generation reactors, the strength of low-alloy A508 and A533B steels for the pressure vessel will be inadequate for most designs. Depending on the operating temperature, the use of one of the high-chromium steels discussed above may be required to provide adequate corrosion and oxidation resistance. However, there are economic and technical advantages of using lower-chromium (2.25–3%Cr) steels. For example, the steels can be welded without the use of a post-weld heat treatment under certain conditions, a considerable economic advantage.

The first such choice would be the 2.25Cr–1Mo steel (Grade 22), for which there is considerable experience for pressure-boundary applications in the power-generation and petrochemical industries. Also, an advanced 2.25Cr–1.6WVNb steel (Grade 23) (Table 1) has received ASME code approval for pressure-boundary applications. The steel has elevated-temperature strength approaching and exceeding that of some of the high-chromium steels. Similarly, a 2.25Cr–1MoVTi steel (Grade 24) has improved properties over 2.25Cr–1Mo steel, although it is not as strong as Grade 23. Any of these steels could be considered for pressure vessel and other out-of-core applications.

A steel developed at ORNL also deserves consideration [57–60]. This steel was developed as a reduced-activation steel in the US Fusion Program based on observations on the microstructures developed during different heat treatments [57,58]. As a result of these studies, a steel was produced with a base composition of nominally Fe–3Cr–3W–0.25V–0.1C (3Cr–3WV). An addition of 0.07% Ta (3Cr–3WVTa) to this base composition was found to further improve strength and toughness (Table 1). The elevated-temperature strength of these steels is obtained from a bainitic microstructure with a high number density of fine, needle-like MX precipitates in the matrix [60]. During creep, coarsening of these fine matrix precipitates is much more rapid in the steel without tantalum.

In section sizes investigated to date, the 3Cr–3WV and 3Cr–3WVTa steels have yield stress over double the 345 MPa (50 ksi) used to design with the A533B steel. Strength properties of the 3Cr–3WV and 3Cr–3WVTa steels also exceed those of T23 and T24 (Fig. 13). A similar advantage is exhibited during creep tests at 550, 600 and 650 °C, especially for the 3Cr–3WVTa steel [60]. For these test conditions, the 3Cr–3WVTa steel even has an advantage over the modified 9Cr–1Mo steel, as seen in Larson-Miller parameter comparisons for the 3Cr–3WVTa with 2.25Cr–1Mo (T22) and 2.25Cr–1.6WVNb (T23) (Fig. 14(a)) and modified 9Cr–1Mo (Fig. 14(b)). The Larson-Miller parameters were chosen based on the data for the T23 [61] and modified 9Cr–1Mo steel [62]. Work in progress at ORNL seeks to commercialize the steels: two 50 ton heats, one with tantalum and one without, have been produced for use in developing a database to apply for an ASME Code Case [59].

In addition to the advantages cited above for a higher-strength 2–3%Cr steel in the steelmaking and vessel fabrication processes, such a steel would also offer advantages for nuclear plant operation for applications where present-day low-alloy pressure-vessel steels are used, because A533B-type steel vessels are clad with stainless steel to prevent corrosion products from contaminating the coolant. The higher chromium level of 2.25–3%Cr steels make them more corrosion resistant, perhaps allowing them to be used without cladding. The higher chromium means the steel is also more resistant to hydrogen embrittlement. Based on observations on various higher alloyed ferritic steels (e.g., 2.25Cr–1Mo, modified 9Cr–1Mo, Sandvik HT9) irradiated to high doses (tens of dpa compared to  $\approx 0.01$  dpa

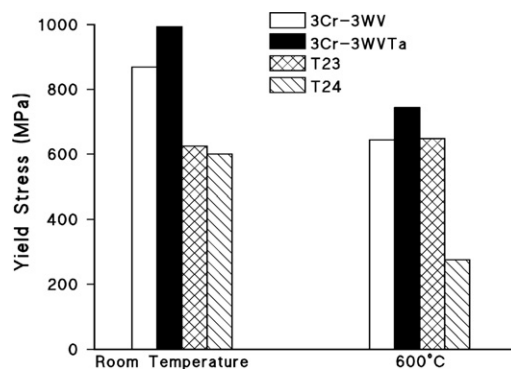


Fig. 13. Yield stress for tests at room temperature and 600 °C for 3Cr–3WV, 3Cr–3WVTa, 2.25Cr–1.6WVNb (T23), and 2.25Cr–1MoVTi steel (T24) steels.

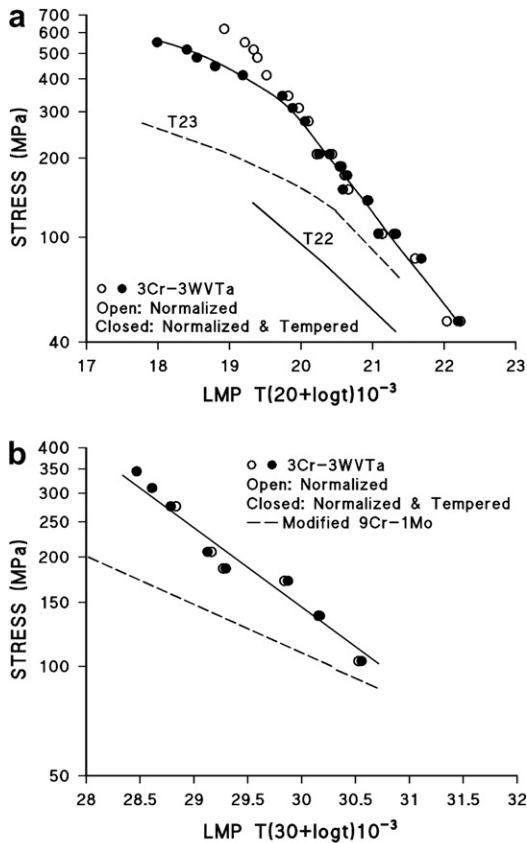


Fig. 14. Larson-Miller parameter for 3Cr-3WVTa steel compared to (a) 2.25Cr-1Mo (T22) and 2.25Cr-1.6WVNb (T23) and (b) modified 9Cr-1Mo (T91) steels [60].

in an LWR) in fast reactors in the breeder reactor and fusion test programs, a steel such as 3Cr-3WV steel should be much more resistant to irradiation embrittlement compared to A533B. This might allow a reactor to be operated to a higher fluence with a smaller coolant gap, which means a smaller-diameter vessel, all other conditions being equal for the two steels.

## 6. Economic considerations

Recent decades have seen an increasing emphasis on the economic viability of nuclear power generation, as vendors have been pressured by utilities to reduce construction and operation costs while increasing capacity factors. Nuclear plants constructed during the coming decades will undoubtedly face similar pressures to continually reduce expenses barring a paradigm shift away from society's current tolerance of high greenhouse gas emis-

sions. As such, designs must consider monetary ramifications of every option throughout a power station's life cycle. Lower construction costs may not correspond with operational savings, which likewise may not necessarily equate to reduced decommissioning costs.

Anticipating the exact lifetime costs associated with the use of advanced steels for nuclear components ranging from in-core fuel structures to core externals and pressure vessels is impractical and would prove explicitly academic given the incomplete nature of advanced plant designs and material properties databases for unirradiated and irradiated conditions. Despite the relative maturity of the development of Cr-Mo-W elevated-temperature steels, ASME codes for irradiated conditions will require no small effort. Still, elevated-temperature design windows provide a starting point to analyze the basic elements that will influence the economic utility of high-chromium steels.

As mentioned, the contribution material selection has in overall plant cost will come from all phases of its operation cycle. While smaller quantities of activated structural components will save in decommissioning costs when waste disposal is of interest, the contribution of structural components to the cost of a plant operation will fall primarily in the construction phase. The specific type, quantity, and essential fabrication, joining, or installation methods required of the selected material will all play a role in determining its economic viability.

Component construction cost is first determined by base price and volume of material required, which is determined primarily by the material's design window that provides maximum allowable stresses for anticipated operating temperatures. Fig. 15 shows allowable stresses for steels of interest [3]

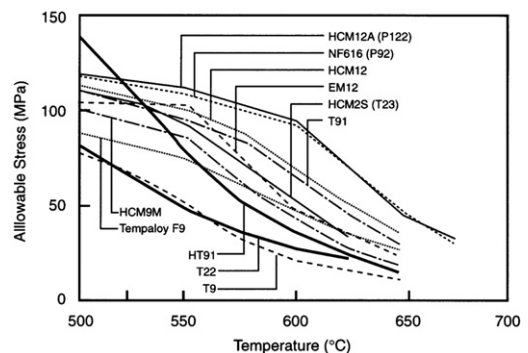


Fig. 15. Allowable stresses for various structural elevated-temperature steels [3].

(note that a curve for Sandvik HT9 is not shown; however, the properties of this steel are similar to those of Sandvik HT91 [63]). A second factor involves transportation and installation costs, which will be governed by the section weight. These may prove to be of increasing importance in Generation IV nuclear plants. For example, Finland's EPR (European pressurized-water reactor) under construction at Olkiluoto is relying largely upon a modular, on-site construction process. Finally, fabrication costs will be controlled by the thickness of the sections being milled, welded, and heat treated.

In generating even a preliminary cost approximation for pressure vessel construction of the various candidate steels, the differences in the current commercial infrastructure for the modern generation of steels becomes problematic. US vendors are currently able to supply A533B plate 'off the shelf' in limited sizes and thicknesses, but new plant construction would entail the commitment of mills to produce plates in the larger sizes and thicknesses required for next-generation designs. Given that large-scale plate production capabilities of the sizes required for present conceptual designs are not available for any of the steels considered, a more basic cost comparison was sought. Steel cost estimates were generated using element-specific prices to reflect the substantial difference that inclusion of an expensive alloying component (i.e. Cr, Mo, V, W, etc.) will have on the cost of a steel composition. Since the candidate steels are compared based on a figure of merit to each other and not external options, only relative costs are important for this discussion, and this procedure should demonstrate how differences in composition and strength can affect the economics of future plants.

As discussed in the previous section, present LWRs do not require advanced steels, such as HT9, modified 9Cr–1Mo, NF616, or 2.25Cr–1Mo, despite potential gains based upon their elevated maximum design stresses. These gains translate to

higher safety factors and smaller, thinner components compared to traditional low-alloy nuclear steels, such as SA302B, SA508-2/3, and SA533B-1. This is shown in Table 3, where two relative figures of merit (FOM) are shown for four steels under the three categories previously identified as influencing relative competitiveness as a candidate material: material cost, mass, and thickness.

If a component could be constructed of a traditional steel, any gains that an advanced steel alloy would offer must be evaluated with respect to the higher initial cost. In this situation, a figure of merit relative to a traditional alternative (such as A533B) is of interest. However, more demanding applications will preclude the use of familiar steels and a figure of merit calculated relative only to other ferritic/martensitic steels is appropriate. Each figure of merit is calculated by comparing the four steels' performance within one of three categories first to a reference traditional steel and second to the mean of the four. As mentioned previously, the three categories of performance considered are material cost, mass cost, and thickness cost. Material cost reflects the initial investment difference that a more expensive material will require. Mass cost is intended to convey the savings that less-massive structures will benefit from in transportation and installation expenses. Finally, thickness cost characterizes the decreased heat treatment, welding, and fabrication times necessary for thinner components.

In these calculations, the material's allowable stress (Fig. 15) dominates the other categories, due to the fact that it directly determines the required thickness of material. Varying prices and slightly varying densities are factored into the calculation, but these values are similar between the steels. These calculations would appear to favor HT9 due to its superior strength below  $\approx 525$  °C. However, HT9 would probably never be chosen for applications at these temperatures, given the availability of steels like 3Cr–3WVTa, T23 and T24. These steels would

Table 3  
Figures of merit for Cr–Mo steels at 300 °C

Steel	Material costs		Mass costs		Thickness costs	
	FOM (vs A533B)	FOM (vs Mo–Cr alloys)	FOM (vs A533B)	FOM (vs Mo–Cr alloys)	FOM (vs A533B)	FOM (vs Mo–Cr alloys)
T22 (2.25Cr–1Mo)	0.627	0.958	0.550	1.222	0.625	1.215
T91 (Mod 9Cr–1Mo)	0.739	1.130	0.497	1.104	0.571	1.111
P92 (9Cr–1.8W–0.5Mo)	0.724	1.107	0.438	0.974	0.497	0.966
HT9 (12Cr–1Mo–0.3V)	0.527	0.805	0.315	0.700	0.364	0.707

have comparable strengths to that of HT9 at these temperatures, and they offer significant advantages in vessel fabrication (welding). In addition to direct savings due to strength, implementation of steels containing higher chromium contents for low-temperature pressure vessels may allow the elimination of the stainless steel cladding necessary to inhibit corrosive attack in traditional steels used in present

LWRs. Besides savings in the liner's cost and installation, the vessel itself could be slightly reduced in overall size with its removal.

When operation at higher temperatures is considered, as is the case with the gas-cooled and liquid-metal-cooled Generation IV designs, low-alloy steels lack the capacity to withstand thermal creep. Similar to the low-temperature figures of merit, Fig. 16 shows the figures of merit for HT9, modified 9Cr–1Mo (T91), NF616 (T92), and 2.25Cr–1Mo (T22) as a function of operating temperature. As was the case with the low-temperature analysis, the allowable stress governs steel performance under all three categories. Of particular interest in these plots is interaction between performance and economic viability over the temperature range shown.

All three figures demonstrate similar trends between the four steels. The HT9 has a slight advantage at the bottom of the Generation IV temperature window (500 °C), but Grades 91 and 92 dominate HT9 at higher temperatures. This shift to a high-temperature operations regime is the most important change in the next generation of reactors compared to those envisioned in the 1970s, when HT9 was the first choice. Grades 91 and 92 clearly become the choice over HT9 between 500 and 550 °C, above which this initial scoping suggests Grade 92 offers advantages that will extend into the economic as well as mechanical regimes.

## 7. Summary

Ferritic/martensitic steels with 9–12%Cr are favored candidates for in-core and out-of-core applications for construction of the next generation of fission nuclear reactors. A natural first choice for high-temperature applications would, at first glance, appear to be Sandvik HT9, since a large amount of mechanical properties data in both the normalized-and-tempered and neutron-irradiated conditions were generated for this steel during the 1970s when it was considered for fast reactor applications. Since that time, however, the steel industry has introduced 9–12%Cr elevated-temperature steels with vastly improved creep properties over those of HT9. These steels are far superior to HT9, and they appear to be the logical choice for the next generation of reactors. Depending on the operating conditions for future reactors, pressure-boundary applications (i.e., pressure vessel, piping, etc.) may exist where temperatures are too high for the low-alloy steels presently used for these applications. However,

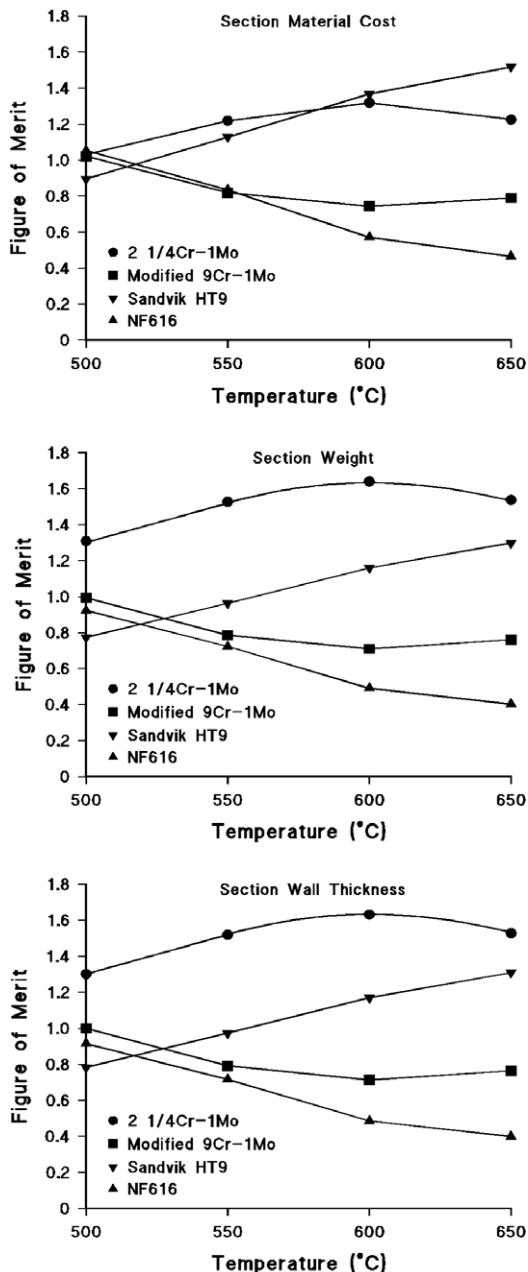


Fig. 16. Estimated figures of merit for Cr–Mo steels over the range 500–650 °C based on material costs (top), weight (middle), and thickness (bottom).

there are now 2.25–3%Cr steels available for this application that would offer technological and economic advantages over both the low-alloy steels and the 9–12%Cr steels.

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The helpful comments and review of the manuscript by Drs L.L. Snead and K.J. Leonard are appreciated. This research was sponsored by the Office of Fusion Energy Sciences, US Department of Energy, under Contract DE-AC05-00OR22725 with U.T.-Battelle, LLC.

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