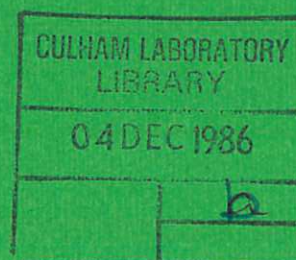UKAEA

Report

A STUDY OF THE PROSPECTS FOR DEVELOPMENT OF LOW-ACTIVATION MARTENSITIC STAINLESS STEELS FOR FIRST WALL AND BLANKET STRUCTURES IN FUSION REACTORS

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Abstract

The concentrations of certain elements in the first wall and blanket structures of fusion reactors must be restricted in order to limit the required nuclear decay time and remanent radioactivity in components withdrawn from service. This study examines the potential of the elemental substitution approach to the design of low-activity martensitic stainless steels, subject to the requirement that the contact γ dose rate falls to a value that would allow essentially unrestricted handling of discarded material after a cooling period of 100 years. The factors governing the structure and properties of the 9-12%Cr martensitic steels are reviewed. Practicable substitutes for the proscribed elements molybdenum, nickel and niobium include tungsten, tantalum and an increased vanadium content in conjunction with optimised carbon, nitrogen and boron levels. Given the generally attractive combination of properties offered by the martensitic steels, the prospects for developing a satisfactory low-activity composition appear favourable. A series of experimental compositions and a programme of investigations are proposed to explore possible alloys with the objective of reproducing, as far as possible, the characteristics of existing fully martensitic high strength stainless steels.

CONTENTS

1. INTRODUCTION

The first wall and blanket structure in a fusion reactor will form the heat exchanging interface between the thermonuclear plasma and the coolant, which will probably be water or helium. The structure will be subjected to fluxes of electromagnetic energy, neutral and charged atoms and neutrons with energies up to about 14 MeV. There is very limited experience of materials behaviour for the fluxes and energies involved. It is envisaged, however, that the structure will operate at temperatures of 500°C and above, with cyclic temperature variations that will result in thermal stress fatigue.

A crucial factor in the choice of a material for this application is the nature of the neutron-induced transmutations that take place, since these will determine the induced radioactivity characteristics of the components. These in turn will govern the radioactive waste management regime for the reactor by dictating the storage periods and handling methods required for expired reactor components.

Various materials have been considered for first wall and blanket structures, including stainless steels, refractory metals, vanadium based alloys and ceramics. The 9-12% Cr martensitic stainless steels are primary candidates for application in near-term fusion reactors. Their strength and corrosion-resistance properties are broadly compatible with the anticipated engineering requirements and they appear to possess a relatively high resistance to thermal fatigue and to radiation damage, as compared with austenitic steels. There is, moreover, a considerable body of experience in their fabrication and use in the power generation, petrochemical and aerospace industries.

The neutron activation and decay characteristics of the chemical elements have been systematically examined by Jarvis[1], who has categorised the elements in terms of their acceptable concentrations in a first wall material the post-service activity of which is required to fall to a specific value during a reasonable cooling period. The classification presented in Table 1 is based on the requirements that the contact dose rate from a first wall made entirely of the element in question should, after irradiation to a first wall neutron power fluence of 14 $MWym^{-2}$, decay to a value not exceeding 2.5×10^{-5} Svh^{-1} at the end of a 100y storage period. This dose rate corresponds roughly to the level at which essentially unrestricted handling of the material could be contemplated.

Some established martensitic stainless steels have been proposed for further study as potential reactor materials and examples of these

Table 1   Summary of element acceptability in structural materials from
           considerations of recycling after 100 years decay time

A. Structural elements (intended constituents)	
Primary constituents:	C, Mg, V, Cr, Mn, Fe, Ta, W
Major constituents (10-50%):	Si
Minor constituents (1-10%):	Cu, Zn
Trace constituents (0.1-1%):	Ti, Co, Ni
Undesirable constituents (10-1000 ppm):	Al, Zr, Mo, Sn
Troublesome constituents (1-10 ppm):	Nb
B. Impurity elements	
Unlimited (> 10%):	Li, Be, B, N, O, F, Na, P, S, Ga, Ge, As, Se, Br, Y, Rh, Pd, Sb, Te, I, Cs, Ce, Pr, Nd, Sm, Ho, Yb, Lu, Hf, Os, Au, Hg, Tl, Pb
Minor impurities (1-10%):	Ru, In
Trace impurities (0.1-1%):	Cl, Rb, La, Gd, Pt
Acceptable impurities (10-1000 ppm):	Ca, Sc, Sr, Cd, Dy, Er, Tm, Re
Troublesome impurities (1-10 ppm):	K, Ba
Unacceptable impurities (< 1 ppm):	Ag, Eu, Tb, Ir, Bi, Th, U
C. Omissions	
Hydrogen:	H, D
Unstable elements:	Tc, Pm
Inert gases:	He, Ne, Ar, Kr, Xe

are given in Table 2. The objective of the present study was to consider these existing steels and to propose alternatives within the compositional limitations imposed by the elemental concentration limits given in Table 1. The service requirements of the first wall material with respect to fabrication methods, operating stresses and temperatures and design codes are not yet well defined. The following guidelines have therefore been adopted in the present study:

1. Compositions chosen must conform as closely as possible to the permitted concentrations of alloying additions represented by Table 1.

2. The selected compositions should permit the manufacture and fabrication of components by established methods, preferably with no greater difficulties than would apply for the steels listed in Table 2.

3. The mechanical properties of the new compositions should generally approximate those of the established steels, particularly FV448 and DIN 1.4914. Any property deficiencies to be expected as the result of compliance with requirements 1 and 2 should be identified, to assist the selection of compositions for experimental evaluation.

4. The anticipated service life of a steel first wall/blanket component is 2-3 years at about 550°C.

Table 2   Compositions of martensitic stainless steels suggested for fusion

Alloy	Fe	Cr	Mo	Ni	V	Nb	Mn	W	Si	C
FV448	85.8	10.6	0.6	0.8	0.2	0.4	1.0	–	0.5	0.12
EM12	86.3	9.5	2.0	0	0.35	0.5	1.05	–	0.25	0.09
1.4914	85.7	11.5	0.5	0.8	0.3	0.25	0.35	–	0.45	0.17
HT-9	85.3	11.5	1.0	0.5	0.3	–	0.5	0.5	0.25	0.2
E5	86.4	10.6	2.0	–	0.09	0.057	–	–	0.29	0.05

With the above boundary conditions a study of available information on the martensitic stainless steels has been made. The principal metallurgical features of this class of steels are summarised and new low activation compositions are suggested for further investigation.

The numerous commercial variants of the 12%Cr steels are described in a comprehensive review of their properties and characteristics by Briggs

and Parker [2]. The present paper concentrates on the probable effects that would result from the elimination of the proscribed elements from the existing steels and their substitution by permitted alloying additions.

2.   BASIC METALLURGY OF THE MARTENSITIC STAINLESS STEELS

2.1   Matrix phase constitution

Steels containing between 9 and 13% chromium and which are capable of hardening to martensite on air cooling have a compositional balance that gives a predominantly austenitic structure at both the hot working temperatures and those used for austenitising prior to hardening. Depending on the balance of alloying elements in solution at these temperatures, however, some delta ferrite may be present.   After cooling to ambient temperature the martensitic matrix may contain either or both delta ferrite and retained austenite.

Some commercial steels have been developed with duplex ferrite-martensite or ferrite-austenite structures.   The former, described briefly in Appendix 1, have the claimed advantage of generally improved weldability, though relatively little information is available on their overall performance.   In this study the emphasis has been placed on the identification of compositions capable of providing predominantly martensitic structures with the required properties in the hardened and tempered condition.   The duplex steels could warrant examination, however, particularly if difficulties were experienced in balancing the requirements of hardness in the tempered condition with austenite phase stability.

The propensity to form delta ferrite is often represented by the Schaeffler diagram, or its modifications, which takes into account the effect of the alloying elements, weighted in accordance with their influence on austenite or ferrite formation, on the phase stability of the steel.   The version of the diagram given by Schneider [3] is shown in Fig.1 and the equivalence factors for the principal alloying additions are given in Table 3.   In an alternative method that may be used the change in the phase proportions that result from a given adjustment of the alloy content from a specified starting composition may be estimated.   Examples of the coefficients available for this type of calculation are shown in Table 4 [4].   The extent of the austenite phase field as a function of carbon content for the basic Fe12%Cr system is shown in Fig.2.

The quantitative relationships referred to above must be used with caution in predicting phase stability since they do not, for example, indicate the variation in delta ferrite content that may be associated
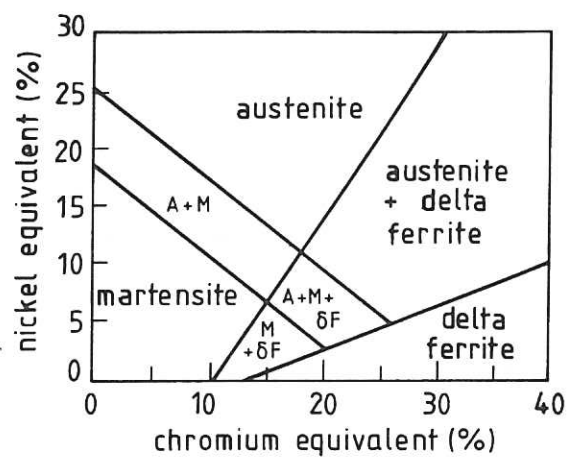
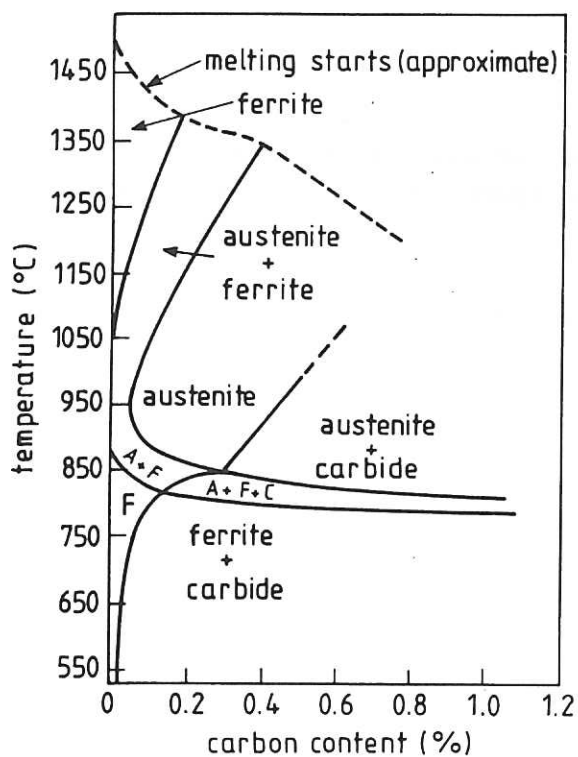Fig. 1 Schaeffler diagram as modified by Schneider.

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Fig. 2 Phase diagram showing effect of carbon content on equilibrium relationships in 12% Cr steels.

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Table 3   Effect of alloying elements on the chromium and nickel
          equivalents[3]. ( ) represents the mass percentage
          concentration of the element in solution

Ferrite forming elements	Austenite forming elements
Cr equivalent %	Ni equivalent %
(Cr) + 2 x (Si) + 1.5 x (Mo) + 5 x (V) + 5.5 x (Al) + 1.75 x (Nb) + 1.5 x (Ti) + 0.75 x (W)	(Ni) + (Co) + 0.5 x (Mn) + 30 x (C) + 0.3 x (Cu) + 25 x (N)

Table 4   The effect of various elements on the delta ferrite content,
          M_s and Ac_1 temperatures for a 15Cr-2Ni-1.5Mo-0.3V steel[4]

| Element | Effect of 1 wt% alloying addition | | |
	change in delta ferrite concentration %	change in M_s (C°)	change in Ac_1 (C°)
N	−22*		
C	−21*	−47*	
Ni	−20	−17	−30
Co	−7		−5
Cu	−7		
Mn	−6	−33	−25
W		−11	
Si	+6	−11	
Mo	+5	−21	+25
Cr	+14	−17	
V	+18		+50
Al	+54		+30

* these values are for 0.1 wt% additions

with variations of austenitising temperature. More significantly, they relate only to mean compositions and do not take account of segregation effects. They nevertheless provide a starting point from which to predict the effects of variations in phase stability with composition.

A section of the ternary iron-chromium-carbon equilibrium phase diagram[2] is shown in Fig.2, where it can be seen that a base composition of 0.1%C and 12%Cr is fully austenitic at temperatures between about 900° and 1100°C. Increasing the carbon content to 0.2% provides a wider temperature range within which only austenite exists. Subsequent transformation of a 0.1%C, 12%Cr steel will result in the range of microstructures indicated in the continuous cooling transformation (CCT) diagram given in Fig.3. For comparison, the transformation characteristics of a more highly alloyed 12%Cr steel containing 1% Mo and 0.3% V are shown in Fig.4.

So far as the development of the matrix microstructure on heat treatment is concerned, the main factors governed by composition may be summarised thus:

● the range of optimum austenitising and hot working temperatures

● the volume fraction of delta ferrite and undissolved carbide or nitride phases retained after transformation to martensite

● the martensite start temperature and thus the tendency to retain austenite on hardening and to autotemper during the martensite formation

On tempering, the alloying additions affect the following:

● the maximum permissible reheating temperature before reversion to austenite begins

● solid solution strengthening, solubility of the interstitials and the matrix-tempered carbides lattice parameter differentials, all of which will govern the strength in the tempered condition

● the propensity to form intermetallic phases, generally considered to be detrimental to toughness and comparatively ineffective for strengthening.

2.2   Strengthening mechanisms

In alloys where the compositional balance has been designed to give a predominantly martensitic structure the initial martensitic hardness

CONTINUOUS COOLING TRANSFORMATION DIAGRAM

13 Cr

AUSTENITISED AT 980°C

PREVIOUS TREATMENT ROLLED, SOFTENED 650°C 1 h

ANALYSIS Wt %

C	Si	Mn	P	S	Cr	Mo	Ni	Al	Nb	V
0.12	0.40	0.50	0.020	0.010	12.5	—	0.20	—	—	—

Fig. 3 Continuous cooling transformation diagram for a 12.5%
Cr steel austenitised at 980°C, rolled and softened for 1 h at 650°C.

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CONTINUOUS COOLING TRANSFORMATION DIAGRAM

12 Cr Mo V

AUSTENITISED AT 1000°C

PREVIOUS TREATMENT   ROLLED. SOFTENED 650 C 1 h

ANALYSIS Wt %

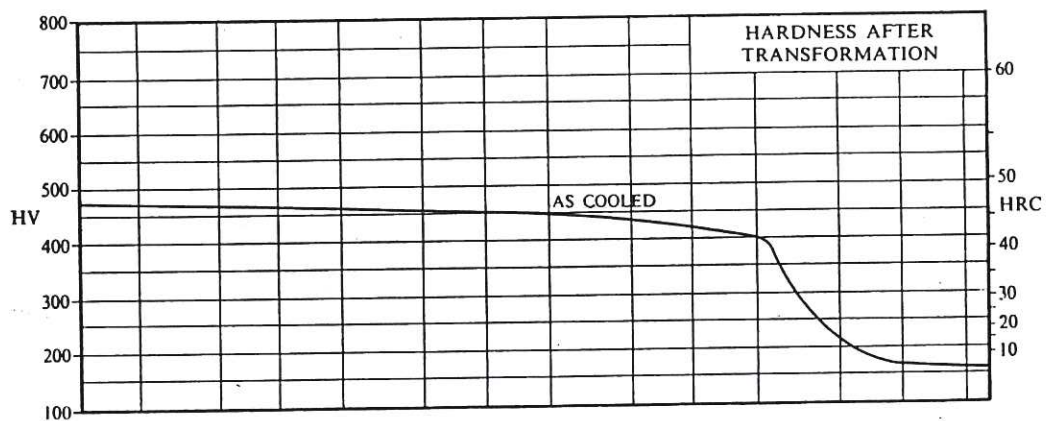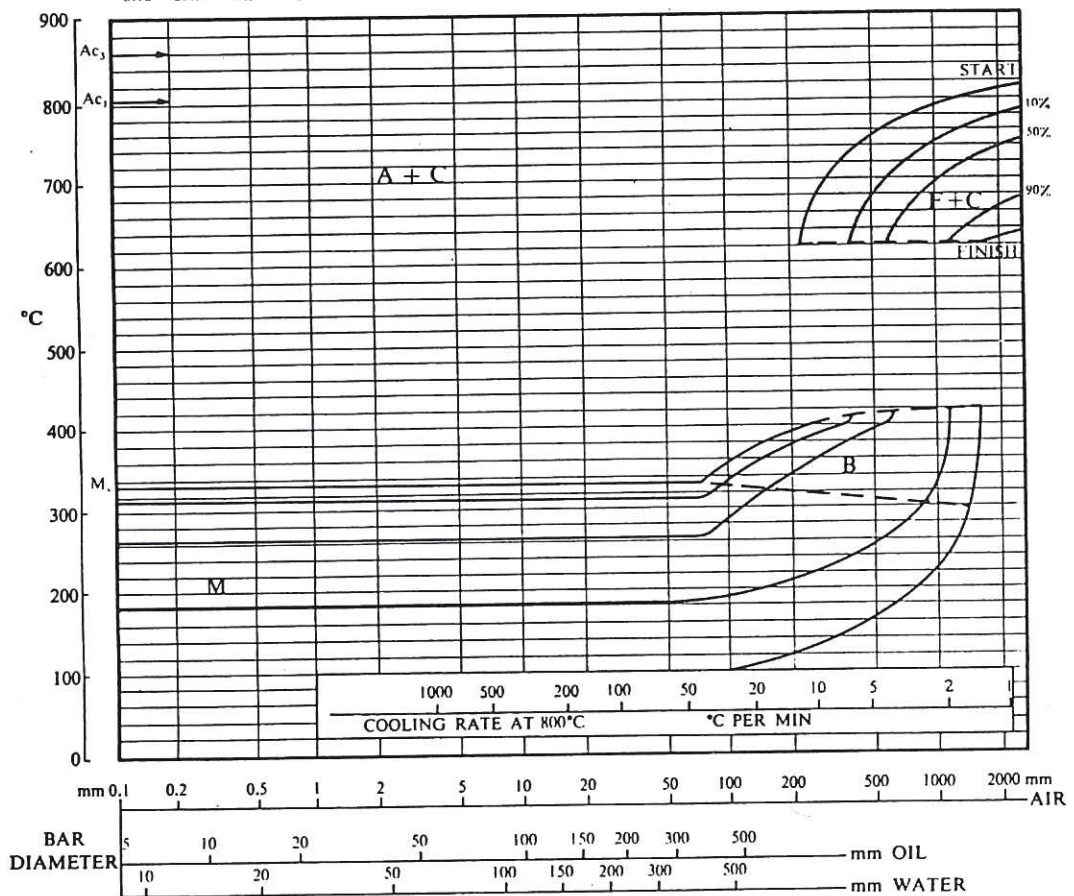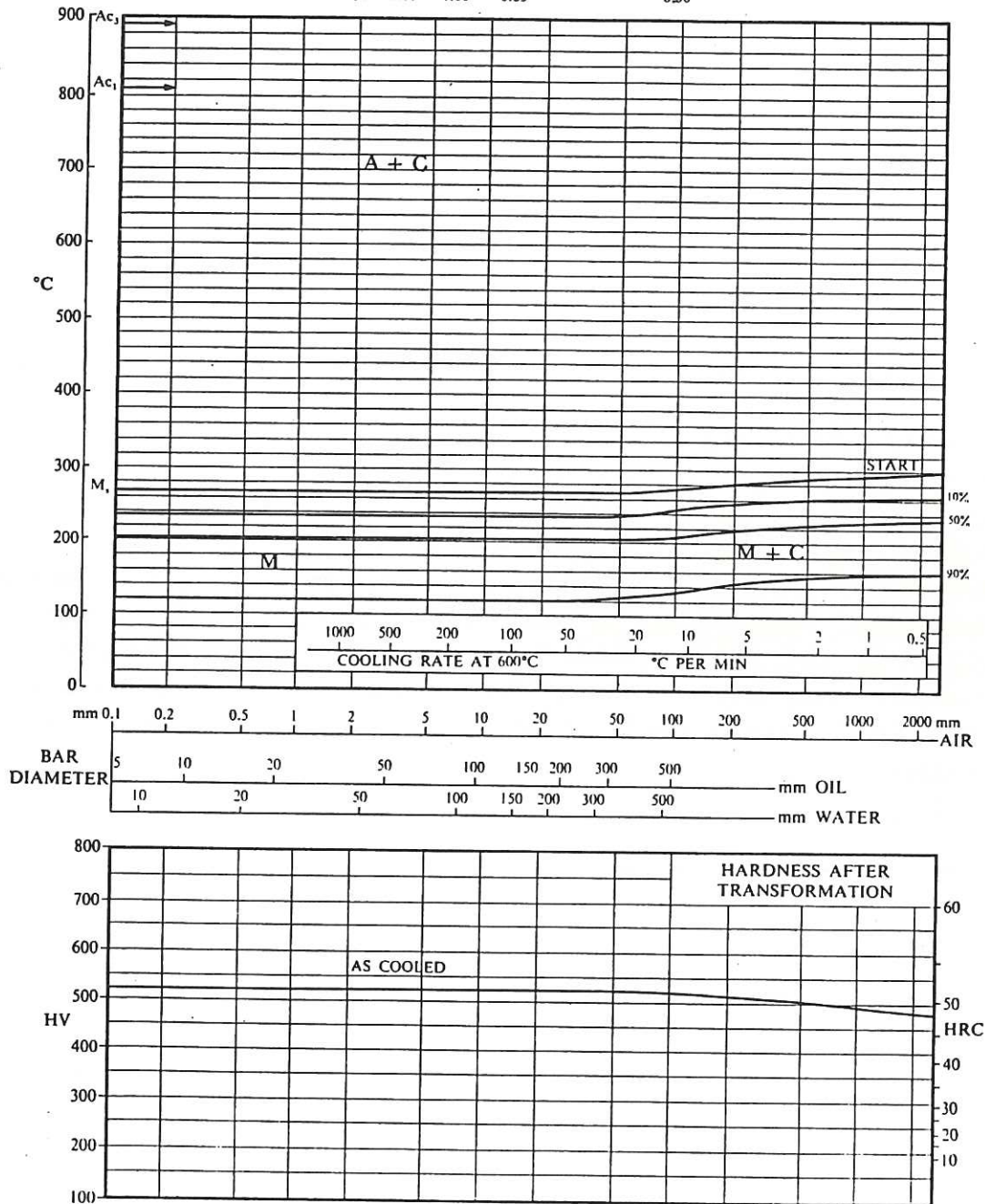| C	Si	Mn	P	S	Cr	Mo	Ni	Al	Nb	V
0.20	0.25	0.70	0.030	0.030	12.00	1.00	0.65	—	—	0.30

Fig. 4 Continuous cooling transformation diagram for a 12CrMoV
steel austenitised at 1000°C, rolled and softened for 1 h at 650°C.

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level is governed by the dissolved carbon content. This is an important factor with respect to hardening and welding fabrication and to the control of internal stresses, as discussed more fully in Appendix 2. For service at elevated temperatures, however, the steels are tempered at temperatures above 650°C and develop relatively stable tempered martensite microstructures containing various carbide types and morphologies. Thus the properties at the commencement of service depend on the elements in solid solution, the tempered martensitic structure and the type, location and volume fraction of precipitates.

The development of the tempered structures may best be considered with reference to individual alloying elements, although much of the available information applies to observations on proprietary alloys, in which more than one compositional variable has been changed during the experiments. Some general points may usefully be outlined before proceeding to the consideration of individual alloying elements.

The carbon and nitrogen contents are clearly important in determining the volume fraction of carbide and nitride phases formed both on tempering and during service exposure. In the unalloyed 12%Cr steels $(Fe,Cr)_3C$ forms initially on autotempering or tempering at low temperatures. This phase is replaced by dispersed $(Cr,Fe)_7C_3$ at higher temperatures, while overaging leads to the formation of grain boundary $M_{23}C_6$. In the alloyed 12%Cr steels the principal carbide-nitride phases are $M_{23}X_6$ based on $Cr_{23}C_6$, M_2X based on Mo_2C, V_4C_3 if relatively high V levels are present and NbC if niobium is present. Table 5 summarises the principal carbide phases found in some commercial steels.

A wide range of intermetallic phases has been reported for various compositions and conditions. They may be classified into two broad types, the Laves and the chromium-bearing phases. The former, typified by Fe_2Mo and Fe_2W are found at high levels of molybdenum and tungsten, such as may arise by segregation of these elements in delta ferrite. The bulk composition of an alloy is normally adjusted to avoid their formation. The chromium-bearing phases range from chi, found in alloys with high molybdenum, titanium or cobalt contents, through sigma phase to the low temperature chromium-rich alpha-prime. As discussed below, the avoidance of Laves and other intermetallic phases is one of the constraints to the development of novel alloy steels based on tungsten and vanadium.

Complex silicides and boride phases have been reported. These phases may form at unusually high concentrations of silicon or boron and usually occur in relatively coarse particles which confer no strengthening advantage. There is an extensive literature on the phase

Table 5 Phases present in chromium-based steel types

Steel	Phases present after hardening and tempering	Phases present after 30,000h at 550°C
2.5Cr-1Mo	$M_2X + M_7C_3 + M_{23}C_6$	$M_{23}C_6 + M_6C$
9Cr-1Mo	$M_{23}C_6 + (M_2X)$	$M_{23}C_6 + M_2X$
12Cr-1Mo-0.25V	$M_{23}C_6$ M_7C_3	$M_{23}C_6 + M_2X$ $+(VC)$
11Cr-0.3V-0.75W *	$M_{23}C_6$	$M_{23}C_6 + VC$ $+ WC$ or (M_2X)
11CrVWB *	$M_7(C,B)_3 + M_{23}(C,B)_6$	$M_{23}(C,B)_6 + VC + WC$

* the phases listed for these steels are anticipated and not experimentally verified.

chemistry of the 12%Cr,Mo,V,W,Nb steels, of which Refs.4-12 are representative.

3.   THE EFFECTS OF SPECIFIC ALLOYING ADDITIONS

3.1   Permissible low activity elements

3.1.1 Carbon

As is indicated in Table 3 and Fig.2, carbon is a strong austenite stabilising element. When dissolved, carbon will determine the as-quenched martensitic hardness[13], the dependence on concentration being as shown by Fig.5. This is an important factor for welding fabrication because of the risk of cracking in the weld heat-affected zone (HAZ) and this practical consideration limits the carbon level to about 0.2% maximum.

In the well-tempered structure developed at temperatures above 650°C, however, the effect of the carbon content depends on the relative concentrations of the carbide-forming elements. If strength values typical of current 12%CrMoV steels are sought then it is unlikely that carbon contents below 0.1% will give an adequate carbide volume fraction, hence the permissible range is established at between 0.1 and 0.2%.
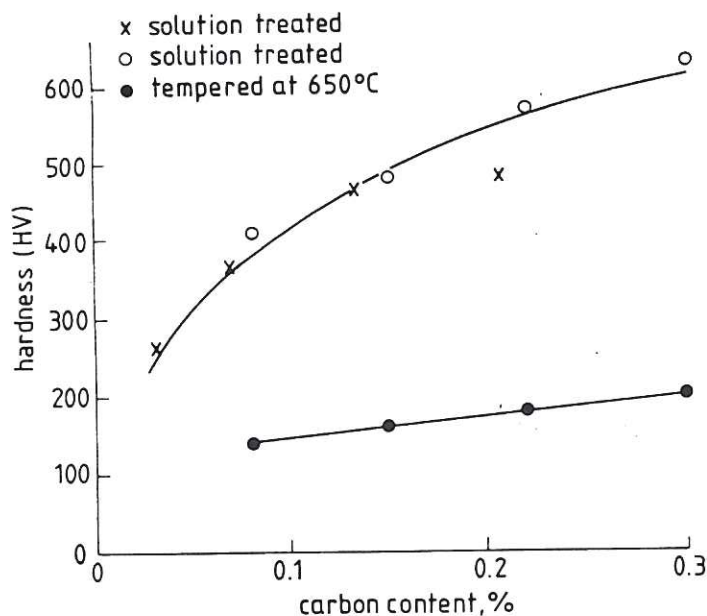
Fig. 5 Graph showing the effect of carbon on
the martensitic hardness of 12% Cr steels.

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3.1.2 Chromium

The element chromium confers the hardenability and corrosion resistance
characteristics of the 12%Cr martensitic stainless steels. Because of
the strong effects of chromium in promoting the formation of delta
ferrite and in depressing the M_s temperature (Table 4), however, the
development of a predominantly martensitic structure on cooling from
the austenitising temperature depends on balancing the concentrations
of chromium and other ferrite stabilising elements, as illustrated by
Figs. 3 and 4. Table 6 gives typical compositions and properties of a
range of standard commercial steels containing 2-12% Cr and other
elements. In the present work it will be assumed that the corrosion
resistance requirements in the fusion application will require a
minimum chromium content of 9%. Thus the permissible range can be
taken to be between 9 and 12%. A brief summary of the properties of
the 9%Cr-Mo commercial steels is given in Appendix 3.

3.1.3 Nitrogen

Nitrogen exerts similar effects to those of carbon. During tempering
it promotes strengthening through precipitation of the $(Cr,Mo,Fe)_2(C,N)$
phase, the effect being shown by Fig. 6[14]. It has been reported[15]
that additions of up to 0.15% N to a 0.17C-13Cr-1.3Mo-0.35V steel
confer increased strength on tempering, whilst an optimum addition of

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Table 6   Typical compositions and properties of a range of commercial chromium-based steels.   Typical values are shown in brackets.

Steel	Ac₁ °C	Ac₃ °C	M_s °C	Maximum section size for full hardening on air cooling	Typical heat treatment temperature °C	Minimum room temperature properties (typical values)		Minimum properties at 500°C (typical values)		Typical stress rupture value 3x10⁴h at 550°C	Stress for creep at 3x10⁴h at 550°C	
						0.2% PS MPa	Tensile MPa	0.2%PS MPa	Tensile MPa		0.5%	1.0%
2¼Cr-1Mo BS3059:622	735	880	420	20 mm	950 + 720	272 (350)	490	189 (230)		90	60	70
9Cr-1Mo BS3059:629	810	875	315	500 mm	1000 + 760	398 (450)	590	290 (360)		70	47	55
12Cr-0.1%C BS1449: 410S21	805	860	335	50 mm	1000 + 750	388 (500)	(590 to 680)	218 (350)	(350 to 420)	111	53	65
12CrMoV BS3059:762	810	890	270	1000 mm	1000 + 750	470 (660)	720 (780)	296 (380)		168	122	140
12CrMoVNb (FV448)	800	880	270	1000 mm	1150 + 650	755* (820)	925 (965)	540* (555)	(660)	(200)		(220)

* 0.1% Proof Stress

Typical compositions weight %

Steel	C	Si	Mn	Cr	Mo	Ni	V	Nb	N
2¼Cr-1Mo BS3059:622	0.08-0.15	0.5 max	0.4-0.7	2-2.5	0.9-1.20	-	-	-	-
9Cr-1Mo BS3059:629	0.15 max	0.25-1.0	0.3-0.6	8-10	0.9-1.1	-	-	-	-
12Cr-0.1%Cr BS1449: 410S21	0.09-0.15	0.8 max	1 max	11.5-13.5	-	1 max	-	-	-
12CrMoV BS3059:762	0.17-0.23	0.5 max	1 max	10-12.5	0.8-1.0	0.3-0.8	2.5-3.5	-	0.02-0.045
12CrMoVNb (FV448)	0.15	0.35	0.75	10.5	0.65	0.75	0.25	0.3	0.06

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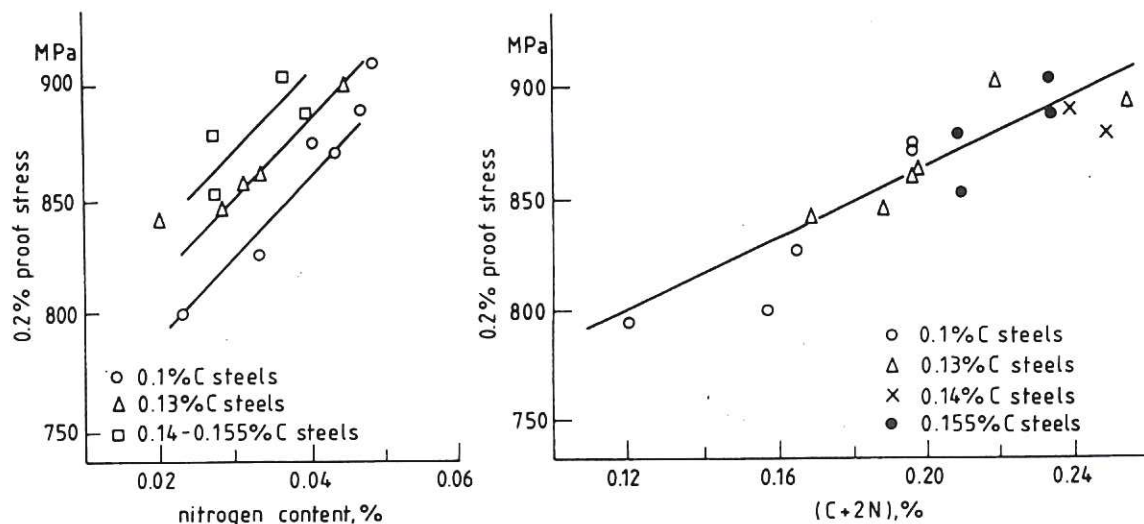
Fig. 6 Graphs illustrating the influence of carbon and nitrogen on a 12% CrMoV steel (treatment 1050°C, AC, 1h at 650°C)[14].

0.05-0.1% N has been recommended for 0.15C-11Cr-1.8W-1.6Ni-0.4Mo steels[16].

3.1.4 Manganese

Manganese is an austenite stabilising element, approximately half as effective on a weight for weight basis as nickel. In the martensitic steels it is normally present at concentrations which reflect its use as a deoxidant in steelmaking rather than as an intentional addition. It has been reported that, by decreasing the lattice solubility of carbon, manganese increases the degree of M_7C_3 precipitation. It has little effect on the tempered strength of 13Cr-0.1C-0.4Ni-0.2Mo steels when present up to 2.6%[17] and it has been added up to this level in developmental compositions[18], though for purposes other than improvement of the mechanical properties, which were not significantly affected. Excessive additions of manganese could impair the oxidation resistance and the element is best regarded as a compensating austenite stabiliser, for use at concentrations up to about 2.0%.

3.1.5 Silicon

Silicon is a ferrite stabilising element and contributes to solid solution strengthening in the tempered ferrite matrix. It plays no role in the formation of the common carbide and nitride phases but has an indirect influence on strength by reducing the ferrite lattice parameter and thus increasing the mismatch between the matrix and the precipitated carbides.

Silicon has been found to enhance the corrosion resistance of the 9%Cr-1%Mo steels in gaseous carbon dioxide and additions up to 0.8% are

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used for this purpose. There is an associated increase in tensile strength at both room and elevated temperature but no appreciable change of the creep rupture properties[19]. The use of silicon will be limited by considerations of austenite phase stability and the available evidence as to its effect on strength suggests that a practical upper limit is about 1%.

3.1.6 Vanadium

Vanadium is a ferrite stabiliser, acting directly in solid solution and also indirectly by removing carbon and nitrogen from solution if the austenitising conditions are such that carbide and nitride phases are not fully dissolved. For a 0.2C-10.4Cr-1.4Mo steel containing 0.2% V and 0.042% B it was found that the vanadium addition accelerated the transformation of M_7C_3 to $M_{23}C_6$ on ageing at 650°C, vanadium being detected in the $M_{23}C_6$ phase[7]. Vanadium concentrations above about 1% result in the formation of a discrete V_4C_3 precipitate while at even higher contents delta ferrite is stabilised. The effect of vanadium concentration on the tempering resistance of a 0.1C-12Cr-2Ni steel is illustrated in Fig.7.

The influence of vanadium as the sole alloying element in 9-12% Cr steels is to cause secondary hardening at about 550°C with the precipitation of vanadium-enriched M_7C_3[20]. After tempering at 700°C for up to 2000h only $M_{23}C_6$ was found except with vanadium contents above 1.3%, when some V_4C_3 was observed[21]. The effect of vanadium on hardness after tempering for short periods at 700°C was found to be proportionately greater up to 0.38% V than over the higher range 0.38-0.97%, as shown by Fig.8. Thus a small increase in vanadium content from the nominal 0.3% in the steels FV448 and DIN 1.4914 could yield some improvement in strength.

3.1.7 Tungsten

Tungsten is a ferrite stabilising element and a solid solution strengthener at concentrations up to 1%. On account of its higher atomic mass it is only about half as effective, on a mass percentage basis, as molybdenum. Some tempering curves for tungsten-bearing steels are given in Fig.9[4].

Tungsten is sometimes added to 12%CrMoV steels with the claim that it improves the stress rupture strength at around 600°C. Experimental work, however, did not reveal any significant benefit from an addition of 0.5% tungsten[22]. The role of tungsten appears to be one of stabilising the M_2X precipitate and it has been found to be effective in combination with 1% Mo at the 1% level[7]. There was no report of
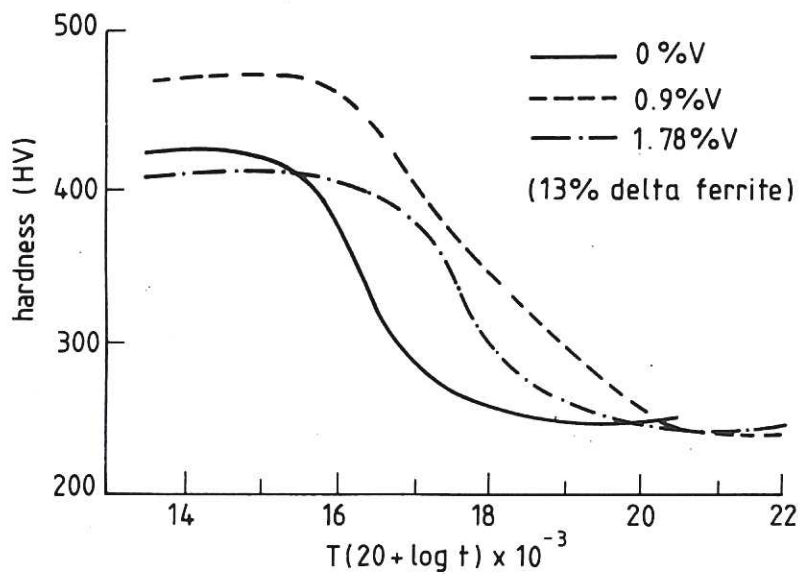
Fig. 7 Curves showing the effect of vanadium on the
tempering resistance of 0.1 C-12 Cr-2 Ni steels[4]
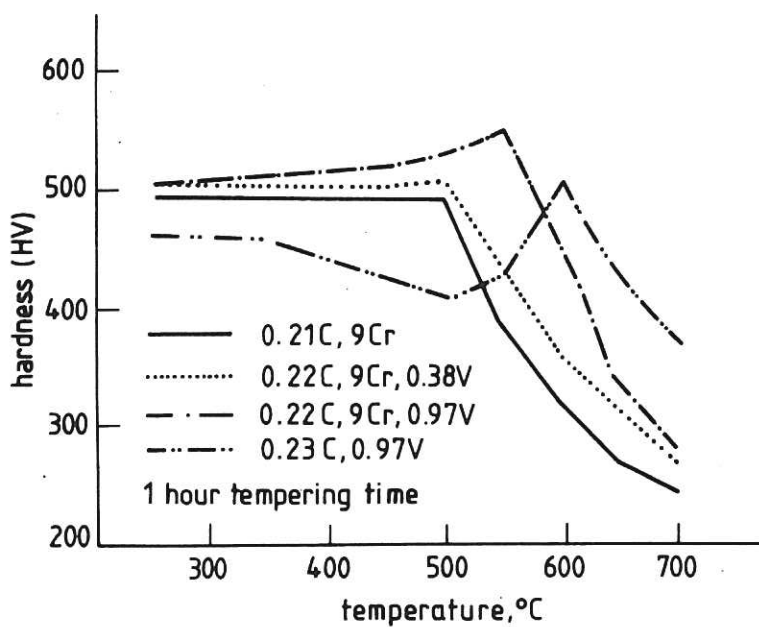
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Fig. 8 Hardness curves for 9% Cr-V steels for 1 h
tempering time[20].

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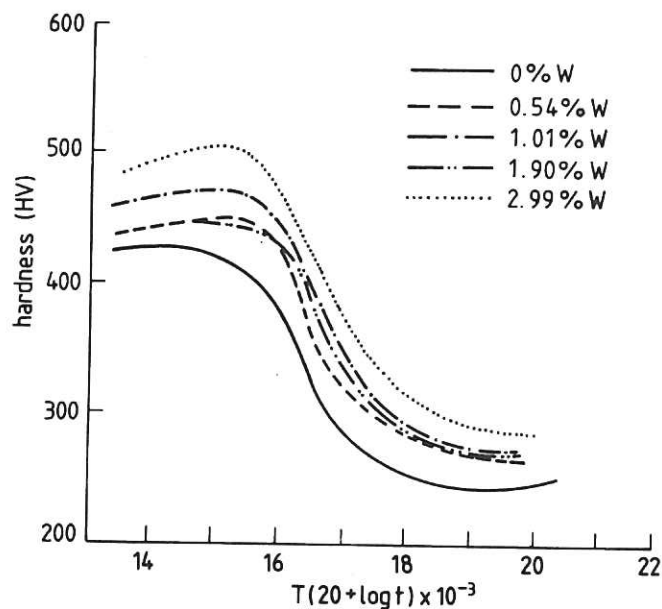
Fig. 9 Effect of tungsten on the tempering
resistance of 0.1 C-12 Cr-2 Ni steels[4].

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Laves phase formation in this steel during long term ageing but in
steels with 1.5-4% W, aged for 3000h at 600°C, both $M_{23}C_6$ and Laves
phase were observed. The higher tungsten steels were also found to
contain delta ferrite.

3.1.8 Boron

Boron dissolves in the $M_{23}C_6$ phase and its effect in improving the
creep rupture behaviour of both ferritic and martensitic steels may be
attributed in part to the finer distributions of the precipitates
obtained[23]. Thus an addition of 0.037% B to a 10.5Cr-0.2C-1.6Mo-
0.2V-2Nb martensitic stainless steel was found, as shown by Fig.10, to
give an appreciable increase in creep strength[23].

3.1.9 Other elements

A range of strong carbide-forming elements such as tantalum and hafnium
could, in principle, be used in the low activity martensitic steels.
There are, however, few solubility data or reports of their practical
application. Tantalum might be expected to behave in a similar way to
niobium, though it will not be considered further at this stage on
account of the combined problems of its high cost and the difficulty of
obtaining a steelmaking grade of the metal with a sufficiently low
niobium content.

-17-
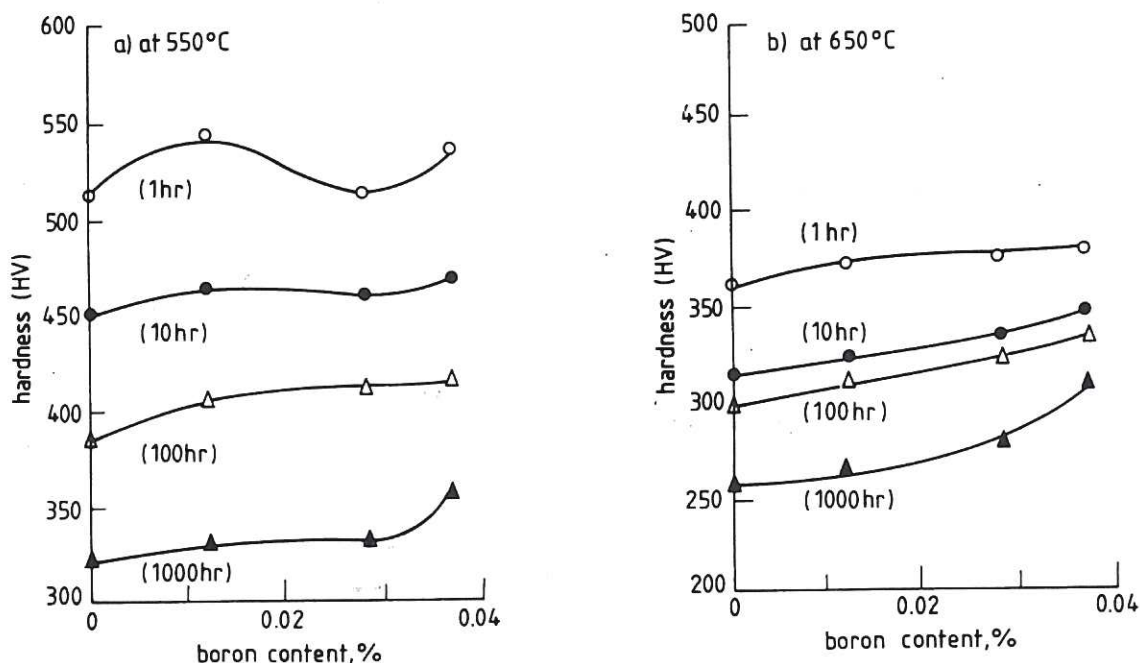
Fig. 10 Effect of boron content on the
hardness of 0.2C-10.5Cr-1.5Mo steel.

CLM-R264

3.2   The proscribed elements

3.2.1 Molybdenum

Molybdenum has several important roles in the high strength martensitic
stainless steels. It confers solid solution strength, hardenability
(cf. Figs.3 and 4) and appears in most of the carbides that give
precipitation strengthening, of which the most important type is M_2X.
The substantial hardening effect resulting from additions of molybdenum
up to 1% is indicated in Fig.11 by measurements on a 12Cr-2 Ni-0.09N
steel. Although concentrations up to 2% may be present in commercial
steels the strong ferrite-forming tendency of molybdenum usually
dictates that 1% or less is used in cases where a fully martensitic
structure is required. High concentrations of molybdenum can,
moreover, lead to the generation of Laves phase during ageing. The
removal of the 0.6% Mo present in the reference FV448 composition
(Table 2) will therefore result in a substantial decrease in hardness
and strength at elevated temperatures, especially where creep is the
dominant deformation process.

3.2.2 Nickel

Nickel is an austenite stabiliser and, like manganese, it depresses the
M_s temperature and thus increases the martensitic hardness for most

-18-
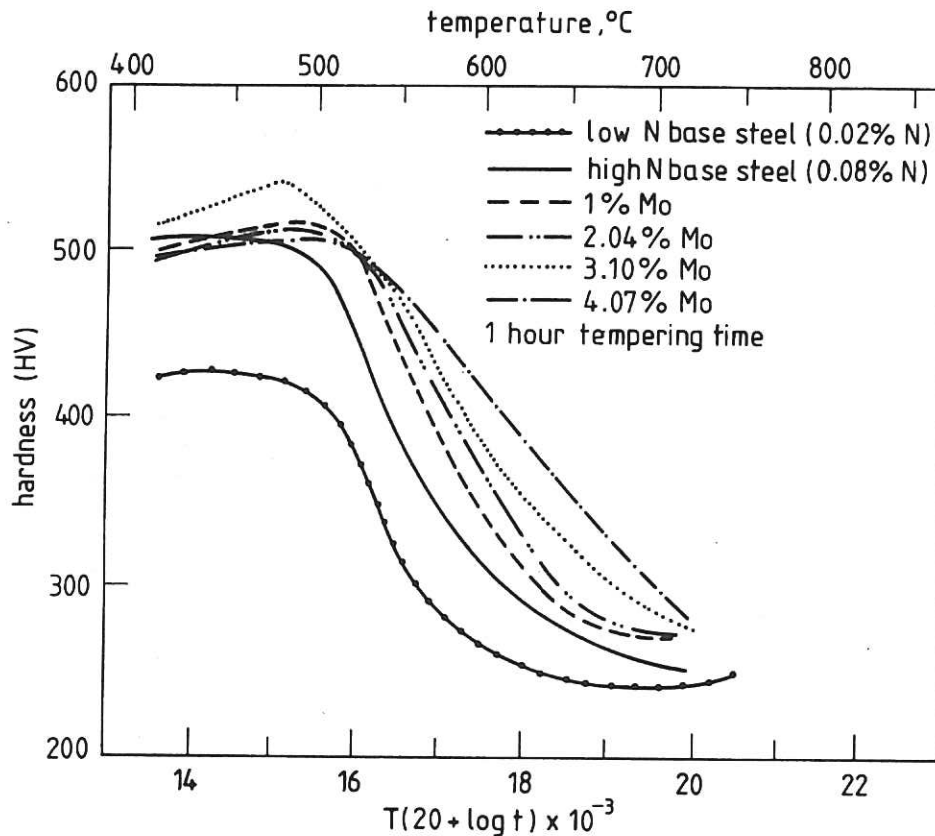
Fig. 11 Effect of molybdenum on the
tempering resistance of 0.1 C-12 Cr-2 Ni steel.

CLM-R264

steels by suppressing auto-tempering. In concentrations up to 1% it
has an appreciable effect on the solid solution strengthening of the
matrix[4]. Nickel has no direct role in the formation of precipitates
but, by reducing the solubility of carbon, it favours the increased
precipitation of M_7C_3 and M_2X[2]. Thus the elimination of nickel will
lead to some reduction in strength, though not to the same extent as
with molybdenum.

3.2.3 Cobalt

Cobalt is an austenite stabilising element which, like nickel, does not
participate in the formation of the carbide and intermetallic phases
but contributes to solid solution strengthening. Unlike nickel, it has
little effect on the transformation temperatures and can be utilised to
adjust the austenite stability without depressing the M_s temperature.

The concentrations of cobalt in normal martensitic stainless steels are
usually below 0.05% and its absence is not expected to lead to any
appreciable change in properties.

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3.2.4 Niobium

Niobium is a ferrite stabiliser and strong carbide former, similar in its effect to vanadium. Additions of up to about 0.25% have been found to raise the creep strength through the formation of NbC precipitates. An optimum content of 0.15% Nb with 0.2% V was found for exposure of 10,000h at 600°C[7]. Inadequate solution treatment will lead to a reduction in martensitic hardness as a result of the removal of carbon from solution as Nb(C,N). The elimination of niobium from the reference compositions will therefore lead to some reduction in strength.

3.2.5 Titanium

Titanium is similar to niobium in its influence, though more effective on a mass percentage basis because of its lower atomic mass. In low alloy steels the nitride phase is less soluble than that of either vanadium or niobium. Where titanium is dissolved at the austenitising temperature subsequent precipitation of TiC would be expected, though this has not been reported as a feasible strengthening mechanism in commercial martensitic stainless steels. At concentrations above 1.5% and when combined with silicon, titanium gives a strong precipitation hardening reaction with the silicon in ferrite[24]. These precipitates, however, are less stable than those formed during carbide strengthening at high temperatures and the combined additions would effectively prevent the development of a fully austenitic structure.

Titanium is not normally added to the high-chromium martensitic steels of the type being considered in this study. Moreover, the rather restricted concentration permitted by the long term dose rate criterion (Table 1) implies that it must be disregarded as a significant alloying addition in the present context.

3.2.6 Copper

Copper is an austenite stabiliser but has no direct effect on martensitic hardness. It is employed in commercial high strength stainless martensitic steels at concentrations up to 4% to give dispersion strengthening on ageing at 450-650°C through the precipitation of a copper-rich phase. At higher tempering temperatures this phase overages rapidly, however. Thus copper cannot be considered as giving an effective strength contribution in the 9-12%Cr martensitic steels, though it might confer some increase in toughness.

3.3 Residual elements

The elements that are normally reported as minor constituents of steels

may be divided into the metallic, metalloid and non-metallic residual elements and can be classified as follows:

- Metallic elements present as a component of ferro-alloy impurities or scrap metal charges and not specified as an alloying addition, e.g. antimony, tin

- Metallic elements usually present in the form of oxides as a result of deoxidation reactions or liquid steel-refractory reactions, e.g. aluminium, calcium, magnesium

- The metalloid elements, again most frequently present as a consequence of the use of mixed scrap, e.g. arsenic

- Non-metallic elements derived from impurities in the iron and ferro-alloys, reactions with refractories or dissolved gases, e.g. sulphur, phosphorus, hydrogen

Aluminium and zirconium are restricted to very low concentrations by the constraints on long term contact dose rate, though their elimination to the levels of 10-1000 ppm given in Table 1 should not be difficult. Aluminium can be replaced as a deoxidant and zirconium occurs only at very low concentrations in normal production and mainly as a result of refractories attack.

Restriction of the tin content to 0.001% (Table 1) would exclude the possibility of using normal scrap-based melting routes, with a consequent increase in steelmaking cost. The adoption of a special melting base to restrict the ingress of tin would also allow the reduction of phosphorus, arsenic and antimony concentrations and thus decrease any risk of temper embrittlement.

In cases where low residual element levels are specified for current steel production they are usually achieved through the use of specially selected sources of iron and of steel scrap that have been derived from a virgin iron ore, rather than from scrap-contaminated processes. Table 7 gives the reported elemental analyses for two alloy steel products made in this way. There is scarcely any data, however, for the occurrence in steels of particular trace elements included in sections B and C of Table 1. The question of the feasibility of excluding particular impurity elements to the high degree demanded by the radiological requirements will need to be addressed in future studies.

As indicated by Table 1, silver is a highly undesirable residual element. There is only limited information on the silver content of

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Table 7   Typical residual element concentrations (wt%) in two types of
low alloy steel made from selected iron units and ferro alloys
to control residual levels under full scale production
conditions

Steel Type \ Residual Element wt%	P	S	As	Cu	Nb	Sb	Sn	Bi	Pb	Co
3½% NCMV Rotor Steel (240t BEA+VAD)	0.006	0.007	0.008	0.04	unknown	0.0012	0.003	unknown	<0.0005	<0.01
Cr-Mo-V Bolt Steel (120t BEA)	0.008	0.009	0.014	0.06	0.009	0.0016	0.008	<0.001	<0.005	unknown

normal steels; a concentration of 0.0002% has been measured in a type
316 steel[25] and this is introduced mainly via the nickel addition.
Since nickel will not form a constituent of low-activation steels it
should not provide a primary route for contamination by silver.

4.   METHODS OF MANUFACTURE

Before considering the selection of optimised compositions it is
appropriate to outline the steelmaking routes that may be used to
produce the intermediate steel products required for reactor
construction. The basic steelmaking units are the electric furnace and
the converter processes, of which the Argon Oxygen Decarburisation
(AOD) is the most suitable for the manufacture of high-chromium alloys.
The former melting unit may be used to feed an AOD converter.

Plates, billets and bars of the 12%CrMoV steels would normally be made
from ingots of weight between 4 and 10 tonnes, depending on plate size
and thickness.   Large forgings are most often made from single,
purpose-shaped ingots of similar weight although, as noted below,
larger ingots may be produced. Seamless tube and strip would normally
be made from ingots of less than 8 tonnes weight. The ingot size is of
considerable importance as the alloys are prone to segregation on
solidification, a problem that increases in severity with the size of
the ingot. Local formation of delta ferrite is one possible result.
For example, negative segregation at the bottoms of large ingots has
been observed; the consequent carbon depletion leads to formation of

delta ferrite at the cores of primary dendrites, even though the nominal alloy composition may indicate its absence. In the manufacture of large forgings for the power generation industry this problem has been overcome by the adoption of electroslag remelting (ESR). In this process an electrode initially produced by conventional means is remelted through a suitable slag. The maintenance of a small molten pool and the broadly directional solidification pattern help to minimise macrosegregation[26]. The ESR manufacturing capacity currently ranges from about 3 to 160 tonnes ingot weight.

The importance of compositional control to offset the formation of delta ferrite on initial solidification will depend on the product form and the tolerable ferrite content. A chromium equivalence formula has been proposed to predict compositions that will be immune to formation of delta ferrite in large section sizes[27], similar in form to that used to predict phase stability from the Schaeffler diagram.

5.   THE COMPOSITIONAL DESIGN OF LOW-ACTIVITY 12%Cr STEELS

Examination of Table 1 indicates that the elements nickel, molybdenum and niobium must be excluded on radiological grounds from any low-activation stainless steel compositions. As discussed in section 3 the practicable alternative additions to the iron-chromium-carbon matrix of 12%Cr martensitic steels comprise manganese, nitrogen, tungsten, vanadium and boron.

As a starting point in the design of alternative compositions it is instructive to estimate the properties to be expected of the base material obtained by removal of the undesirable elements from the standard FV448 or 1.4914 compositions. The effects of eliminating molybdenum, nickel and niobium from these steels on the hardness in the tempered condition and the transformation temperatures and delta ferrite content have been estimated and the results are shown in Table 8. On the assumption that the effects of the individual elements are additive, the main consequences are a loss in hardness of 100 HV, equivalent to a reduction in room temperature tensile strength from about 960 to 640 MPa, a potential increase in the delta ferrite content and an increase in the M_s temperature. The expected decrease in room and elevated temperature strengths is supported by a comparison of the properties of the steels BS 1449:410S21 and FV448, shown in Table 5. It must be emphasised that the above approach is simplistic, in that it neglects any synergistic effects of the individual elements.

It should be mentioned that in the above and in subsequent estimations it has been necessary to employ hardness values as an indirect measure of room temperature strength. This need arises from the fact that most

Table 8 Summary of anticipated effects on properties resulting from the removal of Mo, Ni and Nb and addition of V and W

Data are taken from Table 4. Figures in brackets are estimates for elements not included in this table

Element	Amount to be removed %	Effect of removal on properties			
		Tempered hardness HV	Change in M_s °C	Change in Ac_1 °C	Predicted change in delta ferrite content %*
Mo	0.6	−30	+12	−15	−3
Ni	0.8	−30	+13	+24	+16
Nb	0.3	−40	(+10)	(−10)	(−7)
	Amount to be added %	Effect of addition on properties			
V	0.25	+25	(−10)	+12	+4
W	1	+60	−11	(+6)	(+2)
	2	+120	−22	(+12)	(+4)
Net additive effect of removing Mo, Ni and Nb, increasing V to 0.5% and adding					
	1% W	−15	(+14)	(+17)	(+12)
	2% W	+45	(+3)	(+23)	(+14)
relative to FV 448		280	270	800	≠

* Actual δ ferrite content not directly calculable
≠ Although the propensity for delta ferrite formation has increased, all of the modified alloys should contain less than 5% delta ferrite.

systematic studies of the influence of individual alloying elements have been conducted on the basis of tempering curves, with hardness as the measured parameter, rather than on complete evaluations of the mechanical properties. The hardness values may be taken as a relative measure of the tensile strength.

The first consideration in designing a low-activity composition is the austenite phase stability. In general, the presence of delta ferrite is to be avoided since it results in impaired hot working characteristics, loss of strength and a heterogeneous distribution of alloying elements. The latter feature may cause embrittlement after long term exposure at elevated temperatures and, in addition, local variations in corrosion and oxidation resistance. The reported properties of duplex 12%CrMoV steels containing up to 30% delta ferrite are summarised in Appendix 1 and these indicate that it is possible to obtain satisfactory conventional and short term elevated temperature properties with delta ferrite present[28]. If, however, reliance is placed on vanadium and tungsten to promote strength then there is an increased risk of intermetallic phase formation as a result of the segregation of these elements into the ferrite. For this reason it is proposed initially to examine compositions that should possess fully martensitic structures, though the possible future need to consider steels having duplex structures cannot be ruled out at this stage. Thus the aim will be to achieve, where possible, fully austenitic structures prior to hardening and to identify compositions which, under normal conditions of segregation, will have acceptable delta ferrite contents, generally below 5%.

The behaviour of the permissible alloying elements and the concentration ranges that can usually be employed are summarised in Table 9. There are some uncertainties regarding the choice of the combined concentrations for study. The first relates to the optimum ratio of the interstitial and the carbide-forming elements. Optimum vanadium to carbon ratios are known empirically for rupture strength in the 12%CrMoV steels but remain to be established for the steels in which the vanadium content is increased and tungsten is substituted for molybdenum. The second uncertainty concerns the limitations placed on the upper concentrations of vanadium and tungsten by intermetallic phase formation. There is a problem in the interpretation of the relevant literature in that many of the chemical or electrolytic isolation techniques used in the early X-ray and electron optical phase studies are known to give selective phase isolation. Thus Laves and possibly other intermetallic phases may well be present at earlier stages of formation than those reported in the literature.

The toughness of a 12%Cr steel containing vanadium and tungsten may be affected by unfavourable carbide or intermetallic phase distributions, an aspect that will require examination for both the initial service condition and after exposure simulating service thermal history. It is generally held that nickel is beneficial to the toughness of the martensitic stainless steels, hence some inherent loss of toughness in comparison with FV448 may be anticipated, even if a favourable phase distribution is obtained on tempering.

For the present application there is some concern as to the role of carbon and nitrogen in the processes of corrosion in the presence of lithium. The lowest practicable levels of carbon and nitrogen in current commercial production of stainless steels are 0.002 and 0.003 wt % respectively. Reduction of the carbon and nitrogen contents to such low levels in order to retard lithium attack would lead to a ferritic structure and, as noted above, a consequent drastic reduction in strengthening from precipitation on tempering. Although balanced additions of manganese may be used to eliminate the ferritic structure there is no practicable way of recovering the elevated temperature strength. It is therefore proposed that the martensitic steels continue to be considered for applications involving contact with liquid lithium, with reliance on surface treatments such as chromium deposition (e.g. 'chromising') to prevent exposure of carbides if this is necessary. If such a technique were adopted the possibility of carbon migration through the protective layer would need to be considered. There appears to be no benefit at this stage in considering carbon contents greatly reduced below 0.1%, until further information is available on the control of possible embrittlement reactions.

In addition to the above considerations regarding the microstructure, the effects of changes in alloy composition on the transformation temperatures will need to be taken into account, particularly with respect to the M_s temperature, which is about 260°C for 12%CrMoV steels. The data in Table 8 suggest that the removal of molybdenum, nickel and niobium may result in an increase to about 290-300°C. A greater negative effect could, however, accumulate from the elements added or decreased, as indicated by Table 4, with the possibility that M_f will lie below room temperature and austenite will thus be retained in the structure on hardening. Examples of possible effects are illustrated by selected compositions in Table 8, using the information of Table 4.

6. COMPOSITIONS PROPOSED FOR STUDY

From the factors given in Table 9 a range of compositions for experimental assessment may be proposed and these are listed in

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<u>Table 9</u> Range of alloying additions proposed as basis for experimental evaluation

Element	Practicable range	Strengthening increment within range for 650°C-750°C tempered condition	Comments
Carbon	0.1-0.20%	Not relevant	Upper limit set by martensitic hardness. Content would need to be optimised against levels of carbide-forming elements, 0.15% proposed as initial base content.
Chromium	9.0-12.0%	Not relevant	Reduction in chromium reduces ferrite-forming potential of composition. Concentrations of 9.0 and 11.0% proposed.
Vanadium	0.25-0.9%	85HV/1.0%	Additional precipitation strengthening required, but upper limit is set by delta ferrite formation and tendency to precipitate as non-strengthening intermetallic, rather than carbide phase.
Tungsten	0.25-3.0%	45HV/1.0%	Substitutes broadly at 2:1 ratio for molybdenum with respect to temper embrittlement, solid solution and precipitation strengthening. Ferrite stabiliser.
Nitrogen	0.06-0.10%	Not relevant	Acts as both austenite stabiliser and participates in precipitation.
Boron	0.01-0.03%	Not relevant	Retards coalescence of carbides and stabilises the $M_{23}(C,B)_6$ precipitate phase.
Manganese	0.5-1.5%	Not relevant	Acts as austenite stabiliser.

Table 10   Experimental compositions for evaluation

Steel No.	Composition weight %													Cr equiv.	Ni equiv.	estimated delta ferrite content %
	C	Si	Mn	P	S	Cr	Mo	Ni	W	V	Nb	B	N			
1	0.15	0.4	0.75	0.01	0.015	11	0.65	0.75	-	0.25	0.3	-	0.06	12.4	7.2	0
2	0.15	0.4	0.75	0.01	0.015	11	-	-	-	0.25	0	-	0.06	13.0	6.4	0
3	"	"	"	"	"	"	-	-	0.25	0.25	0	-	"	13.2	6.4	0
4	"	"	"	"	"	"	-	-	0.75	0.25	0	-	"	13.5	6.4	0
5	"	"	"	"	"	"	-	-	1.25	0.25	0	-	"	13.9	6.4	0
6	"	"	"	"	"	"	-	-	2.0	0.25	0	-	"	14.5	6.4	0
7	"	"	"	"	"	"	-	-	3.0	0.25	0	-	"	15.2	6.4	5
8	"	"	"	"	"	"	-	-	0.75	0.5	0	-	"	14.8	6.4	0
9	"	"	"	"	"	"	-	-	0.75	0.9	0	-	"	16.5	6.4	10
10	"	"	"	"	"	"	-	-	0.75	0.25	0	0.01	"	13.9	6.7	0
11	"	"	"	"	"	"	-	-	0.75	0.25	0	-	0.10	13.9	7.4	0
12	"	"	"	"	"	9	-	-	0.75	0.25	0	-	0.06	11.5	6.4	0
13	"	"	"	"	"	9	-	-	3.0	0.25	0	-	0.06	13.2	6.4	0

Table 10 together with calculated values of the delta ferrite content. The rationale for the selection of these compositions is presented below.

Steel 1 is the reference base alloy, made to the typical FV448 composition given in Table 5. The residual element concentrations have been chosen to represent those occurring in conventional production steelmaking practice. The phosphorus content of 0.010% could be reduced further in production if necessary for toughness control. Steel 2 represents the base alloy with the elements Mo, Ni and Nb removed and provides a reference against which to measure the effects of added elements.

Steels 3-7 provide for a systematic exploration of the contribution from tungsten, with vanadium present at the nominal concentration of the FV448 alloy. No adjustment has been made to compensate for the formation of delta ferrite in the 3%W Steel 7. The composition proposed will provide an indication of the effects of delta ferrite in a molybdenum-free steel (cf. Appendix 1) and any necessary adjustment could be made at a later stage.

Steels 8 and 9 allow the role of vanadium in the presence of 0.75% W to be established while Steels 10 and 11 explore the effects of separate additions of boron and nitrogen relative to Steel 4. The Steels 12 and 13 duplicate 4 and 7 but with reduced chromium contents of 9%.

The influence of boron could be examined further in a composition providing a suitable tempered carbide distribution containing $M_{23}C_6$.

7. SUGGESTED PROCEDURE FOR EVALUATION OF THE PROPOSED COMPOSITIONS

An experimental programme for assessment of the proposed low-activity compositions is outlined schematically in Table 11. The preparation of the experimental steels, their homogenisation and conversion to a convenient starting form would follow standard practices. The first tests would establish the incidence of delta ferrite after austenitising at a standard temperature. For economy of effort the full range of austenite stability need not be explored initially unless specific problems are encountered with the dissolution of carbides and nitrides or excessive volume fractions of delta ferrite are formed.

An investigation of the tempering response is fundamental to an estimation of the strength values that can be achieved and to gain an initial indication of the thermal stability of the tempered martensitic structures. During this phase of the assessment the stability would be judged with reference to an assumed maximum service exposure equivalent

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Table 11 Work plan for the evaluation of proposed experimental Cr-W-V martensitic stainless steels

Phase I	1. Manufacture to proposed compositions 50kg ingots, forge, homogenise and roll to 50 mm sq. and 19 mm round stock.	
	2. Anneal 19 mm stock for metallographic studies. Austenitise at 1100°C and air cool. Examine for the presence of delta ferrite, undissolved carbide or other phases. If absent	If present Explore austenitising temperatures in range 1000–1200°C. Choose optimum austenitising treatment. Refrigerate, if required, to deal with retained austenite.
	3. Perform tempering for 1h at temperatures between 450 and 750°C. Establish hardness and make metallographic assessment of phases present at temperatures above 600°C.	
	4. Select temperature above 600°C and carry out isothermal tempering for times up to 500h. Characteristic phases present.	
	5. Assess results of tempering experiments in terms of hardness results, precipitated phase chemistry, distribution and morphology.	

Table 11 cont

Phase II		If selected compositions are satisfactory	If no composition is satisfactory
	6.	Select, after further tests as necessary, austenitising and tempering conditions appropriate to each candidate composition.	Revert to stage 1 and reselect compositions.
Phase III	7.	Establish room temperature tensile properties and perform tensile tests at temperatures up to 650°C. Establish Charpy impact transition curves for standard tempered conditions and after 500h at 500°C. **If properties judged acceptable** Mount stress rupture tests at 500–550°C for a planned duration of 10,000h on selected compositions. Characterise transformation characteristics by dilatometry. Evaluate microstructures and hardness levels produced by weld cycle simulation. Conduct initial corrosion evaluation to assess relevance of chromium level. Initiate thermal exposure trials at 500°C to assess toughness, fracture toughness and tensile properties after exposure times in excess of 10,000h. Verify sensitivity to embrittlement at lower temperatures by isothermal exposure at temperatures of 400° and 450°C.	

to 2 years at 575°C. At this point it may be possible to suspend study of some of the compositions on the grounds of excessive delta ferrite content or the incidence of unfavourable precipitate types and morphologies. Investigations could then proceed either on compositions selected from those in the initial series or on optimised variants indicated by the preliminary results. In either case it is suggested that the heat treatment condition be optimised and the basic tensile and impact toughness properties of the steels be established.

From this stage, if suitable compositions have been chosen, it is possible to proceed to tests more closely related to the anticipated service conditions. For example, current design codes require stress rupture data relevant to the proposed application. From the materials development standpoint it is advantageous that the service life currently anticipated for steel reactor components is relatively short in comparison with the lives required of components for conventional power generation. One result is that relatively short elevated temperature test programmes, up to 2 years' duration, will give useful data.

In the final phase of the experimental study stress rupture tests should be initiated, primarily at 500-550°C but with some supporting tests at higher temperatures, and fabrication and corrosion aspects could be studied in more detail. It would also be essential to confirm the predictions of thermal stability derived from metallographic examinations, with tests to assess the variations in properties following thermal exposure. By the time this stage of the assessment has been reached, more engineering design information may be available to allow the selection of further test conditions to evaluate, for instance, the thermal fatigue behaviour and radiation damage susceptibility.

8.   SUMMARY

The 9-12%Cr martensitic stainless steels are being considered for fusion reactor first wall and blanket applications on the grounds of their strength, resistance to radiation damage and thermal fatigue and compatibility with lithium-based breeding materials. In order to achieve a strong reduction in the levels of long-term remanent radioactivity in components removed from reactor service it is necessary to eliminate certain of the chemical elements normally employed as alloying additions in stainless steels. The most important of these elements metallurgically are molybdenum, nickel, niobium and aluminium. The metallurgical factors governing the structure and properties of the 12%CrMoV steels have been reviewed to determine whether high strength martensitic steels can be developed without the use of these elements. The consequences of eliminating the proscribed

elements, in terms of the alloy strength and phase balance, have been assessed and the use of alternative alloying additions has been considered, with the objective of attaining a service performance comparable to that of existing steels, subject to certain assumptions as to the anticipated service conditions. It has been assumed that the component life in a power reactor will be 2-3 years at a mean operating temperature of 500°C, with thermal excursions.

The principal conclusions of the study are as follows:

1. The elimination of molybdenum and niobium from the compositions of established martensitic stainless steels leads to a substantial reduction in room and elevated temperature strength. The practicable substitutes that can be employed to restore the strength are tungsten, in place of molybdenum, with increased additions of vanadium and appropriately adjusted concentrations of carbon, nitrogen and possibly also boron.

2. The overall alloy balance must be such that a predominantly martensitic structure is obtained on hardening, with sufficiently high M_s and M_f temperatures to ensure a controllable retained austenite content on hardening and an Ac_1 temperature high enough to allow full tempering and stress relieving without austenite reversion. Although the use of duplex steels cannot be excluded, the employment of vanadium and tungsten introduces a risk of segregation and intermetallic phase formation within regions of delta ferrite. For this reason it is proposed in the first instance that substitute steels should have predominantly martensitic structures.

3. Existing tempering data indicate that suitable strengthening should be obtained with additions of vanadium up to 1% and of tungsten up to 3%, with suitable adjustment to the concentrations of carbon and nitrogen. The synergistic effects of these additions will, however, need to be investigated.

4. It is considered that there is a reasonable probability that a low-activity composition will be identified, within the operational boundary conditions assumed in this study, namely a 2-3 year component life, 500°C normal operating temperature, with thermal excursions to a maximum of 600°C.

5. In addition to 12%Cr steels, the characteristics of the commercially available 9%Cr steels have also been summarised and it is proposed that consideration be given to the use of a 9%Cr matrix, since the reduction in chromium content aids the prevention of delta ferrite formation.

6. A programme has been proposed for the evaluation of selected experimental compositions, to establish the optimum concentrations of vanadium and tungsten and to assess the problems of austenite phase stability and the incidence of intermetallic phases in both the initial tempered condition and after simulation of thermal exposure in service.

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APPENDIX 1

DUPLEX FERRITIC-MARTENSITIC STAINLESS STEELS

Whilst the declared objective of the present study is the development of a direct replacement for the conventional martensitic steels, it is worth noting that duplex ferritic-martensitic steels with ferrite contents up to 50% have been developed commercially. The aim in designing these compositions has been to improve the weldability; by relaxing the requirement for a fully martensitic structure and by reducing the carbon content the hardness of the weld HAZ can be reduced.

Available commercial steels are based on a matrix consisting of 9-10% Cr and 1.5-2% Mo, some with additions of vanadium and niobium (Appendix 3). Wada et al[29] have proposed compositions based on, nominally, 0.1%C, 12%Cr, 2%Mo, 0.25%V and 0.05%Nb, with an optional addition of 0.5%W, as illustrated by Table A1.1. These steels contain between 15 and 40% delta ferrite. Tensile strengths comparable with that of FV448 were obtained at room temperature with satisfactory elevated temperature stress rupture properties, on the basis of tests to 3000h, at temperatures of 593° and 649°C.

Studies of Fe-Cr-Mn microduplex ferritic-martensitic steels have been reported[30], based on 12%Cr, 3%Mn steels with low interstitial content, the carbon and nitrogen concentrations being below 0.05 and 0.03 wt % respectively. These steels contain up to 25% delta ferrite. Their properties are of only limited interest as there were no additions to confer strength at elevated temperatures. It was claimed, however, that the toughness characteristics of, typically, a material comprising 85% martensite and 15% ferrite were superior to those expected from a fully martensitic FeCrMn steel. In principle, the properties claimed at least for short term elevated temperature exposure justify the consideration of structures with delta ferrite contents above 10%[28]. The case would be strengthened if it were found that the replacement of nickel by manganese appreciably impaired the toughness of the fully martensitic steels. It is not known, however, to what extent the claimed advantages in welding offset any problems of hot workability.

In the absence of information on the strengthening contributions from the individual alloying elements used in these steels it is not possible to suggest candidate compositions based directly on the reported work. It may be noted, however, that the elimination of nickel, molybdenum and niobium from the alloys proposed by Wada

et al leads to compositions similar to those given in Table 10, except for the carbon and nitrogen contents. Further consideration of duplex steels may be warranted in the light of the behaviour of Steels 7 and 9 in the development programme.

Table Al.1 Recommended composition of duplex structure 12Cr-Mo steels[29]

Type	Element, %											
	C	Mn	Si	Cr	Mo	W	Ni	V	Nb	P	S	N (ppm)
12Cr-2Mo	0.07 – 0.11	0.6 – 0.8	0.15 – 0.5	11.0 – 12.0	1.7 – 2.1	–	0.5 – 2.0	0.2 – 0.3	0.0 – 0.1	0.03	0.02	150 – 350
12Cr-2(Mo,W)	0.07 – 0.11	0.6 – 0.8	0.15 – 0.5	11.0 – 13.0	1.4 – 1.7	0.4 – 0.6	0.5 – 2.0	0.2 – 0.3	0.03 – 0.01	0.03	0.02	150 – 350

Typical room temperature properties

Type	Yield strength (MPa)	UTS (MPa)	elongation %
12Cr-2Mo	690	840	22
12Cr2(Mo,W)	750	900	19

APPENDIX 2

WELDING FABRICATION ASPECTS OF THE 12%Cr STEELS

An outline of welding methods for the 12%Cr martensitic steels is given in Ref.2. It is accepted that the steels are not easily welded but can be fabricated satisfactorily provided suitable preheating and post-welding stress relief heat treatments are applied. A minimum preheat temperature just above the M_s temperature of about 260°C is normally specified, though temperatures up to 450°C may be employed[2]. A laboratory study of welding conditions for a 12%CrMoVW steel, a martensitic stainless composition under consideration for fusion application in the USA, confirmed 300°C as a suitable preheat temperature[31].

Problems of HAZ cracking can be reduced by recourse to a lower carbon content but this is feasible only to an extent permitted by the tolerable delta ferrite content and by the ratio of the interstitial elements to vanadium and tungsten to achieve adequate strengthening in the tempered condition. In developing any new steels a balance must be achieved between the attainable strength values and the weldability. For this reason a study of simulated weld HAZ structures has been incorporated in the third phase of the proposed experimental assessment.

Post weld heat treatments for stress relief are required for fabrications. The temperature range used must be high enough to ensure stress relaxation and is usually specified in the design codes for individual steels. Temperature ranges are usually just below the normal tempering temperatures thus, for the 12%Cr alloy steels, treatments up to some 3h at 750°C could be applied, following the original tempering operation.

APPENDIX 3

MARTENSITIC 9%Cr-Mo STEELS

The basic commercial steel in the 9%Cr-Mo family is the 9%Cr, 1%Mo composition BS 3604:629 and BS 3059:629, which was developed to provide the required corrosion resistance in certain oil industry applications. Its high strength at ambient and elevated temperatures led to its adoption as tube material in the AGR heat exchangers and as a candidate for similar fast reactor applications. High silicon contents up to 0.8% are specified for the former to increase corrosion resistance in hot carbon dioxide gas but these have little attendant effect on elevated temperature creep strengths[32].

The 9Cr-1Mo steel has a high hardenability and a fully martensitic structure after air cooling in sections up to 500 mm thick. The material is normally used tempered at 760-780°C, and has the property values shown in Table 6. The strength may be raised towards those of the 12%CrMoV steels by increasing the molybdenum content to 2% and/or by the addition of vanadium and niobium. Examples of these modified compositions are given in Table A3.1. The relatively low carbon contents of these steels confer low HAZ hardness levels in welding, though pre- and post-weld heat treatments are still necessary. As a consequence of the low carbon content, however, the delta ferrite content is increased in the more highly alloyed compositions. The steels EM12, NCM9M and Tempaloy F9 have been used commercially and an ASME code case is in preparation to give design values for the application of the Grade 91 composition, primarily for both conventional and nuclear heat exchangers.

The carbide phases present in all the steels are principally $M_{23}C_6$ and M_2X. Experimental variants of 9%CrMo steels with up to 3% Mo and 1.6% V have been described but there appear to be no studies of these more highly alloyed compositions balanced by increased carbon and manganese contents to give fully martensitic structures.

Table A3.1   Typical compositions of 9%Cr-Mo Steels

Steel Type	Trade name or origin	mass percent									Typical room temp. 0.2% P.S. Mpa	Approx. delta ferrite content %
		C	Si	Mn	Cr	Mo	Nb	V	N	B		
9Cr-1Mo (UK AGR)	-	0.10	0.5 (0.65-0.80)	0.6	9	1	-	-	0.02	-	450	5
9Cr-2Mo (Ref 33,34)	HCM9M (Japan)	0.07	0.3	0.5	9	2	-	-	0.02	-	400	30-40
9Cr-2MoNbV (Ref 35)	EM12 (Belgium, France)	0.1	0.4	1.0	9.5	2	0.4	0.3	0.02	-	500	30
9Cr-1MoNbV (B) (Ref 36)	Tempaloy F9 (Japan)	0.06	0.4	0.5	9	1	0.3	0.2	-	0.004	420	30
9Cr-1MoNbV (Ref 37)	Grade 91 (USA)	0.1	0.3	0.4	9	1	0.06	0.2	0.05	-	585	5
10Cr-2MoNbV (Ref 38)	TAF experimental (Japan)	0.06	0.5	0.5	10-11	2	0.06	0.1	-	-	not available	not available

APPENDIX 4

AUSTENITIC STAINLESS STEELS

Although the primary objective of this survey is the reproduction of the properties of martensitic stainless steels in suitable low-activation compositions, the potential of austenitic stainless steels in this application are considered briefly here. The martensitic steels appear to be less susceptible to neutron irradiation damage, having in particular a greater resistance to void swelling than the austenitic steels[39]. If it were necessary to use an austenitic alloy, however, then the low-activation elements for stabilisation of the austenitic structure are carbon, nitrogen and manganese. Whilst an austenitic structure can be stabilised by quenching a 0.8-1.0%C, 12%Cr steel from a suitably high austenitising temperature, this material is of scientific interest only. All commercially developed nickel-free austenitic steels have low carbon contents with the austenite stabilised by nitrogen in the present of manganese.

Typical proprietary grades are indicated in Table A4.1[40] and, of those included, Tenelon XM31 satisfies the basic compositional criteria for low remanent dose rate. These steels have been considered primarily for use at room temperature and few data exist on their elevated temperature properties. For high oxidation resistance, replacements for the standard austenitic steels have been suggested based on the use of aluminium-manganese-iron alloys, though these are precluded in the present application by their high aluminium contents of around 10%[41]. The British Steel Corporation has under development a manganese-chromium austenitic steel that is dispersion strengthened by a vanadium addition and is thus likely to have superior elevated temperature strength to the currently available commercial MnGrN compositions.

Table A4.1 Commercial high manganese austenitic stainless steels[40]

Steel	C	Mn	Cr	Mo	Ni	N	Cu	Room temperature tensile strength MPa
Carpenter 18-18 plus	0.10	18	18	1	–	0.5	1	835
Croloy 299	0.18	14.7	17.2	–	1.45	0.36	–	770–1175
Crucible 16-16-1	0.10	16	16	–	1.0	0.18	–	725
Crucible 223	0.10	12	15.5	–	0.6	0.28	–	760
Tenelon XM31	0.10	15	18	–	–	0.4	–	860
AISI 205	0.18	15	17	–	1.25	0.35	–	860