CULHAM LIBRARY
REFERENCE ONLY

CLM-R271

CLM-R271

UKAEA

Report

CULHAM LABORATORY
LIBRARY
19 JAN 1987
b
L

INVESTIGATIONS ON LOW ACTIVATION 9 AND 12%Cr, V, W STEELS FOR NUCLEAR FUSION REACTOR COMPONENTS

K. W. TUPHOLME
D. DULIEU
G. J. BUTTERWORTH

CULHAM LABORATORY
Abingdon, Oxfordshire

1986

Available from H. M. Stationery Office

Price £5.00

© - UNITED KINGDOM ATOMIC ENERGY AUTHORITY - 1986
Enquiries about copyright and reproduction should be addressed to the Librarian, UKAEA, Culham Laboratory, Abingdon, Oxon. OX14 3DB, England.

CLM-R271

INVESTIGATIONS ON LOW ACTIVATION 9 AND 12%Cr, V, W STEELS FOR NUCLEAR FUSION REACTOR COMPONENTS

K W Tupholme and D Dulieu
British Steel Corporation Swinden Laboratories
Moorgate, Rotherham, S60 3AR

G J Butterworth
Culham Laboratory, Abingdon, Oxon., OX14 3DB
Euratom/UKAEA Fusion Association

ABSTRACT

The results of an initial evaluation of the properties obtainable from a series of experimental low-activation martensitic stainless steels are presented. The effects of tungsten, vanadium, boron and nitrogen on the structure and strength of 0.15%C, 9 and 11%Cr steels have been investigated. The compositions studied were balanced so that no more than 5% delta ferrite was present on austenitising at 1100-1150°C. Isochronal tempering curves were established for the temperature range 450°-750°C and isothermal curves determined at 675°C, judged to be the optimum tempering temperature for service around 500°C. Room and elevated temperature tensile and impact toughness properties were established for selected steels after tempering. Of the alloys examined, the one most closely approaching the strength of the reference steel FV448 contained 11%Cr, 3.0%W and 0.23%V. On tempering for 2h at 675°C this steel had a strength close to that of FV448, with slightly lower impact toughness and a proof strength 60 MPa lower at 800 MPa. Exposure for 500h at 500°C after tempering caused a slight loss of toughness with the proof strength falling to 90 MPa below that of the reference steel. The 9%Cr variant of the 11%Cr steel exhibited similar properties but was slightly weaker. In all the steels the principal precipitate at 675°C was $M_{23}C_6$, this phase dissolving 1 in 23 metal atoms of tungsten. Laves phase M_2W was found generally precipitated in the 3%W steels overaged for 500h at 675°C and this phase, together with the coarser austenite grain structure resulting from the absence of niobium, probably causes the relatively low toughness of the tungsten steel in the overaged condition.

July 1986

ISBN 085311 1553

CONTENTS

1.	INTRODUCTION	1
2.	SELECTION OF COMPOSITIONS FOR EVALUATION	3
3.	EXPERIMENTAL PROCEDURES	5
	3.1 Preparation of the experimental steels	5
	3.2 Determination of mechanical properties	5
	3.3 Metallographic examination and phase characterisation	6
4.	EXPERIMENTAL RESULTS	7
	4.1 Microstructures after austenitising	7
	4.2 Results of isochronal tempering for 1h at temperatures between 450° and 750°C	11
	4.3 Results of isothermal tempering for times up to 500h at 675°C	15
	4.4 The mechanical properties of Steels 1, 2, 6, 7, 9 and 13	20
	4.5 Metallographic examination and phase characterisation	27
	4.5.1 Structures observed after tempering for 1h at 700°C	27
	4.5.2 Structures and phases present after tempering for 500h at 675°C	33
5.	DISCUSSION OF RESULTS	41
	5.1 Structures on austenitising	41
	5.2 Hardening response	48
	5.3 The mechanical property values obtained	48
	5.4 The roles of the alloying elements	50
6.	CHARACTERISTICS OF THE EXPERIMENTAL STEELS IN RELATION TO THE OBJECTIVES OF THE LOW-ACTIVATION MATERIALS DEVELOPMENT PROGRAMME	53
7.	SUMMARY OF PRINCIPAL FINDINGS	54
8.	GENERAL CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK	55
9.	REFERENCES	57

1. INTRODUCTION

In parallel with the development of conceptual designs of fusion power reactors a range of potentially suitable structural materials is being examined. The critical materials applications lie in the first wall and blanket components, which contain the breeder material and coolant circuits and are exposed to fluxes of high energy neutrons. Materials for their construction must meet two major requirements in addition to possessing the basic engineering properties for the structural role. These requirements are, firstly, an adequate resistance to microstructural degradation resulting from the neutron bombardment and, secondly, a favourable set of transmutation products induced by neutron-nucleus interactions. The latter requirement is an important one since the major source of solid radioactive wastes created by the fusion reactor will comprise the activated first wall and blanket structural components withdrawn from the reactor after relatively short service lives that are governed either by radiation damage degradation or by burn-up of the tritium breeding materials. The subsequent management of this time-expired material will be greatly simplified by the selection of structural alloys that exhibit a relatively rapid decay of their induced radioactivity.

Among the materials that have been considered, the martensitic stainless steels emerge as attractive candidates [1]. Their resistance to radiation damage is generally superior to that of the comparable austenitic steels and their thermo-mechanical properties and fabricability are commensurate with current perceptions of the engineering design requirements of the reactor components.

The specific radioactivity, contact dose rate and biological hazard indices for a given material during and after service in a reactor can be calculated with the aid of established computer codes, given a knowledge of the cross sections for the nuclear reactions in the elements present and of the product decay paths involved. To aid the selection and development of low-activation compositions having favourable decay characteristics, the chemical elements have been classified in terms of their allowable concentrations in a first wall material, the activity or contact dose rate of which is required to fall to some chosen value during an appropriate storage period. Table 1 summarises the results of some 'first order' activation calculations by Jarvis [2] and gives the maximum concentrations permissible if the surface dose rate is not to exceed $25\mu Svh^{-1}$ after a storage time of 100 years. The choice of the above value is to some extent arbitrary but it is considered to represent the level below which 'hands on' processing of the scrap material, with only minimal shielding requirements, could be contemplated.

Table 1 indicates the maximum permitted concentrations of the principal elements that govern the level of long term activation. Of the normal constituents of steels, it will be noted from the table that the use of cobalt and nickel is restricted, that molybdenum, aluminium and tin must be held to concentrations below about 10 ppm and that niobium and certain

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 (10-1000ppm)	Al, Zr, Mo, Sn
Troublesome constituents (1-10ppm)	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 (10-1000ppm)	Ca, Sc, Sr, Cd, Dy, Er, Tm, Re
Troublesome impurities (1-10ppm)	K, Ba
Unacceptable impurities (<1ppm)	Ag, Eu, Tb, Ir, Bi, Th, U
C. Omissions	
Hydrogen	H, D
Unstable elements	Tc, Pm
Inert gases	He, Ne, Ar, Kr, Xe

trace elements such as silver, europium, terbium and bismuth must essentially be totally excluded.

In developing a low-activation steel the metallurgical design objective is to devise a steel composition that will have adequate conventional properties and also give an acceptably low post-service activation level after a realistic cooling time. An earlier report [3] presents the outcome of a literature survey covering the effects of alloying additions on the structure and properties of the martensitic stainless steels. Existing compositions are based on matrices consisting of iron and 9-12% chromium with additions of nickel to adjust the ferrite-austenite phase stability and control the transformation temperature. Molybdenum and vanadium are added to form stable carbides on tempering of the martensitic structure whilst niobium is used for additional carbide precipitation and to give austenite grain refinement at the high austenitising temperatures employed for hardening. The carbide precipitates govern the strength at both room and elevated temperatures.

The literature review indicated that, with nickel restricted and molybdenum and niobium effectively excluded, the most promising candidate additions to yield properties equivalent to those of the CrMoVNb steels are tungsten and vanadium in combination, with possible further strengthening contributions from the effects of nitrogen and boron on the precipitates formed on tempering. On this basis a number of compositions were selected for preliminary experimental evaluation, with the following guidelines:

1. The composition must be balanced so as to give a fully austenitic structure at practicable austenitising and hot working temperatures. This requirement avoids the problems of poor hot workability and loss of strength that would result from the presence of excessive delta ferrite in the martensitic structure formed on hardening.

2. The carbon content and the martensite transformation temperature range must be such that a suitable martensitic structure, free from retained austenite, is formed.

3. The tempering reactions must yield a suitable strengthening precipitate dispersion. Tempering temperatures of 650°C or above are required, for stability and to allow adequate stress relief after welding.

4. There must be no embrittling reactions during long term service exposure and a stable microstructure will be required to maintain creep strength at service temperatures in the region of 500°C.

In the present experimental programme, the compositions proposed in the earlier study [3] as having the potential to fulfil these requirements have been subjected to an initial experimental assessment. The objective has been to determine the heat treatment response and the conventional mechanical properties obtainable with the candidate low-activation compositions. Throughout this work a widely used high strength martensitic stainless steel of the 12%CrNiMoVNb type has been adopted as the basis for comparison with the behaviour of the experimental steels. The overall objective has been the identification of compositions with basic properties justifying more detailed examination as candidate materials for reactor construction.

2. SELECTION OF COMPOSITIONS FOR EVALUATION

The rationale underlying the selection of the experimental compositions has been fully discussed in an earlier publication [3] and is summarised only briefly here. The reference material is a proprietary martensitic stainless steel manufactured by Firth Vickers and known as FV448. This steel was developed primarily for aviation gas turbine components [4,5]. Details of the typical composition and basic mechanical properties of this steel in the heat treated condition are given in Table 2. The elimination of nickel, molybdenum and niobium from the FV448 composition affects the austenite phase field, the prior austenite grain size developed on austenitising, the temperature of formation of the martensite on hardening and the precipitation sequence, and hence the strength, obtained on

Table 2

Properties of FV448 commercial martensitic stainless steel

Data from Firth Vickers Publication No. 104

Typical analysis, mass percent

Fe	C	Si	Mn	Cr	Ni	Mo	V	Nb	N
bal	0.15	0.35	0.75	10.5	0.75	0.65	0.25	0.3	0.06

Heat treatment

Oil quench or air harden from 1150° - 1170°C, temper at 650° - 700°C

Mechanical properties measured on hot rolled and heat treated bar

temperature °C	0.1% proof stress MPa	UTS MPa	elongation %	reduction of area %
20	870	1035	20	56
100	830	990	20	58
200	780	925	20	56
300	750	880	19	55
400	710	865	17	55
500	635	745	21	58
600	415	560	32	74
650	325	450	29	77
700	255	355	28	77

Table 3

Compositional patterns in the experimental casts studied

Steel number	SL cast number	nominal composition, mass percent	notes
1	928	0.65Mo, 0.75Ni, 0.06N, 0.3Nb, 0.25V	FV448 type steel with 11% Cr for comparison with experimental casts
2	886	0.06N, 0.25V	Base steel with 11% Cr. FV448 without nickel, molybdenum or niobium
3	887	0.06N, 0.25V, 0.25W	To examine the effect of increasing the tungsten content, relative to Steel 2, on the properties and δ ferrite content
4	888	0.06N, 0.25V, 0.675W	
5	889	0.06N, 0.25V, 1.1W	
6	870	0.06N, 0.25V, 2W	
7	890	0.06N, 0.25V, 3W	
8	891	0.06N, 0.5V, 0.65W	To examine the effect of increasing vanadium at nominally 0.7%W with respect to steel 4
9	871	0.06N, 0.8V, 0.75W	
10	892	0.06N, 0.25V, 0.75W, 0.01B	To examine the effect of a boron addition to Steel 4
11	893	0.1N, 0.25V, 0.75W	To examine the effect of increased nitrogen in Steel 4
12	894	9Cr, 0.06N, 0.25V, 0.7W	Reduction of the Cr content of Steel 4 to 9%
13	895	9Cr, 0.06N, 0.25V, 3W	Reduction of the Cr content of Steel 7 to 9%

tempering. The basis for the selection of the 12 experimental compositions is presented in summary form in Table 3. In each case the overall compositional balance was chosen so as to give, as far as possible, a fully austenitic structure, free from delta ferrite and undissolved phases at practicable austenitising temperatures. Tungsten and vanadium were identified as the primary candidates to replace molybdenum for the control of strength in the tempered condition. The concentrations of these elements in the experimental steels were chosen so as to explore their strengthening effects, up to limits indicated by the literature and believed to be governed by the formation of intermetallic phases on ageing or the difficulty of obtaining adequate solution treatment on hardening.

Because both tungsten and vanadium are ferrite stabilising elements, steels based on a 9% chromium content were also examined, the lower concentration of chromium discouraging the formation of delta ferrite. The roles of boron and nitrogen, added in higher concentrations than those normally found in commercial steels, were also explored as these elements have been reported as influencing the precipitation on tempering.

3. EXPERIMENTAL PROCEDURES

3.1 Preparation of the experimental steels

It was intended that the experimental steels should be prepared with as high a degree of purity as was attainable using generally available charge materials. For the reference experimental cast of FV448, mild steel strip punchings were used to provide the iron matrix. These are obtained from strip manufactured by the basic oxygen steelmaking route, which does not use high proportions of steel scrap and is thus inherently low in residual tramp elements. For the experimental low-activity steels, on the other hand, a refined electrolytic iron charge was used. The latter represents one of the purest forms of iron available on a tonnage basis. The analyses reported for the charge materials are given in Table 4.

The charge materials were melted in air by electric induction, the 50 kg weight cast being direct teemed into two 25 kg weight ingots. One ingot was retained for future studies and the second reheated and hot rolled to 19 mm round bar, which was used for all experimental studies in the present work. The compositions of the experimental steels, as determined by standard metallurgical analysis techniques, are indicated in Table 5. All heat treatments of the bar samples were performed in air in electrically heated furnaces.

3.2 Determination of mechanical properties

The hardness tests, used as comparative indications of strength, were conducted at mid-radial locations on transverse sections of the heat-treated bars using a 30 kg load Vickers indentation.

Room and elevated temperature tensile tests were performed on 100 mm^2 cross section test pieces machined from the heat treated bars and tested in

Table 4

Reported compositions of the charge materials used in manufacture of the experimental steels

charge material	element, mass percent														
	C	Si	Mn	P	S	Cr	Mo	Ni	Al	B	Co	Cu	N	V	W
electrolytic iron	0.005	0.005	0.002	0.003	0.003	0.002	0.001	0.003		0.0003	0.005	0.003			
chromium metal	0.005	0.095			0.003	99.5			0.04						
Warner iron	4.21	0.31	0.22	0.028	0.01	0.08	0.002	0.05				0.05	<0.005		
N_2FeCr	0.032	0.66	0.38			66.9		0.59					4.73		
FeSi		75													
manganese metal			99.5												
FeW															81
FeV														59	
FeS					31										
FeP				26.6											
mild steel punchings*	0.03		0.03	0.015	0.015	0.02	0.01	0.04				0.04			
FeCr*						70									

* Used only for Steel 1.

accordance with British Standards BS18 Part 2: 1971 and BS3688 Part 1: 1963 (1981), respectively.

Charpy impact transition curves for absorbed energy and fracture appearance were derived from tests on standard 2 mm V-notch specimens, in accordance with BS 131 Part 2: 1972 (1982).

3.3 Metallographic examination and phase characterisation

The general microstructure and the prior austenite grains were revealed for optical examination by etching in Villelas reagent, the grain size being estimated by the ASTM E112:82 method. A general characterisation of the microstructures of six selected experimental steels was made by means of carbon extraction replicas prepared from samples hardened and tempered for 1h at 700°C and for 500h at 675°C. Scanning transmission electron diffraction (STED) and energy dispersive analysis (EDA) techniques were employed to determine the nature of the precipitated phases in the steel having the highest tungsten content. To supplement this determination, the phases present in the six selected steels after exposure to 675°C for 500h were identified by X-ray powder diffraction with the aid of a Nonius focussing camera, after electrolytic isolation by potentiostatically-controlled dissolution of the matrix in a 10% aqueous solution of HCl.

Table 5

Chemical analysis of the experimental steels in mass percent

element	Steel number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
C	0.15	0.16	0.16	0.17	0.16	0.15	0.17	0.16	0.15	0.16	0.16	0.16	0.17
Si	0.26	0.46	0.45	0.45	0.42	0.43	0.44	0.47	0.41	0.45	0.45	0.37	0.42
Mn	0.88	0.87	0.81	0.78	0.77	0.80	0.76	0.78	0.80	0.80	0.79	0.79	0.74
P	0.011	0.008	0.008	0.007	0.009	0.009	0.010	0.008	0.009	0.008	0.007	0.008	0.011
S	0.012	0.012	0.013	0.013	0.013	0.014	0.012	0.013	0.016	0.013	0.013	0.012	0.012
Cr	11.3	11.4	11.5	10.9	10.9	11.7	11.2	11.1	11.7	11.4	11.2	9.1	9.22
Mo	0.66	<0.01	<0.01	<0.01	<0.01	0.04	0.02	<0.01	0.03	<0.01	<0.01	<0.01	0.02
Ni	0.75	0.02	0.02	0.02	0.02	0.01	<0.02	<0.02	0.01	<0.02	<0.02	<0.02	<0.02
Al	0.003	<0.005	<0.005	<0.005	<0.005	0.006	<0.005	<0.005	0.004	<0.005	<0.005	<0.005	<0.005
B	—	<0.0005	<0.0005	<0.0005	<0.0005	0.0002	0.0007	0.0005	0.0002	0.0083	0.0006	<0.0005	0.0013
Co	0.02	0.009	0.008	0.009	0.01	0.006	0.014	0.013	0.005	0.013	0.014	0.013	0.014
Cu	0.03	<0.02	<0.02	<0.02	<0.02	0.007	0.02	<0.02	0.01	<0.02	<0.02	<0.02	<0.02
N	0.057	0.054	0.060	0.060	0.056	0.076	0.068	0.069	0.082	0.060	0.103	0.060	0.059
Nb	0.3	<0.01	<0.01	<0.01	<0.01	0.002	<0.01	<0.01	0.002	<0.01	<0.01	<0.01	<0.01
Pb	—	—	—	—	—	0.002	—	—	0.001	—	—	—	—
Sn	—	<0.005	<0.005	<0.005	<0.005	<0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ti	—	<0.01	<0.01	<0.01	<0.01	0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001
V	0.25	0.26	0.25	0.25	0.24	0.24	0.23	0.46	0.80	0.25	0.25	0.24	0.25
W	<0.02	<0.02	0.24	0.65	1.12	1.95	3.04	0.66	0.77	0.70	0.69	0.68	2.90
Zr	—	—	—	—	—	0.003	—	—	—	—	—	—	—
chromium equivalent	—	13.6	14.0	13.5	13.7	15.2	15.5	14.8	17.1	14.1	13.9	11.5	13.4
nickel * equivalent	—	6.8	6.7	7.0	6.6	6.9	7.2	6.9	7.0	6.7	7.8	6.7	7.0

*Calculated in accordance with the Schaeffler—Schneider relationship [3]

4. EXPERIMENTAL RESULTS

4.1 Microstructures after austenitising

Samples of all the experimental alloys were austenitised for 1h at 1100°C then air cooled. The resulting delta ferrite content, austenite grain size and as-cooled hardness values are shown in Table 6. In the experimental version of the reference commercial steel, the structure on an optical scale comprised martensite with some undissolved carbide/nitride particles. There was little dissolution of these particles when the austenitising temperature was raised to 1150°C. Both the as-cooled hardness and the prior austenite grain size were unchanged and the appearance of the microstructure was similar to that in a reference sample of industrially-produced FV448 bar. It was thus confirmed that 1150°C (within the specified range of 1150°-1170°C) was a satisfactory austenitising treatment for Steel 1.

With the exceptions of Steels 6, 7 and 9, the remaining steels all had fully martensitic structures after austenitising at 1100°C. In all cases

Table 6

Prior austenite grain sizes (ASTM values), delta ferrite contents and hardness values of the steels air cooled after austenitising

Steel number	austenitising temperature °C	grain size ASTM	δ ferrite content	as-cooled hardness HV30
1	1100	9	0	462
	1150	9-9.5	0	457
2	1100	4.5	0	487
3	1100	5	0	496
4	1100	5	0	504
5	1100	4.5	0	497
6	1100	4.5	<5	557
7	1100	5	<5	546
8	1100	5	0	500
9	1100	7	0	470
	1150	7	0	498
10	1100	4.5-5	0	500
11	1100	4.5	0	528
12	1100	4.5-5	0	469
13	1100	5	0	497
commercial FV448	1150	6-6.5	0	434

the prior austenite grains were coarser than those in both Steel 1 and the commercially-produced alloy, as shown by Table 6. Steels 6 and 7, containing respectively 2 and 3% tungsten, both contained a small proportion, less than 5%, of delta ferrite in the structure obtained on cooling from 1100°C. Steel 9, containing 0.8% vanadium, contained undissolved carbide/nitride particles on cooling from 1100°C. Their presence was associated with a prior austenite grain size intermediate between the values observed for the other experimental steels and the FV448 steels. A reduction in the proportion of undissolved phases was observed in Steel 9 as the austenitising temperature was raised to 1150°C, the corresponding as-cooled hardness value increasing from 470 to 498 HV. Accordingly, 1150°C was adopted as the austenitising temperature for this composition.

Typical optical micrographs, showing principally the variations in prior austenite grain size, are shown in Figures 1 and 2. The hardness values after hardening, given in Table 6, are plotted as a function of the analysed interstitial element (C+N) contents in Fig.3.

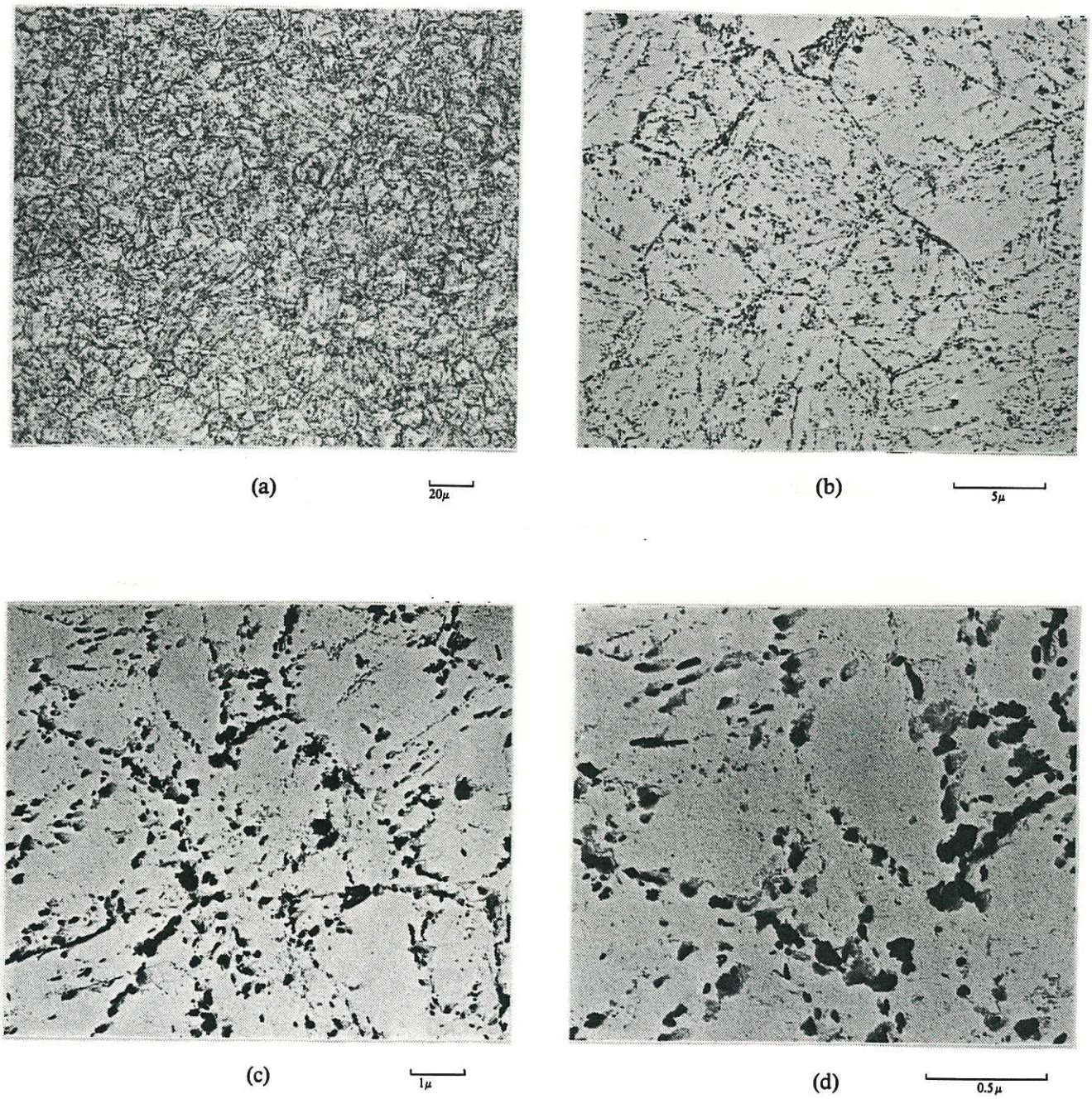
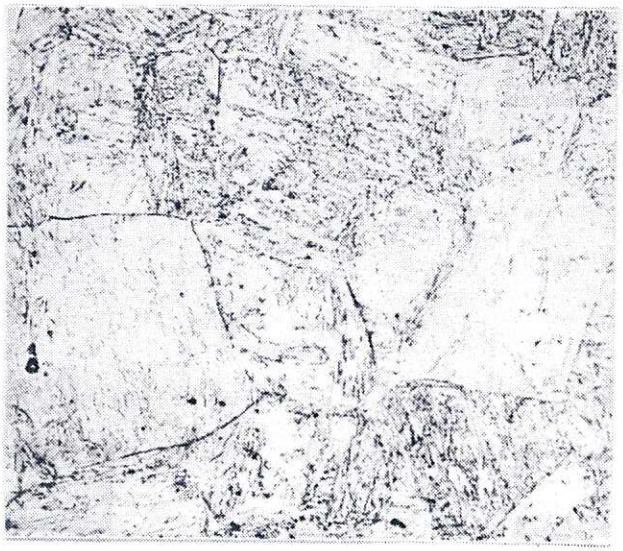
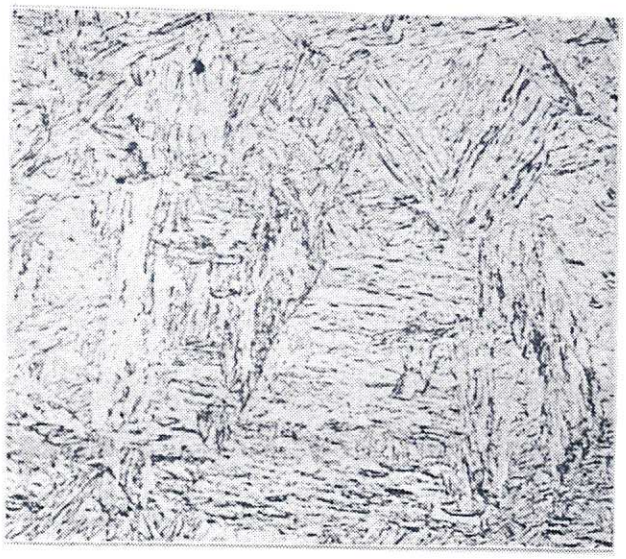


Fig. 1 Optical and carbon extraction replica electron micrographs of Steel 1 (FV448 type) after hardening from 1150°C and tempering for 1 h at 700°C.

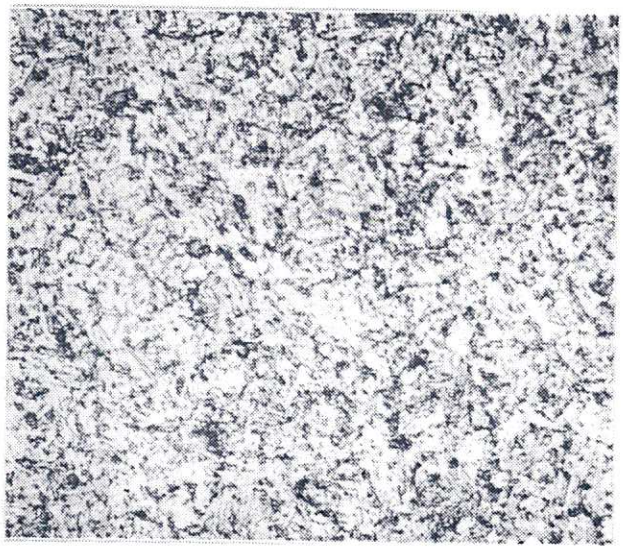


(a) Steel 6

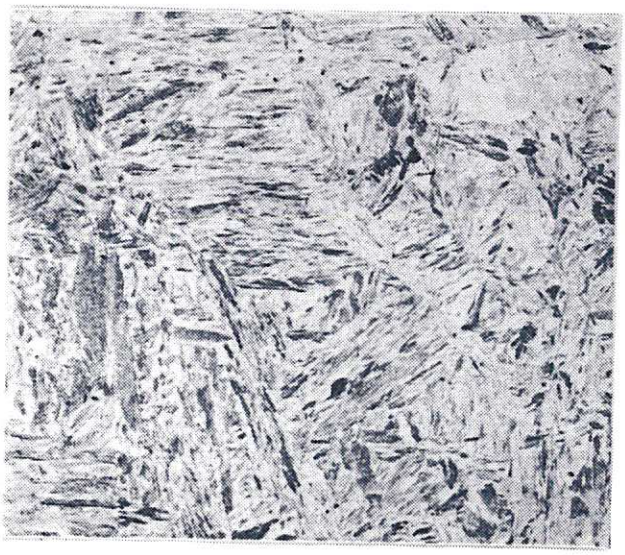


(b) Steel 7

50μ



(c) Steel 9



(d) Steel 12

Fig. 2 Optical micrographs of Steels 6, 7, 9 and 12 in the as-hardened condition.

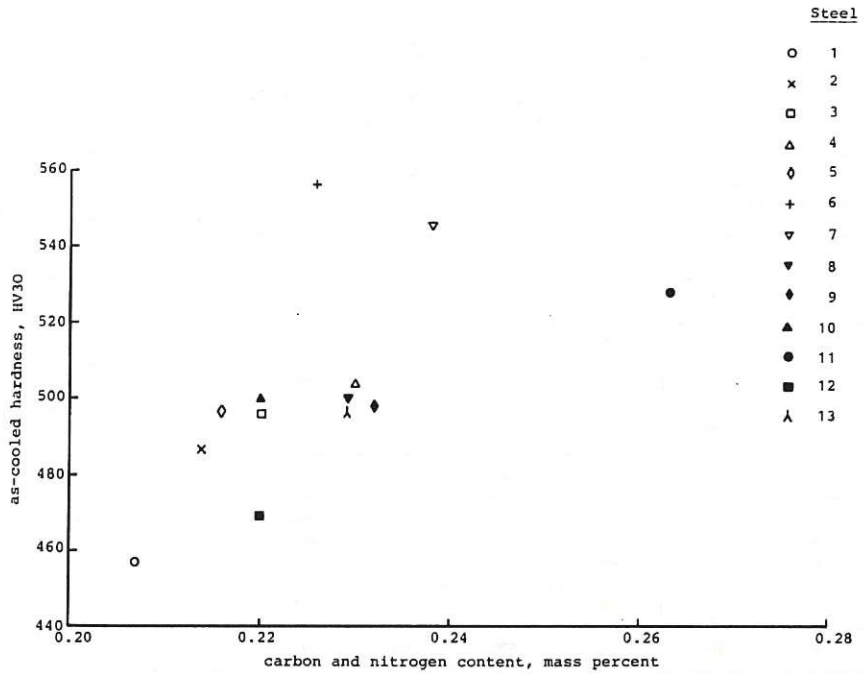


Fig.3 Dependence of the as-air cooled hardnesses of the steels on the carbon and nitrogen contents.

4.2 Results of isochronal tempering for 1h at temperatures between 450° and 750°C

The hardness values measured after tempering are presented in Table 7 and are shown graphically in Figures 4-8 as follows:

Fig.4 The tempering response of the experimental FV448 composition

Fig.5 The tempering response of Steels 2-7, showing the effect of increasing the tungsten content over the range from the residual level below 0.02% up to 3.04%

Fig.6 The tempering response of Steels 4, 8, 9 showing the effect of increasing the vanadium content from 0.25% to 0.80% in the presence of nominally 0.65% tungsten

Fig.7 The tempering response of Steels 4, 10, 11 showing the effect of individual increases in nitrogen and boron contents in the composition containing 0.65%W, 0.25%V

Fig.8 The tempering response of the 9%Cr, 0.25%V; 0.65% and 3.0%W steels 12 and 13.

The results show that the peak hardness in the tempered condition was obtained at 500°C for all the steels examined. Figure 5 shows that the

Table 7

Hardness of the steels after isochronal tempering within the temperature range 450° - 750°C

Steel number	hardness as-hardened*	hardness (HV30) after 1 h at temperature:						
		450°C	500°C	550°C	600°C	650°C	700°C	750°C
1	457	469	485	449	403	352	338	290
2	487	495	498	448	372	342	309	261
3	496	492	498	453	369	340	303	265
4	504	496	510	457	396	348	312	268
5	497	499	506	451	396	344	299	273
6	557	522	563	501	411	368	322	276
7	546	531	542	496	457	360	333	294
8	500	489	513	493	445	365	318	252
9	498	503	506	485	419	371	310	251
10	500	491	502	446	402	341	302	262
11	528	551	559	521	458	347	318	262
12	469	484	493	470	396	342	303	245
13	497	507	529	503	442	365	333	—

**All steels were austenitised at 1100°C for 1 h and air cooled, except for Steels 1 and 9 which were austenitised at 1150°C.*

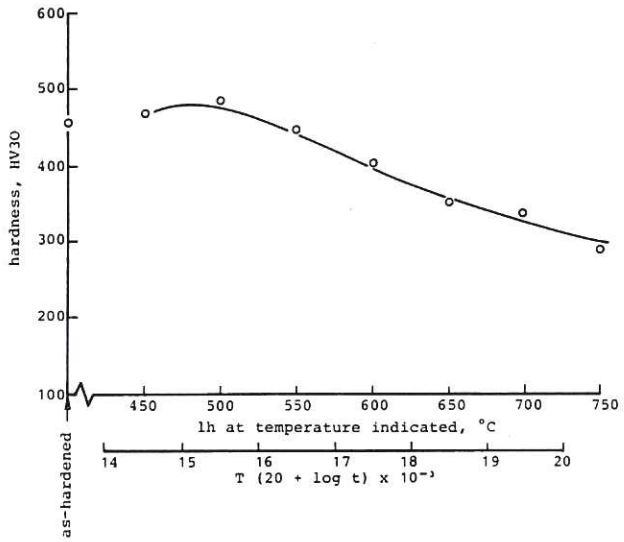


Fig. 4 Isochronal tempering characteristics of Steel 1 (FV448 type).

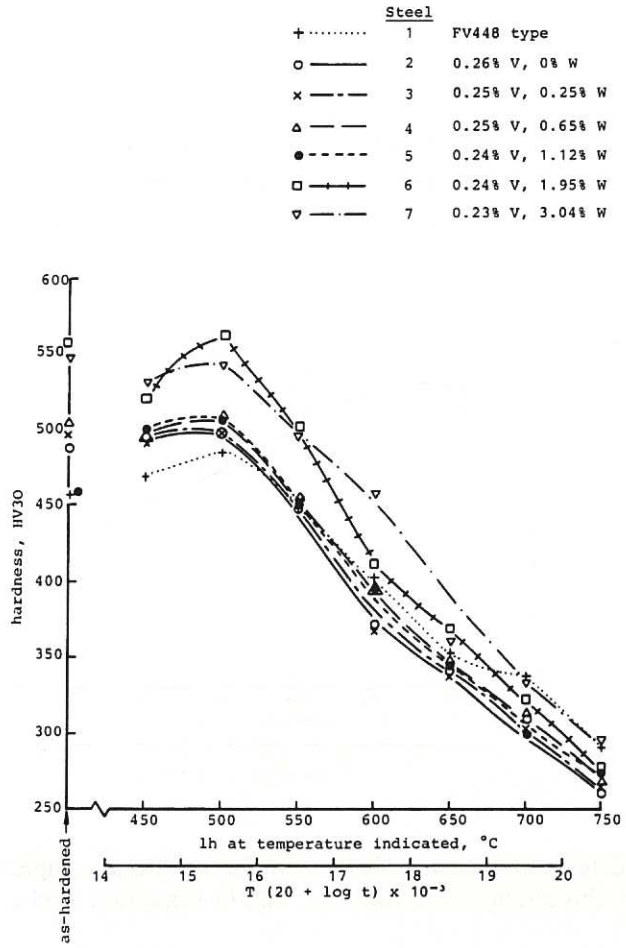


Fig. 5 Effect of tungsten on the isochronal tempering characteristics of 11% chromium, 0.7% tungsten steels.

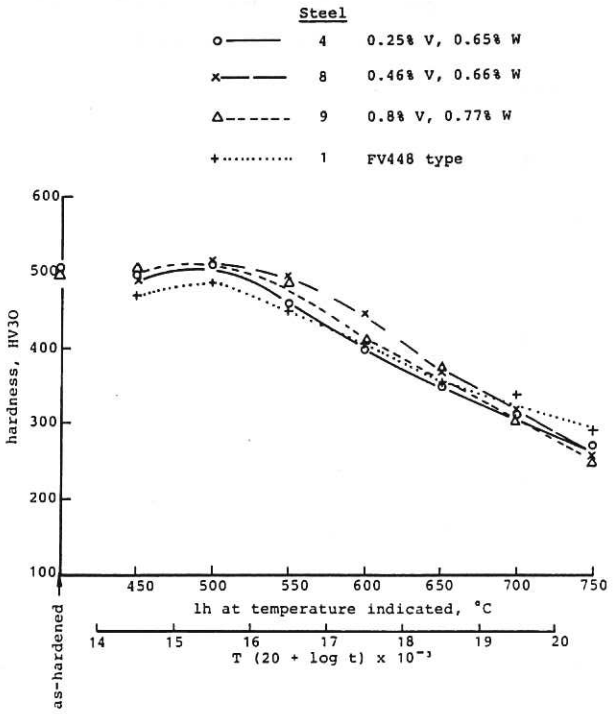


Fig. 6 Effect of vanadium on the isochronal tempering characteristics of 11% chromium, 0.7% tungsten steels.

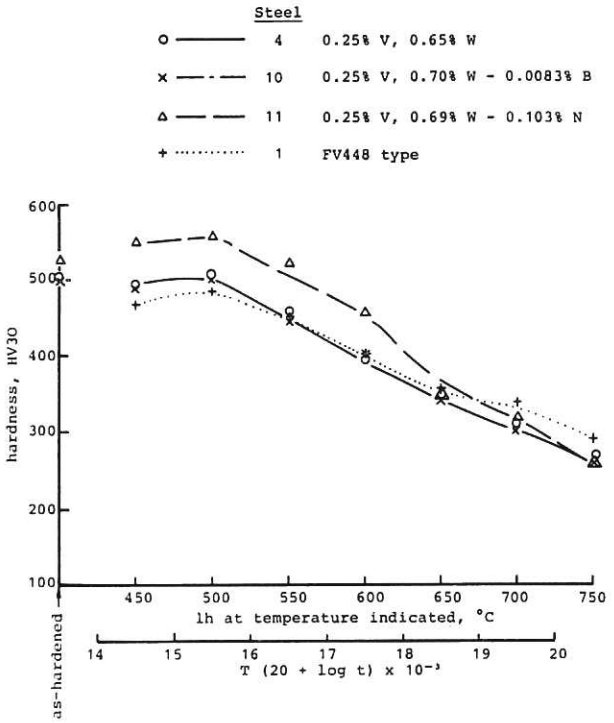


Fig. 7 Effect of boron and nitrogen on the isochronal tempering characteristics of 11% chromium, 0.7% tungsten, 0.25% vanadium steels.

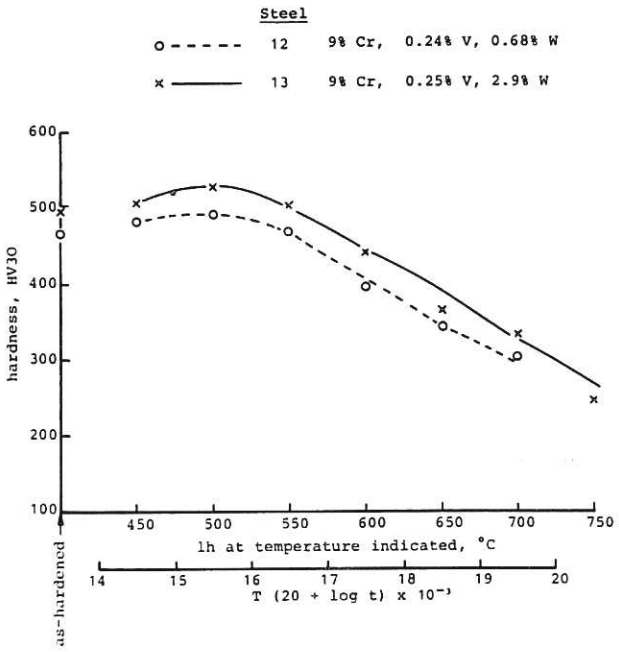


Fig. 8 Isochronal tempering characteristics of 9% chromium steels.

hardness level on tempering increased as the tungsten content was raised above 1% while Fig.6 indicates that vanadium exerts a maximum effect at the 0.46% concentration.

As shown by Fig.7, boron appeared to have little influence on the tempered hardness of Steel 4 in the 1h tempered condition. The effect of nitrogen in promoting a high initial hardness, however, persisted to tempering temperatures of 600°C. The tempering characteristics of the 9%Cr steels, illustrated in Fig.8, were broadly similar to those of the 11%Cr compositions having similar tungsten contents, falling below the hardness of the FV448 material at temperatures above 700°C. Although it exhibited a relatively low as-hardened hardness value, the FV448 steel showed a tempering resistance at temperatures above 650°C superior to that of all except the 3% tungsten steels. From these preliminary isochronal tempering results, a temperature of 675°C was chosen for further studies of tempering.

4.3 Results of isothermal tempering for times up to 500h at 675°C

The hardness values measured during isothermal tempering are given in Table 8 and are plotted in Figures 9-13, grouped in a similar form of presentation as for the isochronal data. The hardness values at 1h are in fact derived by interpolation from the isochronal measurements. Included in Table 8 are the absolute decrements in hardness, ΔH_1, between the

Table 8

Hardnesses after isothermal tempering at 675°C for times up to 500h

Steel number	hardness as-hardened	hardness after isothermal tempering at 675°C					ΔH_1 AH to 500h at 675°C	ΔH_2 4h to 500h at 675°C
		4h	16h	48h	96h	500h		
1	457	330	325	312	297	256	201	74
2	487	293	274	256	245	217	270	76
3	496	293	276	255	244	219	277	74
4	504	298	286	264	252	226	278	72
5	497	304	289	274	255	232	265	72
6	557	314	298	280	266	244	313	70
7	546	319	306	290	279	247	299	72
8	500	306	278	254	246	223	277	83
9	498	284	253	239	234	215	283	69
10	500	305	285	267	257	229	271	76
11	528	295	277	260	255	230	298	65
12	469	291	270	249	240	212	257	79
13	497	319	302	280	268	236	261	83

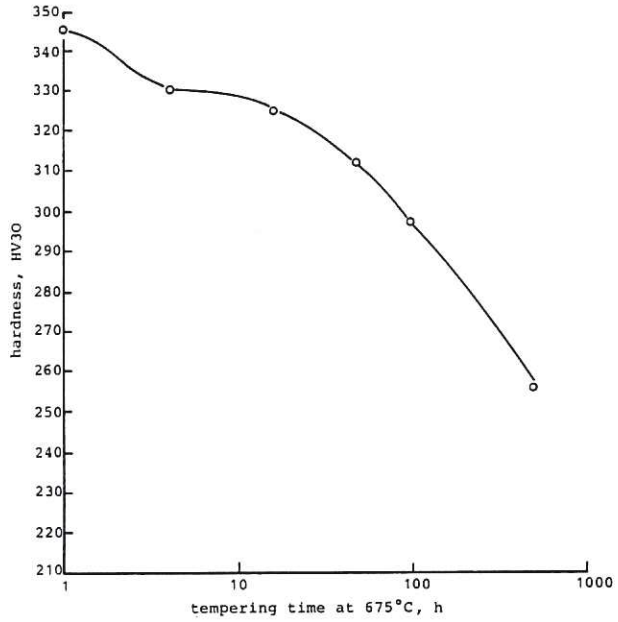


Fig. 9 Hardness of Steel 1 (FV448 type) after tempering at 675°C for times up to 500h.

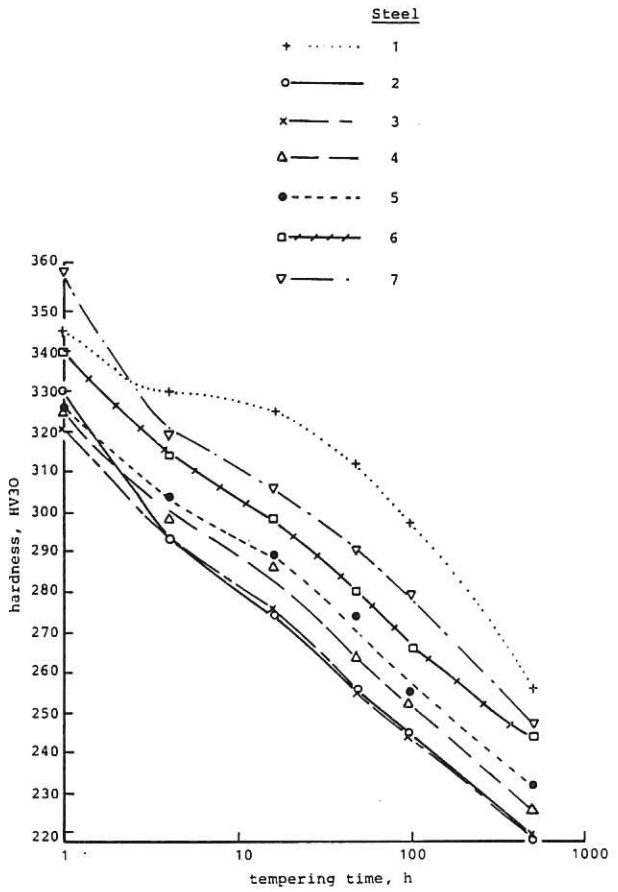


Fig. 10 Effect of tungsten content on the hardness of 11% chromium steels after tempering at 675°C for times up to 500h.

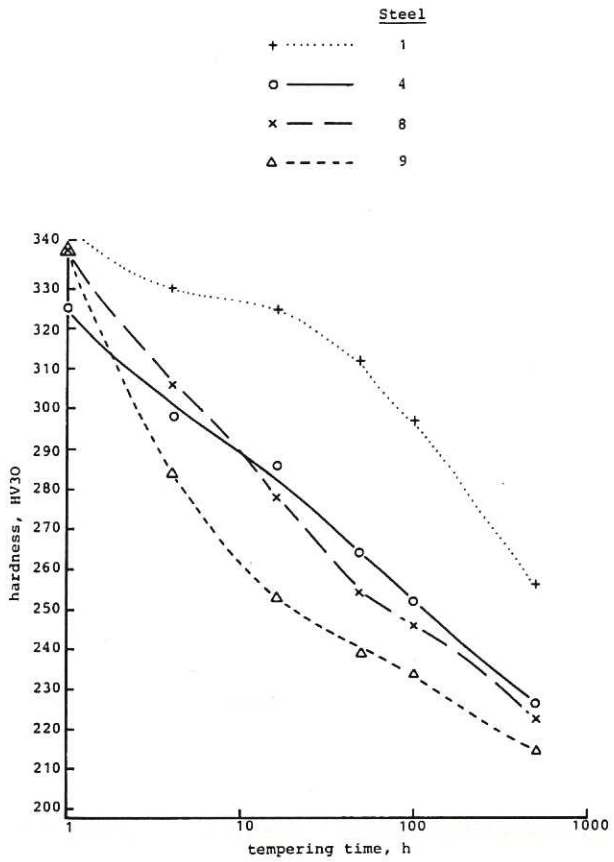


Fig. 11 Effect of vanadium content on the hardness of 11% chromium steels after tempering at 675°C for times up to 500h.

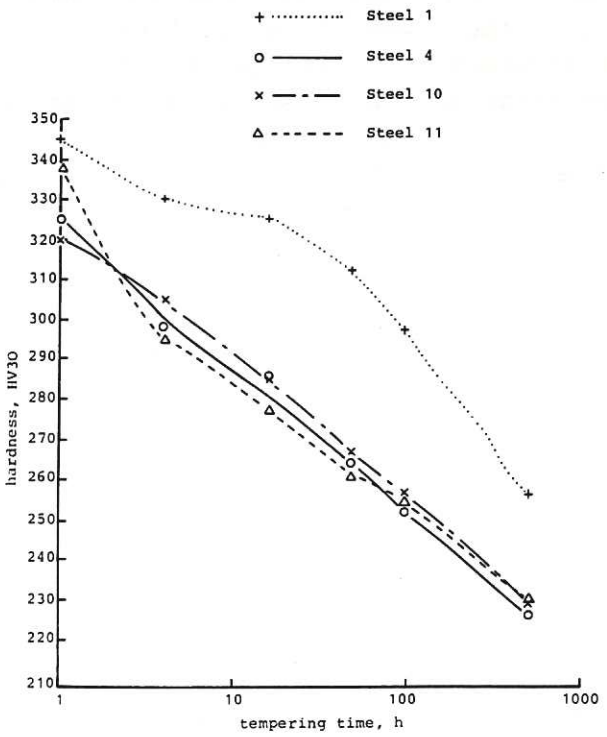


Fig. 12 Effect of boron and nitrogen content on the hardness of 11% chromium steels after tempering at 675°C for times up to 500h.

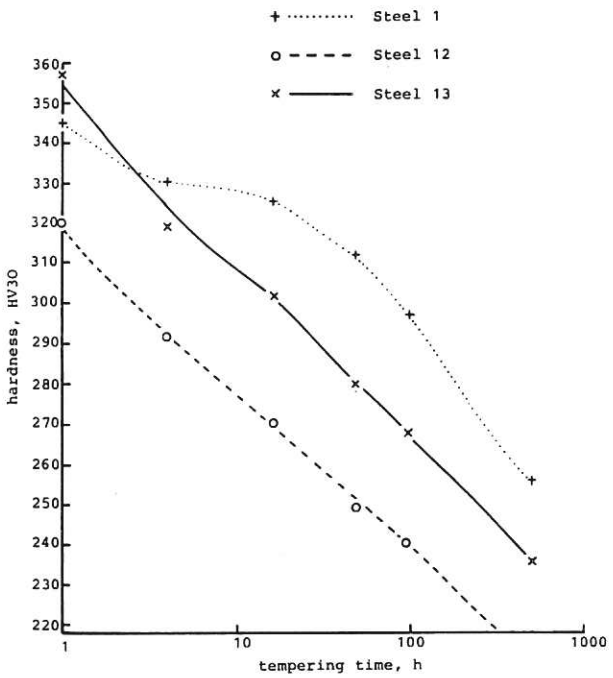


Fig. 13 Hardness of 9% chromium steels after tempering at 675°C for times up to 500h.

material in the as-hardened condition and after tempering for 500h at 675°C. These values show that all the molybdenum-free steels lost some 60-110 HV more than the FV448 alloy, reflecting in part its comparatively low as-hardened hardness. An indication of the tempering resistance is given by the decrement ΔH_2, also shown in the table, between the hardness values measured at 4h and 500h, at 675°C. The extent of softening was found to be similar for all the steels, being especially uniform for Steels 1, 6, 7 and 13, which exhibited comparable hardness in the 4h tempered condition.

The tempering curves of Fig.10 indicate that the effect of tungsten in increasing the tempered hardness persists up to 500h at 675°C. As seen in Fig.11, however, the addition of vanadium over 0.25% led to more rapid overageing. The effects of boron or nitrogen in Steel 4 were very weak after ageing for 10h or longer. The 9%Cr steels, 12 and 13, gave tempering curves at 675°C of similar slope, the hardness difference at a particular time reflecting the initial difference in hardness. Steel 13 with 3%W, 0.25%V was some 10HV softer than the corresponding 11%Cr steel after 500h.

On the basis of the tempering data, steels were selected for a more detailed assessment of their properties. Steel 7 was chosen on the basis of its giving the closest match to the FV448 alloy, in terms of the hardness value on tempering at temperatures above 650°C. An indication of relative tempering resistance is given in Fig.14, which shows the hardness

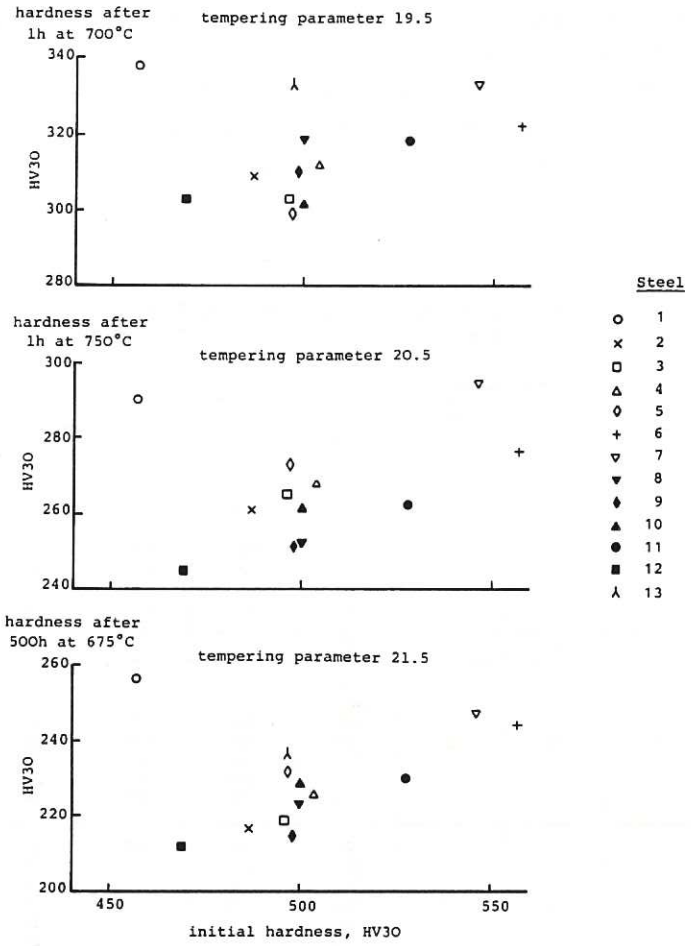


Fig. 14 Tempering data, summary presentation as a function of as-cooled hardness value.

values attained after 500h at 675°C and 1h at 700° and 750°C, corresponding to tempering parameters of 21.5, 19.5 and 20.5, respectively. The tempering parameter P is defined by the relation

$$P = T\ (20 + \log t) \times 10^{-3}$$

where T is the absolute tempering temperature and t is the time of tempering. The hardness values are shown as a function of the as-hardened hardness level. A roughly linear relationship is obtained for the molybdenum-free compositions, with the 3%W steels lying on the upper bound. From this plot, Steel 13 was chosen as the stronger of the 9%Cr compositions and Steel 6, with 1.95%W, was chosen as a close match to Steel 7 in hardness. Though not the optimum composition among the vanadium-bearing series, Steel 9 was selected in order to examine the effects of a high vanadium concentration. Steel 2, the base composition, was included for comparison purposes.

4.4 The mechanical properties of Steels 1, 2, 6, 7, 9 and 13

The tensile and Charpy impact toughness properties of the selected steels were determined on bar material austenitised at 1100°C, or 1150°C in the cases of Steels 1 and 9, air cooled and tempered for 2h at 675°C. The results are presented in Table 9 whilst the impact transition curves, in the form of absorbed energy and percentage brittle fracture appearance plots as a function of temperature, are shown in Figures 15-20.

Table 9

Mechanical properties of six selected experimental steels after hardening and tempering for 2h at 675°C

Steel number	impact toughness		tensile properties				
	50% brittle °C	room temp. impact J	test temperature °C	0.1% proof stress MPa	UTS MPa	elongation %	reduction in area %
1	30	27	20	861	1039	16	59
			400	725	848	12	56
			450	641	813	12	60
			500	603	749	16	65
			550	503	656	15	74
			600	387	583	20	67
			650	344	485	20	71
2	72	10	20	739	915	17	56
6	35	29	20	742	965	16	49
			400	624	777	12	52
			450	593	737	15	55
			500	529	665	18	75
			550	461	587	18	72
			600	359	499	24	78
			650	270	402	24	82
7	44	22	20	801	1022	14	58
			400	646	814	12	51
			450	601	774	13	56
			500	578	715	16	65
			550	495	634	18	71
			600	401	538	24	76
			650	318	436	23	80
9	42	22	20	731	924	16	50
			400	628	750	12	51
			450	559	697	14	57
			500	521	630	16	65
			550	428	548	17	67
			600	333	477	22	64
			650	220	375	20	72
	19*	54*	20*	704	889	16	57
13	44	29	20	772	972	16	52
			400	626	791	13	53
			450	630	747	13	55
			500	561	698	18	69
			550	473	600	18	76
			600	376	531	22	74
			650	322	457	20	78

**results for Steel 9 austenitised at 1100°C*

The room temperature tensile properties were found to be consistent with the tempering data, demonstrating that Steel 7 gives the closest approach to the strength of the FV448 steel at room temperature. This steel was slightly lower in strength at elevated temperature and it may be noted that the 9%Cr, 3%W alloy, Steel 13, was found to be slightly stronger than the equivalent 11%Cr steel on testing at 650°C.

Table 9 shows that the elimination of molybdenum, nickel and niobium from the FV448 composition resulted in a reduction of 122 MPa in the 0.1% proof

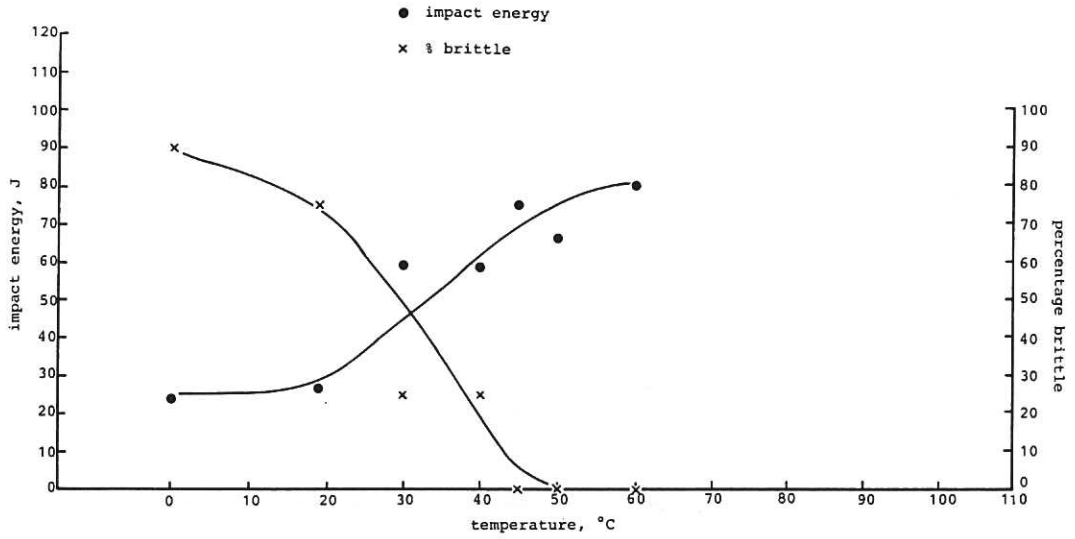


Fig. 15 Impact transition temperature data for Steel 1 (FV448 type) after 1 h at 1150°C and 2h at 675°C.

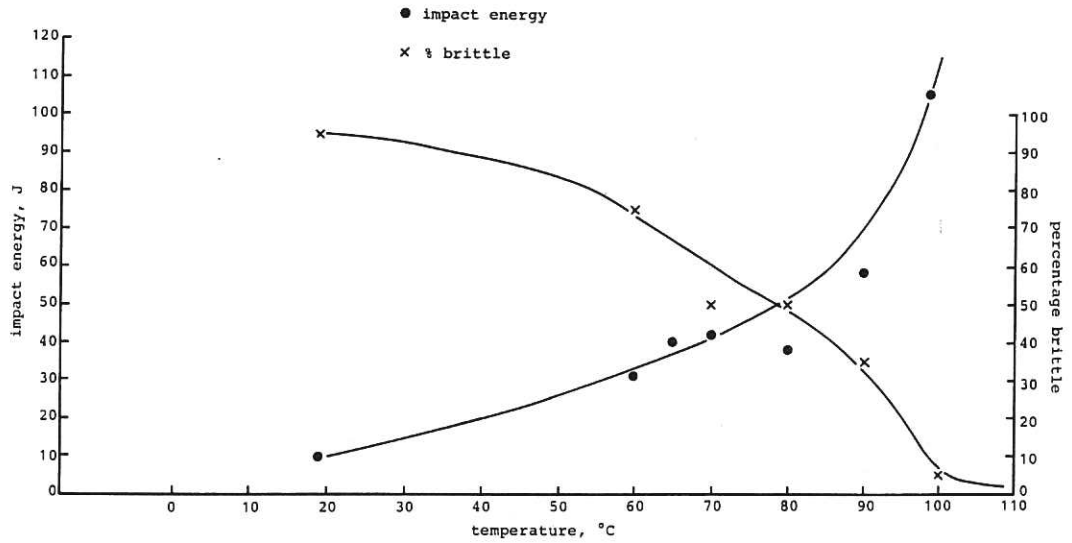


Fig. 16 Impact transition temperature data for Steel 2 (0.25% V) after 1 h at 1100°C and 2h at 675°C.

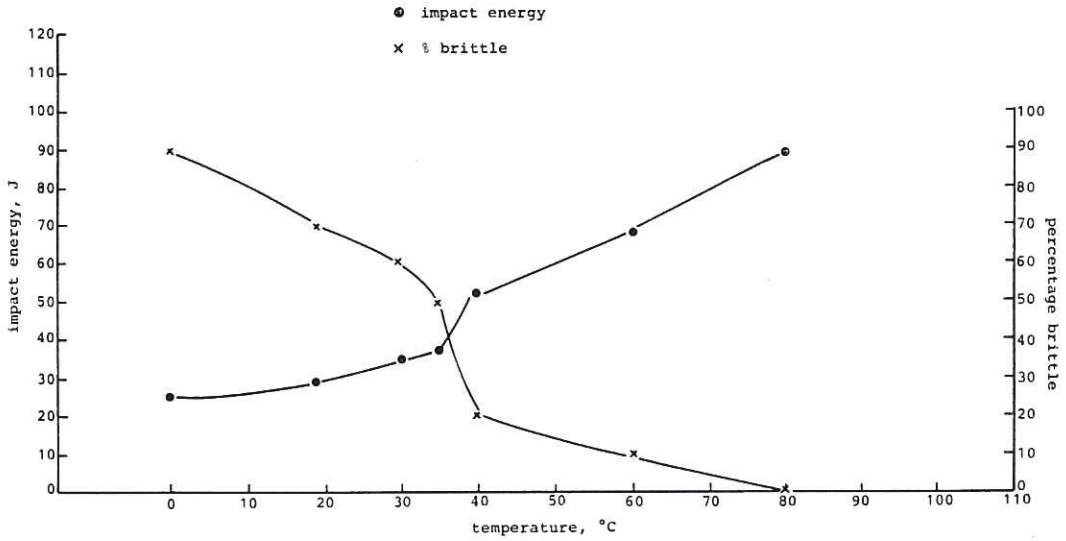


Fig. 17 Impact transition temperature data for Steel 6 (0.25% V, 2% W) after 1 h at 1100°C and 2 h at 675°C.

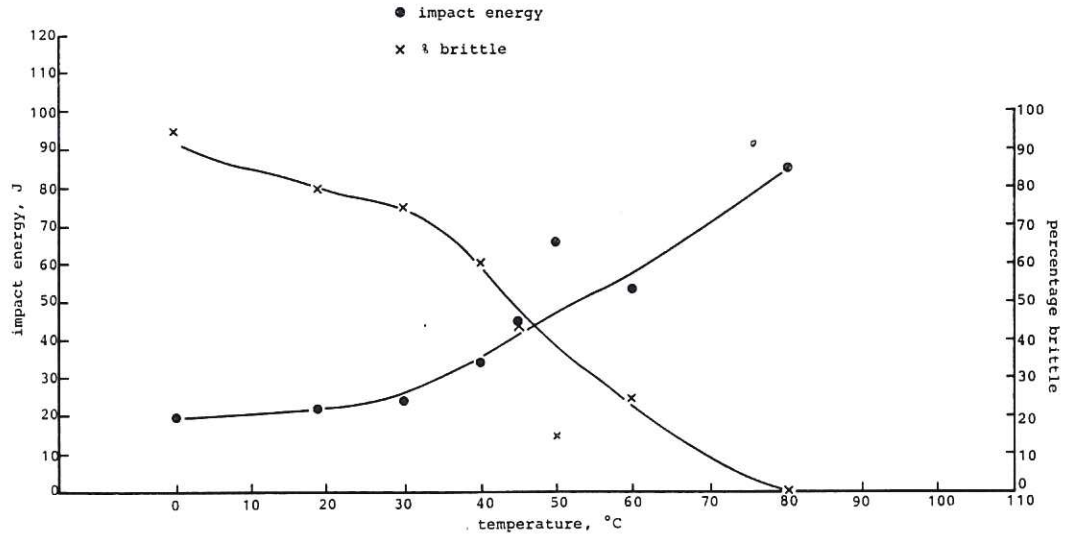


Fig. 18 Impact transition temperature data for Steel 7 (0.25% V, 3% W) after 1 h at 1100°C and 2 h at 675°C.

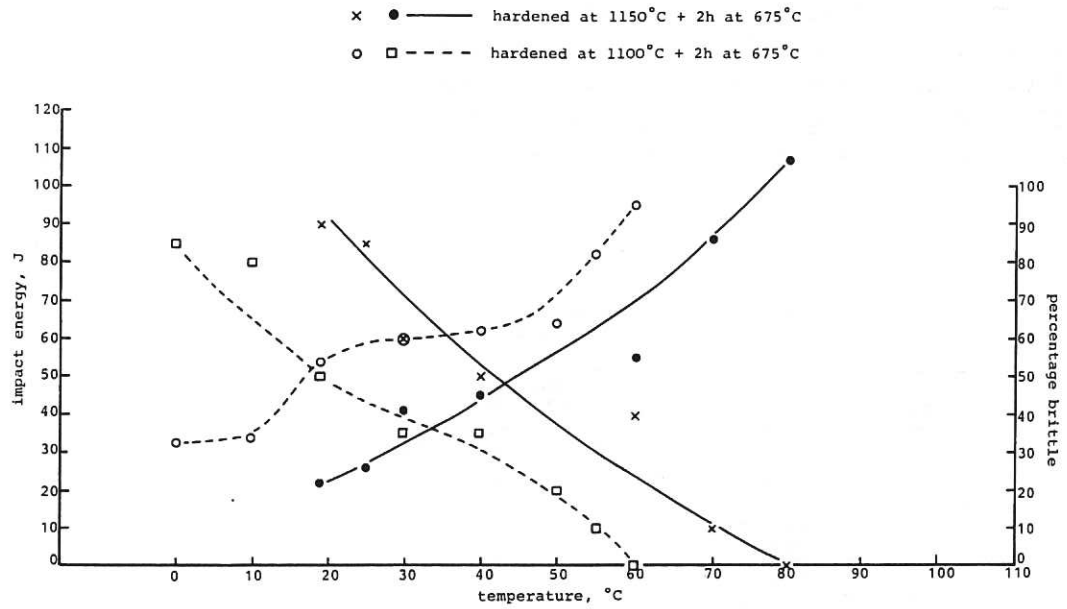


Fig. 19 Impact transition temperature data for Steel 9 (0.8% V, 0.75% W) after treatment at two different austenitising temperatures, 1150°C or 1100°C, followed by 2h at 675°C.

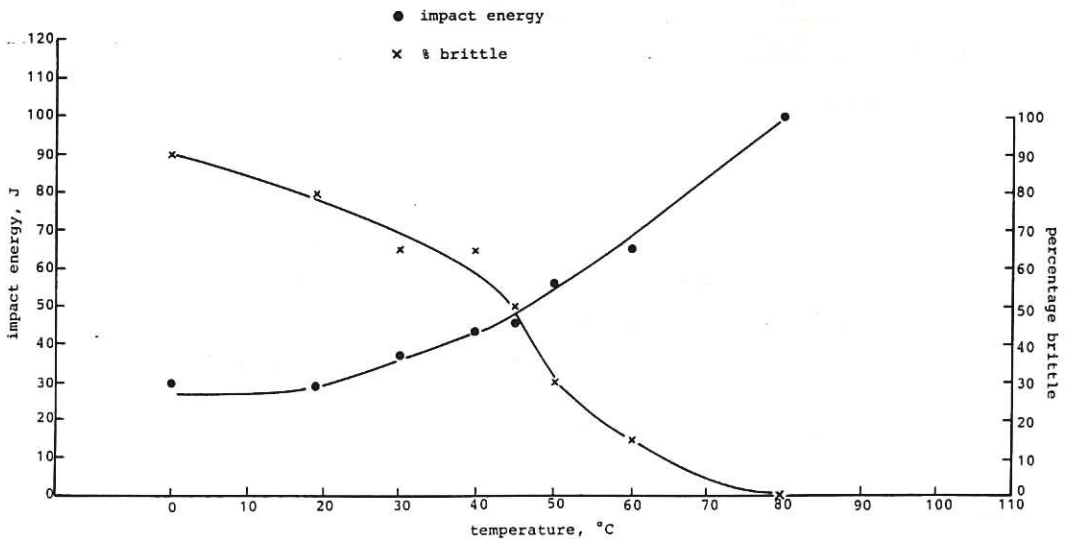


Fig. 20 Impact transition temperature data for Steel 13 (9% Cr, 0.25% V, 3% W) after 1h at 1100°C and 2h at 675°C.

stress value and a deterioration in impact toughness from a brittle fracture mode at room temperature. To obtain an indication of the effects of service exposure on overageing of the precipitates, the properties of Steels 1, 6, 7, 9 and 13 were also determined after tempering for 500h at 675°C. The properties were established for material tempered for 2h at 675°C and then exposed for a further 500h at 500°C. The results obtained on samples subjected to these treatments are presented in Table 10 and the

Table 10

Mechanical properties of selected experimental steels after tempering for 500h at 500° and 675°C

Steel number	tempering treatment	impact toughness Charpy 2mm V-notch		tensile properties			
		50% brittle °C	room temp Impact J	0.1% proof stress MPa	UTS MPa	elongation %	reduction in area %
1	2h at 675°C	30	27	861	1039	16	59
	2h at 675°C + 500h at 500°C	38	23	882	1043	17	55
	500h at 675°C	−18	105	614	778	20	63
6	2h at 675°C	35	29	742	965	16	49
	2h at 675°C + 500h at 500°C	38	25	743	961	18	53
	500h at 675°C	4	87	529	766	20	59
7	2h at 675°C	44	22	801	1022	14	58
	2h at 675°C + 500h at 500°C	55	22	790	1014	16	47
	500h at 675°C	38	25	542	795	18	53
9	2h at 675°C	44	22	731	924	16	50
	2h at 675°C + 500h at 500°C	73	17	723	913	18	49
	500h at 675°C	3	124	452	683	28	68
13	2h at 675°C	44	29	772	972	16	52
	2h at 675°C + 500h at 500°C	51	23	770	973	15	49
	500h at 675°C	31	33	528	773	19	54

impact transition curves are shown in Figures 21-25. For Steel 1, with the FV448 composition, the 500h exposure at 675°C resulted in a 270 MPa reduction in the 0.1% proof stress, a similar fall in the tensile strength, a small increase in tensile ductility and a significant improvement of the impact toughness. In contrast, although the 3%W steel, number 7, also decreased in strength by a similar amount, with a moderate increase in tensile ductility, the impact toughness was only marginally improved. The behaviour of the 9%Cr steel, number 13, was similar, both with respect to the tensile strength and insofar as no appreciable improvement in toughness was observed after tempering for 500h. Exposure to 500°C for 500h following the initial tempering treatment was found to cause a minor loss of toughness for each steel, with no major change in strength value. The impact transition temperature was raised in all cases and the shift was especially pronounced for the high vanadium steel, number 9.

To summarise the mechanical property results, the 11Cr-3W-0.23V alloy was the strongest of the experimental steels examined. It was some 60 MPa

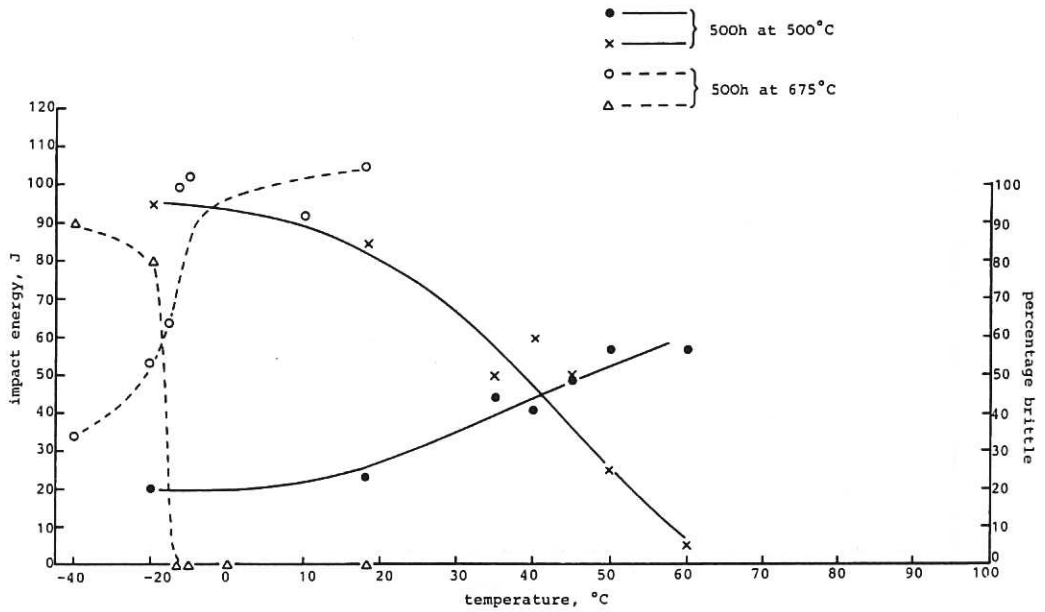


Fig. 21 Impact transition temperature data for Steel 1 (FV448 type) after 500h tempers.

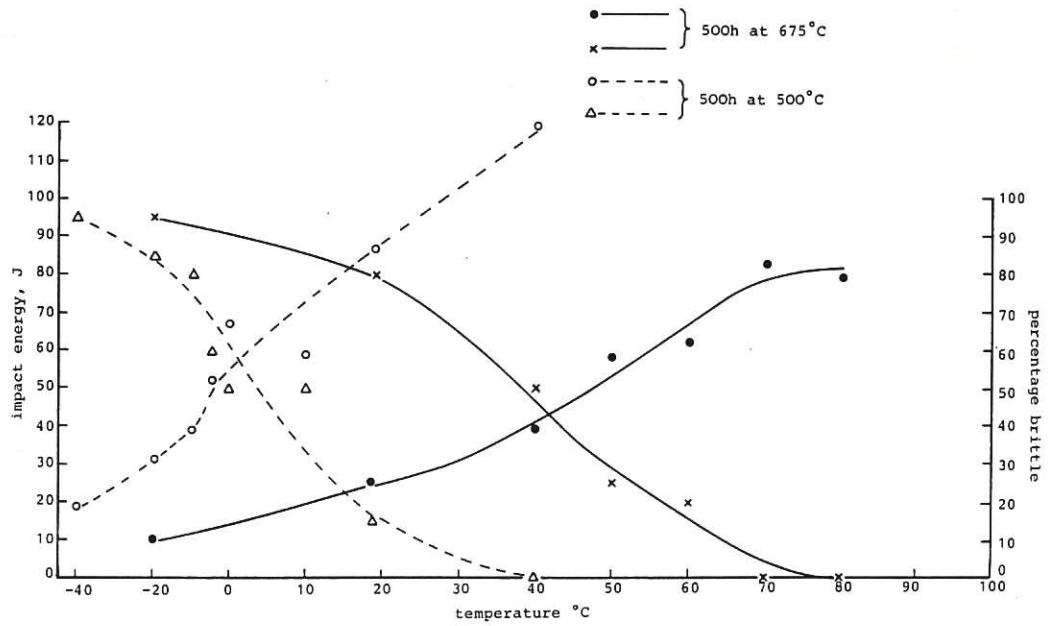


Fig. 22 Impact transition temperature data for Steel 6 (0.25% V, 2% W) after 500h tempers.

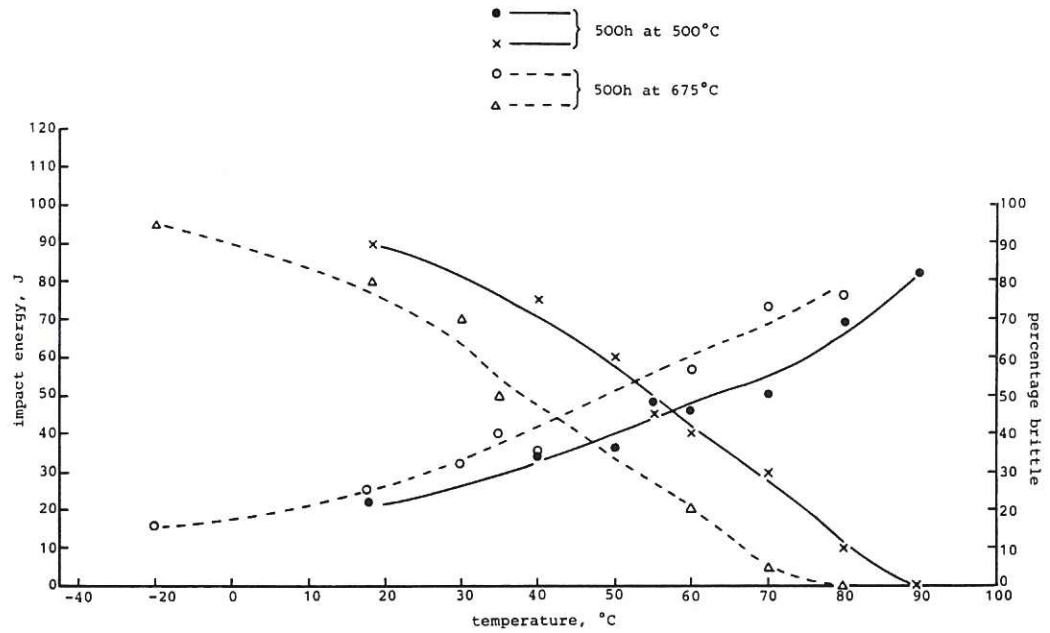


Fig. 23 Impact transition temperature data for Steel 7 (0.25% V, 3% W) after 500 h tempers.

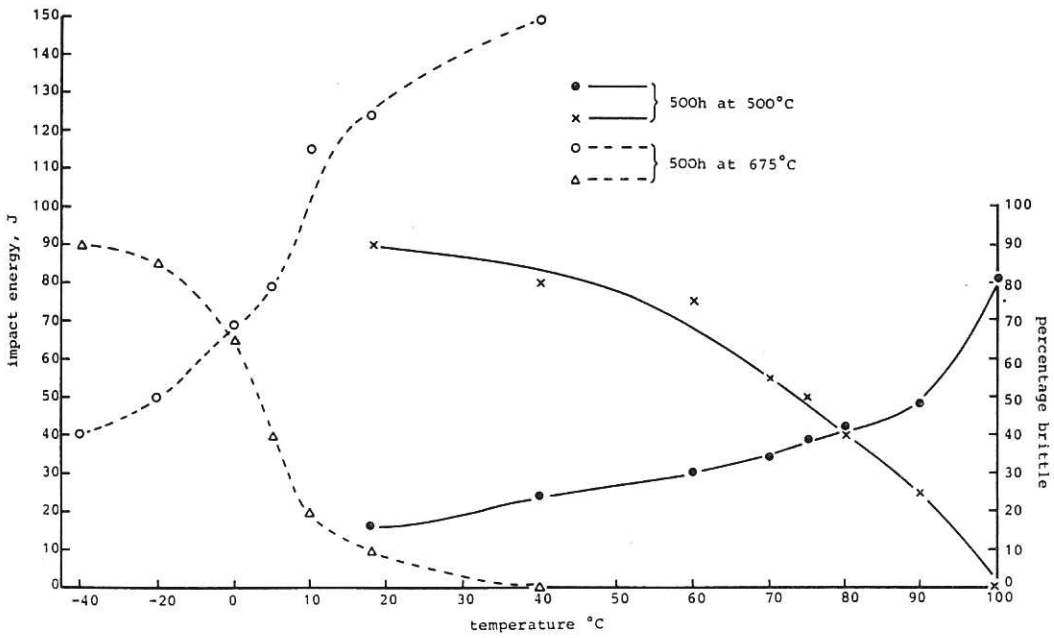


Fig. 24 Impact transition temperature data for Steel 9 (0.8% V, 0.75% W) after 500 h tempers.

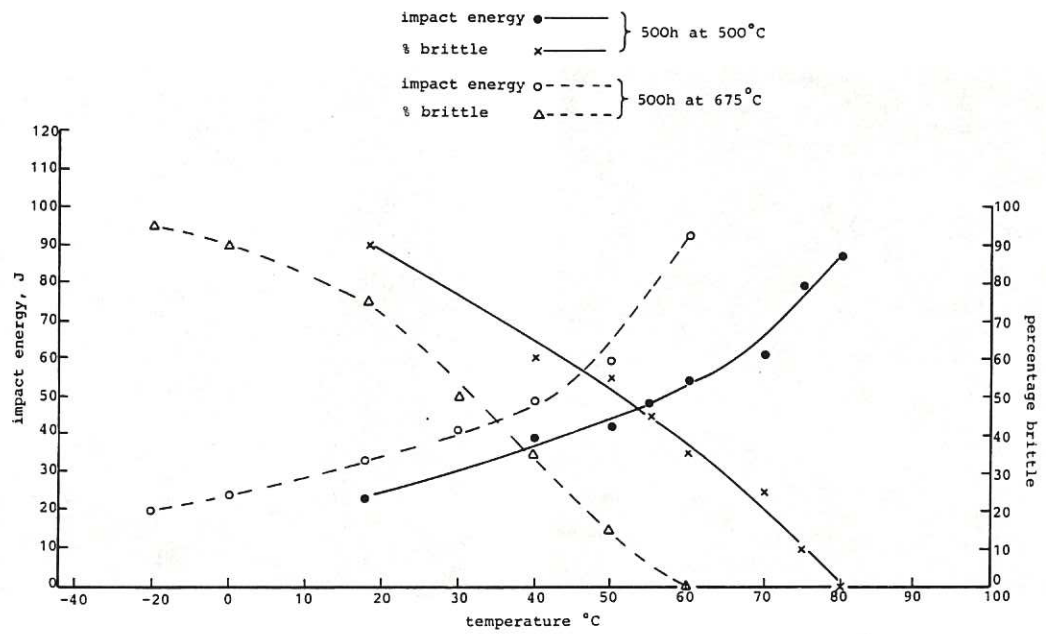


Fig. 25 Impact transition temperature data for Steel 13 (9% Cr, 0.25% V, 3% W) after 500h tempers.

weaker in proof strength than the FV448 steel, with a marginally inferior impact toughness and ductility, after tempering for 2h at 675°C. The 9%Cr variant of the same composition was weaker. In terms of proof strength the 2%W, 0.25%V steel was only marginally stronger than the tungsten-free base alloy, though it exhibited significantly greater toughness. After ageing for 500h at 675°C the 9 and 11%Cr, 3%W, 0.25%V steels possessed similar strengths, being about 70 MPa lower in proof stress than the FV448 steel. The toughness of the tungsten-bearing steels was, however, markedly inferior in this condition. With the exception of the high vanadium steel, the properties of the alloys studied were not greatly affected by exposure at 500°C for 500h subsequent to the initial temper.

4.5 Metallographic examination and phase characteristation

4.5.1 Structures observed after tempering for 1h at 700°C

An initial examination of the structures of Steels 1, 2, 6, 7, 9 and 13 was made using carbon extraction replicas in the transmission electron microscope, after a preliminary optical examination had indicated that the structures were all predominantly tempered martensite. Typical micrographs are shown in Figures 26-30 and these may be compared with the structure of Steel 1 shown in Fig.1. The micrographs showed that the tempered structures contained relatively coarse precipitates on the prior austenite and intermartensite unit boundaries, together with finer precipitates within the martensite, as seen for example in Steel 6, Fig.27(d). The finer austenite grain size of Steel 1 was associated with the presence of finer boundary precipitate particles than those in Steels 2, 6, 7 and 9, as

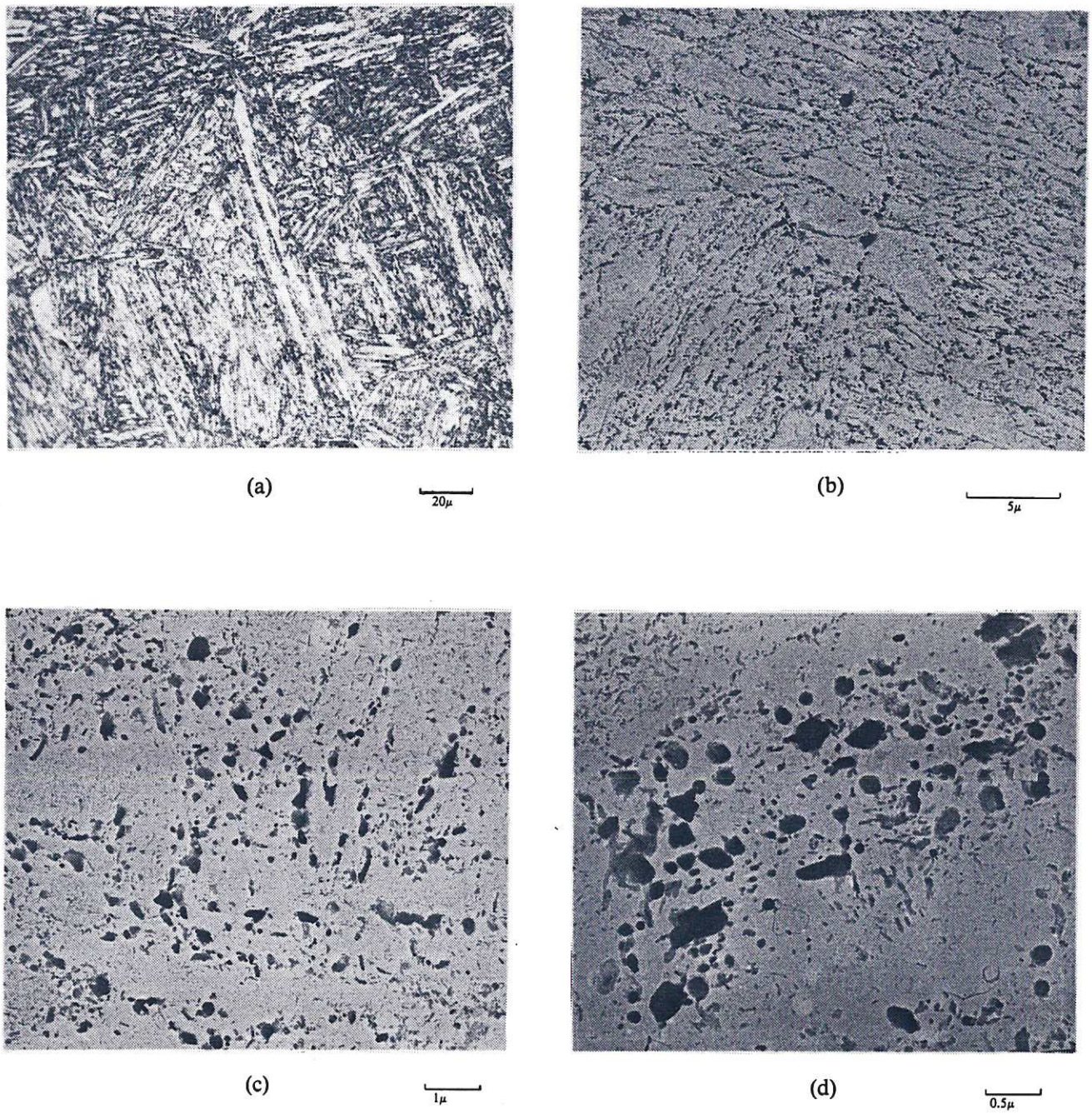


Fig. 26 Optical and carbon extraction replica electron micrographs of Steel 2 (0.25% V) after hardening from 1100°C and tempering for 1 h at 700°C.

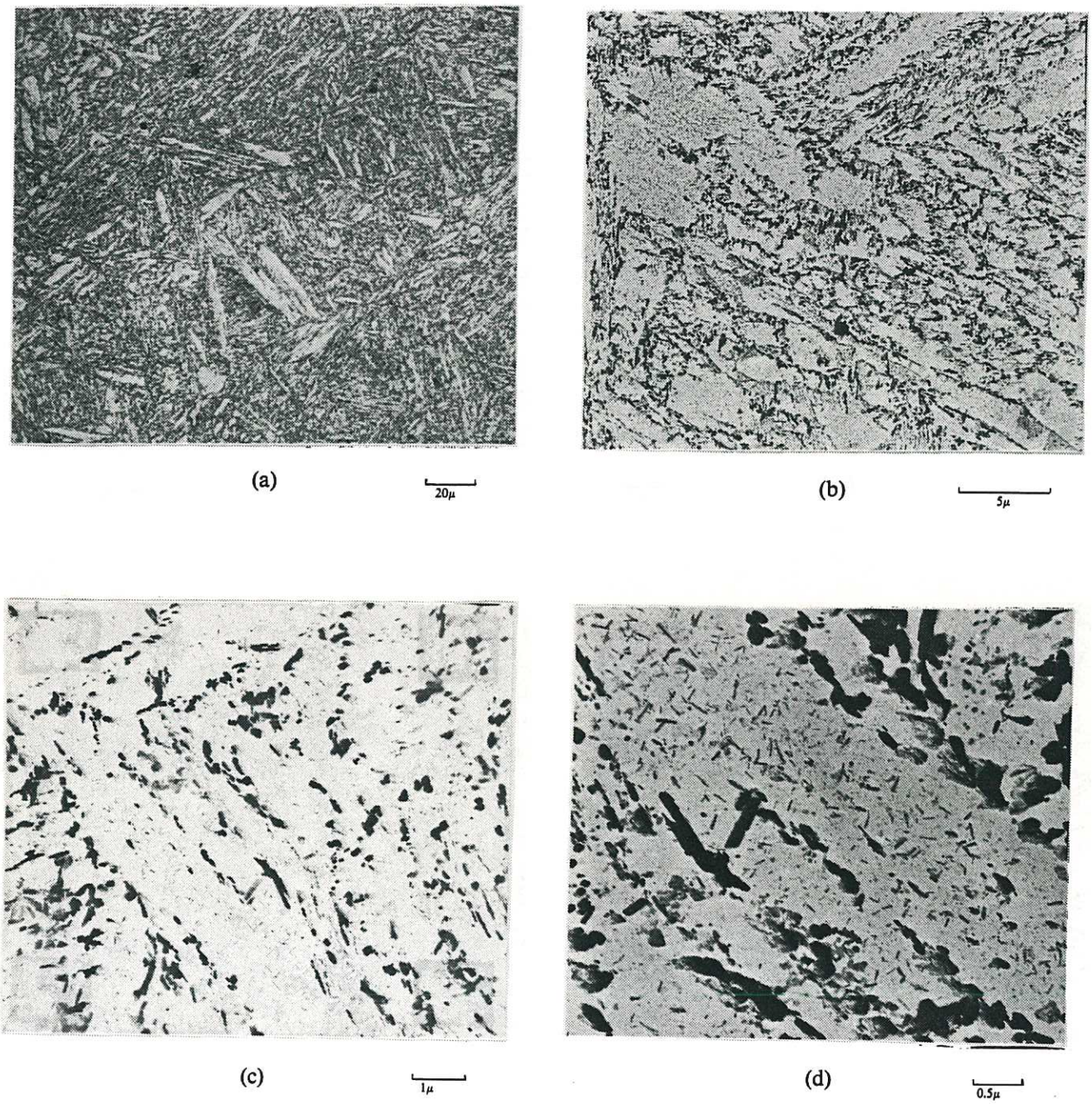


Fig. 27 Optical and carbon extraction replica electron micrographs of Steel 6 (0.25% V, 2% W) after hardening from 1100°C and tempering for 1 h at 700°C.

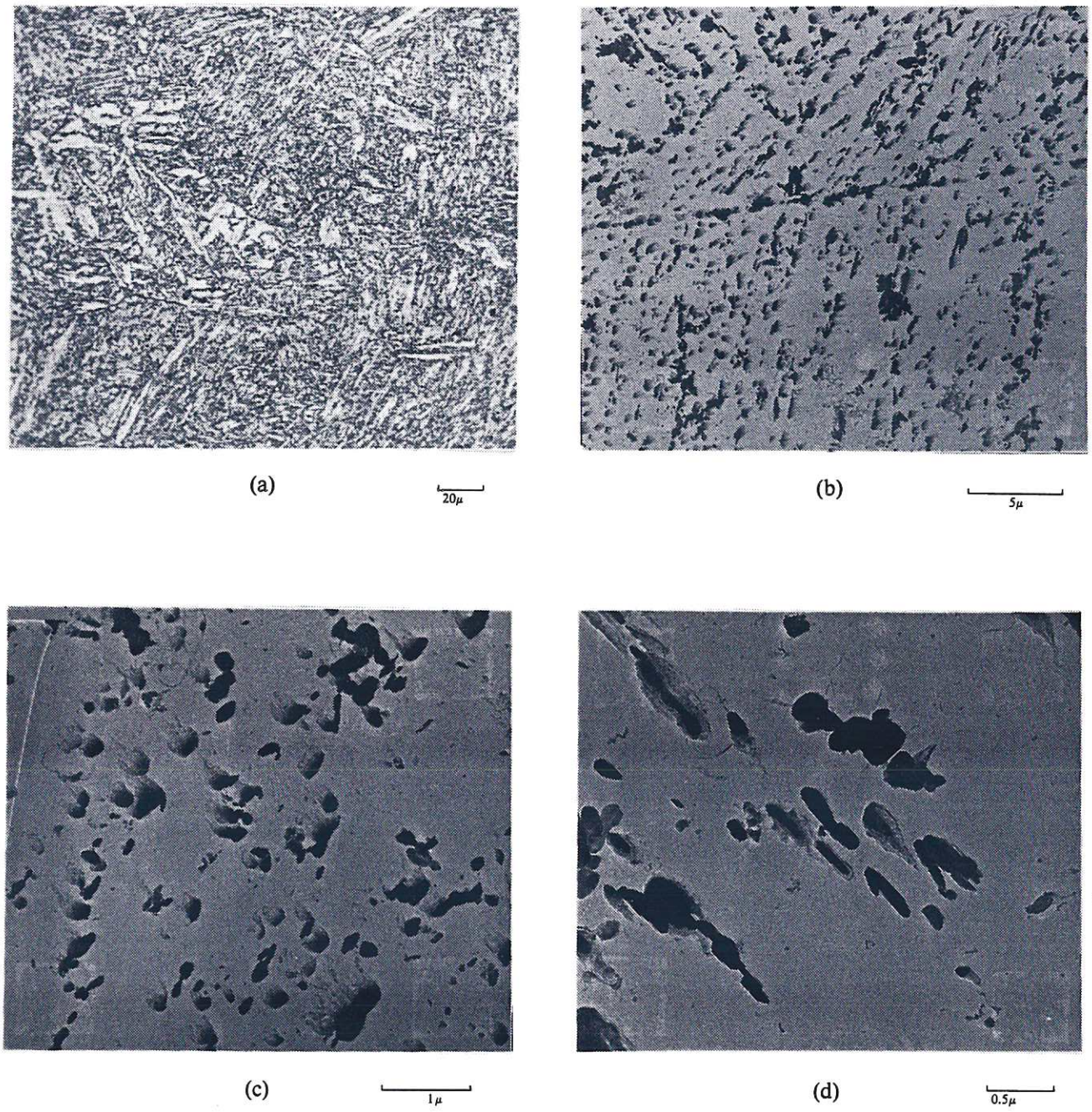


Fig. 28 Optical and carbon extraction replica electron micrographs of Steel 7 (0.25% V, 3% W) after hardening from 1100°C and tempering for 1 h at 700°C.

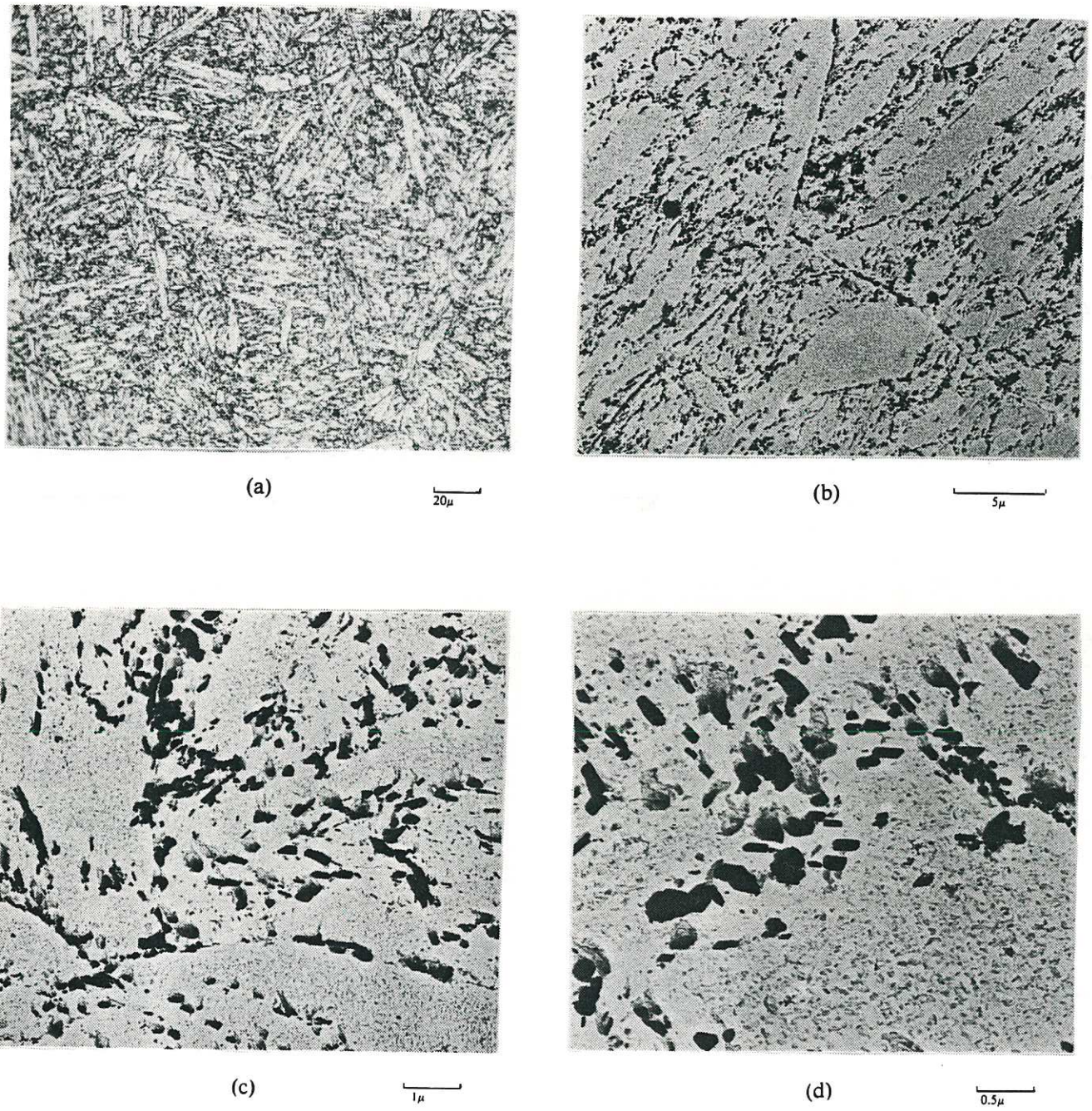
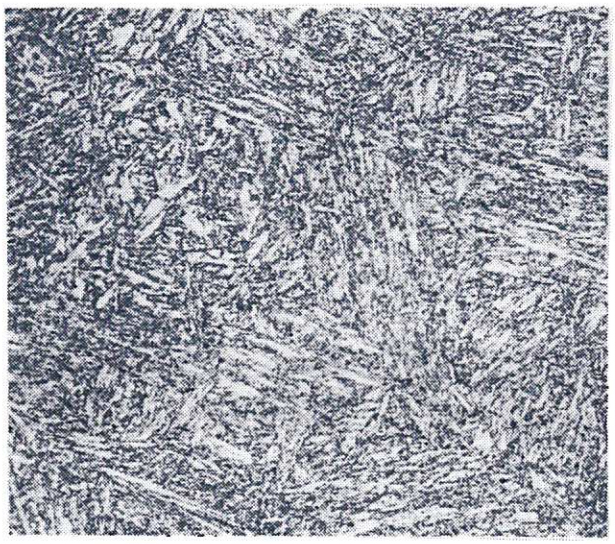


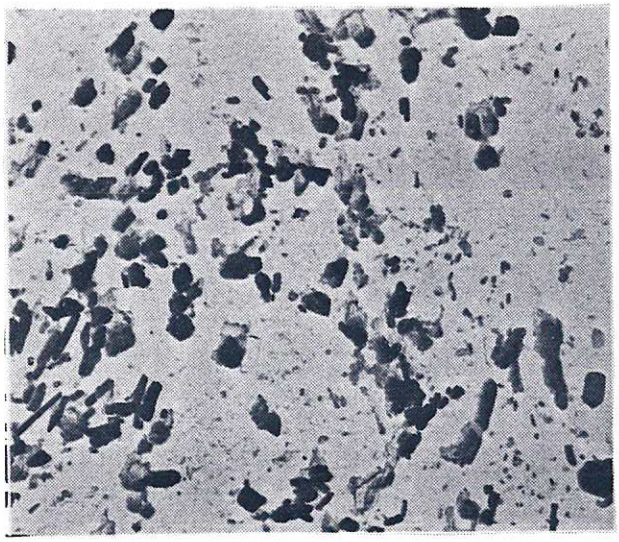
Fig. 29 Optical and carbon extraction replica electron micrographs of Steel 9 (0.8% V, 0.75% W) after hardening from 1100°C and tempering for 1 h at 700°C.



(a) 20μ

(b) 5μ

(c) 1μ



(d) 0.5μ

Fig. 30 Optical and carbon extraction replica electron micrographs of Steel 13 (9% Cr, 0.25% V, 3% W) after hardening from 1100°C and tempering for 1 h at 700°C.

may be seen by comparing the higher magnification fields shown at (d) in the appropriate figures.

4.5.2 Structures and phases present after tempering for 500h at 675°C

The tempering treatment of 500h at 675°C corresponded to the highest tempering parameter in the present series of tests and was chosen to represent overageing at the likely tempering temperature. In relation to the condition produced by a 1h temper at 700°C, particle distributions were found to be similar, with particle coarsening and a tendency for the particles in the tungsten-bearing steels to be elongated rather than equiaxed, as illustrated by Figures 31-37.

The results of the X-ray powder phase identifications are given in Table 11 and these show that in all the steels $M_{23}C_6$ carbide was the principal precipitate phase isolated. In Steel 1 the next most abundant phase was the NbC type, followed by Cr_2N and trace amounts of NbN. In Steel 2, without molybdenum and niobium, only $M_{23}C_6$ and Cr_2N were found. The intermetallic Laves phase Fe_2X was detected only in the 3%W steels, 7 and 13. An appreciable proportion of V(C,N) was found only in the high vanadium composition, Steel 9. This alloy, together with the 9%Cr, 3%W, V variant, Steel 13, showed traces of Cr_2N.

Table 11

Phases observed in the steels aged for 500h at 675°C, as determined by X-ray diffraction from powder residues prepared by electrolytic isolation

Steel number	phases identified					
	$M_{23}C_6$	Laves Fe_2X	Cr_2N	fcc $a_0 \approx 4.45$ Å (probably NbC)	fcc $a_0 \approx 4.44$ Å (probably NbN)	fcc $a_0 \approx 4.10$ Å (probably VC/VN)
1	m	—	s	s-m	tr	—
2	m-l	—	s-m	—	—	—
6	m-l	—	s-m	—	—	—
7	m	s-m	s	—	—	tr(?)
9	m-l	—	tr(?)	—	—	s
13	m	s-m	tr(?)	—	—	tr(?)

Concentrations: l=large, m=medium, s=small, tr=trace

Steel 7 contained all of the major phases detected by X-ray diffraction, with the exception of the niobium carbide and nitride found only in FV448. A more detailed phase characterisation was therefore performed for this steel, employing a combination of convergent beam electron diffraction and energy dispersive analysis in a scanning transmission electron microscope, to obtain mean particle compositions from several individual particles.

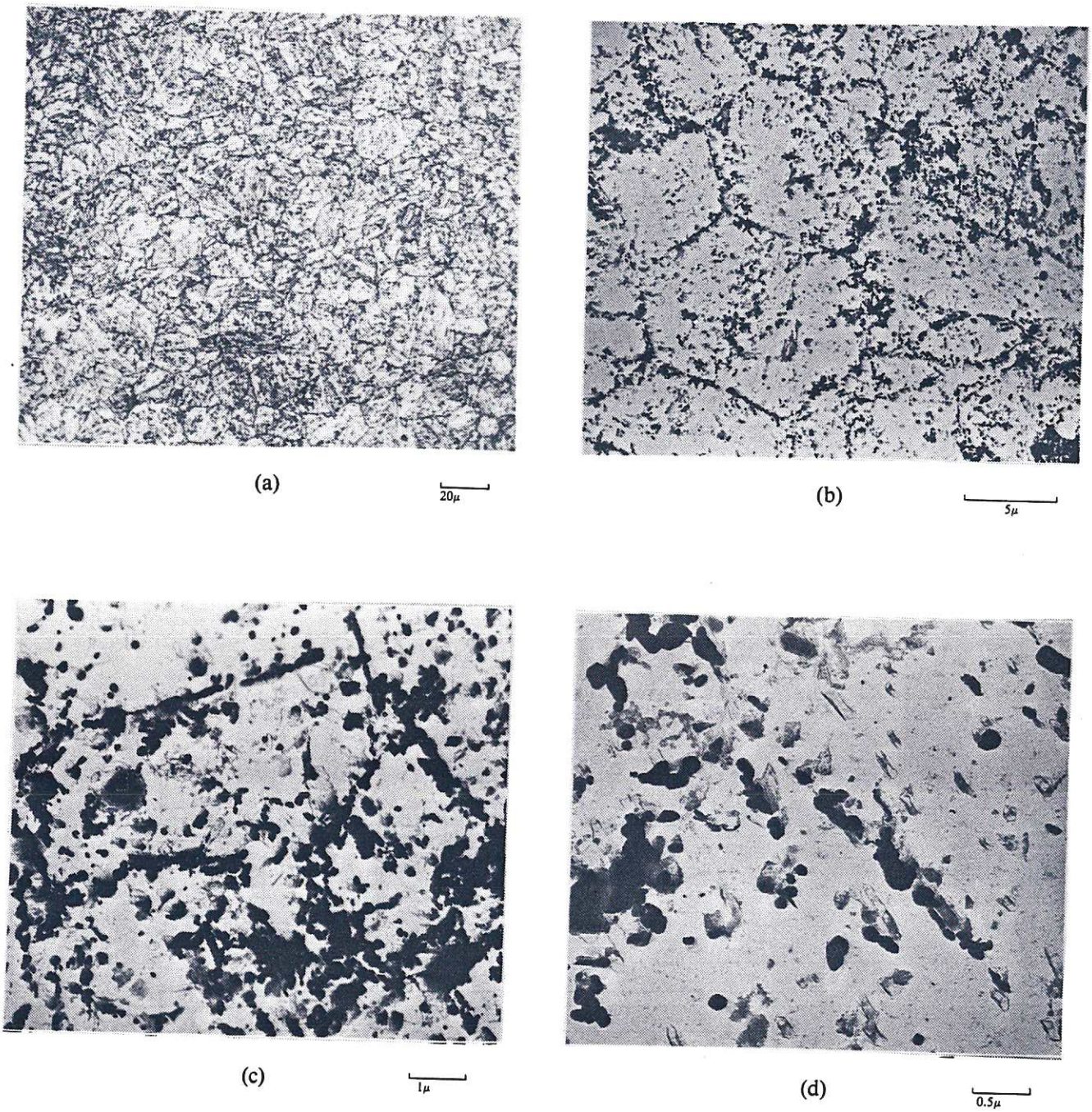


Fig. 31 Optical and carbon extraction replica electron micrographs of Steel 1 (FV448 type) after hardening and tempering for 500h at 675°C.

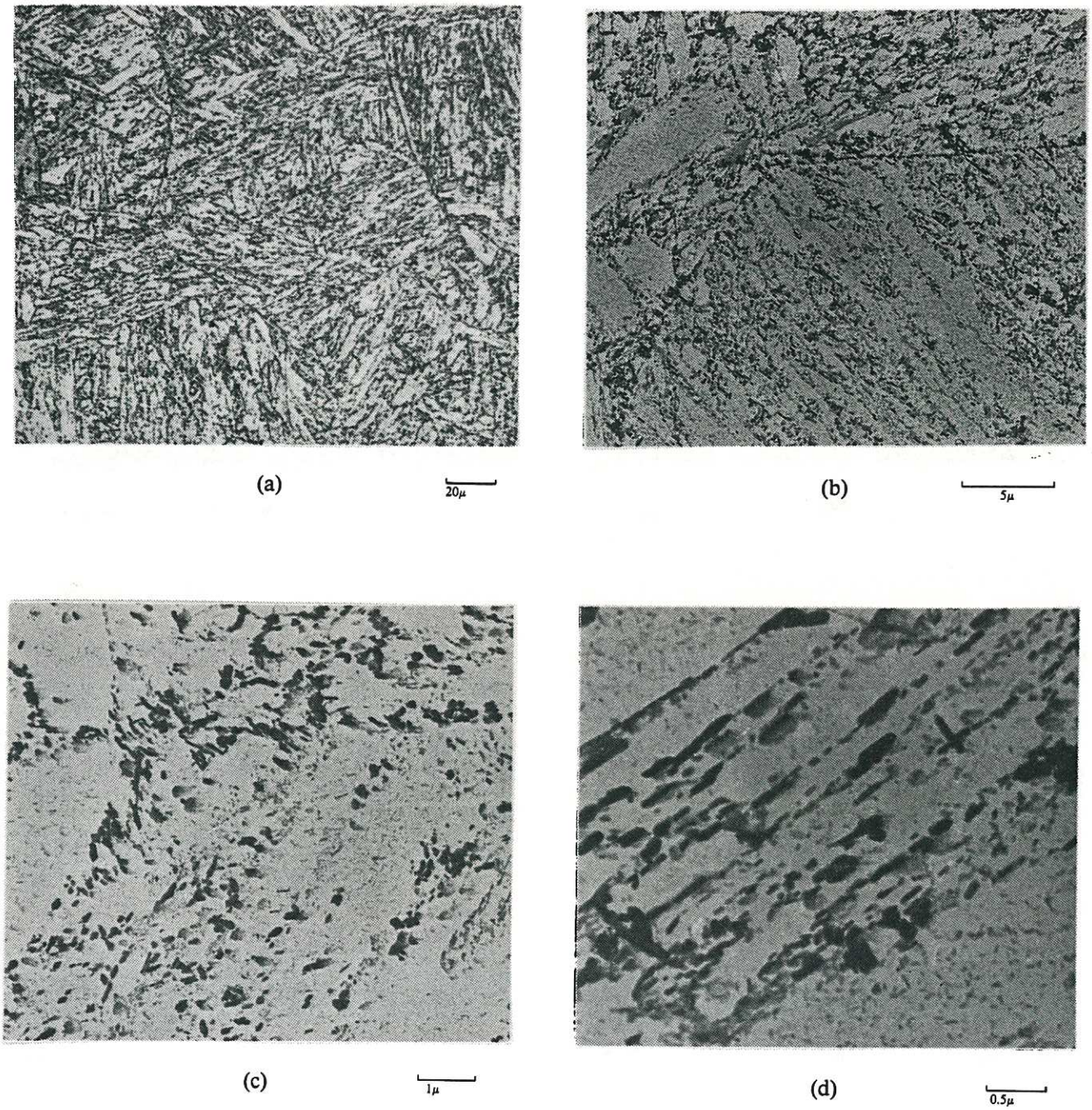


Fig. 32 Optical and carbon extraction replica electron micrographs of Steel 2 (0.25% V) after hardening and tempering for 500h at 675°C.

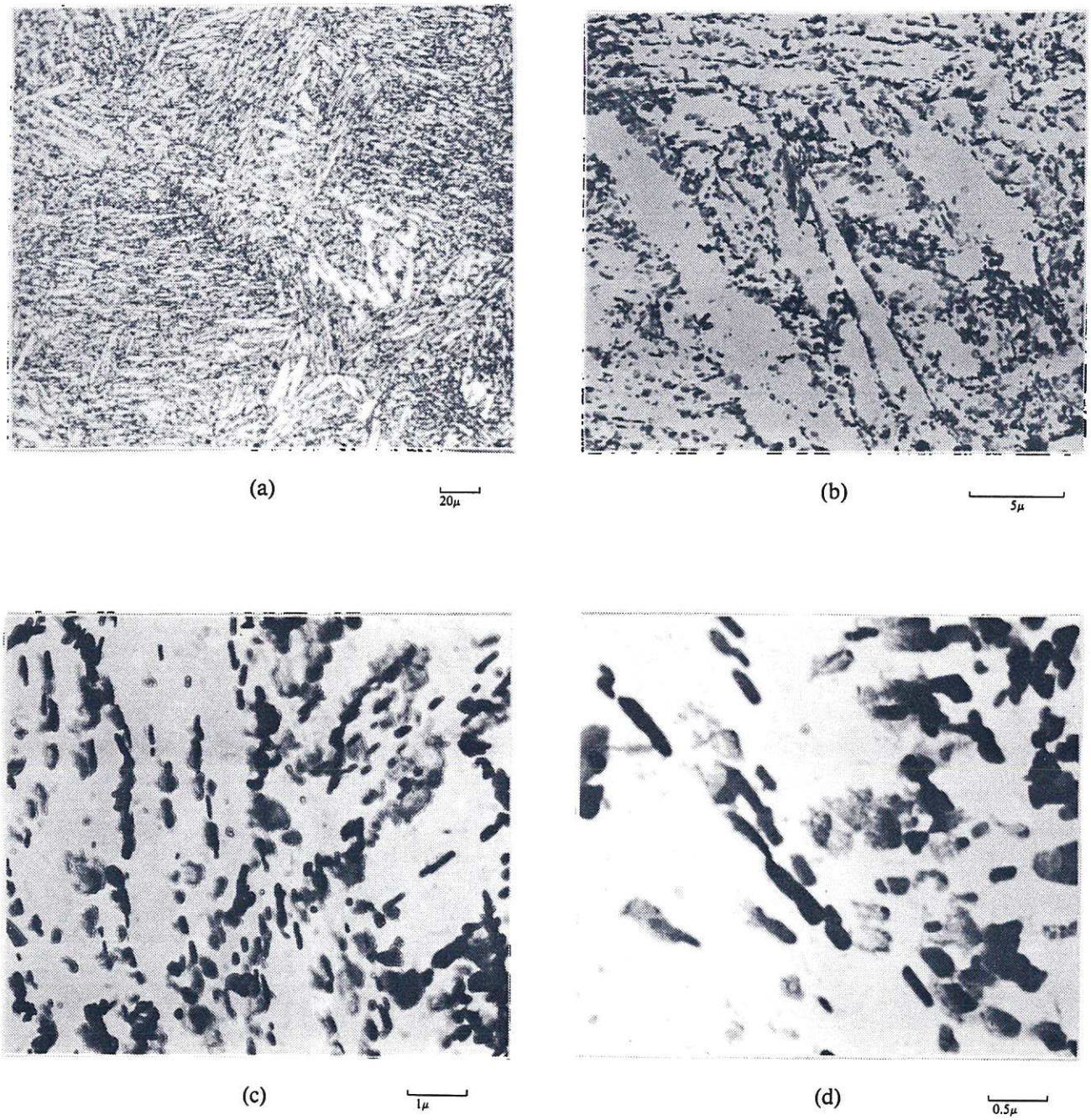


Fig. 33 Optical and carbon extraction replica electron micrographs of Steel 6 (0.25% V, 2% W) after hardening and tempering for 500h at 675°C.

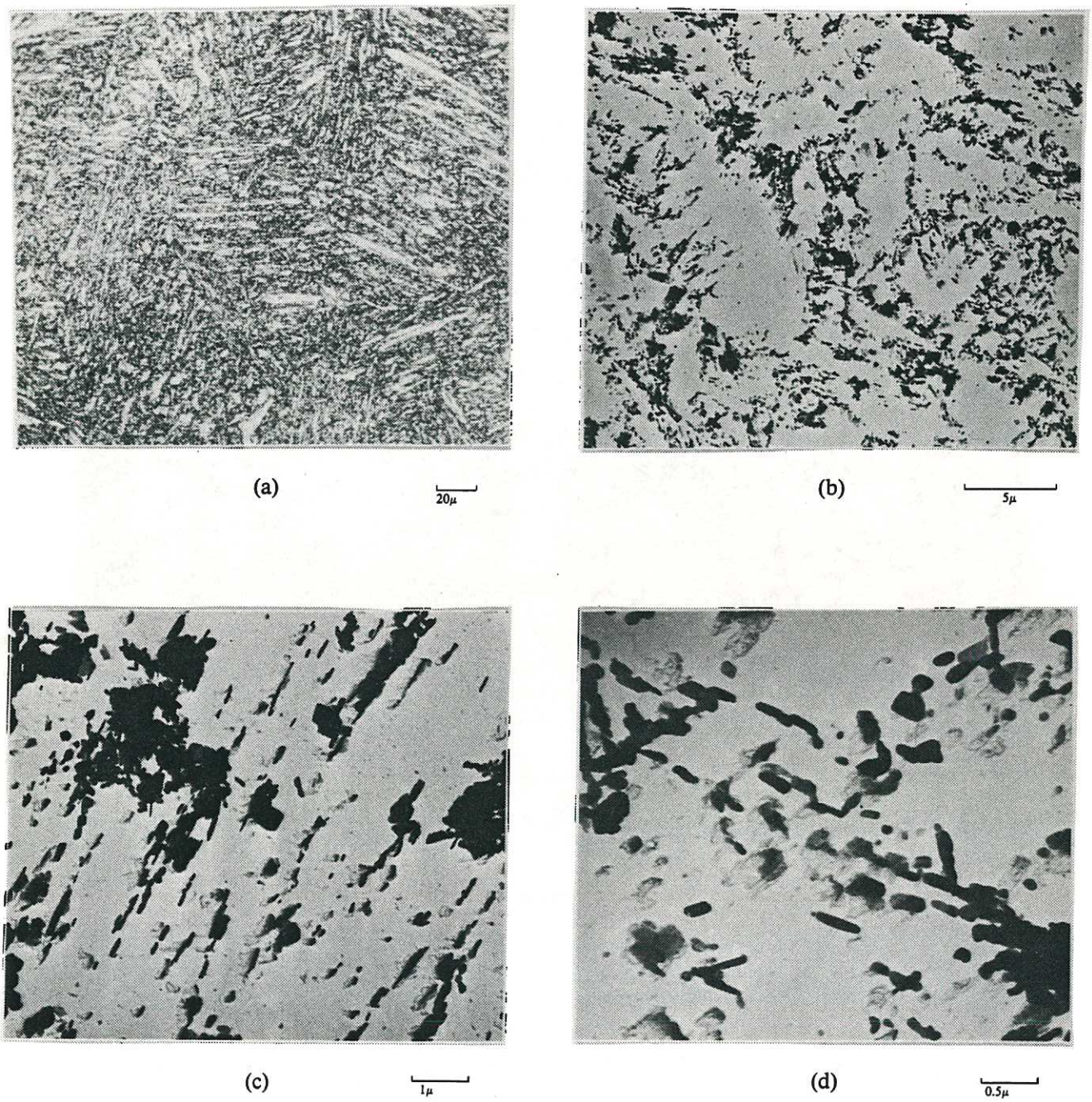


Fig. 34 Optical and carbon extraction replica electron micrographs of Steel 7 (0.25% V, 3% W) after hardening and tempering for 500 h at 675°C.

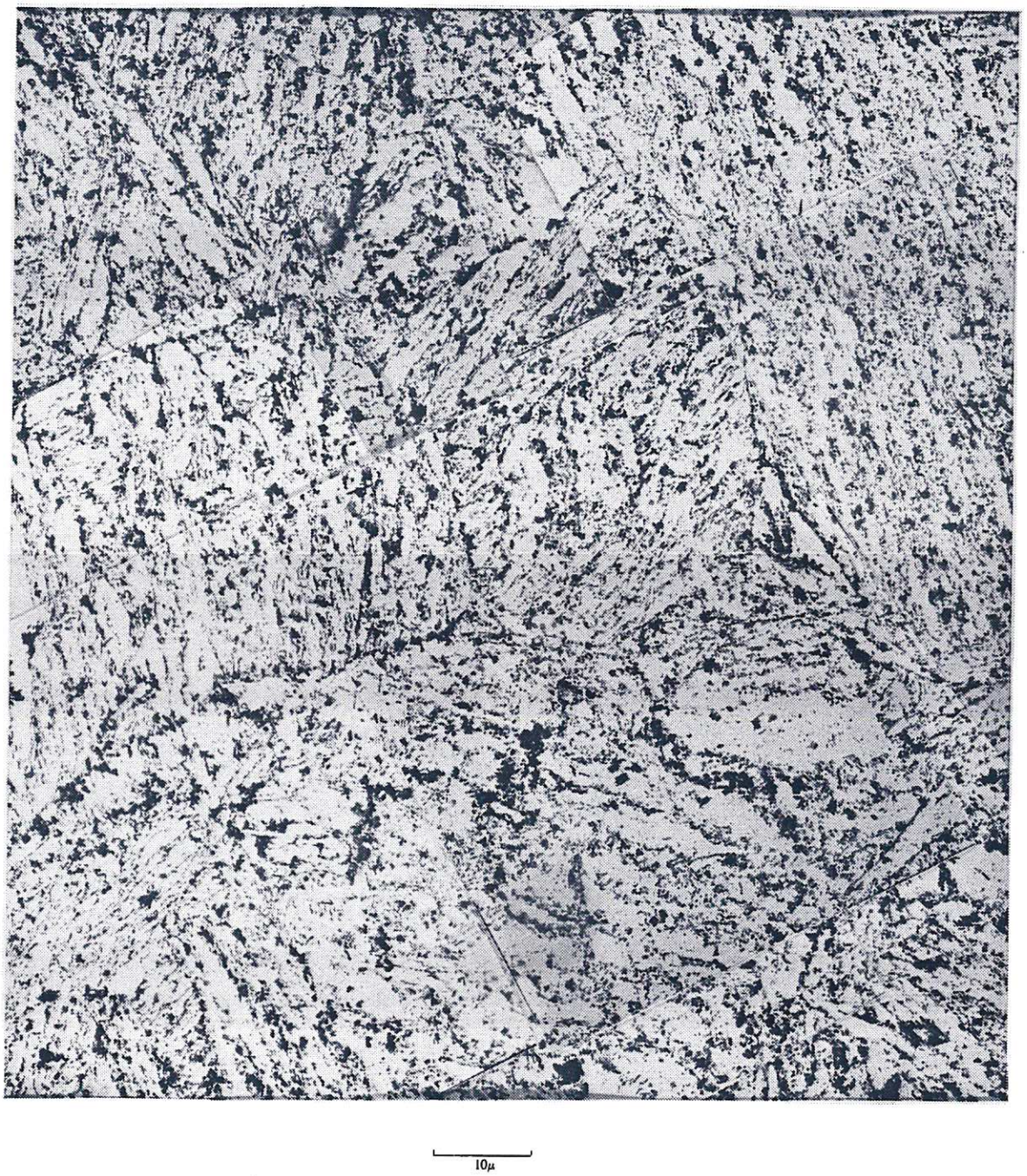


Fig. 35 Carbon extraction replica of Steel 7 (0.25% V, 3% W) after hardening and tempering for 500h at 675°C.

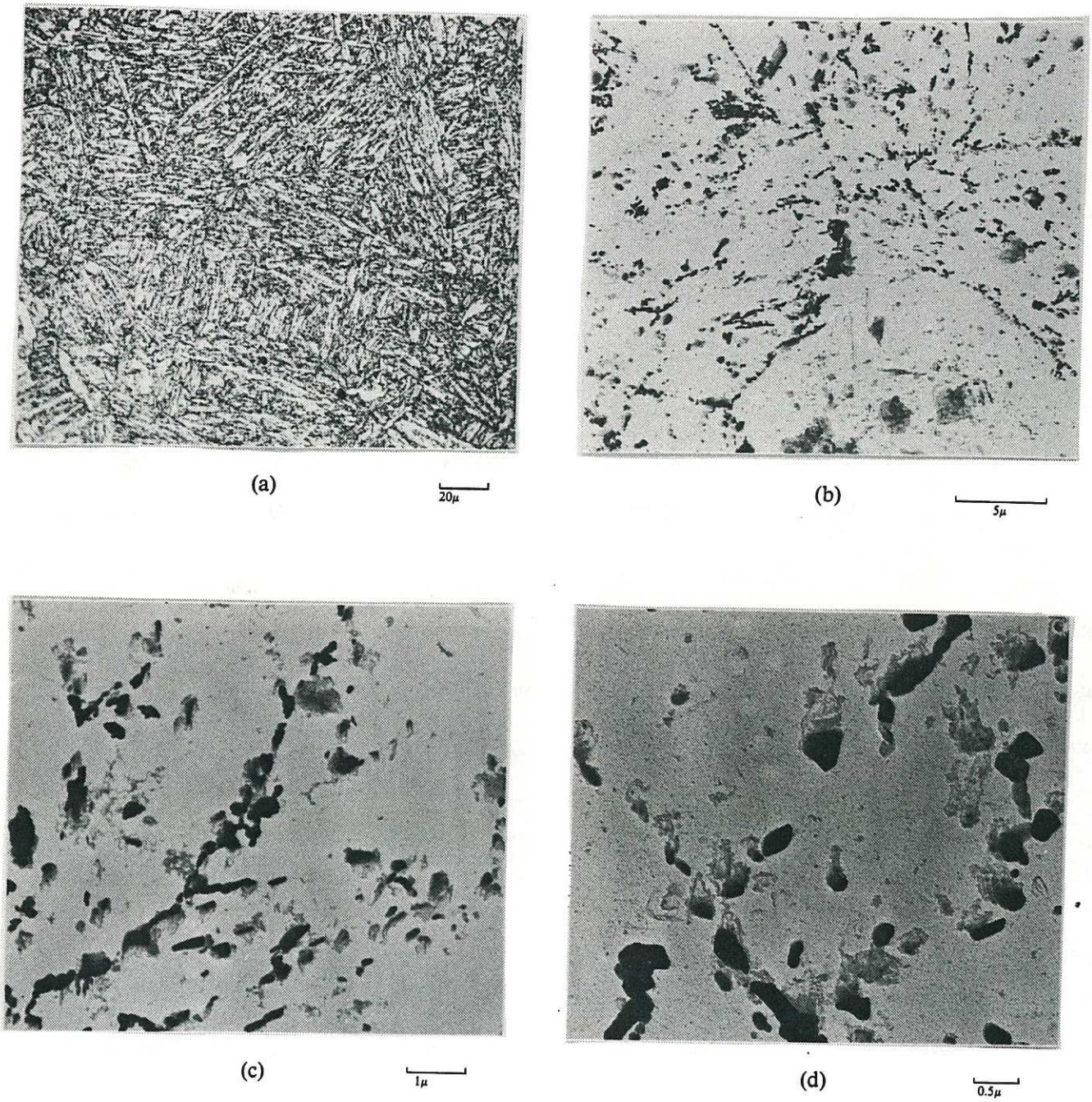


Fig. 36 Optical and carbon extraction replica electron micrographs of Steel 9 (0.8% V, 0.75% W) after hardening and tempering for 500h at 675°C.

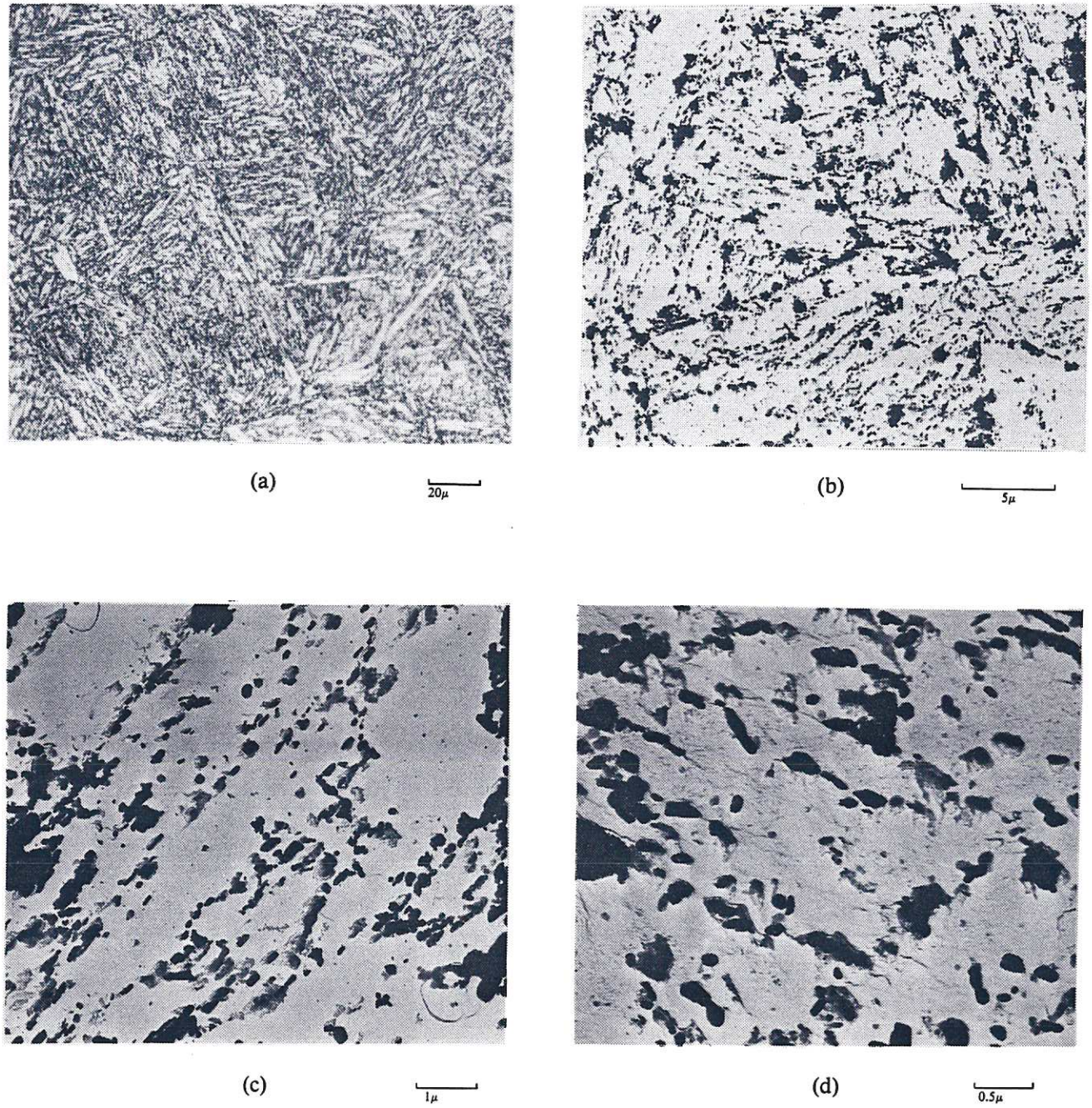


Fig. 37 Optical and carbon extraction replica electron micrographs of Steel 13 (9% Cr, 0.25% V, 3% W) after hardening and tempering for 500h at 675°C.

Table 12

Approximate compositions of precipitated phases in Steel 7

heat treatment condition	type	composition determined from EDA of individual particles
after 500h at 675°C	$M_{23}C_6$	$(Cr_{16.5}, Fe_{5.5}, W_{1.0})\ C_6$
	M_2X	$(Cr_{1.55}, V_{0.4}, (Fe,W)_{0.05})\ N$
	Fe_2X	$(Fe_{1.6}, Cr_{0.4})\ W$
	MC	$(V_{0.55}, Cr_{0.38}, Fe_{0.06}, W_{0.01})\ (C, N)$
after 1h at 700°C	$M_{23}C_6$	$(Cr_{16.0}, Fe_{6.0}, W_{1.0})\ C_6$
	M_2X	$(Cr_{1.55}, V_{0.2}, Fe_{0.2}, W_{0.05})\ N$
	Fe_2X	$(Fe_{1.6}, Cr_{0.4})\ W$

The phases detected and the mean compositions are given in Table 12. It will be noted that little change in the composition of the $M_{23}C_6$ carbide occurred between the two tempering treatments and that this carbide contains only a limited amount of tungsten. Also, only a small amount of tungsten was detected in the MC type carbonitride observed after 500h at 675°C. The results indicate that the vanadium content of the M_2X phase increases with the tempering parameter.

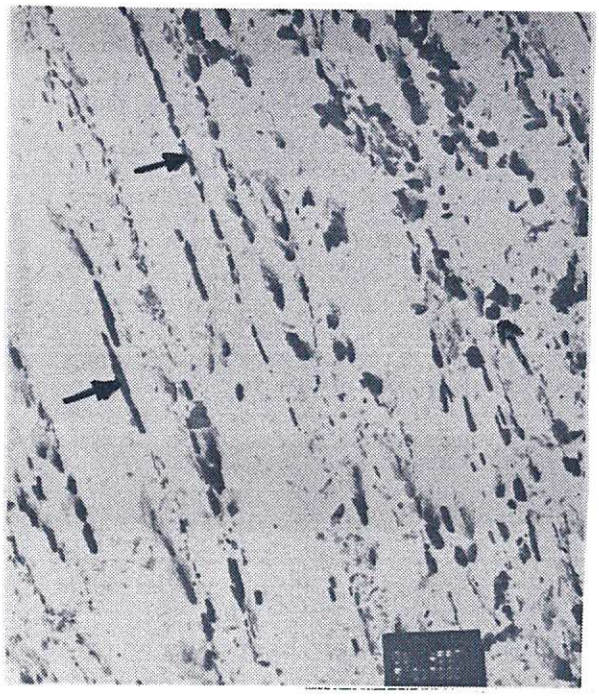
Examples of the morphologies of the particles and their associated EDA spectra are given in Figures 38-40 and 41-47. These observations confirm that the majority of the larger precipitate particles consist of $M_{23}C_6$, with some Laves phase. The finer, needle-like M_2X particles were found to be non-uniformly distributed over the replicas but tended to occur in scattered regions. The larger disc-like V(C,N) particles, shown for example by Fig.40(c), were found infrequently.

5. DISCUSSION

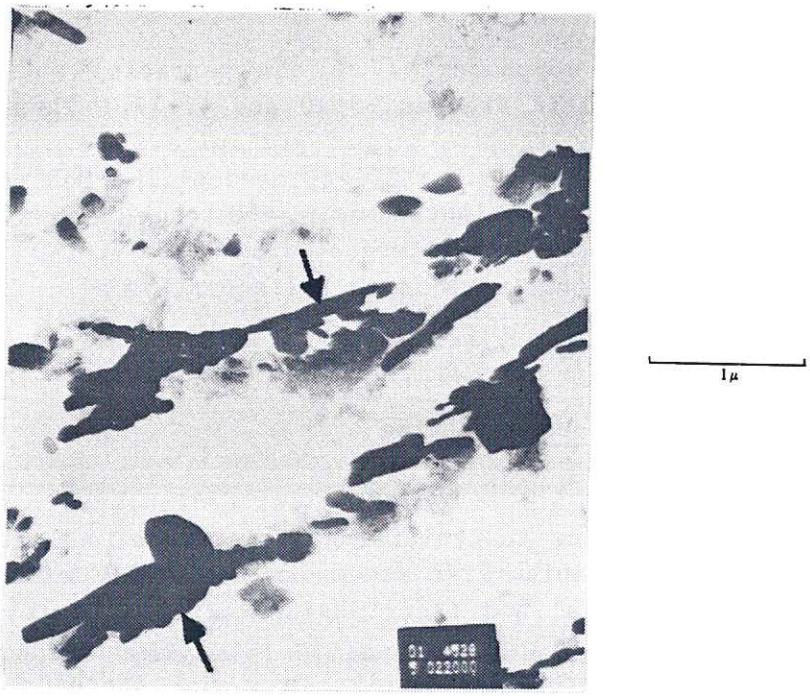
5.1 Structure on austenitising

The data in Table 6 show that, unless undissolved particles are present as the result of a low austenitising temperature, as for example with Steel 8 at 1100°C, the niobium-free steels have coarser prior austenite grains than both the commercial and the experimental FV448 materials. The reason for the appreciable difference in grain size between the latter two samples is uncertain. It probably results from a difference in the prior thermal histories of the two samples, that of the commercial material being unknown.

If an effective low-activation substitute for niobium were available then the resulting grain refinement would clearly be expected to benefit the toughness of the niobium-free steels. Titanium forms stable carbonitride

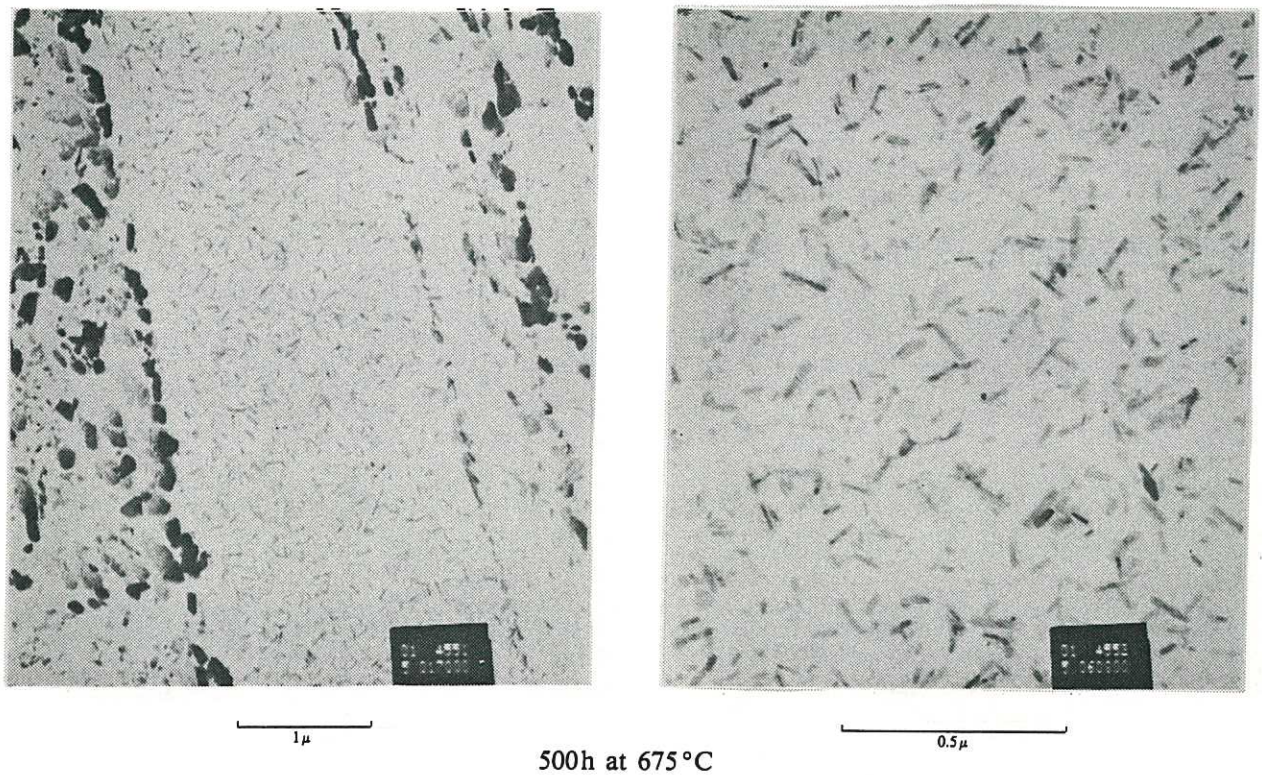


(a) 1h at 700°C

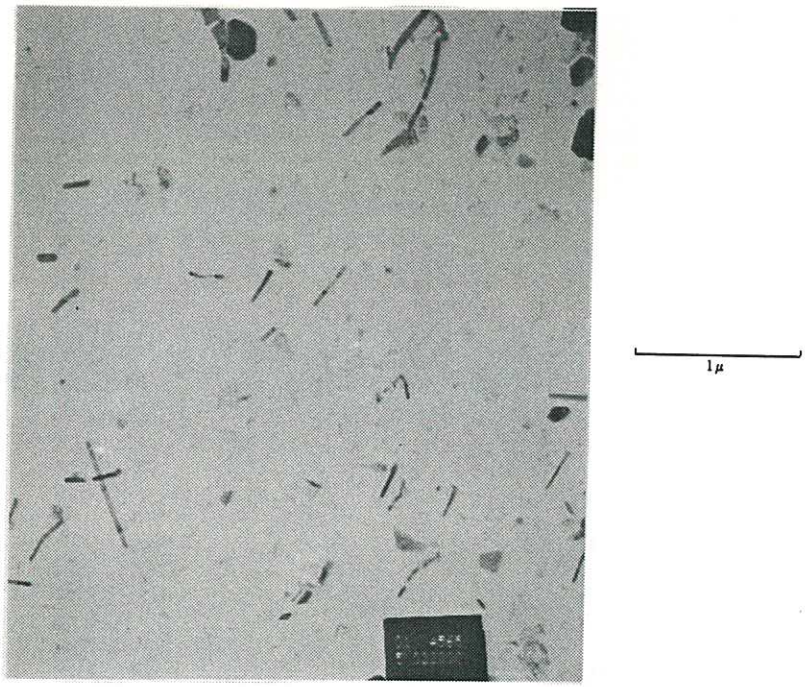


(b) 500h at 675°C

Fig. 38 Electron micrographs of $M_{23}C_6$ precipitates in Steel 7 after tempering.



500h at 675 °C

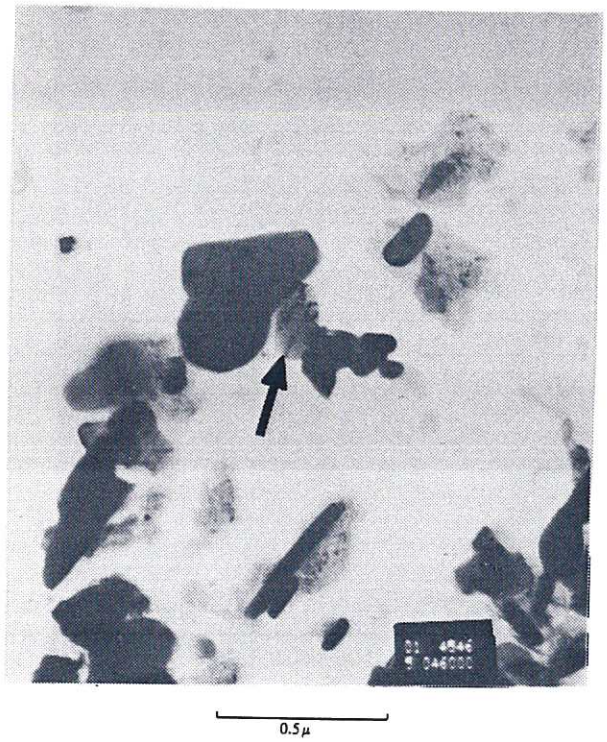


1h at 700 °C

Fig. 39 Electron micrographs of Cr_2N precipitates present in Steel 7 after tempering.

(a) Fe_2W after 1h at 700°C

(b) Fe_2W after 500h at 675°C



(c) V(C,N) after 500h at 675°C

Fig. 40 Electron micrographs of other precipitates in Steel 7 after tempering.

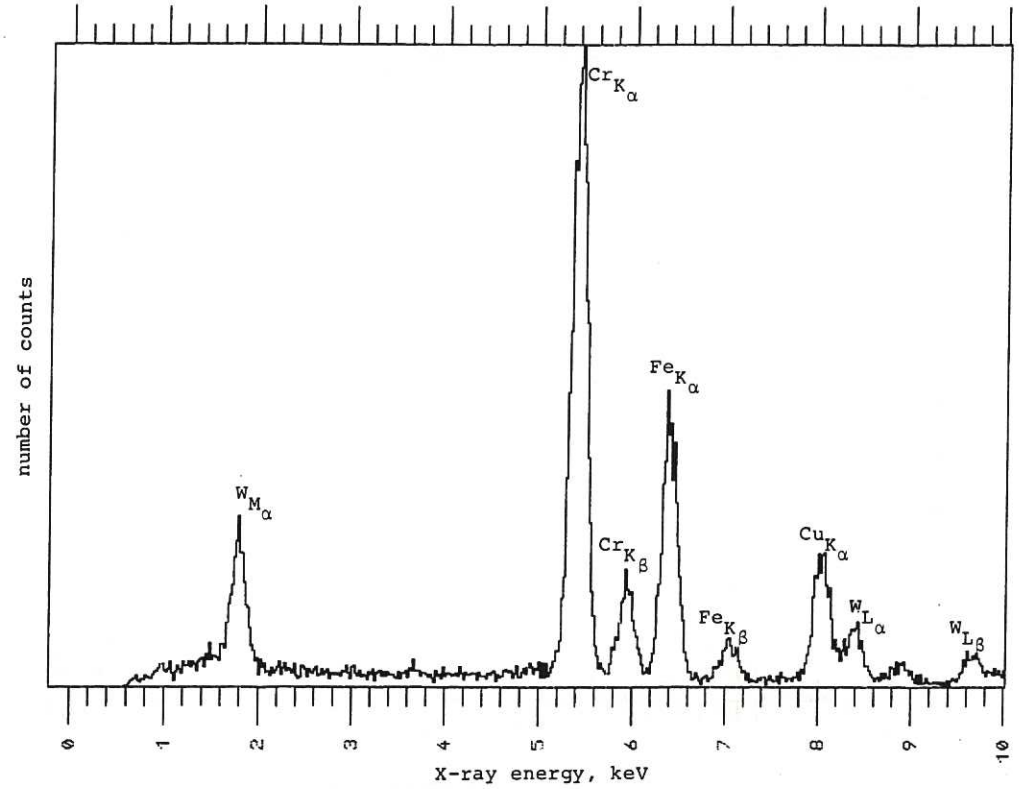


Fig. 41 Typical EDA trace of $M_{23}C_6$ in Steel 7 after 1h at 700°C.

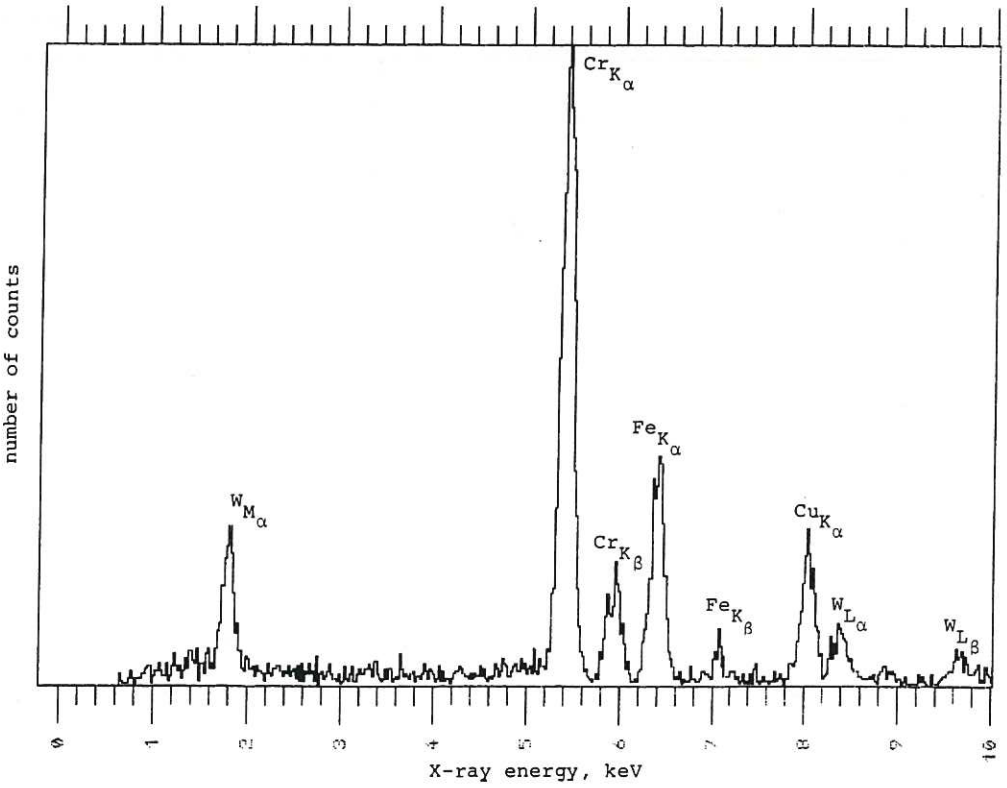


Fig. 42 Typical EDA trace of $M_{23}C_6$ in Steel 7 after 500h at 675°C.

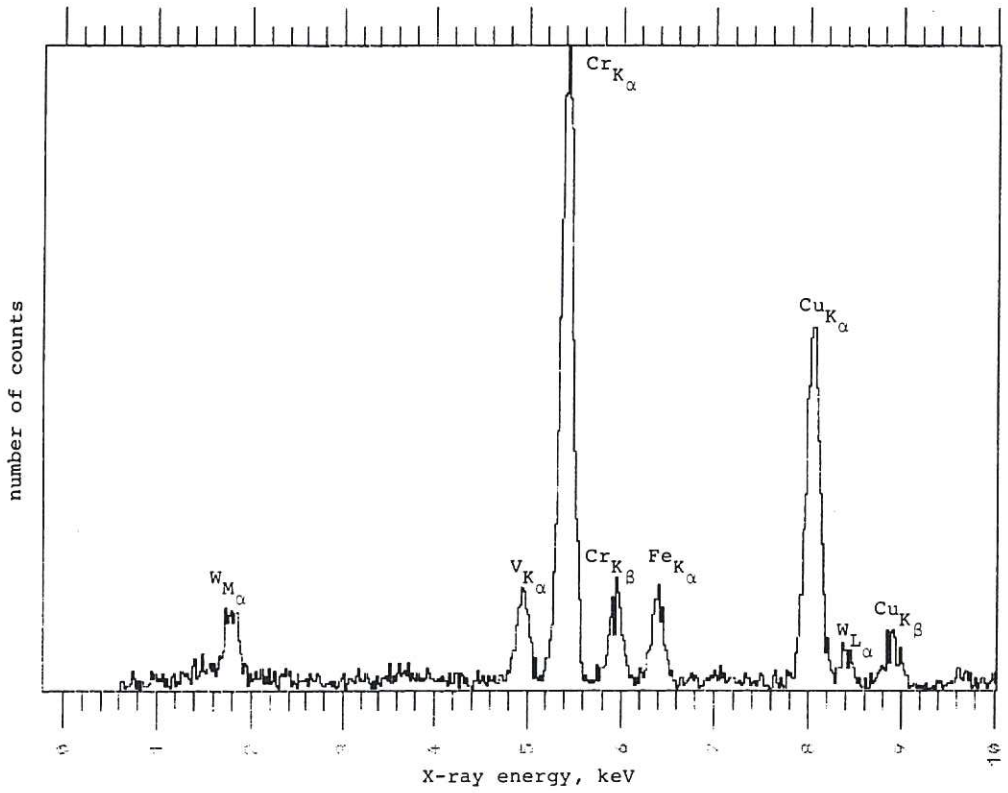


Fig. 43 Typical EDA trace of Cr_2N in Steel 7 after 1h at 700°C.

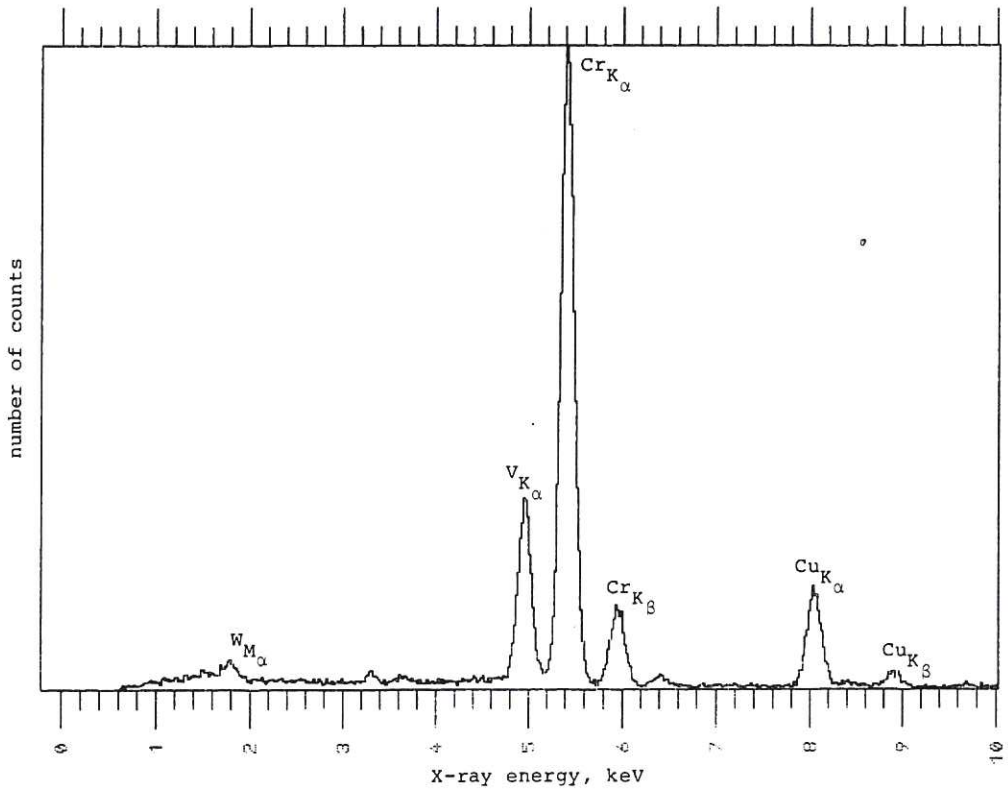


Fig. 44 Typical EDA trace of Cr_2N in Steel 7 after 500h at 675°C.

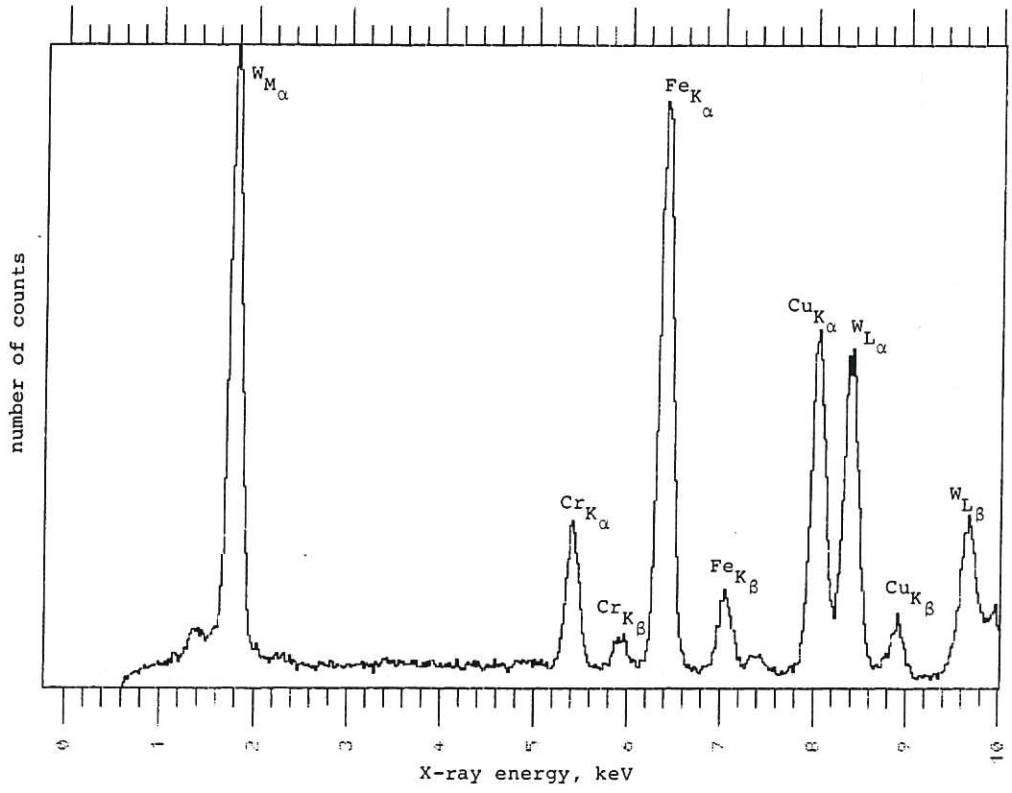


Fig. 45 Typical EDA trace of Fe_2W in Steel 7 after 1h at 700°C.

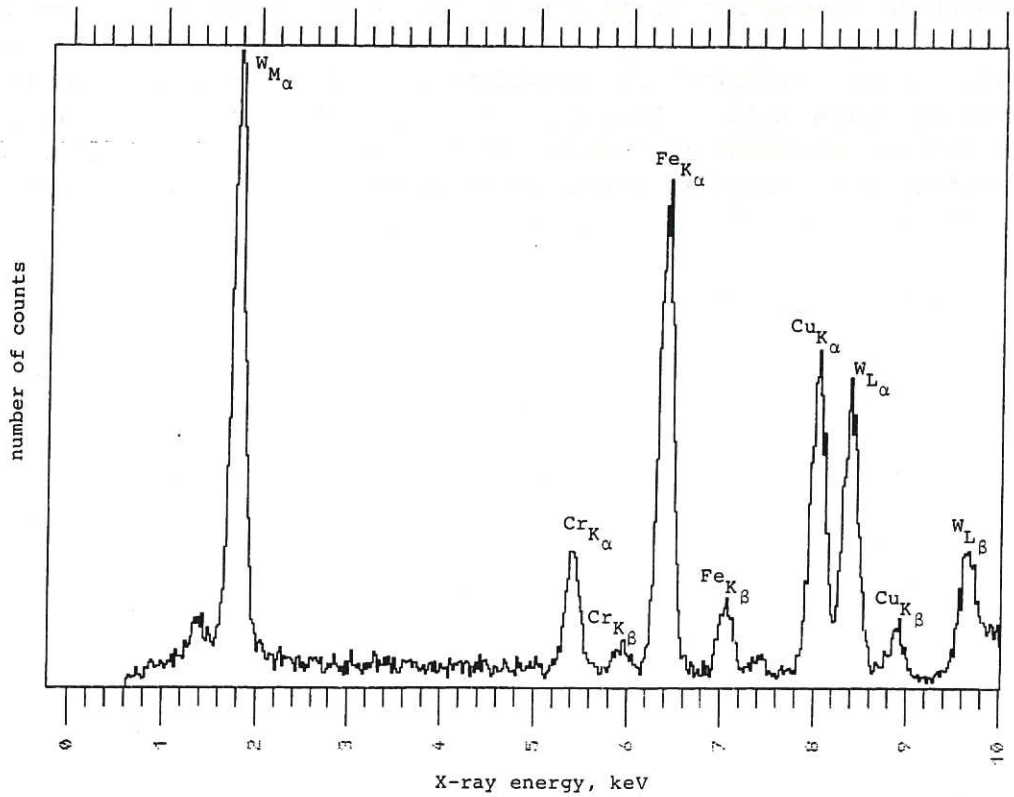


Fig. 46 Typical EDA trace of Fe_2W in Steel 7 after 500h at 675°C.

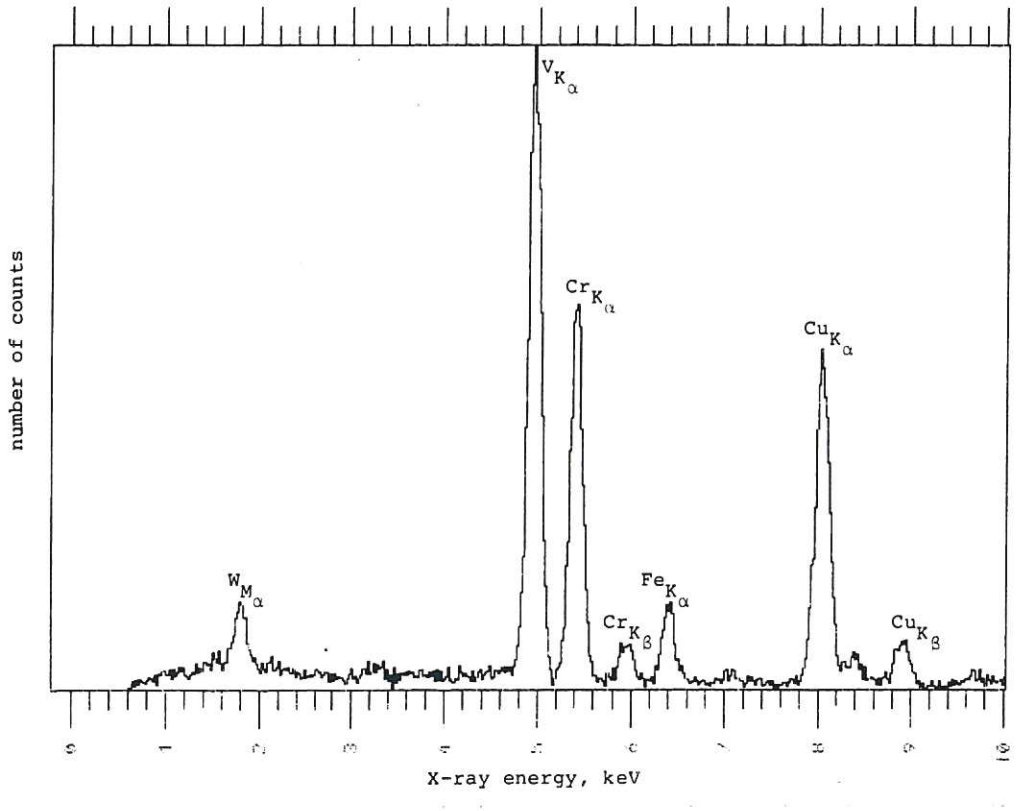


Fig. 47 Typical EDA trace of V(C,N) in Steel 7 after 500h at 675°C.

and nitride phases but it is likely that these would be present on a scale too coarse for effective grain refinement in the presence of nitrogen at 0.05%. Also, radiological considerations limit the use of titanium to additions below 0.1%. Tantalum is chemically related to niobium in the same way as tungsten is related to molybdenum. Its carbide and nitride solubility relationships could advantageously be explored since it is an acceptable element for a low-activation composition.

5.2 Hardening response

The hardening responses of the steels are summarised in Fig.3. Though this supposition was not verified by direct observation, it is likely that the relatively low as-hardened hardness value for the laboratory-prepared FV448 steel is related to the presence of retained austenite. The hardnesses of the low-activation compositions can be correlated with their interstitial and solid solution element contents, the 11%Cr, 3%W steel being slightly softer than the analogous 1.95%W steel as a consequence of the presence of delta ferrite.

5.3 The mechanical property values obtained

Within the range of compositions examined, the 11Cr-3.04W-0.23V alloy gave a strength value closest to that of the reference conventional steel for the tempering conditions investigated. The isochronal data demonstrate

that this strength comparability is maintained for tempering temperatures up to 750°C. The tensile properties following a 2h tempering at 675°C, however, indicate that, although the tensile strengths of the two steels are comparable, the FV448 composition possesses a higher proof strength. After ageing for 500h the proof strength of the tungsten steel has fallen lower in relation to the tensile strength. Thus the isochronal data do not permit an accurate comparison of the strengths of the two steels. Nevertheless, in order to allow some extrapolation from the hardness measurements to tensile properties for the steels not fully tested in this programme, correlations between the hardness and the proof strength and ultimate tensile strength for the steels tested are given in Figures 48 and 49.

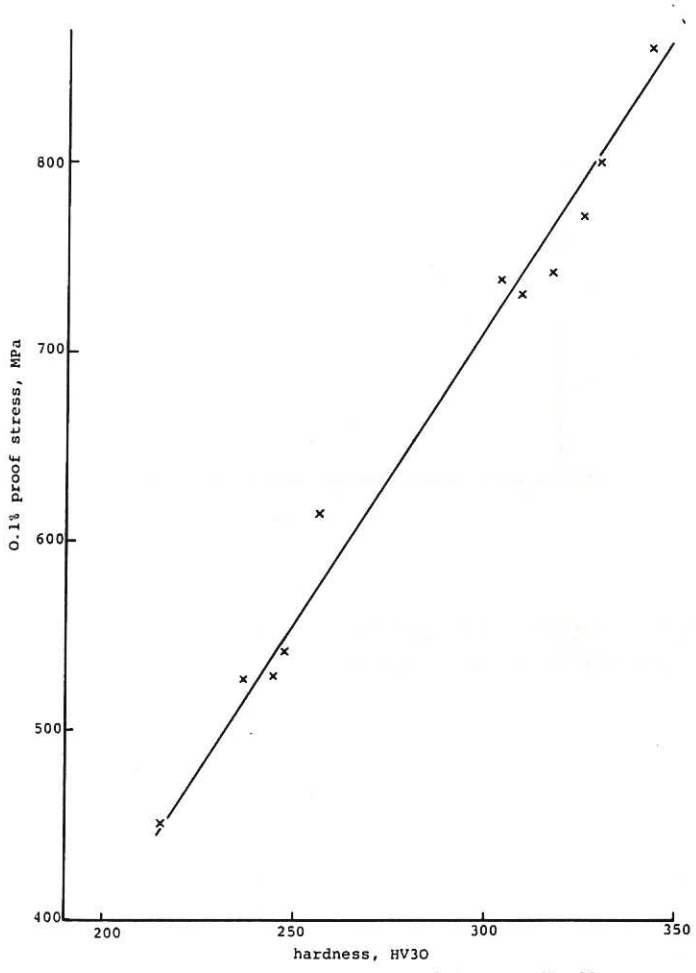


Fig. 48 Correlation between hardness and 0.1% proof stress of the experimental martensitic stainless steels.

Of the other steels the 9%Cr variant of Steel 7 offers the best combination of properties and its apparent equivalence to the 11%Cr steel in terms of elevated temperature tensile properties at 600°-650°C requires confirmation and further investigation. On the basis of the criteria adopted for the current evaluation, none of the other compositions offers any special advantage over these two steels.

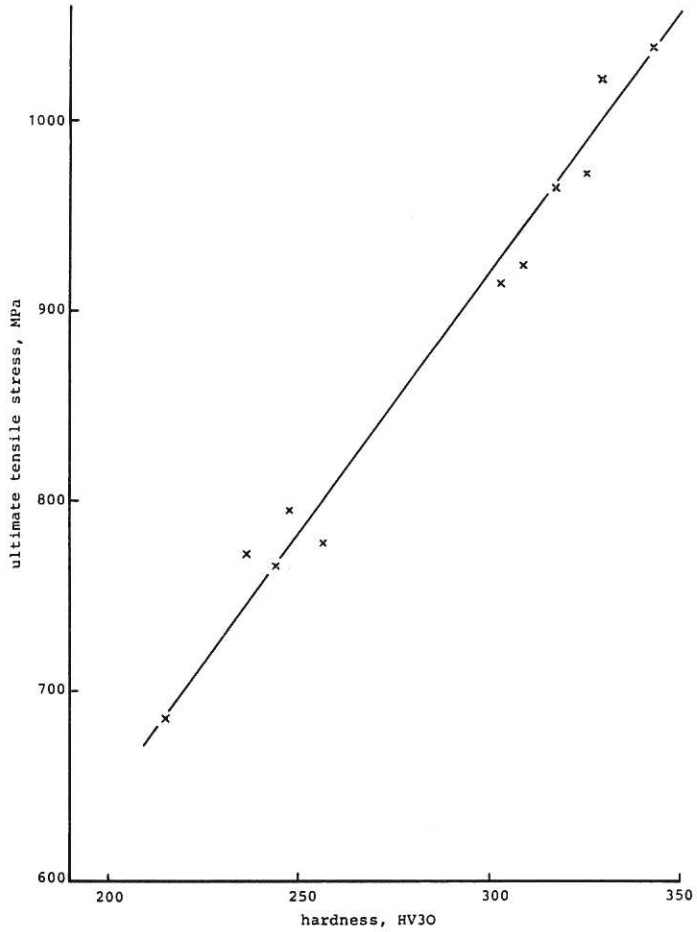


Fig.49 Correlation between hardness and ultimate tensile strength of the experimental martensitic stainless steels.

Correlations between the fracture appearance transition temperature (FATT) and the proof strength are often of value in assessing the toughness of steels, provided they are established for materials with similar microstructures and are used within reasonable limits. Figure 50 shows the relationship for the steels tested in the present study. It will be noted, for the three heat treatment conditions employed, that the observations for the low-activation steels all lie above the trend line for the FV448 alloy. This figure highlights the loss of toughness in the high vanadium steel after post-tempering exposure at 500°C and it also demonstrates that, with the exception of this composition, the steels are not subject to significant embrittlement on exposure at 500°C.

5.4 The roles of the alloying elements

Figure 3 shows that tungsten, when present in concentrations above 1%, raises appreciably the as-hardened hardness when compared with the FV448 steel. The effect of tungsten on the tempering response can be summarised

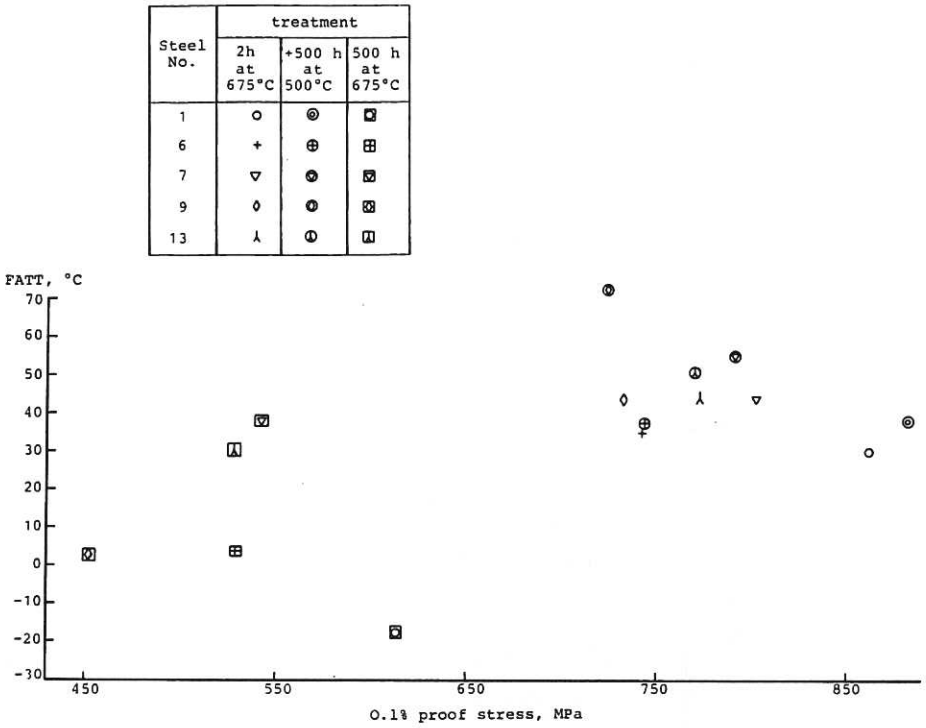


Fig. 50 Relationship between fracture appearance transition temperature and 0.1% proof stress of selected experimental steels after optimum heat treatment and overageing.

as in Fig.51, which shows the increment in hardness relative to the base material, Steel 2, as a function of tungsten content for tempering temperatures in the range 550°-700°C. Also shown for reference are the respective hardness values of the FV448 composition. The summary diagram shows that the optimum tungsten content for hardening depends on the tempering temperature and that the increment obtained continues to increase with tungsten content above 2% for tempering temperatures above 650°C. The phase characterisation observations indicate that this effect of tungsten is not related to any significant modification of the chemistry and structure of the $M_{23}C_6$ carbide formed. The presence of both a small proportion of tungsten in the carbide and tungsten in solid solution may, however, influence the rate of carbide particle growth. It may be mentioned that Vitek and Klueh [6] found only a small proportion of tungsten in the $M_{23}C_6$ phase which occurs as the dominant precipitate in Sandvik HT-9 (12Cr-1Mo-0.5W-0.27V). Koutsky and Jezek [7] detected a similar atomic proportion of molybdenum and tungsten in their experimental steels. Table 13 compares the compositions of extracts of $M_{23}C_6$ with the extracts of Steel 7 and in all instances the $M_{23}C_6$ molecule is found to contain one atom of either tungsten or molybdenum. In the higher tungsten steels of the present work there will also be a strength contribution from the Laves phase.

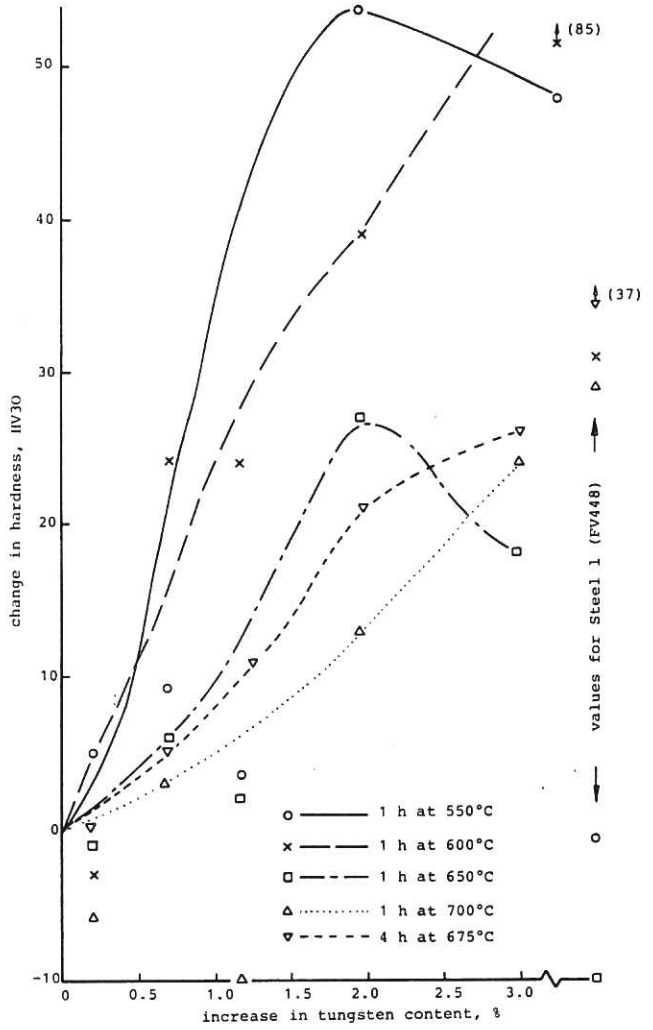


Fig. 51 Effect of increasing tungsten content on the hardness of Steels 3-7 in comparison with Steel 2.

Figure 52 illustrates the effects of an increasing vanadium concentration relative to Steel 4, which contains 0.25%V, in the same form of presentation as employed for Fig.50. This plot clearly shows that the maximum strengthening in the 0.7%W steel base is obtained with a vanadium content of about 0.5%. Furthermore, this strengthening is greatly reduced, under the conditions studied, at tempering temperatures above 600°C. As noted earlier, the effectiveness of additions of boron or nitrogen is also limited to this temperature range.

The toughness data of Table 10 indicate that precipitation in the 3%W or 0.8%V steels can impair toughness in comparison with the FV448 alloy. Thus overageing the 3%W steel at 675°C leads to a FATT increase of +40°C. The differential is smaller for the high vanadium steel at 675°C, though this

Table 13

Comparison of compositions of extracts from selected steels after hardening and tempering

origin of extract	chemical composition of experimental cast mass percent				composition of extract after quench and temper mass percent				approximate composition of $M_{23}C_6$
	C	Cr	Mo	W	Fe	Cr	W	Mo	
Ref. 7	0.27	11.8		2.12	16	54	14		$(Cr_{17}Fe_5W_1)\ C_6$
Ref. 7	0.21	11.9	0.55		17	59.5		5.7	$(Cr_{19}Fe_3Mo_1)\ C_6$
Swinden Laboratories Steel 7	0.16	11.2		3.04	25.2	63	13.9		$(Cr_{16}Fe_6W_1)\ C_6$

composition suffers a severe loss of toughness after exposure at 500°C, as shown by Fig.50.

6. CHARACTERISTICS OF THE EXPERIMENTAL STEELS IN RELATION TO THE OBJECTIVES OF THE LOW-ACTIVATION MATERIALS DEVELOPMENT PROGRAMME

Of the steels examined, none has completely met the equivalent strength, tempering characteristics or toughness of the commercial reference steel FV448. Nevertheless, the 9 and 11%Cr, 3%W, 0.25%V steels approach the target strength level in the useful tempering temperature range above 650°C, the deficiencies in proof strength for the two steels after tempering at 675°C being 60 and 90 MPa respectively. No significant deterioration in properties was found after a 500h exposure at 500°C, though this observation provides only a limited indication of the changes that might occur under actual operating conditions.

If it is accepted that the 3%W steels provide the starting point in terms of strength then the present work indicates that the major line of compositional development should aim at the achievement of a finer grain structure, closer to that of the commercial niobium-bearing material. Alternative approaches may be opened up by accepting a lower strength or by considering a relaxation of the tempering temperature requirements.

The tempering studies suggest a lower tungsten and a higher vanadium content, e.g. 2%W, 0.5%V, as an alternative strengthening combination. Such an adjustment would reduce the incidence of Laves phase precipitation but would be practicable only if lower tempering temperatures could be tolerated. Practical problems, associated with the narrow gap between anticipated service temperatures and stress relief temperatures required during fabrication, might be introduced if the tempering temperature were reduced much below 675°C. Examination of this option may be worthwhile, but at a lower priority than a more detailed investigation of the behaviour of the 3%W steels, as proposed below.

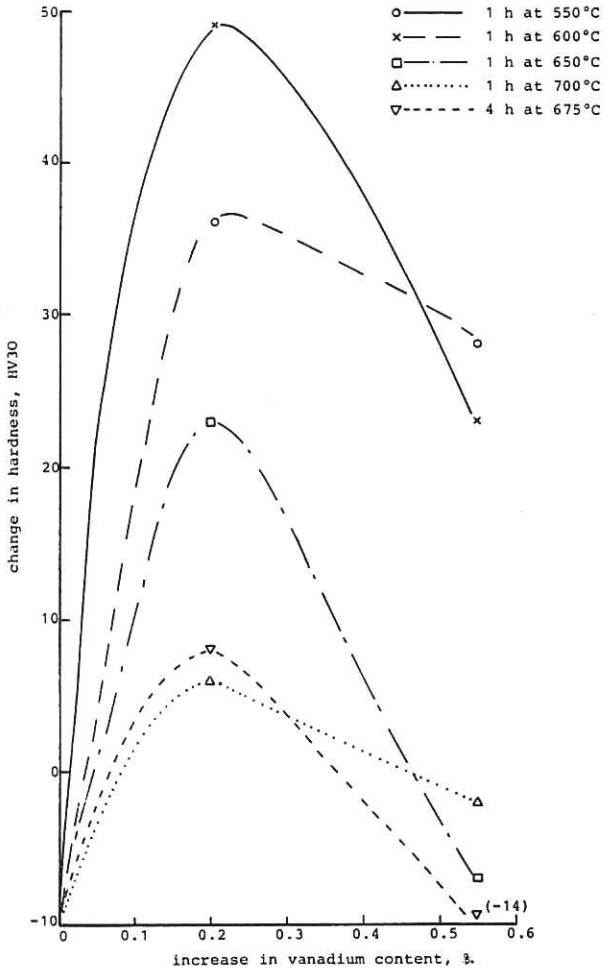


Fig. 52 Effect of increasing vanadium content on the hardness of Steels 8 and 9 in comparison with Steel 4.

7. SUMMARY OF THE PRINCIPAL FINDINGS

Examination of 13 experimental 0.15%C, 9 and 12%Cr martensitic stainless steels in which molybdenum has been replaced by additions of tungsten or increased concentrations of vanadium has shown the following:

1. The austenite grain size of an experimental 12%Cr steel corresponding to the commercial steel FV448 from which the molybdenum, nickel and niobium contents had been removed was found to be ASTM 4.5 on hardening from 1100°C. A value of ASTM 9 was found for the laboratory cast of the FV448 composition and 6.5 for commercial samples of FV448 austenitised from 1150°C. The observed grain coarsening was attributable to the absence of niobium. The elimination of the above elements did not cause any loss of hardness

on air cooling from the austenitising temperature but the tempering resistance was reduced, such that a decrease in proof stress from 860 to 740 MPa occurred for material tempered for 2h at 675°C. The impact toughness was also significantly impaired.

2. Additions of tungsten up to 3 mass percent as a replacement for molybdenum led to improved tempering resistance for 1h treatments at temperatures up to 750°C. Additions of vanadium above the 0.25% concentration already present gave no advantage for tempering temperatures above 650°C. Higher contents of boron or nitrogen were not effective in increasing the tempering resistance for temperatures above 650°C.

3. The composition giving the closest approach to the properties of the reference steel FV448 on tempering at 675°C contained 3.0% tungsten and 0.23% vanadium. Although of similar tensile strength to FV448, this steel had a proof stress 65 MPa lower and a marginally inferior impact toughness.

4. On overageing for 500h at 675°C the tungsten steel remained some 70 MPa lower in proof strength than the FV448 steel, which exhibited an appreciable increase in toughness not shown by the tungsten steel.

5. Exposure for 500h at 500°C after an initial temper for 2h at 675°C caused no major change in the strength or toughness of either the FV448 or the 3%W, V steels.

6. In all the steels the principal phase precipitated during tempering was the $M_{23}C_6$ carbide. The molecular unit of this carbide contained one atom of tungsten when formed in the 3%W steel on tempering at 675° and 700°C. The difference in toughness observed in the overaged condition between the FV448 and 3%W steels is attributed to the generally precipitated Laves phase.

7. A 9%Cr, 3%W, 0.25%V steel was found to be slightly weaker than the 11%Cr variant but contained no delta ferrite, less than 5% of the latter being present in the higher chromium steel.

8. GENERAL CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The present study indicates that the 9 and 11%Cr, 3%W, 0.25%V steels offer the closest approximation to the properties of the reference material. Aspects requiring further study include the possibility of austenite grain refinement for improvement of toughness and investigation of the longer term stability of the structures. It is suggested that future work should include the following investigations:

1. Creep testing to determine the strength, ductility and phase stability of the low-activation alloys.

2. Exploration of the potential for austenite grain refinement by additions alternative to niobium. Of the candidates, titanium is believed to be of marginal value but tantalum warrants investigation.

3. Since the fabrication of reactor components is almost certain to involve welding it is essential to confirm the phase stability of the low-activation tungsten steels under thermal cycles typical of those encountered during welding. The susceptibility to HAZ cracking may also require examination.

4. The properties obtainable from lower tungsten alloys, possibly with increased vanadium contents, may be worthy of study. Since the use of these alloys would necessitate a reduction in tempering temperature, however, such a study would be justified only if problems from Laves phase precipitation or other difficulties were experienced with the 3%W steels.

5. Further work is needed to proceed from a typical composition to the definition of a compositional range. This range must take account of changes in composition arising from transmutations during service, if the fullest potential of the recycling techniques being developed for these materials are to be realised.

REFERENCES

1. G J Butterworth, Some initial considerations on the suitability of ferritic/martensitic stainless steels as first wall and blanket materials in fusion reactors, Culham Laboratory Report CLM-R217 (1982).

2. O N Jarvis, Low-activity material: Reuse and disposal, Harwell Laboratory Report AERE-R10860 (1983).

3. K W Tupholme, J Orr, D Dulieu and G J Butterworth, A study of the prospects for development of low-activation martensitic stainless steels for first wall and blanket structures, Culham Laboratory Report CLM-R264 (1986).

4. Steels for turbine and compressor components, Firth Brown Ltd.

5. H W Kirby and R J Trueman, 12%Cr steels, creep resisting and high strength variants, BISRA/ISI Conference, Eastbourne, April 1966.

6. J M Vitek and R L Klueh, Precipitation reactions during the heat treatment of ferritic steels, Met. Trans. A 14A (1983) 1047.

7. J Koutsky and J Jezek, High temperature properties of 12%Cr steels alloyed with tungsten, molybdenum and vanadium, JISI July 1965.