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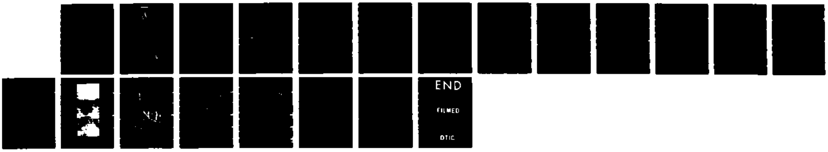

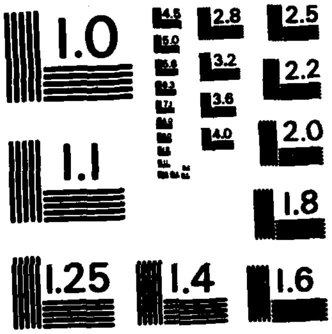

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REPORT 1/85

The Effect of Alloy Steel Design and Heat Treatment on the Mechanical Properties of $3\frac{1}{4}$ NiCrMoV Steel

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Fort Halstead
Kent.

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REPORT 1/85

The Effect of Alloy Steel Design and Heat Treatment on the Mechanical Properties of 3½ NiCrMoV Steel*

T D Andrews
R Hawkins
S R Keown**

Summary

This report describes work carried out to optimise the composition of 3½ NiCrMoV steels through a stoichiometric balance of the carbon content with the carbide-forming elements Cr, Mo and V. Reduction of the carbon content to the stoichiometric level gives a steel having a very high Charpy upper shelf energy, but the grain refining effect of the carbides is lost and the impact transition temperature increases. An optimised steel containing a slight excess of carbon has been developed that gives a better strength/toughness combination than the commercial steel.

Approved for issue:

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Head of Explosives, Pyrotechnics and Materials Group

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** Beta Metallographic Services Ltd, Sheffield

CONTENTS

1 INTRODUCTION

3½ NiCrMoV steels are ultra high strength quenched and tempered steels offering a good combination of strength, ductility and toughness (Refs 1&2) for applications such as pressure vessels and armaments. The steel composition is controlled to give a high degree of hardenability for plate sections/wall thicknesses approaching about 150mm.

Carbon content is very important because this controls the strength level (via solid solution and carbide dispersion hardening) and in addition has a significant influence on hardenability. In these steels a 'medium' carbon level of about 0.3-0.4% is used which makes the steel very difficult to weld due to the formation of brittle high carbon martensite in heat affected zones.

Chromium, molybdenum and vanadium are all carbide-forming elements influencing secondary hardening on tempering in addition to providing increased strength and hardenability by solid solution effects. It is generally considered that the alloy carbides Cr_7C_3, Mo_2C and V_4C_3 precipitate on tempering at 500°C-600°C and that at higher tempering the overaging carbides $M_{23}C_6$ and M_6C precipitate at the expense of Cr_7C_3 and Mo_2C (Ref 3). At lower tempering temperatures cementite, Fe_3C, probably containing alloying elements in solid solution as $(CrMoVFe)_3C$, is the predominant phase. Nickel and manganese increase hardenability, strength and possibly toughness by solid solution effects.

Tempered martensite is generally considered to be the best microstructure for an optimum strength/toughness combination (Ref 4). Increasing the tempering temperature generally reduces strength and increases toughness as the high dislocation density of the martensite is reduced and interstitial carbon is rejected from solid solution. Martensitic steels have two interrelated grain boundary structures. The prior austenite grain size is always retained, since martensite laths never grow across these boundaries. Within an austenite grain, 'packets' of martensite laths are formed with lath and packet size related to the prior austenite grain size (Ref 5). The austenite grain boundaries and the boundaries between packets are high angle boundaries, while within the packets, the individual laths have lower angle grain boundaries and the lath width is known to control yield strength by the well known Hall-Petch relationship (Ref 6).

Grain refinement of the prior austenite will bring about toughening and strengthening of the steels as packet sizes and lath widths respectively are correspondingly decreased. A low hardening temperature is the simplest heat treatment method for austenite grain refinement, although particle pinning of austenite grain boundaries by undissolved precipitates will give even better grain refinement (Ref 4). Rapid heat treatment cycling is also a very effective experimental procedure for grain refining these steels (Ref 7).

Empirical optimisation of the heat treatment of 3½ NiCrMoV steels has resulted in the use of low hardening temperatures (typically 860-870°C), the Ac_3 of these steels being around 800°C. With an Ac_1 temperature of about 675°C it is important to limit the tempering temperature to about 640°C, to avoid partial re-austenitisation on tempering with subsequent transformation to brittle, untempered martensite on cooling after tempering.

2 STOICHIOMETRY

It has been suggested (Ref 8) that steels achieve optimum mechanical properties when the alloy elements are present in their stoichiometric ratio with respect to the carbon content of the steel. The stoichiometic ratio of a two-element compound is simply the atomic weight ratio of the elements present. For example, the stoichiometric ratio of molybdenum carbide Mo_2C will be:

$$\frac{\text{ATOMIC WEIGHT of Mo} \times 2}{\text{ATOMIC WEIGHT of C}} = \frac{95.95 \times 2}{12.01} = 15.98$$

The Mo:C ratio is, therefore, 15.98:1 and it follows that for every 1%Mo there should be 1/15.98 (ie 0.063)%C present for potentially complete combination of molybdenum and carbon as Mo_2C.

Using this approach it is possible to analyse the 3½ NiCrMoV steel to assess whether or not the steel has sufficient carbon for combination with all the carbide-forming elements:

Element	Carbide	Stoichiometric Ratio M:C	% Carbon for 1% Alloy	% Alloy in Steel	% Carbon Required
Chromium	Cr_2C_3	16.59:1	0.060	1.0	0.060
Molybdenum	Mo_2C	15.98:1	0.063	0.6	0.038
Vanadium	V_4C_3	5.66:1	0.176	0.2	0.035
				Carbon required for stoichiometry =	0.133

With a typical 3½ NiCrMoV steel containing 0.33%C it can be seen that the steel has a large excess of carbon (approx 0.2%). If this carbon is in solid solution it will contribute to both the strength and the brittleness of the steel. However, this carbon will only be in solution in the 'as quenched' condition; on tempering it will be rejected owing to the metastability of the martensite and the low solubility of carbon in ferrite. The influence of tempering temperature on the yield strength and Charpy energy at -18°C for 5Ni ½Cr ½Mo 0.07V steels (Ref 9) with varying carbon contents (nominally 0.1,0.2 and 0.3%C) is shown in Figure 1. It can be seen that on tempering at a typical commercial tempering temperature of 630°C the effect of excess carbon on toughness is quite significant but the effect on strength is only marginal. Stoichiometric calculations for the steels shown in this Figure (due to Porter et al) are given below:

Steel	Nominal Carbon %	Actual Carbon %	Stoichiometric Carbon Required %	Excess Carbon %
A	0.1	0.10	0.074	0.026
B	0.2	0.22	0.074	0.146
C	0.3	0.27	0.074	0.196

This suggests that the carbon content of the steel can be reduced to achieve increased toughness with only a slight reduction in yield strength on tempering at 630°C.

A series of experimental 3½ NiCrMoV steels with varying carbon contents was therefore designed to test this stoichiometric concept with the aim of replacing the embrittling cementite with alloy carbides and eliminating solid solution carbon at the same time.

3 EXPERIMENTAL PROCEDURE

Three steels were manufactured to represent the normal commercial grade (C), a perfectly balanced stoichiometric steel (S), and a hyperstoichiometric composition with a small excess of carbon (H). The steels were melted in a vacuum induction melting furnace to give steel compositions and purity equivalent to those of commercial electroslag remelted material in terms of residual elements such as oxygen, phosphorus and sulphur. The steels were cast as 50kg ingots approximately 150 x 150 x 250mm and the ingots were reheated to 1150°C, drop forged and hot rolled to give plates 500 x 125 x 16mm. This gave a reduction in thickness of about 8:1 compared with about 4:1 in a typical commercial operation.

All these steels were normalised at 890°C - 4h, air cooled, hardened at 870°C - 3h, oil quenched, and tempered at 630°C - 6h, followed by oil quenching to simulate a commercial heat treatment. The stoichiometric steel, S, exhibited a rather low yield strength using this heat treatment, so a lower tempering temperature of 610°C was used to raise the yield strength for comparison with the other steels.

Tables 1 and 2 show the chemical analysis and mechanical properties of the three steels.

TABLE 1 Chemical Analysis of 3½ NiCrMoV Steels

	Analysis Weight (%)										
Steel	C	Ni	Cr	Mo	V	Mn	Si	S	P	O	N
C	0.33	3.33	1.05	0.66	0.20	0.45	0.24	0.003	0.001	0.003	0.002
S	0.12	3.35	1.07	0.64	0.20	0.45	0.21	0.003	0.001	0.004	0.002
H	0.20	3.33	1.04	0.60	0.20	0.45	0.25	0.003	0.003	0.004	0.001

TABLE 2 Mechanical Properties of 3½ NiCrMoV Steels

Steel	Tempering Temp (°C)	Hardness HV30	Tensile Properties		Impact Properties (J)			
			0.2% PS (MN/m^2)	UTS (MN/m^2)	-40 (°C)	ITT++ (°C)	USE	LSE
C	630	379	1075	1158	40	-80	55	15
S	610	375	1027	1129	42	-25	90	7
H	630	361	1048	1125	57	-60	80	9

++ Impact transition temperature taken to be 50% of the upper and lower shelf energies.

Tempering curves were also produced on samples tempered for 6h at temperatures between 500° and 700°C and these are shown in Figure 2.

The complete Charpy impact transition curves are shown in Figure 3.

Samples of all three steels were prepared for microstructural analysis by diamond polishing and etching in 2% nital. The micrographs shown in Figure 4 indicate that steel C had the finest austenite grain size and that steel S had the coarsest grain size. Hence the grain size increases with decreasing carbon content. Samples of the as quenched steels were given an 'embrittling' heat treatment of 510°C for 24h and etched in aqueous picric acid to reveal the austenite grain boundaries. This technique tends to over-estimate the grain size (since some of the smaller grains in these mixed grain microstructures are not well delineated). The average grain sizes of the three steels C,N and S were 36,47 and 70 microns respectively.

4 DISCUSSION OF RESULTS

The results demonstrate that the carbon content of 3½ NiCrMoV steels can be reduced from 0.33 to 0.12% whilst still achieving the required strength/toughness combination of $1050 MN/m^{-2}$ yield strength and 40J at -40°C Charpy impact energy. This is in agreement with predictions that the commercial 0.33% carbon steel contains carbon in excess of that necessary to give carbides of Cr Mo and V and that the effects of solid solution carbon are eliminated on tempering at the commercial tempering temperature of 630°C.

This simplistic stoichiometric approach predicts that all the embrittling cementite will have been replaced by alloy carbides at the commercial tempering temperature. However, recent electron microscope results show (Ref 10) that cementite occurs at all tempering temperatures and it appears to be stabilised by the alloying elements to make it the predominant second phase in the commercially heat treated condition. It has been shown in fact, that the Fe_3C, whilst being an almost pure iron carbide (98.8%Fe) in the as quenched steel, becomes an alloy cementite eg $(FeCrMo)_3C$ containing ~12%Cr and ~4%Mo on tempering the steel at 625°C for 10h (Ref 10).

Therefore the stoichiometric design concept appears to be at fault because of the existence of alloy cementite. However, the experiments have confirmed that 0.33% carbon is not essential and alternative explanations are required. In looking at solubility aspects and grain size effects an explanation has been reached based on the solubility and grain controlling effects of vanadium carbide.

4.1 Solubility Product of Vanadium Carbide

Alloying elements in steel influence the mechanical properties either by solid solution effects or by the formation of second phase precipitate particles. Small precipitates can be used for precipitation hardening, whilst coarser, more widely distributed precipitates can control grain size by particle pinning of grain boundaries. The amount of precipitate phase available and the volume fraction of coarse particles depend on the solubility of the precipitates in the matrix at heat treatment temperatures. This solubility can be defined in terms of the temperature-dependent solubility product in the form:

$$\mathrm{Log}[M][C] = -\frac{W}{T} + Y \qquad (1)$$

where M is metal concentration, C is carbon concentration, W and Y are constants and T is the absolute temperature (Ref 11).

Electron microscopy of commercially heat treated 3½ NiCrMoV steel (Ref 10) has shown that undissolved vanadium carbide particles always occur, and so it is interesting to consider the solubility product for vanadium carbide in austenite. The solubility product for this system has been given by Narita (Ref 12) as

$$\mathrm{Log}[V][C] = -\frac{9500}{T} + 6.72 \qquad (2)$$

This relationship is shown plotted for the hardening temperature of 870°C in Figure 5. The stoichiometric tie-line for V_4C_3 is shown with a slope of 5.66 and the compositions of all three steels are indicated with tie-lines parallel to that for V_4C_3. Steel S(0.2%V,0.12%C) lies on the 870°C solubility curve indicating that all the vanadium and carbon will be in solid solution with no undissolved carbides (electron microscopy has since confirmed this prediction (Ref 10)). Figure 5 also suggests that steels H and C should contain increasing amounts of undissolved carbides with correspondingly reducing amounts of soluble vanadium and carbon.

4.2 Impact Properties

The Charpy impact transition curve for bcc steels is shown schematically in Figure 6 with a generalised summary (Ref 13) of the factors that influence impact transition temperature (ITT) and upper shelf energy (USE). Figure 7 shows the effects of coarse undissolved V_4C_3 particles on the ITT and USE for steels C and S. The stoichiometric steel S(0.12%C) has the advantage over the commercial steel C (0.33%C) of a higher USE, but is still inferior because the loss of the grain refining effect has raised the ITT above that of steel C. The actual impact data (Fig 3) show that the slightly carbon-rich steel, H (0.20%C), achieves the best compromise with adequate grain refinement (as shown by the grain size values) to give a low ITT and fewer coarse particles to lower the shelf energy.

5 CONCLUSIONS

Experiments designed to investigate the effect of carbon content on the mechanical properties of 3½ NiCrMoV steels have shown that the carbon content can be reduced without any impairment of the tensile properties.

The carbon content was reduced initially to the stoichiometric level (0.12%C) with respect to the carbide-forming elements (Cr,Mo and V) in an attempt to eliminate harmful cementite and interstitial carbon. However, although this concept was found to be incorrect due to the unexpected formation of alloy cementite, the low carbon steels exhibited similar tensile properties but with a higher upper shelf energy.

The results are explained in terms of the solubility of vanadium carbide and the influence of coarse V_4C_3 particles on the pinning of grain boundaries and on the properties.

An optimised steel composition containing 0.20%C, which is slightly hyper-stoichiometric with respect to carbon content, was developed with the optimum balance of grain refinement and a reduced volume fraction of coarse particles. This steel is slightly better than the commercial grade and has the major advantage of improved weldability.

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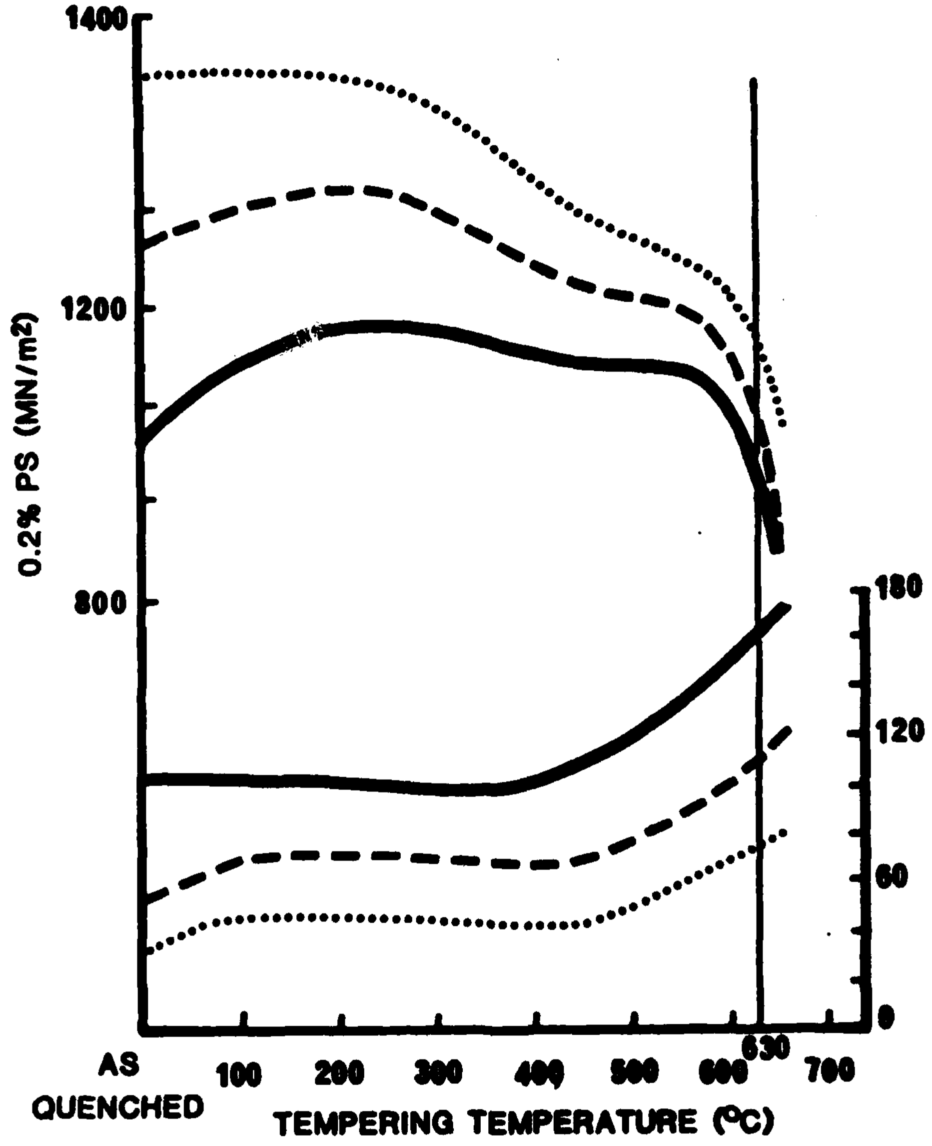


FIG. 1 EFFECT OF CARBON CONTENT ON THE TEMPERING CHARACTERISTICS OF 5 NiCrMoV STEELS (AFTER PORTER et al (9))

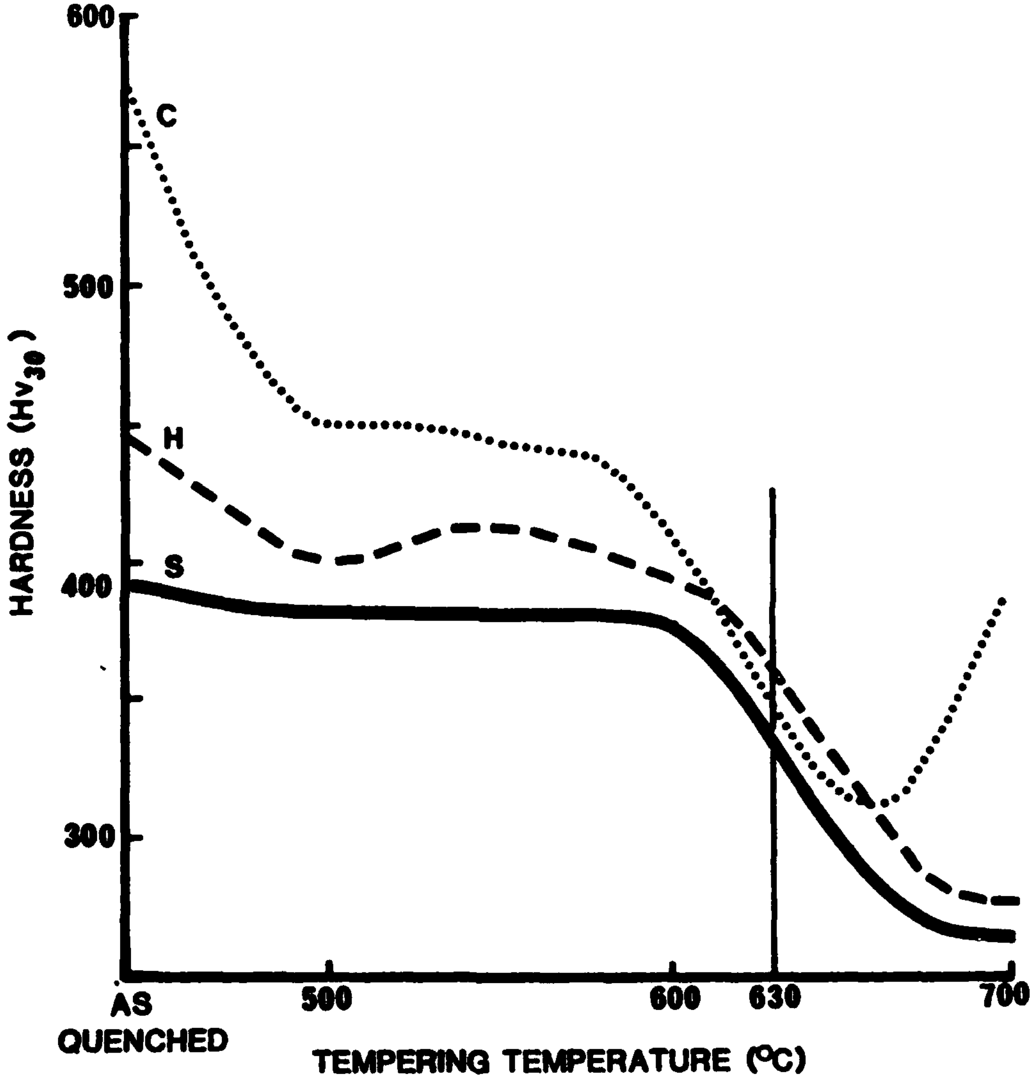


FIG.2 TEMPERING CURVES FOR STEELS C, H & S

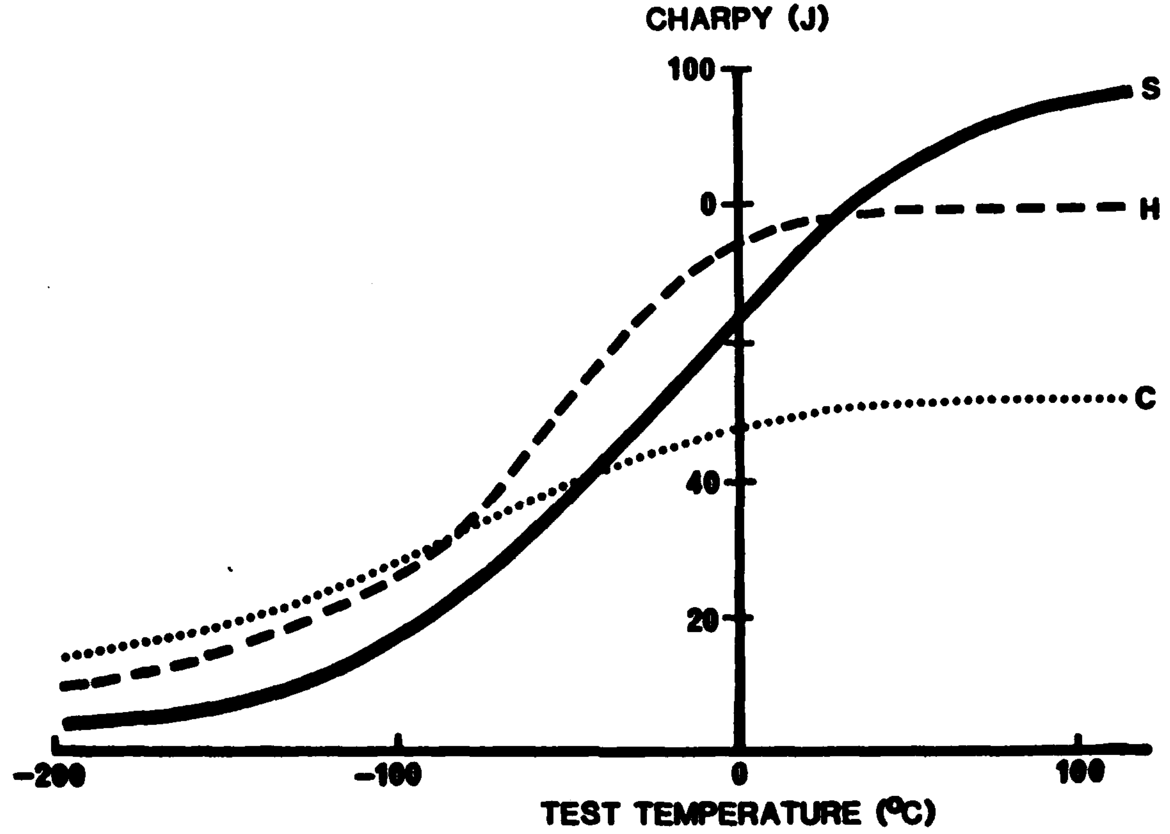


FIG.3 IMPACT TRANSITION CURVES FOR STEELS C, H & S

FIG.4

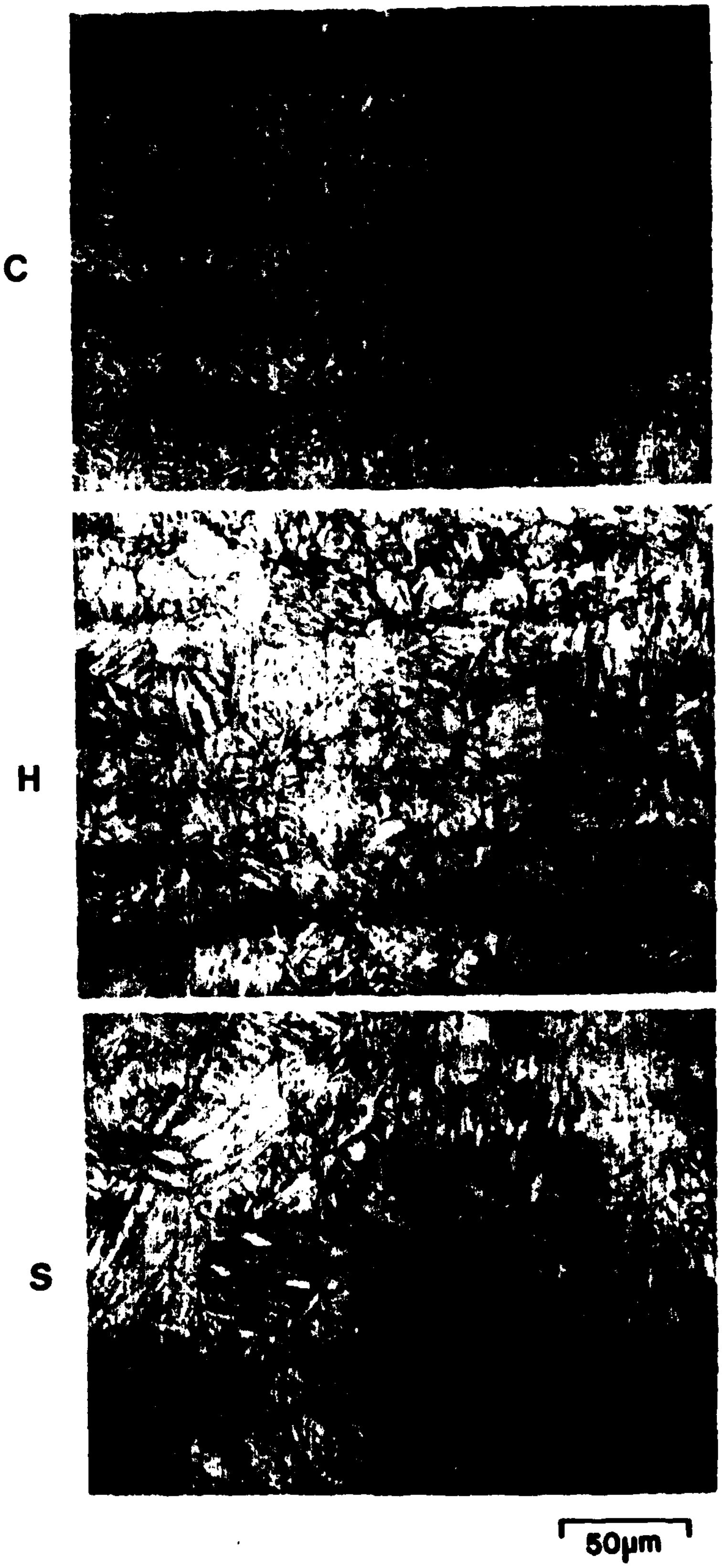


FIG.4 OPTICAL MICROGRAPHS FOR STEELS C, H & S

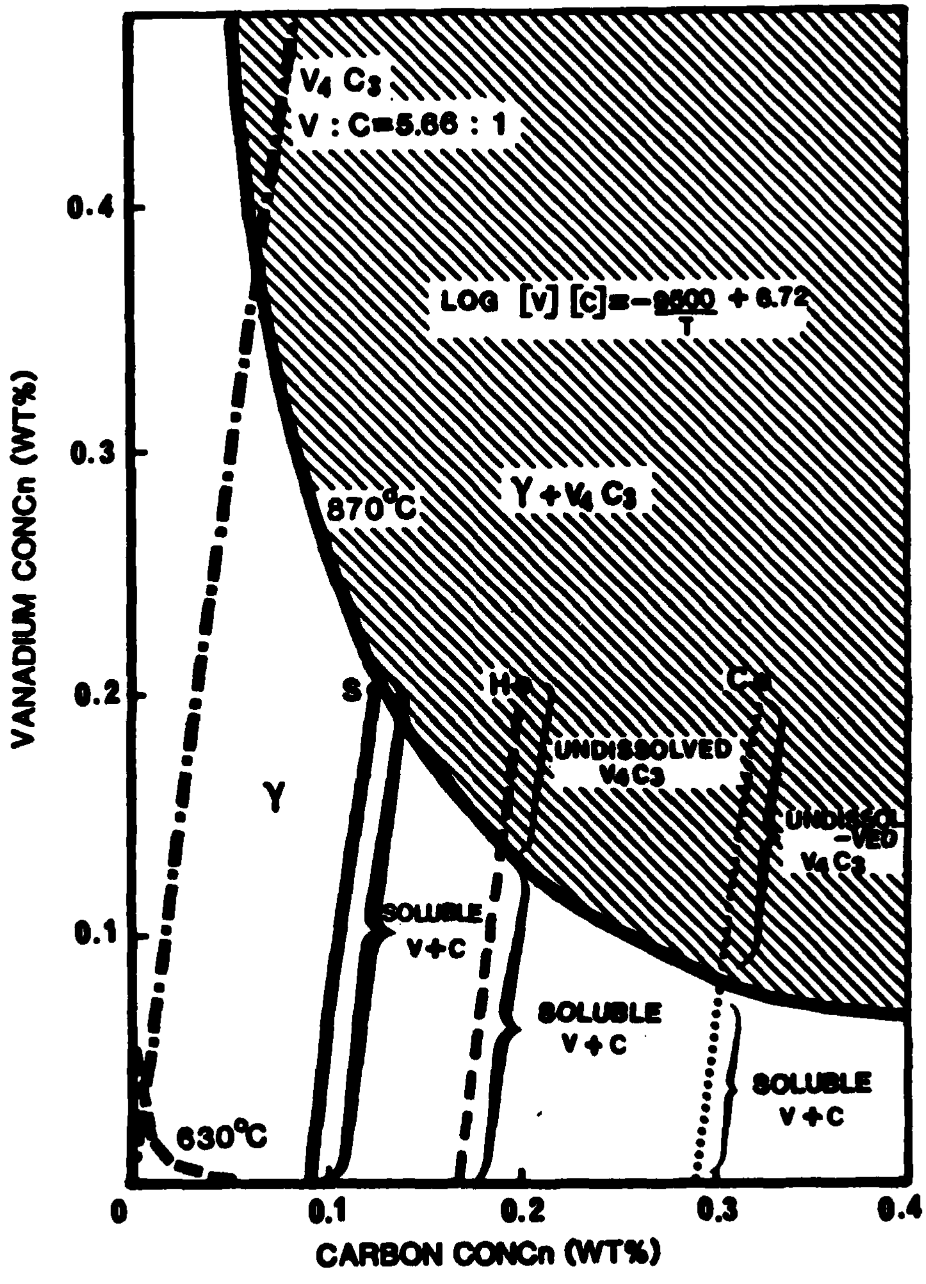
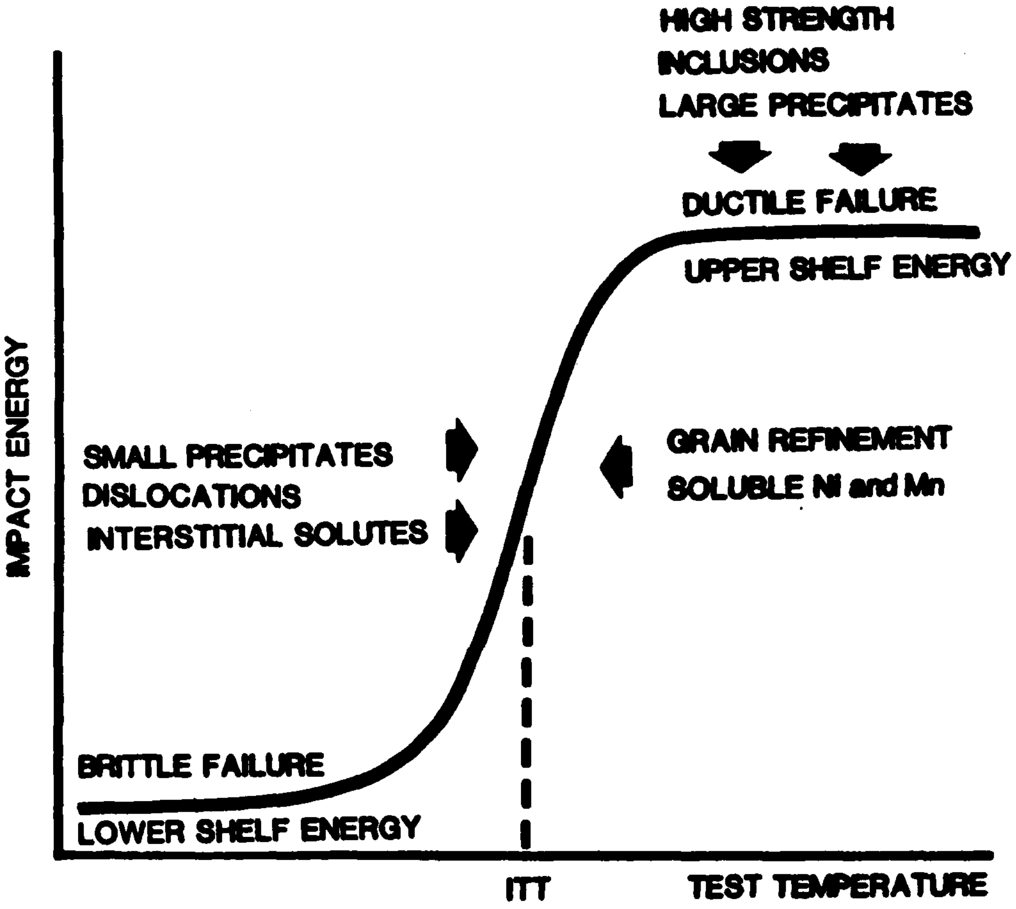


FIG.5 SOLUBILITY DATA FOR V_4C_3 IN AUSTENITE



<u>FIG.6 MICROSTRUCTURAL AND COMPOSITIONAL VARIABLES INFLUENCING THE CHARPY IMPACT TRANSITION CURVE FOR FERRITIC OR MARTENSITIC STEELS (AFTER KEOWN (13))</u>

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FIG.7

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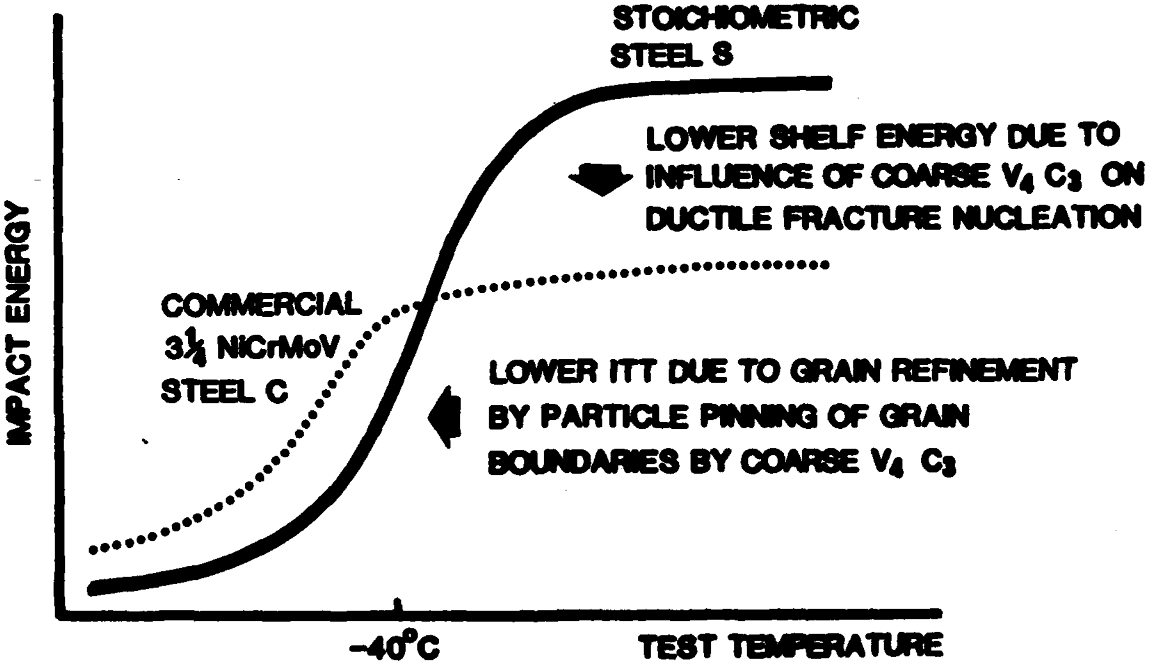

FIG.7 SCHEMATIC INFLUENCE OF COARSE VANADIUM CARBIDES ON UPPER SHELF ENERGY AND IMPACT TRANSITION TEMPERATURE

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Heat treatment	Chromium containing alloys	Carbides
Mechanical properties	Molybdenum containing alloys	

Abstract This report describes work carried out to optimise the composition of 3½ NiCrMoV steels through a stoichiometric balance of the carbon content with the carbide-forming elements Cr, Mo and V. Reduction of the carbon content to the stoichiometric level gives a steel having a very high Charpy upper shelf energy, but the grain refining effect of the carbides is lost and the impact transition temperature increases. An optimised steel containing a slight excess of carbon has been developed that gives a better strength/toughness combination than the commercial steel.

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