

The effect of vanadium on the reversible temper-embrittlement behaviour of low-alloy chromium and chromium-nickel steels

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SYNOPSIS

The effect of vanadium on the susceptibilities of chromium and chromium-nickel steels to reversible temper embrittlement was evaluated. The steels investigated were approximately equivalent to steels of BS 970 Grade 708A42 and BS 970 Grade 817M40, the major difference being that molybdenum had been replaced by vanadium in various concentrations.

It was found that the vanadium had a detrimental effect and, in all the concentrations tested, enhanced the susceptibility to reversible temper embrittlement of both the chromium and the chromium-nickel steel. The detrimental role played by vanadium in reversible temper embrittlement is explained by a consideration of the effect of vanadium carbide, as well as of free vanadium, in solid solution in ferrite.

SAMEVATTING

'n Ondersoek is gedoen om die effek van vanadium op die vatbaarheid vir omkeerbare temperbroshheid van beide chroom- en chroom-nikkel stalle te bepaal. Die staalsamestellings wat ondersoek is, kom ooreen met BS 970 Graad 708A42 en BS 970 Graad 817M40 staaltipes, maar met die verskil dat die molibdeen deur verskillende hoeveelhede vanadium vervang is.

Dit is bevind dat vanadium die vatbaarheid vir omkeerbare temperbroshheid in beide chroom- en chroom-nikkel stalle aanhelp. Die effek van vanadium op omkeerbare temperbroshheid word verklaar met behulp van 'n hipotese wat beide die effek van vanadiumkarbiede asook vanadium in oplossing in ferriet inkorporeer.

Introduction

Reversible temper embrittlement is a phenomenon that affects all alloy steels by causing brittle failures. This embrittlement, which is characterized by an increase in ductile-brittle transition temperature or fracture-appearance transition temperature (FATT) and by a tendency to intergranular fracture along prior austenite boundaries, occurs primarily during exposure in the temperature range 325 to 575°C. The transition temperature of commercial-purity steels can increase from -100°C to greater than 100°C, while specially prepared laboratory alloys can be made to fail in a brittle mode at temperatures as high as 500 to 600°C.

Heating for short times above 600°C will cause the FATT of an embrittled alloy to fall to its non-embrittled value (de-embrittling). In addition, the mode of brittle failure will change from intercrystalline to transcrystalline cleavage.

Since the term *reversible temper embrittlement* (RTE) was first coined by Dickenson in 1917¹, a great deal of work has been done on this intriguing problem. It is well known that some or all of the impurity elements phosphorus, tin, antimony, and arsenic have to be present in a steel before RTE can occur¹⁻³. In addition to these four embrittling impurities normally causing RTE, ger-

manium, bismuth, selenium, and tellurium have been reported as being capable of causing RTE⁴⁻⁶. The effects of alloying elements frequently used in steels are also well known: chromium, nickel, manganese, silicon, and carbon enhance RTE^{1-3,6-11}, while molybdenum, titanium, wolfram (tungsten), and lanthanum retard it^{1,2,7,8,11,12}.

RTE is a complex metallurgical phenomenon, and no single mechanism has yet been devised to explain all its manifestations. However, all the recent models appear to rely on segregation of the elements in solution to the grain boundaries, and the interaction of these elements with carbides. The mechanisms proposed involve equilibrium segregation^{1,13-15}, non-equilibrium segregation⁷, and pinning of dislocations by carbide and nitride particles¹⁶.

Ohtani *et al.*¹⁷ have postulated that RTE can be prevented by stabilization of the carbides through alloying additions of titanium, molybdenum, and vanadium. The beneficial effect of molybdenum is well known^{19,20}, while that of titanium was proved by Ohtani *et al.*¹⁸.

No clear picture of the effect of vanadium and its carbides on RTE has yet emerged, and some controversy is to be found in the literature. Powers has shown that vanadium enhances the beneficial effects of molybdenum, and Comon *et al.* have indicated that additions of vanadium are very beneficial². However, it has also been reported that vanadium, in all the concentrations tested, enhances RTE¹.

Ustinovshchikov²¹ postulated that, if vanadium can be kept in solution, RTE will be retarded but, if vanadium

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TABLE I
CHEMICAL ANALYSES OF THE EXPERIMENTAL ALLOYS

Experimental Procedures

A commercial steel, BS 970 Grade 530A40 (EN18D), was used as feed material for this investigation. The steel was melted in a vacuum-induction furnace under an argon atmosphere, and was modified with alloying elements to produce the experimental melts. The analyses of these alloys are given in Table I. It is evident that the experimental alloys are basically of the BS 970 Grade 708A42 (EN19C) and BS 970 Grade 817M40 (EN24) types, the major difference being that vanadium replaces molybdenum in varying amounts.

After being melted, the samples were cast into 15 kg ingots and hot-rolled to slabs 12 mm thick. Charpy specimens, without notches, were machined with the long axes parallel to the rolling direction of the slabs. The notches were machined, subsequent to the final heat treatment, in the short transverse direction of the slab.

For complete dissolution of vanadium carbides, Collins²⁴ suggested an austenitizing treatment of 1250°C for at least 30 minutes. The first step of the experimental heat-treatment cycle, shown in Fig. 1, was accordingly designed to completely dissolve vanadium carbide and ensure a fully martensitic structure upon oil quenching. However, this treatment yields a very large austenite grain size, and a subsequent grain-refining austenitizing treatment was given at 1250°C for 1 minute. The final austenite grain size ranged between 4 and 5 ASTM, which was adequate for the purpose of this investigation.

So that the RTE behaviour of the experimental steels could be evaluated, a two-stage tempering procedure was followed as suggested by Taran²⁵. The samples were first stabilized at a tempering temperature well above the em-

tempered to the same hardness during the stabilizing tempering cycle. Table II summarizes the tempering temperatures that were required for the various samples to attain a final hardness of approximately 325 Vickers.

TABLE II
TEMPERING TEMPERATURES USED TO GIVE A FINAL HARDNESS OF 325 VICKERS

Sample number	Tempering temperature, °C
K1	644
V1	676
V2	678
V3	692
K2	630
2V1	674
2V2	685
2V3	698

An embrittling temperature of 510°C was chosen because this temperature falls within the range at which a maximum rate of embrittlement can be expected²⁶. The embrittling times ranged from 0 to 192 hours, as indicated in Fig. 1.

In an assessment of the susceptibility of the experimental steels to RTE, a change in fracture-appearance transition temperature ($\Delta FATT$) was used as the measure. These temperatures were determined by measurement of the percentage brittle fracture of the fractured surfaces after impact testing of the Charpy specimens. A ductile

TABLE III
FATT OF LOW-ALLOY CHROMIUM AND CHROMIUM-NICKEL STEELS
IN UNEMBRITTLED CONDITION

Sample number	Ni %	V %	FATT, °C
K1	0,13	0,05	-33
V1	0,18	0,20	-36
V2	0,14	0,28	-33
V3	0,15	0,40	-38
K2	1,50	0,05	-53
2V1	1,53	0,21	-58

nickel to the experimental steels in the unembrittled condition decreased the FATT significantly. Additions of vanadium, on the other hand, had no adverse effect on the FATT for both the chromium and the chromium-nickel steel.

The effect of vanadium and embrittling time on the RTE susceptibility of the chromium and chromium-nickel steels under discussion are shown in Figs. 2 and 3 respectively, where the susceptibility to RTE is compared by means of the Δ FATT.

From the positive Δ FATT values with embrittling time (Fig. 2), it is clear that all the experimental steels containing 1 per cent chromium exhibited a susceptibility to RTE. It is interesting to note that, for the embrittling times used in this study, the steels containing 1 per cent chromium exhibited the greatest susceptibility to RTE at an embrittlement time of 48 hours. At longer times, the recuperative tendency is apparent for all the samples. This diminishing susceptibility to RTE at long embrittling times has also been reported by others^{4,18,27,28}, but with

the marked difference that these authors found the turning point to be at times in excess of 100 hours.

The diminution in Δ FATT values after embrittlement of the low-alloy chromium steels for 48 hours cannot be attributed to any changes in hardness during aging of the samples. In order to prove this conclusion, hardness measurements were made on all the samples before and after embrittlement, but no change was detected. Also, the diminishing susceptibility to RTE cannot be attributed to the effect of vanadium, since the control sample, K1, exhibited the same tendency. Takayama *et al.*²⁸ proposed that this effect may rather be due to non-equilibrium in the structure.

It appears from the results portrayed in Figs. 2 and 3 that vanadium affects the susceptibility to RTE differently for the chromium steel than for the chromium-nickel steel. In the chromium steel, an increase in the vanadium content increased the susceptibility to RTE. Although an increase in susceptibility to RTE was found for the chromium-nickel steel when small amounts of vanadium were added, a further increase in the vanadium content resulted in a minimal increase in Δ FATT. This difference was more pronounced at longer embrittling times.

Fig. 4 gives an even better indication of the effect of vanadium on the susceptibilities to RTE of the two steels after various embrittling times. It is quite clear that the susceptibility to RTE was increased by the addition of vanadium to the chromium steel, as well as to the chromium-nickel steel. However, the mechanism by which vanadium increased the susceptibility to RTE was different for the two types of steel. A gradual increase in susceptibility with increasing vanadium content was

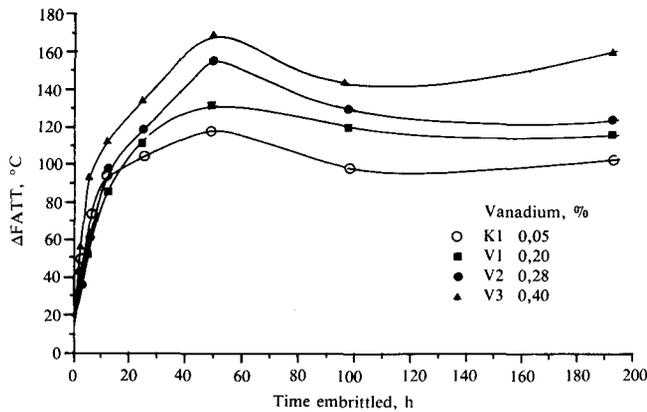


Fig. 2— Δ FATT as a function of time of embrittlement for steel containing 1 per cent chromium

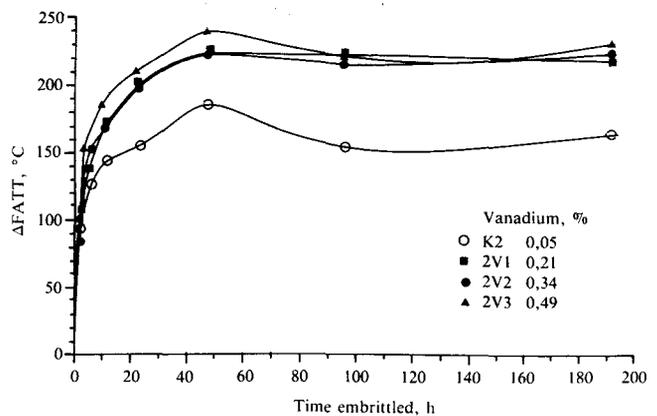


Fig. 3— Δ FATT as a function of time of embrittlement for the steels containing 1 per cent chromium and 1,5 per cent nickel

experienced by the chromium steel over the entire range of vanadium contents investigated. However, for the chromium–nickel steel, a sharp initial increase in susceptibility was observed at vanadium contents up to 0,2 per cent, while only a limited further increase was experienced with further vanadium additions. After 48 hours of aging (the time after which embrittlement was most severe), the samples containing 0,2 per cent vanadium showed an increase of 25°C in $\Delta FATT$ in the chromium steel, and 37°C in the chromium–nickel steel. With a vanadium content of 0,4 per cent, the $\Delta FATT$ of the chromium steel increased by 51°C, while that of the chromium–nickel steel increased by 41°C.

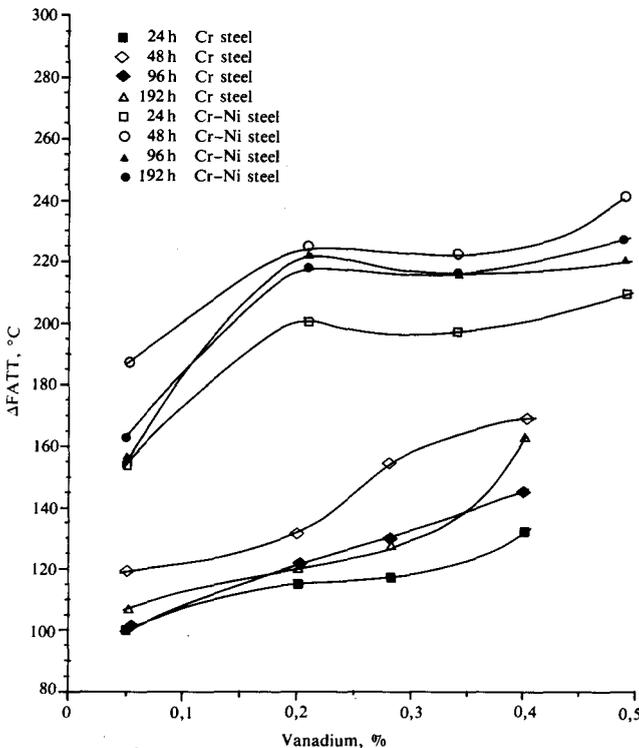


Fig. 4—Effect of vanadium and aging time on the $\Delta FATT$ of chromium and chromium–nickel steels

As to the mechanistic effect of vanadium and aging time on the RTE susceptibilities of the steels under discussion, the co-existence of vanadium carbide and free vanadium in the structure of the steel can be considered in a speculative hypothesis.

On the initial tempering of the chromium steel, carbides (which include vanadium carbides) were precipitated on the grain boundaries and within the matrix. After an embrittling treatment, these carbides had a deleterious effect on RTE, as a result of the presence of impurity elements at the carbide–matrix interfaces, which resulted in an accumulation of impurity elements ahead of the growing carbides^{5,17}. Vanadium carbides, with their very low coarsening rate, might have immobilized dislocations and had a detrimental effect on RTE¹⁶. Thus, with an increase in vanadium content, more vanadium carbides were precipitated and the susceptibility to RTE was increased further. It is well known that chromium, nickel, manganese, silicon, and carbon enhance RTE^{1–3,6,7} by segregating to the grain boundaries^{1,5,13,15}. With the pre-

sence of free vanadium in the steel, the vanadium might also have segregated to grain boundaries to have an additive or synergistic effect with these elements in increasing the susceptibility to RTE.

An increase in the vanadium content of chromium–nickel steel is expected to have the same outcome on the carbides. However, the effect of free vanadium in solution may be different.

In order to explain the beneficial effect of titanium on RTE of low-carbon chromium–nickel steel doped with antimony, Ohtani *et al.*¹⁸ concluded that a benign nickel–titanium interaction occurs on the grain boundaries, partly supplanting the nickel–antimony attraction, which leads to embrittlement. In the same manner, free vanadium may also associate with nickel at the grain boundaries. Thus, the deleterious effect of nickel on RTE is cancelled, and a balancing effect is achieved to partially offset the negative effect of vanadium carbides on RTE. The initial sharp increase in $\Delta FATT$ of the chromium–nickel steels, shown in Fig. 4, can be attributed to the effect of the carbides on RTE. With increasing vanadium contents, more free vanadium will be available for interaction with nickel, and the increasing susceptibility to RTE with increasing vanadium content will be cancelled. This is in contrast to the chromium steels, in which vanadium interacts with the other alloying elements to enhance RTE.

Conclusions

- Vanadium has a deleterious effect on the susceptibility of low-alloy chromium and chromium–nickel steels to RTE. With increasing vanadium contents, the susceptibility to RTE increases for chromium steels, while a benign nickel–vanadium interaction may occur in chromium–nickel steels with vanadium additions of more than 0,2 per cent. The overall susceptibility to RTE is greater for chromium–nickel steels than for chromium steels.
- Both the chromium and chromium–nickel steels examined displayed maximum susceptibility to RTE after 48 hours of embrittlement. At longer embrittling times, lower $\Delta FATT$ s were observed.
- The mechanism by which vanadium affects RTE is complex and needs further investigation. There is a possibility that vanadium affects RTE through free vanadium in solution as well as through vanadium carbide. It also appears that a benign nickel–vanadium interaction occurs to partly supplant the attraction exerted by nickel impurity elements that leads to embrittlement.

Acknowledgements

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Corrigenda: December paper

The following amendments should be made to the paper by D.D. Marsden entitled 'The current limited impact of Witwatersrand gold-mine residues on water pollution in the Vaal River system', which appeared in the December 1986 issue.

On page 497, the references mentioned below should be 18 (official sources), and not 17 (Mrost and Lloyd):

Left-hand column, line 29

Right-hand column, line 14.

Steel rolling

The 4th International Steel Rolling Conference will be held in Deauville (France) from 1st to 3rd June, 1987. The theme of the Conference is 'A new outlook', and the languages are French, English, and German.

The following topics will be discussed:

- Cold Rolling
 - Roll gap modelling, chatter, tandem-mill set-up
 - Flatness criterion
 - Flatness measurement and control
 - Endless rolling and processing
 - Surface phenomena
- Hot Strip Mill
 - Metallurgical and thermal optimization
 - Roughing mill operation
 - Looper operation
 - Thickness, profile, and flatness control of the finisher
- Surface Phenomena in Hot Rolling
- Plate Mill
 - New developments
 - Optimum computer control

- Plate Mill/Hot Strip Mill
 - Roll force prediction
 - Metallurgical optimization of the cooling conditions
- New Technologies for Hot and Cold Rolling
- Hot Levelling of Plates
- Cold Rolling and Cluster Mill Operation
- Pickling, Surface Cleanliness, Automatic Inspection and Measurement
- Application of Advanced Computing Methods to the Rolling Theory
- Flow Stress Determination for Hot and Cold Rolling

Enquiries should be directed to

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ASEAN mining

A committee consisting of representatives from mining associations in the ASEAN region has been formed to organize the First Asia/Pacific Mining Conference and Exhibition. The Committee is chaired by Henry A. Brimo, President of The Chamber of Mines of The Philippines, with Rachan Kanjana-Vanit, President of the Mining Industry Council of Thailand, as co-chairman. Other officers include Achmad Prijono, President of the Indonesian Mining Association, and Ibrahim Menudin, President of the States of Malaya Chamber of Mines, who serve as Vice-Chairman of the eight-man committee.

The Asian/Pacific Mining Conference and Exhibition was conceived as part of the activity of AFMA (Asean Federation of Mining Associations) in the region and is to be held in Bangkok from 24th to 27th February, 1988. Its objective is to establish a long-range programme to monitor the changes in the industry and to facilitate the harmonious promotion and development of the mineral wealth of the region with a view to optimizing the contribution of minerals to economic development. Apart from that, the event creates a forum at which mining professionals and businessmen in the region have the opportunity to meet and exchange information, and to promote closer ties and cooperation with the world mining com-

munity. A brisk amount of business is also expected to be conducted at the accompanying trade exhibition of mining equipment.

The Conference, with its selected theme of 'Mineral and the Economic Development of the Asia/Pacific Region', will cover the full range of issues, both technical and non-technical, related to the development of metals, industrial minerals, and solid fuels in the Asia/Pacific. It is expected to draw hundreds of mining engineers, geologists, and others who are directly associated with mineral development from this region and other parts of the world. The organizers also expect that executives involved in mining finance and mineral trading, as well as government officials, will attend, since many of the topics covered will be of special interest to these groups.

For more information or details, please contact

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