V-Technology

A Vanitec Report on Technical Papers & Publications

Issue - July 2017

Vanitec Limited
Hildenbrook House
The Slade
Tonbridge
Kent
TN9 1HR
UK

Tel: +44 (0)1732 240121
E-mail: info@vanitec.org
website: www.vanitec.org

Vanitec is a technical and scientific committee, which brings together representatives of companies and organisations involved in the mining, processing, manufacture, research and use of vanadium and vanadium-containing products.

Vanitec establishes, collects and makes available information on vanadium, its use, availability, new scientific and technical developments and trends in its application. The object of V-Technology is to provide up to date information and to initiate discussion through the medium of short articles on subjects to the use of vanadium.

2016 Vanadium Award

The Institute of Materials, Minerals and Mining (IOM3) presented the 2016 Vanadium Award on 11th July 2017 to B. Hutchinson, D. Martin, O. Karlsson, F. Lindberg & H. Thoors of SwereaKIMAB, Sweden and R. K. W. Marceau & A. S. Taylor of Deakin University, Australia for their outstanding paper "Vanadium Microalloying for Ultra-high Strength Steel Sheet Treated by Hot-dip Metallising", which was published on the Materials Science and Technology, 4 October 2016. This work demonstrated that vanadium, especially when in combination with a raised nitrogen content, helps to resist the effect of tempering so that a larger proportion of the initial strengthening is preserved in the ultra-high strength martensitic steels after the galvanising cycle, resulting in tensile strength levels exceeding 1000MPa.

The strong demand for weight reduction in vehicle construction and building materials has led to adopt steels with ever higher strength levels to save energy and limit CO2 emissions. The ultimate microstructure for maximising strength is fully martensitic low carbon steel and these steels also possess remarkably good local formability (bending and hole expansion) due to homogeneity and uniformity of the martensite microstructure. For many applications, especially in vehicles it is necessary to apply an anti-corrosive coating. This raises a problem as hot dip galvanising or galvannealing of martensitic steels necessarily involves tempering and loss of strength for the virgin martensite. A possible solution is to develop steels that are resistant to softening so that conventional hot-dip galvanising can be employed. The effect of different alloy elements has been extensively studied in engineering steels with respect to temper-resistance and the occurrence of secondary hardening. One such element that is known to be most effective in this regard is vanadium. For this reason, vanadium was chosen in their study to investigate its influence, especially when in combination with nitrogen, on improving the strength hardened martensitic steel sheets after it is subjected to hot-dip metallising processes.

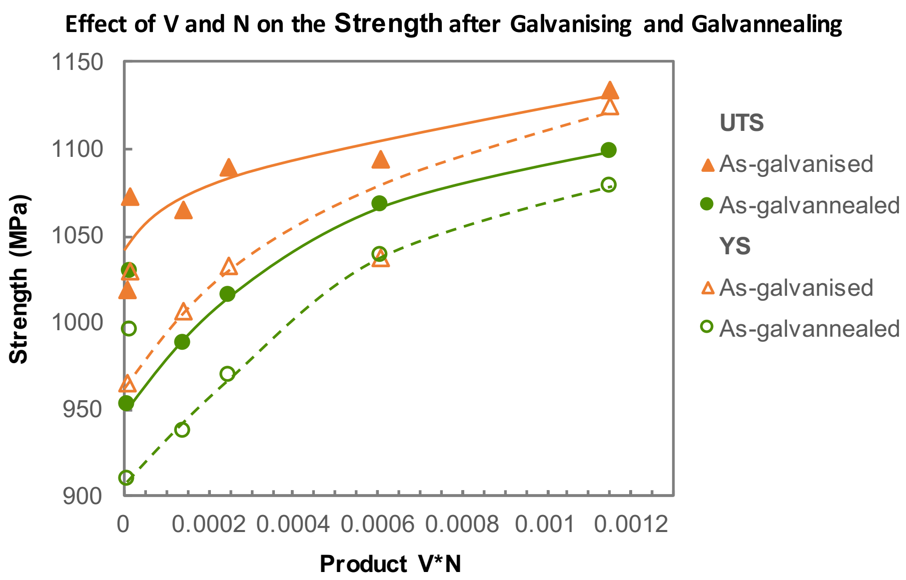

Fig. 1 Yield strength and tensile strength of the steels as a function of the product of vanadium and nitrogen contents

A series of nine steels with base composition of 0.2%C, 1.2%Mn and 0.4%Cr and different contents of vanadium (0–0.1%) and nitrogen (0.002–0.012%) were designed in this study. The steels were first hot rolled to 4 mm thickness, finishing around 900°C and air cooled. After removal of the scale, the sheets were cold rolled to 1.1 mm. Heat treatment for hardening the steels was carried out at 900°C for 3 minutes followed by quenching into cold water. A total annealing time of 5 minutes at 460°C in a salt bath was adopted to simulate Hot dip galvanising and a further heat treatment of 550°C for 15 seconds in a salt bath was used to simulate the galvannealing.

The study showed that in the as-quenched condition the yield strength and tensile strength vary very little with the compositions. The 5 mins annealing at 460°C reduced the strength and the additional treatment of 15s at 550°C led to further reductions in both yield and tensile strength. However, the tensile strength and, especially, the yield strength are seen in figure 1 to rise with increase of the vanadium and nitrogen contents after both the simulated galvanising and galvannealing treatments, despite the strengths being virtually constant in the as-quenched condition. These results point to a potentially useful role of vanadium in ultra-high strength martensitic steels that require galvanising and also show that a raised nitrogen content plays a synergistic role together with vanadium. According to some steel specifications [1] there is a critical requirement for advanced high strength steels with the tensile strength to exceed 980 MPa which can be reliably achieved with this V-N microalloying.

Various metallographic techniques including Scanning Electron Microscope (SEM), Electron Backscatter Diffraction (EBSD), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS), Atom Probe Tomography (APT) were used in order to understand the mechanism by which vanadium together with nitrogen resists the loss of strength in these steels during the galvanising and galvannealing. The reasons(s) why alloying with vanadium improves strength under these conditions is still not fully established.

[1] Bhattacharya D., "Developments in advanced high strength steels", The Joint International Conference of HSLA Steels, 2005, pp. 70-73.

Recent Vanadium Related Publications Review

Vanadium Microalloying Improves Properties of Ultra-high Strength Dual Phase Automotive Steel

Ferrite-martensite Dual Phase (DP) steels are the most widely used advanced high-strength steels (AHSS) in automotive market to achieve lower fuel consumption and better crashworthiness. DP steels possess outstanding mechanical properties, having a low yield ratio as well as a large work-hardening coefficient and large elongation. However, DP steels suffer from poor cut edge sensitivity and stretch flange formability. The latter is an important property of high strength steel sheets for press-forming and typically measured by the hole expansion test as the Hole Expansion Ratio (HER), which is known to correspond well to the local ductility. HER of high strength steels generally decreases as the tensile strength increases, however, HER of DP steels is more strongly dependent on the microstructure due to the presence of multiple phases and strength differential between phases. It is shown [2-3] that HER decreases with increasing martensite hardness and martensite/ferrite hardness ratio for DP steels, attributing this finding to greater strain partitioning to the ferrite during plastic deformation, which resulted in interface incompatibility and decohesion at ferrite-martensite interfaces.

Some recent developments in DP steels have focused on trying to improve stretch flange formability by modifying the strain partitioning between ferrite and martensite phases either by microstructure refinement or by selective strengthening of the ferrite phase using precipitation hardening. Vanadium addition to DP steels has been shown to improve the post uniform elongation as well as increased the strength due to precipitation strengthening of ferrite by nano-sized VC particles [4]. A paper "Properties of Ultra-fine Grained V-microalloyed Dual Phase Steels" by C. P. Scott, et al. presented at the International Symposium on New Developments in Advanced High-Strength Sheet Steels in May 2017 demonstrated that vanadium addition strongly refines the DP microstructure and ferrite is strengthened by grain refinement and selectively VC precipitation strengthening. The mechanical properties of the vanadium microalloyed DP steel are excellent (YS~600 MPa, UTS>1200 MPa, UE 8-10%) and are much less sensitive to the martensite fraction compared to the vanadium-free DP steel.

Two steels (Ref and Ref+V) were designed to study the effect of vanadium microalloying on the microstructure and properties of the ultra-high strength dual phase steel and the compositions are shown in Table 1. The Ref steel was designed to be equivalent to a standard

Table 1 Chemical composition of the steels (wt.%)

Steel	C	Si	Mn	V	N	Mo	Cr	Cu
Ref	0.186	0.19	1.59	0.003	0.008	0.01	0.03	0.011
Ref+V	0.182	0.19	1.65	0.140	0.008	0.01	0.03	0.019

DP1180 grade but with a lower martensite fraction (30%). The Ref+V steel has the same base chemistry with the addition of 0.14 wt.%V.

The steels were hot rolled to a final thickness of 3 mm on the CanmetMATERIALS laboratory (CMAT) pilot rolling mill and several sets of rolling and coiling parameters were explored. The hot strips were cold rolled from 3 mm to 1 mm (66% reduction) using the CMAT pilot mill. Large area sheet annealing was done in specially adapted furnace and the sheets were directly quenched after annealing.

Thermodynamic modelling and physical simulation (dilatometry) were done to determine the optimum intercritical annealing temperature. Various annealing time/temperature combinations were carried out and the resulting DP sheets were characterised by optical microscopy, SEM/EBSD, TEM, EDX and EELS techniques. The mechanical properties of the cold strips were investigated in the as-quenched state by tensile and hole expansion testing.

This study demonstrated that vanadium addition strongly refines the DP microstructure as shown in figures 2a and 2b, which are optical micrographs of the Ref and Ref+V steels annealed at 750^{0}C for 120 s and 180 s respectively. The average ferrite grain size is 4 µm in the Ref steel and 1.6 µm in the Ref+V steel.

After cold rolling and intercritical annealing at 750^{0}C, intense fine V(C,N) precipitates were observed in the ferrite phase whereas precipitates were scarce and much coarser in martensite in the Ref+V steel. Figure 3a shows a STEM bright field image of a direct replica extracted from the Ref+V steel annealed at 750^{0}C/180 s and die quenched. The darker (thicker) regions of the replica show the martensite phase, and the lighter (thinner) regions indicate ferrite. The EDX map in figure 3b confirms that the precipitates are vanadium precipitates (red) and that they are very heavily (but not exclusively) concentrated in ferrite.

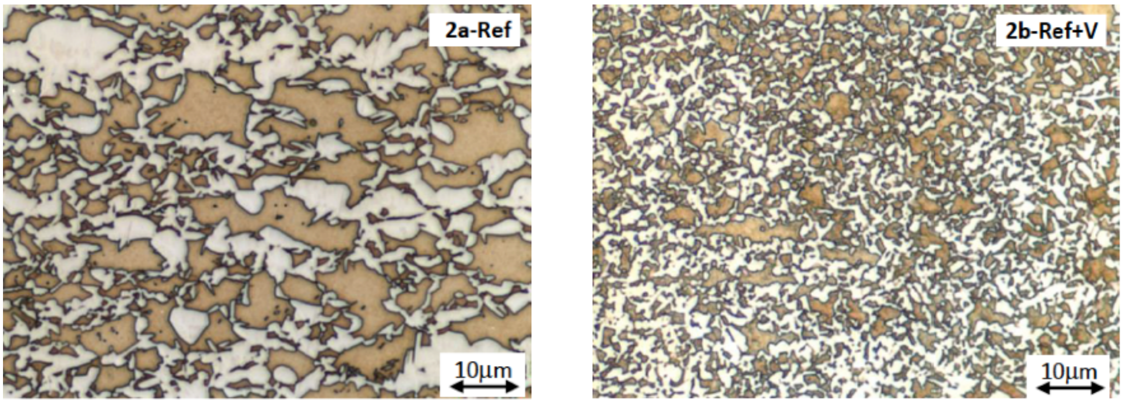

Fig. 2 a) Lepera etch of the Ref steel annealed at 750^{0}C/120s. b) Lepera etch of the Ref+V steel annealed at 750^{0}C/180s. (martensite is white and ferrite is brown)

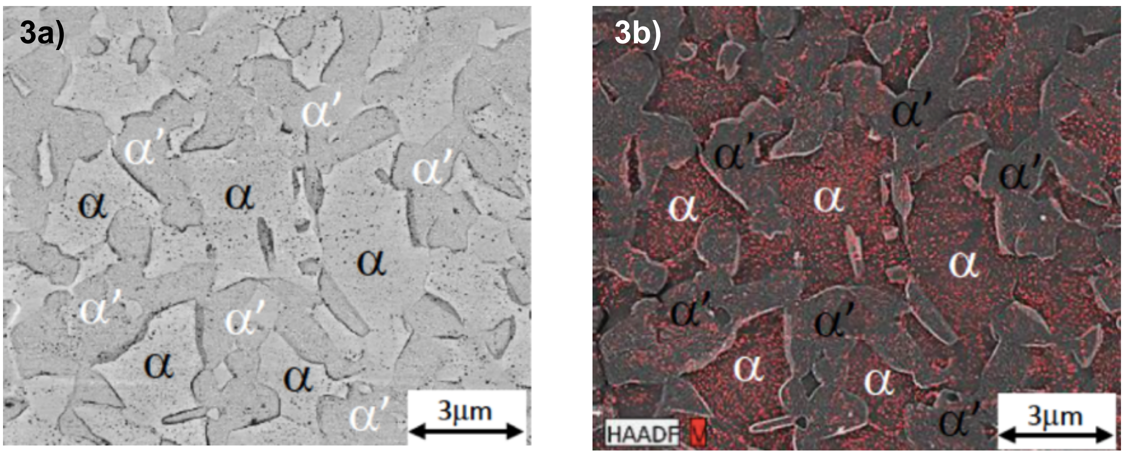

Fig 3 a) BF STEM image of a direct extraction replica (Ref+V steel annealed at 750^{0}C / 180 s and die quenched). b) EDX chemical map superimposed on the HAADF image of figure 3a) (note reversed contrast) showing the localisation of V precipitates (red) in ferrite.

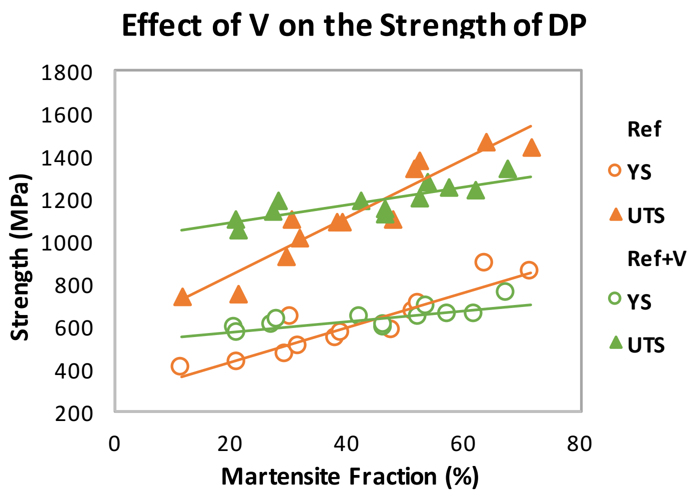

Fig. 4 Relationship between martensite fraction and the strength

The vanadium addition also completely changes the mechanical behaviour of the DP steel. The YS, UTS and work hardening rate of the Ref+V steel are higher at low martensite fractions (<45%) and lower at high martensite fractions, as shown in figure 4. It is suggested that the lower sensitivity of the tensile properties of the V added steel to martensite fraction is mainly due to grain refinement and selective strengthening of the ferrite phase, and also to martensite softening. This unique property implies that for the vanadium containing DP steel, the processing is more robust i.e. the intercritical annealing temperature is not so critical. In addition, lower martensite fraction is required for the same strength i.e. lower annealing temperature and productivity gains. Improvements in the tensile fracture strain and the hole expansion coefficient have also been observed in the vanadium added steel.

[2] Hasegawa, K., Kawamura, K., Urabe, T., & Hosoya, Y., "Effects of microstructure on stretch-flange-formability of 980 MPa grade cold-rolled ultra high strength steel sheets", ISIJ international, 44(3) 2004, pp. 603-609.

[3] Taylor, M. D., Choi, K. S., Sun, X., Matlock, D. K., Packard, C. E., Xu, L., & Barlat, F., "Correlations between nanoindentation hardness and macroscopic mechanical properties in DP980 steels", Materials Science and Engineering A, 597, 2014, pp. 431-439.

[4] Kamikawa, N., Sato, K., Miyamoto, G., Murayama, M., Sekido, N., Tsuzaki, K., & Furuhara, T., "Stress–strain behavior of ferrite and bainite with nano-precipitation in low carbon steels", Acta Materialia, 83, 2015, pp. 383-396.

Vanadium Increases High Temperature Strength, Heat Shock Resistance and Wear Resistance of Ni–Cr–Mo Steel Brake Discs

A recent study "Improvement of High Temperature Strength by Addition of Vanadium Content of Ni–Cr–Mo Steel for Brake Discs" by Naoki HARADA, et al., published in ISIJ International, Vol. 57, No. 3, 2017, pp. 550–557" demonstrated that the significantly increased high temperature strength with increasing vanadium content is attributed to the increase in the density of fine VC precipitation.

In this study, four Ni–Cr–Mo ferritic steels with a similar basic composition, but different vanadium additions from 0wt.% to 0.27wt.% were investigated and the chemical compositions are summarized in Table 2.

The steels were melted by radio frequency induction furnace in SiO2 crucible and cast using 27-mm×27-mm×80-mm cuboid sand mold in air. Cast bars were homogenized at 960˚C for 3 hours in air, followed by furnace cooling to room temperature. Then, steels were heat-treated at 960˚C for 3 hours in air for austenitization and solution treatment, followed by water quenching. After quench, tempering was carried out immediately at 630˚C for 3 hours in air to obtain ferrite microstructure with precipitation of nano-sized vanadium carbide (VC) particles, followed by air cooling. Strain-rate change tensile tests were carried out at strain rates ranging from 1×10^{-5} to 1×10^{-3} s^{-1} and at temperatures of 650˚C, 700˚C and 750˚C in air.

The strain-rate-change tensile testing results showed that the flow stresses of the Ni–Cr–Mo steels at 650˚C, 700˚C and 750˚C were increased significantly along with the increase in concentration of vanadium. The stress exponent, n, which was estimated from the slope of the curves, exhibited values of 7.4, 10.3, 13.1 and 15.4 at 650˚C, 6.6, 7.9, 9.0 and 9.1 at 700˚C and 5.2, 5.2, 6.4 and 6.9 at 750˚C for 00V, 11V, 20V and 27V, respectively. Inductively Coupled Plasma Atomic

Table 2 Chemical composition of the steels (wt.%)

Steel	C	Si	Mn	Ni	Cr	Mo	V	Al
00V	0.24	0.82	0.46	0.79	0.76	0.80	0.00	0.03
110V	0.22	0.74	0.49	0.79	0.81	0.81	0.11	0.05
20V	0.23	0.81	0.51	0.79	0.85	0.79	0.20	0.02
27V	0.21	0.87	0.52	0.78	0.77	0.79	0.27	0.04

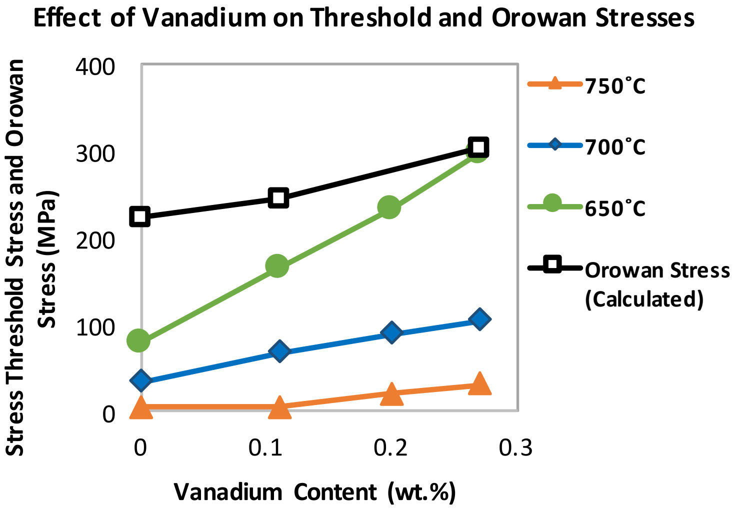

Fig. 5 The threshold stress and the Calculated values of Orowan stress as a function of the concentration of vanadium

Emission Spectroscopy (ICP-AES) and Transmission Electron Microscopy (TEM) revealed that a major part of the vanadium in the steels were precipitated as VC and the VC particle size decreased and the VC particle density increased with increasing vanadium content. Figure 5 shows that the threshold stress and the calculated Orowan stress also increase in proportion to vanadium content. The authors concluded that in the vanadium added Ni–Cr–Mo steels, owing to the increase in the number of fine VC particles that was associated with the increase in the concentration of vanadium, the threshold stress increased due to the Orowan mechanism and as a result, the high-temperature strength also increased.

The authors also showed that 0.1% vanadium addition to a conventional Ni–Cr–Mo cast steel, which is used for production of brake discs in high speed railway cars, improves the heat shock resistance and wear resistance in their paper "Effects of V Addition on Improvement of Heat Shock Resistance and Wear Resistance of Ni–Cr–Mo Cast Steel Brake Disc" published on Wear, Vol. 302, 2013, pages 1444–1452.

The heat shock resistance of the conventional Ni–Cr–Mo cast steel and the Ni-Cr-Mo+ 0.1%V steel was compared using the heat shock tests, which involved repeatedly (50 times) heating the samples up to 1000˚C in 3s with an RF heater followed immediately by cooling with water. The heat shock test results showed that obvious cracks occurred in the conventional Ni–Cr–Mo steel, while no cracks were detected in the V added steel, as shown in figure 6. Full scale dynamo tests were also carried out at a maximum speed of 300 km/h (the maximum speed for railway cars in Japan) for the conventional Ni–Cr–Mo steel disc and at a maximum speed of 430 km/h for the V added steel (in order to determine its potential for its use in higher speed applications). The dynamo tests provided similar results as the heat shock tests. The study concluded that the vanadium addition rises AC_3 point (the temperature at which all of the ferrite has been transformed to austenite) and promotes lower bainite transformation, resulting in improved heat shock resistance. The dynamo test also indicated that the wear loss was larger for the conventional Ni–Cr–Mo steel disc than the V added steel disc.

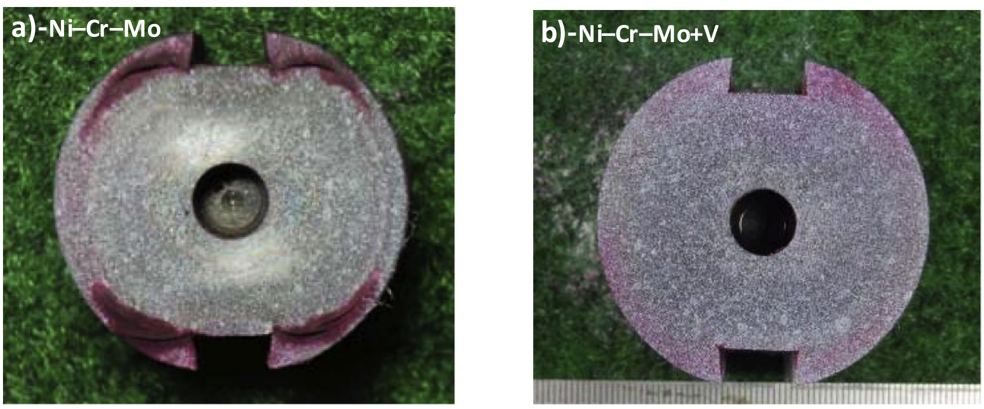

Fig. 6 Results of the heat shock tests (50cycles) (a) conventional Ni–Cr–Mo steel and (b) Ni–Cr–Mo + V steel.

Vanadium Reduces Reheat Cracking Susceptibility of Heat-Resistant Steel

Grade T/P23 heat-resistant steel was developed as an improved version of the standard 2¼Cr-1Mo steel primarily through the substitution of Mo with W, additions of V and Nb to improve the creep rupture strength, and limiting the carbon to less than 0.10% to improve weldability. Grade T/P23 has been shown to exhibit excellent mechanical properties and widely utilised in recent years to reduce section thicknesses in boiler and heat recovery steam generator headers, tubing and other components. However, the T/P23 steel shows a high reheat cracking susceptibility in the welding coarse grained heat affected zone (CGHAZ). Reheat cracking is defined as intergranular cracking in the heat affected zone (HAZ) or in the weld metal that occurs during the exposure of welded assemblies to the elevated temperatures produced by post weld heat treatments (PWHT) or high temperature service. It has been suggested [5] that the high reheat cracking susceptibility of the T/P23 steel is due to the active carbide formation reaction of tungsten in ferrite which depletes carbon within the matrix, resulting in higher segregation concentration of phosphorus at the prior austenite grain boundaries (PAGBs) and the prior austenite grain boundary/carbide interfaces (GCIs). A recent paper "Reduction of Intergranular Cracking Susceptibility by Precipitation Control in 2.25Cr Heat-Resistant Steels", which was published in Metallurgical and Materials Transactions A, Vol. 48A, No. 3, 2017, pages: 1459-1465, demonstrated that the intergranular cracking susceptibility of grade T/P23 is reduced by increasing the vanadium content in the steel.

In this study, two T/P23 steels, which are mainly different in the vanadium content, were used to investigate the role of the vanadium on the reheating cracking susceptibility. The chemical compositions of the steels are given in Table 3.

Table 3 Chemical composition of the steels (wt.%)

Steel	C	Si	Mn	P	S	Cr	Mo	V	Al	W	Nb	N	B	Ti
V255	0.100	0.318	0.509	0.021	<0.002	2.24	-	0.255	0.019	1.55	0.049	0.010	0.0013	0.016
V408	0.100	0.315	0.510	0.021	<0.002	2.24	-	0.408	0.018	1.54	0.051	0.010	0.0011	0.015

The steels were homogenized at 1200˚C for 1 hour and hot-rolled to 12 mm thick plates. Rectangular bars were machined from the plates in the hot-rolling direction and the bars were heat treated at 1050˚C for 0.5 hour followed by air cooling, and then tempered at 750˚C for 0.5 hour under an argon atmosphere. After the heat treatment, tensile specimens (ø7-mmx8-mm) were machined from the rectangular bars. The intergranular cracking susceptibility was evaluated using a thermo-mechanical simulator (FDC,Thermecmastor-Z). The gage part of each specimen was heated to 1300˚C at a heating rate of 25˚C/s and held at the temperature for 5 seconds, followed by fast cooling to room temperature to simulate the welding. After the welding simulation, the specimens showed a typical lath martensitic microstructure. The specimens were again heated to 750˚C, which is usually the post-weld heat treatment (PWHT) temperature, at a heating rate of 10˚C/s. As soon as the temperature reached 750˚C, the tensile tests were carried out on the specimens at a cross-head speed of 0.5 mm/min. The tensile specimens were used for the interfacial segregation investigation, which was carried out using an Auger Electron Spectroscope (AES).

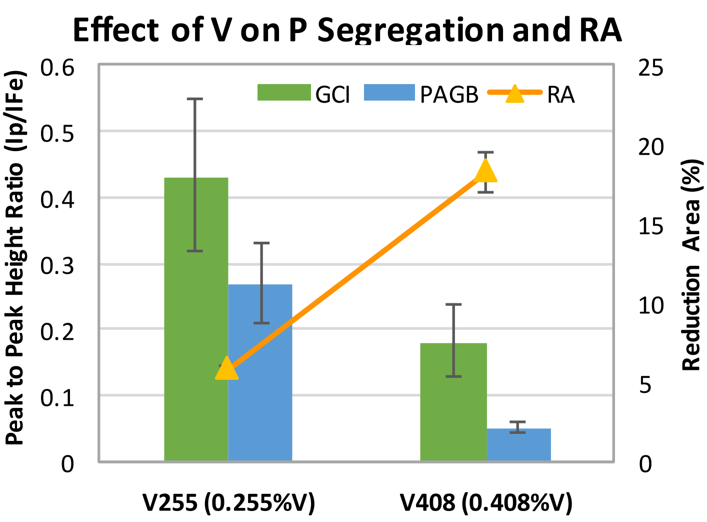

Fig 7 Effect of vanadium content on phosphorus segregation concentration (average peak-to-peak height ratios) and reduction area

The tensile test results showed that the maximum stress at 750˚C increases with increasing vanadium content, even though the room temperature hardness of the martensitic microstructure before the tensile test was around 380 Hv for both of the steels. In addition, the V408 steel has a higher Reduction Area (RA) value than the V255 steel. The V255 steel showed intergranular cracking after the tensile test at 750˚C, while the cracking susceptibility was improved by increasing the vanadium content from 0.255wt.% (V255) to 0.408wt.% (V408). Microstructural examinations revealed that numerous $M_{23}C_6$ carbides precipitated in the V255 steel, while amount of $M_{23}C_6$ carbides was much less in the V408 steel. The increase of vanadium content inhibits the formation of $M_{23}C_6$ carbides, but promotes the precipitation of V-rich MX carbo-nitrides. Auger electron spectroscopy analysis showed that phosphorus segregation concentration at the prior austenite grain boundary/carbide interfaces (GCIs) and at the carbide-free PAGBs decreases with increasing vanadium content, and RA is inversely proportional to segregation concentration of phosphorus, as shown in figure 7. In addition, no sulfur segregation at the GCIs and the carbide-free PAGBs was detected in the V408 steel, but there was sulfur segregation at the interfaces in the V255 steel.

It is suggested that the high reheat cracking susceptibility of the V255 steel is due to the larger amount of $M_{23}C_6$ carbides precipitation, resulting in the depletion of the dissolved carbon, which can segregate to the GCIs and the PAGBs and repel the phosphorus from the interfaces. The increase of vanadium content in the T/P23 steel reduces the amount of $M_{23}C_6$ carbides, leading to lower segregation concentration of phosphorus at the interfaces, higher maximum tensile strength and ductility, and finally reduces the reheat cracking susceptibility. The authors also expected that that the creep-rupture life will be increased with increasing bulk vanadium content.

[5] Sung, Hyun Je, Nam Hoe Heo, and Sung–Joon Kim, "Roles of Molybdenum and Tungsten on Reheat Cracking Susceptibility of 2.25 Cr Heat Resistant Steels", ISIJ International, 57(1), 2017, pages: 176-180.

Recent Vanadium Related Publication List

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Interphase Precipitation – An Interfacial Segregation Model, Samuel Clark, Vit Janik, Yongjun Lan, and Seetharaman Sridhar, ISIJ International, 57(3), 2017: 524-532.

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Theoretical and Experimental Nucleation and Growth of Precipitates in a Medium Carbon–Vanadium Steel, Sebastián F. Medina, Inigo Ruiz-Bustinza, José Robla, and Jessica Calvo, Metals, 7(2), 2017: 1-10.

Calendar of Conferences and Seminars

Date & Place	Vanitec Events
10-11 October 2017, London, UK	93rd Vanitec Meeting
Spring, 2018, Brazil	94th Vanitec Meeting
Fall, 2018, London, UK	95th Vanitec Meeting
Date & Place	**Steel Related Events**
16-18 August 2017, Qingdao, CHINA	The 7th International Conference on Modelling and Simulation of Metallurgical Processes in Steelmaking (STEELSIM2017)
7-8 September 2017, Glasgow, UK	Nanoanalysis of Steels and Structural Alloys
11-14 September 2017, Graz, AUSTRIA	20th International Forgemasters Meeting – IFM 2017
8-12 October 2017, Pittsburgh, USA	Materials Science & Technology 2017 (MS&T17)
9 November 2017, Düsseldorf, GERMANY	STAHL 2017
12-16 November 2017, Tokyo, JAPAN	11th International Conference on Zinc and Zinc Alloy Coated Steel Sheet (GALVATECH)
13-16 November 2017, Kyoto, JAPAN	5th International Symposium on Steel Science (ISSS 2017)
11-13 December 2017, Kanpur, INDIA	3rd International Conference on Science and Technology of Ironmaking & Steelmaking (STIS2017)
6-9 February 2018, Odisha, INDIA	Asia Steel International Conference 2018 (Asia Steel 2018)
7-10 May 2018, Philadelphia, USA	The Iron & Steel Technology Conference and Exposition (AISTech2018)
3–6 June 2018, Orlando, USA	2nd International Symposium on The Recent Developments in Plate Steels
29-31 August 2018, New Delhi, INDIA	Minerals, Metals, Metallurgy & Materials (MMMM 2018)
14-18 October 2018, USA	Materials Science & Technology (MS&T) 2018
6 – 19 October 2018, Stockholm, SWEDEN	3rd International Conference on Ingot Casting, Rolling and Forging (ICRF 2018)

Date & Place	Energy Storage Related Events
27-28 July 2017, Rome, ITALY	2nd International Conference on Battery & Fuel Cell Technology
31 Oct. – 1 Nov. 2017, Arlington, USA	Lithium Battery Materials & Chemistries 2017
28-29 November 2017, Birmingham, UK	Battery and Energy Storage 2017
4-7 December 2017, Tangier, MOROCCO	2017 International Renewable and Sustainable Energy Conference (IRSEC'17)
27-28 February 2018, London, UK	Energy Storage Summit
Date & Place	**Trade Events**
22 - 24 October 2017, Scottsdale, USA	CRU Ryan's Notes Ferroalloys 2017
Date & Place	**Vanitec Sponsored Trade Events**
6 - 8 September 2017, Chicago, USA	AMM North American Ferroalloys Conference **Special Discounted Rate (15%) to Vanitec Members**
19-21 November 2017, Lisbon, PORTUGAL	33rd International Ferroalloys Conference **Special Discounted Rate (15%) to Vanitec Members**

Vanitec Members

AMG Vanadium, Inc.
60790 Southgate Road
Cambridge, OH 43725
USA
Tel.: +1 740 435 4600
E-mail: vanadium@amg-v.com
www.amg-v.com

Atlantic Vanadium Pty Ltd
Level 24, Allendale Square
77 St Georges Terrace
Perth, WA, 6000
Australia
Tel: +61 8 6141 7100
E-mail:info@atlanticltd.com.au
http://atlanticltd.com.au

Australian Vanadium
Level 1, 85 Havelock Street
West Perth WA 6005
Australia
Tel.: +61 8 9321 5594
E-mail:
info@australianvanadium.com.au
www.australianvanadium.com.au

Bear Metallurgical Company
679 East Butler Road
Butler, PA 16002-9127
USA
Tel.: +1 724 431 2800
E-mail: info@bearmet.com
www.bearmet.com

Beijing Zhongkaihongde Technology Co., Ltd.
Tongfang Technology Square
No.1 Wangzhuang Road, Haidian
District, Beijing, 100083
China
Tel.: +86 10 83185988
E-mail: lli@cn-ess.com

Bushveld Minerals Limited
Main Mothotlung Road
0250 Brits
North West
South Africa
Tel.: +27 21 318320
E-mail: info@bushveldminerals.com
www.bushveldminerals.com

Chengde Iron & Steel Group Co., Ltd
No.1 Office Building
General Manager Office
Shuang Luan District
Chengde City
China
Tel.: +86 314 4378909
E-mail: lilanjie20040014@163.com
www.cdsteel.com.cn

Chengde Jianlong Special Steel Co., Ltd
Xinglong County
Chengde City
Hebei, 067201
China
Tel.: +86 314 5316566
E-mail: bfr00@163.com
www.ejianlong.com

China Iron & Steel Research Institute Group
No.76 Xueyuan Nanlu
Haidian,Beijing 100081
China
Tel.: +86 10 62182761
E-mail: chenxuehui@cisri.com.cn
www.cisri.com

De Sheng Gruop
No. 8, Tonghe Road
Shawan District
Leshan
Sichuan
China
Tel: +86 0833 3480171
E-mail: 247222584@qq.com
www.deshenggrp.com

Duferco S. A.
Via Bagutti, 9
6900 Lugano
Switzerland
Tel.: + 41 91 822 56 00
E-mail: info@duferco.com
www.duferco.com

Evraz NTMK
1, Metallurgov Street
Nizhniy Tagil, Sverdlovskaya oblast
622025
Russia
Tel.: +7 3435 497270
E-mail: post@ntmk.ru
www.ntmk.ru

Evraz Vanady Tula 1, Przhevalskogo Street Tula, 300016 Russia Tel.: +7 4872 466 900 E-mail: info@vanady.com www.vanady.com	**Gildemeister Energy Storage GmbH** Carl-Zeiss-Str. 4 97076 Wuerzburg Germany Tel.: +49 (0) 931-25064-250 www.energy.gildemeister.com	**Glencore plc** P. O. Box 3620 Brits, 0230 South Africa Tel.: +27 12 3180700 www.glencore.com
Largo Resources Ltd. 55 University Ave., Suite 1101 Toronto, Ontario, M5J 2H7 Canada Tel.: +1 416 861 9797 E-mail: info@largoresoures.com www.largoresources.com	**Mustavaaran Kaivos Oy** Asemakatu 37 F1-90100 Oulu Finland Tel.: +358 8 370 090 E-mail: info@mustavaarankaivos.com www.mustavaarankaivos.com	**New Zealand Steel Ltd.** Mission Bush Road Private Bag 92121 Auckland 1142 New Zealand Tel.: +64 9 375 8999 www.nzsteel.co.nz
Panzhihua Iron & Steel Group Xiangyang Village East District, Panzhihua, Sichuan 617067 China Tel.: +86 10 5969 5097 www.pzhsteel.com.cn	**PVH Storage** c/ Sepúlveda, 17, Bajo 1 – 2 28108 Alcobendas Madrid Spain Tel.: +34 91 831 0013 E-mail: contact@pvhardware.es www.pvhardware.com	**Queensland Energy & Minerals Pty Ltd.** Level 19, 10 Eagle Street Brisbane Queensland 4000 Australia Tel.: +61 7 3303 0161 www.qldem.com.au
Treibacher Industrie AG Auer-von-Welsbach-Straße 1 9330 Althofen Austria Tel.: +43 42 62 5050 E-mail: treibacher@treibacher.com www.treibacher.com	**U308 Corp** 401 Bay Street, Suite 2702 Toronto, ON M5H 2Y4 Canada Tel.: +1 416 868-1491 www.u3o8corp.com	