V-Technology

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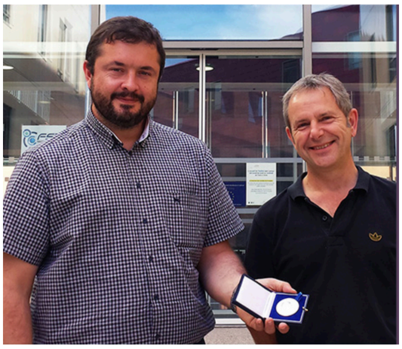
Vanitec is a technical and scientific committee, which brings together representatives of companies and organisations involved in the mining, processing, manufacture, research and use of vanadium and vanadium-containing products.

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.

2017 Vanadium Award



C. P. Scott and S. Y. P. Allain

The Vanadium Award was endowed by Vanitec to The Metal Society (now The Institute of Materials, Minerals and Mining) in 1981 to celebrate the 150th anniversary of the discovery of vanadium. The award has been made annually since that time. The Vanadium Award for 2017 was won by C. P. Scott, F. Fazeli, B. Shalchi Amirkhiz and I. Pushkareva of CanmetMATERIALS, Canada and S. Y. P. Allain of Institut Jean Lamour, France for their paper "Structure-properties Relationship of Ultra-fine Grained V-microalloyed Dual Phase Steels", published in Materials Science and Engineering: A, vol. 703, 2017, pages: 293-303. In this paper, the authors demonstrated that vanadium addition strongly refines the dual phase (DP) microstructure, and ferrite is strengthened by grain refinement and selectively V(C,N) precipitation strengthening, resulting in excellent mechanical properties. In addition, the vanadium microalloyed DP steel is much less sensitive to the martensite fraction compared to the vanadium-free DP steel.

Two steels (Ref and Ref+V) were used to study the effect of vanadium microalloying on the microstructure and properties of high strength DP steel and the chemical compositions are shown in Table 1. The Ref steel was designed to be equivalent to a standard DP1180 grade but with a lower martensite fraction. 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 and the rolling parameters were designed to produce bainitic hot strips with the maximum amount of V maintained in solid solution before cold rolling. The hot strips were cold rolled from 3 mm to 1 mm (66% reduction) under tension in 7 passes. The phase transformation behaviour of full hard cold rolled strips was investigated in a Bahr DIL 805 dilatometer and a Gleeble 3800 simulator. Large area sheet annealing was carried out in a specially adapted furnace and quenched between flat dies in a Macrodyne 1200t press.

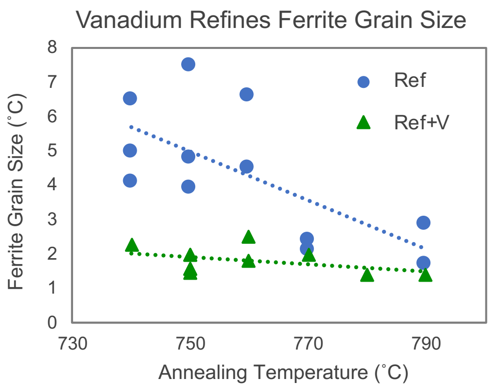


Fig. 1 Effect of vanadium on ferrite grain size of the DP steel

This study showed that vanadium addition strongly refines DP microstructures (ferrite grain size reduced to 1.6 μm) without requiring any new processing requirements, as shown in figure 1. It means that steelmakers without sophisticated annealing lines can produce ultrafine grain DP steels. The authors proposed that this microstructural refinement is due to Zener pinning of newly recrystallized ferrite by V(C,N) precipitates nucleated on dislocations during the heating portion of intercritical annealing. After cold rolling and intercritical annealing at 750^{0}C/180s intense V(C,N) precipitation (mean diameter 7.4 nm) was observed in the ferrite phase

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

whereas precipitates were scarce in martensite (austenite) and much larger (mean diameter 13.4 nm).

The study also showed that vanadium addition strongly delays the formation of austenite during heating and isothermal holding and promotes the reverse transformation to ferrite during cooling while at the same time retarding/suppressing the pearlite and bainite transformations i.e. it provides an overall increase in hardenability. The authors indicated that this increased hardenability is a positive benefit for DP production on older annealing lines with limited fast cooling capability or for the production of thicker gauges (hot strips) where the cooling rate is non-uniform.

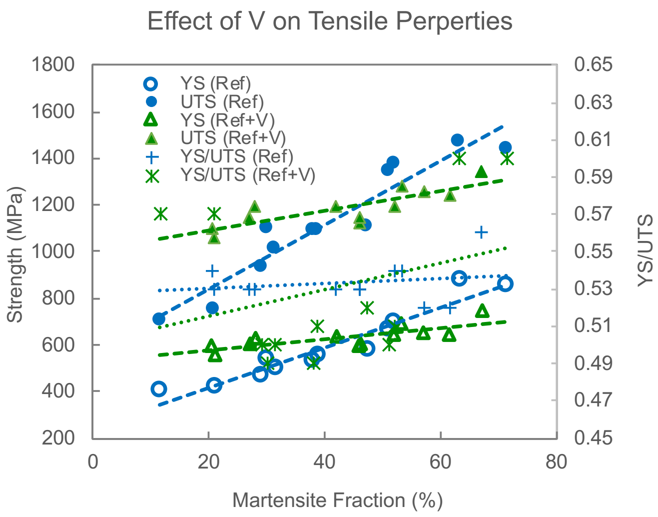


Fig. 2 YS, UTS and YS/UTS plotted as a function of martensite fraction

The mechanical properties of the vanadium added steel are excellent (YS~600MPa, UTS~1200 MPa, UE~8-10%) and this is mostly due to the ferrite phase which is strengthened by grain refinement and selectively strengthened by V(C,N) precipitation. In addition, vanadium addition introduces a rather startling difference in the structure/properties relation. Significant gains in YS, UTS and work hardening rate were observed in the Ref+V steel at low martensite fractions due to a combination of selective precipitation strengthening and grain refinement of ferrite, as shown in figure 2. However, at higher martensite fractions (> 45%) the YS, UTS and work hardening rate became lower than the Ref steel, primarily due to softening of the martensite. The latter was attributed to the fixing of solute carbon by V(C,N). The lower sensitivity of the tensile properties of the V added steel to martensite fraction implies that for the vanadium containing DP steel, the processing is more robust i.e. the product can tolerate much larger variations in the intercritical annealing temperature. Improvements in the tensile fracture strain and the HE coefficient in the Ref+V steel have also been observed.

Recent Vanadium Related Publications Review

Strengthening Mechanism of Vanadium Microalloying in Low-Carbon Bainitic Steel

Bainitic steels are gaining in industrial importance as more arduous service conditions drive up steel property requirements and the avoidance of heat treatment is essential for economic competitiveness. Examples of medium carbon bainitic steels have been seen in forging and rail steels. Developments in strip and plate steels are moving rapidly towards increasingly high strength levels with low carbon contents. Up to yield stress levels of about 600MPa, strengthening can be realised by ferrite grain refinement and precipitation strengthening as in traditional HSLA steels. Higher strength steel necessitates substructure strengthening as in bainite or tempered martensite. However, when bainite is formed during cooling to the coiling temperature or in the coil of bainitic hot rolled strip steels, it is expected to recover and soften significantly during the prolonged holding at elevated temperatures after coiling. There is some evidence[1-4] that vanadium microalloying is effective in preventing the recovery of the bainitic ferrite and leads to retention of the strength of the virgin bainite after coiling. In addition, vanadium microalloying makes the mechanical properties of the hot rolled bainitic strips largely independent of the precision coiling temperature.

A recent paper “Kinetics and Microstructural Change of Low-Carbon Bainite Due To Vanadium Microalloying” by F. Fazeli, B. S. Amirkhiz, C. Scott, M. Arafin and L. Collins, published in Materials Science and Engineering: A, vol. 720, 2018 pages: 248-256 showed that vanadium microalloying significantly increases the strength of API X100 bainitic linepipe steel. The increased strength is due to vanadium in solution, which shifted the bainite transformation to lower temperatures (by 30-40°C) during cooling at 1–50°C/s, resulting in refinement of the lath structure and increase of the dislocation density of bainitic ferrite. The vanadium added steel also showed more resistance to softening during coiling.

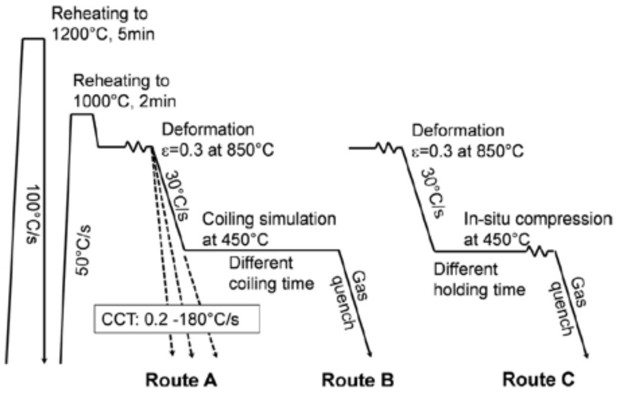


Fig. 3 Different thermomechanical routes by dilatometer: (A) to develop CCT diagram, (B) to simulate cooling and interrupted coiling and (C) in-situ compression to determine softening of fresh bainite upon coiling.

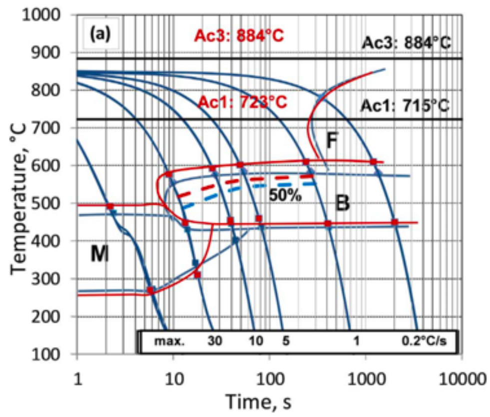


Fig. 4 Dilatometric findings for the Ref. Steel (red) and the 0.06V Steel (blue): Measured CCT diagram, where the solid and dashed lines represent 5% and 50% transformation respectively.

The study was carried out on two API X100 linepipe steels with identical chemical compositions (0.06wt%C-1.95wt%Mn-0.16wt%Cr-0.03wt%Nb-0.005wt%Ti-0.005wt%N) but two levels of vanadium, i.e. a reference steel (Ref.) with residual amount (0.004wt%) of vanadium and a vanadium added steel (0.06V) with 0.063wt%V to study the strengthening mechanism of vanadium microalloying in a low carbon bainitic microstructure. The steels were melted and control rolled to 14 mm simulating a coiled plate production process.

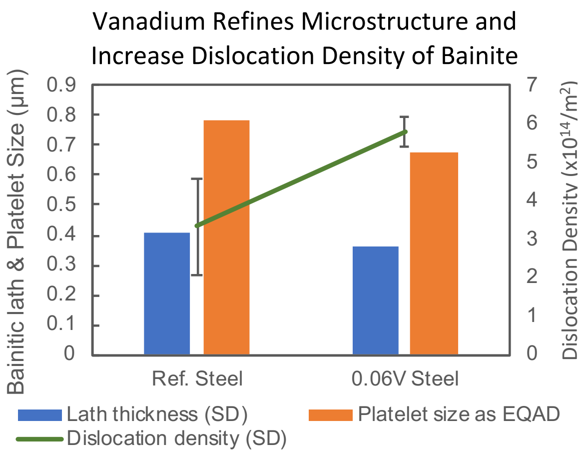


Fig. 5 Microstructural features of fresh bainite (cooled at 30°C/s below Bs and held 30 s at 450°C).

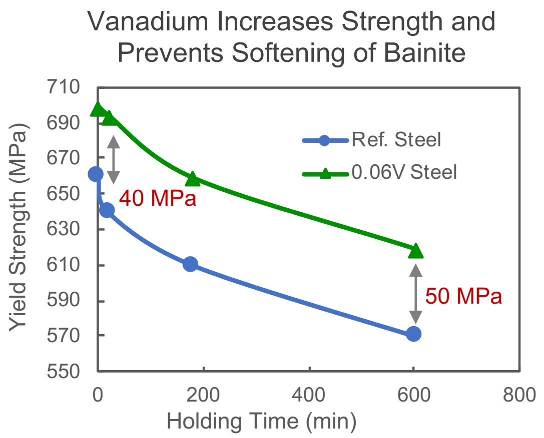


Fig. 6 Strength of fresh bainite and its softening upon coiling

Rod specimens with 10 mm length and 5 mm diameter were machined at the quarter thickness of the plates for dilatometric studies and subsequent microstructure characterization. A quenching, deformation BAHR 805 dilatometer was used to determine the kinetics of austenite decomposition during continuous cooling and cooling-coiling scenarios. Three distinct thermomechanical routes were carried out as shown in Fig. 3. The specimens were soaked for 5 min at 1200°C to simulate reheating of slabs prior to rolling and to ensure the dissolution of Nb and V carbonitrides, followed by sufficiently fast cooling to room temperature to suppress any subsequent precipitation. Route A entailed cooling the specimens at different rates to develop a CCT diagram, whereas route B included a 30°C/s cooling segment to 450°C followed by isothermal holding for different times to simulate complete and interrupted coiling. Route C was a novel in-situ compression test at 0.1 s^{-1} strain rate to measure the flow strength of the material at various stages of coiling, namely the strength of fresh bainite and its softening behaviour for different coiling times up to 10 h.

The dilatometric study (Route A) demonstrated that vanadium in solution delays the bainite reaction to lower transformation temperatures (by 30–40°C) over a wide range of cooling rates (1–50°C/s), as shown in figure 4. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) examinations of the specimens processed through Route B representing fresh bainite microstructures revealed that a fully bainitic microstructure consisting of mainly slender laths with a smaller fraction of equiaxed platelets was obtained in both of the steels and the shift in bainite transformation to lower temperatures resulted in refinement of the lath structure (12%) and an increase of the dislocation density (75%) of the fresh bainite for the 0.06V steel compared to the reference steel (figure 5). In addition, electron backscatter diffraction (EBSD) studies showed that the frequency of low angle (2–10°) boundaries was slightly higher in the 0.06V specimens implying a more refined microstructure. However, no evidence of fine vanadium precipitation during fast cooling and subsequent low temperature coiling (450°) was found from TEM characterization.

The 0.06V steel had a higher strength of fresh bainite compared to the reference steel (figure 6). It is suggested that the refinement in lath structure in combination with the increased dislocation density is the prevailing factor for the strength gain (40 MPa) of the 0.06V steel. Furthermore, interrupted coiling simulations in conjunction with in-situ compression tests (Rout C) confirmed that the fresh bainite softened rapidly at the coiling temperature (450°C); about 90 MPa drop was noted during 10 h for the reference steel whereas the V-added steel demonstrated a higher resistance to softening (figure 6).

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Vanadium Increases Strength and Ductility of Medium Mn Steel

Medium Mn steels containing 5-10 wt% Mn have received much attention as potential candidates for the third generation of advanced high strength steels (AHSS) due to their excellent combination of strength-ductility and lower cost than that required for the second generation AHSS. Medium Mn steels have fine multi-phase microstructures with a large fraction of metastable retained austenite, which are mainly introduced by an intercritical annealing process, i.e. annealing in the ferrite + austenite temperature region. Retained austenite plays a critical role in the tensile properties of medium Mn steels primarily via the transformation induced plasticity (TRIP) effect i.e. strain-induced transformation of retained austenite to martensite. This leads to an enhanced work hardening behaviour over a broad strain regime. By optimizing the mechanical stability of retained austenite, medium Mn steels can achieve excellent mechanical properties with a strength-ductility balance in the range of 35,000 to 45,000 MPa-pct. Despite the high tensile strength and excellent ductility, medium Mn steels have a relatively low yield strength, which could be ascribed to the soft ferrite matrix after intercritical annealing. Vanadium in medium Mn steels has been shown to increase yield strength and enhance the TRIP effect, resulting in exceptionally excellent tensile properties. A recently published paper "Simultaneous Increase of Both Strength and Ductility of Medium Mn Transformation-Induced Plasticity Steel by Vanadium Alloying, B. B. He and M. X. Huang, Metallurgical and Materials Transactions A, vol. 49, no. 5, 2018, pages: 1433-1438" demonstrated that vanadium alloying leads to optimized mechanical stability of austenite grains, resulting in continuous transformation-induced plasticity (TRIP) effect and consequently increases both strength and ductility of the medium Mn steel. The study also showed that vanadium alloying suppresses the formation of intergranular cracks, leading to a ductile fracture of the V-alloyed steel.

The study was carried out on two medium Mn steels with the chemical composition of Fe - 10wt%Mn - 0.45wt%C - 1wt%Al (V-free) and Fe - 10wt%Mn - 0.45wt%C - 1wt%Al - 0.7wt%V (V-alloyed). The steels were cast and forged into billet followed by hot rolling to strips with a final thickness of 4 mm. The tensile samples with a gage length of 25 mm were cut along the rolling direction of the strips. The tensile samples were annealed at 1000°C for 1 hour, followed by water quenching and deep cryogenic treatment in liquid nitrogen for 10 minutes, and then were tempered at 620°C for 5 hours. The heat treatment was termed as quenching, tempering and partitioning (Q-T&P) process. The tensile tests were performed at a strain rate of $5X10^{-4}s^{-1}$ under room temperature.

The scanning electron microscopy (SEM) observation and electron backscattered diffraction (EBSD) analysis of the samples after the Q-T&P treatment showed that both of the V-free steel and V-alloyed steel have a dual phase microstructure with martensite embedded in the

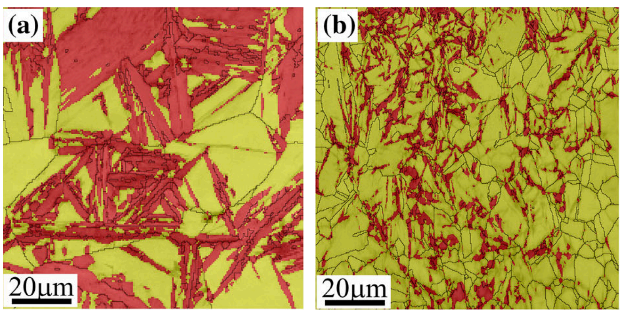

Fig. 7 EBSD phase images of (a) V-free steel and (b) V-alloyed steel. Yellow: austenite; red: martensite; Black lines represent high-angle grain boundaries (>15 deg).

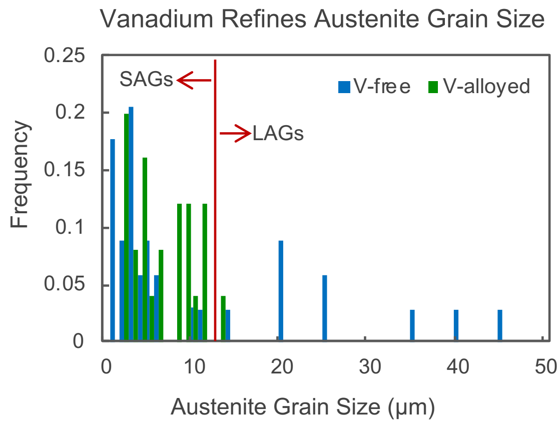

Fig. 8 Austenite grain size distributions for V-free steel and V-alloyed steel

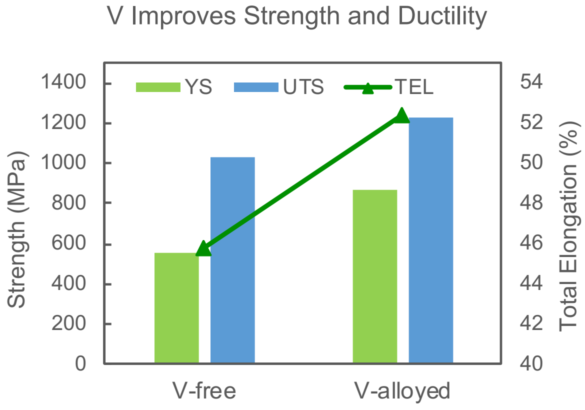

Fig. 9 Tensile properties of the steels

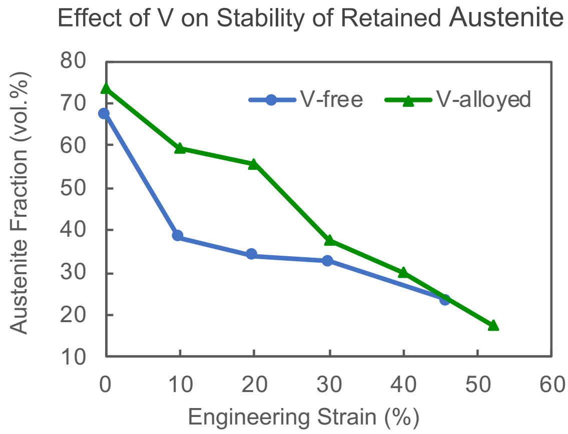

Fig. 10 Evolution of austenite volume fraction at different engineering strains for the steels

austenitic matrix (figure 7), and a similar austenite volume fraction, 67.5% for the V-free steel and 73.7% for the V-alloyed steel. The martensite grain size in the V-alloyed steel is much finer than that in the V-free steel. It is suggested that the finer martensite is due to vanadium carbide precipitates, which could pin prior austenite grain boundaries during recrystallization process, resulting in smaller prior austenite grain size in the V-alloyed steel. In addition, both of the steels contain large austenite grains (LAGs) and small austenite grains (SAGs), as shown in figure 8, but the LAGs in the V-free steel are much coarser than those in the V-alloyed steel.

The study demonstrated that vanadium alloying improves the tensile properties of the medium Mn steel (figure 9). As compared to the V-free steel, the V-alloyed steel has a higher yield strength, which can be ascribed to the precipitation strengthening from V-carbide precipitates and grain refinement due to vanadium alloying. The V-alloyed steel also has an excellent ductility in terms of total elongation, which is contributed by high work hardening rate and the existence of large non-uniform elongation.

The metastable austenite grains could transform to martensite during plastic deformation for both the V-free and V-alloyed steels. However, it seems that retained austenite grains in the V-alloyed steel have improved mechanical stability because the decreased amount of austenite volume fraction in the V-alloyed steel is much smaller than that in the V-free steel at low strain level (10%) as shown in figure 10. It is expected that the LAGs in both steels are less stable as compared to the SAGs due to the coarse grain size and insufficient C partitioning from adjacent martensite, therefore the LAGs shall transform to martensite during initial plastic deformation for both of the steels. Although the LAGs in the V-alloyed steel may have a lower C content due to the formation of V-carbide precipitates, the gradual decrease of austenite volume fraction in the V-alloyed steel during initial plastic deformation indicates that the grain refinement overcomes the reduced C concentration in stabilizing the LAGs. In other words, the vanadium alloying optimizes the mechanical stability of austenite grains, enabling a continuous TRIP effect to enhance work hardening behavior across a wide strain regime.

Furthermore, the study showed that vanadium alloying reduces the amount of Portevin–Le Chatelier (PLC) bands in the medium Mn steel. It is suggested that the formation of vanadium carbide precipitates reduces the available C atoms for dislocation pinning events and consequently, the dynamic strain aging effect, which leads to the formation of PLC bands. The vanadium alloying also suppresses the formation of intergranular cracks in the medium Mn steel, leading to a ductile fracture. Therefore, the V-alloyed steel has a larger non-uniform elongation than the V-free steel, indicating that the V-alloyed steel shall have good formability for automotive application.

Vanadium Microalloyed High Strength Steel for Nitrided Gears

Carburizing is widely employed to case harden gears for improving fatigue strength and wear resistance. During carburizing, the steel is heated to the austenitic temperature and then quenched to obtain martensite. The drawback of this heat treatment is that quenching from a high austenitic temperature may cause extensive distortion, which can have strong negative impact on gear performance and manufacturing costs. Nitriding for surface engineering of gears has been growing steadily in recent years because of the many benefits offered by this technology. Nitriding is performed at low subcritical temperatures and allows gears to be treated with minimal distortion. However, nitriding steel selection is important to obtain a hardness adequate for the machining before nitriding and a fatigue strength equivalent to that of carburized and quenched steel after nitriding. Nippon Steel & Sumitomo Metal Corporation has recently developed a new vanadium microalloyed high-strength nitriding steel for gears (Development of High-strength Nitriding Steel for Gear, H. Imataka, M. Yuya, K. Tanaka, A. Kobayashi and S. Maeda, Nippon Steel & Sumitomo Metal Technical Report No. 116, September 2017). The

Table 2 Chemical composition of the steels (wt%)

Steel	C	Si	Mn	Cr	**V**
V-added Steel	0.10	0.15	0.55	1.25	**0.17**
JIS SCr420H	0.20	0.20	0.80	1.00	
JIS S35C (conventional steel)	0.35	0.20	0.75		

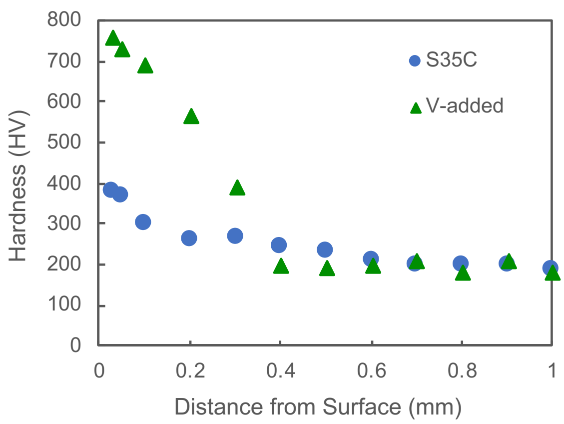

Fig. 11 Hardness profiles of nitrided layers of the V-added steel and S35C steel

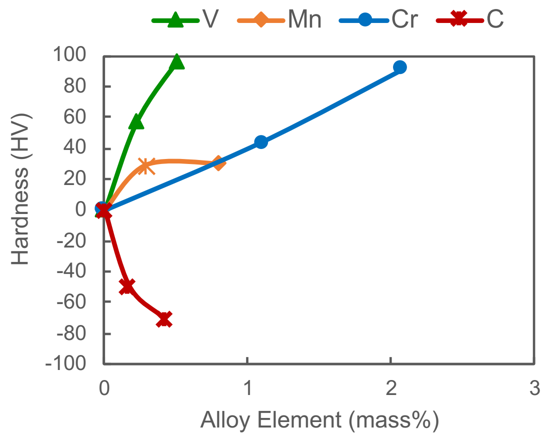

Fig. 12 Influence of alloying elements on surface hardness after nitriding

report demonstrated that fine carbonitrides containing V and Cr at the nitride layer contribute to optimal hardness distribution and excellent fatigue properties of the developed steel.

The new vanadium microalloyed (V-added) nitriding steel was designed according to a popular alloy steel (JIS SCr420H) for machine structural use to obtain good machinability for gear cutting before nitriding as well as high fatigue strength after the treatment. Comparison with the JIS SCr420H steel, vanadium was added and chromium content was increased in the new nitriding steel to form nitrides in the surface layer during nitriding, thus improving surface hardness. In addition, carbon content was reduced to lower the material hardness before nitriding by increasing the volume fraction of ferrite. Silicon and manganese contents were modified in order to obtain a ferrite-pearlite structure without bainite for good machinability. A popular carbon steel (JIS S35C) for machine structural use was also included for comparison. The chemical compositions of the steels are shown in Table 2. The V-added steel and the S35C steel were prepared using a converter, continuously cast into blooms, rolled into billets and then into bars. The bars were then machined into test pieces, and subjected to a turning test before nitriding. Then, the steels underwent gas nitriding at 600°C for 2 h, and their properties were examined.

The V-added steel and the S35C steel had similar hardness (V-added: HRB 86; S35C: HRB 85) and good machinability before the nitriding. After the nitriding, hardness at the surface layer of the V-added steel was much higher than that of the S35C steel and similar to that (HV 700-800) of carburized steel (figure 11). The nitrogen concentration in the surface layer of the V-

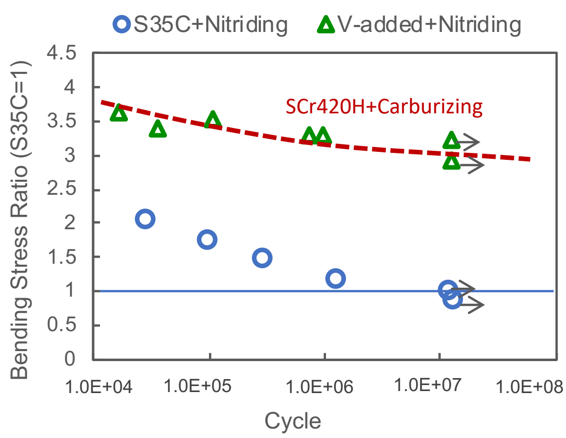

Fig. 13 Results of Ono-type bending fatigue test

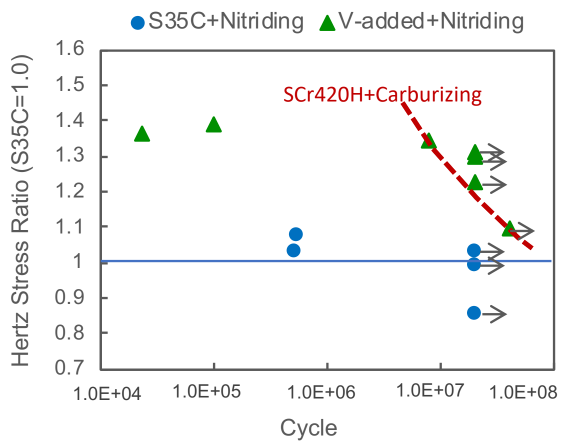

Fig. 14 Results of roller pitting fatigue test

added steel was more than twice that of the S35C steel. It is suggested that this may be due to V and Cr, which have an affinity for N. The report also indicated that vanadium is the most effective element for increasing the hardness of surface layer after nitriding (figure 12).

The rotary bending and roller pitting fatigue tests after nitriding showed that the V-added steel has higher bending fatigue strength (figure 13) and higher anti-pitting strength (figure 14) than that of S35C and substantially equal to that of the gas carburized JIS SCr420H steel. Fine carbonitrides containing V and Cr were observed in the surface layer of the steels by transmission electron microscopy (TEM) and the precipitates were much finer and denser in the V-added steel than that in the S35C steel. The reported suggested that addition of appropriate amounts of V and Cr to low-C steel is effective for improving surface hardness and fatigue strength of nitriding steel for gears.

Recent Vanadium Related Publication List

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Calendar of Technical & Trade Conferences

Date & Place	Vanitec Events
9-10 October 2018, London, UK	95th Vanitec Meeting
Spring 2019, Xichang, CHINA	96th Vanitec Meeting
Date & Place	**Steel Related Events**
20-22 August 2018, Hefei, CHINA	The 4th International Conference on Advanced High Strength Steel and Press Hardening (ICHSU 2018)
29-31 August 2018, New Delhi, INDIA	12th International Exhibition and Conference Minerals, Metals, Metallurgy & Materials
6-7 September 2018, Istanbul, TURKEY	20th International Conference on Advanced High Strength Steels (ICAHSS 2018)
26-28 September 2018, Darmstadt, Germany	Materials Science and Engineering
14-18 October 2018, Columbus, USA	Materials Science & Technology (MS&T) 2018
16-19 October 2018, Stockholm, SWEDEN	3rd International Conference on Ingot Casting, Rolling and Forging (ICRF 2018)
30-31 October 2018, Shanghai, CHINA	7th Baosteel Biennial Academic Conference (Baosteel BAC 2018)
18-21 November 2018, Jeju, KOREA	6th International Conference on Advanced Steels (ICAS 2018)
1-3 April 2019, Aachen, GERMANY	4th International Conference on Medium and High Manganese Steels
6-9 May 2019, Pittsburgh, USA	The Iron & Steel Technology Conference and Exposition (AISTech2019)
2-5 June 2019, Luleå, SWEDEN	The 7th International Conference on Hot Sheet Metal Forming of High-Performance Steel (CHS² 2019)

Date & Place	Steel Related Events
18-22 August 2019, Xi'an, CHINA	The 10th Pacific Rim International Conference on Advanced Materials and Processing (PRICM-10)
Date & Place	**Energy Storage Related Events**
19-20 September 2018, Toronto, CANADA	Energy Storage Canada
19-20 September 2018, Tangshan, CHINA	Energy Storage China 2018
24-26 October 2018, Brussels, BELGIUM	Energy Storage Global Conference 2018
4-5 December 2018, Warwick, UK	Battery and Energy Storage 2018
26-27 February 2019, London, UK	Energy Storage Summit
10-11 April 2019, Berlin, GERMANY	Energy Storage Innovations Europe 2019
7-9 May 2019, Guangzhou, CHINA	The 4th International Battery and Energy Storage Technology Expo and the 9th China lithium battery industry summit
15-17 May 2019, Munich, GERMANY	ees Europe 2019
27-28 May 2019, Barcelona, SPAIN	5th International Conference on Electrochemistry
Date & Place	**Trade Events**
12-14 September 2018, Xiamen, CHINA	FerroAlloyNet 7th International Vanadium Products Summit
26-28 September 2018, Chicago, USA	North American Ferroalloys Conference 2018
21-23 October 2018, Orlando, USA	CRU Ryan`s Notes Ferroalloys Conference 2018
11-13 November 2018, PORTUGAL	34th International Ferroalloys Conference
Date & Place	**Other Events**
5-8 November 2018, Montevideo, URUGUAY	11th International Vanadium Symposium

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