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The effect of nitrogen and vanadium on hardenability of medium carbon 0.4 %C and 1.8 %Cr steel

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ABSTRACT

Purpose: To investigate the effect of V and N on hardenability of steel containing 0.4 % C and 1.8 % Cr.

Design/methodology/approach: Four laboratory melts with different N and V contents were used. Hardenability of steel was investigated using standard Jominy test and Grossmann analytical method. The effect of calculated undissolved carbonitride V(C,N) content on austenite grain size was investigated.

Findings: Nitrogen addition without microalloying elements increased the austenite grain size. Very high hardenability was obtained in steel containing 0.004 %N and 0.08 %V at 870°C. Addition of 0.08 %V at elevated nitrogen content significantly decreased the grain size and at 870°C increased the hardenability of steel.

Practical implications: Investigated steel showed very high hardenability with ideal critical diameter DiJ approximately 200 mm, at appropriate austenitizing temperature. Higher nitrogen content in steel with vanadium addition retards austenite grain growth in broad austenitizing temperature range.

Originality/value: Results of investigations provide valuable information on the effect of vanadium and nitrogen content on the hardenability of quenched and tempered steel with 1.8 % Cr. Thermodynamic calculations enable to select the optimum austenitizing temperature range.

Keywords: Manufacturing; Hardenability of steel; High strength low alloy steels; Quenched and tempered steels; Microalloying elements

MATERIALS

1. Introduction

Hardenability is a very important property of quenched and tempered steels. The microstructure formed during decomposition of undercooled austenite, which determines the mechanical properties of heat treated steel strongly depends on the hardenability. The main factors influencing the hardenability of steels are: chemical composition of steel, austenite grain size, uniformity of chemical composition of austenite and content of undissolved non-metallic inclusions. Except cobalt, all elements dissolved in austenite increase the hardenability. There is little information concerning the effect of nitrogen on hardenability of steel [1]. Most data shows the detrimental effect of nitrogen on hardenability [2, 3] but it may be due to the low content of dissolved nitrogen in austenite which is mostly combined in nitrides and carbonitrides at conventional austenitizing

Table 1.
Chemical compositions of experimental steels (wt-%)

Melt	C	Mn	Si	N	Ti	V	Nb	Cr	Al	P	S	Fe
N1	0.39	0.91	0.28	0.0038	0.012	<0.004	<0.006	1.92	0.006	0.008	0.006	Bal.
V-N1	0.41	0.94	0.27	0.0047	0.016	0.075	<0.004	1.98	0.020	0.009	0.007	Bal.
N2	0.38	0.97	0.29	0.032	0.003	<0.004	<0.004	1.84	0.009	0.009	0.006	Bal.
V-N2	0.36	0.93	0.27	0.0412	0.003	0.078	<0.004	1.88	0.013	0.009	0.006	Bal.

temperature. Particles of these compounds decrease the austenite grain size, what can decrease the hardenability because increasing the austenite grain boundaries area as well as area of interphase boundaries austenite/compound and thus increasing the rate for nucleation of diffusional products during austenite decomposition. But inhibiting austenite grain growth by undissolved nitrides and carbonitrides can be useful for final mechanical properties of heat treated steel. Moreover, some data shows [2, 3], that inhibition of austenite grain boundaries can create conditions for segregation of dissolved elements on immobiled boundaries and decreasing their surface energy. This may improve the hardenability in way similar to effect of boron [4, 5].

In order to control the austenite grain size the microalloying elements such as V, Nb and Ti, showing high chemical affinity to interstitial elements, C and N, are added. Morover in steel is always present Al, which form nitride, AlN. Microalloying elements form carbides, MC and nitrides, MN. These compounds have similar lattice what results in their mutual solubility and formation of carbonitrides with composition and dissolution temperature, dependant on chemical composition of steel [6, 7].

In work [8] the increase of the hardenability of steel containing 0.3% C and 2% Cr with increasing nitrogen content and microalloying additions of Ti, Nb, V and Al was reported.

In microalloyed steel the austenitizing temperature is a very important factor, influencing hardenability and final mechanical properties. Too low temperature results in low hardenability because of excess of undissolved compounds favouring nucleation for diffusional products of austenite decomposition whilst too high temperature may result in austenite grain growth and decrease of mechanical properties of heat treated steel.

The aim of present work was to investigate the effect of nitrogen and microalloying element V, on the hardenability of steel containing 0.4%C and 1.8%Cr.

2. Materials and experimental procedures

Four casts were air melted in laboratory induction furnace and poured at temperature 1515-1520°C [9]. The ingots were surface dressed and hot rolled to 30 mm square bars. The bars were annealed in argon atmosphere at 900°C for 1 h with subsequent air cooling. The experimental steels contained 0.36/0.41% C and 1.85/1.98%Cr with different amounts of V and N. All compositions and percentages quoted in the present work are in weight % unless otherwise stated. The chemical compositions of the steels are presented in Table 1. Two melts – N1 and N2 – contained different amount of nitrogen (0.0038 and 0.032%) with trace amount of vanadium and two melts – V-N1 and V-N2 – contained different amounts of nitrogen (0.0047 and 0.0412%) with similar content of vanadium (0.075 and 0.078%). Melts N1 and V-N1 contained 0.012 – 0.016% Ti, whilst in N2 and V-N2 this content was in the range 0.003%. The effect of vanadium and nitrogen on hardenability of steels was determined in relation to the hardenability of the base melt N1 with low nitrogen content.

Jominy hardenability tests were carried out according to a standard procedure [10]. Standard Jominy specimens were austenitised in argon atmosphere for 30 min. at temperatures in the range 840-970°C. The austenitizing time was measured from when specimen reached the austenitizing temperature according to the couple placed near the specimen. One specimen was end quenched for each heat treatment condition. Hardness profiles, using Rockwell hardness tester, scale C, were measured on parallel flats ground to a depth of 2 mm to avoid any decarburisation, and mean hardness profile was then used for assessing the hardenability.

After hardness testing, a section of 20 mm long from the quenched end of Jominy specimen was removed for metallographic examination. The prior austenite grain size was measured after etching specimens for 15-30 min at room temperature in saturated aqueous picric acid solution containing 10 mL wetting agent. The mean linear chord length l of austenite grain size was measured using computer program SigmaScan Pro [11] on ~500 grain intercepts for each specimen. The mean chord length was converted to ASTM grain size number, GS.

The ideal critical diameters were calculated using two methods: Grossmann analytical method and his multiplying formula and using hardenability curves. These parameters were notified as D_i and D_{iJ} respectively. For calculation of D_i the data provided by Kramer at. al. [12] were used except for multiplying factor for Mn. For Mn the data of De Retana and Doane [13] were used, because of such combination of applied data resulted in best agreement of values of D_i and D_{iJ} for base melt N1. In calculation of D_i the contents of nitrogen and microalloying elements were omitted

The ideal critical diameters D_{iJ} of the steels were estimated using the measured Jominy distances to the 50 % martensitic point. The positions for 50 % martensite on the Jominy specimens, $x_{50\%}$ were determined using the Hodge and Orehoski relationships between hardness, carbon content and amount of martensite [14] adding 3 HRC for this hardness because in chromium steel in ferrite the dispersion hardening effect by chromium carbide is possible. As it was described in [3], the distance of $x_{50\%}$ values were corrected to constant quenching temperature of 840°C, using Jackson and Christenson data [15]. The ideal critical diameters D_{iJ} of investigated steels were determined from the corrected distances, x_{cor}, using conversion curve presented by Grossman [16] and corrected by Jatczak for distances above 50 mm [17], using the following equations:

$$D_{iJ} = 6.7 \cdot x_{cor} \qquad (1)$$

for: x_{cor}<8 mm

$$D_{iJ} = 5.1130 + 7.4350 \cdot x_{cor} - 0.1807 \cdot x_{cor}^2 + \\ + 2.7264 \cdot 10^{-3} \cdot x_{cor}^3 - 1.67 \cdot 10^{-5} x_{cor}^4 \qquad (2)$$

for: $8 \le x_{cor} \le 50$ mm

$$D_{iJ} = -46.07 + 7.0998 \cdot x_{cor} - 0.07165 \cdot x_{cor}^2 + \\ + 2.523 \cdot 10^{-4} \cdot x_{cor}^3 \qquad (3)$$

for: $x_{cor} > 50$ mm, where D_{iJ} and x_{cor} are both expressed in mm.

In order to estimate the effect of nitrogen and vanadium on hardenability the ideal critical diameters were further corrected to a common prior austenite grain size of GS=8 and to the chemical composition of a base melt (melt N1). The correction was carried out using data such as for D_i calculation.

Two measures of nitrogen and microalloying elements effect on hardenability of investigated steels were used. The first, parameter f_1 was expressed by the ratio of D_{iJ} and D_i and second - f_2 - by equation:

$$f_2 = \frac{D_{iJc}}{D_{iJc}^{base}} \qquad (4)$$

where: D_{iJc} is the ideal critical diameter of microalloyed steel corrected to austenite grain size number GS = 8 and chemical composition of base steel and D_{iJc}^{base} is the ideal critical diameter of base melt corrected to GS = 8.

All above estimations were carried out using developed computer program, of which details are given elsewhere [18].

In order to calculate the chemical composition of austenite at austenitizing temperature as well as the volume fraction of undissolved carbonitride M(C,N) and aluminium nitride AlN the thermodynamic model for the system Fe-M’-M’’-M’’’-Al-C-N was used [6, 7]. Because of low content of Ti and Nb in investigated steels resulted in low dissolved content of these elements in austenite in further text only effect of dissolved vanadium and aluminium contents on hardenability of steel is discussed. Also at applied austenitizing temperatures range the chemical composition of carbonitride was close to V(C,N).

3. Results

Results of quantitative analysis of austenite grain size with calculated total volume fractions of undissolved carbonitride V(C,N) and nitride AlN of investigated steels are shown in Table 2.

Example of microstructures with revealed prior austenite grain boundaries for temperature 970°C is shown in Fig. 1.

The effect of austenitizing temperature on mean chord lengths is presented in Fig. 2.

The lowest austenite grain size in austenitizing temperature range showed melt V-N2, for which the mean chord length of austenite grains was in the range 5.44 – 6.65 μm. The highest austenite grain size showed melt N2 with mean chord length in the range 9.91 – 26 μm. It is worthy to emphasize, that larger changes of austenite grain size was observed in the range of 840 - 870°C whilst over 870 to 970°C change of austenite grain size was insignificant.

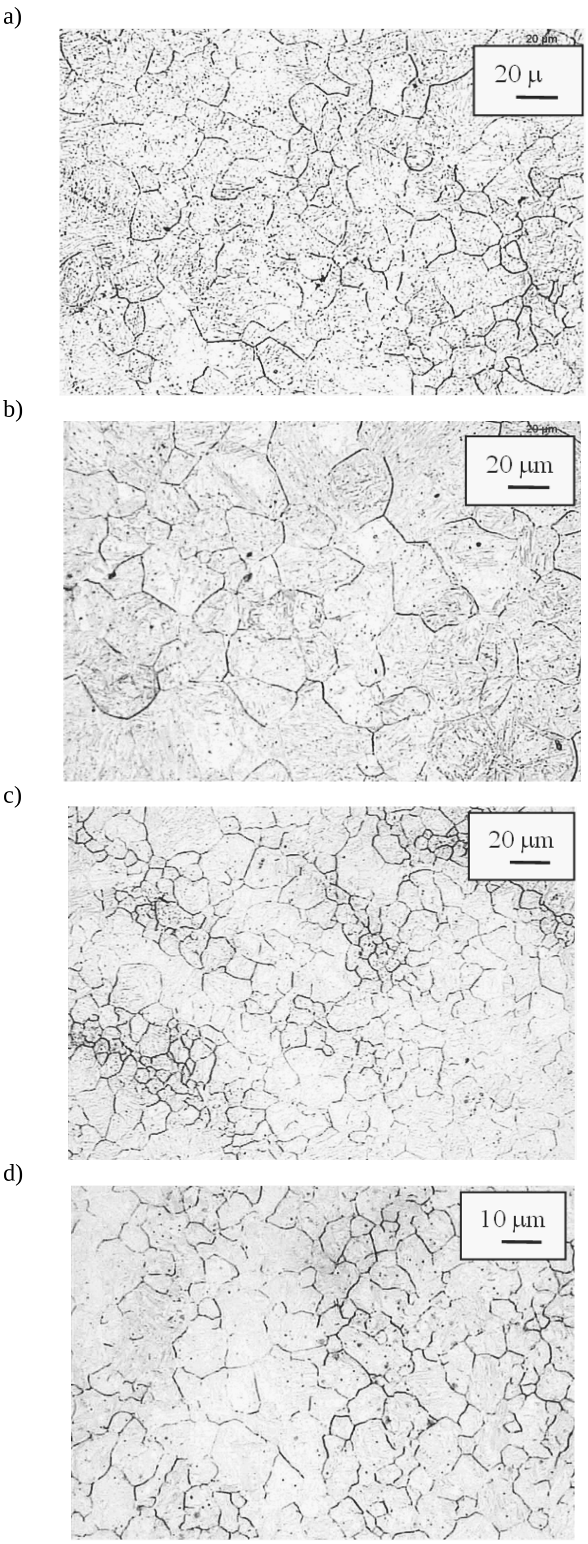

Fig. 1. Examples of microstructures with revealed austenite grain boundaries for austenitizing temperature of 970°C, a) N1, b)N2, c) V-N1, d) V-N2

Table 2.
Data of mean chord lengths, l, austenite grain size number, GS and calculated of total volume fractionV_v of carbonitride V(C,N) and nitride AlN

T, ^{0}C	melt	l, µm	GS	Vv,%
840	N1	9.91	9.93	0.056
	N2	12.08	9.36	0.0458
	V-N1	6.19	11.28	0.177
	V-N2	5.44	11.66	0.2826
870	N1	16.04	8.54	0.0552
	N2	25.95	7.16	0.0424
	V-N1	11.77	9.43	0.1178
	V-N2	5.43	11.66	0.2675
970	N1	15	8.74	0.0507
	N2	25.67	7.19	0.0271
	V-N1	10.46	9.77	0.0679
	V-N2	6.65	11.08	0.1856

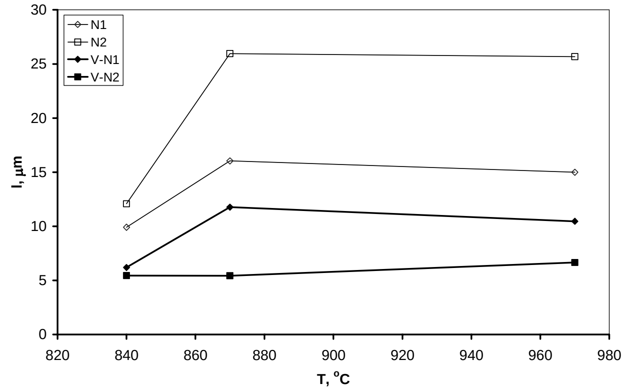

Fig. 2. Relationship between mean chord length and austenitizing temperature

The effect of calculated contents of carbonitride, V(C,N) and nitride, AlN, on the mean chord length is shown in Fig. 3. The data show some scatter but it is visible the tendency of austenite grain size decrease with increasing total volume fraction of undissolved carbonitride V(C,N) and nitride AlN.

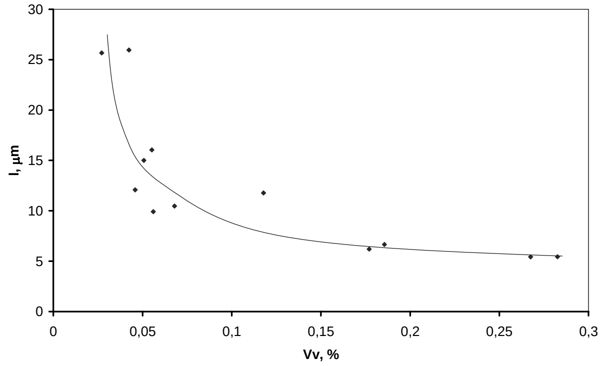

Fig. 3. Relationship between mean chord length of austenite grains and calculated volume fraction, V_v, of undissolved V(C,N) and AlN

The hardenability parameters of investigated steels with calculated content of vanadium, [V] and aluminium, [Al], dissolved in austenite (notified as [M]) are given in Table 3.

Depending on the composition of steel and austenitizing temperature the hardenability parameters show significant differences. Ideal critical diameters, D_{iJ}, estimated directly from Jominy curves are in the range 75.6 mm to 198.4 mm. The highest hardenability showed melt V-N1, quenched from 870°C. In this case almost all hardness data on the length of Jominy curves were placed over HRC_{50}, what means, that Jominy specimen was fully hardened. After corrections of D_{iJ} to base composition and constant austenite grain size of GS = 8 the values of ideal critical diameters were in the range 101.1 – 220 mm. Calculated multiplying factors, f_1 and f_2 showed close values, what supports the credibility of data used for hardenability analysis. Multiplying factors, f_2, expressed the combined effect of vanadium and nitrogen on hardenability of steel were in the range 0.59 to 1.28.

Table 3.
Hardenability parameters of investigated steels and content of dissolved [V]+[Al]=[M]

T, ^{0}C	melt	HRC_{50}	x_{50},mm	x_{cor},mm	D_{iJ}, mm	D_{iJc}, mm	D_{iJk},mm	D_i,mm	f_1	f_2	[M], %
840	N1	44.3	49.9	49.9	158.7	158.7	180.8	155.9	0.96	1	0.0093
	N2	43.8	34.1	34.1	133.1	133.1	145.0	163.0	0.72	0.75	0.0031
	V-N1	45.2	41.9	41.9	146.4	146.4	169.5	153.3	0.91	0.95	0.0629
	V-N2	42.8	15.8	15.8	86.9	86.9	116.8	132.1	0.57	0.59	0.0101
870	N1	45.3	50.4	52.0	159.5	164.6	171.4	170.6	0.95	1	0.0096
	N2	44.8	37.4	38.5	139.0	140.9	134.2	186.4	0.75	0.79	0.0042
	V-N1	46.2	95.9	98.8	198.4	199.2	203.7	173.6	1.14	1.18	0.0802
	V-N2	43.8	50.1	51.6	159.0	164.1	220.6	132.0	1.22	1.28	0.0147
970	N1	45.3	60.9	71.2	177.2	186.9	197.0	168.5	1.05	1	0.0114
	N2	44.8	41.1	48.0	145.2	155.9	148.7	186.1	0.79	0.76	0.0093
	V-N1	46.2	70.8	82.7	186.7	193.7	202.6	169.8	1.1	1.02	0.0951
	V-N2	43.8	35.4	41.3	135.5	145.5	187.8	137.5	0.99	0.96	0.0399

The effect of austenitizing temperature on ideal critical diameter, D_{ijk}, is presented in Fig. 4. In austenitizing temperature range steel N2 with higher content of N and without microalloying elements has lower ideal critical diameter, D_{ijc}, in comparison with steel N1 with lower amount of nitrogen. At 840°C both vanadium microalloyed steels, V-N1 and V-N2 shows lower hardenability in comparison with non-microalloyed steels with similar N content. The difference between miroalloyed and non-amicrolloyed steels is much bigger for elevated nitrogen content.

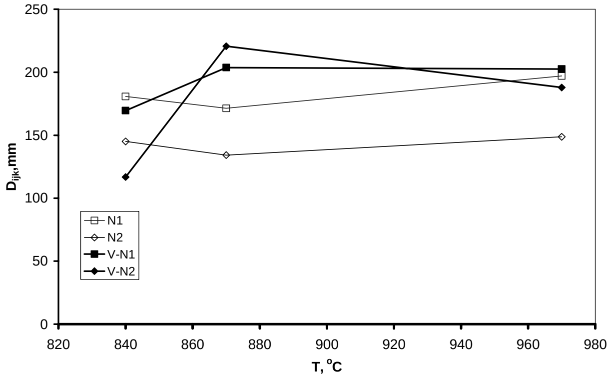

Fig. 4. The effect of austenitizing temperature on ideal diameter of investigated steels

The effect of total vanadium and aluminium content, dissolved in austenite on ideal critical diameter is demonstrated in Fig. 5.

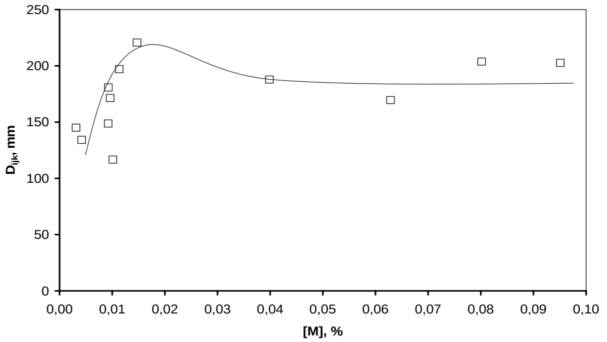

Fig. 5. The effect of calculated dissolved microalloying elements, [V]+[Al]=[M], on ideal critical diameter D_{ijk}

4. Discussion of results

Vanadium is common microalloying element in high strength low alloy steel, used to control the austenite grain growth and increasing their mechanical properties because of precipitation strengthening effect. Its effect depends on the chemical composition of steel, especially on nitrogen content.

There is little data on the effect of nitrogen on hardenability of quenched and tempered constructional steels [1, 8]. There are some evidence, that nitrogen itself in pure carbon steel increases the hardenability but in presence of nitride forming alloying elements it can decrease the hardenability because combining alloying elements and thus decreasing their potential as hardenability agents. Present investigations show, that in 0.4% C steel containing 1.8% Cr nitrogen decreases hardenability in investigated austenitizing temperature range of 840 – 970°C, although it increases the austenite grain size. It can be explained that nitrogen forms chromium nitrides, and these precipitations enable the nucleation for diffusional products of undercooled austenite decomposition, with lower dissolved Cr content. Results of investigations show, that the effect of vanadium on hardenability depends on nitrogen content as well as on austenitizing temperature. At 840°C for steel with low and high nitrogen content the vanadium addition results in decrease of hardenability and this effect is more pronounced with higher nitrogen content. For steels V-N1 and V-N2 the multiplying factors f_2 were 0.95 and 0.59. This effect is due to high undissolved carbonitride content. With increasing austenitizing temperature to 870°C quite significant increase of is hardenability of vanadium alloyed stels is observed and multiplying factors for V-N1 and V-N2 steels reach value of 1.18 and 1.28. These effects can be related to substantial dissolution of carbonitride and increase of dissolved vanadium [V] and aluminium [Al] content which effectively decrease the rate of austenite decomposition. Furher increase of austenitizing temperature results in slight decrease of multiplying factor to 1.02 and 0.96 at 970°C. Obtained results support the grain boundary pinning hipothesis of Garbarz and Pickering [2], according to which the increase of hardenability is due to the grain boundary pinning by carbonitride particles, which enables the dissolved vanadium (and other alloying elements) atoms to segregate to these immobile boundaries. Decrease in the grain boundary energy reduces their potential for the nucleation of non-martensitic products. Important evidence supporting the above hypothesis is shown in Fig. 5, presenting the relationship between ideal diameter, D_{ijk} and calculated content of [M]. The shape of curve is similar to the well known relationship between hardenability parameters and dissolved boron in austenite [4]. With addition of vanadium the hardenability of steel with higher nitrogen content can be increased at appropriate austenitizing temperature. Results of investigations show, that nitrogen in steel not containing microalloying elements increases the austenite grain size. It may be due to decrease of iron self diffusion coefficient for iron by nitrogen dissolved in austenite [19].

5. Conclusions

- Nitrogen decreased hardenability of non-alloyed steel in applied austenitizing temperature range;
- Nitrogen increased the austenite grain size of investigated steel;
- Addition of 0.075/0.078%V significantly influenced the hardenability of steel in a level depended on austenitizing temperature and nitrogen content;
- At 840°C vanadium microalloyed steels shows lower hardenability compare to base steel and multiplying factor f_2 was equal 0.95 and 0.59 for steel V-N1 and V-N2;

- Maximum hardenability effect of vanadium microalloyed steels was observed at 870°C and f_2 was equal 1.18 and 1.28 for V-N1 and V-N2 steels;
- Increase of austenitizing temperature over 870°C resulted in slight decrease of hardenability effect;
- Results of investigations support the Garbarz and Pickering hypothesis on the effect of immobile austenite grain boundaries for increasing the efficiency of microalloying elements as hardenability agents;
- Vanadium with elevated nitrogen content significantly decreased the austenite grain size in applied austenitizing temperature range.

Acknowledgements

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