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THE NITROGEN CONTENT EFFECT ON CARBONITRIDE COAGULATION IN 40Cr8 STEEL WITH MICRO-ADDITIONS V AND V + Al

WPŁYW ZAWARTOŚCI AZOTU NA KOAGULACJĘ WĘGLIKOAZOTKÓW W STALI 40Cr8 Z MIKRODODATKAMI V I V+Al

The work examines the effect of nitrogen and micro-additions V and V+Al on the austenite grain size and the coagulation of carbonitride precipitates in 40Cr8 steel. The analyzed materials underwent heat treatment consisting in holding the material at 1200°C for 1h, which was next exposed to furnace cooling down to 820°C and maintained at this temperature for 20hrs, and subsequently quenched in water. With the application of electron microscopy, the microstructure and the formed carbonitride precipitates were examined. The SigmaScanPro software was used to perform the quantitative metallographic analysis of the precipitates. The study demonstrated that increase in the content of nitrogen inhibits the coagulation rate of carbonitrides, whereas aluminium favours the tendency for coagulation and efficiently inhibits the austenite grain growth.

Keywords: Coagulation; Carbonitrides; HSLA steels

W pracy badano wpływ azotu i mikrododatków V, V+Al na wielkość ziarna austenitu oraz koagulację wydzieleń węglikoazotku w stali 40Cr8. Próbki z badanych wytopów poddano obróbce cieplnej polegającej na wygrzewaniu przy temperaturze 1200°C przez czas 1h, następnym chłodzeniem z piecem do temperatury 820°C i wytrzymaniu przy tej temperaturze przez czas 20h oraz chłodzeniu w wodzie. Przy wykorzystaniu mikroskopii elektronowej badano mikrostrukturę oraz powstałe wydzielenia węglikoazotku. Za pomocą programu SigmaScan Pro przeprowadzono ilościową analizę metalograficzną wydzieleń. Badania wykazały, że wzrost zawartości azotu hamuje szybkość koagulacji węglikoazotku, podczas gdy aluminium sprzyja skłonności do koagulacji i skutecznie hamuje rozrost ziarn austenitu.

1. Introduction

Such alloy micro-additions as V, Nb or Ti, introduced into microalloyed steels, characterize in high chemical affinity for carbon and nitrogen. In steel, they form stable compounds – carbides and nitrides and the products of their mutual solubility, that is carbonitrides. The formed precipitates significantly affect the microstructure of steel by inhibiting the growth of the austenite grains at high temperature and assuring a fine-grained microstructure of the transformation products of the supercooled austenite. The effectiveness of the precipitates as the inhibitors of austenite grain growth is influenced by the chemical composition of steel, which determines the stereological parameters of the precipitates: the mean particle radius r, and the volume fraction V_V. The dependence between the mean radius of the austenite grains, R_a, and the mentioned precipitate parameters (under conditions of thermodynamic equilibrium) is described by the Smith-Zener equation [1]:

$$R_a = \frac{4r}{3V_V} \qquad (1)$$

The above equation implies that the degree of refinement of the microstructure formed during the cooling of the austenite increases with the decreasing sizes of the formed precipitates and their increasing volume fraction. At higher temperature, the precipitate particles can increase their size as a result of the coagulation process. In consequence, they become ineffective as the inhibitors of the austenite grain growth. The process of the precipitate coagulation is described by the Lifschitz-Slyozov–Wagner equation [2,3]:

$$r^3 - r_0^3 = \frac{8Dc_0\gamma V_m^2}{9RT}t \qquad (2)$$

where: r_0, r – mean initial and after holding time, t, radius, R – gas constant, T – temperature, D, c_0 – diffusion coefficient and concentration of the element controlling the rate of particles coagulation in austenite, γ – energy of interface: austenite–carbonitride, V_m – molar volume of precipitates.

The more rapid the coagulation process, the less effective are the precipitates as the inhibitors of the austenite grain growth. As is implied by equation (2), the rate of the precipitate coagulation is affected by several factors. The most important one is the concentration of the substituting element in the austenite, c_0, which is part of the composition of the precipitates. The higher its concentration in the austenite, the

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TABLE 1

Chemical composition of steels, %mass

steel	C	Mn	Si	N	Ti	V	Nb	Cr	Al	P	S
VN1	0,41	0,94	0,27	0,0047	0,016	0,075	<0,004	1,98	0,020	0,009	0,007
VN2	0,36	0,93	0,27	0,0412	0,003	0,078	<0,004	1,88	0,013	0,009	0,006
VAlN2	0,40	0,92	0,26	0,0362	0,001	0,079	<0,004	1,85	0,060	0,010	0,006

more significant tendency for coagulation. Lowering the concentration of the substituting element at a given temperature T can be achieved by the content increase of the non-metallic element which is part of the precipitate composition. It is worthy to emphasize, that main parameters influencing on the austenite grain size (volume fraction V_V of precipitates inhibiting austenite grain growth) and rate of precipitation coarsening (concentration, c_o, of the element controlling the coagulation rate in austenite) can be calculated using a thermodynamic model [4-7].

The aim of the investigations was to analyze the effect of nitrogen on the austenite grain size and the precipitate coagulation of 40Cr8 steel with micro-additions V and V+Al, after a long-term austenitizing at high temperature.

2. Material and investigations methodology

The investigating material were three laboratory melts of 40Cr8 steel with different contents of nitrogen (0,0047-0,0412%), containing micro-additions: V and V+Al. The examined steels were denoted by the following symbols: VN1, VN2 and VAlN2, which demonstrate the alloy element content (V, Al) and a low or high content of nitrogen (N1 and N2, respectively). The chemical composition of the investigated steels is given in Table 1. Work [8] presents the parameters of the technological production process of the examined steels. The preliminary heat treatment of the steels included homogenizing and normalizing annealing of 40×40×110 mm bars. The homogenizing annealing was performed at 1200°C for the period of 4hrs (furnace cooling), and the normalizing annealing was carried out at 870°C for 30mins followed by air cooling. Both annealing processes operated in the protective atmosphere of argon. The performed initial heat treatment aimed at the homogenization of the chemical composition of the materials, the elimination of the alloy element segregation and the refinement of the coarse-grained microstructure formed as result of the long-term holding at high temperature.

Then 20×20×15 mm samples were cut off the heat treated bars and next they underwent the main heat treatment. The latter included austenitizing at 1200°C for 1h, furnace cooling down to 820°C and holding at that temperature for 20hrs, followed by water cooling. The scheme of the preformed heat treatment is presented in Figure 1.

2.1. Methodology of investigations

2.1.1. Austenite grain size analysis

For each steel, metallographic microsections were made, which were then etched with saturated water picric acid with the addition of an agent reducing the surface tension, which aimed at the revealing of the grain boundaries of the former austenite. The microstructure observation was performed with the use of a Leica light microscope. For each steel, a series of images was taken, which were then used in the examinations of the austenite grain size, performed with the application of the SigmaScan Pro software [9]. On the microstructure image of each steel, approximately 50 secants (test lines) were plotted,
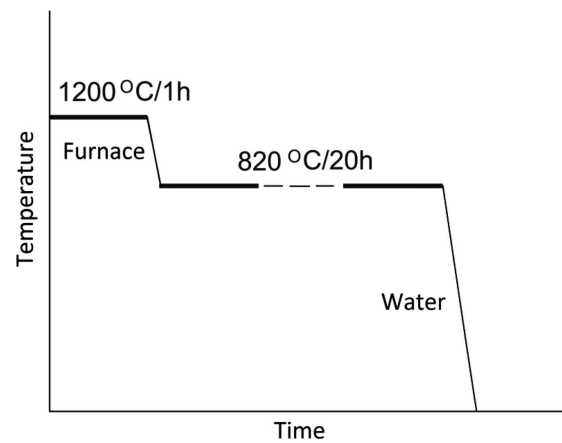

Fig. 1. Scheme of the performed heat treatment

which crossed from 1383 to 1511 grains, N_{grain}, and chords length were measured. The obtained results were used to determine: the mean length of chords $\bar{l}$, the standard deviation $s(l)$ and the variation coefficient, $v = s(l)/\bar{l}$. Also determined was the limiting measurement error δ, for the confidence level of $1-\alpha = 0,95$. On the basis of the formula:

$$GS = 16,54 - 2,88 \ln(\bar{l}) \qquad (3)$$

the mean chords length $\bar{l}$ (in μm) was recalculated to the grain size number GS according to the ASTM scale (for practical reasons). For each steel, empirical cumulative distribution functions, $F(l)$, of the linear fractions, L_L of the length of austenite grain chords were made.

2.1.2. Microstructure and precipitate analysis

The analysis of the microstructure and precipitates of carbonitrides was performed with the use of transmission electron microscopy. For each steel, thin foils and double-sided extraction replicas were prepared, which were then observed under a JEM 200CX by JEOL transmission microscope.

One 1 mm-thick slice was cut off each heat treated sample with the use of a diamond blade saw. The slices were grounded with abrasive papers until the thickness of the order of 0,07 – 0,1 mm was obtained. 3 mm-diameter disks were cut out

of the slices, which were then used to make thin foils and double-sided extraction replicas. The disks assigned for thin foils were electrolytically polished with the application of a double-stream grinder by Struers. Acetic acid and perchloric acid solution in the ratio of 10:1 were used as the electrolyte. The disks assigned for the replicas were electrolytically sheared till the thickness of 0,03 – 0,04 mm was reached. After the shearing process, the disks were vacuum coated with a carbon layer and placed in a 10% solution of bromine in ethanol for approximately 20 hrs, with the aim of dissolving the metal matrix. Next, the replicas were rinsed successively in: ethyl alcohol, a 10% HCl solution in ethyl alcohol and a mixture of 60% ethyl alcohol + 40% of distilled water.

2.2. Quantitative metallography of precipitates

In the quantitative analysis of the carbonitride precipitates, the double-sided extraction replicas were applied. For each steel, series of images was performed, which recorded from 277 to 1009 precipitates. With the use of the SigmaScan Pro software [9], the Feret diameter, d, of precipitates was measured. On the basis of the obtained results, the mean values of d, the standard deviation $s(d)$ and the variation coefficient, $v = s(d)/\bar{d}$ were calculated. Also determined was the limiting measurement error δ, for the confidence level of $1-\alpha = 0,95$. In addition the empiric cumulative distribution functions, $F(d)$, were made.

3. Results of investigations

Figure 2 presents examplary images of the steels microstructure with the revealed grain boundaries of the former austenite. Steels VN1 and VN2 characterized in a homogeneous distribution of grains. In the case of steel VAlN2, one could observe clusters of very fine grains present next to very large grains. Table 2 compiles the results of the grain size analysis of the former austenite. The finest grain was stated for steel VAlN2, which contained a higher amount of nitrogen (0,0362%) and an Al addition. The mean length of the austenite grain chords of this steel equaled 32,76 μm (GS=6,5) and it was much smaller than in the case of steel VN2 (101,94 μm, GS=3,2), which contained a smaller amount of Al than steel VAlN2.
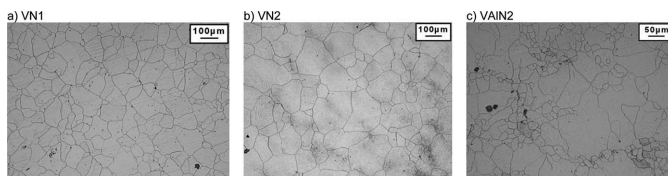

Fig. 2. Examples of microstructures with revealed grain boundaries of former austenite

The empiric F(l) distribution functions are presented in Fig. 3. The distribution functions are different but significant difference between distribution curve for VAlN2 and rest of steels is visible.
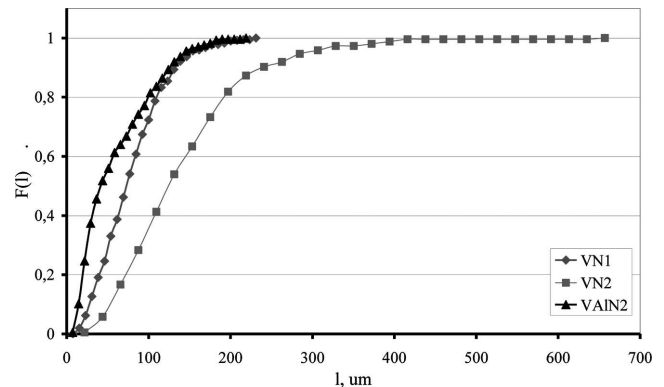

Fig. 3. Empiric distribution functions F(l) of linear fractions L_L of austenite grain chords length

The electron microscopic analysis of the microstructure of the investigated steels shows it martensitic character (Fig. 4), (α martensite). Figure 5 presents the examples of the precipitates recorded on the replicas. The diffraction analysis confirms the VC type of the precipitates (Fig. 6).
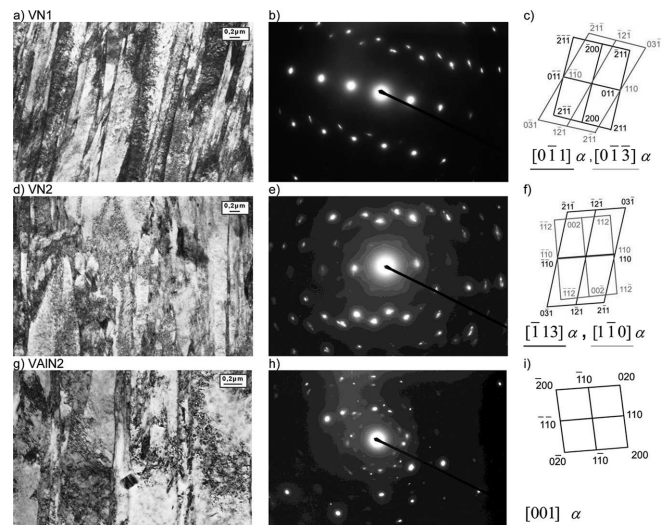

Fig. 4. Images of microstructures (a, d, g), diffraction patterns (b, e, h) and solutions of diffraction patterns (c, f, i) of steels VN1 (a, b,c), VN2 (d, e, f) and VAlN2 (g, h, i)
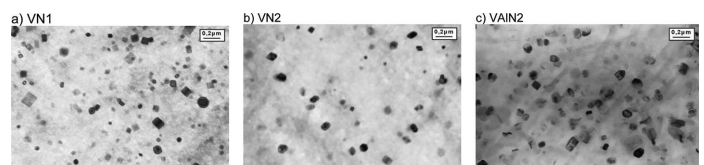

Fig. 5. Images of carbonitride precipitates recorded on extraction replicas

TABLE 2

Results of grain size analysis of the former austenite

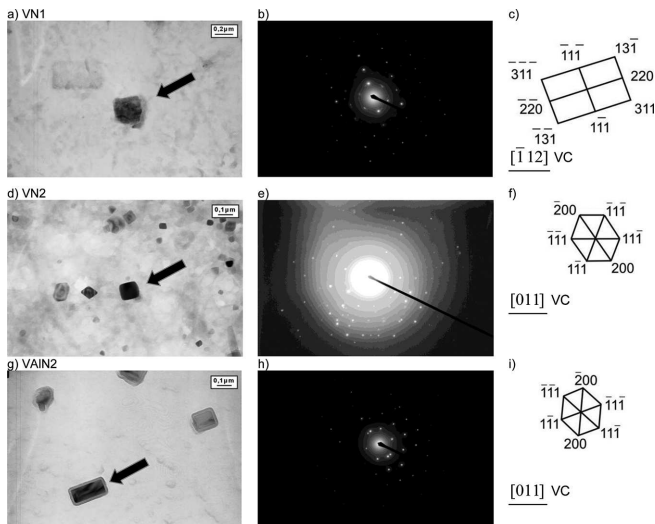| steel	N_{grain}	$\bar{l}, \mu m$	$s(l), \mu m$	v	$\delta, \mu m$	GS
VN1	1445	55,70	36,37	1,53	1,87	4,96
VN2	1383	101,94	65,00	1,57	3,42	3,22
VAlN2	1511	32,76	30,55	1,07	1,54	6,49

Fig. 6. Precipitate images (a, d, g), diffraction patterns (b, e, h) and solutions of diffraction patterns (c, f, i) of steels VN1 (a, b,c), VN2 (d, e, f) and VAlN2 (g, h, i)

Table 3 gives the analysis results of the mean Feret diameter $\bar{d}$, the standard deviations, $s(d)$, the coefficients of variation, $v = s(d)/\bar{d}$, and the measuring error δ.

TABLE 3

Results of precipitates size analysis of the carbonitride

steel	$N_{precipitates}$	$\bar{d}, \mu m$	$s(d), \mu m$	v	$\delta, \mu m$
VN1	1009	0,063	0,033	1,91	0,002
VN2	277	0,045	0,021	2,14	0,002
VAlN2	346	0,101	0,036	2,80	0,004

The largest precipitates were recorded for steel VAlN2. The mean Feret diameter for this steel equaled 0,101 μm. For steels VN1 and VN2, this quantity equaled 0,063 and 0,045 μm, respectively. The empiric $F(d)$ distribution functions are presented in Fig. 7.
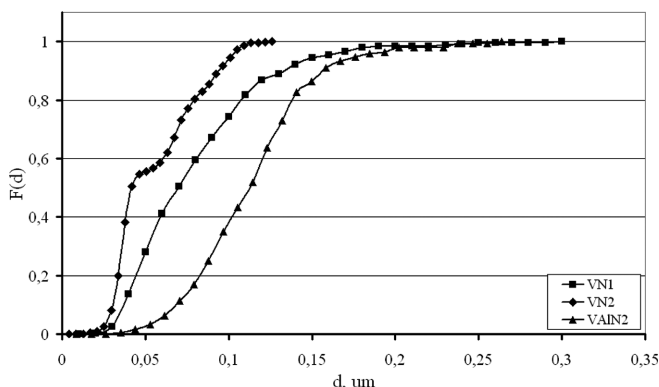

Fig. 7. Empiric distribution functions F(d) of precipitates Feret diameters

4. Discussion of results

The investigation results showed that the chemical composition of steel has a significant effect on the size of vanadium carobnitride precipitates V(C,N) and their tendency for coagulation at higher temperature. An especially strong effect on the precipitate size is observed in the case of nitrogen and aluminium contained in steel. The increase of the nitrogen content lowers the tendency for coagulation of V(C,N), as it decreases the amount of vanadium dissolved in the austenite. According to equation (2), one of the basic factors affecting the coagulation rate of the compound's precipitates under the given austenitizing conditions (temperature T, time τ) is the content of microalloying element dissolved in austenite, c_o, being part of the precipitates composition. This is because the rate of diffusion of metallic element, V, is lower in comparison with the rate of diffusion of interstitial elements (C,N). The content of the vanadium dissolved in the austenite is also affected by aluminium, as it bonds the nitrogen, forming AlN.

In the investigated steels, after a high temperature austenitizing at 1200°C and the following long-term holding at 820°C, the content of precipitates of the sizes below 50 nm equaled over 50% in steel VN2, whereas in steel VAlN2, it was lower than 5%.

The investigation results of the austenite grain size confirm the data from [10-13], according to which the nitrogen dissolved in the austenite affects the grain growth by lowering the activation energy of iron's self-diffusion. Thus for steel VN2 the austenite grain size is almost twice as big as that for steel VN1. The lowest austenite grain size was demonstrated by steel VAlN2. This material, however, also showed a disadvantageous phenomenon of an abnormal grain growth, connected with the fact that two types of grain growth inhibiting precipitates where present: carbonitride V(C,N) and nitride AlN. The former is dissolved at 1200°C. The non-dissolved AlN precipitates block parts of the austenite grain boundaries, ie., inhibits the austenite grain growth, which is the cause of the inhomogeneity of the austenite grains distribution in this steel.

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