H. ADRIAN[*], E. GŁOWACZ[*]

THE EFFECT OF NITROGEN AND MICROALLOYING ELEMENTS (V AND V+Al) ON AUSTENITE GRAIN GROWTH OF 40Cr8 STEEL

WPŁYW AZOTU I PIERWIASTKÓW MIKROSTOPOWYCH (V i V+Al) NA ROZROST ZIARNA AUSTENITU STALI 40Cr8

The effect of nitrogen and microalloying elements V and V+Al on austenite grain growth of steel containing 0,4 %C and 2 %Cr in austenitizing temperature range of 850-1200 °C and time range of 1 to 5h was investigated. Using a thermodynamic model the contents of undissolved vanadium carbonitride, V(C,N), and aluminium nitride, AlN, were calculated at austenitizing temperatures. Using Smith-Zener equation [1] and calculated undissolved carbonitride and aluminium nitride contents as well as austenite grain size, the mean radius, r, of precipitates was calculated. The size distributions of intercept length of austenite grains were analysed. Strong effect of nitrogen content on austenite grain growth of microalloyed steel was observed.

W pracy analizowano wpływ azotu oraz mikrododatków V i V+Al na wielkość ziarna austenitu stali zawierającej 0,4 %C i 2 %Cr w zakresie temperatur od 850 do 1200 °C, i czasu od 1 do 5 godzin. Za pomocą modelu termodynamicznego obliczono zawartość nierozpuszczonych wydzieleń węglikoazotku wanadu, V(C,N), oraz azotku aluminium, AlN, przy temperaturach austenityzowania. Na podstawie analizy wielkości ziarna austenitu i zawartości nierozpuszczonych wydzieleń V(C,N) i AlN, za pomocą równania Smith'a-Zener'a [1], wyznaczono rozmiar wydzieleń V(C,N) i AlN dla analizowanych czasów. Analizowano rozkłady długości cięciw ziarn austenitu. Zaobserwowano znaczący wpływ zawartości azotu na rozrost ziarn austenitu badanej stali mikrostopowej.

1. Introduction

Microalloying elements V, Nb, Ti and Al are used in high strength low alloy steels in order to prevent the austenite grain growth at elevated austenitizing temperatures and to decrease the grain size of product of transformations of undercooled austenite. Microalloying elements show high chemical affinity to carbon and/or nitrogen, and form carbides and nitrides. Because of the similarity of lattice structure of carbides, MC, and nitrides, MN, except AlN the carbonitrides, M(C,N), are formed as an effect of mutual solubility of carbides and nitrides. Their chemical composition and temperature of dissolution in austenite depends on the chemical composition of steel [2,3]. The precipitations of nitrides, carbides and carbonitrides inhibit the austenite grain growth at elevated austenitizing temperatures. The efficiency of inhibitors depends on the mean size of precipitations, r, and volume content, V_V, of undissolved compounds. The effect of stereological parameters of precipitations on the mean radius, R_a, of austenite grains is described by Smith-Zener equation [1]:

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

The austenite grain size, R_a, is low if precipitations have lower size, r, and their content is higher. On the efficiency of precipitations as austenite grain growth inhibitors strong effect exert their susceptibility to particle coarsening. The process of coarsening of precipitations is described quantitatively by the Lifschitz-Wagner equation [4,5]:

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

where: r, r_0 – average radius of precipitations after time of τ and τ_0; R, T – gas constant and absolute temperature; D, c_0 – diffusion coefficient and dissolved content of element controlling the coarsening process; γ – energy of austenite/precipitates interphase; V_m – molar volume of the precipitated compound.

[*] FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, 30-059 KRAKÓW, 30 MICKIEWICZA AV., POLAND

For austenitizing parameters, T and τ the rate of coarsening of precipitates depends on the diffusion coefficient of microalloying element and its dissolved in austenite content. Lower content, c_0, of microalloying element decrease the coarsening rate of precipitations at high austenitizing temperature. For decreasing the rate of precipitations coarsening in microalloyed steel higher content of nitrogen is used [6,8].

The aim of investigations was to analyse the effect of nitrogen content and microalloying elements V and V+Al on austenite grain growth in medium carbon low alloyed 40Cr8 steel using longer time of austenitizing at elevated temperatures.

2. Materials and experimental procedure

For investigations three laboratory melts of 40Cr8 steel were used. The chemical composition of steels is presented in table 1. The steels contained two level of nitrogen: 0,0047 and 0,036/0,041 % with different microalloying elements. Steel denoted as V-N1 contained 0,0047 %N and 0,075 %V, V-N2 contained 0,0412 %N and 0,078 %V. Steel V-Al-N2 contained simultaneous addition of 0,079 %V and 0,06 %Al with high content of nitrogen equal 0,0362 %. Details of the technological process of investigated steels production were described in [8].

TABLE 1

Chemical composition of investigated steel (% mass.)

Ozn.	C	Mn	Si	N	Ti	V	Cr	Al	P	S
V-N1	0,41	0,94	0,27	0,0047	0,016	0,075	1,98	0,020	0,009	0,007
V-N2	0,36	0,93	0,27	0,0412	0,003	0,078	1,88	0,013	0,009	0,006
V-Al-N2	0,40	0,92	0,26	0,0362	0,001	0,079	1,85	0,060	0,010	0,006

Bars with square section of 40x40 mm and 110 mm long were homogenized in electric furnace with argon atmosphere at 1200 °C for 4h following by slow cooling with furnace. After homogenizing bars were normalized at 870 °C for 30 min and air cooled. For investigation of the effect of temperature and time of austenitizing, series of samples of size 20x20x15 in mm were prepared. Then specimens were austenitized in temperature range of 850 - 1200 °C for 1h in order to investigate the effect of temperature on the austenite grain size. For investigation the effect of time of austenitization at elevated temperature on austenite grain size, series of samples were annealed at 1000 and 1100 °C for 3 and 5h. The austenitization was carried out in the argon atmosphere in order to avoid the decarbonization of surface. Then, the samples were quenched in water. For microstructure investigation the metallographic microsections were prepared by grounding on abrasive papers of grades 150 to 2000 with following polishing of surface using the water suspension Al_2O_3. The polished surfaces were chemically etched in saturated water solution of picric acid with addition of softening agent. Optical light microscope Leica was used for observation of the etched samples surfaces. For each sample the series of images of microstructure were recorded in order to perform the quantitative analysis using the computer program SigmaScan Pro [9]. The austenite grain size was estimated on the basis of measurement of the length of chords of the austenite grains cut by random secant superimposed on the microstructure image. For every sample was used about 50 secants, which cut N_g =600 - 2600 of austenite grains. On the basis of measurements the mean chord length, $< l >$, and standard deviation, $s(l)$, were calculated. The measuring error, δ, for α=0,05 (u_α=1,96) was estimated according to equation [10]:

$$\delta = u_\alpha \frac{s(l)}{\sqrt{N_g}}. \qquad (3)$$

For each sample the frequency (f) and cumulative (F) distribution of chord length of austenite grains were prepared. Using χ^2 test available in the computer program Statistica 6.0 [11], the empirical distributions of chord lengths were compared with theoretical distributions: logarithmic normal and gamma.

Using a thermodynamic model [2,3] the volume fraction V_V of undissolved in austenite vanadium carbonitride, V(C,N), and aluminium nitride, AlN were calculated for each austenitizing temperature, T. For the carbonitride and Al nitride particles the mean radius (r) was estimated by equation (1) for empirical V_V and $R_a = < l >$.

3. Results of investigations

Examples of microstructures of investigated samples with revealled prior austenite grain boundaries for temperatures 850, 1000 and 1200 °C and austenitizing time

1h are presented in Fig. 1. It is worthy to emphasize a very low austenite grain size of steel V-Al-N2 containing simultaneous additions of V and Al for temperatures up to 1100 °C. However, at 1200 °C the abnormal austen- ite grain growth in this steel was observed (Fig. 1i). The effect of temperature and time of austenitizing on the austenite grain size is presented in Fig. 2 and 3.
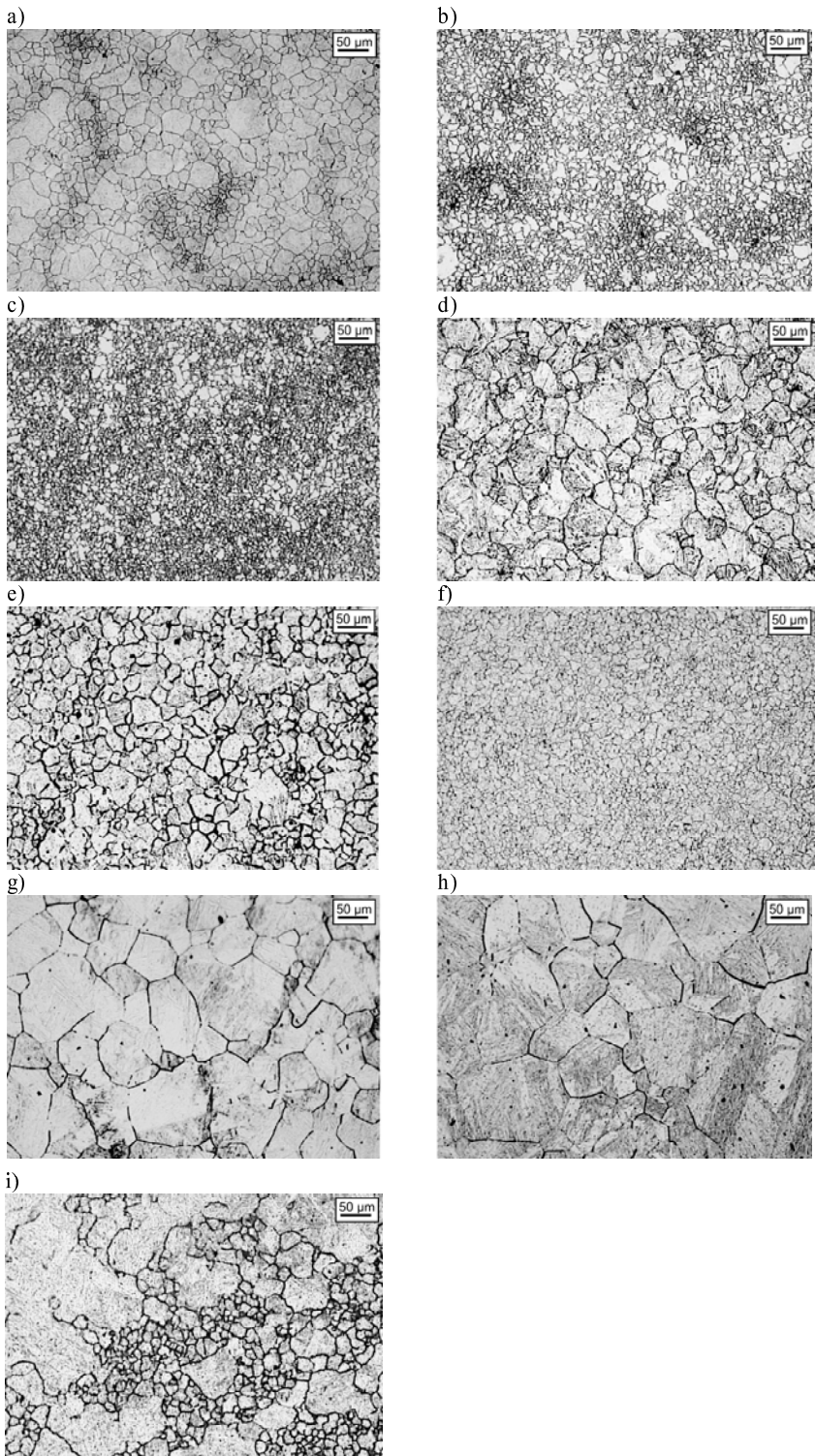

Fig. 1. Examples of microstructures with revealed austenite grains boundaries. Melt V-N1: 850 °C (a), 1000 °C (d), 1200 °C (g); Melt V-N2: 850 °C (b), 1000 °C (e), 1200 °C (h); Melt V-Al-N2: 850 °C (c), 1000 °C (f), 1200 °C (i); Austenitization time: 1h
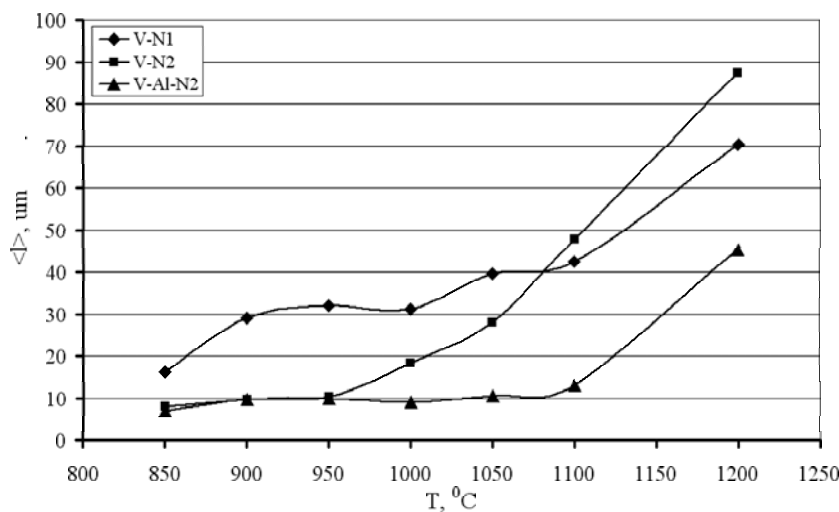
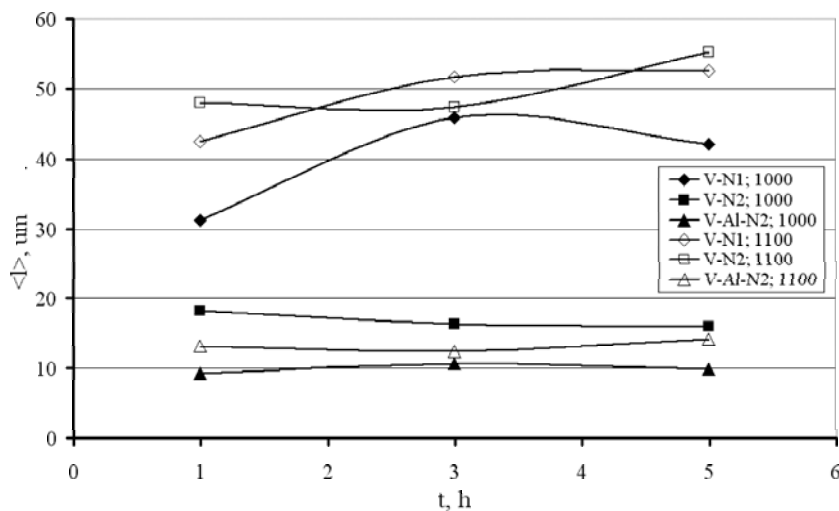Fig. 2. The effect of austenitizing temperature, T, on mean chord length, $< l >$, of austenite grains

Fig. 3. The effect of temperature, T, and time, t, of austenitization on austenite grain chord mean length, $< l >$, in steels V-N1, V-N2, V-Al-N2

Mean chord length of austenite grains at the austenitizing temperature range of 850 - 1200 °C for 1h was in the range: 16,3-70,5, 8,1-87,5 and 7,1-45,4 μm for steels V-N1, V-N2 and V-Al-N2, respectively. No significant effect of prolonged time of austenitizing at 1000 and 1100 °C on the austenite grain size was observed (Fig. 3). Results of calculation of the undissolved vanadium carbonitride, V(C,N) and aluminium nitride, AlN, as a function of austenitizing temperature is presented in Fig. 4. The effect of austenitization parameters on the calculated size of undissolved precipitations, r, is presented in Fig. 5. The calculated size of particles was in the range of 1 to 2,3 μm. The austenite chord length distribution for selected heat treatment parameters are presented in

Fig. 6. For comparison of the effect of austenitizing parameters on austenite grain size distributions, the data of investigated steels are placed in the same figures. Presented data show that austenite grain size of the steel V-N1 with low content of N is bigger in comparison with steels with higher nitrogen content at the temperatures up to 1000 °C. At 1100 °C higher austenite grain size show steel V-N2 compare to V-N1. For prolongated time of austenitzation the austenite grain size both steels are similar. At 1200 °C the steels V-N2 with high nitrogen content shows bigger austenite grain size in comparison with V-N1. Selected cumulative curves for linear fraction of chord length of austenite grains are presented in Fig. 7. It is worthy to emphasize the change of cumulative

curve for the steel V-Al-N2 at 1200 °C when abnormal austenite grain growth occurred. Comparative analysis of experimental distribution of chord length logarithmic normal and gamma distributions showed that most of the size distributions are close to the logarithmic normal distribution (27 cases from total number of 32). In the case of steel V-Al-N2 with abnormal grain growth none of the considered theoretical distributions describes experimental data. Results of χ^2 test for goodness of fit experimental and theoretical distributions are given in table 2.
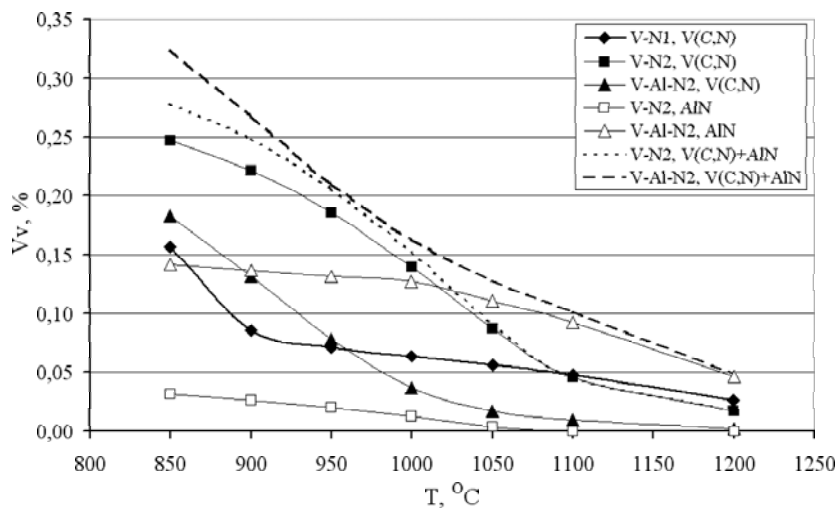

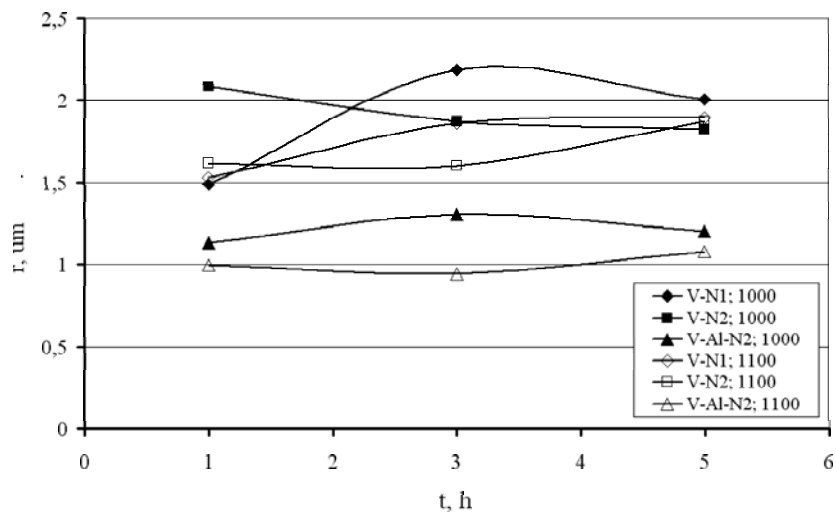Fig. 4. The effect of temperature on content of V(C,N) and AlN

Fig. 5. The effect of temperature and time of austenitization on mean radius of precipitations V(C,N) and AlN
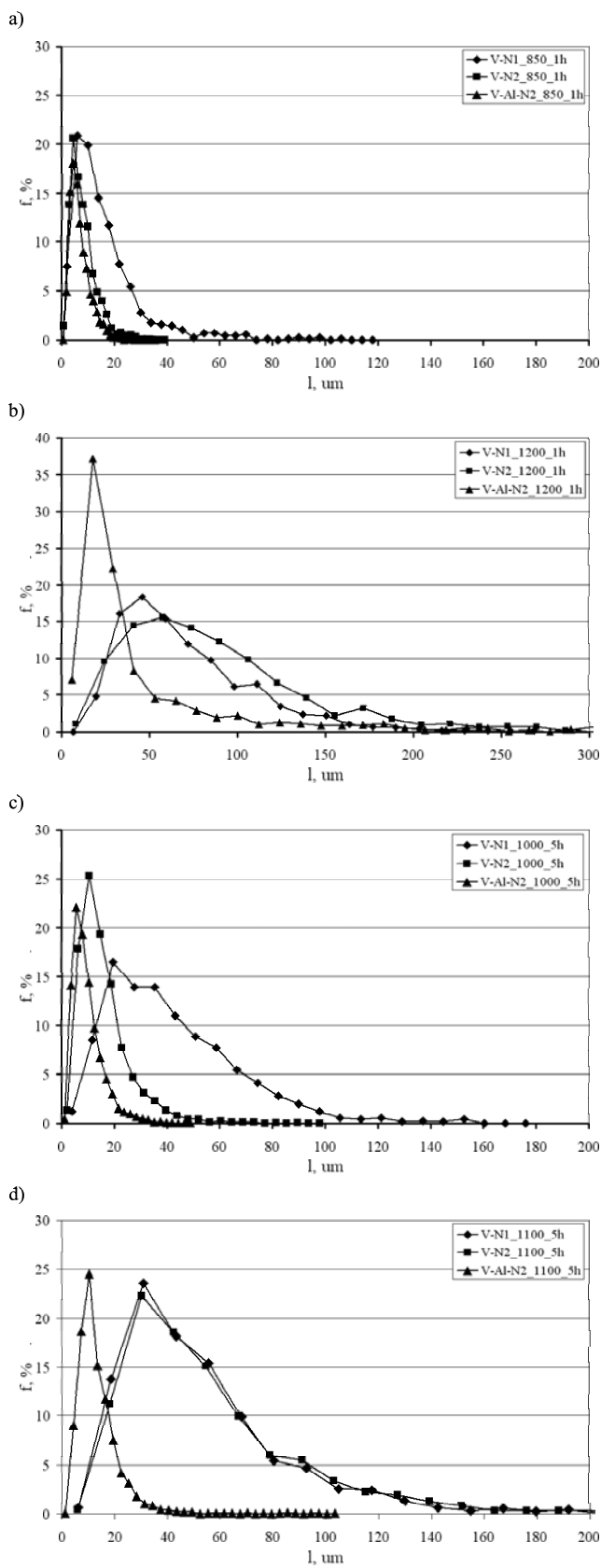
a)

b)

c)

d)

Fig. 6. Comparison of austenite grain chord length distributions after austenitization for 1h at temperatures: 850 °C (a), 1200 °C (b) and for 5h at temperatures: 1000 °C (c), 1100 °C (d)
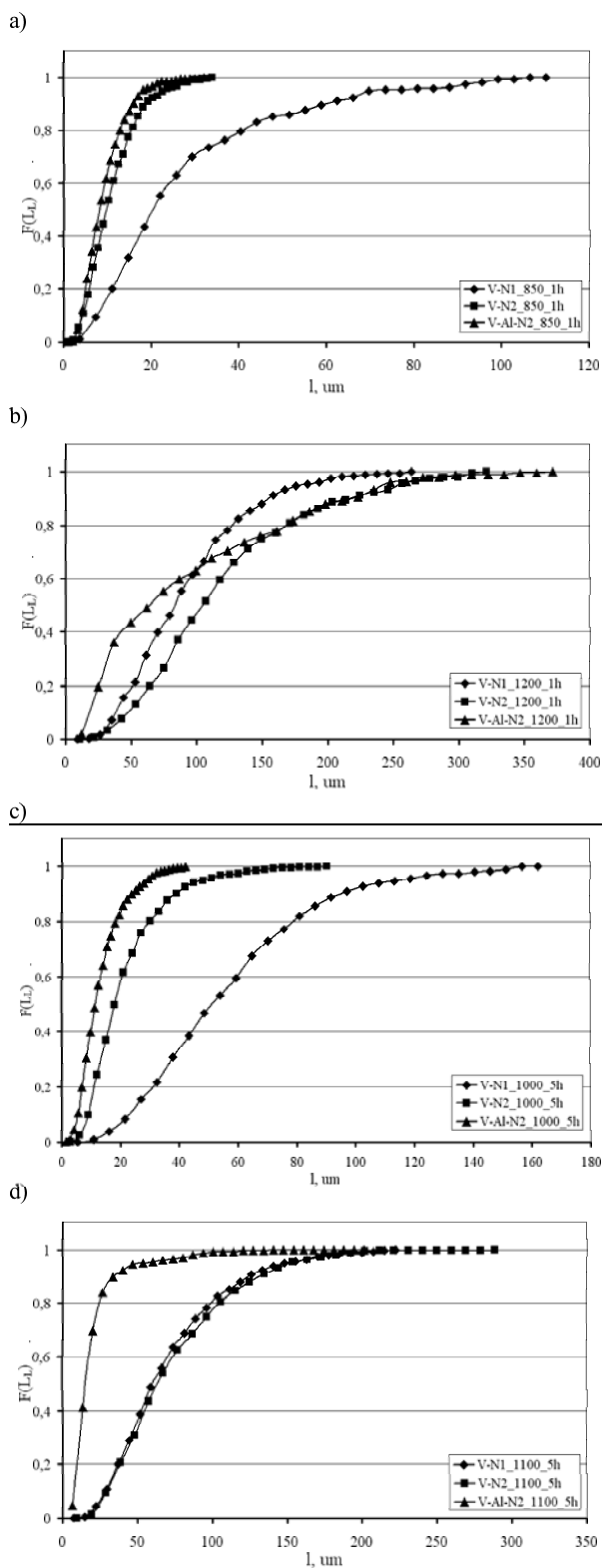
a)

b)

c)

d)

Fig. 7. Cumulative curves for linear fraction (L_L) distribution of austenite grain chord lengths for austenitizing temperatures: 850 °C (a), 1200 °C (d) for 1h and for austenitizing temperatures: 1000 °C (b), 1100 °C (c) for 5h

TABLE 2

Resluts of χ^2 test for goodness of fit of experimental and theoretical distributions of austenite grains chords lengths

Melt	Temp., °C	Time, h	Degrees of freedom	χ^2 for logarithmic normal	χ^2 for gamma	Better approximation
V-N1	850	1	14	13,25	89,35	Log-norm
	900		13	21,75	22,60	Log-norm
	950		14	17,03	36,96	Log-norm
	1000		14	22,77	33,67	Log-norm
	1050		14	23,34	19,24	Gamma
	1100		14	15,41	12,72	Gamma
	1200		14	23,51	76,74	Log-norm
	1000	3	13	21,19	41,92	Log-norm
	1100		14	15,59	39,25	Log-norm
	1000	5	14	32,27	21,80	Gamma
	1100		13	19,51	88,20	Log-norm
V-N2	850	1	13	20,70	54,31	Log-norm
	900		14	19,55	29,26	Log-norm
	950		13	20,43	23,34	Log-norm
	1000		14	15,84	78,93	Log-norm
	1050		14	17,78	76,03	Log-norm
	1100		14	17,60	72,15	Log-norm
	1200		14	15,51	22,04	Log-norm
	1000	3	14	18,40	162,42	Log-norm
	1100		14	22,37	91,82	Log-norm
	1000	5	13	20,63	193,00	Log-norm
	1100		13	18,98	78,95	Log-norm
V-Al-N2	850	1	14	11,56	57,94	Log-norm
	900		14	14,20	28,89	Log-norm
	950		14	15,33	53,80	Log-norm
	1000		13	15,47	17,52	Log-norm
	1050		14	12,36	68,95	Log-norm
	1100		14	19,93	70,99	Log-norm
	1200		14	220,98	581,29	none
	1000	3	14	20,39	42,80	Log-norm
	1100		14	12,69	30,76	Log-norm
	1000	5	14	18,36	141,34	Log-norm
	1100		14	71,07	199,76	none

4. Discussion of results

In high strength low alloy steels microalloying addition of vanadium is used in order to decrease the austenite grain size [12-14]. Additional effects of vanadium results in the hardenability increase and precipitation hardening of diffusional products of the austenite decom-

position. The effect of vanadium on austenite grain size depends on the chemical composition of steel, especially on the nitrogen content. The vanadium carbonitride, V(C,N), content as well as its dissolution temperature increase with nitrogen content. Also the coarsening rate of V(C,N) precipitations decrease with nitrogen content. Simultaneous addition of V and Al to steel with high nitrogen content should effectively decrease the austenite grain size because, apart carbonitride V(C,N), the aluminium nitride AlN is formed. However, total increase of metallic elements forming the austenite grain boundary pinning compound particles may affect the coarsening rate of precipitations (increase of c_0 in equation (2)). Results of the investigations of the effect of temperature and time of austenitizing show, that at temperatures up to 1100 °C simultaneous addition of V+Al effectively inhibit the austenite grain growth even at elevated time of austenitizing up to 5h. From it may be concluded that the addition V+Al does not affect the coarsening rate of V(C,N) and AlN precipitations and higher volume fraction of the compounds results in low austenite grain size. However, at high temperature, when one of the compound giving the grain boundary pinning effect is dissolved (V(C,N)) and second (AlN) is coarsened, the abnormal austenite grain growth occur, which can decrease of the mechanical properties of heat treated steel. Such abnormal austenite grain growth in V-Al-N2 steel was observed at 1200 °C. In present work the average size of carbonitrides particles was calculated but it need the experimental verification. The stereological characteristics [15] of compounds giving the grain boundary pinning effect has to be investigated.

In steels with singular addition of V the elevated content of nitrogen effectively decreased the austenite grain growth at temperatures up to 950 °C. Above this temperature gradual increase of austenite grain size is observed as the effect of carbonitride V(C,N) coarsening and dissolution. It is necessary to emphasize that in steel containing high N at temperatures when almost all V(C,N) precipitations are dissolved, the austenite grain size is bigger compare to steel with low N content. This effect is possibly due to the decrease of iron self diffusion coefficient, D_{Fe}^{γ}, by dissolved nitrogen. Such effect is observed in case of carbon. The explanation is that atoms of interstitial elements dissolved in austenite decrease the interatomic forces between iron atoms [7,16].

5. Conclusions

1. Nitrogen increases the austenite grain growth temperature in steel 40Cr8 containing microalloying addition of V and V+Al.

2. Simultaneous addition of 0,06 %Al and 0,079 %V increased the austenite grain growth temperature up to 1100 °C.

3. In steel with simultaneous addition of Al and V the abnormal austenite grain growth at 1200 °C was observed.

4. The austenite grain chord length distribution is close to the logarithmic normal distribution.

5. Elevated nitrogen content in 40Cr8 steel with microalloying elements results in low austenite grain size even during austenitizing time up to 5h at temperatures up to 1100 °C.

6. At austenitizing temperatures above temperature of V(C,N) dissolution nitrogen increases the austenite grain growth possibly because of the decrease of Fe self diffusion coefficient (in case of AlN absence).

REFERENCES

[1] C. S. S m i t h, Grains, phases and interfaces: an interpretation of microstructure. Trans AIME **175**, 15-31 (1948).

[2] H. A d r i a n, Thermodynamic model for precipitation of carbonitrides in high strength low alloy steels containing up to three microalloying elements with or without additions of aluminium. Mater Sci Technol **8**, 406-20 (1992).

[3] H. A d r i a n, Thermodynamic calculations of carbonitride precipitation as a guide for alloy design of microalloyed steels. In: Korchynsky M, DeArdo AJ, Repasi P, Tither G, editors. Proceedings of the International Conference "Microalloying '95"; Pittsburgh, 285-307 (1995).

[4] I. M. L i f s h i t z, V. V. S l y o z o v, The kinetics of precipitation from supersaturated solid solutions. J Phys Chem Solids **19**, 35-50 (1961).

[5] C. W a g n e r, Theorie der Alterung von Niederschlägen durch Umlösen (Ostwald-Reifung). Elektrochem **65**, 581-591 (1961).

[6] F. B. P i c k e r i n g, Some beneficial effects of nitrogen in steel. In: Korchynsky M, Gorczyca S, Blicharski M, editors. Proceedings of International Symposium "Microalloyed Vanadium Steels", Cracow, 24-26 April; 33-62; (1990).

[7] R. S t a ś k o, H. A d r i a n, A. A d r i a n, Effect of nitrogen and vanadium on austenite grain growth kinetics of a low alloy steel. Materials Characterization **56**, 340-347 (2006).

[8] R. S t a ś k o, The effect of nitrogen and microalloying elements on the hardenability of medium carbon steel with 2% Cr. PhD thesis, AGH, Cracow 2007.

[9] SigmaScan Pro Automated Image Analysis Software, User's Manual, Handel Scientific Software; (1995).

[10] L. L. L a p i n, Probability and statistics for modern engineering. Boston, MA: PWS Engineering; (1983).

[11] Statistica (Release 5), Quick Reference, StatSoft, Inc; (1995).

[12] F. B. P i c k e r i n g, Vanadium as a hardenability and temperability additice in quenched and tempered steels. In: Gray JM, et al. Proceedings of an International Conference on HSLA Steels '85, 305-324 (1985).

[13] B. G a r b a r z, F. B. P i c k e r i n g, Mater Sci Technol **4**, 967-975 (1988).

[14] H. A d r i a n, A mechanism for the effect of vanadium on the hardenability of medium carbon manganese steel. Mater Sci Technol. **15**, 366-378 (1999).

[15] K. W i e n c e k, Archives of Metallurgy and Materials, **53**, 711-720 (2008).

[16] M. E. B l a n t e r, Tieoria tiermiczeskoj obrabotki, Moskwa, Mietalurgija (in Russian); (1984).