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DECREASING THE CARBONITRIDE SIZE AND AMOUNT IN AUSTENITIC STEEL WITH HEAT TREATMENT AND THERMOMECHANICAL PROCESSING

ZMANJŠANJE VELIKOSTI KARBONITRIDOV V AVSTENITNEM JEKLU S TOPLOTNO OBDELAVO IN TERMOMEHANSKO PREDELAVO

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The article deals with the heat treatment and forging of AISI 321 austenitic stainless steel with a combination of the main alloying elements, Cr-Ni, in the mass ratio of about 18 : 10 and its variants used in the energy industry. The experiment was focused on the influence of heat treatment and thermomechanical processing on the microstructure and, especially, on the distribution of titanium carbo/nitrides and their agglomerations. Three experimental heats with various amounts of carbon, titanium and boron were prepared and subjected to different heat-treatment regimes. Also, different solution-annealing treatments were applied after the forging. The distribution of titanium carbo/nitrides was analyzed in different areas of the tested ingots. The microstructure of the samples was analyzed by means of light and scanning electron microscopy. A numerical simulation in the DEFORM HT software was used for simulating the cooling in different environments after the forging.

Keywords: austenitic steels, heat treatment, titanium carbonitrides

Članek obravnava toplotno obdelavo in kovanje avstenitnega nerjavnega jekla AISI 321 s kombinacijo glavnih legirnih elementov Cr-Ni v masnem razmerju 18 : 10 in njegovih različic, ki se uporabljajo v energetiki. Preizkus je bil usmerjen na vpliv toplotne obdelave in termomehanske predelave na mikrostrukturo in predvsem na razporeditev titanovih karbonitridov in njihovo grupiranje. Pripravljene so bile tri eksperimentalne taline z različno vsebnostjo ogljika, titana in bora ter izpostavljene različnim načinom toplotne obdelave. Po kovanju so bila izvršena različna raztopna žarjenja. Na različnih področjih eksperimentalmih ingotov je bila analizirana razporeditev titanovih karbonitridov. Mikrostruktura vzorcev je bila analizirana s svetlobno in vrstično elektronsko mikroskopijo. Za simulacijo ohlajanja v različnih okoljih po kovanju je bila uporabljena numerična simulacija s programsko opremo DEFORM HT.

Ključne besede: avstenitna jekla, toplotna obdelava, titanovi karbonitridi

1 INTRODUCTION

Stainless steels with an austenitic microstructure and an approximate composition of mass fractions w = 18 % chromium, 10 % nickel and additions of molybdenum, titanium or niobium are today widely used in the components designed for high-temperature applications like nuclear power stations, boilers or superheaters.[1] AISI 321 is a typical austenitic stainless steel with this combination of the main alloying elements of Cr-Ni.

The main goal of this study was to reduce the amount of large carbo/nitride agglomerations. Large agglomerations usually cause echoes during ultrasonic inspections and, thus, almost finished products have to be rejected.

In normal practice, a sufficient amount of titanium is added to steel to combine with all the carbon. Titanium prevents the formation of $Cr_{23}C_6$ carbides, which locally deplete the matrix of chromium[2]; however, a reduction in the carbon amount below w = 0.03 % does more to improve the sensitization resistance than an increase in the Ti amount.[3]

Titanium and niobium carbides are much less soluble in austenite than chromium carbide, so they form at much higher temperatures as relatively stable particles. These should remain relatively inert during commercial heat treatments involving solution temperatures no higher than 1050 °C, thus minimizing the possible nucleation of $Cr_{23}C_6$. However, TiC and NbC have some solubility in austenite at 1050 °C and can subsequently precipitate at lower temperatures. During high-temperature processes, these carbides dissolve to a greater extent in austenite and can then reprecipitate at lower temperatures. Therefore, NbC and TiC do not always form inert dispersions and are often likely to be redistributed due to heat treatment. They do, however, have a great advantage of not depleting the matrix of chromium, particularly in the sensitive areas such as grain boundaries.[4]

The precipitation of carbides and nitrides also occurs during the rapid quenching from high solution temperatures;[4] nevertheless, if only the final heat treatment is applied on thermomechanically processed products (long-time annealing at the temperatures above 1150 °C), grain coarsening can be observed. $M_{23}C_6$ particles precipitated predominantly at the grain boundaries, causing an earlier onset of an abnormal grain growth as compared to the samples, in which precipitation occurred

in the interior of the grains (at the lowest temperature, 1090 °C). This effect is associated with the stability and kinetics of the dissolution of $M_{23}C_6$ particles.[5]

The solution heat treatment in the range of 1100–1250 °C also has a beneficial effect on the creep resistance due to the subsequent precipitation of MX precipitates.[6]

2 EXPERIMENT

Three different heats of austenitic stainless steel were prepared. The chemical composition meets the requirement of the Russian standard 08Ch18N10T and American standards AISI 321 and AISI 321H (in the case of a heat enrichment with boron). The chemical composition of the experimental material is summarized in **Table 1**.

Table 1: Chemical composition of experimental heats
Tabela 1: Kemijska sestava eksperimentalnih talin

Element	Heat number		
(*w*/%)	46471	46736	46777
C	**0.0400**	**0.0400**	**0.0600**
Mn	1.5100	1.6100	1.7000
Si	0.5300	0.5100	0.5700
P	0.0250	0.0220	0.0210
S	0.0070	0.0020	0.0020
Cr	17.600	17.650	17.600
Ni	10.300	10.100	10.100
Ti	**0.2200**	**0.2800**	**0.3900**
B	**0.0001**	**0.0037**	**0.0045**
N	0.0215	0.0265	0.0116

The main variation of the chemical composition consists of different amounts of titanium, carbon and boron. The experiment was mainly focused on the microstructure examination and image analysis. This was done on the ingots. The ingot size and shape were 8K 1.1 with a mass of 1000 kg (the mean diameter was about 500 mm, the length without the head was 1120 mm). The microstructure was inspected in three localities (the ingot axis – 1; the half of radius – 2; the edge – 3), of the ingots after different heat treatments, on the samples forged from the ingots and cooled in two different environments and on these samples after the high-temperature annealing. The microstructure examination and image analyses were focused on the amount and distribution of titanium carbonitrides, on the volume fraction of delta ferrite and the grain size after forging and heat treatment. The particular parameters of the experiment described above are shown in **Table 2**. All the samples for the microstructure documentation were cut in a cubic shape with the dimensions of about 12 mm × 12 mm × 12 mm.

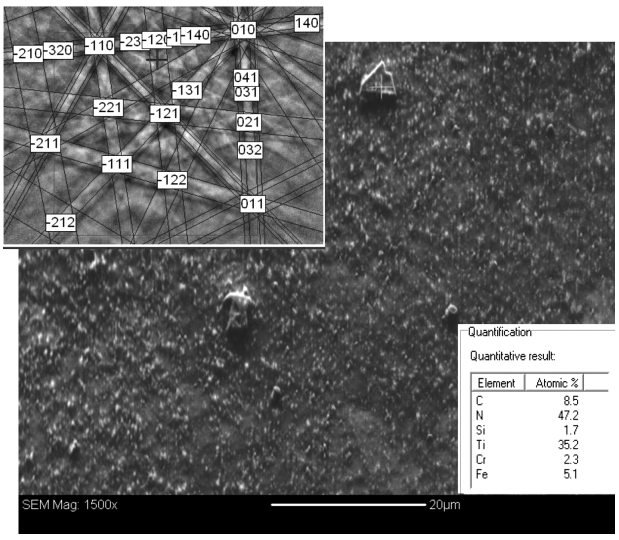

Figure 1: EBSD and EDX analysis of TiCN
Slika 1: EBSD- in EDX-analiza TiCN

Table 2: Parameters of the experiment (for the samples from ingots and the samples forged from ingots)
Tabela 2: Parametri preizkusa (na vzorcih iz ingotov in na kovanih vzorcih iz ingotov)

Experimental procedure	Experiments on ingots		Experiments on forged samples	
	Heat treatment of the samples from ingots (solution annealing)		Cooling after forging (forging at 1200 °C)	Annealing temperature (°C)
Parameters	Temp. (°C)	Time (h)	Vermiculite or water quenching	1020 or 1100
	900	1; 5; 10		
	1100	1; 5; 10		
	1300	1; 5; 10		
Analyses	Microstructure examination and image analysis			

The ingots were cut with a conventional cutting saw. The samples for the microstructure examination were subjected to a conventional metallographic procedure (grinding and subsequent polishing with an alumina suspension). The Beraha 2 etchant was used for revealing delta ferrite. Austenite grains were revealed by means of the V2A etchant.

The identification of carbonitrides was done by means of an HKL Nordlyss EBSD camera and EDS detector INCAx-sight on a JEOL 7400F scanning electron microscope (**Figure 1**).

The image analysis was made with a Nikon MA 200 light microscope with the NIS Elements software for image analyses.

All the samples were evaluated at a 500× magnification and inspected in 30 image fields of each sample (one image field represents an area of 0.022728 mm^2).

The entire experimental heat treatment was done with an annealing furnace Heraus. The forging of the samples from the experimental ingots was done with a hydraulic press Zeulenroda (PYE 40).

3 RESULTS AND DISCUSSION

3.1 Microstructure of the ingots

A quantitative image analysis of the carbonitride count and the carbonitride size found that there is no essential difference between particular heats. However, it was found that there are substantial differences between the localities within an ingot. The highest amount of carbonitrides was concentrated on the edge (near the surface) of an ingot. On the other hand, the size (the average area) of these particles near the surface is the lowest (see **Figure 2** where locality 1 is the ingot axis, locality 2 is at the half of its radius and locality 3 is on the edge of the ingot). The term "object count" in the figure represents the amount of particles per analysed image field, while "object area" represents the average area of one particle.

Agglomerations of carbonitrides are classified as one large carbonitride during the image analyses. Histograms show the distribution of carbonitrides into 10 size factors on the *x*-axis (from 0 μm^2 to 10 μm^2 with a 1 μm^2 step). Class "other" indicates carbonitride agglomerations. It is clearly visible that the amount (the *y*-axis) of large carbonitride agglomerations decreases from the ingot axis to its surface (**Figure 3**).

Delta ferrite formed a complex network around the as-cast grains in the middle of the ingot (**Figures 4** and

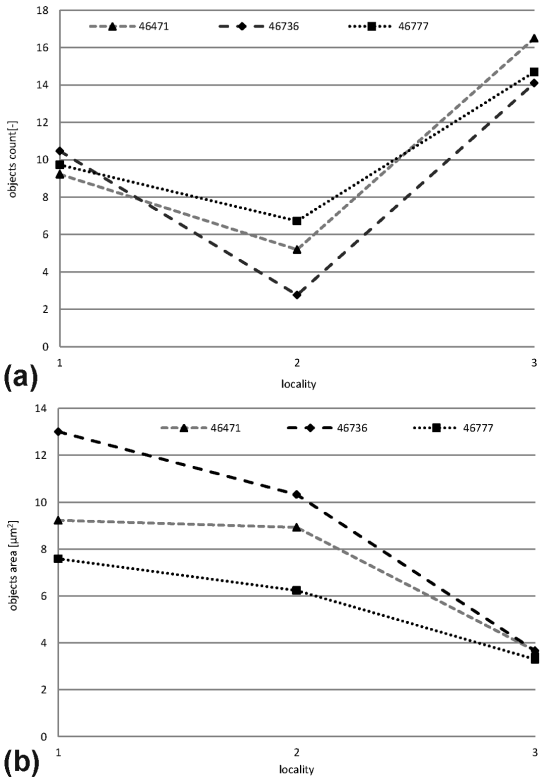

Figure 2: Amount of carbonitride particles and the average area of carbonitride particles in ingots: a) amount of particles per field, b) average area of particles

Slika 2: Delež delcev karbonitridov in povprečna velikost karbonitridnih delcev v ingotih: a) količina delcev v enem polju, b) povprečna velikost področja delcev

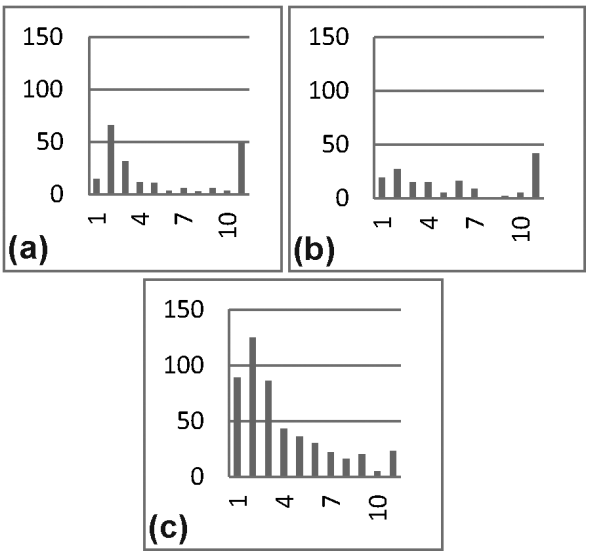

Figure 3: Histograms of carbonitride classification for ingot 46471: a) ingot axis, b) half of radius, c) edge of ingot

Slika 3: Histogrami razporeditve velikosti karbonitridov v ingotu 46471: a) os ingota, b) polovica polmera ingota, c) rob ingota

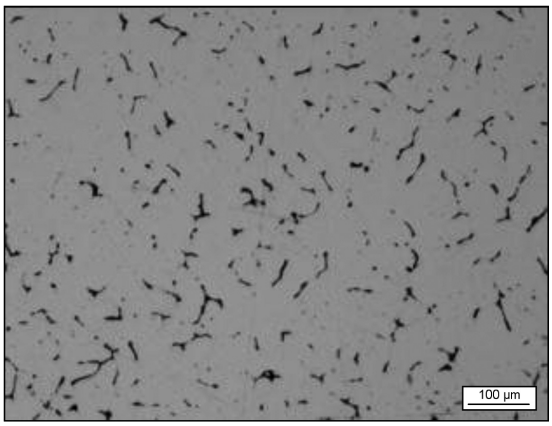

Figure 4: Size and distribution of delta ferrite in ingot 46471 – the middle part of the ingot, Beraha 2 etchant

Slika 4: Velikost in razporeditev delta ferita v ingotu 46471 – sredina ingota, jedkalo Beraha 2

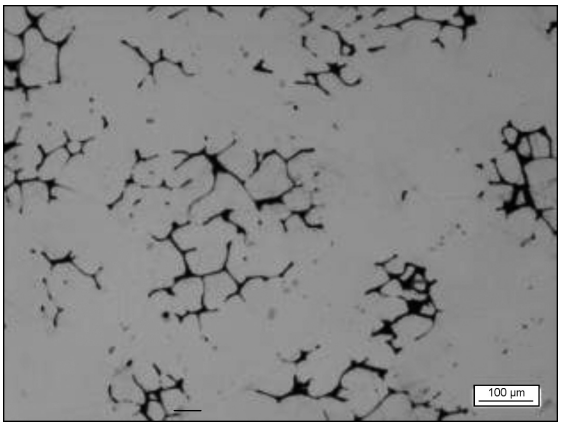

Figure 5: Size and distribution of delta ferrite in ingot 46471 – the edge of the ingot, Beraha 2 etchant

Slika 5: Velikost in razporeditev delta ferita v ingotu 46471 – rob ingota, jedkalo Beraha 2

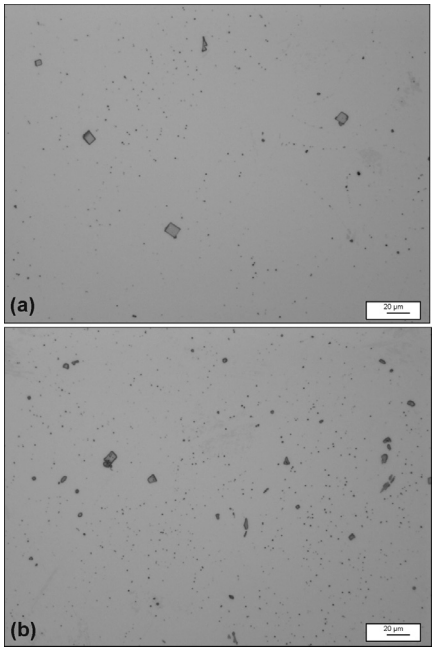

Figure 6: Size and distribution of carbonitrides in ingot 46471: a) initial state, as polished, b) after the heat treatment (1300 °C, 5 hours), as polished

Slika 6: Velikost in razporeditev karbonitridov v ingotu 46471: a) začetno stanje, polirano, b) po toplotni obdelavi (1300 °C, 5 h), polirano

5). Near the edge of the ingot, delta ferrite forms more separate islands and its volume fraction is lower. Both delta-ferrite and carbonitride distribution within the ingot are related to the ingot solidification. Carbonitrides form agglomerations due to the reduced speed of solidification and delta ferrite is formed due to the segregation of the alpha-phase-forming elements.

3.2 Heat treatment of ingots

The samples from the ingots were annealed at (900, 1100 and 1300) °C for (1, 5 or 10) h. The results of the image analyses after the solution annealing are shown **Table 3**.

The annealing at 900 °C for a short time (1 h and 5 h) does not substantially affect the size and count of carbonitrides. The effect of annealing on this temperature is only visible after the annealing for 10 h when the amount of carbonitrides decreases and its average area slightly increases.

An increase in the solution temperature to 1100 °C led to a similar effect on the particle size even after 1 h. But the average amount of carbonitrides per inspected field did not change substantially. A longer annealing at this temperature did not bring any other effect.

The best result was obtained with the annealing at 1300 °C for 1 h and 5 h (**Figure 6**). The average area of one particle decreased and the average count of particles increased. However, the annealing prolonged to 10 h gave almost the same values of the particle count and the average area was the same as in the initial state before the annealing. Nevertheless, the annealing at this temperature for 10 h led to a more homogeneous distribution of carbonitrides.

The best result was reached after the annealing at 1300 °C for 1 h and 5 h when the average area of particles decreased and the average amount of particles per inspected image field increased.

3.3 Forging of the samples from the ingots and different cooling processes

The samples made from the edges of the ingots were heated up to 1200 °C and solution annealed for 2 h and after that they were forged, with a degree of reduction of 2.5. Two different cooling processes were applied: quenching in water and simulation of cooling a whole forged bar with a 250 mm diameter in the air. An insertion of a forged sample into insulating vermiculite simulated this process. The condition of cooling was verified by means of the DEFORM HT software, which proved a similarity of the cooling conditions for a small sample in vermiculite. The influence of forging and the way of cooling on the carbonitride size and distribution were then studied. The forging itself has a substantial

Table 3: Results of the image analyses after the solution annealing (object count represents the amount of particles per analysed image field, object area represents the average area of one particle)

Tabela 3: Rezultati analize slik po raztopnem žarjenju ("število objektov" pomeni število delcev na enem analiziranem polju, velikost področja pomeni povprečno velikost enega delca)

TiCN		46471		46736		46777	
		Obj. count	Obj. area	Obj. count	Obj. area	Obj. count	Obj. area
Temperature	Time	(–)	(µm^2)	(–)	(µm^2)	(–)	(µm^2)
	0	13.00	3.49	14.1	3.67	14.70	3.31
900 °C	1	12.10	3.48	12.2	3.21	14.17	3.05
	5	12.87	3.37	13.67	3.04	14.47	3.33
	10	10.57	5.40	6.8	5.90	14.53	5.33
1100 °C	1	16.57	4.15	8.93	5.77	12.80	4.88
	5	16.33	4.60	10.53	4.68	18.33	5.67
	10	12.37	4.06	7.67	6.64	14.77	5.32
1300 °C	1	36.13	1.72	30.13	2.10	25.43	2.05
	5	37.03	1.98	28.23	2.31	26.27	1.84
	10	20.53	2.50	12.77	3.44	15.20	2.60

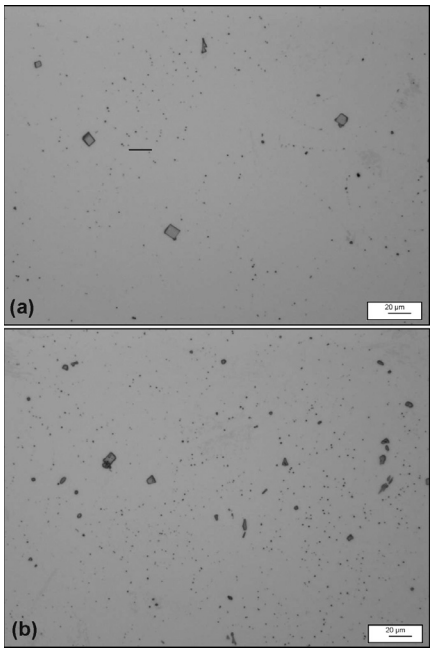

Figure 7: Microstructure of a forged sample after forging, cooling in vermiculite and annealing: a) heat 46736 annealed at 1020 °C, polished, b) heat 46777 annealed at 1020 °C, polished

Slika 7: Mikrostruktura kovanega vzorca po kovanju, ohlajanju v vermikulitu in žarjenju: a) talina 46736, žarjena pri 1020 °C, polirano, b) talina 46777, žarjena pri 1020 °C, polirano

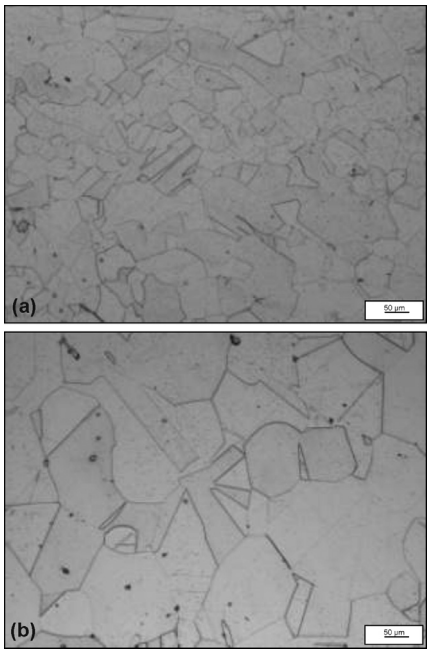

Figure 8: Microstructure of a forged sample after forging, cooling in vermiculite and annealing: a) heat 46736 annealed at 1020 °C, V2A etchant, b) heat 46736 annealed at 1100 °C, V2A etchant

Slika 8: Mikrostruktura kovanega vzorca po kovanju, ohlajanju v vermikulitu in žarjenju: a) talina 46736, žarjena pri 1020 °C, jedkalo V2A, b) talina 46736, žarjena pri 1100 °C, jedkalo V2A

influence on the size and distribution of carbonitrides. An increase in the amount of carbonitrides was observed for all three heats. Heat 46777 showed the strongest increase in carbonitrides due to forging. The observed particles were unfortunately too small for an EDS analysis. But with respect to their positioning within the grain interior, the carbides are not detrimental. Only a low increase in the particle count was observed after the cooling in vermiculite in comparison to the cooling in water. The forging of all the samples led to a decrease in the size of carbonitrides.

3.4 Annealing of forged samples

The forged samples were afterwards annealed at two different temperatures, 1020 °C and 1100 °C, to achieve a further dissolution of carbonitrides. It was found that in the case of heats 46736 and 46777 annealing the forgings quenched in water at 1020 °C led to a further increase in the particle count (**Figure 7**) and a decrease in the average area of particles (**Table 4**).

Increasing the annealing temperature for these heats was beneficial for a further particle refinement but negligible for the final grain size. The grain size increased from 8 (after the forging) to 5 (after the annealing at 1100 °C) according to ASTM E 112 (**Figure 8**). This result was the same for all the heats, there were only minor differences between them.

3.5 Mechanical testing

There was not enough material for standard mechanical testing, thus, mini-tensile test samples were made

Table 4: Average values of the particle count and size for the initial state, after the forging (1 – quenching in water, 2 – cooling in vermiculite) and annealing

Tabela 4: Povprečne vrednosti štetja delcev in velikost v začetnem stanju, po kovanju (1 – ohlajanje v vodi, 2 – ohlajanje v vermikulitu) in po žarjenju

TiCN	46471		46736		46777	
	Obj. count	Obj. area	Obj. count	Obj. area	Obj. count	Obj. area
state	–	µm^2	–	µm^2	–	µm^2
initial state	13.0	3.49	14.1	3.67	14.70	3.31
forging 1	27.97	2.17	18.13	2.86	166.53	0.92
1020 °C	23.9	2.63	24.87	2.83	192.57	0.90
1100 °C	23.73	2.95	45.13	2.10	203.83	0.89
forging 2	25.7	3.05	46.20	2.70	171.73	0.95
1020 °C	23.03	2.81	32.73	1.98	180.37	0.97
1100 °C	19.43	3.05	57.23	1.56	215.57	0.90

from the forged specimens. A sample for the mini-tensile testing is flat, with very small dimensions (the functional-body length is in units of millimetres). The tests were done on a mini-tensile test machine MTS with a video-extensometer MESSPHYSIK. The results of testing the samples annealed at 1020 °C are in **Table 5**. The yield strength increases due to the increasing count of carbonitride particles (precipitation strengthening). Thus, heat 46777 shows the highest *YS* and *TS* of all the heats. The mechanical test of the samples annealed at 1100 °C was not performed because of insufficient grain size.

Table 5: Results of mechanical testing after forging 1 (subsequent quenching in water) and annealing at 1020 °C
Tabela 5: Rezultati mehanskih preizkusov po kovanju 1 (sledilo je ohlajanje v vodi) in žarjenju pri 1020 °C

Specimen	$R_{p0.2}$/MPa	R_m/MPa	A/%
46471	295.5	609.3	70.5
46736	323.4	595.4	56.7
46777	343.2	628.7	63.0

4 CONCLUSIONS

Complex experiments were performed on austenitic stainless steel. Three experimental heats of AISI 321(H) with various amounts of carbon, titanium and boron were subjected to a particular annealing heat treatment, forging with various cooling procedures and a further annealing. Three different temperatures of solution annealing were applied on the ingots – (900, 1100 and 1300) °C, with different holding times – (1, 5 and 10) h. The forged samples were cooled in two different environments – rapid quenching in water and slow cooling in vermiculite. The last heat treatment – solution annealing – was applied on the forged samples – at 1020 °C and 1100 °C for 1 h.

The highest amount of carbonitrides is concentrated on the edge (near the surface) of an ingot where rapid solidification takes place. Carbonitrides become coarsened, forming agglomerations towards the ingot axis, together with the decreasing solidification velocity. Delta ferrite forms a network structure near the ingot axis; it divides into separate islands near the ingot surface.

A substantial decrease in the carbonitride amount was reached after the heat treatment of the ingots at the temperature 1300 °C for 1 h or 5 h when the average area of particles decreased and the average amount of particles per inspected image field increased. Increasing both the annealing temperature and the holding time led to a substantial decrease in the delta-ferrite volume fraction. No substantial differences between the amounts of the observed carbonitrides, in dependence of particular carbon and titanium amounts in the ingots were observed.

Further experiments were concentrated on the samples taken from the edges of the ingots. Thermomechanical processing – the forging itself – substantially decreased the size of particles in all the heats. On the other hand, the amount of carbonitrides increased. The minimum increase was observed on heat 46471 with the lowest carbon and titanium amounts. The highest increase in the carbonitride amount was observed on heat 4677 with the highest titanium, carbon and boron amounts. Considering the difference between the cooling procedures in two environments, a substantial increase in the particle count was observed for heat 46736 after the cooling in vermiculite in comparison to the cooling in water. However, the differences for the other heats were not crucial.

The highest increase in carbonitrides after the solution annealing at 1020 °C was observed in heat 46777 (the heat with the highest carbon and boron amounts). Using a higher annealing temperature (1100 °C) was not beneficial because of the coarsening of the grain size. The grain size increased from 8 (after the forging) to 5 (after the annealing at 1100 °C) according to ASTM E 112. This correlates with the other studies[5]. The heats with higher titanium and boron amounts (46736 and 46777) exhibited good mechanical properties. The precipitation of very fine carbonitrides has a positive effect on the yield strength, as previously stated by Sourmail[6].

Acknowledgments

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