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CENTRELINE FORMATION OF Nb(C, N) EUTECTIC IN STRUCTURAL STEEL

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The reduction of area in the through thickness direction is an essential mechanical property of thick steel heavy plates. By a routine control, a very small through thickness reduction of area was found for tensile specimen of a 90 mm plate. Careful investigations of the fracture and section of specimens cut from the as solidified continuously cast 250 mm thick slab showed that the cause was the presence of coarse particles of niobium carbonitride as constituent of the quasi eutectic Fe-Nb(C, N) that form because of the centerline segregation of niobium.

Key words: structural steel, heavy plates, through thickness reduction of area, eutectic niobium carbonitride

Nastajanje niobij karbonitridnog eutektika u konstrukcijskom čeliku. Kontrakcija u smjeru debeljine je vrlo važno mehaničko svojstvo debelih limova od konstrukcijskih čelika. Pri rutinskoj kontroli svojstava čelika utvrđena je ispitivanjem na razvlačenje na uzorku lima debljine 90 mm, vrlo mala kontrakcija u smjeru debljine lima. Ispitivanja prijelomne površine i presjeka uzoraka izrezanih iz kontinuirano odlivenog 250 mm debelog slaba pokazala su da je uzrok tome prisutnost grubih čestica niobijevih karbonitrida u kvazieutektiku Fe-Nb(C, N) koji je nastao zbog središnjih segregacija niobija.

Ključne riječi: konstrukcijski čelik, debele ploče, kontrakcija u smjeru debljine, niobij karbonitridni eutektik

INTRODUCTION

The reduction of area in the through thickness direction is an essential mechanical property of thick steel heavy plates intended for fillet welds. In the standard EN 10164 [1] three quality classes Z15, Z25 and Z35 with minimal average values for through thickness reduction of area of three tests 15, 25 and 35 % and minimal individual value 10, 15 and 25 %, respectively, are specified. During a routine testing in the Mechanical testing laboratory in Slovenian steelwork Acroni d.o.o. for one specimen only 9,5 % of through thickness reduction of area was found although the declared plate class was Z35.

The sample is shown in Figure 1. According to reference [2] the content of sulphur is the primary responsible for the low ductility in the through thickness direction because of lamelar tearing with fracture propagation also along the interface between sulphide inclusion and the ferrite matrix [3]. The mass friction of sulphur in the tested steel, which was only 0,003 mass %, excludes the possibility of low reduction of area because of sulphide inclusions. A small content of niobium is added to the investigated structural steel to achieve the required mechanical properties [4]. The addition of Nb could also affect the through thickness ductility of heavy plates because of the formation of coarse niobium carbontride particles as constituents of the degenerated eutectic Fe-Nb(C, N), that may form at high content of niobium or because of a defective steel solidification [5, 6].



Figure 1. Image of S 355 J2+N structural steel, showing the reduction of area specimen taken from 90 mm heavy plate in thickness direction.

Table 1. Chemical composition of the 5 355 J2+N steel gra-	Table 1.	. Chemical	composition	of the S	355 J	12+N	steel gr	rade
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Element	С	Si	Mn	Р	S	Cr	Cu	Ni	AI	Nb	Ti	N
Mass/ %	0,15	0,49	1,1	0,018	0,003	0,14	0,29	0,12	0,033	0,022	0,005	0,0071

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To identify the cause for the low reduction of area a detailed investigations of specimens cut at different distances from the surface of the as solidified slab were carried out [7].

EXPERIMENTAL WORK

The structural steel S 355 J2+N was melted in electric arc furnace (EAF), vacuum degassing (VD) treated, continuously cast, and cut into slabs of dimensions 250 \times 1085 \times 4770 mm. The slabs were cooled to ambient temperature and after surface grinding reheated in pusher-type furnace to the temperature 1250 °C and hot rolled to 90-mm thick plates. The chemical composition of the steel is listed in Table 1. First, samples perpendicular to the slab casting direction were examined after grinding and deep-etching for 40 minutes in 25 % H₂SO₄ at 70 °C that revealed the as cast macrostructure.

From this specimen, samples A, B and C in thickness direction were cut out for metallographical examination,



Figure 2. As-cast sample taken from slab perpendicular to casting direction.

	Element	с	Fe	Mn	S	Ti	Nb	AI	Pb
Mass/ %	(Nb,Ti) (C, N)	3,18	33,09	-	-	3,76	59,97	-	-
	MnS	-	3,56	61,89	33,09	-	-	-	-
	Pb	2,03	8,72	-	-	-	-	0,96	88,29

Table 2. Results of the spot EDXS analyses (see Figure 3)

Table 3. Results of the spot EDXS analyses (see Figure 5)

	Element	С	Fe	Mn	S	Ti	Nb	AI	Pb
Mass/ %	(Nb,Ti) (C, N)	4,27	26,95	-	-	2,47	66,31	-	-
	MnS	-	3,56	61,89	33,09	-	-	-	-
	Pb	1,73	5,14	1,1	-	-	-	1,62	90,41

as shown in Figure 2. From the 90 mm heavy plate specimens were cut out in thickness direction and submitted to tensile testing and examination with electron scanning microscopy (SEM) as well as energy dispersive X-ray spectroscopy (EDXS).

RESULTS AND DISCUSSION

In Figure 3 the secondary electron image of fracture surface of one specimen with coarse niobium carbonitride inclusions and small MnS inclusions is shown.

The spots of the EDXS analysis of three inclusions are marked with arrows in Figure 3, and the results are given in Table 2.

In the mapping micrographies in Figure 4 bright areas represent the element in the particles and shows the morphology of the particles and the main element in large inclusions [8]. Most of the particles observed on the fracture surface showed a high content of niobium. On the base of fractographies it was concluded that niobium containing particles (Nb, Ti)(C, N) were the main cause for the poor through thickness reduction of area of the steel plate.



Figure 3. SEM fractograph of the reduction of area specimen. Analysed particles are marked with arrows, EDXS analyses are presented in Table 2.



Figure 4. EPMA mapping of Nb(C, N) and MnS particles.

From the location of the fracture of tensile specimen shown in Figure 1, we assumed that the source of the coarse precipitates was very strong centreline segregation during solidification of the steel slab.

This conclusion is confirmed by the fact that from three samples, as shown in Figure 2 the niobium rich precipitates were found only in the specimen cut from the slab centre in the sample A. The precipitates are very similar to the Fe-Nb(C, N) eutectic called as »Chinese script« [9]. Beside the niobium rich particles, a minor number of very small manganese sulphide inclusions and lead droplets were found, also. All those phases were found only in the centreline of the cast slab. Results of the spot EDXS analyses from the cast slab are presented in Table 3 and the spots of analyses are marked in Figure 5.



Figure 5. SEM picture of degenerated eutectic in form of "Chinese script" from the sample A of the as cast slab.

The analyses show, that niobium carbonitride particles contain also approximately 2 to 4 mass % of Ti despite of only 0,005 mass % of titanium in steel originating from the steel scrap used. A similar composition of niobium carbonitride was reported in Nb-Ti microalloyed steels [10]. The solubility of niobium carbonitride of approximate composition Nb($C_{0,9}$, N_{0,1}) in structural steel is given by the equation [11,12]:

$$\log\left[[Nb]\left[C + \frac{12N}{14}\right]\right] = 226 - \frac{6770}{T}$$
(1)

with [Nb], [C], [N] as weight contents of the elements in the steel and T as temperature in K. Considering the actual contents of niobium, carbon and nitrogen, the solution temperature of 1140 °C was deduced indicating that the slab soaking temperature was sufficient for a complete, solution in austenite of the niobium carbontride of approximate composition $Nb(C_{0,9}, N_{0,1})$.

The fact that coarse niobium rich precipitates were found also in the hot rolled plate after heating the slabs to 1250 °C indicates that their composition differs from that of soluble niobium carbonitride. The solubility for niobium carbide in austenite is greater than the solubility for niobium nitride [13]. It is assumed that the stability of particles in the investigated steel is due to their high content of nitrogen [14]. The shape and size of coarse carbonitride particles suggest that they are constituents of a degenerated quasi eutectic Fe-Nb(C, N). The location of the eutectic in the centre of the slab and the composition of the steel suggest that its formation is an improper solidification process related to a high casting temperature, a high slab solidification rate or a deficiency in the secondary slab cooling.

CONCLUSIONS

Considering the content of carbon, nitrogen and niobium in the steel, all carbonitride phase with the approximate composition Nb($C_{0,9}$, $N_{0,1}$) is in solid solution in austenite at 1140 °C. Since the slab soaking temperature was 1250 °C, it is evident that the carbonitride found in the examined steel has not the quoted composition and that it has a higher content of nitrogen and correspondingly higher solution temperature in austenite.

The shape and size of the niobium rich particles suggest that they are the constituents of a degenerated eutectic Fe-Nb(C, N) that formed during solidification process of continuous cast slabs due to micro segregation of niobium.

The dissolution of this part of carbonitride eutectic does not follow the solubility product as is the case for niobium carbonitride formed by precipitation and is not dissolved during reheating even at low initial Nb contents. This is the fact that niobium carbonitride eutectic results in reduced ductility particulary in the through thickness direction.

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