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INOCULATION-INDUCED CHANGE IN CARBIDES CONTENT IN THE COLUMNAR AND EQUIAXED STRUCTURE OF CENTRIFUGALLY CAST TUBES FROM 32Ni-25Cr-Nb STEEL

1. INTRODUCTION

Striving for better efficiency of chemical and petrochemical processes contributes to the increased requirements imposed on materials intended for construction of the catalytic systems. Consequently, these materials should offer not only high chemical resistance but also withstand the creep-related effects. For this reason, new materials capable of meeting such requirements are searched for all the time. Past decades have seen numerous changes introduced to the chemical composition and hence also to the properties of alloys used for catalytic installations. Originally, tubes that are an essential element of catalytic stoves were hot-rolled from low carbon steel of 35Ni-25Cr type, but poor creep resistance that they offered was the main reason to replace them with tubes centrifugally cast from the steel grades with higher carbon content and additions of niobium. The coarse structure of austenite with carbide precipitates in the centrifugally cast tubes confers to various cast steel grades high creep resistance even at temperatures reaching 950 ^{o}C [1–5]. Alloys developed currently contain, apart from the previously introduced additives of Nb, Ti and V, also other microalloying elements, to mention e.g. cerium or other rare earth metals often used in the form of mischmetal. The addition of strong carbide-forming elements has greatly improved the stability of carbides hardening the alloy during long-term operation, increasing also the resistance to the effect of chemically active environments [1–3]. Tubes made by centrifugal casting are characterised by structure changing on the casting cross-section: the outer layer is composed of columnar crystals, while inner layer has the structure of equiaxed crystals. The properties of these two zones differ [4, 5] and have a significant impact on casting behaviour at the operating temperatures.

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2. METHODOLOGY

The amount and type of the applied inoculants are not given by the manufacturers of catalytic tubes. For this reason, sections of these tubes were centrifugally cast on a laboratory equipment, [7] using 32Ni-25Cr-Nb cast steel with various additional microalloying elements introduced in different proportions. The chemical composition and the modifier used for cast tube sections are given in Table 1.

Table 1. Chemical composition of the examined alloys

Alloy designation modifier	Chemical composition [wt.%]											
	C	Fe	Ni	Cr	Nb	Ti	Zr	Ce	V	Si	Mn	P	S
11 (–)	0.29	39.3	30.8	25.0	1.16	–	–	–	–	1.99	1.06	0.016	0.012
22 (Ti+Zr)	0.28	39.5	30.9	24.6	1.12	0.075	0.083	–	–	2.15	0.97	0.014	0.011
33 (Ti+Zr+Ce)	0.28	39.3	31.3	24.4	1.14	0.069	0.083	0.064	–	2.12	0.97	0.020	0.003
44 (Ce)	0.28	39.0	31.8	24.3	1.17	–	–	0.160	–	2.04	0.99	0.021	0.004
55 (2xTi+Zr)	0.29	39.0	31.4	24.2	1.13	0.120	0.082	–	–	2.44	0.88	0.015	0.012
66 (4xTi+Zr+V)	0.31	41.5	28.6	23.0	1.41	0.231	0.082	–	0.108	3.11	0.66	0.014	0.041
77 (2xTi+2xZr+V)	0.29	39.7	29.6	24.0	1.45	0.137	0.158	–	0.100	3.20	0.60	0.035	0.019
88 (4xTi+Zr+2xV)	0.26	40.7	28.7	23.7	1.55	0.248	0.082	–	0.236	2.92	0.60	0.036	0.020

Fragments of the cast tube sections were collected, and from them, in a direction normal to the tube axis, specimens were cut out for microstructure evaluation. Figure 1 schematically shows the procedure used in cutting out of the specimens. The specimen surface normal to the tube axis was mechanically ground with „1200" abrasive paper and then polished mechanically with alumina. To reveal the microstructure, the polished surfaces were etched with a solution of HNO_3 + HCl + glycerine in a 1:2:3 ratio; microstructures were examined at a magnification of 500×. Figure 2 shows an example of the microstructure of columnar crystals with superimposed measuring grid.

The volume fraction of the Nb and Cr carbides was measured by point method [6]. The measurement of V_V parameter by point method was based on the equation $V_V = P_P$ and consisted in calculating the fraction of points P_P in a planar microstructure incident on the examined phase. The measurement was taken by superimposing onto the images of microstructure (taken at a magnification of 500×) a grid with 400 points of intersection. Altogether 15 grid superimpositions were made, counting next the number of points falling to the corresponding structural constituents. The measured fraction of points was equal to a relative volume of the examined phase. The necessary number of grid superimpositions was calculated assuming the average volume fraction of carbides equal to 4.5%, the relative error of analysis $\gamma = 0.1$ and the probability that the error of analysis shall not exceed the preset value of $1 - \alpha = 0.9$ ($\alpha = 0.1$). The relative volume of carbides was measured in zones of columnar and equiaxed crystals after inoculation with different types of inoculants.

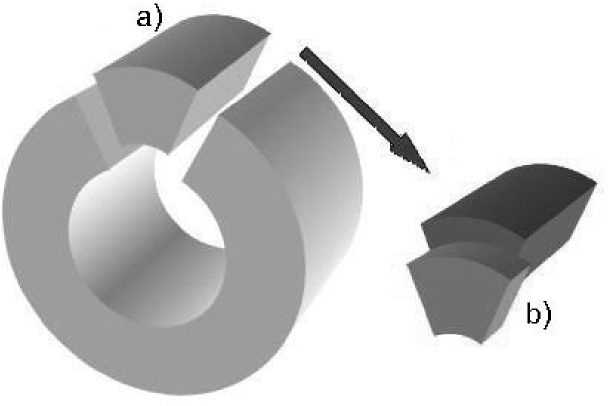

Fig. 1. *Schematic representation of specimen cutting out for microscopic examinations: a) cutting out of tube section; b) specimen cut out in direction normal to the tube axis*

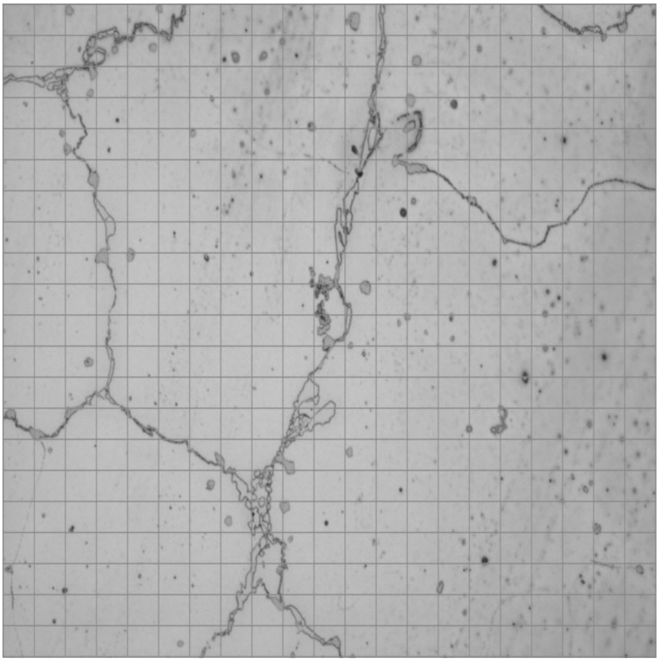

Fig. 2. *Example of microstructure in the zone of columnar crystals with superimposed measuring grid; 500×*

3. TEST RESULTS

Microstructure of the tested alloys is consisted of an austenitic matrix with carbide precipitates at the grain boundaries and inside the grains. Based on previous studies [8, 9], it was found that the bright and faceted precipitates are niobium carbides, while the grey precipitates forming clusters and a grid on the austenite grain boundaries are complex chromium carbides. Inside the grains, single small carbides of both types were observed. The relative volume fraction of Nb and Cr carbides is shown in Table 2 together with the absolute error of measurement calculated for individual types of inoculants in the zone of columnar and equiaxed crystals. It was found that the type of the used microalloying elements induces quantitative changes in the content of carbides in the investigated casting zones.

Table 2. Volume fraction of Nb and Cr carbides in the zone of columnar and equiaxed crystals

Alloy designation modifier	Volume fraction [%]							
	Zone of crystals columnar		Zone of crystals equiaxed		Zone of crystals columnar		Zone of crystals equiaxed	
	Carbides Nb	Error δ	Carbides Nb	Error δ	Carbides Cr	Error δ	Carbides Cr	Error δ
11 (–)	3.33	± 0.38	0.90	± 0.20	2.61	± 0.34	4.46	± 0.44
22 (Ti+Zr)	2.08	± 0.30	1.72	± 0.28	4.52	± 0.44	4.88	± 0.46
33 (Ti+Zr+Ce)	1.84	± 0.28	1.84	± 0.28	3.87	± 0.41	5.53	± 0.48
44 (Ce)	1.96	± 0.29	1.84	± 0.28	4.05	± 0.42	5.05	± 0.46
55 (2xTi+Zr)	2.94	± 0.36	1.60	± 0.27	7.35	± 0.55	5.83	± 0.50
66 (4xTi+Zr+V)	1.49	± 0.26	1.60	± 0.27	5.59	± 0.49	7.32	± 0.55
77 (2xTi+2xZr+V)	1.49	± 0.26	1.42	± 0.25	4.76	± 0.45	5.35	± 0.48
88 (4xTi+Zr+2xV)	2.38	± 0.32	1.60	± 0.27	3.99	± 0.42	5.77	± 0.49

Based on the data presented in Table 2, it was found that the volume fraction of Nb carbides is higher in the zone of columnar crystals than in the zone of equiaxed crystals, while in the case of Cr carbides their volume fraction in the zone of columnar crystals is lower than in the zone of equiaxed crystals.

In the zone of columnar crystals, introducing the inoculants in the form of Ti + Zr (alloy 22), 2xTi + Zr (alloy 55) or 4xTi + Zr 2 xV (alloy 88) has increased the content of Cr carbides, thereby reducing the amount of Nb carbides (compared to base alloy). The addition of Ce (alloy 44) or Ce together with Ti + Zr (alloy 33) had similar effect, and the amount of Nb carbides was even lower. The lowest amount of Nb carbides was obtained in vanadium-inoculated alloys with high content of Ti and Zr (alloys 66 and 77).

In the zone of equiaxed crystals, the impact of the inoculation technique on the calculated content of Cr and Nb carbides was definitely weaker. Additionally, compared with the zone of columnar crystals, the scatter of the results was smaller. The observed changes in the amount of carbides correlated well with the properties of the obtained alloys (tensile strength and elongation), determined in a tensile test carried out at the tube operating temperatures, i.e. at 820 and 950 ^{o}C. The results are shown in the previous author's studies [4, 5].

4. CONCLUSIONS

In contrast to studies done previously on the 32Ni-25Cr-Nb cast steel, the experimental part of the work has demonstrated differences in the structure, namely in the volume fraction of Cr and Nb carbides. Depending on the applied method of alloy inoculation, in both zones of columnar and equiaxed crystals, so characteristic of the centrifugally cast tubes, the following effects were noted:

1. The volume fraction of Nb carbides in the zone of columnar crystals was larger than in the zone of equiaxed crystals.
2. The volume fraction of Cr carbides in the zone of columnar crystals was smaller than in the zone of equiaxed crystals.
3. In the zone of columnar crystals, the outcome of modification was the differentiated carbides content. The introduction of Ti, Zr, Ce and V reduced the amount of Nb carbides and increased the amount of Cr carbides (compared to base alloy).
4. In the zone of equiaxed crystals, the impact of modification technique on the calculated amount of both Cr and Nb carbides was much weaker.

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