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Effect of Silicon Addition on the Microstructure of Cast 24Cr-5Ni-2.5Mo-xSi Duplex Steel

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Abstract

Characteristics of the microstructure of corrosion-resistant cast 24Cr-5Ni-2.5Mo duplex steel after introduction of 0.98, 1.67 and 4.3% Si were described. Based on the test results it has been found that silicon addition introduced to the corrosion-resistant cast two-phase duplex steel significantly reduces austenite content in the alloy matrix. Increasing silicon content in the test alloy to 4.3% has resulted, in addition to the elimination of austenite, also in the precipitation of Si-containing intermetallic phases at the grain boundaries and inside the grains. The precipitates were characterized by varying content of Cr and Mo, indicating the presence in the structure of more than one type of the brittle phase characteristic for this group of materials. The simulation using Thermo-Calc software has confirmed the presence of ferrite in all tested alloys. In the material containing 4.3% Si, the Cr and Si enriched precipitates, such as G phase and Cr_3Si were additionally observed to occur.

Keywords: Cast stainless steels, Microstructure, ThermoCalc

1. Introduction

Duplex Stainless Steels (DSSs) mainly contain Cr, Ni, Mo and small amounts of Si, Mn and Cu [1-3]. Grades are also known in which Ni is replaced by large amounts of Mn and N [3]. In these materials, the content of ferrite and austenite stabilizers is selected in such a way as to provide a 40-60% ferrite fraction in the microstructure. Compared to austenitic stainless steels, the mixed ferritic-austenitic microstructure allows obtaining better mechanical and corrosion properties, this being also true in the cast steel variations. The two-phase structure of these alloys (ferrite and austenite) enriched with alloying additives provides two times higher yield strength and superior corrosion resistance, mainly in local areas (crevice and pitting corrosion PREN = %Cr + 3.3%Mo + 16%N >30 [1]). Containing ferrite in their microstructure, DSSs are classified as ferromagnetic materials. The high content of Cr and the addition of Mo provide good corrosion properties under reducing conditions. In contrast, increasing the corrosion resistance of DSSs under oxidizing conditions and in the environment of hot oxidizing gases requires the addition of Si [4]. This additive stabilizes the passive layer, and also acts as a strongly ferrite-forming element. According to authors [4], 1% Si can balance the effect of 2.5% Cr.

Table 1.
Chemical composition of investigated cast steel

Materials	C	Mn	Si	P	S	Cr	Ni	Mo	other
	wt. %								
1	0.03	0.92	0.98	0.001	0.002	24.00	5.75	2.37	0.03% Nb 0.06% V 0.04% N
2	0.02	1.22	1.67	0.002	0.003	24.81	5.61	2.45	0.03% Nb 0.06% V 0.04% N
3	0.03	1.23	4.30	0.004	0.004	24.34	5.42	2.28	0.03% Nb 0.06% V 0.05% N

The high content of alloying additives in the cast Cr-Ni-Mo duplex stainless steels results in the presence of numerous intermetallic phases like σ, χ, R, $Fe_3Cr_3Mo_2Si_2$ which may appear in the microstructure besides γ, γ_2, carbides and chromium nitrides (Cr_2N, CrN) [4-6].

This article characterizes changes in the microstructure of cast duplex stainless steel after the introduction of different amounts of silicon.

2. Materials and methods

The test material was melted in a vacuum furnace of 1 kg capacity. The furnace charge consisted of armco iron, Cr, FeSi, FeMo and Cr-Ni steel scrap (containing 0.02% C). Thus prepared alloy was poured into ceramic moulds. The chemical composition of cast ingots is given in Table 1.

Simulation of the phase precipitation process during solidification was made with TermoCalc software using a thermodynamic TCFE7 database developed for iron alloys. Metallographic studies were performed with use of a Neophot 32 light microscope and JSM - 7100F scanning electron microscope with EDS detector. Identification of phases included in the cast steel composition was carried out by X-ray diffraction analysis using a D500 diffractometer with CuKα tube (angle 2θ). Based on the records received, the amount of austenite was determined in the samples tested.
Since the authors' intention was to capture changes in the microstructure of the examined cast steel caused by an increased content of the ferrite-forming silicon addition, the article discusses only the changes observed in the microstructure in the starting state. On the other hand, the X-ray diffraction records show the results obtained for both the starting state and the state after the solution heat treatment at 1050°C. An overview of the impact of different heat treatment conditions on the microstructure of the examined cast steel requires further studies and will be the subject of the next article.

3. Results and discussion

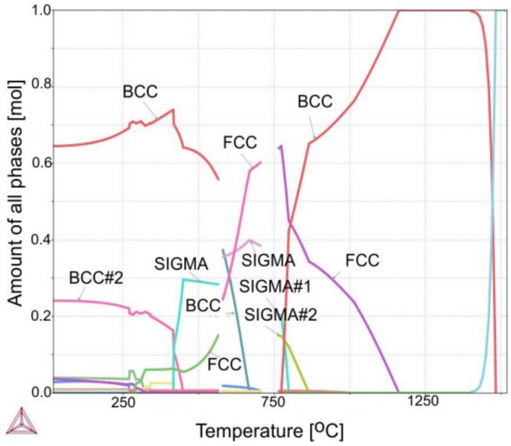
The cast Cr-Ni steel supplied for proper selection of ferrite and austenite stabilizing elements provides the required content of ferrite in the DSSs at a level of 40-60%.

Increasing the content of silicon, which acts as a ferrite stabilizer, while maintaining constant the content of other ferrite- and austenite-forming elements, should increase the ferrite fraction in cast steel [4]. This is indicated by the Cr and Ni equivalents calculated for the tested material:
$Cr_{eq} = \%Cr + 1,55\%Si + 1,4\%Mo + \%Nb - 4,99$,
$Ni_{eq} = \%Ni + 30\%C + 0,5\%Mn + 26(\%N - 0,02) + 2,77$ [1].
Table 2 summarizes the obtained values of the Cr and Ni equivalents and Cr_{eq} / Ni_{eq} ratio. It has been found that with the increasing Si content in cast steel, the values of Cr equivalent and Cr_{eq} / Ni_{eq} ratio are increasing, too. The high, i.e. exceeding 1.95, Cr_{eq} / Ni_{eq} value indicates the ferritic mode of crystallization [7-9].

Table 2.
Cr and Ni equivalents and Cr_{eq} / Ni_{eq} ratio

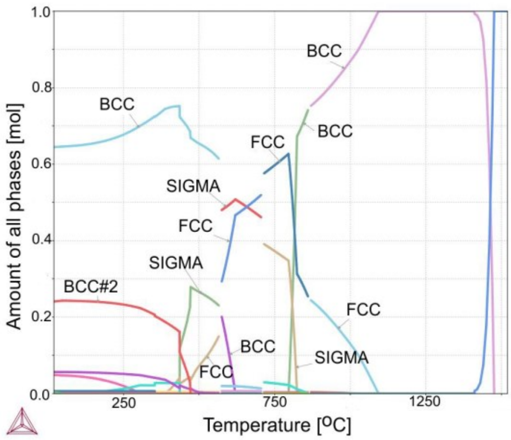
Materials	Cr_{eq}	Ni_{eq}	Cr_{eq} / Ni_{eq}
1	23.88	10.40	2.30
2	25.86	10.11	2.56
3	29.24	10.49	2.80

Thermodynamic calculations of the test alloys crystallization made with the ThermoCalc software have confirmed that for all the tested alloy compositions, the high-temperature ferrite crystallizes as the first one from the liquid, and then, already in the solid state, partial transformation of the matrix into a two-phase mixture, i.e. austenite and σ phase, occurs (Fig. 1). Compared to the duplex steel containing approx. 0.5% Si, the examined material shows significant changes at ambient temperature. In the microstructure of the examined alloys, besides the ferritic matrix, with the increasing Si content increases the content of other two phases, i.e. G and P, and in the alloy containing 4.3% Si, in addition to the previously mentioned intermetallic phases, the phase enriched in Cr and Si, identified as Cr_3Si, also appears (Fig. 1c).



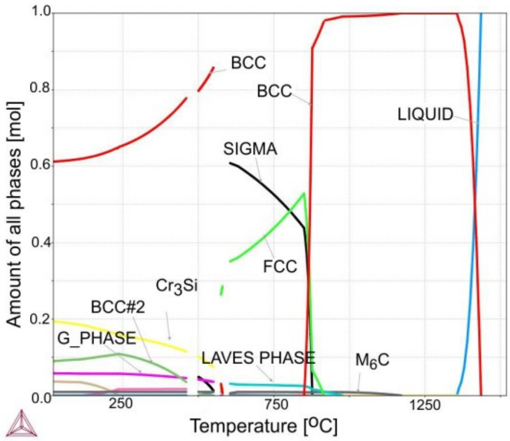
a)

material „1"



b)

material „2"



c)

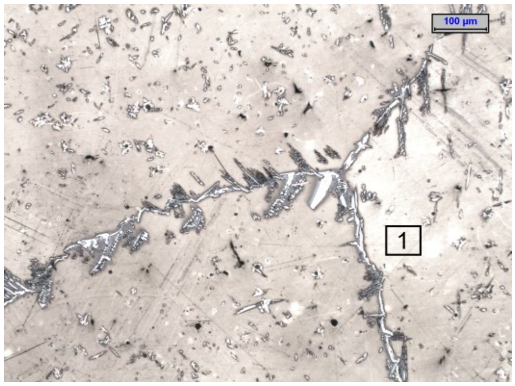
material „3"

Fig. 1. Equilibrium predicted by ThermoCalc for investigated cast steel

2.1. Metallographic studies

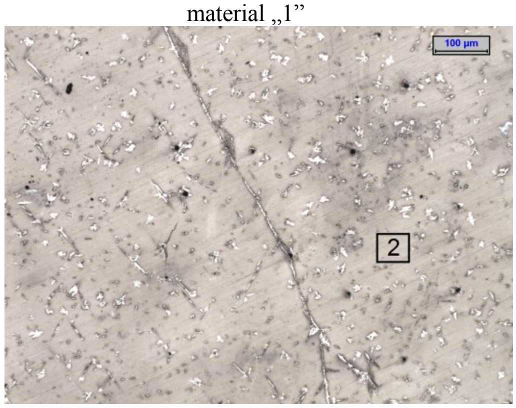
In its base condition, the tested corrosion-resistant cast duplex steel containing 0.98, 1.67 and 4.3% Si is characterized by the structure of predominantly ferritic matrix with austenite precipitates located along the grain boundaries (Fig. 2a,b). As the Si content increases in cast steel, the amount of austenite is rapidly decreasing. In alloy no. 3 containing 4.3% Si, austenite is absent both in the base condition and after the solution heat treatment at 1050°C (Fig. 2c), as confirmed by the XRD records of austenite reflections.

a)



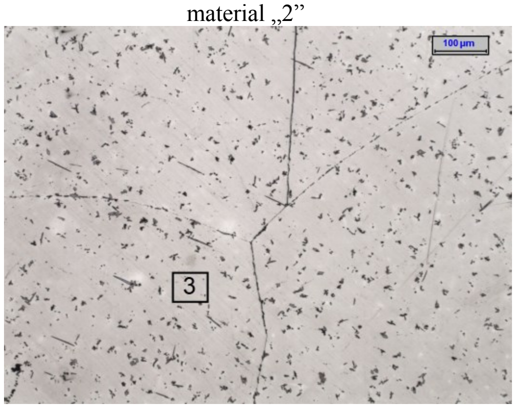
material „1"

b)



material „2"

c)



material „3"

Fig. 2. Microstructure of investigated cast steel (Table 1)

SEM analysis of the chemical composition of phases occurring in the test cast steel has confirmed the enrichment of the ferritic matrix in elements such as Cr, Mo and Si, as compared to the precipitates in the area of grains and grain boundaries identified as austenite (mainly enriched in Ni and Mn). Based on the results obtained, it has been proved that nearly all the silicon dissolved in the matrix of the test material (Table 3). The precipitates of austenite observed in cast steels nos. 1 and 2 contained approximately 22.1% Cr, 7.7% Ni, 1.7% Mo and 0.8% Si. Additionally, in these cast steels, the occurrence in the microstructure of the precipitates of σ phase, characteristic for this group of materials, was observed (Fig. 3).

Table 3.
Chemical composition obtained with Energy Dispersive Spectroscopy in matrix regions from Fig. 2

Materials	Cr	Ni	Mo	Mn	Si	Fe
	wt. %					
1	25.40	5.20	2.30	1.10	0.95	Balance
2	24.80	5.60	2.60	1.60	1.60	Balance
3	24.50	5.60	2.50	1.50	4.10	Balance

Fig. 3. BSE image of material „1"– the σ phase

Moreover, in cast steels nos. 1 and 2, compared to the typical cast duplex steel, the precipitates of a characteristic shape designated in Figure 4 as A appeared in the grain area and crystallized on alumina precipitates. The performed analysis of the chemical composition of a single precipitate has revealed its enrichment in Cr (22.0-24%), Ni (5.8-7), Mo (1.7-2.3) and Si (1% for materials „1"; 1.5% for materials „2") (Fig. 4).

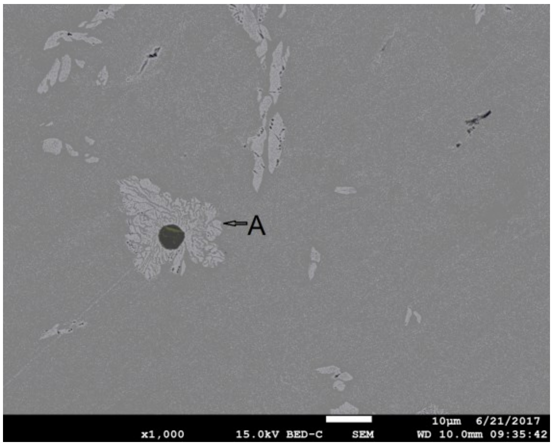


Fig. 4. BSE image of material „1"– the precipitates of a characteristic shape

Microstructure examinations of cast steel no. 3 show at the grain boundaries the presence of precipitates mainly enriched in Si. The variable content of Cr and Mo in these precipitates suggests the possibility of the existence of more than one type of intermetallic phase in the alloy (Table 4). It seems, however, that without additional studies it would be difficult to determine whether this is the intermetallic phase of G or R type (the phase rich in Mo), or whether this is another one of the phases occurring in the DSSs, e.g. a hard phase of the $Fe_3Cr_3Mo_2Si_2$ type [6]. On the other hand, the grains comprise compact precipitates containing a comparable Si content with Cr content increased to 30% and Mo content reduced to about 4%.

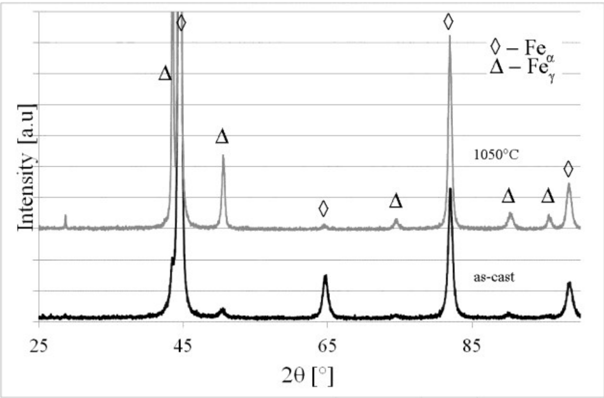
Besides these precipitates, the microstructure also contains other small, needle-like precipitates. The conducted linear analysis shows their enrichment in N and Cr, which suggests that they are likely to be the Cr_2N or CrN compounds [5].

Table 4.
Chemical composition obtained with Energy Dispersive Spectroscopy from selected inclusions in material „3"

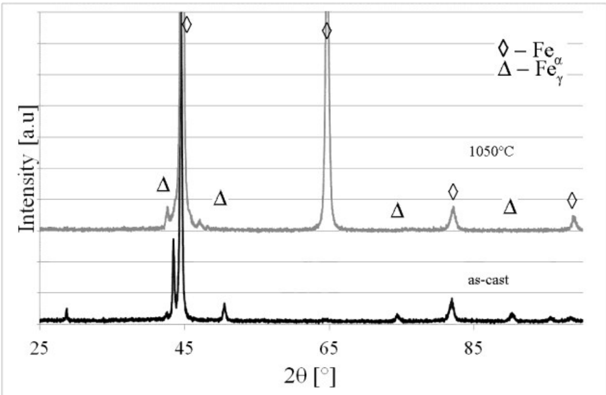
Inclusion	Cr	Ni	Mo	Mn	Si	Fe
	wt. %					
„a"	25.3	6.4	8.3	1.5	5.7	Balance
„b"	29.7	5.0	4.8	1.4	4.9	Balance

*/ a) on the grain boundry, b) within the grain

The X-ray phase analysis has revealed in the diffraction records the presence of reflections coming from ferrite and austenite. Based on the XRD studies, calculations have confirmed the decrease in austenite content with increasing Si content. In cast steel no. 3, the presence of austenite has not been traced (Fig. 5).



a)



b)

Fig. 5. XRD pattern of investigated cast steel – a) material „1” b) material „2”,

3. Conclusions

- In base condition, the cast high-alloyed 24Cr-5Ni-2.5Mo-xSi duplex steel containing 0.98, 1.67 and 4.3% Si has a ferritic matrix with a maximum 22% austenite content, which decreases with the increasing Si content. Austenite has not been detected in the cast steel containing 4.3% Si.
- X-ray diffraction analysis has confirmed the occurrence of both ferrite and austenite in the cast steel containing 0.98 and 1.67% Si, and of sole ferrite in the cast steel containing 4.3% Si.
- In the microstructure of the investigated material containing 0.98 and 1.67% Si, characteristic precipitates of the σ phase and precipitates containing about 1% Si crystallizing on oxide substrates have been traced.
- With the Si content raised to 4.3%, the precipitates with high Si content, additionally enriched in Cr and Mo, were observed to emerge in the alloy ferritic matrix.
- The variable content of Cr and Mo in the precipitates at grain boundaries indicates the presence of not one but many intermetallic phases.
- All intermetallic phases occurring in the test cast steel exhibit the enrichment in Cr, Mo and Si.
- Using ThermoCalc software, detailed analysis of the crystallization process taking place in the examined cast steel has shown that with the 4.3% Si content, the cast steel microstructure comprises the G and Cr_3Si phases, but confirming their presence without additional tests might be difficult.

Acknowledgements

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