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Optimization of Sigma Phase Precipitates with Respect to the Functional Properties of Duplex Cast Steel

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Abstract

The paper presents the results of examination concerning optimization of the σ phase precipitates with respect to the functional properties of ferritic-austenitic cast steel. The examined material comprised two grades of corrosion-resistant cast steel, namely GX2CrNiMoN25-6-3 and GX2CrNiMoCuN25-6-3-3, used for example in elements of systems of wet flue gas desulphurisation in power industry. The operating conditions in media heated up to 70°C and containing Cl⁻ and SO₄ ions and solid particles produce high erosive and corrosive wear. The work proposes an application of the σ phase as a component of precipitation strengthening mechanism in order to increase the functional properties of the material. Morphology and quantities of σ phase precipitates were determined, as well as its influence on the erosion and corrosion wear resistance. It was shown that annealing at 800°C or 900°C significantly improves tribological properties as compared with the supersaturated state, and the best erosion and corrosion wear resistance achieved due to the ferrite decomposition $\delta \rightarrow \gamma' + \sigma$ was exhibited in the case of annealing at the temperature of 800°C for 3 hours.

Keywords: Innovative Foundry Materials and Technologies, Duplex Cast Steel, Sigma Phase, Heat Treatment, Shape Factor

1. Introduction

Ferritic-austenitic steels and cast steels are examples of alloys which functional properties result from the synergetic action of basic microstructural components and advantageous combination of corrosion resistivity and high strength properties [1-3]. High content of chromium, molybdenum, and often nitrogen distinctly increase their pitting resistance, the measure of which is the PRE (Pitting Resistance Equivalent) value, described by the relationship: $PRE = \%Cr + 3,3 \%Mo + 30 \%N$. One of the important fields of application of ferritic-austenitic steels and cast steels are elements of machines and devices used in exploitation of fossil resources and in systems of wet flue gas desulphurisation in coal-fired power plants. Some of them, especially pump impellers and pump casings, which mostly are produced as castings, are subjected to the intensive action of strong erosive

and/or corrosive media, their operating time being considerably shortened due to the severe operating condition [4, 5]. It seems that duplex steels and cast steels, due to the presence of a series of elements – both ferrite- and austenite-forming – as well as multiple intermetallic phases, create possibilities of optimization the functional properties of the material for example by means of heat treatment. The σ phase arising during the treatment is a structural component exerting a negative influence with respect to the plastic properties of the material. Chemical composition of this intermetallic phase precipitating within temperature range from 600°C to 1000°C varies in respect both to the alloying elements present in steel and to the temperature and time of precipitation. The degree of its influence on the mechanical and corrosive properties depends on the heat treatment parameters, and the precipitates generated at lower temperature values generally promote brittleness to the greater degree [6]. Therefore

using the mechanism of σ phase precipitation to increase functional properties of elements subjected to the erosive and corrosive influence of media have to be preceded by optimization of the morphology of the precipitates themselves.

The paper presents the results of examination of corrosion and erosion of cast steel containing σ phase, for which the morphology of precipitates was determined by methods of quantitative metallography.

2. Material and methods of examination

The examined material consisted of two grades of corrosion-resistant ferritic-austenitic cast steel, namely GX2CrNiMoCuN25-6-3-3 and GX2CrNiMoN25-6-3 cast steels, of chemical composition shown in Table 1.

Table 1.

Chemical composition of the examined cast steels, %wt.

C	Cr	Ni	Cu	Mo	Mn	Si	S	P	N
GX2CrNiMoN25-6-3									
0.021	26.70	6.48	0.02	3.10	1.46	0.93	0.012	0.008	0.24
GX2CrNiMoCuN25-6-3-3									
0.024	25.84	6.34	2.75	2.93	1.32	0.81	0.011	0.008	0.23

The heat treatment consisted of the solution heat treatment carried out at 1120°C for 2 hours and subsequent annealing at 800°C for 3h or 900°C for 1.5h in order to achieve full ferrite decomposition according to the reaction $\delta \rightarrow \sigma + \gamma'$. The scope of examination included examination of microstructure, quantitative metallographic analysis and inspection of erosive and corrosive wear. Metallographic examination were carried out for specimens etched with Mi21Fe reagent (30 g of potassium ferrocyanide, 30 g of potassium hydroxide, and 60 ml of distilled water) by means of Neophot 32 optical microscope and SEM JOEL JSM 5400 scanning electron microscope. Images of microstructures after full decomposition of δ ferrite were graphically transformed into binary images of sigma phase and austenite. The shape factor R and the area of each σ phase precipitate were determined by means of ImageProPlus program. The shape factor was determined according to the formula (1).

$$R = \frac{L^2}{4\pi a} \quad (1)$$

where: L – perimeter of a precipitate; a – area of a precipitate.

The results of quantitative analysis served as a basis for creating histograms of shape factor distribution, assuming the division into six classes. The limits of individual ranges and the corresponding shapes of precipitates are schematically shown in Fig. 1.

The examination of erosion and corrosion resistivity were carried out at the laboratory stand realised according to the authors' design [7]. The selection of test parameters was related to the conditions which occur during the wet flue gas desulphurisation in lignite-fired power plants. Examinations were performed at the rotational speed value of 950 rpm in the suspension of silica sand of grain size <0.4 mm in the 0.6M NaCl

solution acidified with sulphuric acid to the pH=4. The relative mass loss of a sample during each examination cycle was taken as a measure of erosion and corrosion resistivity of the examined alloys.

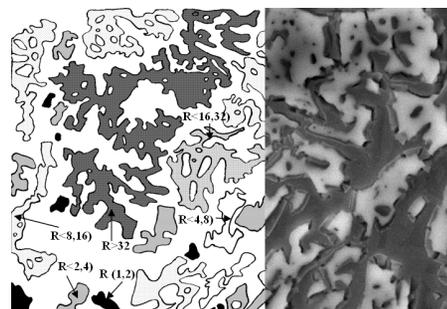


Fig. 1. Sample microstructure of the analysed cast steel with visible sigma phase and the corresponding binary image

3. Results and discussion

Sample microstructures of supersaturated cast steel and the cast steel after complete decomposition of ferrite are presented in Figure 2. The cast steel after solution heat treatment exhibited ferritic-austenitic structure (Fig. 2a) with ferrite fraction of either 48% for the alloy without Cu addition or 58% for the Cu-containing alloy. The complete decomposition of ferrite into austenite and sigma phase was observed after annealing (Fig. 2b), and the ferrite percentage for the annealing temperature of either 800°C or 900°C was equal to, respectively:

- 31.3% or 21.2% in the case of cast steel without Cu addition;
- 20.7% or 15.7% in the case of cast steel with Cu addition.

The results of examination concerning the erosive and corrosive wear after annealing at either 800°C or 900°C show an improvement as compared with the results obtained for the supersaturated material, either by 41-45% in the case of cast steel without Cu, or by 22-40% in the case of cast steel containing Cu. Moreover, the best wear resistance was found for the cast steel annealed at 800°C for 3 hours, for which the mass loss (%m) was equal to 0.212%.

The examinations point out that copper addition slightly deteriorates the erosion and corrosion wear resistance of the cast steel annealed at either 800°C or 900°C, what is shown in Figure 3. It can be noticed that also the increase in temperature from 800°C to 900°C deteriorates this functional property of cast steel.

The less favourable functional properties in the case of cast steel containing Cu are related to the smaller volume fraction of σ phase in the material. The volume percentage of σ phase was taken into account by applying the proposed correcting factor (2) in order to determine the effective influence of the σ phase on the erosion and corrosion wear resistance. Higher values of the coefficient indicate better wear resistance of the material.

$$R_{\sigma} = \frac{100 - \%m}{V_{V\sigma}} \quad (2)$$

where: R_{σ} – compensating factor concerning σ phase percentage; %m – percentage of the mass loss; $V_{V\sigma}$ – volume fraction of σ phase in the cast steel.

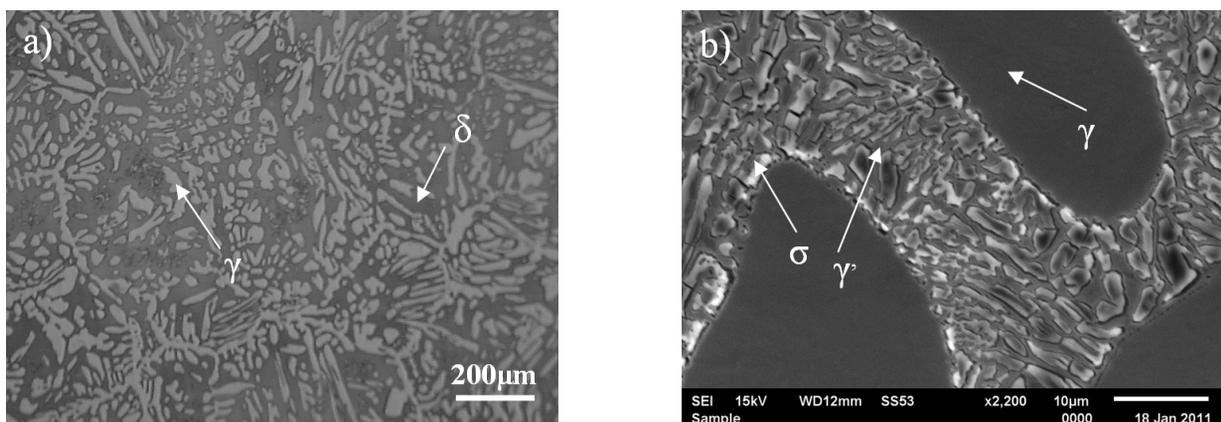


Fig. 2. Microstructures of cast steel: a) GX2CrNiMoCuN25-6-3-3 – solution heat treatment, b) GX2CrNiMoN25-6-3-1120°C/2h/water+800°C/3h, SEM

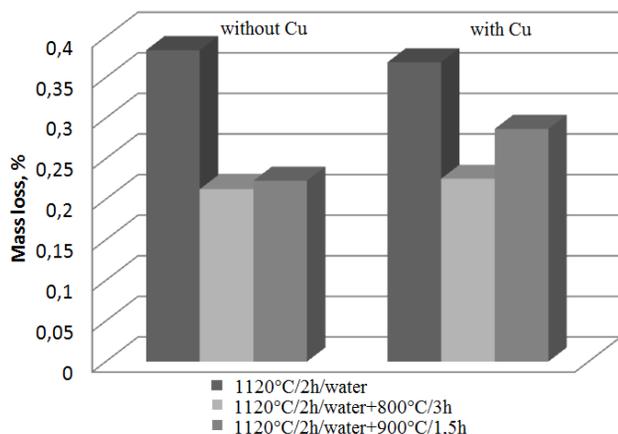


Fig. 3. The erosive and corrosive wear of the cast steel depending on heat treatment, after 24 hours' test

Table 2 juxtaposes values of the R_{σ} factor calculated according to the proposed formula.

Table 2.

R_{σ} factor for the examined cast steels

Volume percentage of σ phase			
without Cu addition		with Cu addition	
800°C/3h	900°C/1.5h	800°C/3h	900°C/1.5h
3.19	4.69	4.82	6.36

The calculations show that the best erosion and corrosion wear resistance (given the volume percentages of sigma phase are equal) would be exhibited by cast steel annealed at 900°C for 1.5h.

The influence of sigma phase morphology on the erosive and corrosive wear was found taking into account the results of quantitative metallographic analysis presented in the form of histograms in Figures 4 and 5.

While analysing the distribution, it was found that the higher temperature of annealing of cast steel without Cu addition caused the disappearance of σ phase particles exhibiting very large area combined with high surface development (shape factor $R > 32$), and 85% of the phase is constituted by regular or oval particles with protrusions, exhibiting the shape factor $R \geq 4$. In the case of annealing at 800°C the fraction of regular particles is somewhat lesser and equal to about 73%, with simultaneous increase in the percentage of large particles with highly developed (rough) surface. This is also indicated by the average shape factor values, being equal to 3.72 and 2.79 for the temperature of 800°C and 900°C, respectively. Similar observations were taken for specimens containing Cu. The more irregular σ phase particles were achieved as a result of annealing performed at 900°C. During the analysis of the influence of chemical composition on the morphology of sigma phase, it was found that if complete decomposition of δ ferrite into σ phase and γ' austenite takes place, the copper addition promotes occurring of particles with more rough surfaces, the average shape factor R_{sr} being then 5.11 and 4.29 for the annealing temperature of 800°C and 900°C, respectively.

The average area of σ phase precipitate after annealing the cast steel without Cu addition at 800°C and 900°C is $5.61 \mu\text{m}^2$ and $7.34 \mu\text{m}^2$, respectively. In the case of Cu addition, the average area of the σ phase precipitate achieved after annealing at 900°C is almost twice as large as the average area of a precipitate obtained after annealing at lower temperature, and is equal to $11.14 \mu\text{m}^2$.

The performed examination of erosive and corrosive wear taking into account the proposed R_{σ} factor as well as the quantitative analysis created a basis for conclusion that the most effective influence is exhibited by these σ phase particles which are characterised by large areas and considerable surface roughness (i.e. by high values of the shape factor). Such particles create a skeleton which prevent the austenitic matrix from wearing away during the work of a cast steel element.

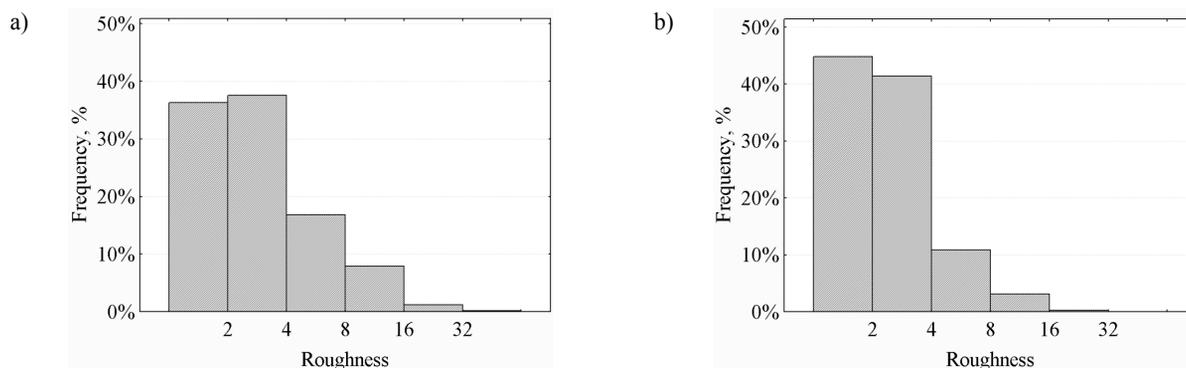


Fig. 4. Distribution of the shape factor R of the σ phase precipitates in cast steel without Cu addition annealed at the temperature of: a) 800°C, b) 900°C

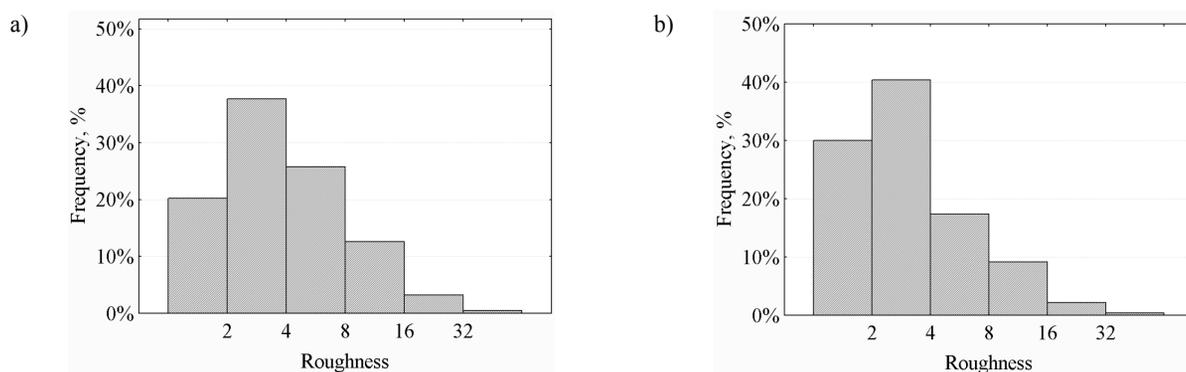


Fig. 5. Distribution of the shape factor R of the σ phase precipitates in cast steel with Cu addition annealed at the temperature of: a) 800°C, b) 900°C

4. Conclusions

The work presents the examination results concerning the erosion and corrosion wear resistance of GX2CrNiMoN25-6-3 and copper-containing GX2CrNiMoCuN25-6-3-3 cast steels, subjected to annealing at the temperature of 800°C for 3 hours or 900°C for 1.5 hour, which led to the σ phase precipitation.

The results of quantitative metallographic analysis, both for cast steel containing copper and for the material without such addition, indicate that the higher annealing temperature results in the disappearance of the σ phase particles characterised by very large area and a considerable value of surface development, with simultaneous increase in percentage of regular and oval particles with protrusions.

The highest value of erosion and corrosion wear resistance was found for GX2CrNiMoN25-6-3 cast steel annealed at the temperature of 800°C for 3 hours. Further, it was found that Cu addition deteriorates the functional properties of cast steel.

The analysis of influence of morphology of σ phase precipitates on the functional properties of the material proved that the most effective improvement is given by particles with large area and high shape factor.

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