Kinetics of the $\sigma$ Phase Precipitation in Respect of Erosion-corrosion Wear of Duplex Cast Steel

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Abstract

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 SO$_4^{2-}$ ions and solid particles produce high erosive and corrosive wear. The work proposes an application of the $\sigma$ phase as a component of precipitation strengthening mechanism in order to increase the functional properties of the material. The paper presents the results of examination of the kinetics of $\sigma$ phase precipitation at a temperature of 800°C and at times ranging from 30 to 180 minutes. Changes in the morphology of precipitates of the $\sigma$ phase were determined using the value of shape factor $R$. Resistance to erosion-corrosion wear of duplex cast steel was correlated with the kinetics of sigma phase precipitating.

Keywords: Innovative foundry materials and technologies, Duplex cast steel, Sigma phase, Shape factor, Erosive-corrosive wear

1. Introduction

Duplex stainless steels (DSS) that contain approximately equal amounts of ferrite and austenite offer an attractive combination of mechanical properties and corrosion resistance [1].

One of the major fields of application of the ferritic-austenitic cast steel include pump rotors or casings, or valves, to be used in wet combustion gas desulphurization systems. The elements of pumps, which are most commonly manufactured in the form of castings, are often exposed to media with an intensive erosive and corrosive action. The hard conditions of operation of parts being exposed to such agents make the life of those parts unsatisfactory.

The occurrence of a number of elements, both ferrite- and austenite-forming, and numerous intermetallic phases in the duplex-type steels and cast steels creates possibilities for the optimization of the service properties of these materials [2]. The $\sigma$ phase arising during the treatment is a structural component exerting a negative influence with respect to the plastic properties of the material [3, 4]. Sigma phase forms after long holding times at temperatures between 600 and 1000°C and after cooling from high temperatures. It seems that in some applications, at low dynamics of parts' operation and a predominance of erosive phenomena over corrosive ones, there is a potential for using the $\sigma$ phase as a structural constituent that enhances the tribological properties, as show in this work.

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  |
|--------|----|-----|-----|-----|-----|-----|-----|-----|-----|----|
| GX2CrNiMoCuN25-6-3 | 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 the temperature of 800°C and at times ranging from 30 to 180 minutes. 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 6610LV scanning electron microscope. The shape factor R of each σ phase precipitate were determined by means of ImageProPlus program, as shown in work [5].

The examination of erosion and corrosion resistivity were carried out at the laboratory stand realised according to the authors’ design [6]. 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 1050 rpm in the suspension of silica sand of grain size 0.5÷1.0 mm in the 0.6M NaCl solution acidified with sulphuric acid to the pH=7. 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.

3. Results and discussion

After hyperquenching of GX2CrNiMoCuN25-6-3-3 and GX2CrNiMoN25-6-3 cast steel at the temperature of 1120°C/2h, the structure consisting of δ ferrite and γ austenite was obtained, which is a typical structure for this type of material. Examples of microstructures of these cast steels have been presented in earlier works [6]. Figures 1 and 2 illustrate examples of microstructures of the cast steels after holding at the temperature of 800°C and at times ranging from 30 to 180 minutes.

![Microstructures of cast steel: GX2CrNiMoCuN25-6-3-3](image)

Fig. 1. Microstructures of cast steel: GX2CrNiMoCuN25-6-3-3 a) 1120°C/water + 800°C/30min, c) 1120°C/water + 800°C/60min, GX2CrNiMoN25-6-3 b) 1120°C/water + 800°C/30min, d) 1120°C/water + 800°C/60min
Analysis of the obtained microstructure proves that the addition of Cu in such a cast steel type speeds up the reaction of ferrite disintegration: \( \delta \rightarrow \sigma + \gamma \). Moreover, it can be stated that after 180 minutes of holding at the temperature of 800°C, there is practically complete disintegration of \( \delta \) ferrite, which can be observed in Fig. 2c. On the basis of microstructure observation after the subsequent times of holding, it was possible to work out the curves of kinetics of the \( \sigma \) phase precipitation in the examined cast steels (Fig.3).

It can be concluded from the graph of kinetics curves that the addition of Cu speeds up the \( \sigma \) phase precipitation. It can already be seen for the first holding time (30 minutes), where the \( \sigma \) phase volume fraction in GX2CrNiMoCuN25-6-3-3 cast steel was two times as high. Moreover, the Cu volume fraction in the cast steel had an influence on the growth of sigma phase volume fraction. For the cast steel containing the Cu addition, it amounted to 43%, while for the cast steel without Cu – 34%. Comparing the practically complete disintegration of \( \delta \) ferrite obtained after 180 minutes of holding at the temperature of 800°C with the volume fraction of ferrite after hyperquenching, it can be concluded that in the cast steel with Cu, ferrite is transformed into the \( \sigma \) phase practically in 90% compared to the cast steel without Cu. Increased content of the \( \sigma \) phase in the cast steel implies higher functional properties of this material. The results of research on the erosion-corrosion wear are presented in Table 2.

Due to the conditions of environment for the erosion-corrosion wear investigation, the erosion can mostly be considered ignoring the participation of the corrosive medium with pH=7. Table 2 shows that in both GX2CrNiMoCuN25-6-3-3 and GX2CrNiMoN25-6-3 cast steel, the growth of sigma phase precipitation is accompanied by the growth of erosion-corrosion resistance. Additionally, it can be observed that after the first hour of holding at the temperature of 800°C the erosion-corrosion wear is on the same level of 1.72 for both cast steels.
Influence of the parameters of heat treatment of the cast steel on the morphology of σ phase and the erosion-corrosion wear of the examined cast steel

| Caststeel           | Heat treatment | Sigma phase [%] | Shape factor | Mass loss [%] |
|---------------------|----------------|-----------------|--------------|---------------|
| GX2CrNiMoCuN25-6-3-3| 1120°C/2h/water| 0               | 0            | 1.89          |
|                     | 800°C/60 min   | 25              | 7.2          | 1.72          |
|                     | 800°C/180 min  | 43              | 5.11         | 1.24          |
| GX2CrNiMoN25-6-3    | 1120°C/2h/water| 0               | 0            | 1.96          |
|                     | 800°C/60 min   | 23              | 5.1          | 1.72          |
|                     | 800°C/180 min  | 34              | 3.72         | 1.01          |

In the case of complete disintegration, i.e. after 180 minutes, definitely better functional properties can be observed for the cast steel without Cu. Higher (~20%) resistance to wear in spite of smaller volume fraction of the σ phase (~20%) can be explained by the morphology of sigma phase described with the shape coefficient, R. Typical morphologies of sigma phase in these cast steels are presented in Fig. 4a and b.

![Fig. 4. Microstructures of cast steel: a) GX2CrNiMoN25-6-3 1120°C/water+800°C/180min, b) GX2CrNiMoCuN25-6-3-3 1120°C/water + 800°C/180min](image)

In the case of the cast steel without copper, particles of relatively regular shape can be observed ($R_{sh} = 3.7$). Whilst in the cast steel with copper, particles with higher development of surface can be seen ($R_{sh} = 5.1$).

### 4. Conclusions

The paper presents the results of research on the kinetics of the σ phase precipitation in GX2CrNiMoN25-6-3 and GX2CrNiMoCuN25-6-3-3 cast steel, hyperquenched at the temperature of 1120°C/2h and after the subsequent holding at the temperature of 800°C at times ranging from 30 to 180 minutes. It has been stated that the addition of copper favours the quickened precipitation of σ phase, as well as increases the volume fraction of this phase. Additionally, complete disintegration of the sigma phase after 180 minutes was observed for both cast steels.

The erosion-corrosion properties of this material were determined for the hyperquenched state and after holding times of 60 and 180 minutes. The research has proved that for the complete disintegration of δ ferrite in this erosion-corrosion environment, the cast steel without copper shows higher resistance, which can be caused by the morphology of sigma phase (with lower degree of surface development). It can be expected that for the improvement of functional properties in the cast steel with Cu, the time of holding should be longer in order to decrease the development degree in the surface of the precipitated σ phase.

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