

# Quench ageing behaviour of duplex cast steel with nano-scale $\epsilon$ -Cu particles

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## Manufacturing and processing

### ABSTRACT

**Purpose:** The aim of the study was to examine the effectiveness and usefulness of the quench ageing on the service properties of massive duplex cast steel. The mechanism of precipitation of a  $\epsilon$ -Cu phase and its effect on the mechanical properties of the cast steel were investigated.

**Design/methodology/approach:** The ferrite substructure was examined on a JOEL JEM HREM. The analysis of chemical composition of selected micro-regions was carried out using a scanning electron microscope. The verification of the metallographic examination results was done using the Thermo-Calc program.

**Findings:** Quench ageing causes an increase in hardness and drop in impact resistance, which results from the formation of the  $\epsilon$ -Cu phase. The ageing parameters have a substantial influence on the ferrite substructure and the degree of coherence, dispersion and amount of the  $\epsilon$ -Cu phase. The ageing treatment at 480°C causes, in addition to the precipitation of the  $\epsilon$ -Cu phase coherent with the matrix, the formation of a  $\alpha'$ -Cr phase and an  $\alpha$ -Fe phase.

**Practical implications:** Duplex cast steels are becoming an irreplaceable material in the elements of equipment exposed to the simultaneous action of corrosive and erosive environment. In the case of massive elements, such as pump (rotors and guide vanes) and pipeline elements etc., which are operated in corrosive environments of water suspensions of solids of different type and gradation, the effect of ageing will be much lower than in small laboratory specimens, which is associated with the presence of a large amount of the incoherent  $\epsilon$ -Cu phase in the cast steel after the solution heat treatment.

**Originality/value:** The lower limit of ageing temperature (480°C) coincide with the temperature of an undesirable spinodal decomposition of the ferrite, which is partially responsible for the slight increase in hardness and a drop in plastic properties. This is the indication that the lower temperature of ageing duplex cast steels with copper should not be lower than 500°C.

**Keywords:** Casting; Heat treatment; Quench ageing;  $\epsilon$ -Cu precipitation

## 1. Introduction

Ferritic-austenitic cast steels are widely used in many branches of industry. The interest in materials of this type resulting chiefly from the fact, that by exhibiting high resistance to different types of corrosion, they fill the gap between ferritic and austenitic steels [1]. Duplex stainless and cast steels exhibit resistance to stress corrosion in solution containing chlorine ions and in environments containing H<sub>2</sub>S, which is better than that of

austenitic materials [2]. The high content of alloying components, mainly chromium, molybdenum and nickel provides also high resistance to pitting and crevice corrosion [3-6]. Elements of duplex-type cast steels are also unrivalled in environments exposed to erosive and corrosive media [7]. Compared to traditional corrosion-resistant steels, chemical composition of duplex cast steels and the heat treatment parameters, which determine the amount and type of precipitating phases, indicate considerable possibilities of modification of the

service properties in the aspect of the final product properties [8-10]. In addition to the basic ferrite- and austenite-forming elements, part of the duplex cast steel grades contain also Cu. Copper is a weak austenite-forming element, whereby its content in the cast steel does not substantially effect the amount of austenite. It has relatively high solubility in austenite (~ 4%) and little solubility in ferrite (~ 0,2%) [11]. It is added primarily in order to increase corrosion resistance [12], but in the light of investigations and literature reports, by taking advantage of the effect of ageing and precipitating the fine-dispersion  $\epsilon$ -Cu phase, it also increases the abrasion resistance of duplex-type cast steels [13]. Aside from the anticorrosion and hardening effect, copper substantially improves castability, which makes cast steels with 3÷5% of Cu particularly suitable for making thin-walled and complex-shape casts. According to [14], the  $\epsilon$ -Cu phase precipitates in duplex cast steel cause a reduction in corrosion resistance by disrupting the integrity of the passive film, and stimulate the formation of pits. Copper-rich  $\epsilon$  phase particles cause also a reduction in resistance to pitting corrosion in a chloride environment. In their work, Smuk *et al* [11] report that heat treatment, which resulted in the precipitation of the copper-rich  $\epsilon$  phase in the ferrite, caused an increase in yield strength and tensile strength moreover a slight decrease in elongation and the reduction of area at fracture, which indicates an undoubtedly positive effect of copper in the precipitation hardening process. However Stradomski and Stachura have found in work [15] that in relation to massive casts, the quench ageing treatment of the GX2CrNiMoCu25-6-3-3 cast steel does not change its resistance to erosive-corrosive wear. They propose to abandon it due to the unnecessary increase in production costs.

Within the present work, the analysis was carried out to determine the effectiveness and suitability of quench ageing treatment in respect of the service properties of elements, such as pump and pipeline elements which are working in corrosive environments of water suspensions of solids of different type and gradation.

## 2. Methodology and materials

The chemical composition of the duplex cast steel type GX2CrNiMoCu25-6-3-3 used for the present work is listed in table 1. For the purpose of the optimisation of the structure and service properties of duplex cast steel, the following heat treatment processes were carried out: solution heat treatment in water after 2h of soaking at a temperature of 1080°C and quench ageing of the cast steel for 4h in the temperature range of 480÷520°C. The microscopic analysis of the cast steel was performed on a Zeiss Axiovert 25 optical microscope. The substructure of ferrite was examined on a JOEL JEM 3010 high resolution electron microscope. Hardness was measured by the Brinell method, according to the PN-EN ISO 6506-1:2002. Impact resistance was measured on the Charpy V specimens.

## 3. Results and discussion

The analysis of the cast steel structure in a as-cast conditions (Fig. 1) showed that, in the case of cast steel with an increased carbon content (heat No. 2), the precipitation of a hard and brittle  $\sigma$  phases took place in the boundary regions of the solidification

grain. Forming of a characteristic network along the boundaries of the primary solidification grain (Fig. 1 b), precipitates caused a distinct impairment of the impact strength of the cast steel in as-cast condition (Tab. 2). Cast steel containing 0.024 %C (heat No. 1) is characterized by a "pure" ferritic-austenitic structure with no  $\sigma$  phase precipitates in the boundary regions of the solidification grain. That structure provides high impact resistance of cast steel already in as-cast conditions (Tab. 2).

Table 1.

Chemical composition of the investigated cast steel

Heat	C	Cr	Ni	Cu	Mo	Mn	Si
No. 1	0.024	25.8	6.34	2.75	2.99	1.32	0.81
No. 2	0.055	24.4	6.71	3.08	2.40	0.14	0.81

After the solution heat treatment the cast steel is characterized by a diphasic ferritic-austenitic structure (Fig. 2). The temperature of 1080°C provided the dissolution of the  $\sigma$  phase precipitated during cooling after the solidification of the cast steel from heat No. 2, whereas the high cooling rate (>40°C/s) prevented its re-precipitation. The examination results show that, in duplex cast steel, the solution temperature of 1080°C provides a ferritic-austenitic structure of a comparable volumetric fraction of both phases. Water solutioning of small specimens, as was the case in the laboratory conditions, prevented the precipitation of the  $\sigma$  phase in the structure of the cast steel.

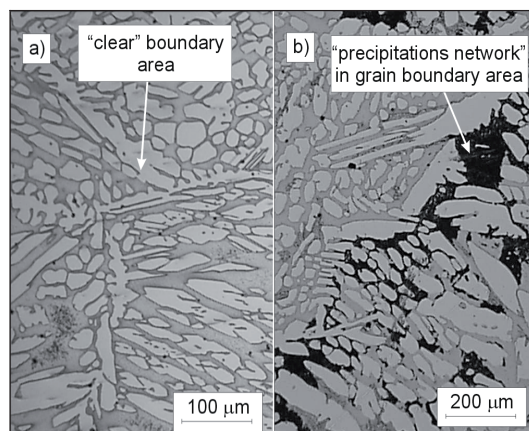


Fig. 1. The microstructure of GX2CrNiMoCu25-6-3-3 duplex cast steel in as-cast conditions: a) heat No. 1, b) heat No. 2

In industrial conditions, during the solution heat treatment of the massive casts at a considerably lower and diverse cooling rates, an increase in the volumetric fraction of the  $\sigma$  phase and an associated impairment in the properties of the material should be expected. This is demonstrated by the results of the authors' investigation presented in the paper [5]. In the solutioned cast steel, in the presence of about 3% of the  $\sigma$  phase remained after the solution heat treatment, the impact resistance amounted to 70 J, compared to 142 J obtained for the pure ferritic-austenitic structure, with a similar volumetric fraction of ferrite and austenite.

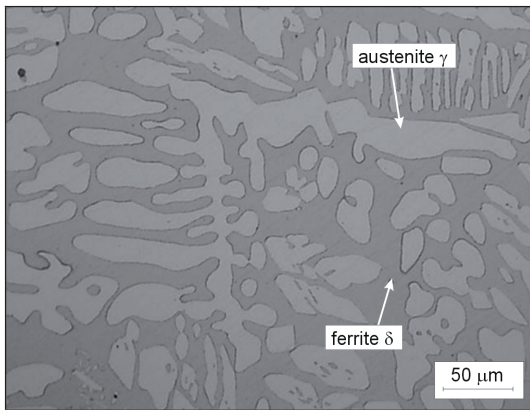


Fig. 2. The microstructure of investigated cast steel after the solution heat treatment 1080°C/2h/water

Three of the six duplex cast steel grades listed in the PN-EN 10283:1998 standard contain copper, whose addition, besides the improvement in castability, should also enhance the resistance to corrosive-erosive wear. The cause of the improvement of tribological properties in duplex cast steels is sought in the dispersive, sub-microscopic-size precipitates of the  $\epsilon$ -Cu phase. Hence the heat treatment process recommended for them is quench ageing in the temperature range from 480°C to 520°C. Examination carried out on a high-resolution electron microscope showed that the applied two hours' time of soaking prior to the solution heat treatment did not allowed the complete dissolution of the copper-rich  $\epsilon$  phase precipitated in the massive cast during cooling. In Figure 3 a, fine, globular precipitates of that phase, uniformly distributed within the ferrite, are visible, whereas the lack of stress contrast indicates that they are incoherent. The ageing parameters have a substantial effect on the degree of coherence and on the dispersion and amount of the  $\epsilon$ -Cu phase. As a result of ageing at a temperature of 480°C for 4 h, a large amount of  $\epsilon$ -Cu phase precipitates coherent with the matrix are formed (Fig. 3 b). The uniformly distributed within the ferritic matrix, fine, globular precipitates of this phase, of an average size of approx. 15 nm, are fully coherent with the matrix. Such precipitates contribute to the increase in the hardness of the alloy (Tab. 2). Increasing ageing temperature from 480°C to 500°C caused the increase of the amount of the  $\epsilon$ -Cu phase, both coherent and incoherent with the matrix. Ageing at a temperature of 520°C resulted in an over-ageing effect involving the coagulation of  $\epsilon$ -Cu phase precipitates and the disappearance of their coherence, which caused a reduction in the hardness of the cast steel with a simultaneous increase in its plastic properties (Tab. 2).

As a result of ageing at the temperature of 480°C which, according to the PN-EN 10283:1998, should lie between 480°C and 510°C, in addition to the precipitation hardening processes described above, the spinodal decomposition of ferrite was found to have occurred with the formation of an iron-enriched  $\alpha$  phase and a chromium-rich  $\alpha'$  phase.

The ageing carried out at three temperatures: 480°C, 500°C, 520°C caused an increase in hardness. The highest increment, by approx. 15%, was obtained for ageing at the lowest temperature of

480°C, upon which the hardness increased by over 40 HB. The overall increase in hardness is determined mainly by the distinct increase in the microhardness of ferrite associated with its precipitation hardening, the fine-dispersion  $\epsilon$ -Cu phase and spinodal decomposition into the  $\alpha$ -Fe and  $\alpha'$ -Cr phases at a temperature of 480°C. The increase hardness in cast steel causes, at the same time, a drop in impact resistance by several times (Tab. 2). Higher ageing temperatures proved to be less effective, as they resulted in a lower increase in hardness.

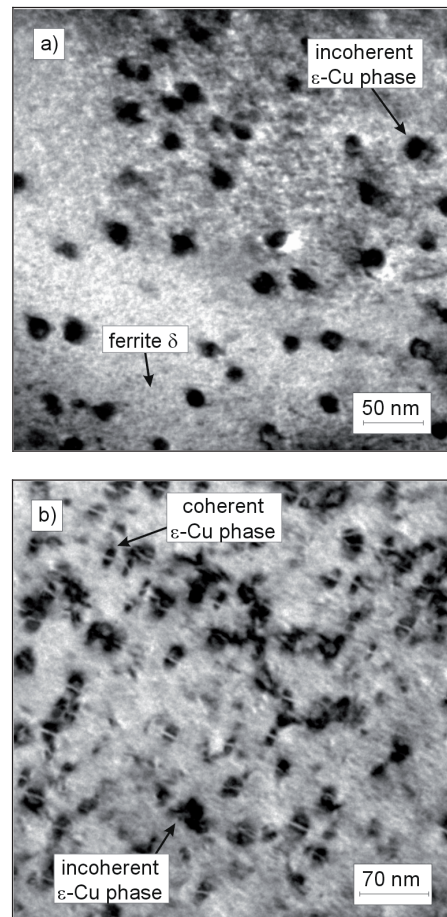


Fig. 3. The HREM microstructure of investigated cast steel after the solution heat treatment 1080°C/2h/water (a) and quench ageing 1080°C/2h/water + 480°C/4h (b)

Solution heat treatment causes a rapid increase in the impact strength of the examined alloys compared to the cast steel in as-cast conditions.

In the cast steel with carbon content at a level of 0.055% (heat No. 2), after solution heat treatment from the temperature of 1080°C, the impact strength was 142 J (Tab. 2), compared to 7 J in the cast steel in as-cast conditions. In the case of the cast steel from heat No. 1, with a pure ferritic-austenitic structure in as-cast conditions, the impact strength after the solution heat treatment increased from 60 J to 120 J (Tab. 2). The quench ageing process causes a drop in duplex cast steel impact strength. The greatest

drop in impact strength is exhibited by the cast steel aged at 480°C, which is accompanied at the same time by the greatest increase in hardness.

Table 2.

Measurements of hardness, microhardness and impact strength of investigated cast steel after different heat treatment

Heat treatment	HB		KV, J	
	heat No. 1		heat No. 2	
as-cast	257	60	268	< 7J
1*	243	120	242	142
2*	282	100	285	50
3*	272	106	271	68
4*	267	118	255	82

\*1- 1080°C/2h/woda, 2- 480°C/4h, 3- 500°C/4h, 4- 520°C/4h

## 4. Conclusions

1. Obtaining a ferritic-austenitic structure of a comparable share of phases is provided by solution heat treatment from the temperature of 1080°C. This temperature assures also the dissolution of the  $\sigma$  phase characterized by high temperature stability.
2. Quench ageing parameters have a substantial effect on the degree of cohesion and the dispersion and amount of the  $\epsilon$ -Cu phase. Ageing at a temperature of 480°C results in an increase in the amount of matrix-coherent  $\epsilon$ -Cu phase precipitates, thereby contributing to a maximum increase in the hardness of the cast steel. As a result of ageing at a temperature of 520°C an over-ageing effect occurred, which consisted in the coagulation of  $\epsilon$ -Cu phase precipitates and the disappearance of their coherence, which resulted in a reduction of hardness with a simultaneous increase in impact strength. In the case of massive casts, the quench ageing effect will be much lower than in small laboratory specimens, which is associated with the presence of a large number of incoherent  $\epsilon$ -Cu phase in the cast steel after the solution heat treatment.
3. Ageing at a temperature of 480°C causes, besides the precipitation of  $\epsilon$ -Cu phase, the formation of a  $\alpha'$ -Cr phase and an  $\alpha$ -Fe phase and associated drop in plastic properties.

## References

- [1] J. Kazior, T. Pieczonka, A. Molinari, Properties of AISI 316L, AISI 434L and duplex stainless steel, AMME'1999, 8 (1999), Gliwice, 289-292
- [2] K. Klyk-Spyra, M. Sozańska, Analysis of the fracture surface of duplex stainless steel after exposure to H<sub>2</sub>S, 8<sup>th</sup> European Congress on Stereology and Image Analysis, Zakopane, Poland, 2005, 246-252
- [3] M.G. Alvarez, R.M. Carranza, The effect of temperature on the passive film properties and pitting behaviour of a Fe-Cr-Ni alloy, Corrosion Science 38 (1996) 909-925
- [4] L.A. Dobrzański, Z. Brytan, M. Grande, M. Rosso, Corrosion resistance of sintered duplex stainless steel evaluated by electrochemical method, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 317-320
- [5] R.A. Perren, T.A. Suter, P.J. Uggowitzer, L. Weber, R. Magdowski, Corrosion resistance of super duplex stainless steels in chloride ion containing environments: investigations by means of a new microelectrochemical method part I, Corrosion Science 43 (2001) 707-726
- [6] J. Nowacki, P. Rybicki, Influence of heat input on corrosion resistance of SAW welded duplex joints, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 113-116
- [7] Z. Pirowski, J. Wodnicki, A. Gwizdź, The Cr26Ni5Mo3 cast steel structure optimization in order to improve erosive-corrosive properties, Acta Metallurgica Slovaca 8 (2002) 381-387.
- [8] Z. Stradomski, D. Dyja, S. Stachura, Technological problem in elaboration of massive casting from duplex cast steel, SSW Conference&Expo, Maastricht, 2005, 363-368
- [9] P. Kangas, J. Nilsson, Influence of phase transformations on mechanical properties and corrosion properties in duplex stainless steels, SSW Conference&Expo, Maastricht, 2005, 278-283
- [10] L.A. Dobrzański, M. Osojca Structure and properties of X2CrNiMoN22-5-3duplex steel, AMME'2003, 12 (2003), Gliwice-Zakopane, 263-266
- [11] O. Smuk, H. Hanninen, J. Liimatainen, Mechanical and corrosion properties of P/M-HIP super duplex stainless steel after different industrial heat treatments as used for large components, Materials Science and Technology 20 (2004) 641-644
- [12] J. Banaś, A. Mazurkiewicz, The effect of cooper on passivity and corrosion behavior of ferritic and ferritic-austenitic stainless steel, Materials Science and Engineering A277 (2000) 183-191
- [13] M. Gajewski, Corrosive and erosive resistance precipitate strengthening cast steel, Foundry Rewiew 1 (2000) 16-21
- [14] J. Banaś, J. Głownia, B. Kalandyk, B. Stypuła, Corrosion and passivity behavior of duplex stainless steel with nitrogen content, 3rd Kurt Schwabe Corrosion Symposium, Zakopane, Poland 2000, 235-240
- [15] Z. Stradomski, S. Stachura, Austenitic-ferritic cast steel optimization for shipbuilding industry, Material Engineering 6 (2003) 377-379