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The structure and mechanical properties of the high chromium and nickel content cast alloy after long duration work in high temperature

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1. Introduction

The technological development of materials is essential in the manufacturing of equipment operating in extreme conditions by incorporating more quality, enabling a longer service life, and lower production costs [1]. Heat resistant alloys have widespread uses in the petrochemical industry in pyrolysis and reformer furnaces. These alloys have replaced the traditional nickel based superalloys and have equivalent properties under conditions of creep, with excellent resistances to high temperature oxidation. In most cases, these complex alloys are used in their as-cast condition but, during service, ageing and phase transformations occur. The typical microstructure of as-cast alloys is an austenite matrix with intergranular eutectic-like primary chromium-rich carbides (M_7C_3 and/or $M_{23}C_6$ types) and niobium carbides (MC type). During service at temperatures of 850–1050°C, all the primary chromium carbides eventually transform into $M_{23}C_6$; intragranular secondary $M_{23}C_6$ carbides also precipitate [2, 3]. For the extreme applications of the petrochemical industry the range of advanced alloys, that reflects the evolution which has taken place in high-temperature materials, are produced. The operation range of these alloys are 533 to 1150°C. High heat transfer coefficient, mechanical strength at elevated temperatures, creep resistance, microstructural stability, carburization resistance, oxidation resistance, and economic considerations are various criteria that should be considered for the appropriate selection of materials for equipment structures [4-6]. For alloys are produced for the petrochemical industry, two requirements are of paramount importance: corrosion resistance and heat resistance.

The demand for higher creep strengths at higher temperatures, with ever diminishing wall or section thickness, has been the major driving force behind these material developments [7, 8].

It should be noted that creep resistant alloys also contain a significant quantity of carbon, required for solid solution strengthening as well as carbide formation. Of further importance of carbon is the secondary carbide formation, where carbides precipitate during operation at high temperatures. Precipitation takes place at operating temperature, within the austenite grains, contributing to strength and creep resistance [9]. In general, they have an austenitic (γ-phase) matrix and contain a wide variety of secondary phases. The most common second phases are metal carbides (MC, $M_{23}C_6$, M_6C, and M_7C_3) and γ', the ordered face-centered cubic strengthening phase [Ni_3(Al, Ti)] found in age-hardenable Fe-Ni-Cr and nickel-base superalloys.

Of particular importance is 35Cr45NiNb Micro (Steloy 1.4889 MA) alloy. The major applications for these alloys are reformer and catalyst tubes. Various international companies are currently producing micro-alloyed HP45. These alloys must be regarded as one of the most significant alloy developments for the petrochemical industry. Microscopic structure and operational conditions are parameters which affect the fracture of the alloy [10]. The failure mechanisms generaly encountered are fatique, stress corrosion cracking and ductile fracture [11].

Most literature sources pointed out that the cause of alloy failure is exposure to an excessively high temperature [12, 13]. Exposure to an excessively high temperature could have two detrimental effects. First, the creep rate can lead to the accelerated formation of grain boundary voids. Furthermore, creep deformation can lead to cracking of the protective oxide scale causing an accelerated carburization attack. Secondly, a higher temperature accelerates the rate of carburization attack. It is very likely that the effect of creep is compounded by the presence of a continuous network of grain boundary carbides [14]. Thirdly, the changes in mechanical properties are connected with the evolution of intermetallic phases and other intermetallic compounds arising in service [15]. The carburization behaviour of the tubes used under the conditions of petrochemical cracking processes depends in a first line on the temperature. Up to 1000°C carbon pickup is low, but above 1050°C heavy carbon pickup and increasing carburization depth must be counted with. This temperature dependence is due to the fact that at 1050°C equilibrium is attained between chromium oxide and carbide, so that the oxide is no longer stable and the original protective effect of the oxide layer is lost. Carburization of a surface layer may set in at temperatures as low as 800°C. Carburization is delayed by high Cr and Ni contents.

2. Material and analysis methods

The research was carried out on high chromium and nickel GX40NiCrNb45-35 steel with its chemical composition given in Table 1. Test pieces for research were taken out from a section of a fractured structure. Examination of chemical composition were carried out using a wavelength dispersive x-ray fluorescence spectrometer Bruker S4 EXPLORER (WDXRF). Areas of examination were cleaned with a sand (abrasive) paper grade 60. The examination with light microscope Keyens VHX-100 (used with magnification from 500× to 1000×) was carried out on cross section of the tube coil sheet. In order to examine microstructure elements in more detail, especially the morphology of precipitations, additional observation was carried out with a Hitachi S-2600N scanning electron microscope.

Table 1

Chemical composition of GX40NiCrNb45-35 steel, % mass

C	Si	Mn	Cr	Ni	Nb	Fe
0.35-0.45	1.76	1.25	34.20	44.33	1.858	16.56

Images were recorded with secondary electron (SE) and backscattered electrons (BSE) detectors. Magnification from 500× to 2000× were applied.

For characterisation of material structures the Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX) was applied (Fig. 1).

Hardness measurement of samples from the tube coil sheet was carried out using Zwick ZHU 2.5. The surface before measurement was cleaned with a sand (abrasive) paper grade 320.

The impact toughness examinations were carried out at room temperature, 300°C, 600°C and 900°C.

Visual inspection of fractures of samples after impact resistance testing was carried out using Hitachi 2600N scanning electron microscope (SEM). Images were recorded with secondary electron (SE) detector. Magnification from 250× to 4000× were applied. The examinations were aimed at determination of fracture character and morphology.

In order to determine resistance properties of the examined material, measurements of uniaxial tension test were carried out with the use of Zwick Z250 static resistance machine. The samples were subjected to tension with initial velocity 5×10^{-4}, s^{-1} at room temperature and 900°C operating temperature.

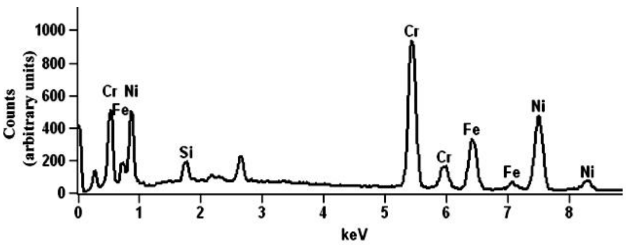


Fig. 1 EDX analysis of the structure (from Fig. 7, point 1)

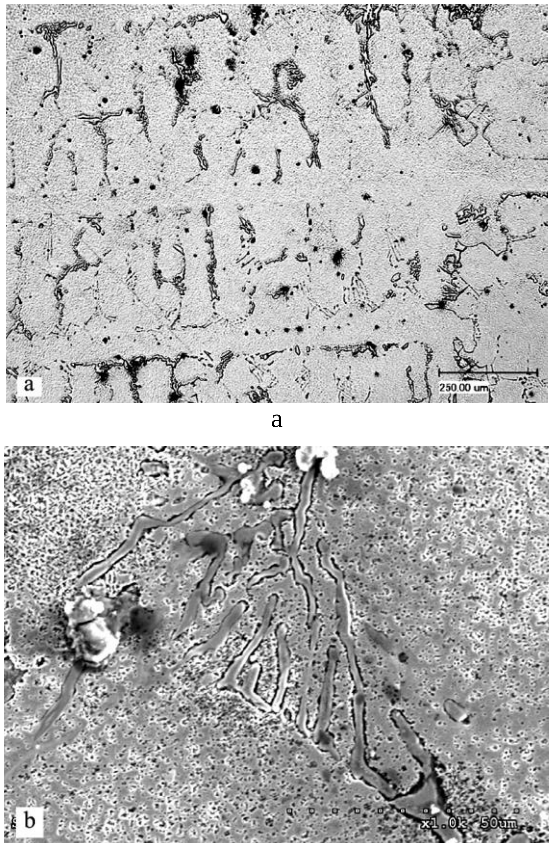
2. Test results and discussion

Fracturing of tube coil sheet. During the visual testing the origins of crack of tube coil sheet were specified.

Fig. 2 Tube coil sheet fractures

The crack was start in the region of stress concentration – the corners of the element (Fig. 2). The fracture on the entire surface has brittle character.

High performance (HP) alloys are complex materials, since they can contain different phases (austenite, M_7C_3, $M_{23}C_6$, MC), with high temperature phase transformations. In the present work have been studied work aged alloy. Different phases with various stoichiometries are present in these alloys: chromium rich-phases ($M_{23}C_6$ and M_7C_3) and niobium carbides (MC). Microstructure of two different regions specimen is shown in Fig. 3.



a

b

Fig. 3 Structure of the tube coil sheet materials after etching: a - light microscope microstructure observation, magnification 200×; b - SEM microscope image of material microstructure, magnification 1000×

As it can be seen in Fig. 3, primary precipitates are well-visible in the fully austenitic matrix and dendritic boundaries. Different environmental conditions, particularly the effect of temperature and carbon diffusion, influence the microstructural and property changes in the service-exposed specimens. Working at high temperatures may result in re-dissolution of primary carbides and re-arrangement of secondary carbides in supersaturated matrix [6, 15, 16].

Cracks are going between dendrites along carbides (Fig. 4). The visual examination shown that the cracks were start in the regions of stress concentration – the corners of the element. The facture on the entire surface has brittle character.

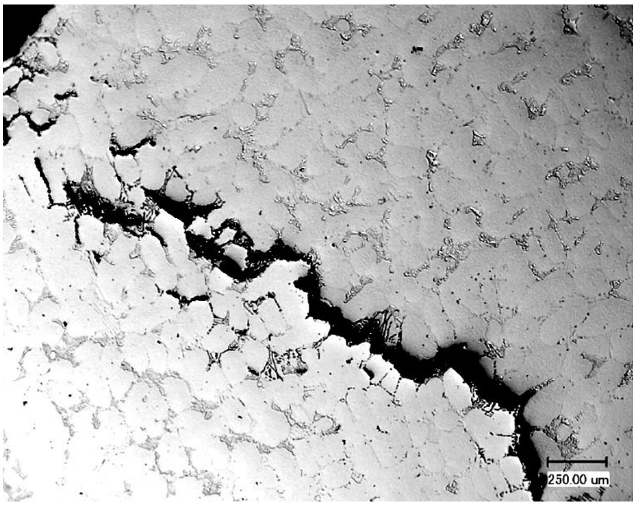


Fig. 4 The character of crack of tube coil sheet (after etching, magnification 100×)

The microstructure of this alloys is composed of primary austenite dendrites with various eutectic cons composed of primary austenite dendrites with various eutectic constituents in interdendritic regions – $\gamma/M_{23}C_6$ and γ/NbC. Cracks are going between dendrites along the chromium carbides. The complex precipitations, consist of different carbides, were not found. The results shown also that transient temperature appear in high temperature at about 900°C. In this coincidence material will have tendency to cracks in low temperature.

Impact resistance testing. Test was performed to establish Facture Appearance Transient Temperature of steel. There is no data for GX40NiCrNb45-35 (1.4889) steel about impact resistance at EN 10295 standards and literature of the subject. Comparison with other Fe-Cr-Ni cast steel alloy shown that impact resistance much lower than the other [17]. The microscope examinations of impact test morphology (Fig. 5) and impact strength test (Table 2) lead to the conclusion that the fracture were examined, in room and elevated temperature, material has brittle character.

Table 2

Impact strength in different temperatures

Sample	Temperature, °C	Impact work, J	Impact strength, J/cm^2
1-3	RT	3	4
4	300	3	4
5-6	600	3	4
7-9	900	11-18	14-23

Room temperature – 17°C

However, it has to be emphasized that some areas of plastic fracture were observed in sample tested in 900°C. These observations can explain the lowered impact resistance of the materials tested in room temperature.

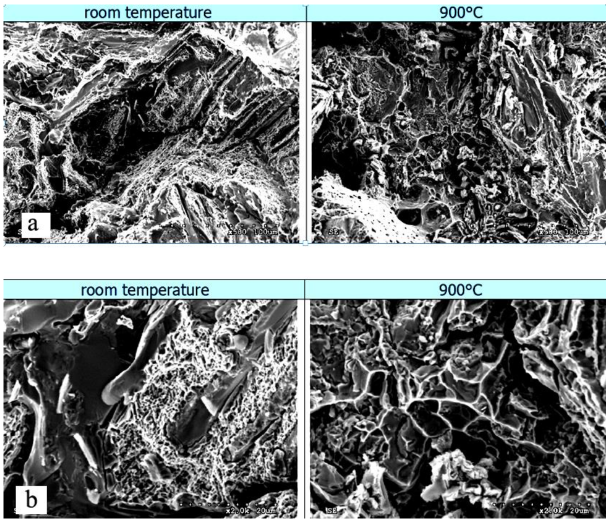


Fig. 5 Morphology of fractures surface of samples after impact resistance testing at room and at 900°C temperature: a - magnification 500×; b - magnification 2000×

Microstructure on Scanning Electron Microscopy. The microstructure of tube coil sheet materials obtained by scanning electron microscope are shown on Fig. 6. The results of microstructure observation are shown typical microstructure in this type of the Fe-Cr-Ni-Nb alloy cast steel. There was no evidence of advance materials microstructure degradation process as a result of the exploitation in the high temperature. The complex precipitations were not found.

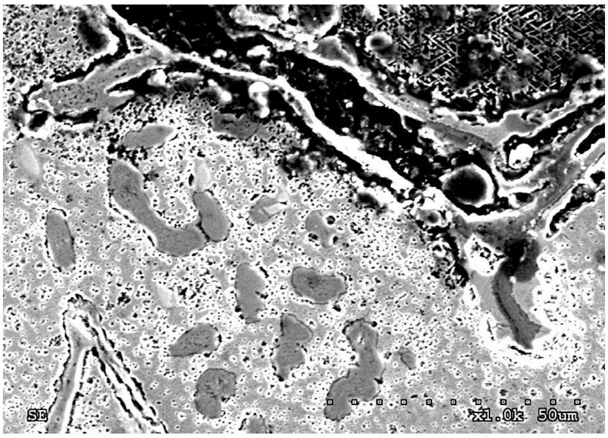


Fig. 6 SEM microscope image of material microstructure (secondary electron detectors, magnification 1000×)

Micro-chemical analysis. During examinations phases rich in chromium (Fig. 1) and niobium (Fig. 7, b) were found. The chemical composition of these phases [16] are following: chromium carbides - $M_7C_{3.07}$ and $M_{23}C_{6.41}$, niobium carbides - $M_{0.55}\,C_{0.45}$.

Tensile test. The samples were subjected to tension with initial velocity 5×10^{-4}, s^{-1} at room temperature and 900°C operating temperature.The results of the tests are shown in Table 2. It can be noted, from the stress-strain curves obtained at room temperature shown in Fig. 8 that the total elongation measured for samples exceeds 0.7%. According to EN 10292 standard material GX40NiCrNb45-35 should have minimum total elongation 3% [17].

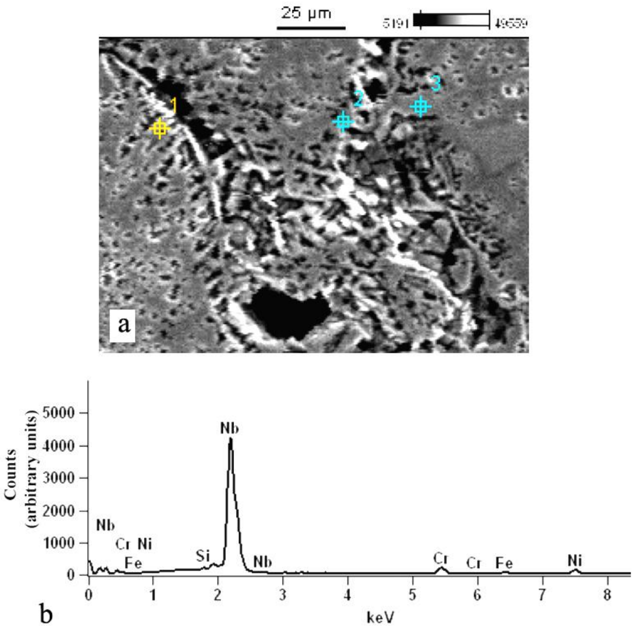


Fig. 7 EDX analysis: a - structure; b - EDX analysis (points 2 and 3)

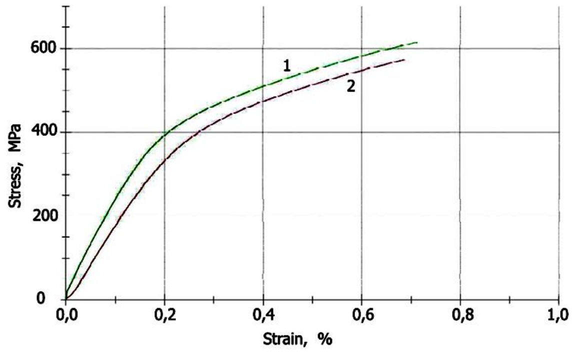


Fig. 8 Tensile stress-strain curves of the samples (1 and 2) tested at room temperature

4. Conclusions

1. The visual examination showed that the cracks start in the region of stress concentration – the corners of the element. The facture on the entire surface has brittle character.

2. Investigated alloy is complex material, since it can contain different phases (austenite, M_7C_3, $M_{23}C_6$, MC), with high temperature phase transformations. The microstructure of this alloys is composed of primary austenite dendrites with various eutectic constituents in interdendritic regions – $\gamma/M_{23}C_6$ and γ/NbC.

3. The results shown also that transient temperature appear in high temperature appear in high temperature at about 900°C. In this coincidence material will have tendency to cracks in low temperature.

4. The microscope examinations of impact test sample lead to the conclusion that the fracture of examined, in room and elevated temperature, material has brittle character.

References

1. **Zumelzu, E.; Goyos, I.; Cabezas, C.; Opitz, O.; Parada, A.** 2002. Wear and corrosion behaviour of high-chromium (14–30% Cr) cast iron alloys, Journal of Materials Processing Technology, 128(1-3): 250-255.
2. **Laigo, J.; Christien, F.; Le Gall, R.; Tancret, V,; Furtado, J**. 2008. SEM, EDS, EPMA-WDS and EBSD characterization of carbides in HP type heat resistant alloys, Materials Characterisation 59(11): 1580-1586. http://dx.doi.org/10.1016/j.matchar.2008.02.001.
3. **de Almeida Soares, G.D.; de Almeida, L.H.; da Silveira, T.L.; Le May, I.** 1992. Niobium additions in HP heat-resistant cast stainless steel, Materials Characterization 29(4): 387-396. http://dx.doi.org/10.1016/1044-5803(92)90045-J.
4. **Culling, J. H.** Iron-chromium-nickel heat resistant alloys. Patent 4861547. http://www.patentgenius.com/patent/4861547. html.
5. **Vasauskas, V.; Baskutis, S.** 2006. Failures and fouling analysis in heat exchangers, Mechanika 5(61): 24-31.
6. **Sadegh Borjali; Saeed Reza Allahkaram; Hamed Khosravi**. 2012. Effects of working temperature and carbon diffusion on the microstructure of high pressure heat-resistant stainless steel tubes used in pyrolysis furnaces during service condition, Materials & Design 34: 65-73. http://dx.doi.org/10.1016/j.matdes.2011.07.069.
7. **Slabbert, D.** Steloy casts its net worldwide. [Retrieved November 10 2011]. Available from: <http://www.steloy.com/upload/news/in-the-spotlight-sep.pdf>.
8. Material catalogue. [Retrieved November 10 2011]. Available from: <http://www.steloy.com/mat-cat/steloy-cat06-full.pdf> (access 16th June 2011).
9. **Kumšlytis, V.;Valiulis, A.V.; Černašejus, O.** 2010. Effect of PWHT on the mechanical properties of P5 steel welded joints, Solid State Phenomena 165: 104-109. http://dx.doi.org/10.4028/www.scientific.net/SSP.165.104.
10. **Karaminezhaad, M.; Kordzadeh, E.; Ebrahimi, S.** 2005. The fracture mechanisms of an austenitic heat resisting steel in copper converter atmosphere, International Journal of ISSI 2(1): 31-36.
11. **Otegui, J.L.; Fazzini, P.G.** 2004. Failure analysis of tube-sheet welds in cracker gas heat exchangers, Engineering failure analysis 11(6): 903-913. http://dx.doi.org/10.1016/j.engfailanal.2004.01.003.
12. **Shipley, R.J.; Becker, W.T.** (ed) 2002. ASM Handbook. Volume 11: Failure Analysis and Prevention. ASM International, 1164 p.
13. ASM Handbook. Volume 1: Properties and Selection: Irons, Steels, and High-Performance Alloys. Edited by: ASM International Handbook Committee, 1990, 1300p.
14. **Ul-Hamid, A.; Tawancy, H.M.; Mohammed, A-R.I.; Abbas, N.M.** 2006. Failure analysis of furnace radiant tubes exposed to excessive temperature, Engineering Failure Analysis 13: 1005-1021. http://dx.doi.org/10.1016/j.engfailanal.2005.04.003.
15. **Makhutov, N.A.; Chirkova, A.G.; Kuzeev, M.I.** 2006. Changes in material characteristics of pyrolysis furnace tube coils, Mechanika, 2(58): 5-10.
16. **Phillips, N.S.L.; Chumbley, L.S.; Gleeson, B.** 2009. Phase transformations in cast superaustenitic stainless steels, Journal of Materials Engineering and Performance 18(9): 1285-1293. http://dx.doi.org/10.1007/s11665-008-9323.

17. Superaustenitic alloys. [Retrieved November 03 2011] Available from: <http://www.fondinox.com/ superausteniticalloys.htm>.

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SENDINTO AUKŠTOJE TEMPERATŪROJE CHROMO IR NIKELIO LYDINIO STRUKTŪRA IR MECHANINĖS SAVYBĖS

R e z i u m ė

Naftos chemijos pramonėje vamzdynų rinklių palaikymui naudojami lieti lakštiniai elementai, pagaminti iš daug chromo ir nikelio turinčių lydinių. Lydinių darbo temperatūra yra 533-1150°C. Lydiniai turi būti atsparūs korozijai ir oksidacijai aukštoje temperatūroje, pasižymėti matmenų stabilumu (t.y., atsparumu matmenų ir geometrijos iškraipymams) ir atsparumu aukšta temperatūriniam valkšnumui. Darbe pateikti šių lydinių konstrukcinių elementų įrimo tyrimai. Tirtų elementų medžiaga dirbo tik 3 metus, tačiau juose buvo pastebėti dideli konstrukcinių elementų supleišėjimai. Darbo metu vyksta intensyvi konstrukcinių elementų paviršiaus oksidacija. Šių elementų aušimo iki aplinkos temperatūros metu, oksidų sluoksnyje gali susidaryti mikroįtrūkiai. Pristatomoje tyrimų medžiagoje nustatyti ir įvertinti lydinio, sendinto 900°C temperatūroje, mikrostruktūros ir mechaninių savybių pokyčiai, chromo, niobio ir kompleksinių karbidų susidarymas ir jų poveikis lydinio eksploatacinėms savybėms.

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THE STRUCTURE AND MECHANICAL PROPERTIES OF THE HIGH CHROMIUM AND NICKEL ALLOY AFTER HIGH TEMPERATURE AGEING

S u m m a r y

In the petrochemical industries cast steel tube coil sheets with high chromium and nickel content are used. The operation range of these alloys are 533 to 1150°C. A paramount for these alloys are: - corrosion and scaling resistance at high temperatures; - dimensional stability, i.e. resistance to warping, cracking and thermal fatigue; - resistance to plastic flow, i.e. creep strength. Tube coil sheet of furnace resulting in aggregate failures have been considered. Life span of the studied specimens obtained from tube coil sheet was 3 years. After a few years of exploitation several hollow cracks on the heater tube-sheet were identified. Pre-oxidation of the tubes surface are possible and it has not only favourable effects: during cooling cracks may form in the oxide layer. The aim of the performed research was to characterize the microstructure and mechanical properties of the investigated alloy after ageing at the temperature of 900°C. The high temperature determine elements diffusion in the structure, emergence of chromium and niobium carbides and other precipitates and cause the changes in the mechanical properties.

Keywords: high chromium-nickel alloys, mechanical properties, fractures, precipitation phases, carbides.

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