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# THE STRUCTURE AND MECHANICAL PROPERTIES OF THE HIGH CHROMIUM AND NICKEL CONTENT ALLOY AFTER WORK IN ELEVATED TEMPERATURE

*Heat resistant alloys replaced the traditional nickel based superalloys and have equivalent properties under conditions of creep, with excellent resistances to high temperature oxidation. In most cases, during service, ageing and phase transformations occur. Of particular importance is 35Cr45NiNb Micro (Steloy 1.4889 MA) alloy. After the long work in high temperature (about 900°C) material will have tendency to cracks. The microscope examinations of the fractures lead to the conclusion that after the cooling material in room and elevated temperature can be characterised as brittle.*

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

## Introduction

Heat resistant alloys have wide spread uses in the petrochemical industry in pyrolysis and reformer furnaces, in the manufacturing of equipment operating in extreme conditions by incorporating more quality, enabling a longer service life, and lower production costs [1]. 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 $M_{23}C_6$. The intragranular secondary $M_{23}C_6$ carbides also precipitate [2]. 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 [3]. 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 [4].

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. 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 [5]. The failure mechanisms generaly encauntered are fatique, stress corrosion cracking and ductile fracture [6].

Most literature sources pointed out that the cause of alloy failure is exposure to an excessively high temperature [7]. 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 [8]. Thirdly, the changes in mechanical properties are connected with the evolution of intermetallic phases and other intermetallic compounds arising in service [9].The carburization behaviour of the tubes used under the conditions of petrochemical cracking processes firstly depends 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.

## Material and analysis methods

The research was carried out on high chromium and nickel steel (GX40NiCrNb45-35) with its chemical composition given in Table 1. Test pieces for research were taken out from a section of a fractured structure.

Table 1.Chemical composition of investigated steel, % mass

| C | Ni | Cr | Mn | Si | Nb | Fe |
|---|---|---|---|---|---|---|
| 0,35÷0,45 | 44.33 | 34.20 | 1.25 | 1.76 | 1.858 | 16.56 |

Examination of chemical composition were carried out using a x-ray fluorescence spectrometer Bruker S4 EXPLORER (WDXRF). The examination with light microscope Keyens VHX-100 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. Images were recorded with secondary electron (SE) and backscattered electrons (BSE) detectors. 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°.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. 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 $5x10^{-4}s^{-1}$ at room temperature and 900°C operating temperature.

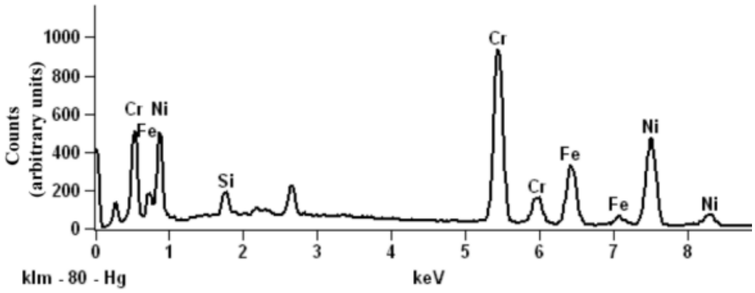


Fig. 1. EDX analysis of the structure (Fig. 7, point 1)

## Test results and discussion

*Fracturing of tube coil sheet*. During the visual testing the origins of crack of tube coil sheet were specified. 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) (Fig. 3).

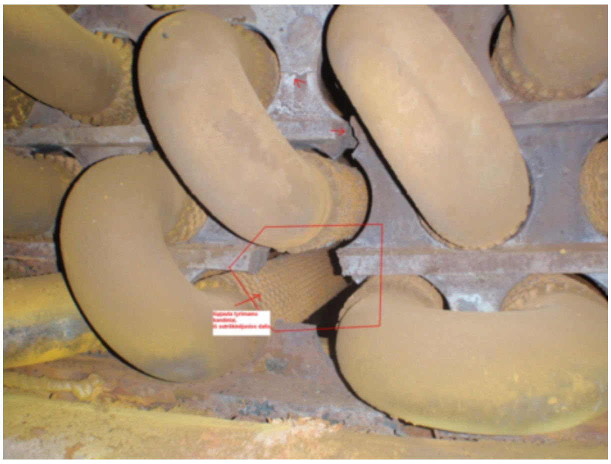


Fig. 2. Tube coil sheet fractures

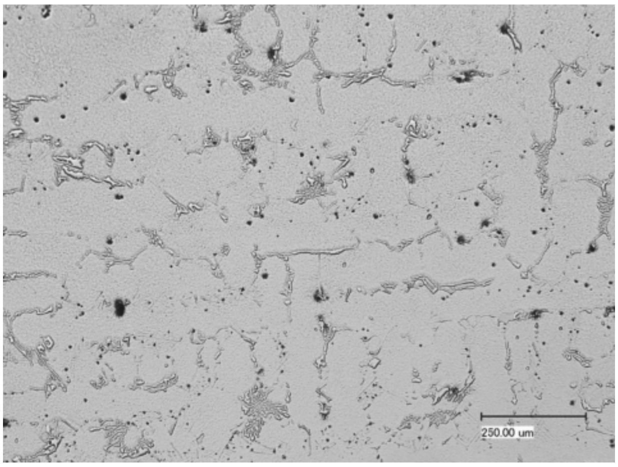


Fig. 3. Structure of the tube coil sheet materials after etching, magnification 200x;

As it can be seen in Fig. 3, primary precipitates are wellvisible 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 [3, 10]. Cracks are going between dendrites along carbides (Fig.4).

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 $\gamma$/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.

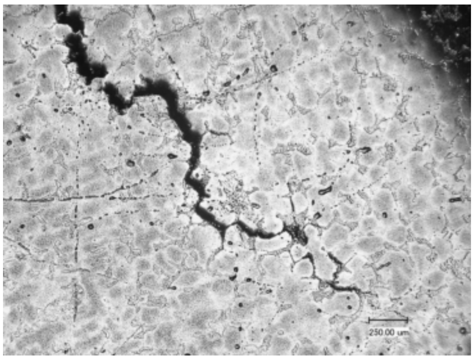


Fig. 4. The character of crack of tube coil sheet (after etching, magnification 100x)

*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 show that impact resistance much lower than the other. The microscope examinations of impact test sample (Fig. 5) and impact strength test (Table 2) lead to the conclusion that from the character of fracture were examined (in room and elevated temperature) that material is brittle.

Table 2.Impact strength in different temperatures

| Sample | Temperature, °C | Impact work, J | Impact strength, J/cm$^2$ |
|---|---|---|---|
| 1-3 | 17 | 3 | 4 |
| 4 | 300 | 3 | 4 |
| 5-6 | 600 | 3 | 4 |
| 7 | 900 | 11 | 14 |
| 8 | 900 | 12 | 15 |
| 9 | 900 | 18 | 23 |

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.

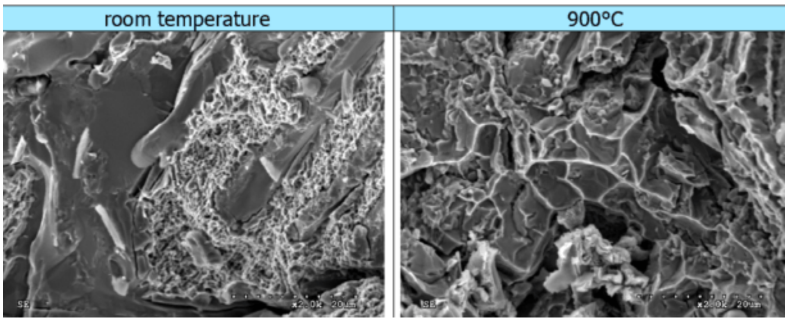


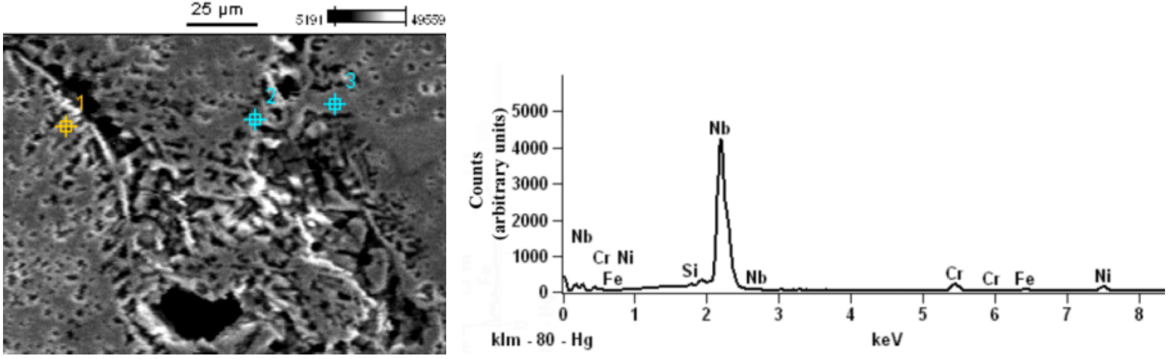
Fig. 5. Morphology of fractures surface of samples after impact resistance testing at room and at 900°C temperature, magnification 2000x.

Fig. 6. SEM microscope image of material microstructure (secondary electron detectors, magnification 2000x)

*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.

*Micro-chemical analysis*. During examinations carbides of chromium (Fig.1 and niobium Fig.7, b) were found. The chemical composition of these carbides [10] 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 5x10$^{-4}$, s$^{-1}$ at room temperature and 900°C operating temperature. 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%.



a) b)

Fig. 7. EDX analysis: a - microstructure: b – 2 and 3 points *Hardness measurement* of samples from the tube coil sheet was carried out using Zwick ZHU 2,5. The standard EN 10295 for GX40NiCrNb45-35 (1.4889) steel is not giving the hardness but it should be notice that it is high (average 317 HV5).

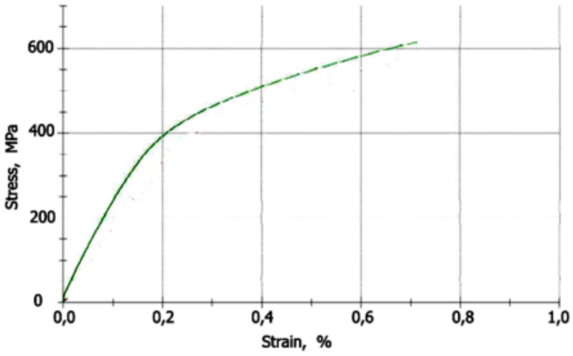


Fig. 8. Tensile stress-strain curves of the samples (1 and 2) tested at room temperature

## Conclusions

1. The transien temperature appear in high temperature at about 900°C. In this coincidence material will have tendency to cracks after cooling in low temperature.
2. Investigated alloy 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 $\gamma$/NbC.
3. The microscope examinations of impact test sample lead to the conclusion that the fracture of examined material (in room and elevated temperature) has brittle character. It should be notice that hardness of material is high.
4. The often cooling of equipment from the work until room temperature can be reason of the tube coil sheets fractures.

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## СТРУКТУРА И МЕХАНИЧЕСКИЕ СВОЙСТВА ВЫСОКОХРОМИСТОГО И ВЫСОКОНИКЕЛЕВОГО СПЛАВА ПОСЛЕ ДЛИТЕЛЬНОЙ РАБОТЫ ПРИ ВЫСОКОЙ ТЕМПЕРАТУРЕ

*Жаропрочные сплавы заменили традиционные жаропрочные сплавы на основе никеля и имеют эквивалентные свойства в условиях ползучести, с превосходным сопротивлением окислению при высокой температуре. В большинстве случаев, во время службы происходят старение и фазовые превращения. В настоящее время особое значение приобрел сплав 35Cr45NiNb Micro (Steloy 1,4889 MA). При высокой температуре работы (около 900°C) материал приобретает склонность к трещинообразованию. Механические испытания образцов и микроскопическое обследования переломов приводят к выводу, что материал длительное время проработав в области высоких температур, при охлаждении до комнатной температуры может быть охарактеризован как хрупкий.*

***Ключевые слова:*** *высокохромникелевые стали, механические свойства высокохромникелевых сталей, трещины, осадочные фазы, карбиды.*

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## СТРУКТУРА І МЕХАНІЧНІ ВЛАСТИВОСТІ ВИСОКОХРОМИСТОГО І ВИСОКОНІКЕЛЕВОГО СПЛАВУ ПІСЛЯ ТРИВАЛОЇ РОБОТИ ПРИ ВИСОКИХ ТЕМПЕРАТУРАХ

*Жароміцні сплави замінили традиційні жароміцні сплави на основі нікелю і мають еквівалентні властивості в умовах повзучості, з чудовим опором окислення при високій температурі. У більшості випадків, під час служби відбуваються старіння і фазові перетворення. В даний час особливе значення набув сплав 35Cr45NiNb Micro (Steloy 1,4889 MA). При високій температурі роботи (близько 900 ° C) набуває схильність до тріщин. Механічні випробування зразків і мікроскопічне обстеження переломів приводять до висновку, що матеріал тривалий час пропрацювавши в області високих температур, при охолодженні до кімнатної температури може бути охарактеризований як тендітний.*

***Ключові слова:*** *високохромнікелевие сталі, механічні властивості високохромнікелевих сталей, тріщини, осадові фази, карбіди.*

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