EFFECT OF LONG-TERM AGEING AT 475 °C ON PROPERTIES AND MICROSTRUCTURE OF CUSTOM 465 STEEL

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Abstract

The steels with high chromium content are known to suffer embrittlement at elevated temperature induced either by decomposition of the microstructure into two arranged solid solutions α+α´ (embrittlement at 475 °C) or by precipitation of chromium-rich brittle phase σ. Martensitic precipitation hardening steels belong among materials having chromium content close to the minimum embrittlement concentration and in some circumstances there could be possibility of prolonged exposure of these steels at elevated temperatures. The effect of long-term ageing (1.000, 2.000 and 3.000 hours at 475 °C) on the material properties, microstructure and substructure of precipitation hardening martensitic stainless steel CUSTOM 465 was analysed and the additional precipitation of very fine particles of intermetallic phases and also decomposition of solid solution α into chromium-rich particles of the phase α´ with nanometric size was found. Despite expectations a slight decrease of strength and impact energy was detected after ageing at 475 °C as a result of stabilization of reverted austenite, which completely compensated the effect of the additional precipitation hardening of martensite. The total content of reverted austenite even doubled after ageing in comparison with the as-received state, although the ageing temperature was significantly lower than the temperature A_{c1} of the steel.

Keywords: Precipitation hardening steel, CUSTOM 465, long-term ageing, mechanical properties, reverted austenite

1. INTRODUCTION

The selection of materials for the extremely demanding operating conditions such as components of landing gear has been ultra-high tensile strength (UHTS) steels such as AISI 4340 and derivatives including 35NCD16THQ and 300M. These low-cost materials provide excellent tensile strength, fatigue resistance, and good fracture toughness [1], but their disadvantage is poor corrosion resistance. The recent development of high-performance structural stainless steels offers a promising alternative material, precipitation-hardened corrosion-resisting steels that have tensile properties approaching the current UHTS steels and moreover provide excellent corrosion resistance. One of these new steel grades is CUSTOM 465 with comparable tensile strength and fracture toughness, better ductility, and very good general corrosion and stress corrosion cracking resistance. As it belongs to the group of high chromium steels that are known to suffer embrittlement at elevated temperature, the aim of the presented work was to analyse the effect of long-term ageing (1,000, 2,000 and 3,000 hours at 475 °C) on the material properties and microstructure changes.

2. STEEL CUSTOM 465 AND ITS PROPERTIES

CUSTOM 465 is a trademark of Carpenter's steel grade; it is martensitic precipitation hardenable stainless steel for use in demanding applications, such as air transport or oil and gas extraction where a tensile strength of more than 1380 MPa is required. A unique combination of high strength, toughness, fatigue strength and corrosion resistance is obtained after ageing of low carbon martensite in the temperature range from 537 to 593 °C. Originally, it was developed for main landing gear of large aircrafts, but it is also used for high-pressure pump components and drilling rigs in oil and gas extraction under extreme conditions, on steam turbine parts, as well as in surgical instruments [2].

The steel is based on 11 % Ni and 12 % Cr and is also alloyed with Mo and Ti. The strengthening mechanism then involves martensitic phase transformation, followed by a strengthening precipitation of hexagonal Ω-phase needles and orthorhombic $Ni_3(Ti,Mo)$ plates. Precipitation introduces strain into the martensitic lattice, and thus it increases strengthening of the alloy. The maximum strength occurs well before precipitates become visible via light optical microscopy. Higher ageing temperature increases the toughness, but at the same time lowers strength. Reverted austenite that occurs in the structure during ageing also plays a significant role in the ductility improvement of the alloy. All these microstructural features give CUSTOM 465® steel its superior strength and toughness. The steel is delivered in four different degrees of strength corresponding to ageing at 510 °C (H 950), 525 °C (H 975), 535 °C (H 1000) and 565 °C (H 1100).

3. 475 °C EMBRITTLEMENT

Embrittlement at 475 °C occurs in Fe-Cr based alloys containing from 12 to 70 wt. % Cr and may significantly change properties of steels that have been exposed for a long time between 425 and 550 °C. This embrittlement is accompanied by increased hardness and ductile-brittle transition temperature. The reason for this embrittlement is the existence of immiscibility gap area in the binary phase diagram of Fe-Cr, where at a temperature of below 550 °C the solid solution α decomposes into areas rich in chromium (α ') and chromium-depleted area, see **Figure 1** [3]. Phase α' is non-magnetic and contains from 61 to 83 wt. % Cr and has a cubic space-centered lattice [4]. The solid solution α transforms either by spinodal decomposition or by nucleation and the growth of the α' phase [5, 6]. The rate and extent of embrittlement is a function of chromium content; at least 100 hours of temperature exposure is required for embrittlement of low and medium Cr-containing steels, while high chromium alloys may exhibit loss of ductility and toughness at shorter times, e.g. in duplex steel, it may become brittle even after 15 minutes of exposure at 475 °C [6].

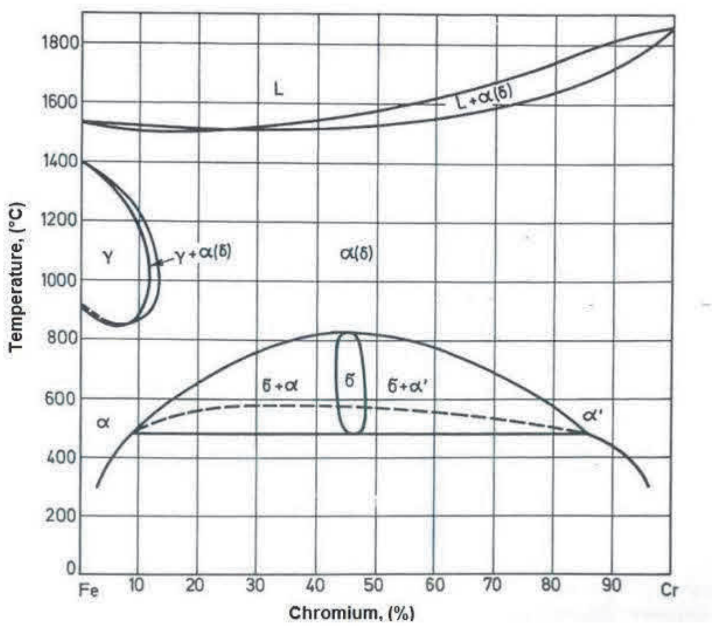

Figure 1 Binary Fe-Cr diagram with miscibility gap and decomposition of solid solution α [3]

Alloying elements (Mo, Co, Cr, Si, Nb, Al, Ti and P) accelerate the start of embrittlement at 475 °C, similarly as cold deformation that promotes the formation of the α'-phase. Embrittlement results in a significant reduction of corrosion resistance, possibly due to the selective attack of iron-rich ferrite. Embrittlement can be removed by short-term heating to a temperature in the range from 550 to 600 °C, where mechanical properties and corrosion resistance are restored to a level corresponding to the initial state [4].

Steel CUSTOM 465 has chromium content close to the lower limit, which is considered to be critical for the possibility of solid solution decomposition and developing of 475 °C embrittlement during long-term annealing at temperatures in the range of about 425 to 550 °C. **Table 1** shows the effect of exposure for 1,000 hours at temperatures 316, 371, 427 and 482 °C on mechanical properties of CUSTOM 465 steel that was initially aged at 535 °C [7]. Long-term exposure at temperatures 371 and 427 °C was accompanied by mild secondary hardening and a gradual decrease of the impact toughness. However, exposure at temperature 482 °C indicates a decrease in strength properties while increasing the impact toughness.

Table 1 Effect of long-term ageing on mechanical properties of steel CUSTOM 465 at room temperature [7]

Ageing	$R_{p0.2}$	R_m	A_5	KV
	[MPa]		**[%]**	**[J]**
316 °C / 1.000 h	1510	1600	18	41
371 °C / 1.000 h	1558	1655	16	34
427 °C / 1.000 h	1579	1689	15	24
482 °C / 1.000 h	1448	1531	20	43

In order to study the influence of long-term annealing of CUSTOM 465 steel at 475 °C, a detailed analysis of mechanical properties and structure after annealing for 1.000, 2.000 and 3.000 hours was carried out.

4. EFFECT OF LONG-TERM ANNEALING ON PROPERTIES OF CUSTOM 465 STEEL

4.1. Experimental material and its properties in as-delivered state

Analysis was performed on the forged rod of Ø 140 mm made from CUSTOM 465 steel. The rod was quenched into oil from 982 °C and further chilled at -80 °C and then age hardened at 524 °C for 8 hours. The chemical composition and mechanical properties of the steel are stated in **Tables 2** and **3** together with transformation temperatures A_{c1}, A_{c3} and M_s.

Table 2 Chemical composition of experimental material [wt. %]

C	**S**	**P**	**Mn**	**Si**	**Ni**	**Cr**	**Mo**	**Ti**	**Al**	**V**	**W**	**Cu**
0.01	0.001	0.006	0.01	0.048	10.82	11.07	0.93	1.55	0.054	<0.003	0.006	0.57

Table 3 Mechanical properties and transformation temperatures

$R_{p0.2}$, [MPa]	**R_m, [MPa]**	**A, [%]**	**Z, [MPa]**	**HV 30**	**KV, [J]**	**A_{c1}, [°C]**	**A_{c3}, [°C]**	**M_s, [°C]**
1531	1617	11.3	44.0	500	18	589	738	131

Despite the high nickel content, the A_{c1} temperature is relatively high and lies about 50 °C above the recommended maximum age hardening temperature. This would, provided that there are no significant segregations in the steels, be sufficient to prevent the partial reaustenitization of the matrix during age hardening. The microstructure was formed by lath martensite with dark segregation bands; see **Figure 2** on the left. The original austenitic grain size was G = 6. Light particles of austenite were detected inside these segregation bands (**Figure 2** on the right). The morphology of the particles suggested that they were reversed austenite formed due to segregation and local enrichment of nickel, which could significantly reduce the temperature A_{c1}. X-ray diffraction analysis found that in the CUSTOM 465 martensitic matrix after age hardening was about 6 - 7 wt. % of austenite, which was approximately about 4 wt. % more than immediately after chilling.

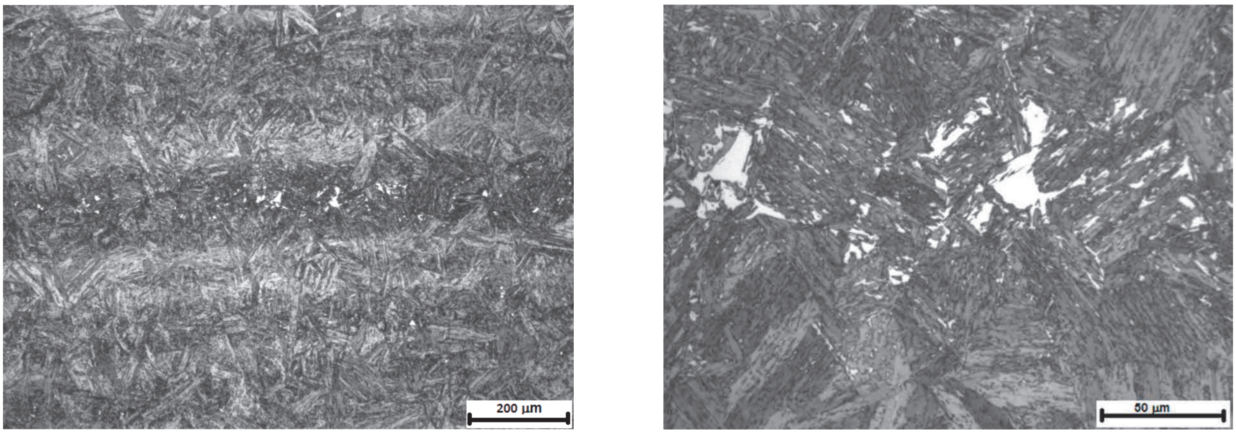

Figure 2 Microstructure of the steel CUSTOM 465, left - overall view, right - detail of reversed austenite

It was found by using EDX microanalysis and electron diffraction on the carbon extraction replicas and thin metal foils that intensive precipitation of nanoparticles started in the martensite during age hardening of the steel CUSTOM 465 at 524 °C, namely:

- MX (TiX) titanium rich particles containing Mo, but the frequency was low,
- particles containing Ti and Ni (Ni_3Ti phase), which was the most important minority phase,
- complex, coarse particles M_6X phase containing Mo, Ti, Cr and Fe situated mainly along the original austenite grain boundaries.

4.2. Mechanical properties and microstructure of CUSTOM 465 steel after ageing at 475 °C

The changes of mechanical properties at room temperature after ageing at 475 °C for 1,000, 2,000 and 3,000 hours are shown in **Figure 3**. These figures show a gradual, more or less smooth decreasing of yield strength and ultimate tensile strength (UTS) during ageing, but the total strength lowering of the steel CUSTOM 465 after 3.000 hour´s exposure was only 10 % in yield strength and 8 % in case of UTS. On the other hand, plasticity (elongation as well as reduction of area) increased after 1.000 hour´s exposure and then remained practically the same. Impact energy KV kept practically the same for the whole ageing time.

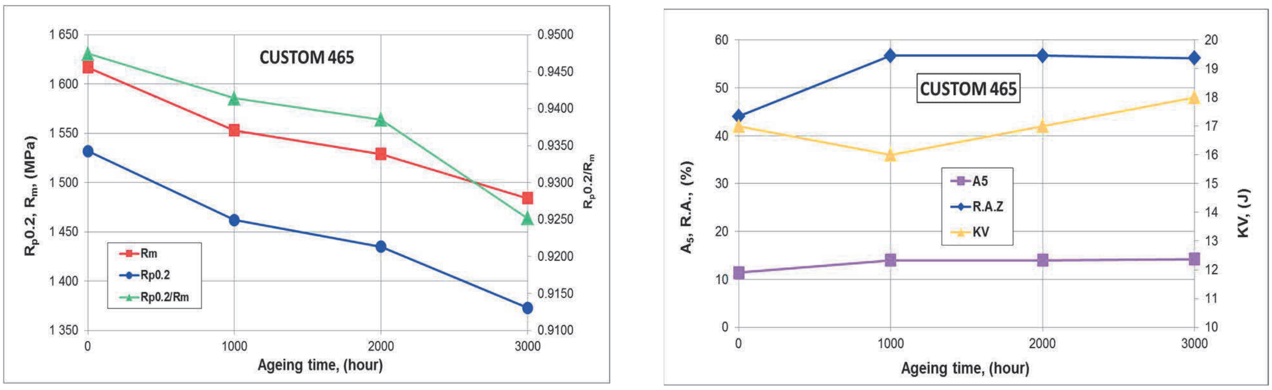

Figure 3 Change of proof stress, tensile strength, elongation, reduction of area and impact energy (KV) during ageing at 475°°C

Bright islands of the reverse austenite were found in the microstructure of the steel also after ageing at 475 °C for 3.000 h, were of irregular shape and size up to several tens of microns and appeared predominantly in the segregation bands, see **Figure 4**. The frequency and size of particles of the reversed austenite in the segregation zone was much greater than in the surrounding matrix and the total reversed austenite content increased up to 11-12 wt. %. The heterogeneous distribution of reversed austenite in aged martensite has a direct relationship with segregation during solidification of the steel. The average nickel concentration determined by the EDX spectral microanalysis in the segregation bands was 12.5 wt. %, while in the surrounding matrix it was only 9.7 wt. %.

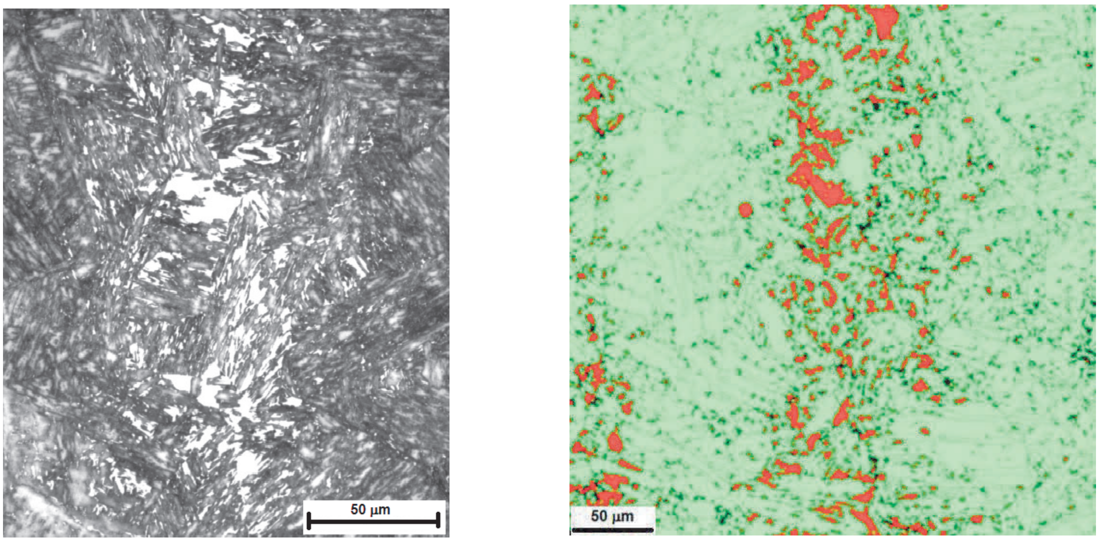

Figure 4 Microstructure (left) and phase distribution map (right) of reversed austenite (red spots) of the steel CUSTOM 465 after ageing at 475 °C for 3,000 h

Analysis of the substructure after long-term ageing revealed the following changes in comparison to the as-received state in the steel CUSTOM 465, see **Figure 5**:

- the increase of molybdenum content in TiX phase,
- the additional precipitation of the Ni_3Ti particles was confirmed after ageing at 475 °C; but no signs of the coarsening of this phase were found,
- very fine particles (about 10 nm) of chromium-rich phase were detected, which can be presumed to be the products of decomposition of the solid solution α. The exact chemical composition of these particles was not possible to analyse due to their very fine size.

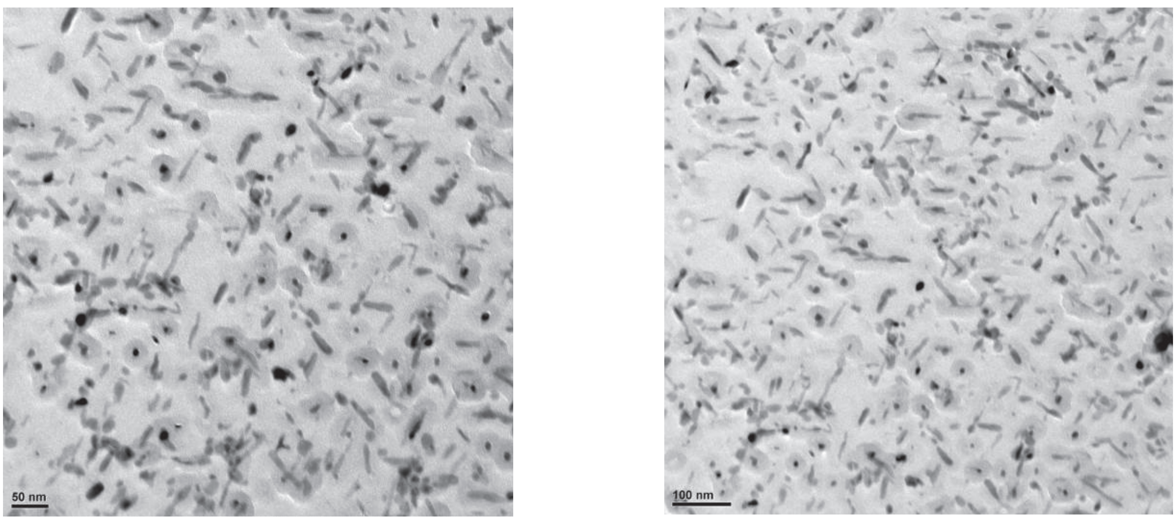

Figure 5 Precipitation in the martensitic matrix of the steel CUSTOM 465 after ageing at 475 °C / 3,000 h, extraction carbon replica

5. CONCLUSIONS

The analysis of material properties, microstructure and substructure of precipitation-hardening steel Custom 465 revealed that:

1) Ageing of the steel at 475 °C for 1.000, 2.000 and 3.000 hours was accompanied by a gradual decrease of strength and increasing of plasticity. On the other hand, notch toughness almost did not change.
2) During ageing at 475 °C the additional particles of intermetallic phases precipitated and the solid solution α decomposed into the chromium-rich particles of nanometric size. Chromium-rich particles were, however, small and they did not significantly affect the precipitation hardening.
3) Ageing at 475 °C had also stabilizing effect on the reversed austenite and its content even increased during ageing.
4) The effect of additional precipitation hardening in martensite during ageing at 475 °C was compensated by the formation of the reversed austenite with lower strength and high toughness.

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