MICROSTRUCTURE AND PROPERTIES OF MARTENSITIC PRECIPITATION-HARDENING STEEL MLX 17 AFTER LONG-TERM AGEING AT 475 °C

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Abstract

Steel MLX 17 (X1CrNiMoAlTi 12-11-2) belongs to a family of martensitic precipitation-hardening steels for use in demanding applications in aviation and offshore oil and gas industry. The unique combination of high strength, toughness, fatigue strength and corrosion resistance is obtained in this steel based on 11 % Ni, 12 % Cr and precipitation hardened by Mo, Al and Ti after ageing of low carbon martensite above 500 °C. Due to its chromium content the steel MLX 17 is a material threatened by embrittlement at 475 °C induced by decomposition of the microstructure into two arranged solid solutions α+α' and/or embrittlement caused by precipitation of chromium-rich brittle σ-phase. Although this steel is not typically exploited at higher temperatures, it is interesting to know the effect of long-term ageing on the material properties, microstructure and substructure. Therefore, the ageing at 475 °C for 1,000, 2,000 and 3,000 hours was performed and material properties, microstructure and substructure were evaluated. Analysis of substructure confirmed the additional precipitation of Lave phase, the main source of precipitation hardening in MLX 17 steel, as well as the decomposition of the solid solution α into the chromium-rich particles of nanometric size. Ageing at 475 °C was also accompanied by increasing of the reverse austenite content, which overcame the possible effect of the additional precipitation hardening of martensite.

Keywords: MLX 17, reverse austenite, mechanical properties, substructure, 475 °C embrittlement, long-term ageing

1. INTRODUCTION

Steel MLX 17 (X1CrNiMoAlTi12-11-2) is a representative of martensitic precipitation-hardening steels for use in demanding applications, namely aerospace industry, marine and defence, offshore oil and gas industry [1]. The unique combination of high strength, toughness, fatigue strength and corrosion resistance is obtained in this steel with balanced chemical composition (11 % Ni and 12 % Cr) and precipitation hardened by Mo, Ti and Al after ageing of low carbon martensite above 500 °C. Excellent corrosion resistance altogether with high tensile strength 1700 MPa and high fracture toughness predetermines this steel for the extremely demanding operating conditions such as components of landing gears, actuators, flaps, rod ends, medical devices. On the other hand, it belongs to the group of high chromium steels that are susceptible to embrittlement at elevated temperatures induced by either decomposition of the microstructure into two arranged solid solutions α+α'(475 °C embrittlement) or by precipitation of brittle chromium-rich σ-phase. Martensitic precipitation-hardening steels belong among materials having chromium content close to the minimum concentration for such an embrittlement, and there is no information about the effect of long-term exposure at elevated temperatures on the possibility of its evolution in the literature. The aim of the presented work is 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 evolution.

2. PROPERTIES OD STEEL MLX 17

MLX 17 is a trademark of Aubert & Duval and represents high strength steel belonging to the family of MLX steel grades with graduated strength levels from 1000 to 1900 MPa. The principal criteria that have been taken into account during the development of this steel grade were [1, 2]:

- nominal tensile strength from 1,700 MPa with Mo, Al and Ti used for precipitation hardening,
- high ductility, fracture toughness and stress corrosion resistance based on optimum Ni content,
- possibility of forging of very large parts with refining grain size during heat treatment at low solutionning temperature.

The steel MLX 17 and the others are based on 11 % Ni and 12 % Cr and is also alloyed with Mo, Al and Ti. In steels containing also copper and especially molybdenum it is expected that at least 11% chromium is necessary to provide good corrosion resistance, on the other hand, higher amount should be restricted due to its strong ferrite stabilizing effect. Nickel is required to provide an austenitic structure at the annealing temperature and also forms the hardening particles together with aluminium and titanium. Molybdenum provides a material resistance to stress corrosion cracking and also strongly increases tempering response and final strength without reducing the ductility.

Steel MLX 17 must undergo a special hardening treatment (age hardening) after quenching. Age hardening is performed at temperatures between 500 and 570 °C when the steel attains the final material properties. The steel is unique for its high metallurgical purity (it is typically produced by electroslag remelting) and for a balanced strength and toughness, excellent fatigue resistance and good resistance to corrosion and stress corrosion cracking. It also exhibits very good weldability, weldments are preferably made before age hardening, which gives the same material properties for the base material as well as all the welded joint.

The nominal chemical composition of the MLX 17 steel is shown in **Table 1**; the mechanical properties after two hardening modes (at 510 °C and 535 °C) in **Table 2**. The strengthening mechanism during heat treatment of MLX steel is based on martensitic phase transformation, followed by a precipitation strengthening involved precipitation of very small Laves phase and possibly also $Ni_3(Ti,Al)$ particles.

Table 1 Chemical composition of steel MLX 17, (mass %) [1]

C_{max}	Mn_{max}	Si_{max}	P_{max}	S_{max}	Ni	Cr	Mo	Al	Ti
0.02	0.25	0.25	-	0.010	10.25-11.25	11.0-12.5	1.75-2.25	1.35-1.75	0.20-0.50

Table 2 Mechanical properties of steel MLX 17 [2]

Hardening at	$R_{p0.2}$	R_m	A_5	KV
	[MPa]		[%]	[J]
510 °C	1610	1725	11	25
535 °C	1500	1590	12	45

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].

Depending on the temperature and chemical composition, the 475 °C embrittlement takes place either by spinodal decomposition of the ferrite phase into two phases (i.e. α and α′) or by nucleation and growth of the ferrite phase i.e. α′ [5]. The two phases α and α′ are rich in iron and chromium respectively. Spinodal decomposition by which Cr-rich and Cr-depleted regions are formed is a process which does not involve the development of nuclei having the ferrite α′ composition but rather the gradual buildup of Cr-rich regions. Nucleation and growth of chromium rich ferrite phase i.e. α′ is another mechanism by which 475 °C embrittlement takes place and is typical for steel with composition.

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. While the rate of 475°C embrittlement is increased by higher chromium and molybdenum contents, it decreases by increasing nickel concentration [6]. For example, 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 [7]. 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].

The development of 475 ºC embrittlement was suggested to be accompanied by an increase in the ductile to brittle fracture transition temperature and a reduction in corrosion resistance, probably due to chromium depletion of the matrix. Although these steels are primarily designed to work at temperatures up to about 300 ° C, it cannot be excluded that, under certain conditions, this limit may be exceeded during exploitation. Therefore, the experimental program for the evaluation of the properties and structure of these steels was focused also on study of the effects of long-term ageing at 475 °C for 1000, 2000 and 3000 hours.

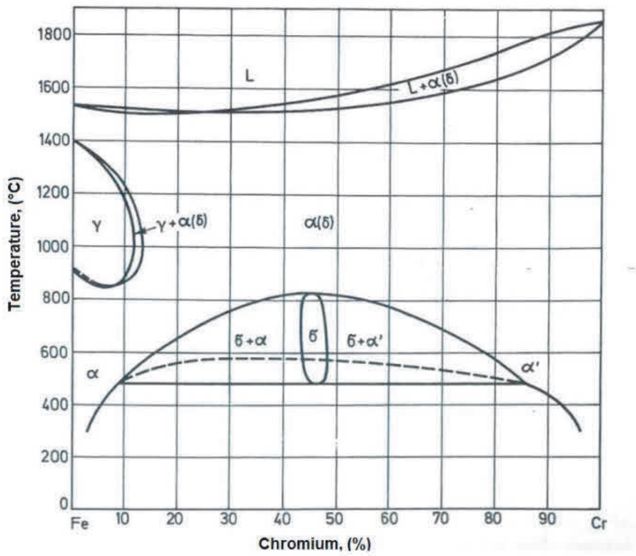

Figure 1 Binary Fe-Cr diagram with miscibility gap and decomposition of solid solution α [3]

4. EFFECT OF LONG-TERM ANNEALING ON PROPERTIES OF MLX 17 STEEL

4.1. Experimental material

Analysis was performed on the forged rod of Ø 140 mm made of MLX 17 steel. The rod was quenched into oil from 840 °C and further chilled at -80 °C and then age hardened at 532 °C for 8 hours. The chemical composition and mechanical properties of the steel are stated in **Tables 3** and **4** together with transformation temperatures A_{c1}, A_{c3} and $M_{s.}$

Table 3 Chemical composition of experimental material [wt. %]

C	S	P	Mn	Si	Ni	Cr	Mo	Al	Ti	V	W	Cu
0.02	0.001	0.007	0.08	<0.01	11.05	11.70	2.06	1.52	0.36	0.009	0.012	0.032

Table 4 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]
1565	1616	10.8	58.7	502	17	586	746	136

The microstructure of the steel was martensitic with about 5.5 wt. % of austenite and was relatively fine with the original austenitic grain size G = 10 (see **Figure 2**). The morphology of austenitic particles suggests that they were formed of reversed austenite transformed during age hardening due to local segregation and enrichment of nickel, which could significantly reduce the temperature A_{c1}.

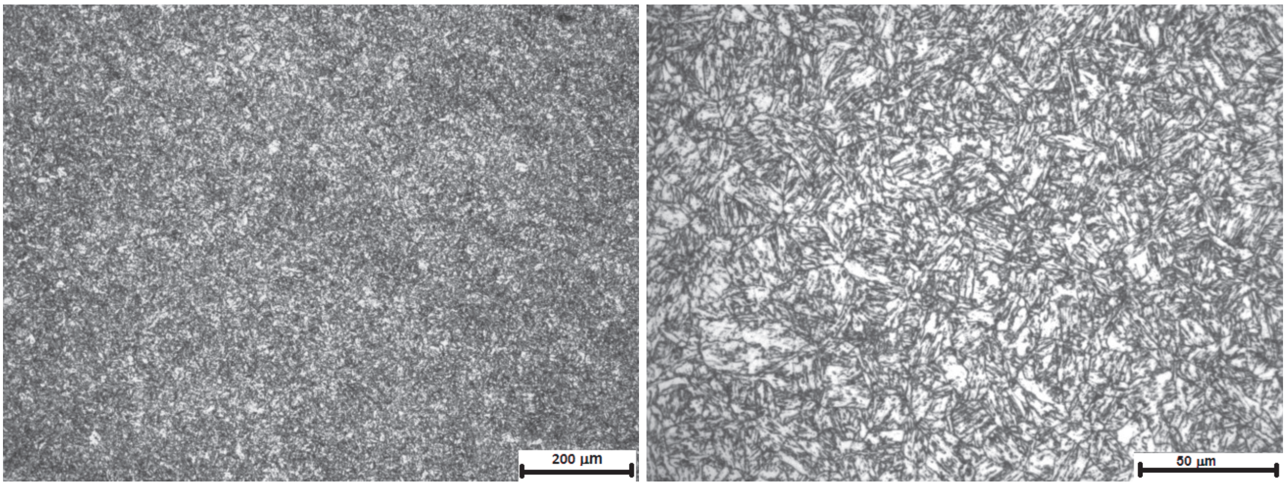

Figure 2 Microstructure of the steel MLX 17.
Left - overall view, right - detail of microstructure

By using EDX microanalysis and electron diffraction on the carbon extraction replicas and thin metal foils It was found that intensive precipitation of nanoparticles started in the martensite of the steel MLX 17 age hardened at 532 °C, namely:

- *TiX* particles containing Mo, a high percentage of Mo indicates their precipitation during age hardening,
- fine particles of intermetallic Laves phase of type Fe_2M containing Mo, Cr and Fe,
- fine carbide particles of Mo_2C,
- particles of complex phosphide of M_2P type (only low frequency).

4.2. Mechanical properties and microstructure of MLX 17 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 decreasing of yield strength (YS) and ultimate tensile strength (UTS) during ageing, but the total strength lowering after 3,000 hour´s exposure was only 8 % (YS) and 6 % (UTS). On the other hand, plasticity (elongation as well as reduction of area) increased. Impact energy KV dropped down in the first 1,000 hours and then slowly increased again after 2,000 hours did not attain the original value.

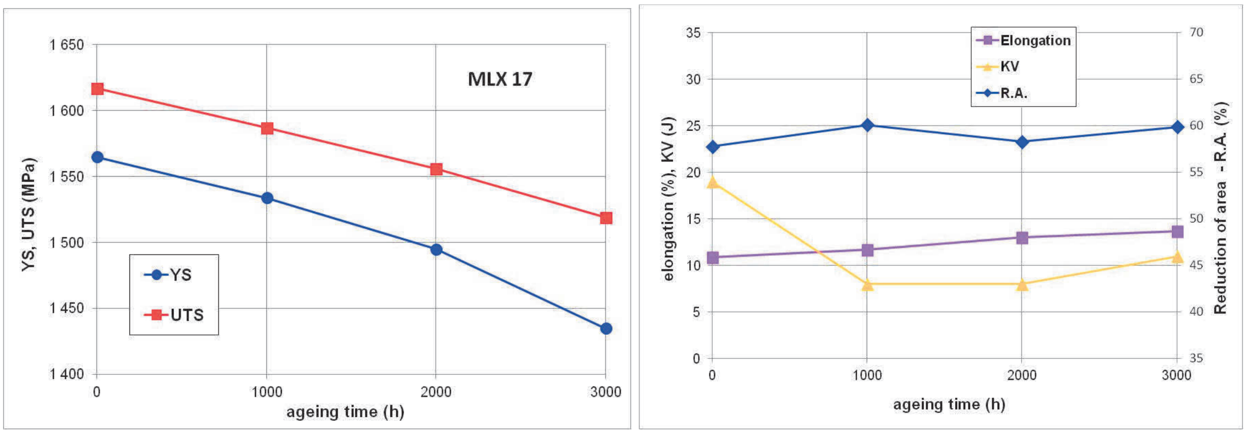

Figure 3 Change of proof stress, tensile strength, elongation, reduction of area and impact energy (KV) of the steel MLX 17 during ageing at 475 °C

After ageing the amount of austenite more than doubled in comparison with the as-received state, which means that the reverse austenite was stabilized during ageing at 475 °C, regardless of the fact that the ageing temperature was significantly lower than the temperature A_{c1}. Phase maps with ferritic and austenitic phases detected by using EBSD technique is shown in **Figure 4**.

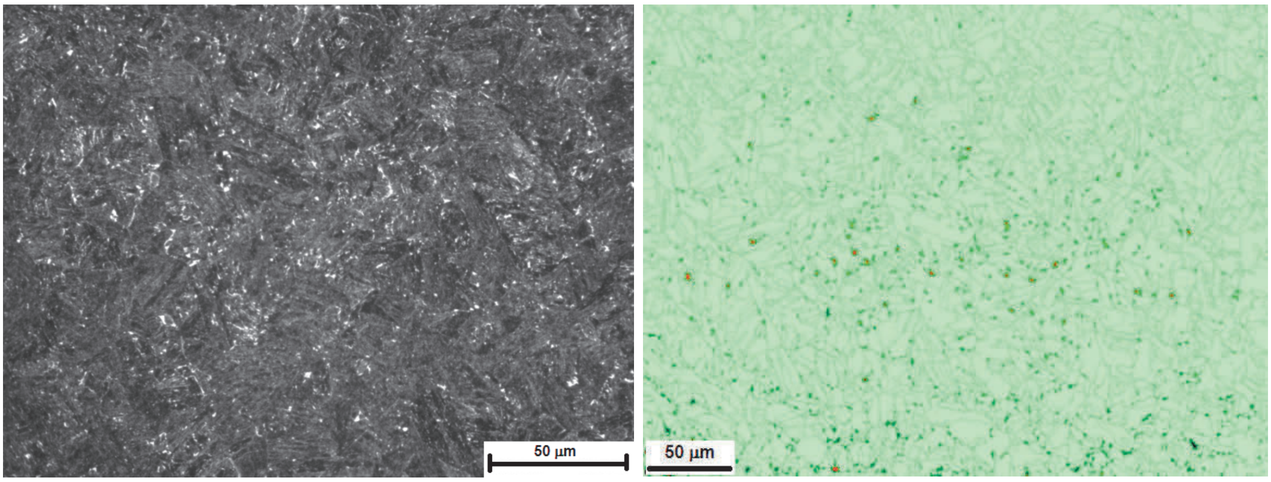

Figure 4 Microstructure (left) and phase distribution map of reverse austenite (right - dark spots) after ageing at 475 °C for 3,000 hours

EDX microanalysis of samples aged for 3,000 hours revealed the following phases in the steel MLX 17, see **Figure 5**:

- *TiX*. Small particles contained, besides titanium, also a significant amount of molybdenum.
- *Fe_2Mo Laves phase*. The precipitation of Laves phase particles was very intensive and these particles were the main source of precipitation hardening in MLX 17 steel. However, the dimensional stability of the particles of this phase was not too high. After ageing 475 °C / 3,000 hours, the mean particle size ranges up to about 100 nm.
- *Cr rich phase*, which can be considered as product of decomposition of α solid solution. Besides Cr were present in these particles also iron and molybdenum. The particle size was very small (about 10 nm) and their amount was small, too.

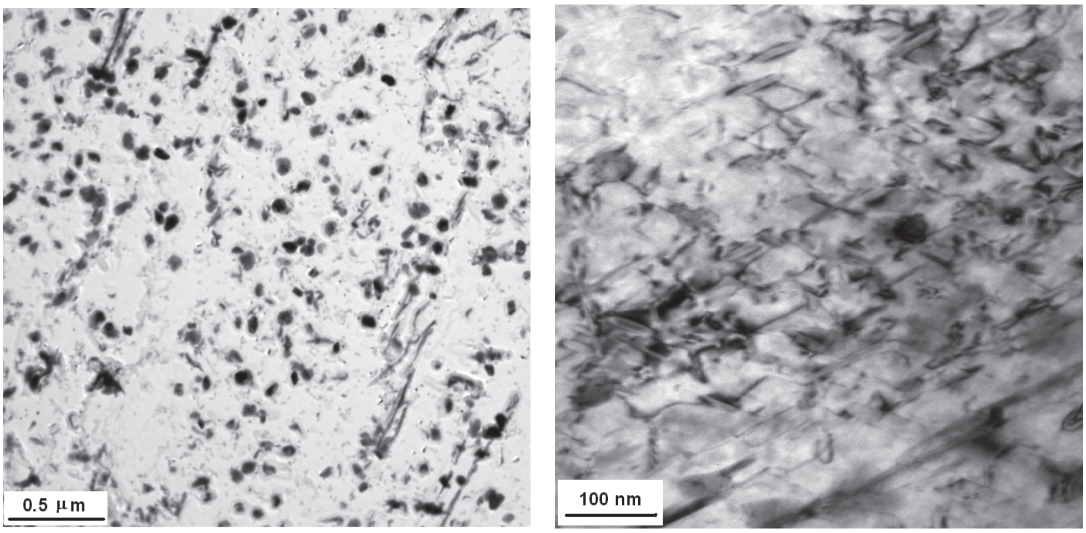

Figure 5 Precipitation in the martensitic matrix of the steel MLX 17 after ageing at 475 °C / 3,000 h, extraction carbon replica (left), thin foil (right)

5. CONCLUSIONS

The analysis of material properties, microstructure and substructure of precipitation-hardening steel MLX 17 revealed that 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. Pronounced decrease of impact strength after the first thousand hours was followed in longer times by small increasing. This phenomenon could be the result of additional precipitation of Laves phase as well as decomposition of the solid solution into the chromium-rich particles of manometric size. Furthermore, ageing at 475 °C also stabilizes the significant amount of the reverse austenite, which compensated the effect of the additional precipitation hardening in martensite.

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