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MECHANICAL PROPERTIES OF VM12 STEEL AFTER 30 000 hrs OF AGEING AT 600°C TEMPERATURE

WŁAŚCIWOŚCI MECHANICZNE STALI VM12 PO 30 000 GODZIN STARZENIA W TEMPERATURZE 600°C

The paper describes the influence of different times of ageing on mechanical properties and microstructure stability in hardened and tempered VM12 steel exposed to service temperature – 600°C. Detailed microstructural and microchemical analysis of secondary phases was carried out using scanning electron microscopy (SEM + EDX) and X-ray phase analysis of carbide isolates. Performed research has proved high stability of strength properties of the investigated steel, which is connected with the lath stability of the microstructure of tempered martensite. Slight changes in strength properties were accompanied by over 50% reduction in impact strength KV of the examined cast steel, from the level of 83 J in the as-received condition to 38 J after 30 000 hrs of ageing at the temperature of 600°C. Significant decrease in impact energy KV of VM12 steel results from the growth of the amount and size of precipitations on grain boundaries.

Keywords: VM12 steel, ageing, microstructure, mechanical properties

W pracy przedstawiono wyniki badań zmian w mikrostrukturze i właściwościach mechanicznych stali VM12 po 30000 godzin starzenia w temperaturze 600°C. Przeprowadzone badania wykazały, że długotrwałe starzenie stali VM12 prowadzi do względnego wzrostu wydzieleń po granicach ziaren, głównie po granicach ziaren byłego austenitu oraz skutkuje zanikiem wydzieleń typu MX oraz wydzielaniem fazy Lavesa. Zmiany w mikrostrukturze w niewielkim stopniu wpłynęły na zmiany właściwości wytrzymałościowych (granicy plastyczności, wytrzymałości na rozciąganie) o ok. 7%, natomiast spowodowały ponad 50% redukcję udarności KV z poziomu 83 J w stanie wyjściowym do 38 J po 30 000 godzin starzenia. Ponadto starzenie stali VM12 skutkowało ok. 16% obniżeniem twardości HV10 co powiązano z zanikiem wydzieleń typu MX.

1. Introduction

The development of new grades of high-temperature creep resisting steels, as well as the welding of these steels, is strictly connected with the development of power industry, especially with raising thermal efficiency of power units. Increase in the units efficiency was forced by the necessity of limiting the emission of pollutants into the atmosphere. As a result of a number of full-scale research projects, new grades of martensitic steels have been developed and introduced, such as: T/P91, T/P92 and E911. High-chromium martensitic steels were obtained through modification and optimization of chemical composition of the steels used so far in the power industry. These steels are characterized by high mechanical properties, most of all creep strength which is higher compared to that of steels used so far by around 20÷25% [1÷5]. However, the volume percentage of chromium in these steels, on the level of 9%, limits their application to the temperature of 580÷600°C. Therefore, higher temperatures of service ~620°C require applying high-temperature creep resisting steels of higher chromium content, on the level of about 12%, which ensures good resistance to oxidation and gas corrosion at the temperature of service. In order to meet these demands in Europe, a new steel has been developed, containing around 12%Cr and defined as X12CrCoWVNbN12-2-2, more commonly known as VM12. This steel was assumed to be characterized by higher creep resistance than T/P92 steel and similar oxidation and gas corrosion resistance as in austenitic PT304/PT347 steel [6÷8]. The paper presents the influence of long-term isothermal ageing at the temperature of 600°C and holding times to 30000 hrs on the microstructure and mechanical properties of VM12 steel.

2. Material and methodology of research

The material under investigation was high-chromium martensitic X12CrCoWVNb12-2-2 (VM12) steel with its chemical composition given in Table 1.

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TABLE 1
Chemical composition of the investigated steel, %mass

C	Si	Mn	Cr	Ni	Mo	V	W	Nb	Co	B	N
0.13	0.48	0.22	11.40	0.19	0.27	0.22	1.30	0.05	1.20	0.003	0.05

Test samples for research were taken out from a pipe section of φ355.6×35 mm along the rolling direction. The VM12 steel was subject to tests in the condition after quenching and tempering (after heat treatment and ageing at the temperature of 600°C for: 1000, 5000, 10 000 and 30 000 hrs). The scope of the research on mechanical properties carried out included: hardness test by the Vickers method using Futre-Tech FV-700 hardness testing machine with the load of 10kG (98,1 N), static tensile test (determiningYS, YT, El., RA) by means of testing machine MTS-810, impact energy test of Charpy V type. The investigation of mechanical properties was performed according to the current standards. The microstructure was examined using metallographic specimens prepared conventionally, etched with the Villela's reagent by means of scanning electron microscope, INSPECT F. Identification of precipitates was performed by means of X-ray phase analysis of the precipitations of carbon isolates using Philips diffractometer.

3. The results of research and their analysis

3.1. Microstructure and mechanical properties of VM12 steel in the as-received condition

The SEM micrographs of normalized and tempered VM12 steel are show in Fig. 1. In the as-received condition (after heat treatment), the VM12 steel was characterized by the microstructure of tempered lath martensite with numerous precipitations. As proved by the study [9], in the as-received condition of VM12 steel, the carbides of $M_{23}C_6$ and precipitations of the MX type were revealed. The $M_{23}C_6$ carbides (carbonborides) were mostly precipitated on the boundaries of prior austenite grains and the boundaries of subgrains/laths of martensite. Nitrides (carbonitrides) of the MX type were mainly precipitated inside the subgrains and on the boundaries of subgrains. The $M_{23}C_6$ carbides stabilize the subgrain microstructure of martensitic steel, while the fine-dispersive precipitates of MX constitute an effective obstacle for the movement of dislocations, at the same time providing high creep resistance.

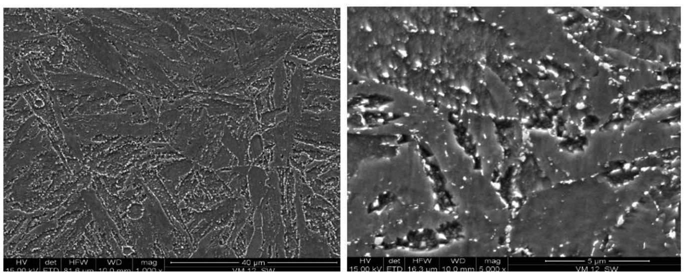

Fig. 1. Microstructure of VM12 steel in the as-received condition, SEM

Moreover, according to [10], in VM12 steel in the as-received condition, also the precipitates called „*V-wings*" can be observed. They consist of spherical shaped NbC carbides and lamellar VN precipitates nucleating on them. Additionally, in the microstructure of the examined steel also the presence of delta ferrite was revealed.

Mechanical properties of VM12 steel in the as-received condition, determined at room temperature, together with the minimum requirements are presented in Table 2. In the as-received state, the VM12 steel was characterized by high strength properties: yield strength and tensile strength which were higher than the required minimum by 20%. High strength properties in the as-received condition is what the examined steel owes to the microstructure of tempered martensite (strengthening by lath boundaries) and numerous precipitates (precipitation strengthening).

TABLE 2
Mechanical properties of VM12 steel in the as-received condition

	YS, MPa	TS, MPa	El. %	RA, %	KV, J	HV10
Investigated steel	571	750	21.5	64	83	259
Requirements [4, 8]	min. 450	620÷850	min. 19	–	min. 27J	–

The VM12 steel in the as-received condition was also characterized by impact energy KV which was over 3-times as high compared to the required minimum of 27J. The value of impact energy KV of 83 J, however, is not impressive, since other grades of high-chromium martensitic steels in the condition after quenching and tempering are characterized by impact energy KV at least on the level of 120 J [7, 8, 11]. High impact energy of high-temperature creep resisting steels in the as-received state is required because, as experience shows, during the steel's service under creeping conditions the decrease in impact energy runs faster in comparison with other mechanical properties [7, 12]. Impact energy of VM12 steel on this level probably results from high carbon content in this steel (it is lower merely by 0.01% than the maximum acceptable content of this element). High volume fraction of carbon results in the growth of the number of $M_{23}C_6$ carbides precipitated on the boundaries of prior austenite grains and the boundaries of martensite laths of $M_{23}C_6$ carbides, which has an unfavourable influence on ductility of the examined steel. Lower volume fraction of carbon, required in order to obtain high impact energy KV>100J, may also have a good effect on the growth of creep strength [13]. Lower impact energy of VM12 steel in the as-received condition, compared to other martensitic steels is also influenced by the presence of delta ferrite observed in the microstructure.

3.2. Precipitate Identification by X – ray Analysis

Table 3 shows results of X – ray diffraction of electrolytic extraction for steel specimens in the as-received condition and after 100, 5000, 10000, 30000 hrs. Performed analysis of the phase composition of precipitates in VM12 steel has shown that the process of ageing at the temperature of 600°C, after 1000 hours contributes to the precipitation of intermetallic Laves phase. The Laves phase, according to literature data [9, 15], is precipitated mostly on the boundaries of prior austenite grain, frequently near $M_{23}C_6$ carbides, and is definitely not a favourable phase due to its low thermodynamic stability. The Laves phase precipitated on grain boundaries increases the steel's susceptibility to intergranular cracking and decreases the creep resistance of steel by depletion of matrix in alloy elements (molybdenum, tungsten) [15-17]. Ageing times longer than 5000 hours cause the disappearance of MN precipitates, which proves their transformation in favour of the stable precipitates of compound nitride Cr(V, Nb)N – the Z phase [18, 19]. In martensitic steels containing at least 10%Cr, fine-dispersive precipitates of MX are metastable and get transformed into more thermodynamically stable precipitates of Z phase, as a result of their enrichment in chromium atoms. Each large precipitation of Z phase occurs at the expense of ca. 1500 fine-dispersive MX precipitates [18]. The transformation of MN precipitate → Z phase results in a rapid fall of creep strength of these steels. Therefore, it should be concluded that the phase composition of precipitates in VM12 steel after long-term ageing is as follows: $M_{23}C_6$ carbides + Laves phase + Z phase + (and probably also single MX precipitates).

TABLE 3
Phase composition of precipitates in VM12 steel in the as-received condition and after long-term ageing

Condition of the material	Phase composition of the precipitates
as-received condition	
	$M_{23}C_6$ – main phase; MN
after ageing at 600°C temperature, h	
1000	$M_{23}C_6$ – main phase; Laves phase (Fe_2Mo) – not much MN – trace amount
5000	$M_{23}C_6$ – main phase; Laves phase (Fe_2Mo) – not much MN – trace amount
10 000	$M_{23}C_6$ – main phase; Laves phase (Fe_2Mo) – not much
30 000	$M_{23}C_6$ – main phase; Laves phase (Fe_2Mo) – not much

3.3. Microstructure and mechanical properties of VM12 steel after ageing

Figure 2 illustrates examples of microstructure of VM12 steel after 10000 and 30000 hours of ageing at the temperature of 600°C. Performed observations of the microstructure of VM12 steel, aged at times up to 10000 hours, have shown that ageing practically did not contribute to any significant changes in the microstructure of the examined steel. Longer times of ageing for VM12 steel most of all result in gradual disappearance of the microstructure of tempered martensite and a visible relative growth in the amount and size of precipitates precipitated on the boundaries of prior austenite grain, on the boundaries of martensite laths and inside the grains. In some areas the number of precipitates on the boundaries of prior austenite grain was so large that they formed the so-called continuous grid of precipitates.

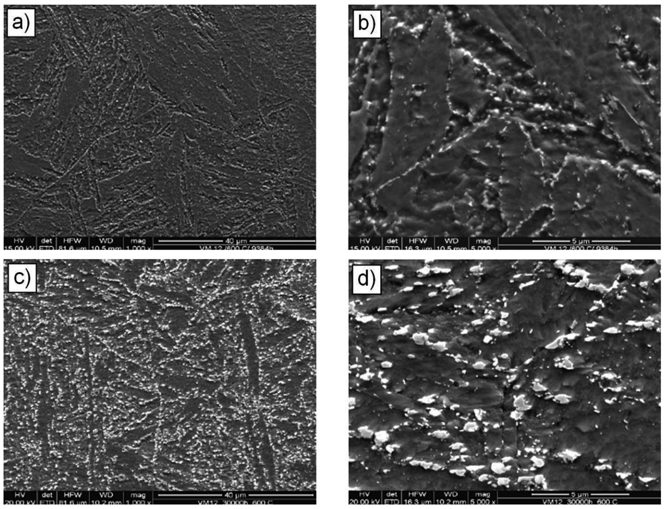

Fig. 2. Microstructure of VM12 steel after ageing at the temperature of 600°C for: a, b) 10 000 hours; c, d) 30 000 hours, SEM

The influence of ageing at the temperature of 600°C on mechanical properties of VM12 steel is shown in Fig. 3.

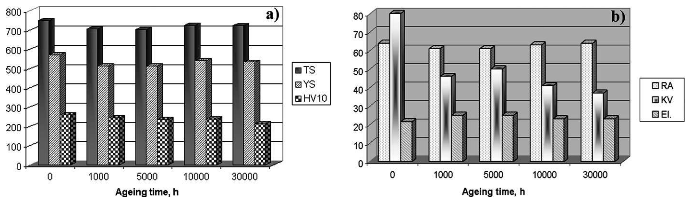

Fig. 3. The influence of ageing of VM12 steel at the temperature of 600°C on the change in mechanical properties

Ageing of VM12 steel at the temperature of 600°C and times up to 30000 hours has little effect on the deterioration in strength properties – yield strength (YS) and tensile strength (TS). The insignificant fall of the strength properties of VM12 steel after the longest ageing time, not exceeding 7%, is a sign of a very slow process of recovery and polygonization of the matrix – disappearance of lath microstructure of tempered martensite. Especially as according to [20], strengthening caused by the refinement with the boundaries of martensite laths in martensitic steels with 9-12% Cr is dominant and constitutes around 33% of the increase in yield strength for this group of steels. Therefore, it is highly important to increase the stability of $M_{23}C_6$ carbides or/and the precipitates of Laves phase, precipitated on the dislocation boundaries and effectively inhibiting the dislocation movement, which allows to retain the lath substructure and slows down the processes of recrystallization of the matrix. Bigger decrease, however, by around 16%, was noted for hardness HV10 (Fig. 3a). Greater fall of hardness of VM12 steel in comparison with yield strength and tensile strength should be associated mostly with the disappearance of fine-dispersive MX precipitates and the related reduction of the precipitation strengthening.

The insignificant decline in strength properties was accompanied by a considerable decrease in impact energy KV of the examined steel from the level of 83 J to 38 J after 30000 hours of ageing at the temperature of 600°C (Fig. 3b). Over 50% reduction in impact energy of VM12 steel after the longest ageing time results most of all from the visible growth of the amount and size of precipitates on grain boundaries (Fig. 1, 2c, 2d). The relationship between precipitates on the boundaries of prior austenite grain and temper brittleness has been discussed, e.g. [21, 22], for tempered martensitic carbon steels. The precipitates on prior austenite grain boundaries (in this case mainly $M_{23}C_6$ and Laves phase) accelerate intergranular fracture and lead to a fall of impact energy and a rise in DBTT. This indicates the necessity of increasing the thermodynamic stability of these precipitates.

4. Conclusions

The influence of long term ageing on the microstructure and mechanical properties of VM12 steel has been investigated. The important conclusions of the study are as follows:

- after long term ageing of VM12 steel microstructure, the steel consists of ferrite + $M_{23}C_6$ carbides + Laves phases + Z phases + probably also single MN precipitates;
- high strength properties after 30000 hours of ageing result from a slow process of recovery and polygonization of the matrix;
- faster softening of the matrix reflected in the hardness decrease, in comparison with yield strength and tensile strength, is connected with the disappearance of the effect of precipitation strengthening by MN particles, as a result of their transformation MN $\rightarrow$ Z phase;
- significant decrease in impact energy KV of VM12 steel is connected with the growth of the amount and size of precipitates on the boundaries of grains.

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