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Possibilities of Restoring the Plasticity of Operationally Degraded Steel EN ISO 14MoV6-3

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The article deals with the possibility of increasing mechanical and utility properties by means of regenerative heat treatment. Experimental program is focused on the heat treatment of low-alloy heat resistant steel EN ISO 14MoV6-3. Currently, due to significant metallographic changes, this steel is already in most cases operated in a very brittle state as a result of operational degradation. The high brittleness of the steel in operation is the source of frequent failures in the piping systems of coal-fired power plants. For this reason it is highly desirable to achieve an increase in its toughness through appropriate heat treatment and thereby achieve an adequate increase in the remaining service life. It should be noted that increasing the residual life using heat treatment is much more economically advantageous and also less time-consuming compared to the implemented repairs of sudden failures. When designing the heat treatment procedure it is also necessary to respect the specifics of heating and cooling of massive material such as thick-walled pipes. In addition the heat treatment process must be feasible directly at the location of the pipeline structure.

Keywords: Coal-fired Power Plants, Heat resistant Steel, Embrittlement, Heat Treatment

1 Introduction

The gradual pressure to increase the efficiency of power plant units inevitably also means an increase in steam parameters. An example can be a comparison of one of the oldes, still operating domestic thermal power plants – Tušimice II plant (inlet steam temperature: 540 °C; inlet steam pressure: 17,46 MPa; efficiency: < 34%) with the most modern Ledvice plant (inlet steam temperature: 600 °C; inlet steam pressure: 28 MPa; efficiency: > 42%) block with supercritical parameters [1, 2]. From the listed parameters of the most technologically advanced type of thermal power plants, it is clear how high demands ared placed on equipment`s materials. Under conditions of long-term exposure of the material to temperautre reaching 600 °C and pressure of 28 MPa, it is no longer possible to describe the action of external influences with standard static or quasi-static strength charakteristics, such as yield strength.

Steel EN ISO 14MoV6-3 has been used since the 1970s for high-temperature exposed components in practi-cally all coal-fired thermal power plants in the Czech Republic. Thus, steel EN ISO 14MoV6-3 is currently the best studied refractory material whose data, collected from experimental creep behaviour tests, exceeds the computational service time 2 . 10^5 hours. In order to remain competitive in the new energy mix, conventional steam power plants are forced to adapt to the requirements of semi-scheduled power generation. However, these plants were not originally designed for such operation and there-fore have to adapt to new demands on the timing of the power provided, including requirements to reduce overall plant emissions and to increase the efficiency of power generation. These components are now subjected to substantially increased cyclic stresses due to power changes during half-cap op-eration. These stresses have a major impact on the material lifetime and therefore on the overall per-formance and lifetime of the plant [3, 4].

Failures of such highly stressed materials can lead to component failure and premature shutdown of the power plant, which can have significant impacts on energy security. Therefore, it is necessary to carry out a detailed analysis of the remaining critical components and develop strategies for their maintenance. Furthermore, it is necessary to look for new mechanisms for the regeneration of materials that could extend the life of these components and thus ensure the possibility of operation of power plants even under current changing conditions (i.e. under conditions of non-constant operating load).

The main purpose of the experiment is to find a possible regenerative heat treatment that will lead to the restoration of the toughness of the thermally and operationally degraded material. Regenerative heat treatment changes the internal structure in such a way as to increase its further service life. The heat treatment process must be set in such a way that there is sufficient dissolution of carbides and carbonitrides in the microstructure followed by their slow precipitation. Furthermore it is also necessary to achieve the refinement of operationally coarsened grain of the material through this process.

2 Characteristics of steel EN ISO 14MoV6-3

Steel EN ISO 14MoV6-3 belongs to the low-alloy heat-resistant CrMoV steels, which are used up to a working temperature of 580 °C (creep area), where the creep strength in 10^5 or 2.10^5 hours is very important. Due to the hardening of these steels by MX vanadium carbide and carbonitride dispersions, this steel is inclinable to secondary hardening. This is a positive process if the steel is loaded in creep conditions, when due to the high temperature high plasticity of the material is guaranteed. In the case of operation in the sub-creep region (lower temperatures), the plastic properties are reduced, which leads to brittle fracture. The most susceptible to brittle damage is the heat-affected zone of the weld [5, 6].

An increase in the heat resistance of this type of steel can be achieved mainly by adding a small content of vanadium. The main reason for the increase in heat resistance of steel EN ISO 14MoV6-3 is the precipitation of stable vanadium carbide V_4C_3 (or carbonitride V(C, N)). Vanadium carbide has little tendency to roughen during prolonged temperature exposure. The optimal content is determined by a V:C ratio equal to approximately 4. Increasing the value of the ratio beyond this limit causes an increase in carbide roughening, which is unsuitable from the point of view of the heat-resistant properties of this steel. Also, when the vanadium content is increased, M_6C carbide is formed, which is also undesirable for these steels. Molybdenum in these CrMoV steels can be purposefully increased to 0.5%. Exceeding this limit results in the formation of Mo_2C carbide and mainly M_6C carbide, which is a complex carbide that consumes molybdenum from the solid solution and thereby reduces the effects of substitution hardening. In addition, the precipitation of coarse particles of M_6C causes the dissolution of small particles of carbides and carbonitrides (VC, VCN, Mo_2C) and thus reduces the effect of precipitation strengthening [7,8].

Steel EN ISO 14MoV6-3 is supplied in two states as standard: 1) EN ISO 14MoV6-3.5 – annealed and tempered, 2) EN ISO 14MoV6-3.9 – accelerated cooling from the austenitizing temperature followed by tempering. The microstructure of the steel, in the right condition, consists of a fine-grained ferritic-bainite structure with homogeneously dispersed carbide phases, which increase the heat resistance of the steel. These are mainly V_4C_3, VCN, Mo_2X, Cr_2C_3, $M_{23}C_6$ or VN carbides [9].

For the examination of the exploited steel EN ISO 14MoV6-3, samples were taken from the steam pipe of the thermal power plant, where the material was exposed to operational pressure, temperature and chemical stress for more than 150 000 hours. The operating parameters of the steam in the given steam line were T=540 °C and p=18 MPa.

3 Experimental material

Operationally loaded material shows an enormously brittle state. The absorbed energy KV_2 is significantly lower than the minimum required 27 J. The value that was found $KV_2 = 8 \pm 0.5$ J. The brittle state of the material is also evidenced by its microstructure, which consists mainly of ferrite and tempered bainite with a considerably coarsened grain. Carbide envelopes are located along the grain boundaries. The aim of the experimental program is therefore to find a solution in the form of a proposal for regenerative heat treatment, which would lead to an improvement of the mechanical properties and above all to an increase in toughness, i.e. to an increase in the value of the absorbed energy above the minimum required value of 27 J. According to previously published reports, regenerative heat treatment with a partially positive result has already been carried out for cast low-alloy heat-resistant steels, specifically for steels of the G21CrMoV4-6 and G17CrMoV5-10 types. For steel EN ISO 14MoV6-3, a similar effect of regenerative heat treatment is assumed as in the case of cast steels. The design of the regenerative heat treatment regime is based on the assumption of structural and chemical changes in the material, which were caused by long-term exposure to elevated temperature and pressure. The expected demands for regenerative heat treatment are therefore as follows [6,7]:

- Reduction of grain size
- Recovery of bainitic structure
- Dissolution of carbides precipitated along grain boundaries

4 Heat treatment

On the basis of these requirements, in accordance with the standard EN ISO 415128 or DIN 17175 proposed a 6 variants of the heat treatment regime, which were further evaluated in order to find the most suitable option. The first step common to all modes is solution annealing at three selected temperatures of

850 °C, 950 °C and 1050 °C followed by cooling in oil. After solution annealing, half of the samples were subsequently tempered at a temperature of 700 °C for 3 hours followed by slow cooling in the furnace.

The overall overview of all used modes of regenerative heat treatment is as follows:

- Solution annealing at a temperature of 850 °C followed by cooling in quenching oil (850 °C).
- Solution annealing at a temperature of 850 °C followed by cooling in quenching oil and tempering at a temperature of 700 °C for 3 hours followed by slow cooling in a furnace. (850 °C + T)
- Solution annealing at a temperature 950 °C followed by cooling in quenching oil. (950 °C)
- Solution annealing at a temperature 950 °C followed by cooling in quenching oil and tempering at a temperature of 700 °C for 3 hours followed by slow cooling in a furnace. (950 °C+ T)
- Solution annealing at a temperature 1050 °C followed by cooling in quenching oil.(1050 °C)
- Solution annealing at a temperature 1050 °C followed by cooling in quenching oil and tempering at a temperature of 700 °C for 3 hours followed by slow cooling in a furnace. (1050 °C + T)

All samples were evaluated for hardness, dynamic toughness and microstructure after regenerative heat treatment. The results of the hardness measurement, including the reference value of the hardness of the degradated material before regenerative heat treatment, are shown in Tab. 1. From the analysis of the hardness measurement, it is clear that the steel sample, which was subjected to regenerative annealing at a temperature of 850 °C followed by tempering, has practically the same hardness as the reference/degradated sample. This result shows that due to the regenerative heat treatment, sufficient austenitization did not occur. This finding is consistent with the CCT diagram (Fig. 1) of the given steel, which shows that the most suitable austenitizing temperature is 880 °C. Furthermore, the hardness measurement results show that subsequent tempering generally leads to lower hardness values. This trend is related to the isothermal transformation of bainite formed during cooling into ferrite during high-temperature tempering. In general, it can be concluded from the above results that the minimum regenerative annealing temperature of 850 °C is not a suitable temperature in terms of the hardness achieved.

The Charpy impact test was performed in accordance with the EN ISO 148 - 1 standard on samples with dimensions of 55 x 10 x 10 mm and a "V" type notch. For the purposes of assessing the effects of regenerative annealing, the absorbed energy value of 27 J is taken in this case. The results of the absorbed energy measurement during the Charpy impact test, including the reference value (degradated steel), are shown in Tab 2. The individual fracture surfaces and therefore their shear and brittle fracture, which are shown in Fig. 2, also correspond to the above specific values of absorbed energy. The absorbed energy results reflect a similar trend that was indicated in the hardness measurements. Along with the rising temperature of regenerative annealing, the value of the energy absorbed during the Charpy impact test gradually increases and the material thus becomes more ductile. In the case of regenerative annealing temperatures of 850 °C and 950 °C, the absorbed energy values are higher than if tempering followed at the same temperature. This phenomenon is probably related, as in the case of the hardness measurement, to insufficient dissolution of the predominantly carbide and carbonitride phases due to the low annealing temperature. During subsequent tempering process these phases which did not fully dissolve in the matrix in the previous thermal process, continue to increase in volume as a result of relatively effective diffusion. Inadequate size and location of undissolved carbidic and carbonotridic phases at the grain boundaries subsequently cause a significant embrittlement of the material, i.e. a lower value of absorbed energy. When annealing at 850 °C and 950 °C it is therefore obviously unsuitable from the point of view of fracture toughness to include any process of subsequent high-temperature tempering of steel.

Tab. 6 *Measured hardness values for individual grades of steel EN ISO 14MoV6-3*

Sample	**Operationally degradated**	**850 °C**	**850 °C + T**	**950 °C**	**950 °C + T**	**1050 °C**	**1050 °C + T**
HV_{10} [-]	155 ± 3.5	229 ± 8.5	152 ± 6.0	349 ± 6.0	256 ± 4.0	392 ± 11.0	287± 3.0

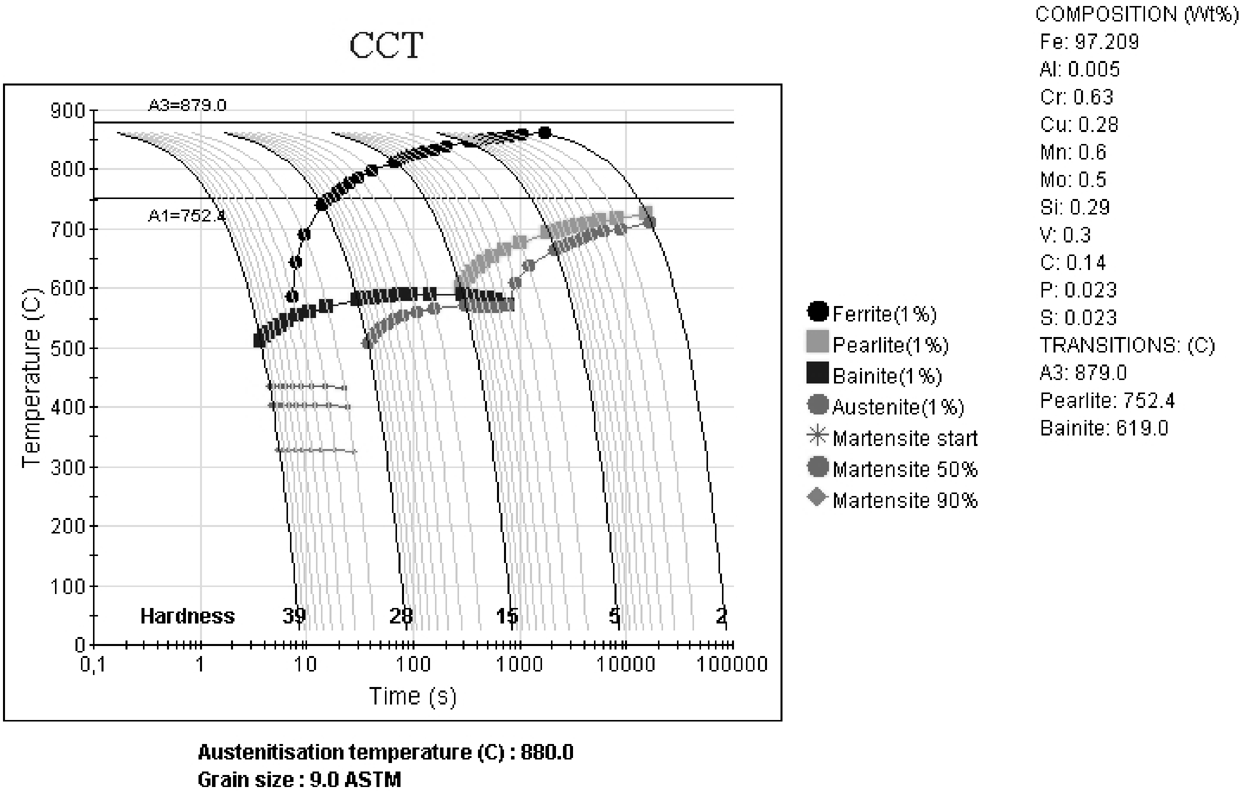

Fig. 10 *CCT diagram of steel EN ISO 14MoV6-3 created on the basis of the detected data by the program JMAT Pro*

Tab. 7 *The results of measuring the absorbed energy of KV_2 steel EN ISO 14MoV6-3 after regenerative heat treatment*

Sample	Degradated sample	850 °C	850 °C + T	950 °C	950 °C + T	1050 °C	1050 °C + T
KV_2 [J]	8 ± 0.5	23 ± 1.5	7 ± 0.5	31 ± 0.5	26 ± 0.0	65 ± 5.0	122 ± 10.0

850°C **850°C + T** **950°C** **950°C + T** **1050°C** **1050°C + T**

Fig. 11 *Fracture surfaces of the samples after the Charpy impact test after individual processes of regenerative heat treatment*

The microstructure of steel after regenerative heat treatment is fundamentally different for different regimes, even when comparing samples annealed at the same temperature, differing only in subsequent tempering. In general, it can be said that in the case of samples annealed to a temperature of 850 °C, the structure is very similar to the structure before regenerative heat treatment. A relatively coarse-grained ferritic structure with carbides excluded along the grain boundaries was found. This microstructure is undesirable from the point of view of mechanical properties. In the case of regenerative heat treatment at 850 °C and tempering, the microstructure is practically identical to the degradated material, including the distribution and proportion of individual structural phases in the material. Regenerative heat treatment with an annealing temperature of 950 °C results in the creation of a significantly finer microstructure, which is desirable in terms of higher toughness of the material. In the case of an annealing temperature of 1050 °C, the samples already show a bainitic structure or a fine-grained tempering ferritic-cementite microstructure without visible particles of carbide or carbonitride phases. The fineness of the matrix is clearly desirable from the point of view of the toughness of the material. Fig. 3 - 6 show the given microstructures of individual samples. There are an images from a light and scanning electron microscope. All images are taken in the etched state, while a 5 % Nital solution was used for etching. LM images were taken with a Zeiss Observer Z.1 microscope. SEM images were taken with a TESCAN MIRA3 GMU microscope.

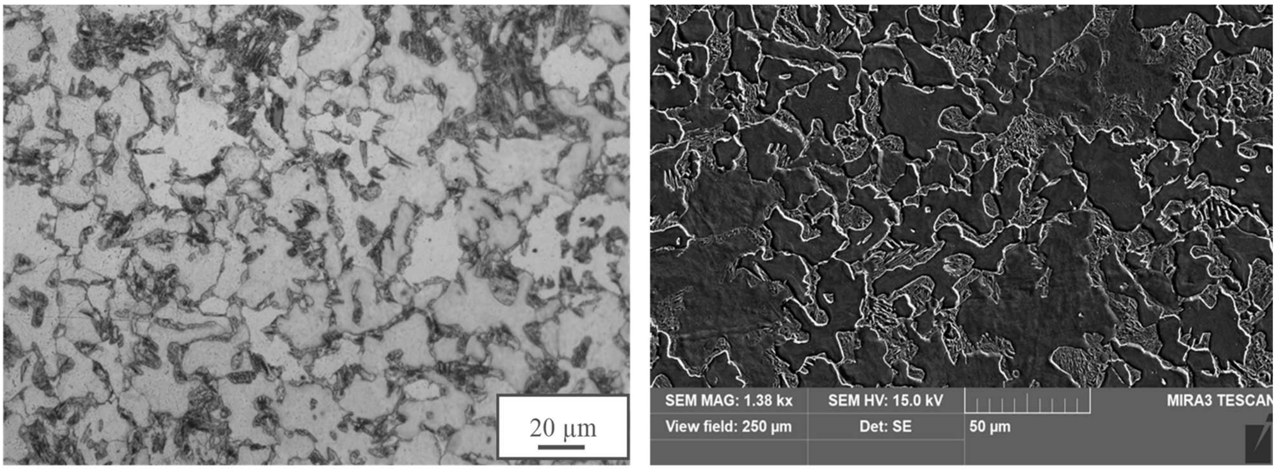

Fig. 12 *Microstructure of steel EN ISO 14MoV6-3 after regenerative heat treatment at 850 °C – coarse-grained ferritic structure with carbides excluded along the grain boundaries*

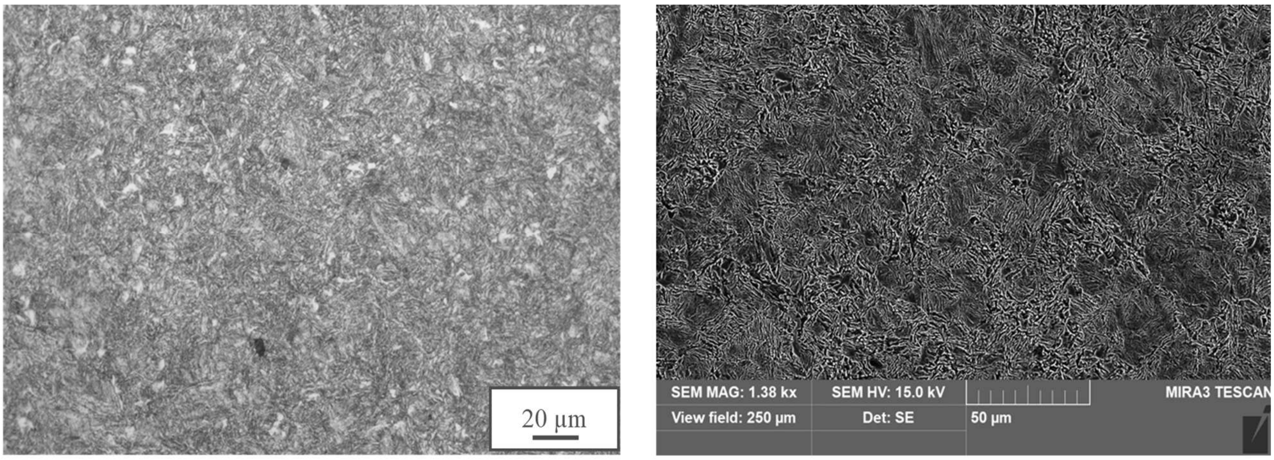

Fig. 13 *Microstructure of steel EN ISO 14MoV6-3 after regenerative heat treatment at 950 °C – fine-grained structure of ferritic – cementitic and bainitic type*

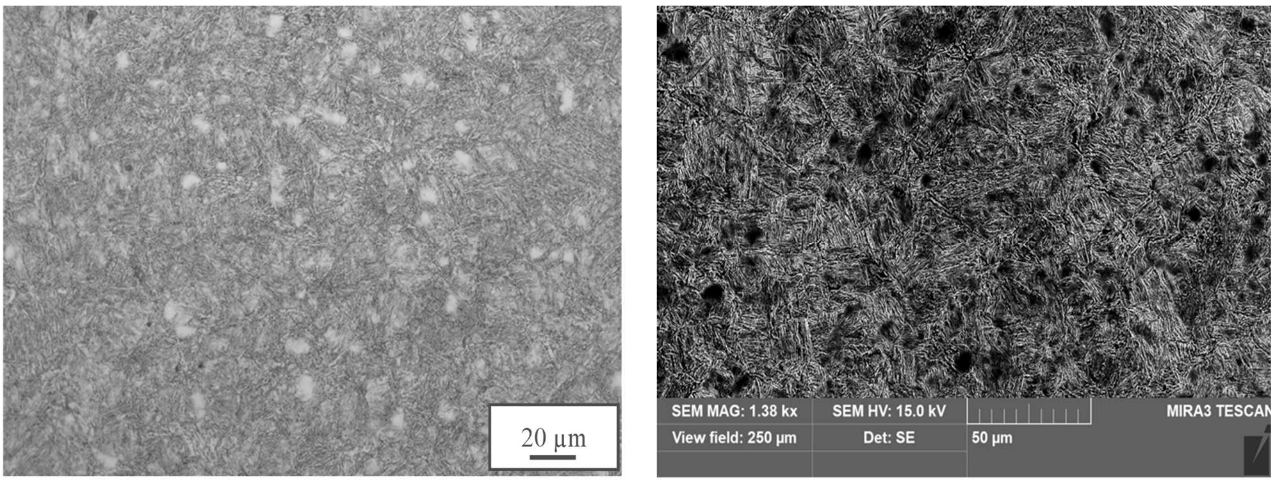

Fig. 14 *Microstructure of steel EN ISO 14MoV6-3 after regenerative heat treatment 1050 °C – fine-grained bainitic structure*

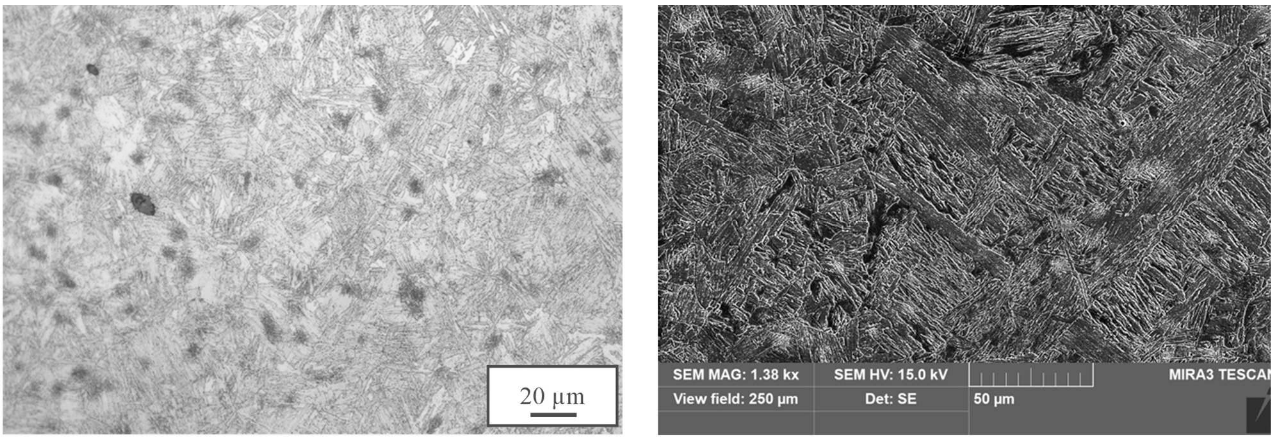

***Fig. 15** Microstructure of steel EN ISO 14MoV6-3 after regenerative heat treatment 1050 °C + T – very fine-grained tempered bainitic type structure*

The structures were also investigated using the EBSD technique (Fig. 7). An Oxford AZtec HKL EBSD analyzer with a NordlysNano detector was used. These measurements confirm the results of previous investigations. It is therefore clear from the obtained results that the original exploitation structure shows a considerably coarser structure and segregation of the carbide and nitride phases occurred at the grain boundaries. Furthermore, this measurement also confirmed that regeneration annealing performed at a temperature of 1050 °C and subsequent tempering led to a refinement of the structure and above all to a positive precipitation of fine phases inside the grains.

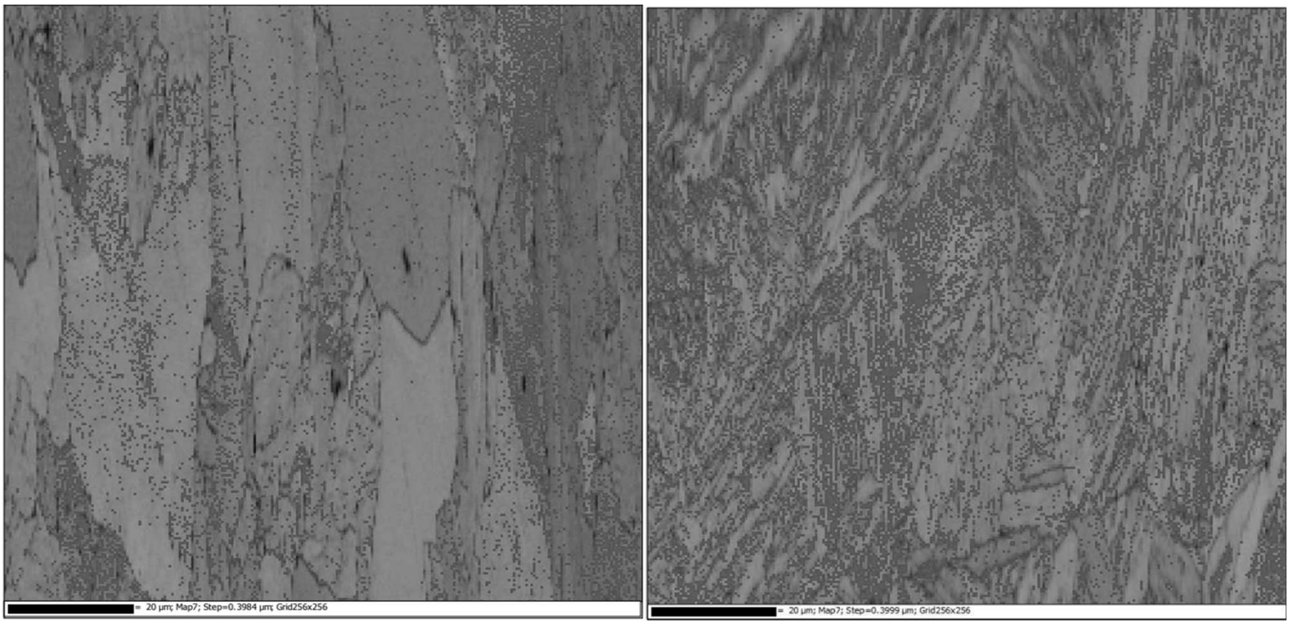

***Fig. 16** Distribution of carbides in steel EN ISO 14MoV6-3 using EBSD analysis; band contrast with phase map of distribution of detected carbides; Left image: operationally degraded steel; right image: steel after regenerative heat treatment 1050 °C + T*

From the above-mentioned results of measuring mechanical properties after regenerative heat treatment, it can be seen that the best results were achieved by solution annealing at a temperature of 1050 °C. The samples tested in this way were cooled in queinching oil. However, such a rapid cooling mode is at least very problematic for the given real application, i.e. for the main steam pipe with a large diameter. In the case of massive constructions, rapid cooling cannot be ensured in real conditions, as in the previous experiment. For this reason, the possibility of cooling the component freely in the air was also investigated. In air-cooled steel, a very fine-grained ferritic-bainitic structure was formed. After the subsequent tempering a troostite structure was created. During the tempering process there was an unwanted precipitation of carbide particles inside the bainitic grains. This is very undesirable in terms of mechanical properties. It was found that slow cooling of the samples in air was not sufficient to prevent the precipitation of carbide and carbonitride phases from the matrix of the material as in rapid oil cooling. This precipitation of unwanted phases subsequently led to a decrease in the impact strength and hardness of the material (Tab. 3). In addition, high-temperature tempering of the material led to the deposition of lamellar carbide phases inside the grains, which further reduced the impact strength (Fig. 8). Precipitation of lamellar carbide phases during high-temperature tempering is a common phenomenon in materials containing carbide-forming elements. This phenomenon occurs due to the diffusion of these elements inside the grains of the material, which leads to the formation of carbide layers. These brittle carbide phases can act as sites for crack initiation and propagation, ultimately reducing the toughness of the material.

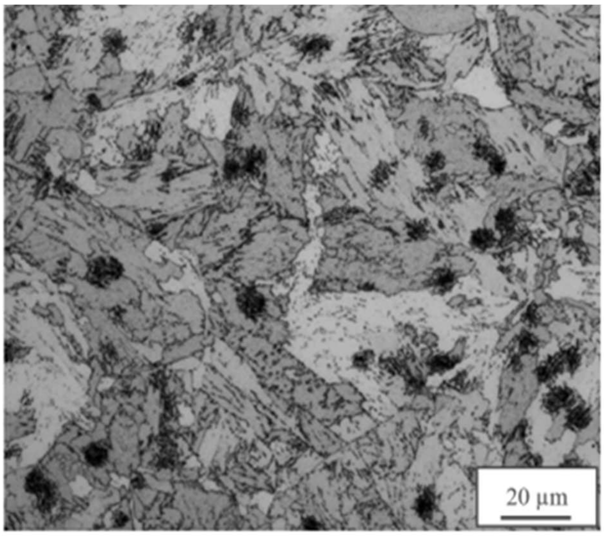

***Fig. 17** Microstructure of steel EN ISO 14MoV6-3 after solution annealing at a temperature of 1050 °C with air cooling + subsequent tempering at a temperature of 700 °C. Presence of excluded lamellar carbides inside the bainitic grains and the formation of troostite*

Due to the relatively massive dimensions of the main steam pipelines of power plants (e.g. Ø 324 mm with a wall thickness of 46 mm), the amount of heat stored in the pipeline during heating is so large that the rapid cooling simulated in the previous text is very difficult to achieve. For this reason a very slow cooling of the samples from the solution annealing temperature was investigated. Specifically, the part was left in the furnace until it cooled down to room temperature, i.e. cooling took place for 13 hours. Slow cooling process in the furnace caused a significant coarsening of the material structure. The microstructure of the material was very similar to the original operationally degraded state. As a result of tempering at a temperature of 700 °C for 3 hours, there was a predicted decrease in grain size and the transformation of lamellar pearlite into globular pearlite, i.e. tempering resulted in spheroidization of carbide particles. Furthermore, as a result of tempering, there was a uniform redistribution of these globular carbide particles within the individual grains. For the 1050 °C+T sample, the precipitation of carbide particles inside the bainitic grains was detected (Fig. 9).

Tab. 3 shows the mechanical properties of the exploited steel after heat treatment at 1050 °C with very slow cooling in the furnace together with the results from previous measurements when the samples were cooled in oil and air for comparison. Even in this case, the negative effect of slow cooling after annealing is clearly distinguishable. Slow cooling could not prevent the re-formation of carbide and carbonitride phases from the material matrix. The coarsening of material grains as a result of very slow cooling is a decisive factor contributing to the reduction of toughness. Subsequent tempering at a temperature of 700 °C contributed to the reduction of the grain size of the given structure and also had an effect on the change in pearlite morphology (from lamellar to globular) and its distribution. For these reasons, the value of KV_2 in the case of the 1050 °C+T regime is still satisfactorily high. It can therefore be stated that even with this method of regenerative annealing, there was an increase in impact strength. Compared to slow cooling in oil, there was a significant decrease in hardness values for all furnace-cooled samples. Despite the fact that the strengthening phases were precipitated due to the slow cooling, no critical embrittlement of the material, which would lead to its total destruction, was detected during this test.

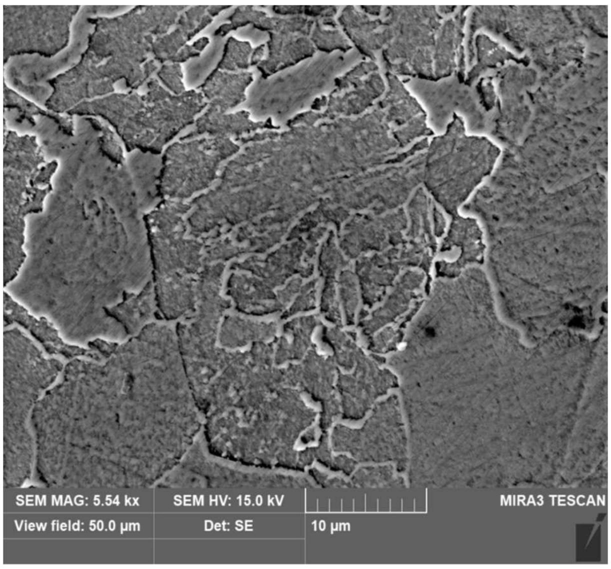

***Fig. 18** Microstructure of steel EN ISO 14MoV6-3 after solution annealing at 1050 °C with furnace cooling + subsequent tempering at 700 °C (1050 °C+T). The precipitation of carbide particles inside the bainitic grain is evident*

***Tab. 8** Comparison of the values of absorbed energy KV_2 and hardness HV_{10} of annealed steel after solution annealing at a temperature of 1050 °C with cooling in air and cooling in oil.*

Sample	1050 °C cooling: quenching oil	1050 °C + T cooling: quenching oil	1050 °C cooling: air	1050 °C + T cooling: air	1050 °C cooling: furnace	1050 °C + T cooling: furnace
KV_2 [J]	65 ± 5.0	122 ± 10.0	39 ± 9.0	54 ± 14.3	27 ± 2.5	78 ± 1.1
HV_{10} [-]	392 ± 11.0	287 ± 3.0	283 ± 5.5	252 ± 5.9	139 ± 12.5	170 ± 2.3

5 Results and discussions

It was found that steel EN ISO 14MoV6-3 exposed to long-term exposure to high temperature and pressure records significant degradation of its mechanical properties, which can have a significant effect on the overall performance and reliability of the equipment. Furthermore, it was found that annealing at a temperature of 850 °C was fundamentally unsuitable for the desired application, while annealing at the highest temperature of 1050 °C produced the best results in all measurements. The optimal procedure for recovery the toughness of the material while maintaining sufficient hardness is solution annealing at 1050 °C followed by cooling in quenching oil and tempering at 700 °C for three hours followed by slow cooling in a furnace. This approach led to a significant improvement in the mechanical properties of the material compared to the original, thermally degradation material.

The basic temperature regimes of heat treatment included only cooling the samples in quenching oil. However, for practical reasons related to the application of regenerative heat treatment to the massive steam pipes of power plants, the work was supplemented with two additional cooling media. Specifically, slow cooling in the air and very slow cooling in the furnace.

It was found by experimental methods that slow cooling led to the expected formation of undesirable carbide or carbonitride phases in the material matrix. Slow cooling also led to other significantly negative phenomena, such as microstructure coarsening, which could be eliminated to some extent by subsequent tempering. However, this process, in addition to creating an unfavorable lamellar morphology, also led to significant precipitation of carbidic phases inside the bainitic grains. Despite these problems, it was found that slow cooling in air reduced the impact toughness and hardness values of the material, but the final values of these quantities were still significantly higher compared to the condition of the operationally degraded material. This finding is quite valuable from a practical point of view, as it enables a certain regeneration of the material without the need to ensure rapid cooling. However, the need for rapid cooling from the annealing temperature of 1050 °C to achieve the highest values of toughness of the regenerated material appears to be a necessary condition.

The results of the experimental program emphasize the importance of careful selection of annealing temperature and cooling medium in regenerative heat treatment. In addition, the need for subsequent tempering to mitigate the negative effects of slow cooling is also emphasized. The experiment also shows the potential of regenerative heat treatment to improve the mechanical properties of degraded steel EN ISO 14MoV6-3, which has practical implications for industries that depend on materials exposed to high temperatures and pressures.

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