THE EFFECTS OF EXTENDED OPERATION PARAMETERS ON X20CrMoV12.1 STEEL GRADE STRUCTURAL STABILITY

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ABSTRACT

Steam superheater coils are one of the most important steam boiler elements operating in sub-critical conditions at a temperature of c.a. 550°C and under pressure ranging from 10 to 18 MPa. X20CrMoV12.1 steel grade in delivery condition has a characteristic tempered martensite structure with ferrite areas. Long-lasting operation of steam superheater coils made of X20CrMoV12.1 steel grade under creep conditions considerably affects the material structural stability (degradation). Steam superheater coils material degradation level depends on operational parameters and mainly on temperature and pressure. Moreover, the effect of a number of boiler start-ups and shutdowns as well as structural conditions is also important. The effect of above-mentioned factors on changes in X20CrMoV12.1 steel grade microstructure and substructure is described in this article. The article also includes the assessment of structure degradation processes which are manifested mainly with destruction of martensitic areas, release of $M_{23}C_6$ type carbides, release of Laves phase and occurrence of recovery and re-crystallisation processes.

KEYWORDS

power generation, operation parameters, creep-resisting steels X20CrMoV12.1, welded joints, microstructure stability,

INTRODUCTION

Continuous development of thermal power generation sector recently saw a considerable increase of importance of creep-resisting steel grades mainly for their application in boilers with supercritical parameters. It is a great step forward when compared with Sixties and Seventies, when the maximum reheat steam temperature of 360 and 500 MW power-generating units ranged from 540 to 560°C under a pressure from 10 to 18 MPa. The group of steel grades, which - during that period - met the requirements concerning heat-resistance and creep-resistance includes X20CrMoV12.1 creep-resisting steel grade elaborated in Germany in accordance with the requirements of DIN 17175 norm. It was widely used in construction of steam boiler elements such as headers and steam superheater coils [6]. X20CrMoV121 steel grade chemical analysis in accordance with DIN 17175 is shown in Table no. 1.

Table 1: X20CrMoV121 steel grade chemical analysis

Steel grade	Elements [%]									
	C	Si	Mn	S	P	Cr	Mo	V	Ni	W
X20CrMoV121	0,17-0,23	0,10-0,50	0,30-0,80	Max 0,025	Max 0,020	11,0-12,5	0,90-1,10	0,25-0,35	0,30-0,80	0,25-0,35

High-temperature creep-resistance properties of X20CrMoV121 steel grade were achieved thanks to introduction of 1%Mo and 0,3%V into a martensitic matrix already containing 12%Cr. Relatively high contents of Cr and other alloy elements makes X20CrMoV121 corrosion-resisting and heat-resisting. Steel grade containing c.a. 12%Cr and 0,2%C, due to its low critical cooling velocity, may be hardened even with ambient air cooling. The addition of molybdenum during steel cooling within the tempering process counteracts tempering brittleness and may cause the secondary hardness effect due to release of M_2C carbide. Such heat treatment results in the achievement of tempered martensite structure. The substructure shows a high dislocation density inside small elongated sub-grains and carbide release at the limits of grains as well as inside sub-grains [3]

Kinetics of release of carbides from X20CrMoV121 appears more intensive when compared with other steel grades applied in power generation sector and that's why it is so important in structural stability assessment to define the advancement of carbide phase transformations. It indicates the degree of passage of alloy components from the matrix to carbides, migration of released particles and growth of large carbide release at the limits of grains and sub-grains resulting in the decrease of material creep-resistance and reduction of its operational service life [4]. Design operational service life amounting to 100 000h is considered a safe operation period. Despite the fact that pressure equipment operated in power generation sector and thermal power sector are designed for a precisely defined operation period (100 000 or 200 000 h), there are numerous plants, which are safely operated well beyond the design service life. On the other hand, there are also examples of damage of elements caused by the loss of operational properties and resulting in their elimination from service before the expiry of aforementioned design service life [2].

Currently, the service period of the majority of elements operated in country's power gene-ration sector - and made of X20CrMoV12.1 steel grade - has already exceeded said design value of 100 000 h. Such a long period of operation of steam superheater coils under creep and fatigue conditions causes - depending on operational parameters - the changes in material structure and the decrease of its operational properties [1]. Changes in properties determining material service life are mainly caused by exceeding of operational temperature and numerous boiler start-ups after - both planned and emergency - shutdowns. Incorrect start-up is related with exceeding of allowable conditions thus accelerating material degradation process and leading to equipment failure.

The effect of non-uniform thermo-mechanical load during the long-term operation under creep condition (local, more or less considerable exceeding of temperature, stress concentration, cyclic changes of operational parameters) results in uneven material wear level thus leading heterogeneous structure and operational properties.

1. EXAMINATION MATERIAL AND METHODS OF EXAMINATION

Steam superheater coils made of X20CrMoV12.1 steel grade in accordance with DIN 17175, after long-lasting (70 ÷ 120 thousand hours) operation were subject to examinations. The effect of pressure, temperature and service time on material degradation degree was analysed. Nominal (design) operational temperature amounted to t = 540÷570°C with pressure p = 16÷19 MPa. Characteristics of microstructure degradation were determined using Reichert MeF2-type luminous microscope and HITACHI scanning electron microscope. Substructure examinations were carried out using JEOL 100B transmission electron microscope with thin foils and extraction replicas. Classification of structural changes after long-lasting operation was based on VGB-TW 507 report [5].

2. RESULTS OF EXAMINATIONS

X20CrMoV121 steel grade in delivery condition has a characteristic tempered martensite structure with δ ferrite areas and measured hardness level of ~240 HV (structure class 0). Long-lasting service of this material (70-100 thousand hours) with boiler nominal operational parameters - not depending on operation time - does not result in considerable changes in structure - structure class 1 (fig. 1). We observe the elongated sub-grains of tempered martensite with high dislocation density. Diffraction examinations and chemical composition analysis have demonstrated the release $M_{23}C_6$ type carbides, mainly at the limits of former austenite grains and at the limits of sub-grains. $M_{23}C_6$ carbide release was mainly elongated (fig. 2). Hardness is slightly lower than the hardness of material in delivery condition and amounts to ~230 HV.

Fig. 1. Tempered martensite structure of X20CrMoV121 steel grade after c.a. 100 000 hours of operation. Structure class 1.
LM Magn. 400×

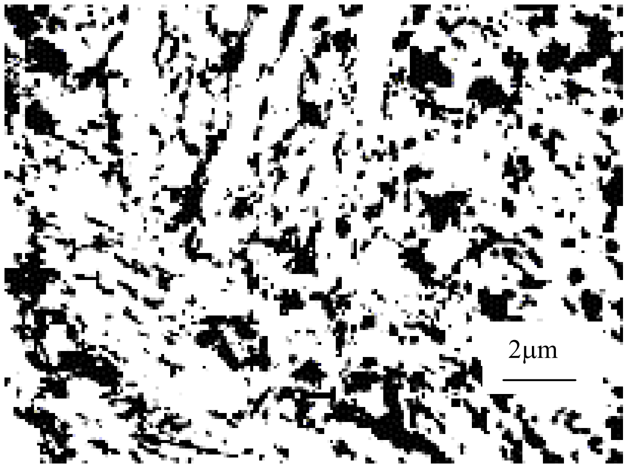

Fig. 2. Extracted $M_{23}C_6$ carbide release in extraction replica reflecting the slat martensite structure.

After long-lasting operation (~100 000 hours) at a temperature of c.a. 580°C - i.e. slightly below the allowable steel temperature - the material shows the evidence of beginning of martensite degradation with its needled structure remaining unchanged and individual creep-related voids starting to appear.

Various size sub-grains are well formed within a recovery process. Their surface is four times larger (average surface P_p=1,3 μm^2) and their dislocation density considerably lower when compared with material of structure class "1". $M_{23}C_6$ carbides are characterised with considerably diversified sizes and occur mainly at the limits of sub-grains. Their average surface amounts to $P_w=60x10^3$ nm^2.

Material hardness has decreased to c.a. 220 HV. Structural changes enable us to classify the examined material into structure class “2a”.

Extension of operation period to the level beyond 120 000 h as well as numerous start-ups considerably affect the changes in steel structure. Coil material classified in structure class “2b” demonstrates higher level of disintegration of martensitic areas with a large number of spherical shape r-type (round) creep-related voids - (fig. 3). At the limits of sub-grains, which are almost four times bigger when compared with “2a” class (P_p=4,5 μm^2), we observe $M_{23}C_6$ carbides and inside the sub-grains dislocation anchoring processes occur in fine-dispersion release of MX-type (fig. 4). Average carbide surface increases to $P_w=180x10^3$ nm^2, which is the evidence of a beginning of coagulation process.

Structural changes have resulted in hardness decrease to a level of c.a. 200 HV.

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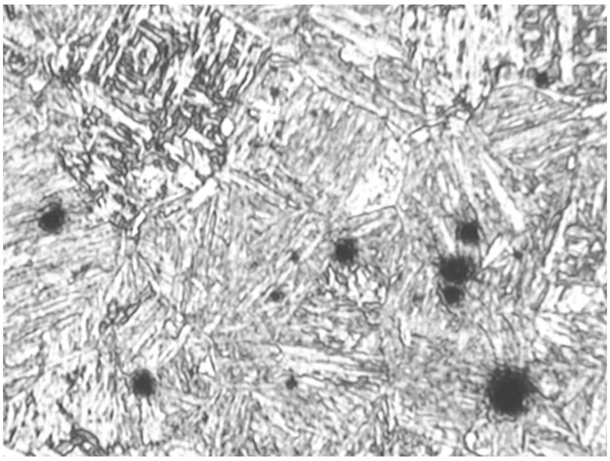

Fig. 3. Numerous creep-related voids in a tempered martensite matrix. Structure class “2a”. LM magn. 400×

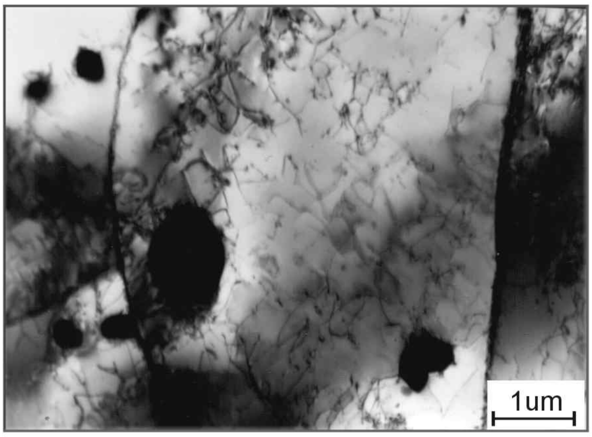

Fig. 4 Dislocation anchoring processes in fine-dispersion release of MX-type.
TEM magn. 400×

Operation (frequently below ~100 000 hours of operation) in the areas of a high risk of temperature exceeding e.g. coil elbows - in case of insufficient steam flow or too high flue gas temperature - causes the total disintegration of martensite, tempered to ferrite and carbides (mainly $M_{23}C_6$) and creation of numerous creep-related voids (fig. 5). We observe well-formed, almost dislocation-free sub-grains - rich in fine-dispersion release of MX-type - with average surface P_p=6,8 μm^2 (fig. 6). Changes of this type cause the decrease of hardness to c.a. 190 HV, thus enabling us to classify this structure into 3a class.

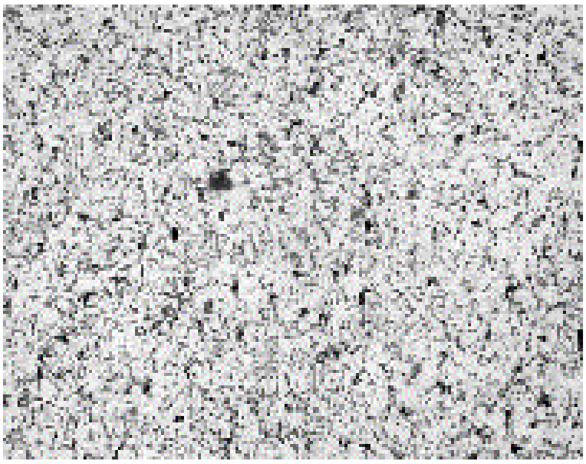

Fig. 5. Ferritic structure with carbides, numerous creep-related voids. Structure class “3a”. LM magn. 400×

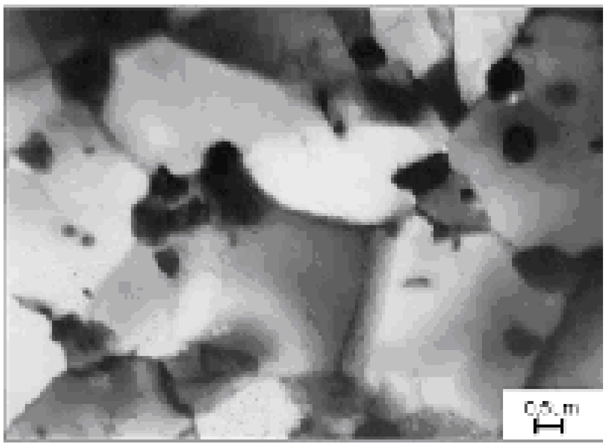

Fig. 6. Ferritic structure with carbides, numerous creep-related voids. Structure class “3a”. LM magn. 400×

Along with the flow of operation time creep-related voids became directed and $M_{23}C_6$ carbides are subject to considerable coagulation - average surface increases to c.a. P_w=240x10^3 nm^2.
Hardness level decreases to c.a. 170 HV. Material is classified in structure class 3b.

Simultaneously, at the areas of coil damage due to e.g. operation at temperatures considerably exceeding the design temperature, we observe the complete degradation of material. Structure of such element consists of carbides in ferritic matrix. We observe the agglomeration of numerous creep-related voids leading to the appearance of micro-cracking and subsequently macro-cracking (fig. 7). This type of changes enables us to classify the material in structure class 4.

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We have also observed intensive recovery and re-crystallisation processes. Average diameter of sub-grains amounts to c.a. 3,3 µm, i.e. more than five times larger then the average diameter of sub-grains measured in a w material examined after 70 000 hours of operation. Inside equiaxial sub-grains we may observe the phenomenon of anchoring of individual dislocations on fine-dispersion release of carbonitrides (fig. 8).
Related material hardness decreased to c.a. 160 HV.

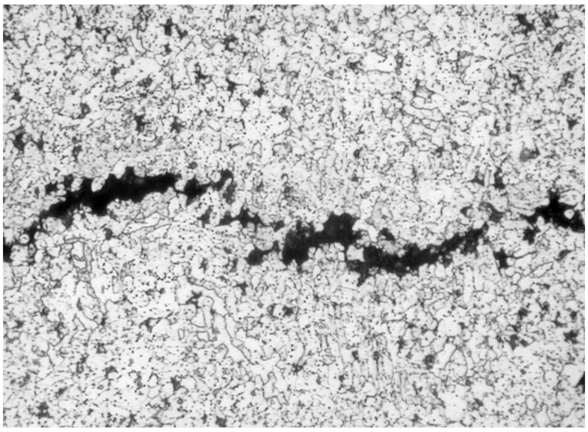


Fig. 7. Micro-cracking in ferritic matrix, directed creep-related voids. Structure class 4. LM magn. 400×

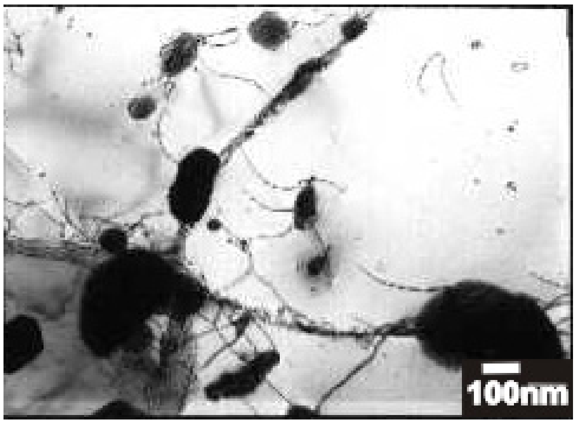


Fig. 8. $M_{23}C_6$ carbide release at the limits of sub-grains and fine-dispersion MX release inside sub-grains.

The increase of average diameter of release with the flow of operation time from c.a. 150 nm after 70.000 hours of operation to 500 nm after 120 000 hours of operation is caused not only by carbides coagulation process but also by the release of large forms of intermetallic phases. The majority of said intermetallic phases released after such long operating time (fig. 9 and 10) have, unlike carbide release, characteristic diversified morphology of particles.
The shape of $M_{23}C_6$ is regular close to spherical (fig.11 and 12).

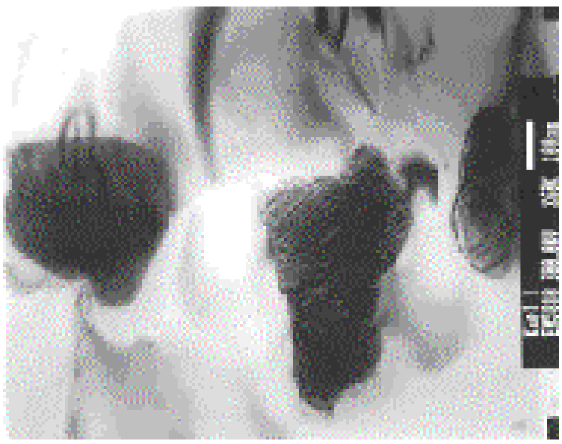
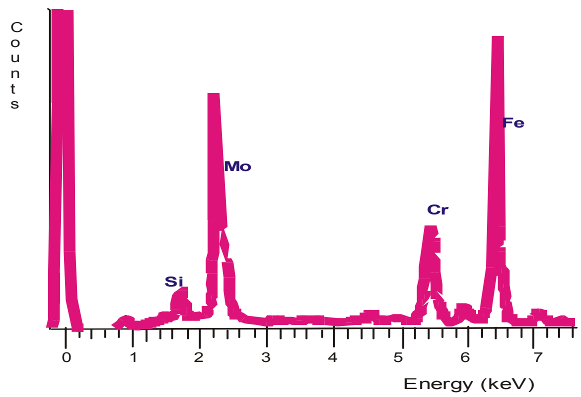


Fig. 9. Laves phase release at the limits of primary austenite grain.



Rys.10. Laves phase chemical analysis (from fig. 9).

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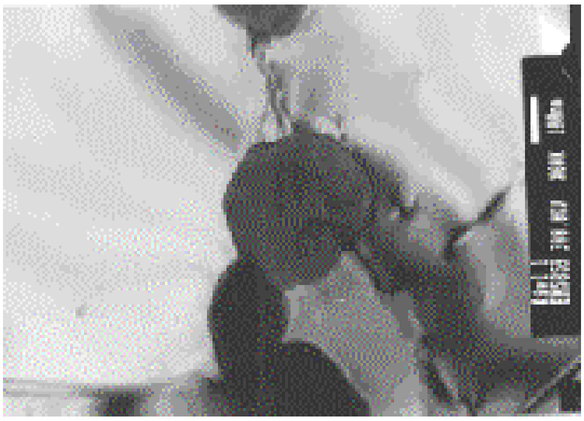

Fig. 11. Equiaxial $M_{23}C_6$ carbide release.

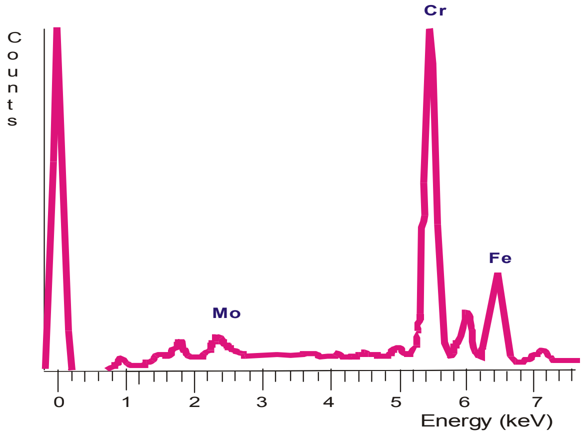

Fig. 12. Chemical analysis of $M_{23}C_6$ carbides (from fig. 11).

The process of Laves phase release in X20CrMoV121 steel grade jest strictly depends on the effect of temperature an operating time. These phases appear at a temperature of 600°C after 100 000 hours of operation. The growth of intermetallic phase release in comparable operational conditions is considerably higher tha the growth of $M_{23}C_6$ carbides due to phase release at the limits of primary austenite grains in the vicinity of $M_{23}C_6$ carbides. They are much larger than simultaneously released $M_{23}C_6$ carbides.
Apart from decrease of dislocation density and increase of sub-grains and release size, the effect of long-lasting operation parameters on changes of structural parameters is also visible in case of intermetallic phase release. Under extreme operating conditions, the effect of strengthening of solid solution for X20CrMoV121 steel grade is reduced due to intensive growth of Laves phase release. Therefore, the positive effect of these phases on material strengthening is highly improbable.
Mechanical properties examinations carried out at a temperature of 550°C have demonstrated that, not-depending on structure class of X20CrMoV121 steel grade, measured yield point of steel is higher than the minimum value required in accordance with provisions of DIN 17175 standard, achieving the level of Re_{550}=250 MPa. In case of material with the highest degradation level (structure class 3b) the yield point at a temperature of 550°C also amounted to R_{e550}=250MPa.

3. FINAL ASSESSMENT OF EXAMINATION RESULTS

The results of metallographic examinations and mechanical properties verification enabled the assessment of the influence of operational parameters - mainly temperature and operating time - on structural stability of steam superheater coils made of X20CrMoV121 steel grade during long-lasting operation.
Long-lasting operation - including excessively high stress concentration and mainly exceeding of allowable operational parameters - causes considerable changes in X20CrMoV121 steel grade microstructure and substructure.

Aforementioned steel structure changes may be divided into three groups depending on disintegration mechanism:

1) Changes in steel martensitic matrix depending on external factors may occur in two ways, as follows:

- <u>excessively high operational temperature</u>

- disintegration of tempered martensite □ creep-related voids □ ferrite + carbides □ micro-cracking;

- <u>correct operational temperature, excessively high stress caused by incorrect flow of medium, structural conditions</u>

- slight degradation of tempered martensite □ individual creep-related voids □ directed voids □ micro-cracking;

2) Processes of release and coagulation of carbides and other phases:

- release of $M_{23}C_6$ carbide □ fine-dispersion MX release □ coagulation of $M_{23}C_6$ carbide □ appearance of Laves phase;

3) Changes in steel substructure:

- sub-grains with high dislocation density □ increase of the average size of sub-grains □ reduction of dislocation density due to the processes of annihilation and dislocation regrouping.

At the same time, degradation of structure causes the considerable reduction of hardness, i.e. from 240HV in delivery condition to c.a. 160HV for a material classified in structure class “4”. Yield point at a temperature of 550°C is subject to similar changes. It was demonstrated that the occurrence of creep-related voids is not determined by the advancement of martensite disintegration into ferrite and carbides.

In a substructure, the increase of material degradation level is combined with clear increase of surface of carbides (mainly $M_{23}C_6$) and sub-grains, which at the same time have fewer and fewer dislocations due to recovery and re-crystallisation processes (fig. 13).

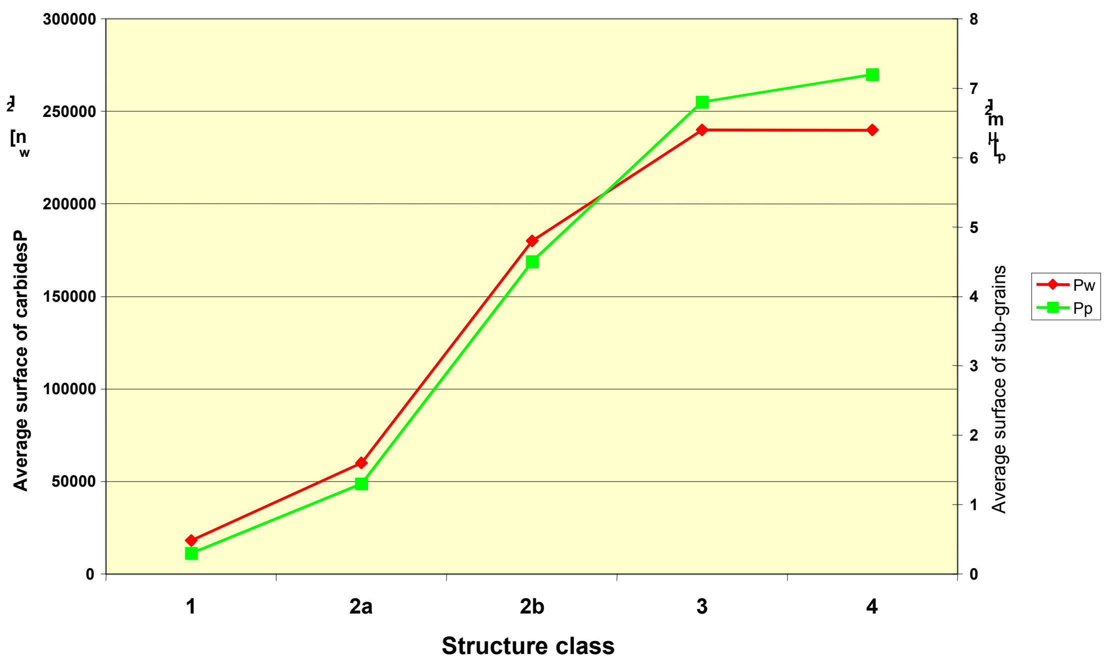

Fig. 13. Changes in average surface of carbides and sub-grains depending material structure class.

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Examinations of mechanical properties have demonstrated that, not depending on X20CrMoV121 steel grade structure class, its yield point is higher than the minimum value required by DIN 17175. It enables us to state that after long-lasting operation under optimum conditions (i.e. not exceeding the allowable ones) the examined steel grade has considerable structure stability and properties.

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