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Analysis of Low Carbon High Chromium Steel on the Conditions of Transformation Plasticity during Long-Lasting Heating

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The article deals with the investigation of transformation plasticity phenomenon of low carbon high chromium steel 0.19C-12.71Cr during 1 hour bending at 520 °C and 650 °C temperatures after long-lasting ageing. One part of steel specimens was bent after hardening, another part was hardened, aged at 520 °C or 650 °C temperatures for 1, 5, 10, 24, 48, 120 or 240 hours and then was bent during tempering at the same temperature. During the test of bending, the curve of plastic deflection of the steel specimen was obtained and remained plastic deflection after bending test was measured. After bending experiment, some steel specimens were picked up for X-ray analysis for determination of carbide particles type, its' parameter of lattice and content of chromium in it. The results obtained have allowed going more into analysis of phenomenon of transformation plasticity of this steel type, evolution of carbide particles and influence of bending stress on transformations of tempering.
Keywords: steel, microstructure, tempering, carbides, transformation plasticity.

1. INTRODUCTION

In the last 30 years, investigations of transformation plasticity (TP) have been significantly made a progress. For analysis of this phenomenon, various models have been created: Kurdjumov-Sachs [1], Magee [2, 3], Greenwood-Johnson [4] et al. – and have been developed successfully by such scientists as Taleb [5], Fischer [6], Tomita [7] et al. Computations under finite elements method (FEM) are invoked for wider conception of TP [8-10] or the results calculated by FEM have been compared with data obtained by experimental investigation [3, 11]. This phenomenon has various determinations. It has been called *superplasticity* [12, 13], *kinetic plasticity* [14], *transformation-induced plasticity* [1 – 11] et al. Essentially, this is the same phenomenon, when enormous plasticity is obtained during phase-structure transformations of steel. Although, plenty of theoretical investigations and experiments have been made for better understanding, they are not fully consummated, yet, whereas many factors have influence on TP: chemical composition of steel (content of carbon, content and type of alloying elements), phase composition dependent on steel heat treatment and conditions. A bigger part of scientific works deals with the investigation based on steel hardening [3, 5 – 7, 10]; however, TP occurs during tempering and it varies depending on steel chemical composition. The processes of tempering can be long-lasting, especially for alloyed steel, when diffusion of alloying elements and formation of special carbides occur during tempering [15 – 17]. Diffusion of alloying elements has influence on steel TP and depends on tempering temperature and duration, as even after ageing at high temperature for a long time, various transformations of tempering occur related with changes of carbide phase [18, 19].

The aim of this work was to research influence of chromium on steel TP during ageing, evolution of special carbides and its effect on TP phenomenon. Stress effect on transformations of tempering was researched, too.

2. EXPERIMENTAL

Steel 20X13 (GOST 5632-72) (equivalent X20Cr13 EN 88-86) was used for the experiments. Its chemical composition is listed in Table 1. This type of steel has a relation Cr/C = 65 (low carbon and high chromium content – that is a special condition for carbides formation). Investigated steel has a very wide application, however, the most interest field – the vanes of steam-turbines, were articles made from this steel work under long-lasting heating and stress effect.

Table 1. Chemical composition of steel 20X13 (GOST 5632-72)

Amount of element, wt. %							
C	Mn	Si	Cr	Ni	S	P	Cu
0.19	0.29	0.23	12.71	0.15	0.020	0.020	0.10

Bending specimens of 6×8×100 mm^3 size were made from the raw steel rod of diameter ∅ 14 mm. The specimens were heated 30 minutes at 1050 °C temperature in protective environment and then were quenched in oil. The initial structure after quenching was composed from martensite and ~ 6 wt. % retained austenite; hardness after quenching was 54 HRC – 57 HRC. After hardening, the specimens were bent during tempering at 520 °C or 650 °C in the special device described in [14]. The bending stress was 90 MPa. This magnitude of stress was about 14 % of yield strength at room temperature for this type of steel [17]. A part of specimens were hardened, aged without load at tempering temperature for certain duration and bent during tempering. Temperature of ageing was the same as

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during the tempering with bending; its duration is listed in Table 2. The curve of plastic deflection on condition of TP was determined during the bending test and remained plastic deflection after experiment was measured with an indicator within 0.01 mm. Some specimens (they marked with "+" in Table 2) were analyzed with X-ray diffractometer DRON-UM2 (Russian design). X-ray diffraction (XRD) measurements were carried out with CuK_α radiation ($\lambda = 0.15405$ nm) on a DRON diffractometer operating at 35 kV and 20 mA equipped with a single-crystal graphite monochromator in step scanning mode of 0.02° in 2θ and counting time of 0.5 s per step. The peaks recorded were identified with those available in PDF-2 data base [20]. The XRD patterns were refined with the program XFIT, using a pseudo-Voigt function for line profiles modeling [21]. The XRD analysis allowed identify the type of carbides, parameter of lattice of carbide and content of chromium.

Table 2. Schedule of steel heat treatment of the experiment and selection of specimens for XRD analysis

Hardening	Ageing	Tempering (with bending)	XRD analysis
1050 °C, oil	0 h	520 °C × 1 h × × 90 MPa	+
	520 °C × 1 h		+
	520 °C × 5 h		
	520 °C × 10 h		+
	520 °C × 24 h		
	520 °C × 48 h		+
	520 °C × 120 h		
	520 °C × 240 h		
	0 h	650 °C × 1 h × × 90 MPa	+
	650 °C × 1 h		+
	650 °C × 5 h		
	650 °C × 10 h		+
	650 °C × 24 h		
	650 °C × 48 h		+

3. RESULTS AND DISCUSSION

During tempering at 520 °C temperature of hardened specimen, plastic flow of steel under TP condition is the result of precipitation of carbon from solid solution and it lasts about 10 minutes of heating (Fig. 1). Later, when temperature of specimens reaches the temperature of tempering, the diffusion of chromium atoms starts, as there is evidence that it originates at 425 °C [22] (in some literature sources were found 450 °C [15]). Chromium atoms move to the grain boundaries, twins, vacancies and other defects of crystal structure, composing special carbides $M_{23}C_6$ [18; 22 – 24] or M_7C_3 [25]. The beginning of chromium diffusion shows about 3 times increased TP of steel comparing with the value of plasticity obtained during carbon segregation from the lattice of martensite. The formation of carbides can precede according to two mechanisms [15]:

1. Because of the diffusion of elements, alloyed cementite $(Fe, Cr)_3C$ becomes special carbide $(Fe, Cr)_7C_3$, and in turn, this carbide becomes more stable $(Fe, Cr)_{23}C_6$.
2. The nuclei of carbide form in the saturated solid α-solution. Generally, the special carbides form in the dislocations or in the boundary of Fe_3C/α-solution.

Chromium not only participates in the formation of carbides, but also reduces the rate of carbides coagulation [15]. Strengthening interatomic binds of α-solution and carbide lattice, and reducing the diffusion of carbon atoms, this element also decreases the motion of metal atoms in the boundary of α-solution/carbide and transport of carbon atoms through solid solution. This is the reason of slower precipitation of carbon from martensite, inconsiderable solution of small carbides and retardation of growing of the bigger ones [15].

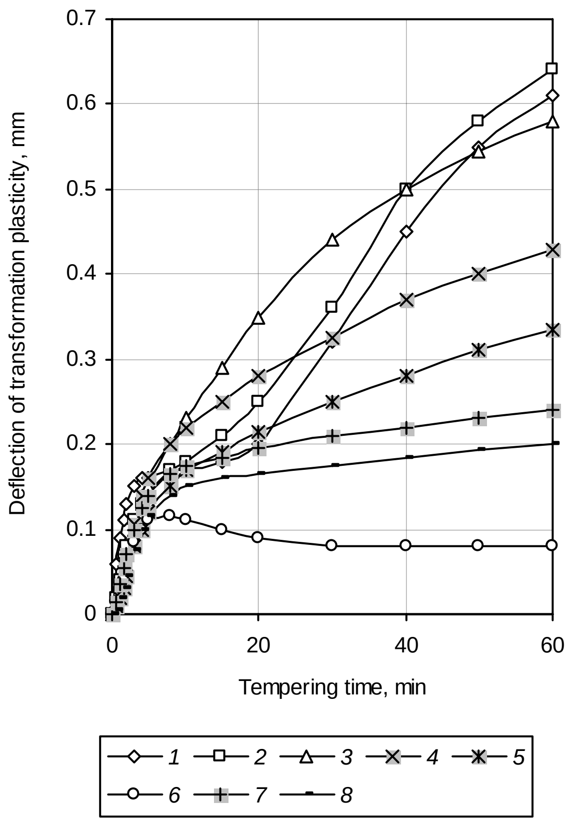

Fig. 1. Influence of ageing on transformation plasticity of steel 20X13 during bending at 520 °C (1 h, 90 MPa). Duration of ageing (h): 1 – 0; 2 – 1; 3 – 5; 4 – 10; 5 – 25; 6 – 48; 7 – 120; 8 – 240

Processes related with carbon precipitation from martensite lattice terminate fully after about 2 hours heating, as different character of plastic deflection curves is obtained. Increasing duration of ageing, even after 48 hours, the processes slow significantly, but are not finished fully, yet. Chose maximum duration of ageing (240 hours) still is not sufficient for termination of transformation, as even after 80 000 heating, slack evolution of carbides and formation of new phases proceed [18].

Increasing temperature up to 650 °C (Fig. 2), the formation of chromium carbide particles becomes very intensive [22]. At this temperature the precipitation of carbon goes with the diffusion of chromium atoms, as, because of favorable conditions, it starts already after ~2 minutes of heating – specimen temperature reaches faster limitary temperature of 425 °C required for the diffusion of chromium atoms. At 650 °C temperature, TP is a result of the diffusion of chromium atoms and formation of carbides, and is greater relatively in ~27 times comparing with the plasticity obtained during the precipitation of carbon. Ageing at 650 °C temperature reduces TP approximately in half. It would be very interesting to perform an experiment or to find information in literature sources that would allow determination of the ending of TP for this type of steel. Even increasing temperature until 650 °C for acceleration of processes, deceleration of transformations just obviously begins. For example, after long-lasting 30 000 hours ageing at 650 °C temperature, the formation of σ-phase (FeCr) just starts [18].

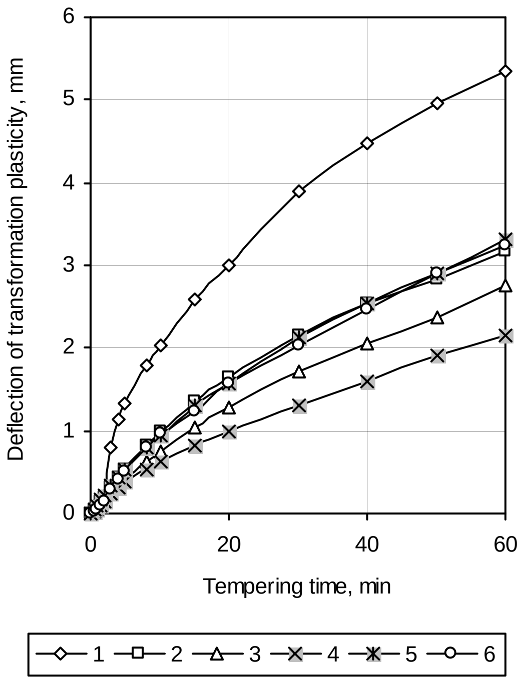

Fig. 2. Influence of ageing on transformation plasticity of steel 20X13 during bending at 650 °C (1 h, 90 MPa). Duration of ageing (h): 1 – 0; 2 – 1; 3 – 5; 4 – 10; 5 – 24; 6 – 48

After tempering at 520 °C temperature, the value of remained plastic deflection decreases as the duration of ageing increases (Fig. 3). This shows the structure approach to the stability, but just at 520 °C. Increasing tempering temperature up to 650 °C, the value of remained plastic deflection declines at 0 – 10 hours duration of heating. Increasing duration of ageing from 10 to 240 hours, the value of remained plastic deflection grows again, obviously, because of started new unexplored processes. What processes? Investigating steel 0.022C-13.4Ni-17.3Cr-1.74Mn-2.13Mo, there was obtained that after 30 000 ageing at 600 °C temperature, η-phase (Fe_2Mo) occurs at the boundaries of grains; after heating 100 000 hours at 600 °C or 30 000 hours at 650 °C temperature, σ-phase (FeCr) originates [18]. Our investigated steel is not so abundantly alloyed like researched one in work [18], but it is obviously, that after 240 hours ageing at high temperature, the processes do not terminate. Increasing duration of ageing, the procedure required for long-lasting heating proceeds: the solution of small carbides and growth of the bigger ones [25].

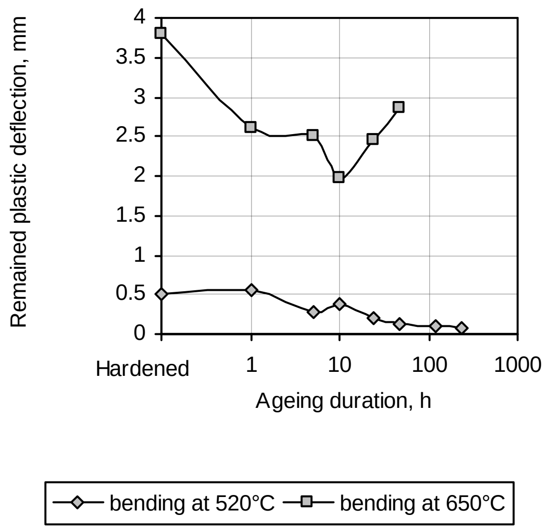

Fig. 3. Influence of ageing on plastic deformation of steel 20X13 during bending

X-ray analysis was performed for the specimens bent after hardening and bent during tempering after hardening and ageing (Table 2). After bending test at 520 °C temperature, carbide $M_{23}C_6$ and traces of carbide M_7C_3 were obtained (Fig. 4). Increasing the duration of ageing, the number and intensity of peaks of carbide M_7C_3 increases, although we know, that evolution of carbides follows from less stable to much stable in such sequence [16, 19, 25]:

$$M_3C \rightarrow M_7C_3 \rightarrow M_{23}C_6. \quad (1)$$

This can be explained by chromium precipitation from solid solution in the conformation of carbide M_7C_3 at the beginning of formation of carbide particle. Later, these carbides become $M_{23}C_6$ as concentration of chromium in surrounding volumes increases. This assumption is in good agreement with [25], where it was affirmed that the concentration of chromium in initial precipitate M_7C_3 is less than concentration required for $M_{23}C_6$ formation. It was found [16], that when content of carbon is small and amount of chromium is great, as in our investigated steel, carbide $(Cr, Fe)_7C_3$ becomes $(Cr, Fe)_{23}C_6$. This process proceeds heavily and demands for long-lasting heating, since chromium reduces diffusive change places of Fe-Cr atoms required for carbon precipitation and carbide formation. Chromium also strengthens interatomic binds in the lattice that reduce diffusion of atoms in the boundary α-solution/carbide, too [15].

Increasing temperature until 650 °C, when diffusion of chromium is the most intensive, we have such sequence of carbide evolution (Fig. 5):

$M_{23}C_6 + Cr_2C$ (after 1 h + 90 MPa) → $M_{23}C_6 + Cr_2C$ (after 1 + 1 h + 90 MPa) → $M_{23}C_6 + (Cr, Fe)_2(C, N)$ (after 10 + 1 h + 90 MPa) → $M_{23}C_6 + (Cr, Fe)_2(C, N)$ (after 48 + 1 h + 90 MPa).

The carbide M_7C_3 has disappeared. Its particles have become $M_{23}C_6$ as diffusion of chromium was sufficient at such high temperature. The carbide M_2C has occurred, which is heavily soluble phase of interposition mentioned

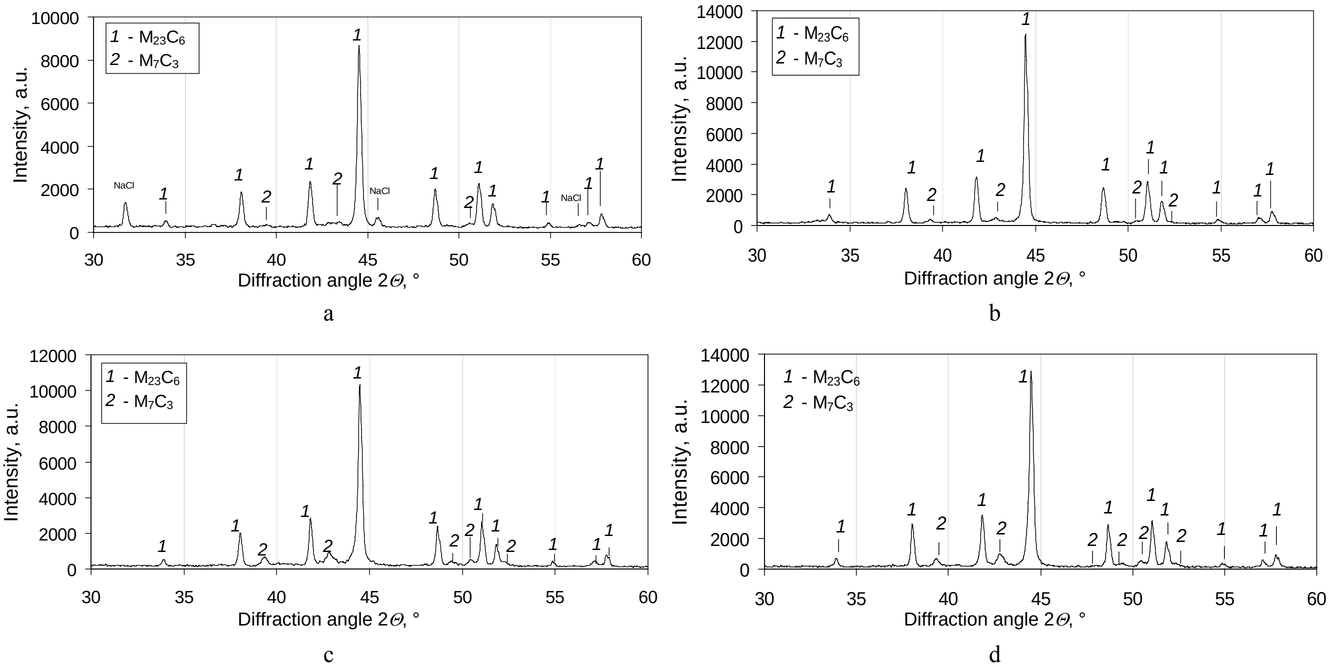

Fig. 4. X-ray diffraction patterns of 20X13 steel bent at 520 °C: a – after hardening; b – after hardening and 1 h ageing; c – after hardening and 10 h ageing; d – after hardening and 48 h ageing.
Note. Traces of NaCl might be obtained because of the electrolytic solution, used for the specimens etching

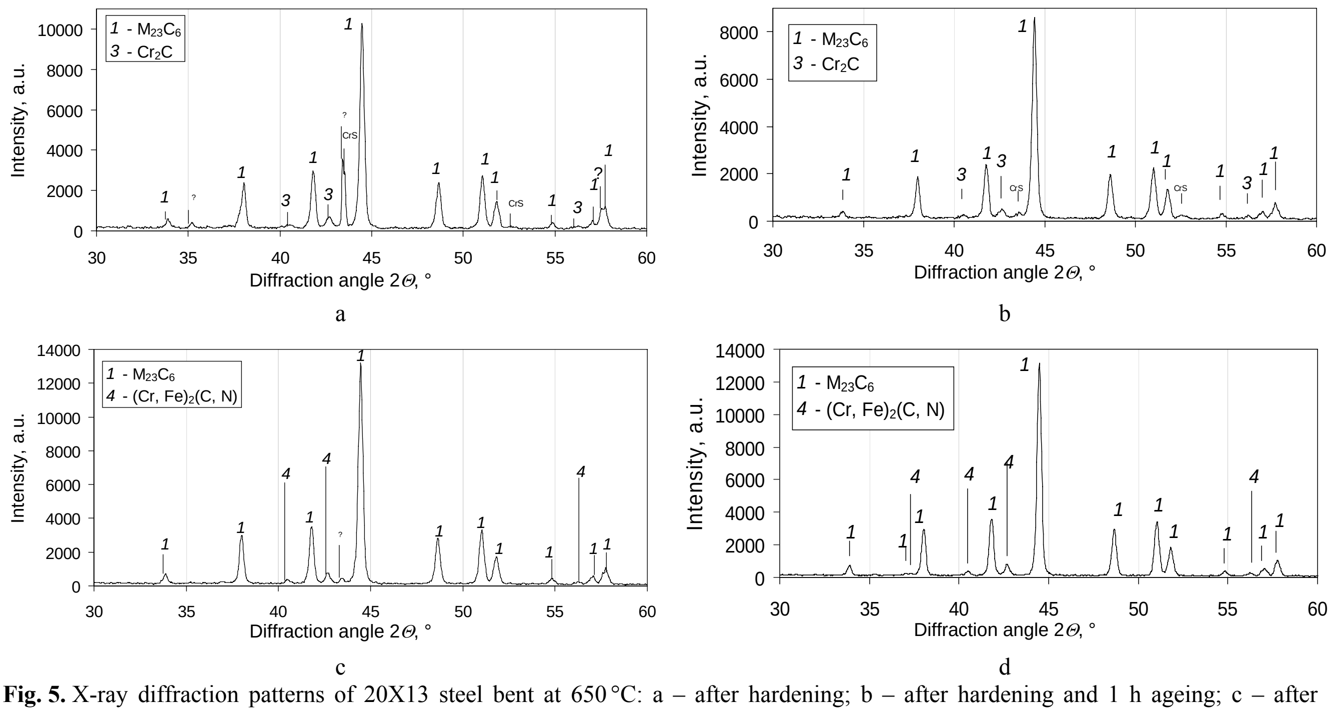

Fig. 5. X-ray diffraction patterns of 20X13 steel bent at 650 °C: a – after hardening; b – after hardening and 1 h ageing; c – after hardening and 10 h ageing; d – after hardening and 48 h ageing.
Note. Traces of CrS might be obtained because of the electrolytic solution, used for the specimens etching

in [16], but there is a lack of information about it. This phase was also found in [19, 26]. Alloyed cementite was not detected at any stage of tempering, as it has been dissolved at the early stage of heating [25].

The investigation of lattice parameter of carbide $M_{23}C_6$ can be closely related with the influence of stress. The lattice parameter and content of chromium in carbide is the least, when the specimen has been bent after hardening without ageing (depending on tempering temperature, Cr ~ (11 – 13) at. %; Figs. 6, 7). This allows assumption that stress reduces diffusion of elements atoms, growth of carbide particles, but stimulates the precipitation of dispersive carbides from solid solution into the boundaries of grains – the density of carbides was measured before and after 20 % deformation in [27]. This assumption is in good agreement with [26], where it was obtained that the stress of load increases the density of dislocations, as in turn, they serve for the formation of carbides nuclei.

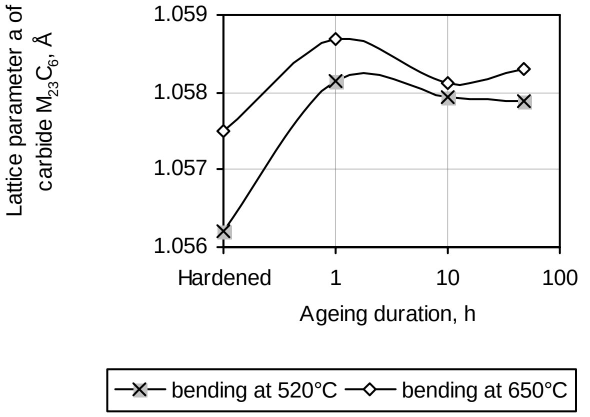

Fig. 6. Influence of ageing on lattice parameter *a* of $M_{23}C_6$

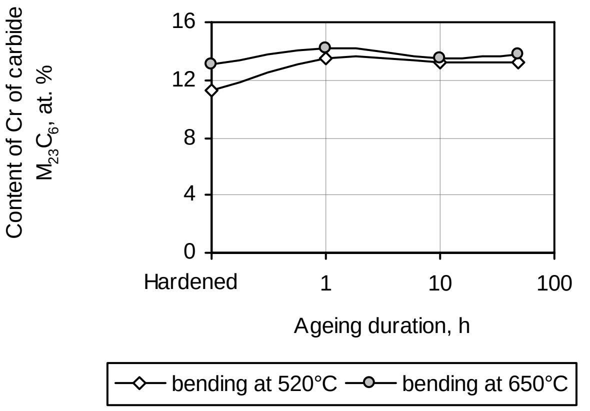

Fig. 7. Influence of ageing on content of chromium of $M_{23}C_6$

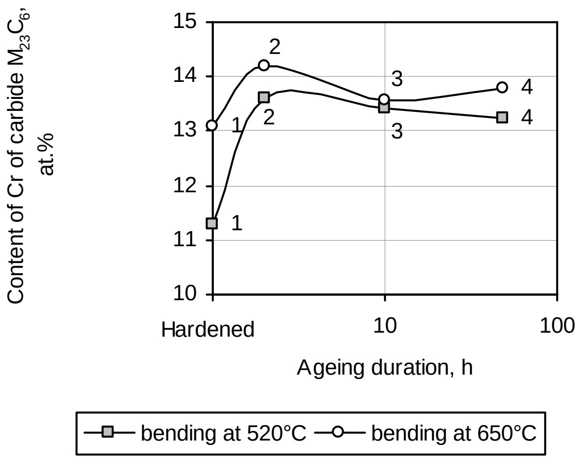

Fig. 8. Influence of duration of ageing on content of chromium of carbide $M_{23}C_6$. Relation between contents of Fe-C-Cr elements pointed as 1, 2, 3, 4 is listed in Table 3

Determining the content of chromium in carbide $M_{23}C_6$ after tempering at 520 °C, the value obtained was 11 at. % – 13 at. %. This value increases by 13 at. % – 14 at. % when tempering temperature reaches 650 °C (Fig. 7). Therefore, we can calculate the content of iron in carbide, whereas the content of carbon is constant (21 at. %) [17]. The results of calculations are listed in Table 3. The least content of chromium in carbide $M_{23}C_6$ was obtained when the specimens were bent without ageing (Fig. 8). Maximum of chromium content in carbide (~14 at. %) was detected after 1 hour ageing and bending during tempering, later the value has decreased. Investigating steel 0.26C-17Cr [22], there was obtained that the content of iron in carbide $M_{23}C_6$ has reached 70 at. % – 80 at. %, as it is very close to our results. However, it stays unclear, why the content of chromium in carbide $M_{23}C_6$ decreases when duration of ageing is prolonged to 48 hours (Fig. 8), as the change of relation between Fe-C-Cr contents and of the condition of heat treatment has a great influence on kinetics of transformations and evolution of carbides, too.

Table 3. Relation between contents of Fe-Cr elements in carbide M23C6 depending on duration of ageing (content of C = 21 % is constant). Content of chromium is determined by XRD, content of iron is calculated

Condition of experiment	Content of elements (at. %) when temperature of ageing and bending experiment is			
	520 °C		650 °	
	Fe	Cr	Fe	Cr
0 h + 1 h × 90 MPa (point 1)	67.69	11.31	63.90	13.10
1 h + 1 h × 90 MPa (point 2)	65.43	13.57	64.80	14.20
10 h + 1 h × 90 MPa (point 3)	65.73	13.27	65.47	13.53
48 h + 1 h × 90 MPa (point 4)	65.72	13.28	65.18	13.82

CONCLUSIONS

The article deals with the investigation of transformation plasticity of steel 20X13 (GOST5632-72) during ageing and bending on tempering. Two ranges of TP increasing were detected: the first range during carbon precipitation from martensite, and another range, accompanied by much greater plastic deflection, is during the diffusion of chromium atoms. X-ray analysis has identified carbide $M_{23}C_6$ and the traces of M_7C_3 at the early stage of heating. Content of carbon in carbide $M_{23}C_6$ was obtained ~13 at. % – 14 at. % as it depends on temperature and duration of tempering. The dependence of the ageing duration on parameter of $M_{23}C_6$ lattice and content of chromium in this carbide was determined. The biggest parameter and the greatest content of chromium in carbide were obtained after hardening, 1 hour ageing and bending during tempering. These values were the least when specimen was bent straight after hardening. Stress effect on evolution of carbides was determined.

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