



Phase transformations in the precipitation hardened cast steel

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ABSTRACT

Purpose: The microstructure of the new ledeburitic, tool cast steel of the precipitation hardened matrix was designed. The concept of this microstructure was based on the microstructure of the steel-bonded carbides [1,2], in which a skeleton is built of sintered carbides. This skeleton is produced by the powder metallurgy methods and then filled with melted steel of the selected chemical composition.

Design/methodology/approach: The new cast steel of the structure analogous to the steel-bonded carbides was conventionally melted in a furnace, however with omitting pressing and sintering operations of the powder metallurgy. The carbides skeleton in the new cast steel is formed by carbides of the MC type forming jointly ledeburite and its matrix constitutes steel hardened by precipitates of intermetallic compounds. This new material will be destined for tools of a moderate hardness (approximately 40 HRC), high abrasion resistance and high strength.

Findings: Utilising hard carbides forming by elements of VB group of the Mendeleev's table it is possible to design the tool material similar to the steel-bonded carbide of the selected matrix composition and primary carbides of MC type.

Research limitations/implications: The chemical composition the matrix of designed material decides on its hardness and strength, the MC type carbides decide on the abrasion resistance and if they occur in the eutectic form they decide on a rather low fracture toughness. Therefore efforts should be undertaken to have non-ledeburitic materials.

Practical implications: As a result of these investigations a new precipitation hardened cast steel have been worked out and a possibility of its industry applied was shown.

Originality/value: The results of investigations of phase transformations in the new cast steel at its heating and cooling from the austenite range, are presented in the hereby paper.

Keywords: Materials; Metallic Alloys; Precipitation hardened cast steel; Phase transformations; Dilatometric investigations

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MATERIALS

1. Introduction

Precipitation hardening (PH) steel (commonly called age-hardening) occurs when, one phases precipitate from a supersaturated solid solution [1,2]. Precipitation of inter-metallic compounds in a martensitic matrix is known as an effective method of producing low-carbon, high-strength and high ductility marage steels. PH stainless steels can be either austenitic, semi austenitic or martensitic depending on the alloying element additions to the composition. Martensitic PH stainless steels usually contain 4-7% nickel to keep the M_s temperature above room temperature. Elements added to form precipitates are copper, molybdenum, aluminum, titanium and niobium [2,3].

These steels are widely used as construction materials for chemical and power plants because of their balanced combination of good mechanical properties and adequate corrosion resistance. After a supersaturation, this alloy is precipitation hardened by tempering at about 580°C for about 4 hours [4].

The concept of the new cast steel microstructure was based on the microstructure of steel-bonded carbides [5,6]. This new material was conventionally produced by casting the melt, of the determined chemical composition, without using the powder metallurgy methods. It was assumed that the matrix will constitute the known, classic martensitic steel hardened by precipitates (PH) of the grade: X5CrNiMoCuNb14-5 (PN-EN 10088-1:1998) of the average chemical composition: 0.05% C; 14.0% Cr; 5.0% Ni; 1.60% Mo; 1.60% Cu and 0.40% Nb. The network of carbides at the grain boundaries will be formed by vanadium carbides MC type, forming jointly ledeburite in the new cast steel.

It was decided to supplement the chemical composition of the mentioned PH steel (for the formation of the primary VC carbides) by adding approximately 1.00% C and 4.25% V. The quotient of the additional vanadium and carbon content resulted from the quotient of their atomic masses:

$$\frac{\text{m. at. V}}{\text{m. at. C}} = \frac{50.941}{12.010} = 4.241 \quad (1)$$

This means that for the formation of the VC carbides the addition of 1% C should be accompanied by the addition of approximately 4.25% V.

The chemical composition of the ingot, made of the new cast steel, is given in Table 1.

As can be easily calculated from the data in Table 1 and from the given above data, concerning the quotient of atomic masses of vanadium and carbon being equal 4.241,

the content of vanadium being 4.05% required only 0.95%°C. It results from the dependence:

$$\frac{\text{V content in the cast steel}}{\text{the ratio of atomic masses V/C}} = \frac{4.05}{4.241} = 0.95 \quad (2)$$

This means that the performed melt contained 1.05% - 0.95% = 0.10% C more than the content resulted from the quotient of atomic masses of V and C.

It should be also mentioned that VC carbides in ferrous alloys have the composition close to V_4C_3 , i.e. that the quotient of V/C content in such carbide equals not 4.241 but:

$$\frac{4 \cdot 50.941}{3 \cdot 12.010} = 5.66 \quad (3)$$

Therefore the content of 4.05% V in the alloy requires:

$$\frac{4.05\% \text{ V}}{5.66 \text{ V/C}} = 0.71\% \text{ C} \quad (4)$$

Assuming that carbides of the V_4C_3 composition were in the melt means that the carbon excess was: 1.05% - 0.71% C = 0.34% C. This excessive carbon was bound by other carbide forming elements, the most probably by Mo and Cr. These two elements can form common $M_{23}C_6$ carbide, which should occur in the performed melt next to the MC (M_4C_3) carbides. Indeed, such carbides can be noticed on metallographic micro-sections of samples taken from the new cast steel ingot. Next to the MC carbides of pointed boundaries, present in the eutectic composition, additional carbides, which are etching by nital into light-pink colour and take grey colour in black-white photographs, are seen (Fig. 1).

The matrix of the new cast steel should be only of martensite. However, inside of crystals etching darker (Fig. 1) there are „products of the austenite transformations”, which, in this work, are conventionally called pearlite, while bright zones separating pearlite from ledeburite are untransformed austenite γ . Along grain boundaries the eutectic (ledeburite) built of the MC type vanadium carbides of pointed boundaries and of „products of the austenite transformation” (pearlite), was formed. Thus, it is the transformed ledeburite.

Large grey precipitates - within the volume of untransformed austenite γ - are the most probably $M_{23}C_6$ carbides typical for Mo and Cr. The pearlite formation, stabilisation of a large austenite volume and additional formation of the $M_{23}C_6$ type carbides occur - the most

Table 1. Chemical composition of the ingot of the new cast steel (mass %)

C	Si	Mn	P	S	Cr	Cu	Mo	Nb	V	Al	Fe
1.05	0.70	0.80	0.015	0.015	14.1	1.70	1.70	0.27	4.05	0.002	bal.

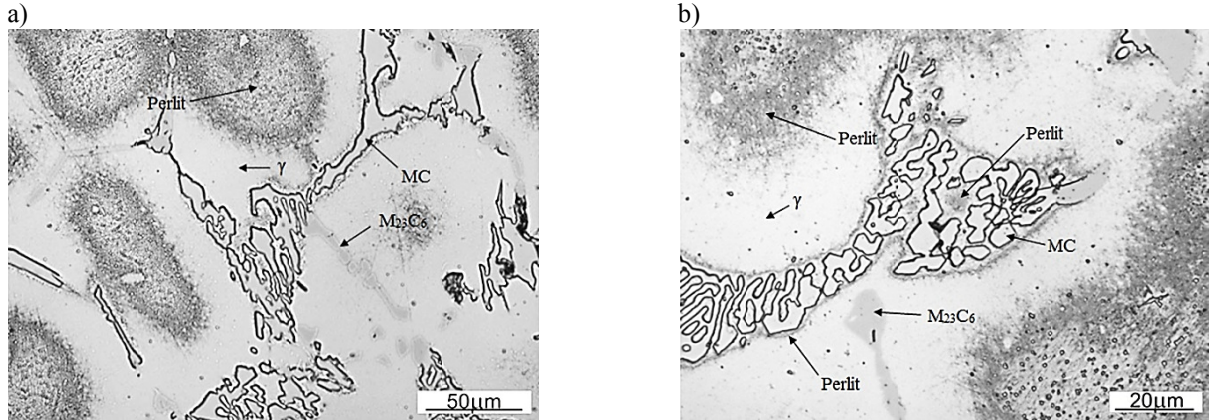


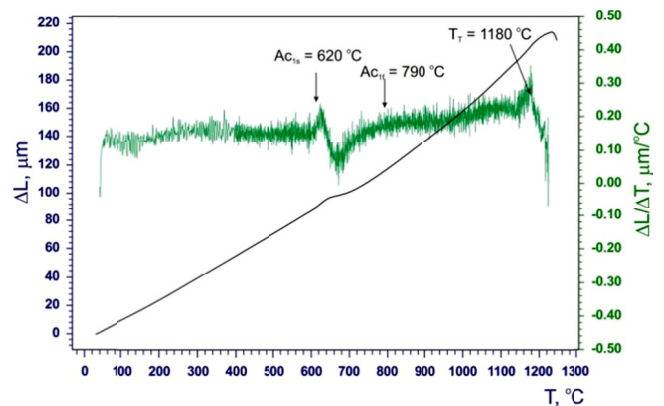
Fig. 1. Microstructure of the tested cast steel in as delivered conditions. Etched by 3% natal

probably - due to the carbon excess in the chemical composition balance of the new cast steel (which was mentioned above). Decreasing of the carbon content should lead to vanishing of pearlite, untransformed austenite and $M_{23}C_6$ carbides. In such case, the cast steel matrix will be formed of low-carbon martensite, which could be precipitation hardened during one tempering treatment (ageing). It can be expected that a partial only decrease of the carbon content in this new cast steel would allow to eliminate the pearlite and $M_{23}C_6$ carbides formation. Its matrix, already after casting, would be formed of martensite and austenite characteristic for the so-called semi-austenitic steels, which should be tempered (aged) at least twice.

2. Results of the investigation and discussion

The heating dilatogram (together with the differential curve) of the new cast steel sample, recorded in the L78 dilatometer of the Linseis Company, is presented in Fig. 2. Critical temperatures Ac_{1s} and Ac_{1f} and the temperature of the melting start: $T_{ms} = 1180^\circ\text{C}$ are marked on the differential curve.

Temperature $T_A = Ac_{1f} + 50^\circ\text{C} = 840^\circ\text{C}$ was assumed for performing the CCT diagram (Fig. 3). At its preparation the austenitic time $t_A = 20$ min was applied.

Fig. 2. Dilatogram of the heating rate: $3^\circ\text{C}/\text{min}$, of samples: $\phi 3 \times 10$ mm of the new cast steel together with the differential curve

It is worth to notice, that for the highest cooling rate of $100^\circ\text{C}/\text{s}$, when only martensite is formed in the matrix and untransformed austenite remains there, the hardness of this cast steel equals only 369 HV10 and it is the highest hardness achieved during its quenching (also from higher temperatures). After ageing, the new material hardness reaches 41 HRC, i.e. app. 402 HV. It limits this material application for tools of a moderate hardness but highly resistant due to the precipitation hardening by intermetallic substances as well as abrasion resistant due to vanadium carbides (MC type) forming jointly transformed ledeburite. This cast steel has no tendency for quenching cracks.

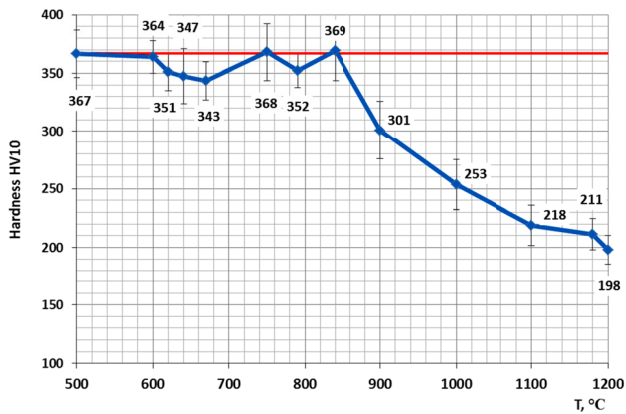


Fig. 4. Hardness changes of the tested cast steel samples after their cooling in water, from the selected temperatures of the range 500-1200°C

The results of hardness measurements of samples (15x15x10 mm) cooled (quenched) in water from increasing temperatures are presented in Figure 4.

The hardness of 367 HV10 in as-delivered condition (as cast state) is marked by the horizontal line. As can be seen, starting from a temperature of 840°C (assumed also for making the CCT diagram) the hardness of samples starts decreasing. Metallographic, magnetic and dilatometric investigations indicate that this is a result of a significant increase of the volume fraction of untransformed austenite. Starting from the austenitising temperature of 1000°C this cast steel matrix after quenching (in water of a room temperature) becomes fully austenitic.

Dilatograms of heating to 620, 840 and 1000°C, holding for 20 minutes, followed by cooling with a rate of 100°C/s to a room temperature the new cast steel samples are shown in Figures 5, 6 and 7.

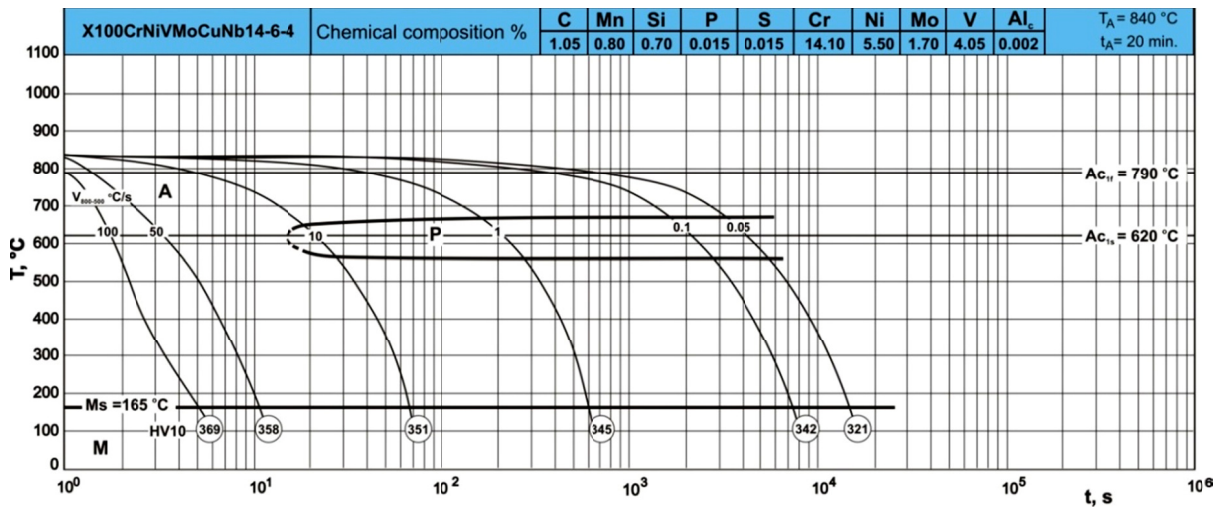


Fig. 3. CCT diagram of the new cast steel

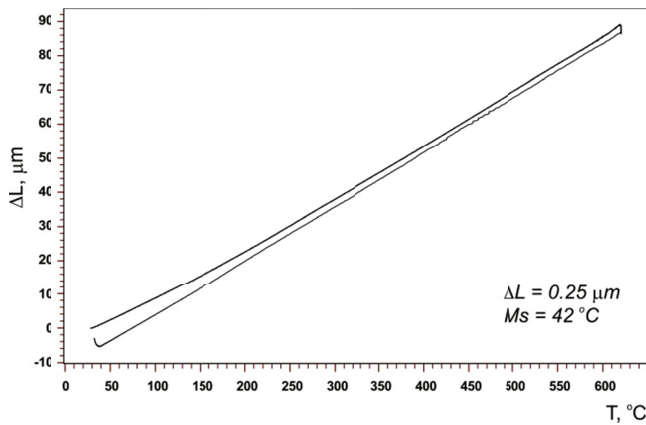


Fig. 5. Dilatogram of the tested cast steel sample heating up to 620°C, holding for 20 min and cooling with a rate of 100°C/s

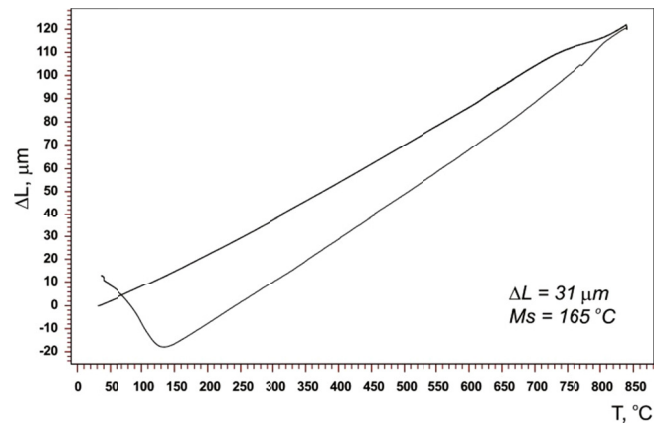


Fig. 6. Dilatogram of the tested cast steel sample heating up to 840°C, holding for 20 min and cooling with a rate of 100°C/s

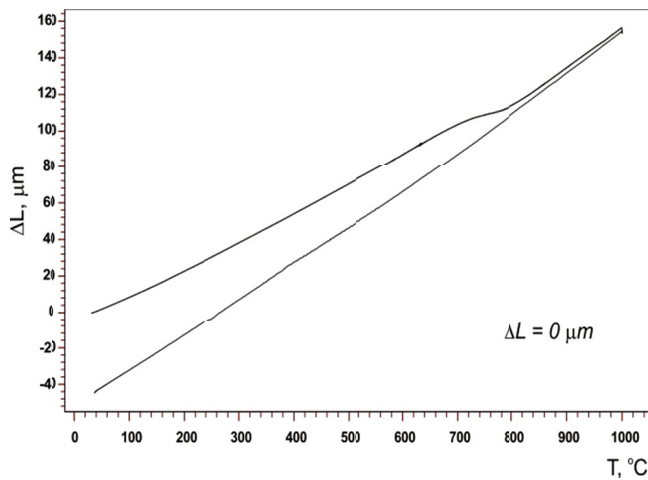


Fig. 7. Dilatogram of the tested cast steel sample heating up to 1000°C, holding for 20 min and cooling with a rate of 100°C/s

It can be noticed, that already after quenching from 620°C (Fig. 5) a small positive dilatational effect ($\Delta L = 0.25 \mu\text{m}$) from the martensitic transformation is seen (temperature $M_s = 42^\circ\text{C}$). At the continuous heating (3°C/min – Fig. 2) a temperature of 620°C is the beginning temperature of the austenite A_{c1s} formation. After austenitising at 840°C (Fig. 6) the dilatation positive effect originated from the martensitic transformation is very large (the largest from all applied austenitising temperatures) and equals $31 \mu\text{m}$, while $M_s = 165^\circ\text{C}$. Starting from $T_A = 1000^\circ\text{C}$ (Fig. 7) the martensitic transformation does not occur and the quenched cast steel matrix is fully austenitic.

Microstructures of the tested cast steel samples after water quenching from 620, 840 and 1000°C are shown in Figure 8. Their hardness equals: 351, 369 and 253 HV₁₀, respectively.

Changes of the dilatation positive effects from the martensitic transformation recorded in cooling dilatograms with the rate of 100°C/s (for the previous heating temperatures in the range: 600–1000°C) are shown in Figure 9. As can be seen, for a temperature of 600°C, when austenite was not yet formed in the tested cast steel, the dilatation effect from martensite: $\Delta L = 0 \mu\text{m}$. The dilatation effect $\Delta L = 0 \mu\text{m}$ also for a temperature of 1000°C and higher. In this case the cast steel matrix remains austenitic. The positive dilatation effect is the largest for a quenching temperature of 840°C, assumed for making the CCT diagram. This means that the advancement of the martensitic transformation at cooling was the highest.

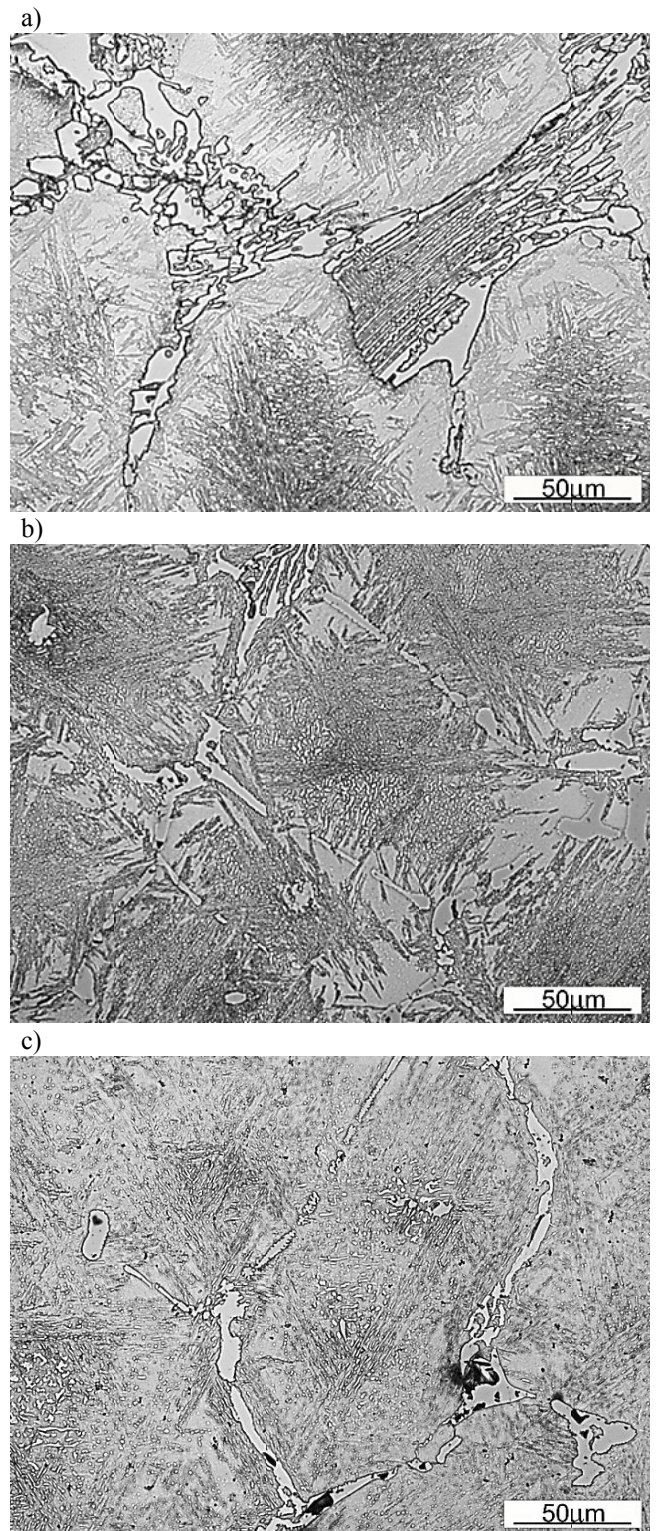


Fig. 8. Microstructures of the tested cast steel after water quenching from: a) 620°C, b) 840°C, c) 1000°C

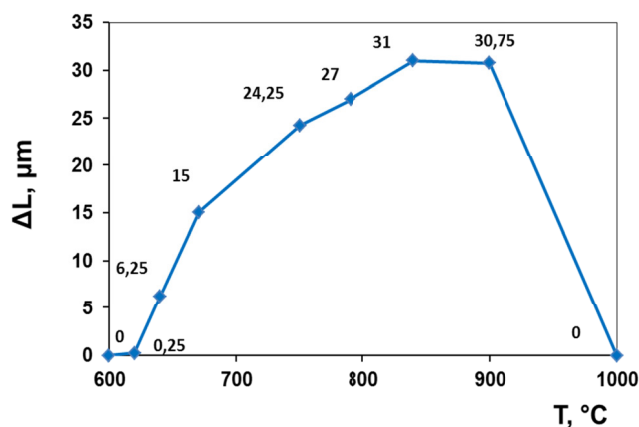


Fig. 9. Influence of the supersaturation temperature on positive dilatation effects originated from the martensitic transformation

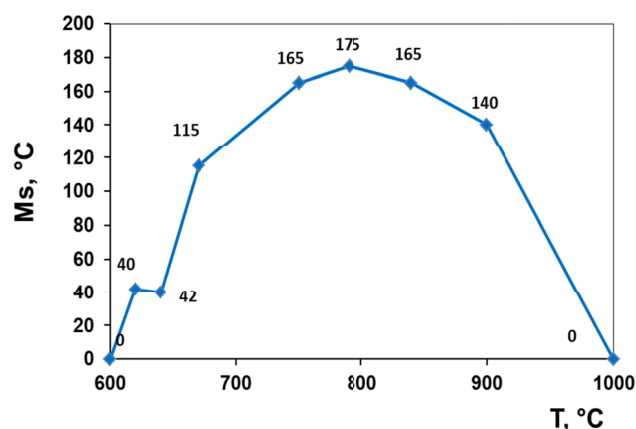


Fig. 10. Influence of the supersaturation temperature on the M_s temperature

The diagram of the temperature changes of the start of the martensitic transformation M_s , for quenching temperatures from the range 600-1000°C, is presented in Figure 10. The highest M_s temperatures were found for the austenitising in the range 750-840°C. This is connected with the chemical composition of austenite. Up to a temperature of 790°C the formed austenite contains less and less alloying elements and carbon, due to which the M_s temperature increases. Instead, above 790°C due to the austenite enrichment in alloying elements and carbon the M_s temperature decreases. For the quenching temperature of 1000°C the M_s temperature is below the room temperature.

3. Conclusions

Utilising strongly carbides forming alloying elements from IVB and VB group of the Mendelejew system it is possible to design the tool material similar to the steel-bonded carbide of the selected matrix composition and primary carbides, MC type.

In case of materials (cast steels) of the precipitation hardened steel matrix (PH), it is possible to produce the martensitic, semi-austenitic or austenitic matrix, which can be later subjected to the heat treatment (quenching and ageing) for obtaining the needed properties.

The chemical composition of the matrix of such designed material decides on its hardness and strength, the MC type carbides decide on the abrasion resistance and if they occur in the eutectic form they decide on rather small fracture toughness. Therefore efforts should be undertaken to have not ledeburic materials [7,8].

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Additional information

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