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Cr-V LEDEBURITIC COLD-WORK TOOL STEELS

LEDEBURITNA JEKLA Cr-V ZA DELO V HLADNEM

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Cold-work tool steels based on Cr-V alloying belong to the most important tool materials for large series manufacturing. To enable high production stability, the tools must withstand various types of degradation processes, concerning firstly plastic deformation and wear. Therefore, the materials should have a high hardness, tensile and/or compressive strength and wear resistance. On the other hand, the materials have to resist brittle fracture, e.g., they must exhibit sufficiently high impact toughness and fracture toughness. This paper deals with an overview of the heat-treatment procedures and surface engineering techniques suitable for Cr-V tool steels. The effect of each of them on the main mechanical properties is also demonstrated and discussed. As a typical example, P/M made from the Cr-V ledeburitic steel Vanadis 6 is presented.

Keywords: P/M cold-work steel Vanadis 6, heat treatment, surface engineering, microstructure, hardness, three-point bending strength, fracture toughness

Orodna jekla za delo v hladnem legirana s Cr-V spadajo med najbolj pomembne materiale za orodja za delo v velikih serijah. Omogočajo veliko stabilnost proizvodnje in prenašajo različne procese degradacije zaradi plastične deformacije in obrabe. Zato morajo imeti visoko trdoto, raztržno in tlačno trdnost ter obrabno obstojnost. Po drugi strani morajo biti jekla dovolj odporna proti krhkemu lomu, kar pomeni, da morajo imeti tudi visoko udarno žilavost in žilavost loma. Članek je pregled postopkov toplotne obdelave in tehnologije površine, primernih za orodna jekla Cr-V, vpliv vsakega postopka pa je opisan in analiziran. Kot tipičen zgled, je obravnavano P/M ledeburitno jeklo Cr-V Vanadis 6.

Ključne besede: P/M hladno orodno jeklo Vanadis 6, toplotna obdelava, inženirstvo površine, mikrostruktura, trdota, tritočkovna upogibna trdnost, lomna žilavost

1 INTRODUCTION

High carbon and chromium ledeburitic steels were developed during World War I as a possible substitution for high-speed steels for cutting operations. However, they have insufficient hot hardness and were too brittle for these purposes. On the other hand, they quickly gained a wide popularity in cold-work applications, due to a high wear resistance and compressive strength. Further development of this group of materials led to two main trends. The first one was characterised by the efforts to get a maximum toughness at an acceptable hardness and wear resistance. A typical representative of this group of materials is the now widely used D2-chromium cold-work tool steel. The second trend was characterized by the development of materials with increased wear resistance. It was found that alloying with vanadium, typically up to the mass-fraction 4 %, combined with an enhanced amount of carbon forms extremely hard MC-carbides. When classically manufactured, unfortunately, the high vanadium containing steels also have important drawbacks. First of all, large segregations take place during slow solidification in industrial ingots, which leads to anisotropy of the physical and mechanical properties. The MC-carbides have a strong tendency to grow during solidification. Large particles of extremely hard phases make the forging and machining of the steels difficult or impossible. In industrial applications, when dynamically loaded, large MC-carbides are responsible for the limitation of toughness. Therefore, the upper limit of the vanadium content for the Cr-V ledeburitic steels manufactured by classical ingot metallurgy was found to be about 4 % V.

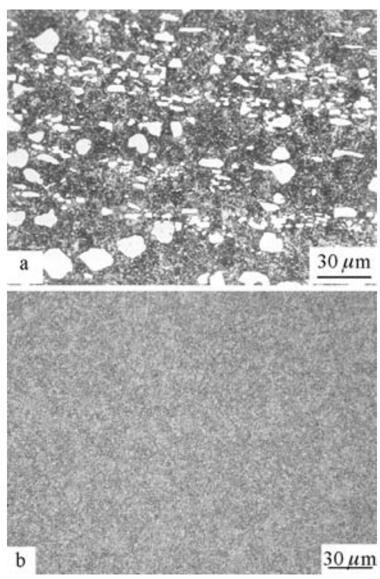

Figure 1: Light micrographs showing the microstructure of ingot metallurgy made Cr-V ledeburitic steel (2 % C, 7,8 % Cr, 6 % V) and PM made steel Vanadis 6 of similar chemical compositions

Slika 1: Optični posnetki mikrostrukture Cr-V-jekla, ki je bilo izdelano z ingotsko tehnologijo (2 % C, 7,8 % Cr, 6 % V) in P/M jekla Vanadis 6 s podobno kemijsko sestavo

For the manufacturing of Cr-V ledeburitic steels with a higher vanadium content, the only possible way to produce them is the powder metallurgy (P/M) of rapidly solidified particles. The technology, based on the rapid solidification of a supercooled melt in small droplets, restricts the segregations in time (due to the rapid solidification itself) and spatially (typical size of powder particles is some tens of micrometers). As a result, materials with an excellent combination of isotropic and fine structure and a high level of mechanical properties can be fabricated (P/M steels). The vanadium content, and proportionally also the amount of carbon, can be increased to more than 10 % without the risks of difficulties in forging and/or machining. Typical examples of conventionally manufactured and P/M steel of similar chemical composition are in **Figure 1**.

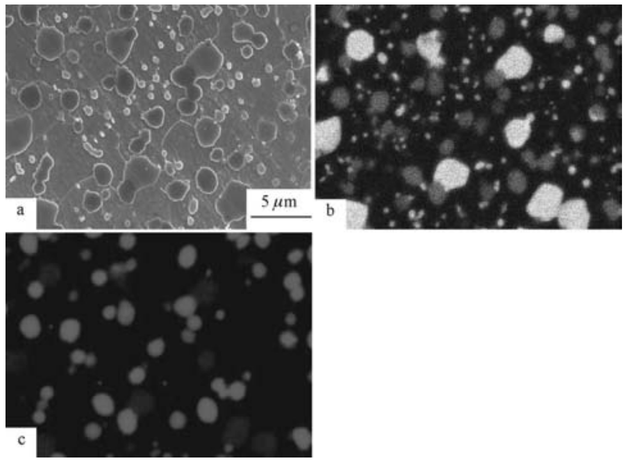

Figure 2: SEM micrograph showing the microstructure of the as-delivered Vanadis 6 steel a – image, b, c – corresponding EDS – maps of Cr and V

Slika 2: SEM-posnetki mikrostrukture dobavljenega jekla Vanadis 6; a – mikrostruktura, b, c – ustrezna EDS-posnetka za Cr in V

2 HEAT TREATMENT

2.1 As-delivered state

Cr-V ledeburitic steels are normally distributed to the end-users in the soft-annealed state. The main reason is to deliver the materials with an acceptable low hardness suitable for machining operations. The microstructure after the soft annealing consists of alloyed pearlite, secondary and eutectic and/or primary carbides, **Figure 2**. As shown in the micrograph, for the P/M made Vanadis 6 steel, the carbides are fine and uniformly distributed throughout the matrix. Previous investigations have shown that the equilibrium of a given alloy is formed by the chromium-based M_7C_3-carbides and vanadium-based MC-carbides [1]. Larger secondary and eutectic particles having a size between 1 μm and 3 μm are of both, e.g., M_7C_3- and MC-type. Ultra-fine carbides with a sub-micron size are the pearlitic ones and they are of M_7C_3-type, **Figures 2a-c**.

2.2 Austenitizing

The tools made from Cr-V ledeburitic steels are used in the heat-treated state only. A proper heat treatment is strictly recommended for the tools, to ensure the appropriate hardness, strength and wear resistance. On the other hand, this procedure should be carried out carefully. Otherwise, there can be a risk of lowering the toughness. The most convenient heat treatment for this type of steels is the so-called vacuum heat treatment.

The first step in heat treatment is austenitizing. Because of the poor thermal conductivity of the materials, the heating up to the final temperature should be slow, with several ramps enabling us to minimize the thermal gradients between the surface and the core, and a subsequent too large distortion of components.

The transformation of pearlite into austenite does not lead to sufficient saturation of the austenite since the amount of alloying elements in pearlite is very low. This is why the Cr-V ledeburitic steels must be heated up to a much higher temperature. During the heating from the A_1 temperature up to the final austenitizing, part of the secondary carbides undergoes a dissolution. Note that the role of the MC- and M_7C_3-phases is clearly different since they differ considerably in terms of thermal stability. As found in our current and previous investigations [2,3], the soft-annealed Cr-V ledeburitic steel Vanadis 6 contains the volume fraction of M_7C_3-carbides 16 % and 13 % of MC-carbides. Even heating up to a temperature of 1000 °C led to a reduction of the M_7C_3-carbides amount to 7 %, while the amount of MC-phase remained almost the same. The M_7C_3-carbides underwent a complete dissolution in the austenite up to 1100 °C, while the MC-phase amount was reduced only slightly, also after austenitizing at 1200 °C, **Figures 3–5** [3]. The dissolution of carbides leads to a saturation of the

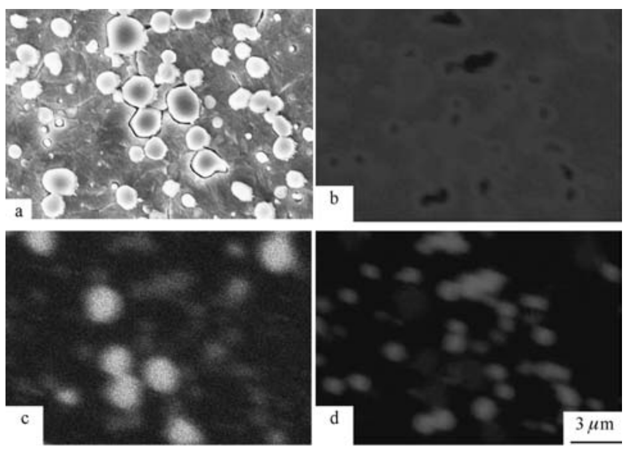

Figure 3: SEM micrograph showing the microstructure of as-quenched Vanadis 6 steel from 1000 °C; a – image, b, c, d – corresponding EDS – maps of Fe, Cr, V

Slika 3: SEM-posnetki mikrostrukture jekla Vanadis 6, kaljenega s 1000 °C; a – mikrostruktura, b, c – ustrezni EDS-posnetki za Fe, Cr in V

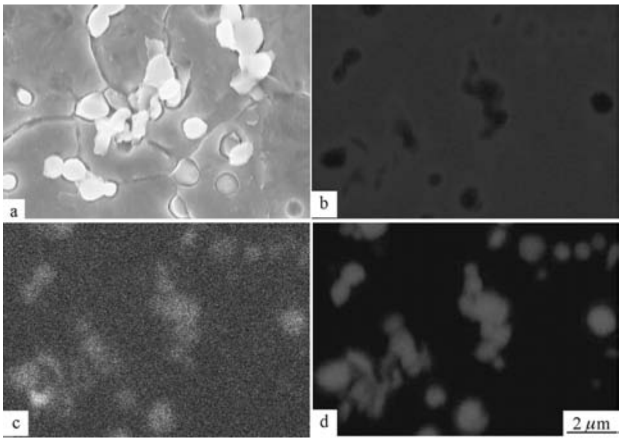

Figure 4: SEM micrograph showing the microstructure of as-quenched Vanadis 6 steel from 1100 °C, a – image, b, c, d – corresponding EDS – maps of Fe, Cr, V

Slika 4: SEM-posnetki mikrostrukture jekla Vanadis 6, kaljenega s 1100 °C; a – mikrostruktura, b, c – ustrezni EDS-posnetki za Fe, Cr in V

matrix with alloying elements. Since the chromium-rich carbides undergo dissolution in a considerably larger extent than the MC-phase, the absolute value of the chromium amount in the matrix increases more rapidly, **Table 1**.

Table 1: Amount of alloying elements dissolved in the matrix
Tabela 1: Vsebnost legirnih elementov, raztopljenih v matici

Austenitizing temperature	1000	1050	1100	1150	1200
Cr	5.66±0.56	5.96±0.22	6.85±0.33	6.96±0.15	7.12±0.09
V	1.72±0.32	1.76±0.48	2.24±0.53	2.18±0.43	2.66±0.37

The upper limit of the austenitizing temperature is determined mainly by the onset of the austenitic grains' coarsening. The second reason why it is essential to keep the recommended austenitizing temperatures is purely economic – a higher austenitizing temperature increases the costs for realizing of heat-treatment procedure. **Figure 6** gives light micrographs of the as-quenched microstructures of Vanadis 6 steels. A measurement of the austenitic grain size according to the ASTM method revealed that after the quenching from a lower tem-

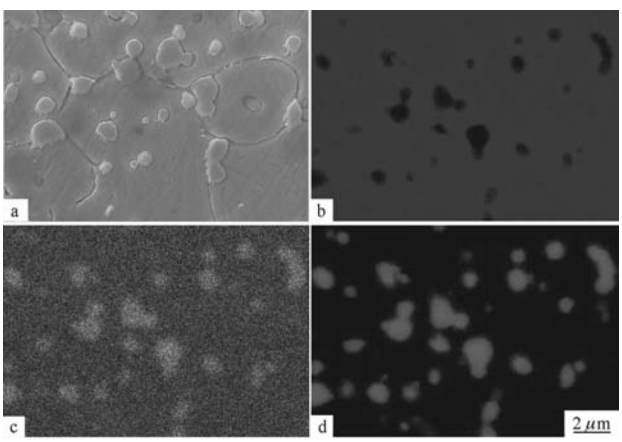

Figure 5: SEM micrograph showing the microstructure of as-quenched Vanadis 6 steel from 1200 °C, a – image, b, c, d – corresponding EDS – maps of Fe, Cr, V

Slika 5: SEM-posnetki mikrostrukture jekla Vanadis 6, kaljenega s 1200 °C; a – mikrostruktura, b, c – ustrezni EDS-posnetki za Fe, Cr in V

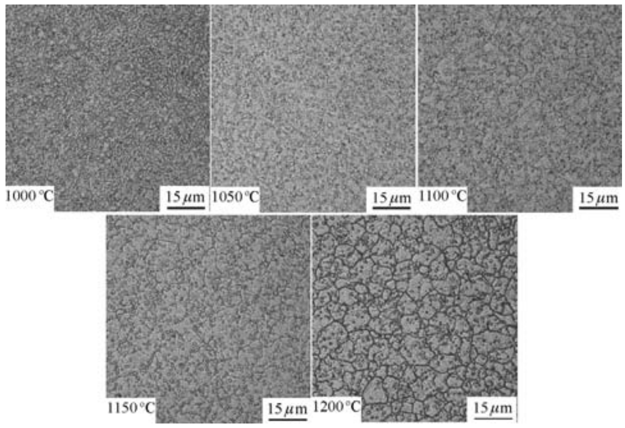

Figure 6: Light micrographs showing the microstructure of the Vanadis 6 ledeburitic steel after quenching from different austenitizing temperatures

Slika 6: Optični posnetki mikrostrukture ledeburitnega jekla Vanadis 6 po kaljenju z različne temperature avstenitizacije

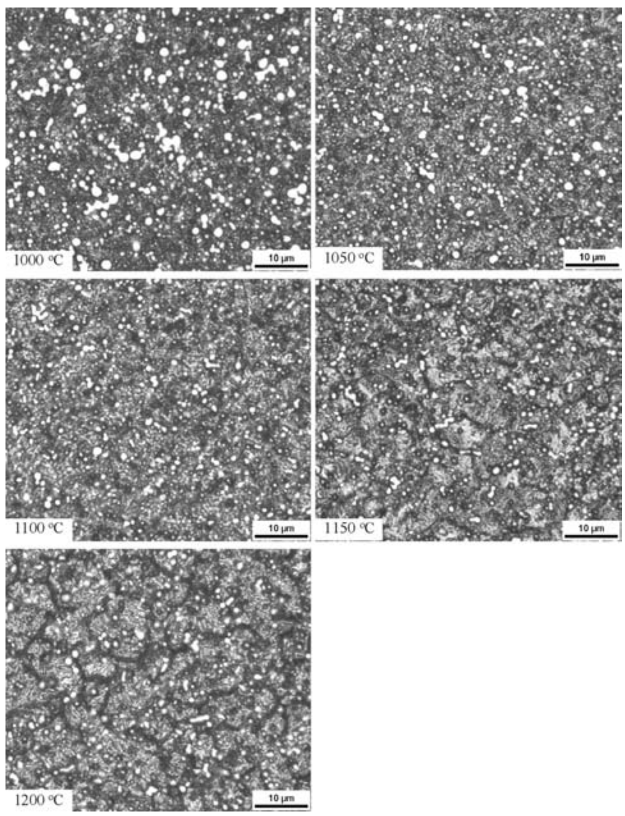

Figure 7: Light micrograph showing the microstructure of the Vanadis 6 ledeburitic steel after quenching from different austenitizing temperatures, colour etching using the Beraha-martensite agent

Slika 7: Optični posnetki mikrostrukture ledeburitnega jekla Vanadis 6 po kaljenju z različne temperature avstenitizacije; barvno jedkanje z Beraha reagentom za martenzit perature it was 11.5, and it increased slightly to 10 after quenching from a temperature of 1200 °C.

2.3 Quenching

The standard quenching medium used for austenitized Cr-V ledeburitic steels is nitrogen gas under a high pressure – 6 bar as the minimum. Due to the good or excellent through hardenability of these steels there is no risk of hardness loss and, in addition, the method enables us to keep smooth and bright surfaces and to minimize the distortion of tools.

The increased saturation of austenite with carbon and alloying elements, **Table 1**, induces a decrease of the temperatures M_s and M_f, respectively. In classical hardening procedures, the materials are quenched to an ambient temperature. As the M_s temperature is located normally around 100 °C and the M_f well below zero, the retained austenite can be found in as-quenched material. The portion of retained austenite increases with an increasing austenitizing temperature because of the decrease of both the M_s and M_f temperatures. When austenitized at temperatures above 1100 °C, also the M_s of Cr- and Cr-V ledeburitic steels is below 0 °C and lower bainite can be found in the material [4]. This fact is clearly evident from the light micrographs, **Figure 7**. The portion of martensite (blue) slightly decreases and the bainite (red-violet) increases with increased austenitizing temperature. In addition, it seems that also the amount of retained austenite increases.

2.4 Sub-zero processing

The sub-zero processing, followed immediately after quenching, is aimed mainly at a reduction of the retained austenite amount and an increase of the hardness and the associated properties of the materials. However, the opinions on the structure and properties of ledeburitic steels are inconsistent and one would say that the development of this technique is not finished yet. What is clear up to now is that the sub-zero processing reduces the retained austenite amount [5], increases the as-quenched hardness [4] and, in some cases, the wear resistance, also [6]. New results obtained within the industrially oriented project TIP gave similar results regarding the as-quenched hardness, **Table 2** [7]. However, subsequent tempering led to a considerable hardness decrease, as discussed in the next section.

Figure 8 shows TEM bright- and dark-field micrographs from the no-sub-zero processed Vanadis 6 steel. The matrix consists of the martensite with a high dislocation density, and of retained austenite.

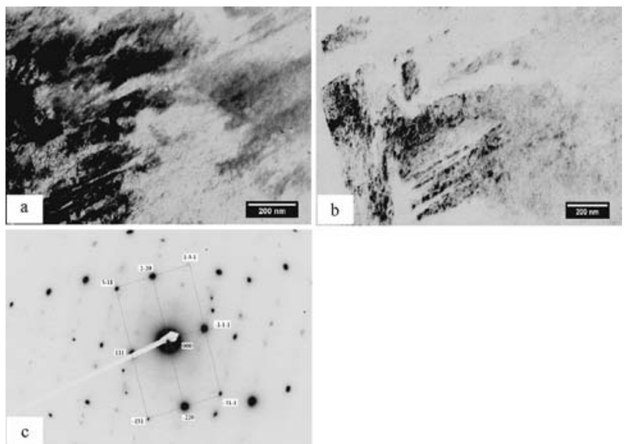

Figure 8: TEM micrographs showing the microstructure of the no-sub-zero processed sample quenched from 1000 °C. a – bright field image, b – dark field image of the same area, c – diffraction patterns from the retained austenite

Slika 8: TEM-posnetki mikrostrukture "sub zero" procesiranega jekla, kaljenega s 1000 °C. a – posnetek v svetlem polju, b – posnetek iste površine v temnem polju, c – difrakcijski odsevi zaostalega avstenita

Table 2: Results of hardness measurements of Vanadis 6 steel after different stages of heat treatment [7]

Tabela 2: Rezultati meritev trdote jekla Vanadis 6 po različnih stopnjah toplotne obdelave [7]

Austenitizing	Sub-zero processing	Tempering	Hardness		
			As-quenched	As-subzero processed	As-tempered
1000	No	2 × 550 °C/2 h	5.5	-	59.5
1000	No	2 × 530 °C/2 h		-	61
1000	– 90 °C/4 h	2 × 550 °C/2 h		66.5	56.5
1000	– 90 °C/4 h	2 × 530 °C/2 h		66.5	58.5
1025	No	2 × 550 °C/2 h	66	-	61
1025	No	2 × 530 °C/2 h		-	61.5
1025	– 90 °C/4 h	2 × 550 °C/2 h		67.5	57.5
1025	– 90 °C/4 h	2 × 530 °C/2 h		67.5	59.5
1050	No	2 × 550 °C/2 h	65.5		61.5
1050	No	2 × 530 °C/2 h			63
1050	– 90 °C/4 h	2 × 550 °C/2 h		68	58
1050	– 90 °C/4 h	2 × 530 °C/2 h		68	60.5
1075	No	2 × 550 °C/2 h	66		62
1075	No	2 × 530 °C/2 h			64
1075	– 90 °C/4 h	2 × 550 °C/2 h		68	58
1075	– 90 °C/4 h	2 × 530 °C/2 h		68	61.5

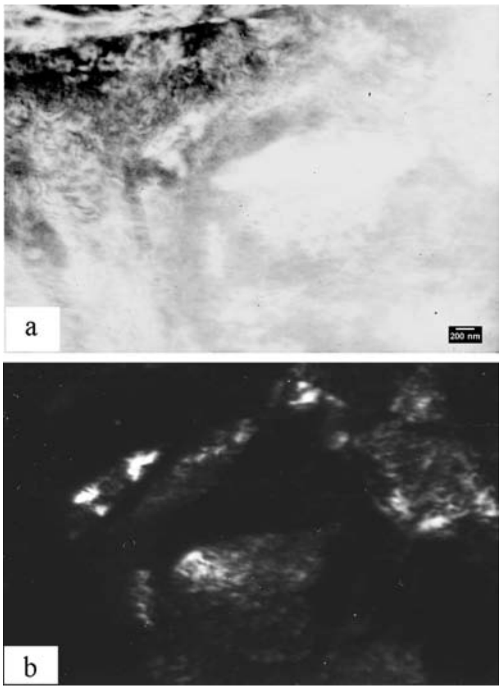

Figure 9: TEM micrographs showing the microstructure of a sample quenched from 1000 °C and sub-zero processed at – 196 °C for 4 h; a – bright field image, b – corresponding dark field image

Slika 9: TEM-posnetki mikrostrukture jekla, kaljenega s 1000 °C, ki je bilo "sub zero" procesirano 4 h pri – 196 °C. a – posnetek v svetlem polju, b – posnetek istega polja v temnem polju

The retained austenite amount was significantly lower at first glance in the sub-zero processed steel quenched from the same austenitizing temperature, **Figure 9**.

Table 3 summarizes the results of the X-ray diffraction measurements of no-sub-zero processed and sub-zero processed Vanadis 6 steel. It is important that the retained austenite amount decreases with the sub-zero treatment period included into the heat processing. Also, the tetragonality of martensite increases, which gives a principal explanation of the higher hardness of the as-sub-zero processed steel than that no-sub-zero processed, see **Table 2**.

2.5 Tempering

As-quenched Cr-V ledeburitic steels contain the martensite (or a mixture of martensite and bainite), retained austenite and undissolved carbides. When

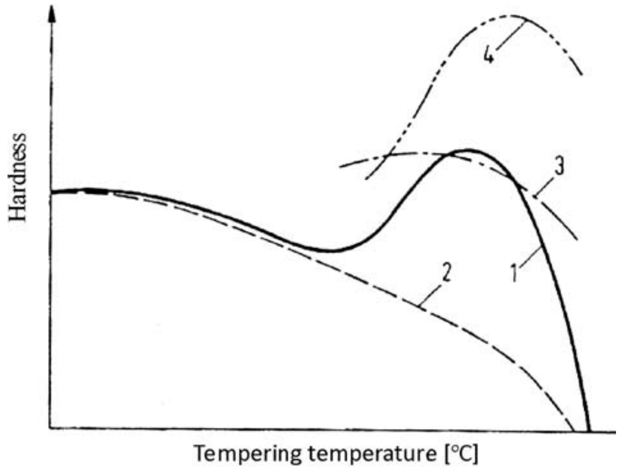

Figure 10: Contribution of main sub-processes to the hardness of ledeburitic steels during tempering [11]. (1 – resulting hardness, 2 – effect of tempering of martensite (softening), 3 – precipitation of carbides, 4 – transformation of retained austenite).

Slika 10: Prispevek glavnih "sub" procesov k trdoti ledeburitnega jekla med popuščanjem [11]. (1 – trdota, 2 – vpliv popuščanja martenzita (mehčanje), 3 – izločanje karbidov, 4 – premena zadržanega avstenita).

sub-zero processed, the structure of some constituents can differ from those conventionally heat processed. Firstly, the amount of retained austenite is significantly lower. Collins and Meng [8–10], in addition, presumed that deep cooling leads to an arrangement of the structure that is responsible for the hindering of the dislocation movement and, the martensite originated at very low temperatures can differ from that transformed at higher temperatures in terms of the lattice parameter. Finally, the martensitic transformation may be probably superposed with the precipitation of nano-sized carbides, which are coherent with the matrix. However, these carbides were not detected by any researchers yet.

Tempering should follow the quenching and/or sub-zero treatment as soon as possible. Otherwise, the retained austenite could have been stabilized. For a more complete transformation of the retained austenite to martensite, as well as for tempering of the newly formed martensite, it is necessary to temper at least twice. During the tempering, the alloying elements and carbon diffuse out as from solid solutions forming precipitates, responsible for a secondary hardening effect. Cooling down from the tempering temperature induces the transformation of retained austenite to new martensite.

Table 3: Results of X-ray diffraction measurements of no-sub-zero and sub-zero processed Vanadis 6 steel

Tabela 3: Rezultati difrakcijskih meritev z rentgenskimi žarki za jeklo Vanadis 6, ki ni in je bilo "sub zero" procesirano

Heat treatment	Martensite /%	Retained austenite /%	Lattice parameter of martensite /nm, tetragonality c/a	Carbides
Quenching	49.45	17.76	a = 0.28623, c = 0.29154 c/a = 1.0186	M_4C_3, M_7C_3
112851 Quenching + sub-zero treatment	63.1	6.1	a = 0.28596, c = 0.29234 c/a = 1.0223	M_4C_3, M_7C_3

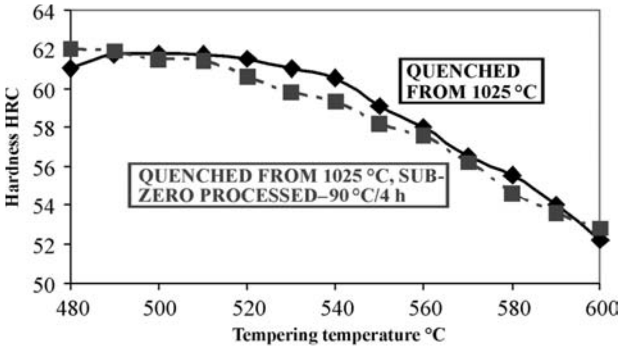

Figure 11: Tempering chart of sub-zero and no-sub-zero processed Vanadis 6 steel

Slika 11: Popuščni diagram za "sub zero" procesirano jeklo Vanadis 6 in za jeklo brez tega procesiranja

Kulmburg et al. schematically divided the total effect of the tempering temperature to the final hardness to the contributions, given by various sub-processes, **Figure 10** [11]. They considered that the final hardness of the material is a result of the competition between the softening of the martensite, due to carbides precipitation, the precipitation of carbides, and the transformation of retained austenite to martensite. For the Cr-V ledeburitic steels there is a hardness decrease up to the tempering temperature of about 350 °C, since the softening of martensite is the dominant process and other sub-processes play only a minor role. At higher temperatures, the sub-processes of the transformation of retained austenite and carbides precipitation become of great importance and if the steel is austenitized and quenched in the right way, the secondary hardness peak occurs at a tempering temperature close 500 °C. Beyond the maximum of the secondary hardness, the Cr-V ledeburitic steels undergo a softening because of the coarsening of precipitates and also due to the fact that during the last tempering cycle, no more austenite can transform to the martensite.

The material tempered after the sub-zero period behaves in a different way, **Figure 11**. In our previous works [7,12], see also **Table 2**, it was established that the tempering at the temperatures of the secondary hardness peak led to a lower hardness of the sub-zero processed material than that of no-sub-zero processed material. The different behaviour (and also rather surprising at first glance) of sub-zero processed material can by indirectly explained using the above-mentioned Kulmburg's consideration: the hardness of as-sub-zero processed material is higher than that of no-sub-zero processed steel due to a more complete martensitic transformation. But, during the tempering, the softening of martensite takes place. On the other hand, a lower retained austenite amount can be transformed into the martensite, thus the contribution of the sub-process 4, **Figure 11**, can be expected to be less significant. And, finally, one would also expect a lower contribution of the sub-process 3 if Meng's assumption [9] on the carbide precipitation at the sub-zero period was confirmed.

2.6 Nitriding

The nitriding of Cr-V ledeburitic steels is mostly carried out in plasma, since the composition of steels can make serious obstacles in gaseous processes. The nitriding temperature should be lower than the tempering temperature. A short processing time is preferred, up to 2h, with a case depth up to 60 μm and with no formation of white compound layers on the surface.

Several beneficial effects on the tool steels can be expected due to the nitriding. The hardness after nitriding can easily reach over 1000 HV, and the wear resistance increased substantially. The nitrogen atoms in the material induces the formation of a high compressive stress, exceeding 1000 MPa for the Vanadis 6 steel [1]. The increased hardness of the plasma-nitrided region has a favourable effect on the adhesion of thin films made with PVD processes. In our previous studies it was found that a properly performed plasma nitriding procedure can enhance the adhesion by two-to-three times [13–15]. Nevertheless, not only the positive effects of plasma nitriding on the material properties were found. Several investigations established that the three-point bending strength decreases with the presence of a nitrided region on the surface [13,16,17]. On the fracture surfaces, some clearly visible transcrystalline cleavages were found, which together with a low fracture toughness makes the material brittle, **Figure 12**.

2.7 Formation of thin ceramic films

For the coating of Cr-V ledeburitic steels, various physical-based low-temperature techniques are used. A variety of thin films can be deposited now onto the

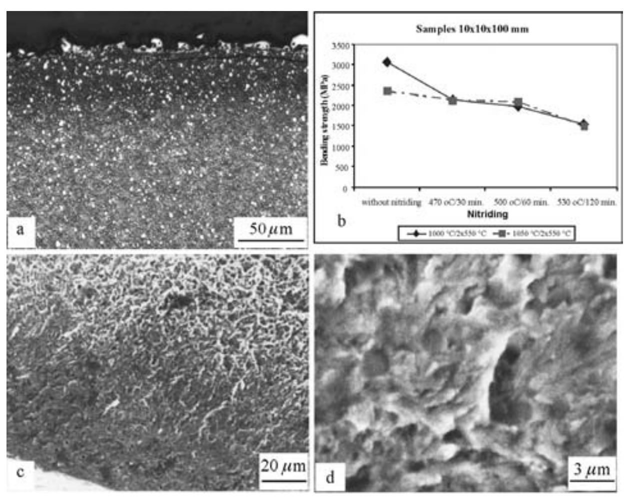

Figure 12: a – light micrograph of plasma-nitrided region formed on the Vanadis 6 steel at 530 °C for 120 min., b – three-point bending strength as a function of processing parameters, c, d – overview and detail SEM micrographs of the fracture surface

Slika 12: a – optični posnetki v plazmi nitrirane površine na jeklu Vanadis 6 po 120 min obdelave pri 530 °C, b – tri točkovna upogibna trdnost v odvisnosti od parametrov procesiranja, c, d – videz in SEM-posnetek površine preloma

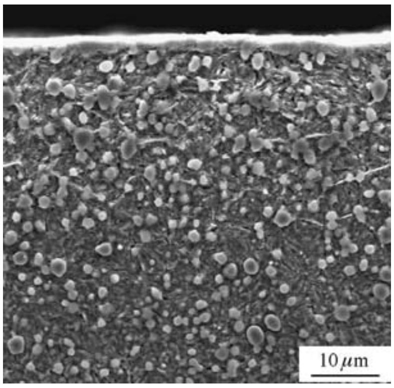

Figure 13: SEM micrograph showing the duplex-layer (plasma nitriding 500 °C/60 min. + CrN 2.5 μm) formed on the Vanadis 6 steel
Slika 13: SEM-posnetek dvojne plasti (plazemsko nitriranje 500 °C/60 min + CrN 2.5 μm), ki je nastala na jeklu Vanadis 6

steels, but the most frequently used are still TiN and CrN and their variations with additions of other elements like Si, Al etc. The main problem in the deposition of thin films is their adhesion to the substrate, since they differ from the metals in many physical and mechanical properties. First of all, they have a much higher hardness and elasticity modulus. Ceramic films generally exhibit very poor fracture toughness and differ from steels also in their thermal expansion coefficient. As a result, they can easily fail when loaded, with heavy normal forces or dynamically.

The current development in PVD coatings is then focused on three main trends. The first one is multilayers with different periodicity of the nano-scaled sub-layers. The effort to develop the multilayers is devoted to the improvement of fracture characteristics of ceramic films based on the assumption that the crack propagation will be hindered by the presence of many interfaces in the film. The second trend in the coatings development is based on the logical consideration that if brittle material contains softer particles of an optimal size and distribution, its resistance to fracture propagation can be improved. Therefore, the addition of small amounts of silver or copper to the CrN (CrAlN, CrSiN) coatings are investigated [18–21]. The last, but not the least, trend in modern coating development is focused on the optimization of the substrate properties before the deposition. For this purpose, plasma nitriding has become of the greatest importance. Nitrided regions have an elevated hardness and a better load-carrying capacity, which led to a several times better coating adhesion in many previous investigations [14,15,22]. **Figure 13** shows an example of a duplex-layer formed on the surface of the PM ledeburitic steel Vanadis 6.

3 MECHANICAL PROPERTIES

3.1 Hardness

Cr-V ledeburitic steels have a heterophaseous composition over their whole lifetime, e.g., from the manufacturing procedure up to the final use of the tools. Therefore, the hardness of the materials is a result of the synergistic effect given by the superposition of the effects of the matrix and the carbides. However, the role of the structural constituents upon the hardness is specific in different stages of the heat treatment of the materials.

In the as-annealed condition, the matrix comprises ferrite and its hardness is low. The hardness of the material is then mainly determined by the quality, size and distribution of carbides. Generally, the hardness increases with increasing amount of carbides. In the group of Cr-V ledeburitic steels, the as-annealed hardness is mainly influenced by the amount of MC-carbides.

In the heat-processed state, the matrix is responsible for the high hardness of the materials. The heat treatment, if properly conducted, leads to the formation of a matrix consisting mainly of martensite and a certain portion of retained austenite. In some cases, bainite can also be formed in as-quenched steels, but, as reported elsewhere, with no risk of a substantial hardness loss [3]. When sub-zero processed, the hardness of steels is increased by several HRC units due to more complete martensitic transformation. Tempering at temperatures up to 450 °C induces a slight hardness decrease. Above that, the hardness increases due to the complex precipitation/transformation process, see section 2.5. Beyond the maximum of the secondary hardness, the coarsening of precipitates proceeds and the hardness decreases.

3.2 Wear resistance

When pure abrasive wear takes place in the use of tools, the resistance of Cr-V ledeburitic steels against it is determined by the amount of large primary and eutectic carbides. But, also the character of the abrasive particles plays an important role. If, for instance, abrasive particles are harder than the hardest structural component of tool steels, no improvement of the wear resistance can be expected [23]. In the case of softer abrasive particles like SiO_2, on the other hand, an enhanced volume fraction of hard MC primary carbides leads to an improvement in the wear resistance by 75–100 %. Nevertheless, also in the case of the SiO_2-abrasive particles the situation is more complex – according to Jacobson [24], better wear resistance of the tool steels can be expected only if the SiO_2-particles are smaller than 100 μm.

However, from various metallurgical aspects it is difficult or impossible to increase the amount of MC-carbides above some limits. A high volume fraction of MC-phase makes serious obstacles in the manufacturing of tool steels, which makes it impossible to obtain a structure and properties, mainly toughness, at an acceptable level [25,26].

If the adhesive wear is the dominant process in the use of ledeburitic tool steels, the presence of hard carbides itself is not relevant for better wear resistance [27]. According to Fontalvo et al. [28], besides the presence of hard MC-carbides, the interparticle spacing is the dominant factor influencing the adhesive wear resistance. The interparticle spacing has to be as small as possible. Otherwise, the contact area between the relatively softer matrix and counterpart material and the probability of adhesion also increases.

The wear resistance can be improved by various surface-treatment techniques. For instance, it has been reported previously that the plasma nitriding applied for the final processing of Vanadis 6 ledeburitic steel reduces the friction coefficient and makes the weight loss due to wear lower by 50 % [29]. Also, the PVD-coating, if properly made, tends to reduce the friction coefficient and makes the abrasive and adhesive wear lower [14,15,22].

For instance, our first experiments with the incorporation of small silver additions to CrN coatings, developed on the Vanadis 6 steel, have shown that the friction coefficient was reduced considerably when the layers were tested at elevated temperatures using a standard pin-on-disc test.

3.3 Three-point bending strength

The three-point bending strength is a standard measure of the resistance of hard ferrous alloys, including Cr-V ledeburitic steels, against the initiation of brittle fracture. For its determination, standard samples with the dimensions (10 × 10 × 100) mm are used. The standard load rate is 1 mm/min and the samples are loaded in the centre.

There are many parameters of the material manufacturing route and processing that influence the three-point bending strength.

3.3.1 Manufacturing route

There are two main manufacturing routes of the Cr-V ledeburitic steels. The first one is based on the ingot casting and subsequent hot rolling and/or forging of as-cast ingots. It often accompanied by the formation of carbide bands, oriented longitudinally to the dominant deformation direction. As a result, also the three-point bending strength is directionally dependent, while the values measured in various directions to the carbide banding may differ significantly [30].

The second production route for the Cr-V ledeburitic steels is the powder metallurgy of rapidly solidified particles. The manufacturing process involves the powder production (mainly by inert-gas spraying of the melt) and powder consolidation (hot isostatic pressing is normally used). In the powder production, the gas spraying disintegrates the melt stream into small droplets, which freeze rapidly, at typical cooling rates of 10^3–10^5 K s^{-1}. This makes a reduction in scale of segregation because of the spatial (typical size of powder particles is several tens of μm) and time (the droplets freeze in mili- or microseconds) restrictions. The consolidation via hot isostatic pressing introduces an isotropic deformation into the material. The resulting microstructure of P/M manufactured steels in much finer than that of conventionally produced materials with no preferred orientation of the structural features, see also **Figure 1**. Nevertheless, an improvement of the mechanical properties of materials due to the use of P/M technique for their manufacturing is closely dependent on the quality of stages of the manufacturing. If, for instance, the molten material is insufficiently homogenized before the spraying, clusters of primary carbides can remain in the structure and might easily cause lowering of the three-point bending strength [31].

Unfortunately, a direct comparison of the effect of manufacturing route on the three-point bending strength is missing up to now since there is not a commercially available Cr-V ledeburitic steel that has been produced by both mentioned techniques.

3.3.2 Surface quality

For brittle materials, like Cr-V ledeburitic steels, the surface quality plays an important role in their fracture behaviour. These problems were analysed in various investigations [32] and for the Cr-V ledeburitic steel Vanadis 6 more precisely in [33]. It was found that a worsened surface quality induces a relatively sharp decrease in the three-point bending strength so the plastic component of the total work of fracture, **Figure 14**. As a consequence, a higher topography of the fracture surfaces of samples with a higher surface quality has been established, **Figure 15**.

3.3.3 Heat treatment

It is well known that the austenitizing and subsequent quenching increases the hardness of Cr-V ledeburitic steels, but, simultaneously, the three-point bending strength drop is lowered. The lowering of the three-point bending strength is more significant with increasing austenitizing temperature because of the grains' coarsening, **Figure 16** [7].

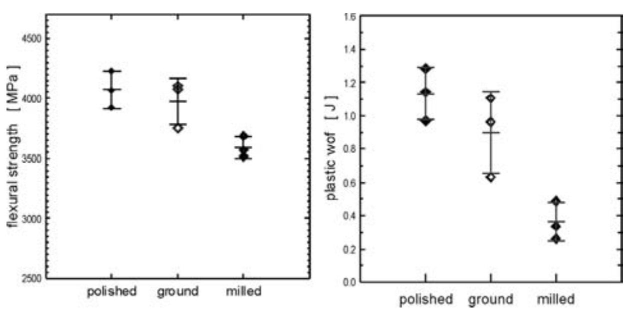

Figure 14: Flexural strength and plastic component of work of the fracture for heat-processed samples from the Vanadis 6 ledeburitic steel with various surface quality: polished – up to mirror finish, ground (R_a = 0.1) and milled (R_a = 6.3).

Slika 14: Upogibna trdnost in plastična komponenta energije preloma za toplotno obdelane vzorce ledeburitnega jekla Vanadis 6 z različno kakovostjo površine: zrcalno polirana, brušena (R_a = 0.1) in rezkana (R_a = 6.3).

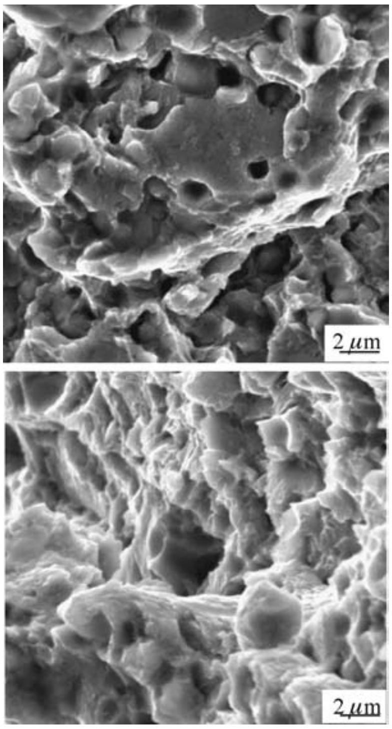

Figure 15: SEM micrographs of fracture surfaces of milled (left) and polished sample (right)

Slika 15: SEM-posnetki površine preloma rezkanega (levo) in poliranega (desno) vzorca.

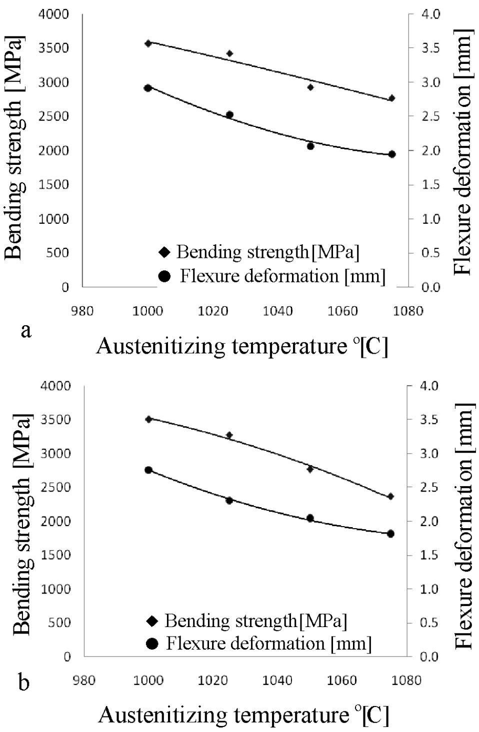

Figure 16: Effect of austenitizing temperature on bending strength after heat treatment. a – austenitizing, tempering 2 × 530 °C/2 h, b – austenitizing, sub-zero period –90 °C/4 h, tempering 2 × 530 °C/2 h

Slika 16: Vpliv temperature avstenitizacije na upogibno trdnost po toplotni obdelavi: a – avstenitizacija, popuščanje 2 × 530 °C/2 h, b – avstenitizacije, "sub zero" obdelava –90 °C/4 h, popuščanje 2 × 530 °C/2 h

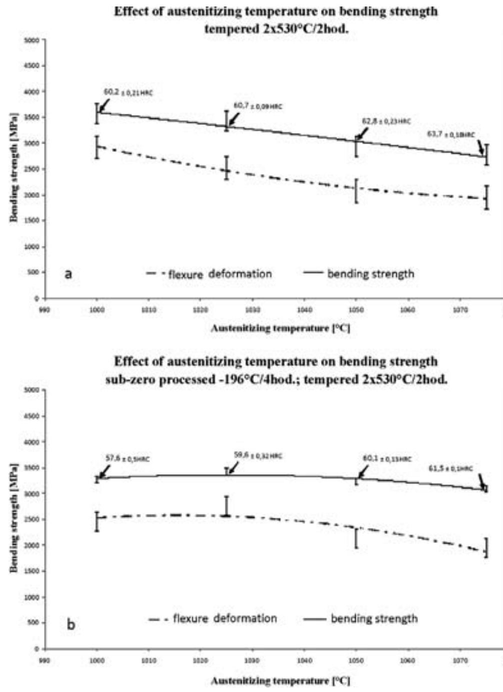

Figure 17: Three-point bending strength and flexure deformation for no-sub-zero and sub-zero processed Vanadis 6 steel

Slika 17: Tri točkovna upogibna trdnost in upogibna deformacija za ne sub zelo in sub zero procesirano jeklo Vanadis 6

Tempering at low temperatures, typically below 400 °C, results in a slight increase of the three-point bending strength because of the martensite softening. The increase of the tempering temperature to the range typical for the secondary hardness peak leads to a lowering of the three-point bending strength. The first

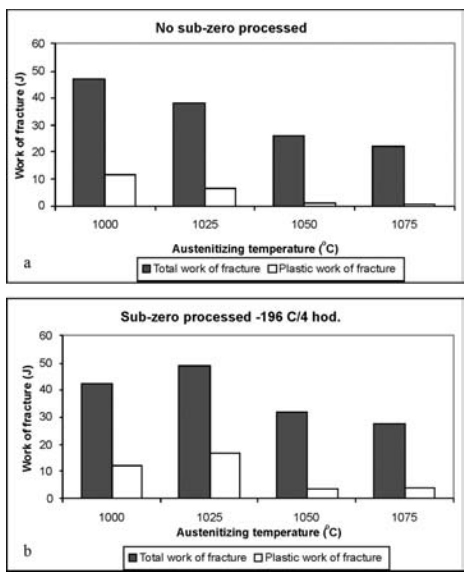

Figure 18: Work of fracture and its plastic component of no-sub-zero (a) and sub-zero (b) processed Vanadis 6 steel as a function of austenitizing temperature

Slika 18: Energija preloma in njena plastična komponenta za ne "sub zero" (a) in "sub zero" (b) procesirano jeklo Vanadis 6 v odvisnosti od temperature avstenitizacije

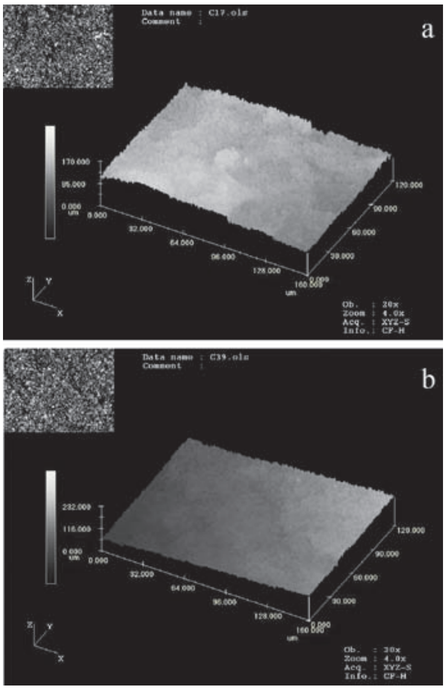

Figure 19: Fracture surfaces of the three-point bending test samples. a – sub-zero processed, b – no-sub-zero processed steel Vanadis 6

Slika 19: Površina preloma vzorcev po tritočkovnem upogibnem preizkusu; a – "sub zero" procesirano, b – ne "sub zero" procesirano jeklo Vadadis 6

process responsible for that is the transformation of the softer retained austenite to the harder martensite. Simultaneously, the precipitation of carbides from martensite and retained austenite contributes to the embrittlement of the materials.

If the sub-zero period is inserted into the heat processing, then the three-point bending strength can slightly increase, in particular when a higher austenitizing temperature was used, **Figure 17**. But some results of the investigations published previously also indicate a slightly opposite tendency, **Figure 21** [12]. The plastic component of the work of fracture increases with the sub-zero treatment, **Figure 18**. This is reflected in the topography of the fracture surfaces, as shown in **Figure 19**. From these two micrographs it can be derived that the sub-zero processing could have a positive effect on the plasticity of the material. This finding is also consistent with the fracture toughness investigations in previous work [12], which is discussed in one of the next paragraphs.

3.3.4 Surface treatment

The effect of the plasma nitriding on the three-point bending strength has been described in Section 2.6.

One would say that the PVD layering cannot influence the three-point bending strength in a negative way since the diffusion bonding of thin ceramic films onto the steel surfaces is poor due to a very low deposition temperature. However, our last investigations have fixed a weak tendency of the material to become more brittle when layered, **Figures 20** [34].

3.4 Fracture toughness

Fracture toughness is a measure that characterizes the resistance of the Cr-V ledeburitic steels against the crack propagation. In these materials, the fractures are typical formed by a "dimple morphology". It is a result of the mechanism of the fracture propagation, where two main mechanisms take place. The first is the carbide cracking. The carbides undergoing fragmentation are mostly the M_7C_3-particles. The second propagation mechanism is decohesion at the carbide/matrix interfaces, which is connected with plastic deformation of the matrix. It is logical that for the second mechanism, much more energy is spent, and also that the capability of the matrix to be deformed is the most important parameter describing the resistance of the materials against crack propagation.

Therefore, in real materials, the hardness of the matrix is the main parameter influencing the fracture toughness. Berns et al. [35,36] have reported that for the steel X210Cr12, the fracture toughness decreases from 31–50 MPa $m^{1/2}$ in the soft-annealed state to 14–22 MPa $m^{1/2}$ after austenitizing and quenching. Subsequent tempering led to a slight increase in K_{IC}, but the level of the K_{IC} increase was proportional to the as-tempered hardness. In addition, the authors of the above-mentioned papers have found that the effect of the morphology of carbides (as-cast networks, as-wrought banding) has an importance only in the soft-annealed state of the material and it becomes much less significant with the increasing hardness of the steels.

For Cr-V ledeburitic steels made via PM, there are practically no relevant data on their fracture toughness. Only in our recent work [12] we attempted to evaluate the fracture toughness of the Vanadis 6 steel after the application of various heat-treatment regimes. Two austenitizing temperatures (1000 °C and 1050 °C) were applied for a standard tempering temperature of 550 °C. Some specimens were also sub-zero processed in liquid nitrogen at –196 °C for 24 h.

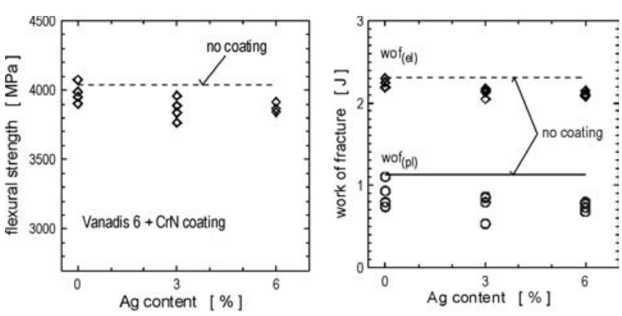

Figure 20: Flexural strength and plastic component of work of fracture for the CrN and CrAgN layered samples made from the Vanadis 6.

Slika 20: Upogibna trdnost in plastična komponenta prelomnega dela za vzorce s pokritjem CrN in CrAgNi iz jekla Vanadis 6

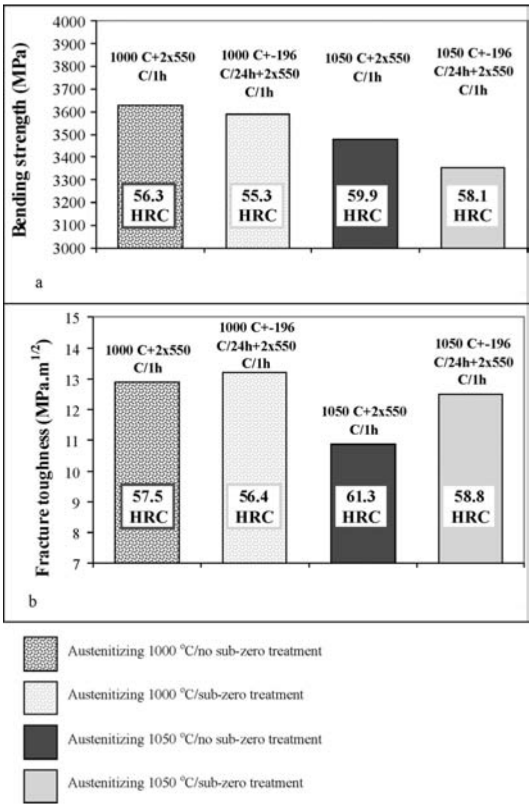

Figure 21: Graphical presentation of the obtained experimental results for a) three-point bending strength and b) average fracture toughness vs. processing route

Slika 21: Grafičen prikaz doseženih eksperimentalnih rezultatov za a) tritočkovno upogibno trdnost in b) povprečno žilavost loma za različne načina procesiranja

The results of the investigations are in **Figure 21**. The fact that a higher austenitizing temperature led to a lower fracture toughness has been expected, since it is logical that the matrix hardness was higher in this case. Nevertheless, the average fracture toughness after the performed heat processing of Vanadis 6 steel was found to be slightly higher for sub-zero processed material. At a first glance, this was rather surprising, since normally it is assumed that as the three-point bending strength so the resistance against crack propagation should be lowered. However, it was found in various investigations [7,12] that the hardness after the tempering was lower for the sub-zero processed material, see also Section 2.5. The observations, that the sub-zero processed Vanadis 6 steel had higher fracture toughness, seems to be consistent with other investigations [35,36].

There is no comparison between the fracture toughness for the Cr-V ledeburitic steels made via classical ingot metallurgy and the PM of rapidly solidified particles, since the only material produced using both manufacturing routes does not exist. The only paper describing the fracture toughness of the ledeburitic steels of the same chemical composition, but manufactured as by ingot metallurgy so via the PM is the pioneer work of Olsson and Fischmeister [37]. They reported that the fracture toughness of the PM made M2-type high-speed steel seems to be slightly better than the conventionally produced material.

4 CONCLUSIONS

As-delivered Cr-V ledeburitic steels should be in the soft-annealed state. When the soft annealing is properly done, they contain primary, eutectic and secondary carbides and spheroidized pearlite. The hardness of the materials should be as low as possible.

During austenitizing, the chromium-based carbides dissolve in the austenite while the vanadium-based particles remain stable up to high temperatures.

The dissolution of carbides induces the enrichment of a solid solution with carbon and alloying elements. As result, the through-hardenability of the materials increases, but also the portion of the retained austenite after quenching tends to increase.

If the optimal austenitizing temperature is exceeded, grain coarsening takes place and the retained austenite amount increases rapidly up to more than 50 %.

Properly quenched materials have a hardness easily exceeding 60 HRC. A too high austenitizing temperature lowers the hardness, due to an increased amount of retained austenite. When sub-zero treated, the materials have slightly elevated hardness due to a more complete martensitic transformation.

Tempering of Cr-V ledeburitic steels is a complex process, which involves the softening of martensite, the formation of new martensite from the retained austenite during cooling down from the tempering temperature and the precipitation of carbides during holding at the tempering temperature. When properly done, the maximum secondary-hardness peak occurs at a temperature of slightly above 500 °C.

It seems that sub-zero processed materials exhibit a tendency to have a slightly lower as-tempered hardness than those no-sub-zero treated. An exact interpretation of the lower as-tempered hardness is not available yet, but its nature should be probably considered in a different structure of deep-cooled material compared to classically heat-processed steels.

Plasma-nitriding possesses an increased hardness, lowered friction coefficient, improved wear resistance and adhesion of thin ceramic films, but, on the other hand, also embrittlement of the materials.

Physical vapour deposition processes are mainly used for the layering of Cr-V ledeburitic steels. Current development trends in the PVD-layering are focused on the development of nano-structured and duplex layers with customer-tailored properties.

The abrasive wear resistance of Cr-V ledeburitic steels is determined mainly by the volume fraction of primary and/or eutectic MC-carbides. However, if the abrasive particles are harder than the MC-phase, the effect of these carbides becomes negligible. In adhesive wear, the interparticle spacing of carbides is important. Surface layering, when properly chosen and made, can lead to a significant increase in the abrasive/adhesive wear resistance.

The toughness of the Cr-V ledeburitic steels is influenced by many parameters. The presence of carbide bands or clusters decreases the toughness. This is why the PM-made steels are tougher than those manufactured via ingot metallurgy. Further, the increased roughness, presence of brittle structures on the surface but also increased matrix hardness, due to heat treatment, make the toughness lower.

The fracture toughness of the discussed materials is mainly dependent on the matrix hardness and it decreases with the increasing matrix hardness. At a constant and low matrix hardness, the fracture toughness depends on the carbide size and distribution also. However, the effect of carbides on the fracture toughness diminishes at a high matrix hardness.

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