DOI 10.1007/s11003-020-00378-1

Materials Science, Vol. 55, No. 6, May, 2020 (Ukrainian Original Vol. 55, No. 6, November–December, 2019)

HYDROGEN-DIFFUSION MECHANICAL TREATMENT OF STRUCTURAL MATERIALS

Ya. M. Hladkyi,[1] **S. S. Bys',**[1,2] **and V. V. Myl'ko**[1]

UDC 621:787.785.9.902

We consider a new approach to the solution of the problems of elevation of the wear resistance of cutting tools and enhancement the serviceability of structural materials. It is based on the analysis of the physicomechanical and physicochemical influence of hydrogen in the cutting zone. The hypothesis of hydrogen-diffusion mechanical treatment and the concept of hydrogen-accumulating tool are proposed. We consider various sources of gaseous hydrogen. The process of cutting in the presence of hydrogen is studied and the obtained results are analyzed.

Keywords: hydrogen-induced wear, structural materials, mechanochemical wear, chip formation, hydrogen accumulators.

Introduction

The possibility of application of difficultly machined structural materials (high-strength, refractory, and heat-resistant steels and alloys) is connected with the problem of chip removal (chip crushing). This may lead to premature failures of tools and a decrease in productivity. The improvement of the methods aimed at increasing the wear resistance of cutting tools, the serviceability of structural materials, and the productivity of cutting is an actual problem for the researchers and producers.

The preliminary saturation of billets or tools with electrolytic hydrogen under certain conditions facilitates the formation of chips and increases the wear resistance. However, the impossibility to control the depth of hydrogen penetration in the process of saturation, the necessity of application of especially high-power equipment for large billets, and a short "lifetime" of electrolytic hydrogen restrict the possibility of extensive application of this method. At the same time, the attempts to deliver hydrogen into the cutting zone from gas vessels and to use a special installation give good results: the temperature-and-force conditions of cutting, the durability of the tool, and the character of chip formation undergo significant changes [1]. However, this technology has numerous significant disadvantages, including the application of gas vessels with liquefied hydrogen, which is, in fact, inadmissible under the production conditions, both for the safety reasons and from the economical point of view.

As a result of the analysis of available methods used for the delivery of hydrogen into the cutting zone and estimation of their positive and negative aspects, it was proposed to use, as a source of atomic hydrogen, the so-called tool-accumulator [2], i.e., a tool covered with hydrogen-containing coating capable of the accumulation of hydrogen at high temperatures and characterized by the possibility of rapid recharging. In [3], the observed intensification of mechanical treatment was theoretically justified and the results of experimental investigations were interpreted.

The effect of hydrogen on the mechanical properties of metals is one of the strongest effects, as compared with the other gases [4]. The unique mobility of hydrogen is explained by the free motion of its nuclei deprived of electrons, i.e., protons, in the crystal lattice of the metal. According to [5], the diffusion coefficient of

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[1] Khmelnytskyi National University, Khmelnytskyi, Ukraine.

[2] Corresponding author; e-mail: serhiibys@gmail.com.

Translated from Fizyko-Khimichna Mekhanika Materialiv, Vol. 55, No. 6, pp. 62–69, November–December, 2019. Original article submitted August 28, 2018.

1068-820X/20/5506–0846

hydrogen in iron varies from 1.5×10^{-5} to 6.3×10^{-4} $\mathrm{cm}^2/\mathrm{sec}$ as temperature increases from 20 to 900°C, respectively.

The hypothesis of elevation of the machinability of materials and increase in the wear resistance of tools is based on the principle of modification of the mechanism of fracture of materials in the process zone.

From the viewpoint of fracture mechanics, the process of chip formation can be regarded as the process connected with the initiation of microcracks in the planes with highest tangential stresses and their merging into a main crack (macrocrack) [3]. In this case, the fracture (chip formation) process may have either transcrystalline or intercrystalline character. Creating special conditions in the material or modifying the stress-strain state in the cutting zone, it is possible to reach the state in which the transition from the high-energy-consuming (intragranular) to the intergranular low-energy-consuming fracture becomes possible. A significant role in the intergranular fracture is played by hydrogen promoting the embrittlement of the material in the cutting zone. In order to increase the wear resistance of the tool and the machinability of materials, it is proposed to deliver hydrogen directly into this zone.

The ability of metal hydrides and intermetallic compounds to perform various tasks is connected with the possibility of accumulation of hydrogen, which turns them into quite promising materials. The application of hydrogen chemically bound in hydrides due to their high sorption capacity gives advantages over the outlined traditional procedures from the viewpoints of economic efficiency and safety.

The highest interest is attracted by $\mathrm{BeH_2}$, $\mathrm{MgH_2}$, $\mathrm{ScH_2}$, $\mathrm{TiH}_{n(n=1.63-2.00)}$, and $\mathrm{ZrH}_{n(n=1.54-2.00)}$ hydrides. However, low fractions of hydrogen in these compounds restrict their applicability.

The intermetallic compounds of metals with hydrogen are capable of accumulation large amounts of hydrogen as compared with the ordinary metals. Among intermetallic compounds that deserve serious attention, we can especially mention the following compounds: $\mathrm{Mg_2Ni}$–H, TiFe–H, and the following mixtures: $(\mathrm{Mg_2Ni} + \mathrm{Mg})\text{–}\mathrm{H_2}$, $(\mathrm{Mg_2Cu} + \mathrm{Mg})$–H, and $\mathrm{LaMg_{12}}$–H.

The hydrogen capacity of these compounds is still insufficiently high (and does not exceed 6%). In order to increase it and prevent the dispersion of intermetallic compounds, it is reasonable to add finely divided hydrogen-sorbing powders, which are not destroyed under the conditions of long-term operation and have improved engineering characteristics, as compared with pure intermetallic compounds. These materials include the so-called frame materials in which the working substance and the filler form a rigid frame, and the components of the material should not interact with each other [the $\mathrm{Ti_2Ni}$–H and (Ti–Mg + additive)–H pseudoalloys]; layered materials, such as metals or intermetallic compounds with deposited coatings of unstable oxides accelerating the processes of sorption and desorption of hydrogen [including, e.g., coatings made of nickel, copper, and (rarely) iron that can be deposited by vacuum spraying, electrolysis, point welding, and other available methods], and mixtures of several intermetallic compounds every component of which is a good accumulator. As the main condition, we can mention the absence of their interaction in the process of operation. Note that the most promising mixtures are $(\mathrm{TiFe} + \mathrm{LaNi_5})$–H and $(\mathrm{Ti_{0.8}Zr_{0.2}Cr_{0.8}Mn_{1.2}})\mathrm{H}$.

The process of synthesis of hydrides is realized by using a low-pressure equipment [6]. There are several special technologies developed for the production of titanium hydrides as coatings on cutting tools. The so-called "barrier layer" is formed on the surface in order to protect the material against the penetration of hydrogen [7]. The titanium coating is formed by the method of condensation with ionic bombardment and subsequent hydrogenation (Fig. 1a). The hydrogen-accumulating coating on the surface of the tool serves as a source of hydrogen. However, this technology does not guarantee the presence of sufficient amounts of hydrogen required for the long-term operation of the cutting tools.

Therefore, as a source of hydrogen, we propose to use a special tool-accumulator. This instrument is formed by an ordinary tool and an accumulator of hydrogen (Fig. 1b), which is pressed to the tool surface by a special protective case (clamp). The service life of this unit is 80–100 min.

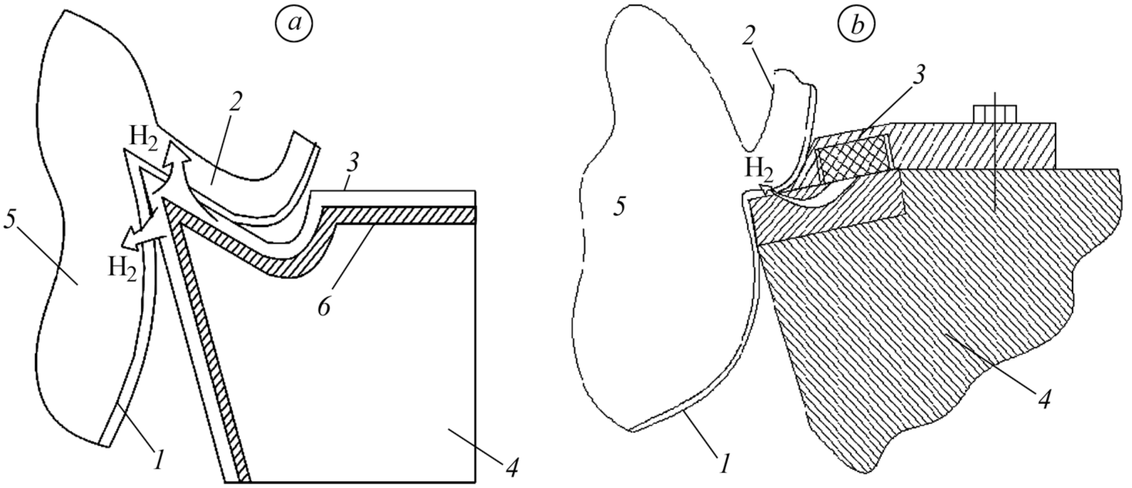

Fig. 1. Schematic diagram of the delivery of hydrogen into the cutting zone: (a) hydrogen-containing coating; (b) tool-accumulator: (1) hydrogenated layer; (2) chips; (3) hydrogen accumulator; (4) tool; (5) treated material; (6) barrier layer.

Procedure of Investigations

We studied the serviceability of tool-accumulators under the conditions of longitudinal turning of structural materials on a 1K62-model lathe with stepless regulation of rotation frequency. We determined the influence of hydrogen on the force characteristics of cutting (i.e., the force components P_Z, P_X, and P_Y), cutting temperature [thermoelectromotive force (TEMF) Ω measured by a thermocouple], optimal cutting velocity V_0, the degree of plastic deformation of the treated material K_L, and its wear resistance. In order to measure the force characteristics of cutting, we used a UDM-600 universal measuring complex. The TEMF in the cutting zone was measured with the help of a natural thermocouple. The level of plastic strains of the treated material K_L was determined according to the DSTU. The degree of wear was measured in a BMI-1 optical microscope. The level of hardness of the surface was found by using a PMT-3 microdurometer according to the DSTU.

We studied the following materials: St3, 40Kh, and 03Kh18N10T steels and KhN35VTYu refractory alloy with different chemical compositions and structures. For turning, we used a tool made of R6M5 high-speed steel and VK6M solid alloy. In the course of turning of steels with the help of a tool made of R6M5 steel with limited heat resistance (by at most 650°C), we used Mg_2NiH_2, MgH_2, TiH_x, and $Ti_2Ni(H_x)$ accumulators as the sources of hydrogen. For these accumulators, the temperature range corresponding to the onset of dissociation of hydrogen is 200–300°C. In analyzing the serviceability of a tool-accumulator based on the VK6M solid alloy, we used Ti_2NiH_x, (Ti–Mg)–H, and TiFe accumulators as sources of hydrogen for which the temperature range of the onset of hydrogen dissociation starts at temperatures higher than 300°C.

Results of Investigations and Discussion

The results of studies of the process of cutting by a tool-accumulator made of R6M5 high-speed steel demonstrate that, in all cases, the procedure of treatment realized with the delivery of hydrogen is characterized by lower cutting forces and a decrease in the degree of plastic deformation of the treated material. The temperature in the contact zone of the couple in hydrogen significantly decreases, which leads to the elevation of the optimal cutting speed V_0 (Fig. 2). The relative changes in some characteristics of the process of cutting of steels performed with the help of a tool-accumulator made of R6M5 steel, as compared with the ordinary tools, are presented in Table 1.

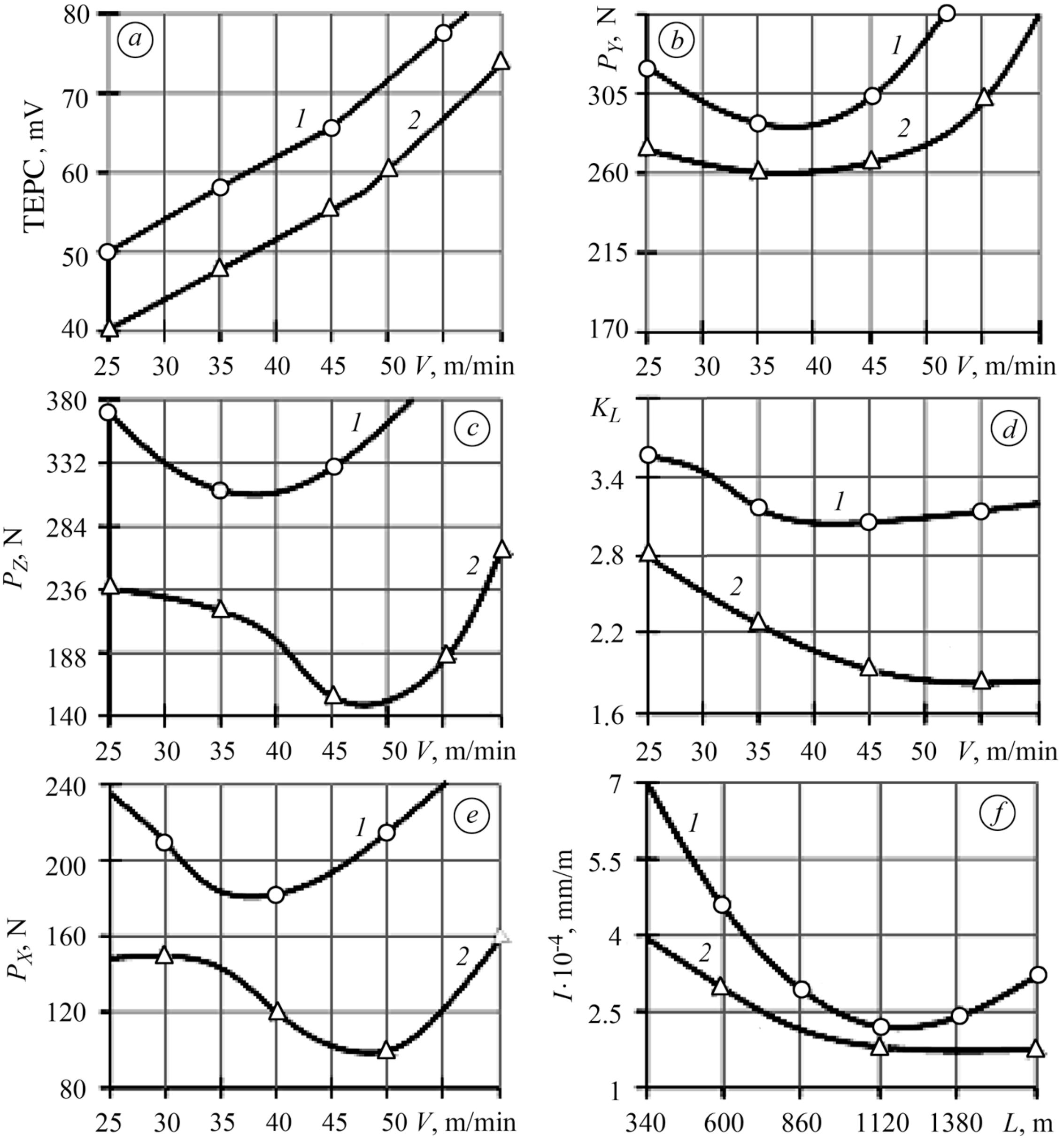

Fig. 2. Dependences of the parameters of the process of cutting for KhN35VTYu heat-resistant alloy [(a) TEMF; (b, c, e) load vector; (d) degree of plastic deformation, and (f) wear resistance] on the rotation speed (a–e) and the path length (f) obtained by using an ordinary tool (1) and a tool-accumulator made of VK6M alloy (2).

The degree of wear of the tool-accumulator based on R6M5 high-speed steel in the course of turning in hydrogen is several times lower than for the ordinary tools under the identical conditions. In addition, within the range of optimal cutting speeds, the process of chip removal is facilitated due to the modification of the mechanism of chip formation. Indeed, instead of continuous chips typical of the process of cutting with ordinary tools, we get articulated chips, which then turn into discontinuous chips.

The changes in the mechanism of fracture of the treated material can be explained by analyzing the regularities of the influence of stresses and strains on the process of hydrogenation. Thus, the deformation of the metal lattice increases its energy level and strongly affects the development of dislocation-vacancy structures, which

Table 1

Treated material	Relative changes in the parameters of cutting in a hydrogen-air environment				
	V_0	P_Z	P_X	P_Y	K_L
	%				
R6M5					
St3	+ 34	– 42	– 33	– 22	– 22
40Kh	+ 43	– 63	– 50	– 45	– 57
03Kh18N10T	+ 34	– 60	– 150	– 88	– 60
VK6M					
40Kh	+ 27	– 20	–	–	–
03Kh18N10Y	+ 33	– 35	– 32	– 15	– 50
KhN35VTYu	+ 36	– 114	– 100	– 30	– 63

determines the hydrogenation of steel [8]. It is reasonable to distinguish three cases of hydrogenation (with increasing intensities): hydrogenation of the metal with nondeformed lattice, hydrogenation of the metal with deformed lattice, and hydrogenation in the course of deformation of the metal. Small deformations accompanied by relatively weak distortions of the lattice (material of the tool) have an insignificant influence on the diffusion of hydrogen and on the susceptibility of the metal to hydrogen embrittlement. High-level deformations (with cutting of the metal) lead to ruptures of the crystal lattice and to the formation of defects in the form of microcavities in the continuous material. The results of investigations carried out in [9] confirm the penetration of hydrogen into the region of plastic strains. Thus, it was shown that the increase in the level of strains by 1% causes an increase in the permeability of hydrogen into steel P_H by 100%.

In Table 1, we present some data on the relative changes in the parameters of cutting of materials in hydrogen as compared with their treatment in air. It follows from these results that there exists a correlation between the effects caused by the hydrogen-diffusion treatment and the properties of structural steels.

The chemical composition of billets affects the diffusion of hydrogen in steel, the solubility in its lattice, and the absorption of hydrogen by collectors. The diffusion of each element is affected by the presence of other elements. It seems likely that some elements change the crystal lattice of iron and the other elements move through this lattice. The presence of Ni in steel (e.g., 03Kh18N10T steel) promotes its high hydrogen permeability. Thus, the activation energy of hydrogen diffusion is equal to 75.6 kJ/mole [10] in 35N3 nickel-containing steel with 3.25% Ni and to 186.1 kJ/mole in 40Kh steel with 0.89% Cr.

We now mention one more regularity. For low speeds of treatment, we do not observe any significant decrease in the cutting force. This can be explained by the fact that the temperature of heated tool-accumulator and strain rate are still insufficient for the onset of intense dissociation of hydrogen accompanied by a significant embrittlement of the material of chips.

For the hydrogen-induced wear, it is necessary to get a hydrophilic state of the layer surface (local increase in the concentration of hydrogen in the surface layer caused by diffusion up to a level higher than the concentration attained outside this layer by at least an order of magnitude). As basic factors affecting this state, we can

Table 2

Structure	Amount of hydrogen absorbed by 100 g of the metal, cm^3
Martensite	6
Troostite	15.9
Sorbite	46.5
Pearlite-ferrite normalized structure	25.5

mention the metal structure, its changes under the conditions of friction, and the chemical composition of the metal.

The changes observed in the surface layer of the metal in the course of friction induce complex structural transformations and leads to an increase in the number of defects, which affects the behavior of hydrogen in this zone. The diffusion of hydrogen from various structural elements of the metal is nonuniform. Hydrogen weakens the boundaries of crystals, decreases the degree of cohesion in cleavage planes, and can move mainly along the indicated directions. It was shown [11] that the rate of hydrogen diffusion depends on the structure of steel. Indeed, metals with different structures absorb different amounts of hydrogen under the same conditions of saturation (Table 2).

It is known that the solubility of hydrogen in austenite is higher than in ferrite and much higher than in martensite. At the same, the rate of hydrogen diffusion in ferrite is higher than in austenite. Hence, it is possible to assume that the absorption of hydrogen by steel and its machinability depend on the structure, parameters of the crystal lattice, and the presence of collectors accumulating molecular hydrogen (this hydrogen may create high pressure and promote the embrittlement of steel). Therefore, as follows from Table 1, the optimal diffusion rate increases, to the greatest extent, in steels with ferrite structures and, to the least extent, in steels of the austenite class (stainless steels).

As one of the most important factors affecting the durability of steel, we can mention the concentration of carbon in it because the diffusion coefficient D_H in alloys of the Fe–C system strongly decreases as the concentration of carbon increases. Thus, the increase in the concentration of carbon from 0.01 up to 0.8% causes a decrease in D_H in steels from $4 \cdot 10^{-3}$ down to $1 \cdot 10^{-3}$ m^2/sec [9]. In addition, the carbon content affects the hydrogen permeability of steels P_H. It is accepted that its increase by each 0.1% decreases P_H by 4.1% [12]. The chemical affinity of hydrogen to carbon may lead to the reduction of carbide phases in steels according to the reaction:

$$Fe_3C + 2H_2 = 3Fe + CH_4.$$

This process is accompanied by a decrease in volume, which induces additional stresses on the grain boundaries. The thickness of the layer susceptible to decarburization and hence, to noticeable changes in its properties decreases as the content of carbon in steel becomes higher [13].

The alloying elements that form chemical compounds (hydrides) affect the ability of steel to absorb hydrogen [14]. Thus, the hydride-forming admixtures of molybdenum, vanadium, chromium, and other elements keep atomic hydrogen in the state of solid permeating solution, decelerate its desorption from the metal and, hence, inhibit the transition of hydrogen into the molecular form and prevent fracture.

In the R6M5 high-speed steel formed by finely divided martensite alloyed with tungsten, molybdenum, vanadium, and chromium and characterized by an elevated (as compared with structural steels) content of carbon (up to 1%), the hydrophilic state does not appear for the period of operation up to returning (durability period). Therefore, we do not observe any catastrophic hydrogen-induced wear.

Under forced operation conditions, high temperatures are formed in the tool-billet contact zone. They lead to the intensification of the processes of oxidation on the contact surfaces and to the overheating (loss of heat resistance) of the tool. Entering this zone, hydrogen, as a strong reducer, first reacts with the oxygen of air and protects the tool against oxidative wear.

In the course of cutting of the metals in gaseous hydrogen, the phenomenon of hydrogen-phase cold hardening (HPCH) is detected in the tool material. The phenomenon of strengthening of the material by HPCH is explained by the following two physical causes: by the internal deformation due to the phase cold hardening of the material under the conditions of saturation with hydrogen and the development of hydride transformations with participation of phases, which have different specific volumes, and by the intense interaction of occluded hydrogen and hydride phases formed with defects of the crystal lattice [15]. The phenomenon of HPCH can be observed for any metal subjected to the action of hydrogen-containing media with the required parameters, such as, e.g., active gaseous hydrogen, hydrogen-containing gases, plasmas, electrolytic hydrogen, etc. In all these cases, under the conditions of HPCH, the density of defects in the crystal structure strongly increases (by 2–4 orders of magnitude). This is accompanied by the refinement of block structure and an increase in the angular disorientation. An additional confirmation of this hypothesis is given by the analysis of the surface microhardness of the cutting edge of the tool-accumulator after operation in gaseous hydrogen. The surface microhardness of the tool made of R6M5 steel becomes almost twice higher.

In the process of cutting with a hard-alloy tool, we observe its rapid wear in hydrogen for the first ten minutes of testing. In connection with this fact, we advanced a hypothesis that atomic hydrogen penetrates into defects in the form of pores and microcracks and also in the regions between tungsten and cobalt carbides. In these zones, hydrogen passes into the molecular form and, hence, destroys the tool by creating high pressures.

Therefore, it was proposed to cure all defects in a sintered powder alloy. The highest hydrogen resistance among chemical elements is exhibited by chromium. Thus, we have used the patented method developed at the Khmelnytskyi National University and aimed at increasing the crack resistance of the tools [2, 3, 7]. A chromium layer, which is called a "barrier" layer, is capable of increasing the fracture toughness of the material. Moreover, it protects the tool against hydrogen penetration. The results of investigations (Fig. 2 and Table 1) demonstrate that both the proposed additional treatment and the application of cutting fluids facilitate the process of chip formation [16].

CONCLUSIONS

The presented results of investigations confirm the improvement of machinability of structural materials in gaseous hydrogen, which penetrates into the cutting zone under the action of high temperatures, high contact stresses, and plastic strains, embrittles the process zone, and facilitates the process of chip formation. As a result of this interaction, the components of the cutting force, the temperature in the cutting zone, and hence, the degree of wear of the tool become lower. As sources of hydrogen, we propose to use its accumulators based on the commercial intermetallic compounds and composite materials and guaranteeing the presence of sufficient amounts of hydrogen for the long-term operation, namely, Mg_2NiH_2, MgH_2, TiH_x, and $Ti_2Ni(H_x)$ for high-speed steels and Ti_2NiH_x, (Ti–Mg)–H, and TiFe for hard alloys.

We establish the relationship between the structure, chemical composition, heat treatment of the tool material, and the load-temperature factor, on the one hand, and the fracture resistance under the influence of hydrogen, on the other hand.

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