1. Introduction

Despite the high quality of cutting tools made from rolled high-speed steels the interest in cast tools has been growing. The reason for this is that foundry technology offers advantages over the traditional way of tool production. First of all the primary focus is on the potential for waste minimization and waste utilization of tool materials. From this point of view investment casting methods allow the most significant high-speed steel savings. Since the machining of tool shaped castings can be restricted to polishing only, energy and labour savings are the other advantages of foundry technology resulting in considerably lower production cost of a cast tool in comparison with the same one made from the wrought material.

The benefit still results from the very as-cast high-speed steel structure that belongs to a natural composite. Just the combination of relatively ductile metallic matrix with reinforcing 3-D skeleton of significantly harder eutectic carbides network provides better wear resistance of as-cast high-speed steels resulting in enhanced tool life.

On the other hand, distinct brittleness of as-cast high-speed steels caused by the presence of eutectic network over grain boundaries of the solid solution, inhibits broad application of chipper cast tools in industry. Therefore, in order to exhibit good all-round performance the impact toughness enhancement of as-cast high-speed steels is obligatorily needed. In general, different methods are used commercially to achieve cast structure refinement and, as a consequence, their properties are improved. Introduction into the melt of inoculant particles or surface-active additions is among most beneficial. However, the effect of modifying additions in as-cast high-speed steels has been studied insufficiently. In fact, a restricted number of modifiers is used for structure and properties improvement in the as-cast high-speed steels compared to the common cast alloys. In the present work several kinds of alloys including tungsten-molybdenum high-speed steels of M2 and T30 types and low-alloy tungsten-free 1.1C–5Mo–1.7V high-speed steel were melted to investigate the effect of bismuth on their structures and properties.

It has been found that additions of bismuth produce a very fine cast structure and affect the shape of the matrix grains and the morphology of the eutectic carbides as well as the redistribution of the main alloying elements of high-speed steels between solid solution and eutectic carbides. The microstructural changes, induced by bismuth during solidification, are explained by the surface activity of bismuth, which segregates to liquid/solid interface, significantly blocking dendrite growth in the direction along certain crystallographic planes. It has been shown that during eutectic solidification, carbides are also exposed to the barrier effect of bismuth being surrounded in the melt by this element. The main metallographic features of the modified cast structure alongside with the purifying effect produced by bismuth are retained after full heat treatment affecting the final mechanical properties of as-cast high-speed steels. As a result, bismuth significantly increases impact toughness and wear resistance of as-cast high-speed steels but decreases their red hardness.

In order to exhibit good all-round performance the impact toughness enhancement of as-cast high-speed steels is obligatorily needed. In general, different methods are used commercially to achieve cast structure refinement and, as a consequence, their properties are improved. Introduction into the melt of inoculant particles or surface-active additions is among most beneficial. However, the effect of modifying additions in as-cast high-speed steels has been studied insufficiently. In fact, a restricted number of modifiers is used for structure and properties improvement in the as-cast high-speed steels compared to the common cast alloys. In the present work several kinds of alloys including tungsten-molybdenum high-speed steels of M2 and T30 types and low-alloy tungsten-free 1.1C–5Mo–1.7V high-speed steel were melted to investigate the effect of bismuth on their structures and properties.

It has been found that additions of bismuth produce a very fine cast structure and affect the shape of the matrix grains and the morphology of the eutectic carbides as well as the redistribution of the main alloying elements of high-speed steels between solid solution and eutectic carbides. The microstructural changes, induced by bismuth during solidification, are explained by the surface activity of bismuth, which segregates to liquid/solid interface, significantly blocking dendrite growth in the direction along certain crystallographic planes. It has been shown that during eutectic solidification, carbides are also exposed to the barrier effect of bismuth being surrounded in the melt by this element. The main metallographic features of the modified cast structure alongside with the purifying effect produced by bismuth are retained after full heat treatment affecting the final mechanical properties of as-cast high-speed steels. As a result, bismuth significantly increases impact toughness and wear resistance of as-cast high-speed steels but decreases their red hardness.

KEY WORDS: high-speed steel; bismuth; modifying effect; structure; properties.
In terms of efficiency and the production cost of all the above-mentioned methods used for as-cast high-speed steels quality improvement, it appears that modification of the melt is more the simple and effective one. However, the effect of modifying additions in as-cast high-speed steels has been studied insufficiently. As a consequence, a restricted number of modifiers is used for structure and properties improvement in the as-cast high-speed steels compared to the common cast alloys. In fact, only titanium, niobium, some rare earth metals, calcium and nitrogen have been extensively employed as modifying elements for as-cast high-speed steels.\textsuperscript{16,19,20,22,33} Moreover, because of insufficient investigation many modifying additions are predicted as non-effective and harmful since they deteriorate plasticity of commercial high-speed steels,\textsuperscript{34} which are obligatory undergone hot plastic deformation after solidification. For example, such elements as bismuth, lead, copper, antimony and tin, at even very low content—0.006 mass% (Bi), 0.04 mass% (Pb), 0.15 mass% (Cu) and 0.20 mass% (for both Sb and Sn)—provoke collapse in wrought high-speed steels when hot plastic deformation is carried out. Just on the contrary, it has been shown that in as-cast high-speed steels, which are not subjected to hot plastic deformation, these elements promote fine solidification structure and therefore benefit to properties enhancement after final heat treatment.\textsuperscript{35–37}

In general, the modifying effect of elements depends on their surface activity.\textsuperscript{38–40} It is known that the lower the surface energy, the more stable the solidifying system, i.e. the more favourable the conditions for nucleation of the melt. It is possible to change the value of the surface energy by adding into the melt surface-active elements. On the one hand, such elements adsorbing on the solid (crystal nuclei)—liquid interface reduce surface stress there that increases the rate of nucleation and the stability of nuclei with smaller critical size. On the other hand, surface-active elements forming the adsorbed monomolecular films on the growing crystals prevent the diffusion of atoms of the crystallizing substance and, as a consequence, decrease the growth rate of crystals that finally results in structure refinement.

From the surface activity point of view the modifiers must have low free surface energy on the solid–gas (vapour) interface: this means they must have the weakest cohesive forces in solid and liquid states and as a result low melting temperature.\textsuperscript{38,40} With the above-mentioned predictions in mind the surface activity of elements in molten iron can be evaluated taking into account the difference between melting temperature ($\Delta T$) and surface energy ($\Delta \sigma$) for iron (Fe) and modifier ($m$) respectively. If:

$$\Delta T = T_{Fe} - T_{m} > 0 \quad \text{......(1)}$$

$$\Delta \sigma = \sigma_{Fe} - \sigma_{m} > 0 \quad \text{......(2)}$$

the modifier is surface active vs. iron.\textsuperscript{38–40}

The value of surface energy on the solid liquid interface can be determined from the equation:\textsuperscript{39}

$$\sigma = \sigma_{1} \left( \frac{\rho_{S}}{\rho_{L}} \right)^{2/3} q / \lambda \quad \text{......(3)}$$

where $\sigma_{1}$ is surface energy (surface tension) on the interface between liquid and gas, $\rho_{S}$ density of the solid phase, $\rho_{L}$ density of the liquid phase, $q$ latent heat of fusion, $\lambda$ latent heat of evaporation.

For evaluation of the surface activity it is possible to use the difference in the specific heat of sublimation ($\Delta P$)\textsuperscript{38–40}:

$$\Delta P = P_{Fe} - P_{m} > 0 \quad \text{......(4)}$$

The total electron potential barrier or energy of cohesion between atoms is also used as another criterion of surface activity and can be calculated as follows:\textsuperscript{39,40}:

$$\psi = \frac{h}{2m} \left( \frac{3N}{8\pi} \right)^{2/3} (\rho / M \cdot z)^{2/3} + \omega \quad \text{......(5)}$$

where $h$ is Planck’s constant, $N$ Avogadro’s number, $\rho$ density, $M$ atomic mass, $z$ number of valence electrons, $m$ electron mass, $\omega$ work function of the solid. The modifier will be surface active if\textsuperscript{38–40}:

$$\Delta \psi = \psi_{Fe} - \psi_{m} > 0 \quad \text{......(6)}$$

Taking into account that in adsorption the electrostatic interaction has significant influence, properties of molecules of the substance, namely their possibility to adsorb or to be adsorbed, can be expressed through the so called statistic generalized moment $m^*$, i.e. the potential of the neutral atom at Goldschmidt’s atomic radius distance from nucleus. Statistic generalized moment can be calculated in accordance with Thomas–Fermi statistic theory as follows:\textsuperscript{39–41}:

$$m^* = \frac{eZ}{r} \varphi(\eta) \quad \text{......(7)}$$

where $e$ is elementary charge, $Z$ atomic number or number of electrons in the neutral atom, $r$ Goldschmidt’s atomic radius (for FCC coordination number), and

$$\varphi(\eta) = \frac{r^3 \sqrt{Z}}{0.468} \cdot 10^9 \quad \text{......(8)}$$

The modifier will reduce surface stress if its statistic generalized moment of ion is less than that of iron:

$$\Delta m^* = m^*_Fe - m^*_m > 0 \quad \text{......(9)}$$

Finally, the surface activity of elements can be estimated using the value of entropy in standard condition $S^{298}$. The modifier is surface active if\textsuperscript{38–40}:

$$\Delta S^{298} = S^{298}_m - S^{298}_Fe > 0 \quad \text{......(10)}$$

In order to evaluate the surface activity of the elements in molten iron the calculations, using the above-mentioned equations, have been carried out in the previous paper.\textsuperscript{17} Calculated results given in Table 1 show that in terms of such criteria as melting temperature, surface energy, specific heat of sublimation, entropy in the standard condition, statistic generalized moment, total electron potential barrier for iron and modifier, respectively, antimony and tin are expected to be very effective surface-active additions in the melt of high-speed steels. According to the received activity series (Table 2),\textsuperscript{17} built up from the derived values on surface activities, bismuth leads the list.
of the most surface-active elements (by ranking the individual averages—for bismuth 18), followed by calcium (27), strontium and tin (35 for both), antimony (36), cadmium (37), magnesium (47), and so on. In this connection the main aim of the present paper is to highlight the effect of bismuth in as-cast high-speed steels.

2. Experimental Procedure

To study the effect of bismuth in high-speed steels, tungsten-molybdenum high-speed steels of AISI M2 and AISI T30 types were used as parent alloys, which were melted in alundum crucibles in electrical resistance furnace with a graphite heater. The steels were deoxidised using 0.2 mass% FMn70 ferromanganese, 0.2 mass% FS75 ferrosilicon, and 0.1 mass% aluminium. The calculated amount of pure bismuth was added into the completely deoxidised melt just before pouring. The chemical compositions of parent steels are presented in Table 3.

The melt temperature before casting was maintained in a range of 1480–1510°C and controlled by a W–Mo thermocouple. The liquid metal was cast into graphite molds preheated to 300°C. The castings with a weight of 0.7 kg were used to prepare specimens for mechanical tests and for metallographic analysis.

The effect of bismuth has been also examined in as-cast low-alloy tungsten-free 1.1C–5Mo–1.7V high-speed steel, which chemical composition is shown in Table 3. The steel was melted in an electric high-frequency induction furnace and after deoxidising was poured into preheated ceramic moulds (the mass of the castings was 3 kg). A part of the melt was modified by 0.1 mass% bismuth.

The castings and the test specimens were isothermally annealed at 850°C for no less than 2 h, cooled to 720°C, and held for 4 h at this temperature. The cooling down to

---

**Table 1.** Calculated differences between melting temperature $\Delta T$, surface energy $\Delta \sigma$, specific heat of sublimation $\Delta P$, entropy in the standard condition $\Delta S^{298}$, statistic generalized moment $\Delta m$, total electron potential barrier $\Delta \psi$ for iron and modifier respectively.17)

| Element | $\Delta T$, K | $\Delta \sigma$, MN/m | $\Delta P$, kJ/m$^3$ | $\Delta S^{298}$, J/K | $\Delta m$, C/cm | $\Delta \psi$, eV |
|---------|--------------|----------------------|---------------------|----------------------|-----------------|-----------------|
| Sn      | 1304±1       | 1328                 | 37.66               | 24.3                 | 0.561           | 4.69            |
| Bi      | 1265±0       | 1494                 | 46.51               | 29.7                 | 0.725           | 7.73            |
| Cd      | 1215±1       | 1302                 | 47.60               | 24.3                 | 0.541           | 3.94            |
| Pb      | 1208±6       | 1404                 | 45.48               | 37.7                 | 0.682           | 5.44            |
| Zn      | 1116±5       | 1090                 | 41.80               | 14.5                 | 0.306           | 0.82            |
| Sb      | 905±5        | 1505                 | 47.04               | 18.4                 | 0.588           | 3.61            |
| Al      | 875±9        | 958                  | 23.81               | 1.14                 | 0.374           | 3.02            |
| Mg      | 887±13       | 1313                 | 45.57               | 5.30                 | 0.597           | 4.75            |
| Sr      | 766±14       | 1569                 | 50.91               | 25.13                | 0.030           | 9.20            |
| Ca      | 697±15       | 1511                 | 48.87               | 14.46                | 0.784           | 8.11            |
| Ge      | 599±12       | 1251                 | 27.36               | 3.99                 | 0.306           | 3.44            |
| Cu      | 452±8        | 887                  | 8.90                | 6.17                 | 0.058           | 0.75            |
| Mn      | 292±7        | 782                  | 6.57                | 0.11                 | 0.045           | 4.33            |
| Si      | 124±3        | 1007                 | 18.48               | 1.64                 | 0.015           | 0.99            |
| Ni      | 81±4         | 94                   | 8.87                | 0.46                 | 0.062           | 0.09            |
| Co      | 44±6         | 46                   | 3.21                | 0.79                 | 0.015           | 0.06            |
| Y       | 17±1         | 1262                 | 34.85               | 17.20                | 0.714           | 4.83            |
| Zr      | –316         | 392                  | 12.40               | 11.70                | 0.570           | 4.31            |
| Ti      | –131         | 222                  | 12.77               | 3.11                 | 0.405           | 2.06            |
| Hf      | –697         | 242                  | 10.67               | 16.80                | 0.570           | 5.36            |
| B       | –764         | 802                  | –67.51              | –21.30               | –4.055          | –8.47           |
| Nb      | –931         | –28                  | –10.47              | 9.35                 | 0.433           | 3.06            |
| Ta      | –1444        | –278                 | –15.70              | 14.20                | 0.420           | 2.98            |

---

**Table 2.** Activity series for elements in melt, built up from the differences between melting temperature $\Delta T$, surface energy $\Delta \sigma$, specific heat of sublimation $\Delta P$, entropy in the standard condition $\Delta S^{298}$, statistic generalized moment $\Delta m$, total electron potential barrier $\Delta \psi$ for iron and modifier respectively. Active elements are placed above the line, and inactive elements below it.17)

| $\Delta T$ | $\Delta \sigma$ | $\Delta P$ | $\Delta S^{298}$ | $\Delta m$ | $\Delta \psi$ |
|------------|----------------|-----------|------------------|------------|--------------|
| Sn         | Sr             | Sr        | Pb               | Cr         | Co           |
| Bi         | Ca             | Ca        | B                | Bi         | Bi           |
| Cd         | Sn             | Cd        | Zn               | Mg         | Mg           |
| Pb         | Bi             | Bi        | Pb               | Pb         | Pb           |
| Zn         | Pb             | Bi        | Sn               | Mg         | Mg           |
| Sb         | Sn             | Mg        | Pb               | Mg         | Y            |
| Al         | Cd             | Zn        | Hf               | Hf         | Sn           |
| Mg         | Mg             | Pb        | Y                | Zr         | Mg           |
| Al         | Cd             | Zn        | Hf               | Hf         | Sn           |
| Ca         | Ge             | Y         | Ca               | Cd         | Cd           |
| Ge         | Zn             | Ge        | Ta               | Nb         | Nb           |
| Cu         | Si             | Al        | Zr               | Ta         | Ta           |
| Mn         | Al             | Mn        | Cu               | Al         | Nb           |
| Si         | B              | Mn        | Ti               | Zn         | Al           |
| Nn         | Mn             | Ti        | Mg               | Zn         | Zn           |
| Co         | Cu             | Zr        | Mn               | Ge         | Ta           |
| Y          | Zr             | Hf        | Ge               | Si         | Zn           |
| Ti         | Hf             | Cu        | Ti               | Mn         | Mn           |
| Zr         | Ti             | Co        | Co               | Cu         | Cu           |
| Hf         | Ni             | Ni        | Ni               | Ni         | Co           |
| B          | Co             | Nb        | Al               | Co         | Ni           |
| Nb         | Ni             | Ta        | Si               | Ni         | Ti           |
| Ta         | Ta             | B         | B                | B          | B            |

---

**Table 3.** Chemical composition of the studied steels. (mass%)

| No. | Steel grade | C   | W   | Mo  | Cr  | V   | Co  | Mn  | Si  | Ni  | P   | S   |
|-----|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1   | AISI M2     | 0.86| 5.38| 5.05| 3.95| 1.96| —   | 0.27| 0.24| 0.25| 0.022| 0.020|
| 2   | AISI T30    | 0.85| 6.48| 5.25| 4.17| 1.78| 5.10| 0.27| 0.29| 0.19| 0.026| 0.024|
| 3   | 1.1C–5Mo–1.7V| 1.02| 0.034| 5.09| 4.26| 1.65| —   | 0.37| 0.29| 0.171| 0.024| 0.029|
500°C was performed in a furnace and, then, in air. To prevent decarburisation, when annealing, the castings were covered with cast-iron chips. The final heat treatment of the materials included quenching from the temperature of 1220 and 1230°C for the M2 and T30 steels, respectively, as well as 1180°C for 1.1C–5Mo–1.7V steel; then triple tempering at 560°C for 1 h. Heating for quenching was two-stage; namely, after heating to 850°C in a molten salt, the temperature of the specimens introduced in the barium chloride bath (95vol%BaCl₂ + 5vol%MgF₂) was increased and the sample was held at austenitizing temperature for 10 s per 1 mm of the specimen cross section. The specimens were tempered at 560°C in a mixture of 50vol%CaCl₂ + 50vol%NaCl and then were cooled in air.

Impact toughness, hardness, and red hardness were determined by standard tests for high-speed steels. Comparisons of wear resistance for the studied steels were done using a plot of mass loses by specimens induced by abrasion wear with a hardmetal counterbody disk versus sliding distance (time). The tribological tests were carried out in sliding friction without any lubricants under the load of 200 N on special specimens with dimensions of 10×10×30 mm. The test specimen worn surfaces were observed using a light microscope Neophot-2.

Chemical composition of both the matrix and carbides, as well as bismuth distribution were examined using microprobe analyser Camebax and scanning electron microscope equipped with microprobe devices Nanolab-7. The steel microstructure was studied using light and electron microscope. The volume of carbide phases, number of nonmetallic inclusions as well as grain size of the steel matrix was determined by the random intersection method followed by statistical treatment. For each steel, minimum 300 grains were measured for solidification grain structure determination. The failure surfaces of the impact specimens were examined using a transmission electron microscope UEMV-100K by the replica method. The X-ray diffraction examination was performed with a diffractometer DRON-3 in the CoKα radiation under the condition of accelerating voltage 30 kV and emission current 20 μA. The content of retained austenite was determined by comparing the integrated intensity of the (110) lines of martensite and (111) lines of austenite.

3. Results and Discussions

The transition of average reciprocal grain size and carbide volume fraction in the modified steels with the additions of bismuth is shown in Figs. 1(a) and 1(b) respectively. After solidification the grain refinement effect induced by bismuth in the steels is evident, while the change in carbide volume fraction is slighter. The grain morphology of the matrix appeared to be affected by bismuth too that is inherited in the structures after full heat treatment as shown in Fig. 2. Micrographs of Fig. 2(a) show that in the parent steel the equiaxed grain matrix has formed during solidifi-

![Fig. 1. Effect of bismuth on (a) average reciprocal grain size and (b) carbide volume fraction in T30 and M2 steels.](image1)

![Fig. 2. (a), (c) Light and (b), (d) scanning electron micrographs of the (a), (b) parent and (c), (d), (e) bismuth-modified high-speed steels: (c), (d) 0.1 mass% Bi; (e) 0.6 mass% Bi.](image2)
cation. Meanwhile bismuth favours a fine columnar grain structure (Figs. 2(c) and 2(e)).

The both grain refinement and transition of microstructure from equiaxed in parent high-speed steels to columnar in modified ones can be explained taking into account predicted high surface activity of bismuth.\(^{17,43}\) It may be assumed that when solidification starts, bismuth segregates to liquid/solid interface, significantly blocking dendrite growth, first of all in a direction along certain crystallographic planes that leads to the fine columnar grain structure. The bismuth concentration profile over the section of a primary grain in Fig. 3(a), which is very typical for surface-active elements as indicated by its presence just in interdendritic space, confirms such assumption.

When carbides form during eutectic solidification, they are also exposed to the barrier effect of bismuth being surrounded in the melt by this element. It is also evident from the bismuth concentration profile over the section of a eutectic colony (Fig. 3(b)). It is seen that bismuth mainly concentrates at matrix/carbide interfaces inside the eutectic colony that is known to impact strongly eutectic reaction first of all in terms of carbides formation. As consequence, by addition of bismuth eutectic network becomes less continuous and finer, and very fine eutectic carbides get favourable shape resulting in more beneficial morphology and more homogeneous structure in general (compare Figs. 2(b) and 2(d) respectively).

The microstructural changes, induced by bismuth during solidification, result in considerable enhancement in impact toughness of the modified steels after full heat treatment (Fig. 4). Fractographical analysis indicates this effect too (Fig. 5). Compared to the parent steel, the signs of plastic deformation on the fracture surfaces of modified steel are more distinguished. For example, when the grain-boundary cracking takes place, smooth grain boundary facets form on fracture surfaces in the regions, being free of eutectic precipitates in the parent steel (Fig. 5(a)), meanwhile in the modified steel grain boundary facets with finely pitted relief are observed in such case (Fig. 5(b)). When the boundary cracking occurs along boundaries covered with eutectic precipitates it is accompanied by carbides failure resulting in formation of intergran and intragrain facets of eutectic carbides, which are coarser in the case of parent steel (Fig. 5(c)) compared to those in the modified steel (Fig. 5(d)). At the transcrystalline crack propagation (the main failure mechanism in heat-treated high-speed steels),\(^7\) observation of corresponding fracture surfaces confirms the higher degree of plastic deformation preceding steel failure in the case of modified structure too. It is indicated by greater number of signs of plastic deformation, which are on the quasi-detachment facets of tempered martensite known as "steps", "crests", and "tongues"\(^7\) (Figs. 5(e) and 5(f) respectively).

However, as seen from Fig. 4, high volumes of impact toughness are achieved in very narrow interval of bismuth additions. In this connection the nature of bismuth should be taken into account.

Bismuth has a low melting temperature (544.5 K) and at 700 K starts to vaporize. This means that at modifying at the temperature of about 1 973 K the melt is treating by bismuth vaporization. On the one hand, it intensifies treatment of the melt, and, on the other hand, leads to occurrence that even upon application of relatively large addition of bismuth (for example, from 0.1 till 0.3 mass%) only traces of this element are retained in solidified steel.\(^{43}\) For this rea-
Introduction of 0.05 mass% addition of bismuth in the melt is not enough to treat it effectively, while addition of 0.6 mass% leads to distinguished overmodification of the melt via steel contamination by non-metallic inclusions, as shown in Fig. 6. In fact, the greatest refining effect is achieved on adding 0.1% bismuth. Probably, in terms of refining effect it can be explained by steel purifying due to bubbling of the melt by bismuth vaporizing, since bismuth has above melting point the lowest vapour pressure that is about of 9–10 orders lower compared to other metals with low melting temperature (Table 4). It seems reasonable to consider that such low vapour pressure can promote better migrating of the microimpurities into the bismuth gas bubbles and then their removing from the melt.

In the case of 0.6 mass% Bi addition, the worse refining effect in comparison with 0.1 mass% Bi addition can be explained, for example, by the larger amount and sizes of non-metallic inclusions forming in the melt. Probably for this reason they have not been removed from the melt despite the stronger bubbling effect produced by the 0.6 mass% Bi addition. Just the overmodification on adding 0.6 mass% Bi can be primarily responsible for the drop in impact toughness of the steel.

For the understanding of impact toughness enhancement, induced in as-cast high-speed steels by bismuth, its behav-

---

**Table 4. Vapour pressure of the metals.**

| Metal       | Vapour pressure (KPa) | Temperature (K) |
|-------------|-----------------------|-----------------|
| Bismuth (Bi)| $181.37 \times 10^{-3}$| 700             |
| Calcium (Ca)| $233.05 \times 10^{-3}$| 900             |
| Magnesium (Mg)| $358.69 \times 10^{-3}$| 700             |
| Antimony (Sb)| $207.72 \times 10^{-3}$| 700             |
bour at the finale stage of heat treatment is also of great importance. The bismuth concentration profile over the section of a primary grain in Fig. 3(c) clearly indicates that its distribution after full heat treatment becomes practically uniform not exceeding the background. Taking into account EPMA results we can suppose that “borders cleaning”, first of all during austenitizing, takes place in modified steel due to diffusion redistribution of bismuth. In this connection it is worth mentioning that the presence of ultrafine bismuth compounds within matrix grains of tempered as-cast high-speed steel has been reported but the origin of those compounds have not been defined by the used means of electron microscopy because of their extremely small sizes.

Table 5 shows hardness of studied steels in the state after solidification and after different operations of heat treatment, including annealing, and quenching. When addition of bismuth is more than 0.1 mass% hardness of modified steels after solidification and annealing is slightly lower compared to that of the parent steels. It is necessary to point out that if decrease in hardness for solidified castings is not principal, just on the contrary, it has very important significance, from machinability point of view, for as-annealed state.

It is seen from Table 5 that after quenching hardness of modified steels is higher, the difference achieves 1–1.5 HRC, and the quantity of retained austenite is less than that of the parent steels. The changes of both the factors, being interrelated, indicate the change of solid solution concentration in the modified steels. Since in high-speed steels, as well as in other ones with martensitic transformation, carbon content in martensite is considered as a primary factor influencing hardness and quantity of retained austenite in structure after quenching, it was assumed that modification by bismuth could provoke redistribution of carbon between carbide phases and metallic matrix. Figure 7 shows that continuous decrease of microhardness of the modified steels with increasing of bismuth additions is in line with above-mentioned assumption. In completely heat treated conditions there is no such difference in hardness for modified and parents steels (Fig. 8). However, in terms of impacting of red hardness (Fig. 9), redistribution of main alloying elements in modified steels, induced by bismuth, is the primary focus.

Table 6 shows that contents of tungsten, molybdenum, and chromium, according to EPMA, are higher in the matrix, and are lower in the eutectic of the modified steel then in those of the parent steel. The reasonable explanation is that bismuth affects significantly redistribution of main alloying elements between liquid and growing solid phases during solidification. Moreover, established relationship between the change of the chemical compositions of the structural components, on the one hand, and the heat resistance, on the other one, are in good correlation. In particular, taking into account high content of tungsten, molybde-
Table 6. Effect of bismuth on the chemical composition of solid solution and eutectic of the high-speed steel T30. (mass%) The numerator gives data for the core of dendrites, and the denominator those for the periphery. Carbon content was not analysed.

| Steel   | Fe  | Co  | W   | Mo  | Cr  | V  |
|---------|-----|-----|-----|-----|-----|----|
|         |     |     | 79.48 | 87.93 | 4.85 | 4.53 | 3.70 | 3.91 | 3.67 | 4.00 | 4.19 | 3.87 | 1.47 | 1.58 |
| T30     |     |     | In solid solution |
| T30 + 0.1 mass% Bi | 71.35 | 64.46 | 3.10 | 5.65 | 5.63 | 4.59 | 5.04 | 4.02 | 4.07 | 1.03 | 1.03 | 1.03 |
|         |     |     | In eutectic |
| T30     | 48.24 | 3.10 | 23.70 | 21.52 | 5.08 | 9.64 |
| T30 + 0.1 mass% Bi | 48.06 | 3.10 | 13.45 | 7.18 | 4.14 | 2.53 |

num, and chromium in solid solution (Table 6), we can suppose that drop in red hardness results, first of all, from lower carbon content in martensite (after quenching) that is not enough to produce proper secondary hardness effect in modified steel due to decrease of the volume fraction of secondary carbides precipitated upon tempering. The second probable reason can be low heat resistance of carbides, both eutectic and secondary origin, to be coagulating at lower temperature.

Returning to impact toughness again, it should be mentioned that in terms of its enhancement the change in chemical composition of eutectic carbides has played the proper role since just carbide particles are known to act as crack initiators in high-speed steels. Therefore, it is evident that the drop in tungsten, molybdenum, and chromium contents in carbides, induced by bismuth during solidification and resulting in lower difference between the thermal-expansion coefficients of the matrix and carbides, can decrease the risk of microcracks initiation in as-cast high-speed steels at heat treatment.

The favourable effect of bismuth on wear resistance of as-cast high-speed steel (Fig. 10) can be explained, first of all, by grain structure refinement. It is seen from Figs. 1 and 10, that linear dependence between both the parameters is evident. Besides this, columnar grain structure, induced by bismuth, is also considered as one of the reasons for enhanced wear resistance. After all, the high wear resistance of modified steels is attributed to the origin of bismuth, which, acting as a lubricant in metal state (due to both specific crystalline structure and physical properties), leads to reducing the friction coefficient in contact zone. Such considerations are confirmed by observations of the test specimen worn surfaces. At the dry sliding, mainly abrasion contributes to the wear of both the parent and modified as-cast high-speed steels, as shown in Fig. 11. It is clear that for worn surface relief, induced by abrasion in the case of modified steel, considerably smaller depth of traces of the abrasive interaction, compared to that of the parent steel, is evident. In both the steels, besides the worn sites with the typical traces of the abrasive interaction produced by counterbody disk, breakdown sites of oxide films, developed on the sliding surface, are also observed, which appear to be considerably larger in the case of the parent steel (Fig. 11).

Compared to the lower bismuth additions, the decrease in wear resistance at adding of 0.6 mass% bismuth (Fig. 10), can be attributed to such factors as primary grain size increase, less continuous network of eutectic carbides over the primary grains, and overmodification (considerably higher content of non-metallic inclusions in the steel).

The favourable effect of bismuth in terms of both the structure refinement and properties improvement is also observed in as-cast low-alloy tungsten-free 1.1C–5Mo–1.7V high-speed steel with the chemical composition given in Table 3. The metallic matrix of the non-modified 1.1C–5Mo–1.7V steel after solidification consists mainly of bainite (Fig. 12) and a certain amount of austenite that has been indicated by X-ray diffraction analysis. It should be mentioned that due to proper chemical composition of this steel, which has been extensively disused in the papers, total amount of the carbide phases in the cast structure is considerably lower than that, for example, in M2 steel and
does not exceed 5%. A previous study has shown that the major fraction of the eutectic precipitates, formed mainly due to liquation processes in the melt, has a rod-like morphology (Fig. 12(a)). Besides this, a proper amount of a lamellar eutectic is observed, Fig. 12(b). The main feature of the present steel cast structure is the presence of coarse carbide particles both on periphery (Fig. 12(b)) or inside (Fig. 12(c)) the colonies of the lamellar eutectic.

At the same time, modified 1.1C–5Mo–1.7V steel, as seen from Fig. 12(d), exhibits only a rod-like eutectic structure being free of any coarse carbide precipitates like in the parent steel. The difference in cast structure between the non-modified and modified steels is due to the role of bismuth that was mentioned earlier in the present paper. In general, the main metallographic features of the steels are retained after full heat treatment as it is shown in Fig. 13. This is despite the minor coagulation of carbides in eutectic colonies of both the types. As consequence, impact toughness of the modified 1.1C–5Mo–1.7V steel is higher than that of the parent steel (Table 7). Enhanced impact toughness can be attributed to finer and more uniform modified structure induced by bismuth.

The results of industrial cutting tests, held at turning and milling have shown that application of the as-cast modified high-speed steels with improved structures and properties benefits to the enhanced tool life compared to that of the same tool made even from the parent wrought steels.5,6

4. Summary

Several kinds of alloys including tungsten-molybdenum high-speed steels of M2 and T30 types and low-alloy tungsten-free 1.1C–5Mo–1.7V high-speed steel were melted to investigate the effect of bismuth on their structures and properties. As a result, the following findings were obtained.

(1) Additions of bismuth produce in tungsten-molybdenum high-speed steels a very fine cast structure concerning both the solid solution and eutectic, simultaneously affect-

Table 7. Mechanical properties of the parent and bismuth-modified 1.1C–5Mo–1.7V high-speed steels in comparison with those of M2 steel in completely heat treated condition.

| Steel             | Hardness (HRC) | Red hardness (HRC) | Impact toughness (MJ/m²) |
|-------------------|----------------|--------------------|--------------------------|
| 1.1C–5Mo–1.7V     | 64.0           | 59.0               | 0.09                     |
| 1.1C–5Mo–1.7V + 0.1 mass% Bi | 64.0           | 58.0               | 0.12                     |
| M2                | 64.0           | 59.0               | 0.035                    |

Fig. 12. Scanning electron micrographs of the (a), (b), (c) parent and (d) 0.1 mass% bismuth-modified 1.1C–5Mo–1.7V high-speed steel after casting.

Fig. 13. Scanning electron micrographs of the (a), (b) parent and (c) 0.1 mass% bismuth-modified 1.1C–5Mo–1.7V high-speed steel after full heat treatment.
muth provokes the redistribution of carbon and main alloying elements between the solid solution and carbide phases.

3) The main metallographic features of the modified cast structure induced by bismuth are retained after full heat treatment. But distribution of bismuth, due to diffusion processes, becomes practically uniform not exceeding its background in steel that provides “borders cleaning” from bismuth during austenitizing.

4) The microstructural changes along with the purifying effect caused by bismuth, result in considerable enhancement in impact toughness of the modified steels. The purifying effect can be attributed to bubbling of the melt by bismuth evaporation, since bismuth has at evaporating temperature extremely low steam pressure compared to other elements. The drop in tungsten, molybdenum, and chromium contents in carbidies, induced by bismuth and resulting in lower difference between the thermal-expansion coefficients of the matrix and carbides, can be also considered as one of the factors enhancing impact toughness of as-cast high-speed steels.

5) At the dry sliding, wear resistance of modified tungsten-molybdenum high-speed steels are significantly higher than that of the parent ones. The favourable effect of bismuth on wear resistance of as-cast high-speed steel can be explained by matrix columnar grain structure refinement, and after all, by the origin of bismuth, which, acting as a lubricant in metal state (due to both specific crystalline structure and physical properties), leads to reducing the friction coefficient in contact zone.

6) Bismuth produces decrease in red hardness of as-cast tungsten-molybdenum high-speed steels. It can be attributed to less carbon content in martensite in modified cast tungsten-molybdenum high-speed steels. It can be attributed to less carbon content in martensite in modified cast tungsten-molybdenum high-speed steels. It can be attributed to less carbon content in martensite in modified cast tungsten-molybdenum high-speed steels. It can be attributed to less carbon content in martensite in modified cast tungsten-molybdenum high-speed steels. It can be attributed to less carbon content in martensite in modified cast tungsten-molybdenum high-speed steels. It can be attributed to less carbon content in martensite in modified cast tungsten-molybdenum high-speed steels. It can be attributed to less carbon content in martensite in modified cast tungsten-molybdenum high-speed steels. It can be attributed to less carbon content in martensite in modified cast tungsten-molybdenum high-speed steels. It can be attributed to less carbon content in martensite in modified cast tungsten-molybdenum high-speed steels. It can be attributed to less carbon content in martensite in modified cast tungsten-molybdenum high-speed steels. It can be attributed to less carbon content in martensite in modified cast tungsten-molybdenum high-speed steels.

7) The favourable effect of bismuth in terms of both the structure and properties improvement (impact toughness and wear resistance) has been also observed in as-cast low-alloy tungsten-free 1.1C–5Mo–1.7V high-speed steel. These effects are also due to the role of bismuth acting in the melt of the steel as a surface-active modifier.

Acknowledgments

The support of a grant VEGA 1/0306/03 from the Ministry of Education of the Slovak Republic is gratefully acknowledged. The author also thanks Alexander Dubko for technical help.

REFERENCES

1) Yu. A. Geller: Tool Steels, Metallurgiya, Moscow, (1983), 527.
2) P. D. Ding, S. Z. Zhou, F. S. Pan and J. L. Liu: Mater. Design, 22 (2001), 137.
3) L. A. Revis and T. A. Lebedev: Structure and Properties of Cast Cutting Tools, Mashinostroenie, Leningrad, (1972), 128.
4) A. S. Chaus: J. Frict. Wear, 20 (1999), 83.
5) A. S. Chaus: J. Frict. Wear, 20 (1999), 30.
6) A. S. Chaus: J. Frict. Wear, 21 (2000), 94.
7) A. S. Chaus, F. I. Rudnickii and M. Murgas: Met. Sci. Heat Treat., 39 (1997), 53.
8) A. N. Popandopulo and A. Seddak: Steel USSR, 13 (1983), 311.
9) A. N. Popandopulo, V. I. Kalinina and A. A. Smirnov: Steel USSR, 15 (1985), 443.
10) A. S. Chaus: Met. Sci. Heat Treat., 40 (1998), 319.
11) F. S. Pan, A. T. Tang, J. Chen, J. Zhang, P. D. Ding and Q. L. Yong: J. Iron Steel Res. Int., 6 (1999), 33.
12) A. S. Chaus and I. V. Latyshev: Phys. Met. Metallogr., 88 (1999), 462.
13) S. Kheirandish, S. Mirdamadi and Y. H. K. Karrazi: Metall., 53 (1999), 339.
14) S. Kheirandish: ISIJ Int., 41 (2001), 1502.
15) M. Boccalini and H. Goldenstein: Int. Mater. Rev., 46 (2001), 92.
16) A. N. Popandopulo and N. A. Pakhomova: Met. Sci. Heat Treat., 27 (1985), 280.
17) A. S. Chaus and F. I. Rudnickii: Met. Sci. Heat Treat., 31 (1989), 121.
18) Y. J. Li, Q. C. Jiang, Y. G. Zhao and Z. M. He: J. Mater. Sci. Lett., 15 (1996), 1584.
19) S. Kheirandish, Y. H. K. Karrazi and S. Mirdamadi: ISIJ Int., 37 (1997), 721.
20) S. Kheirandish, Y. H. K. Karrazi and S. Mirdamadi: Mater. Sci. Technol., 14 (1998), 683.
21) A. S. Chaus: Phys. Met. Metallogr., 91 (2001), 463.
22) A. S. Chaus: Met. Sci. Heat Treat., 46 (2004), 415.
23) S. El-Ghazaly, T. El-Gammal, A. El-Sabbagh, A. Nofal and M. Abbas: Steel Res., 72 (2001), 58.
24) A. S. Chaus and F. I. Rudnickii: Met. Sci. Heat Treat., 45 (2003), 157.
25) B. E. Paton, B. I. Medovar and G. A. Bojko: Electroslag Casting, Naukova dumka, Kiev, (1980), 191.
26) A. S. Chaus and M. Murgas: Phys. Met. Metallogr., 85 (1998), 675.
27) M. Murgas, A. S. Chaus, A. Pokusa and M. Pokusova: ISIJ Int., 40 (2000), 980.
28) A. S. Chaus: Phys. Met. Metallogr., 94 (2002), 616.
29) B. V. Grigorevski: Met. Sci. Heat Treat., 21 (1979), 168.
30) A. S. Chaus: Izv. VUZ. Chernaya Metall., (1998), No. 11, 40.
31) A. S. Chaus, M. Murgash, I. V. Latyshev and R. Tot: Met. Sci. Heat Treat., 43 (2001), 220.
32) H. Y. Li, D. F. Luo, K. H. Lau and C. F. Yeung: J. Mater. Process. Technol., 122 (2002), 179.
33) M. Boccalini, A. V. O. Correa and H. Goldenstein: Mater. Sci. Technol., 15 (1999), 621.
34) S. G. Morozenko and B. E. Napatov: Met. Sci. Heat Treat., 32 (1990), 368.
35) E. I. Belskii, V. F. Sobolev, A. S. Chaus and A. P. Dubko: USSR Inv. Certif. No. 914648—A High-Speed Steel, Discoveries. Inventions, Moscow, (1996), 1584.
36) E. I. Belskii, V. F. Sobolev, F. I. Rudnickii, A. S. Chaus, A. P. Dubko, V. V. Kuzmin and S. V. Sashnev: USSR Inv. Certif. No. 1122746—A High-Speed Steel, Discoveries. Inventions, Moscow, (1982), 120.
37) E. I. Belskii, V. F. Sobolev, F. I. Rudnickii, A. S. Chaus, A. P. Dubko, V. V. Kuzmin and S. V. Sashnev: USSR Inv. Certif. No. 1126624—A High-Speed Steel, Discoveries. Inventions, Moscow, (1984), 84.
38) N. S. Kreshchanovskii and M. F. Sidorenko: Modification of Steel, Metallurgiya, Moscow, (1970), 296.
39) M. P. Braun and N. I. Matushenko: Rare Earth Metals and Alloys, Nauka, Moscow, (1971), 73.
40) M. P. Braun: Microalloying of Steel, Naukova dumka, Kiev, (1982), 303.
41) S. N. Zadumkin: Zh. Neorg. Khim., 5 (1960), 1892.
42) S. A. Salytkov: Stereometric Metallography, Metallurgiya, Moscow, (1970), 375.
43) A. S. Chaus: Izv. Nats. Akad. Nauk Resp. Belarus, Ser. Fiz.-Tekh. Nauk, (2000), No. 2, 10.
44) E. K. Kazenas and G. K. Astakhova: Russ. Metall., (1997), No. 2, 15.
45) M. M. Reinaga: Ph.D. Thesis, Byelorussian Polytechnic Institute (Now Belarus National Technical University), Minsk, (1985).
46) A. S. Chaus: Russ. Metall., (1999), No. 3, 78.
47) L. S. Kremnev: Met. Sci. Heat Treat., 28 (1986), 494.
48) L. S. Kremnev: Met. Sci. Heat Treat., 29 (1987), 870.
49) L. S. Kremnev and Yu. E. Sedov: Met. Sci. Heat Treat., 30 (1988), 429.