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RESEARCH OF INFLUENCE OF ELECTROSPARK PROCESSING ON THE PHASE STRUCTURE OF MOLYBDENUM COVERINGS ON STEEL 20

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Distribution of atoms and phase structure of diffusion zone, which is formed at creation of molybdenum coverings of Iron and steels are investigated by methods X - rays and level-by-level radiometric analyses and Mössbauer spectroscopy. Influence of energy of the spark discharges and contents of carbon in steel or feature formation of phases, speed of process mass-transfer and the laws of distribution of diffused atoms and of non-stoichiometric connections in transitive layers between a covering and basic metal are investigated.

The application of molybdenum as covering material is determined by its high level of wearing resistance. But the formation of a developed diffusion zone between molybdenum and iron or steel is impossible because of the formation of weak intermetallic phases. This is the reason why this method of electro-spark alloying (ESA) which in many cases doesn't lead to the appearance of the above mentioned mineral combinations in the intermediate zone, seems to be quite perspective. The above mentioned process (ESA) can be attributed to the high intensity impulse methods of material processing which stimulate the appearance of abnormal mass-transfer and phase-formation, analogical to mechanic deformation [1] but taking into account the presence of supplementary influence factors. For instance high temperatures lead to the appearance of melting zones or zones with mechanical mixture depending on the properties of the used materials in the surface layers. The migration and the redistribution of atoms between the original and newly-formed phases happen in solid state beginning from a certain depth [2]. Therefore, for a conscious directing of covering formation processes it is necessary to study the peculiarities of the elements interaction in ESA conditions for every concrete case.

In order to apply layers with the help of electrical discharges the "Electron" equipment was used. The processing was done in open air for 1 minute on a surface of 1 cm². Molybdenum and iron anodes were used. The samples were made of steel 20, burned in advance in order to get a grain of considerable size and in order to reduce the tensions. Molybdenum, iron and steel 3 were used for the control samples. The distribution of elements in the layer and the main metal was studied with the help of radio-active isotope of iron ^{55.59}Fe, being applied in advance on the

sample surface made of steel 20 using the layer-by-layer radio-metric analysis [3]. The layer phase content, obtained during the use of ESA, is studied applying the X-Ray structural analysis and Mössbauer spectroscopy method that allows to study the structural state at surface layers with a thickness from 5 to 5000 nm without destroying the samples with the help of the stable iron isotope ^{57}Fe .

The analysis of the concentrated profiles of marked iron atoms distribution in molybdenum and steel 20 showed that they can't be described by a simple exponential dependence as it was observed for other means of impulse actions but have a complex character. In the mean time it is typical presence at least of one concentrated maximum for every value of discharge energy W . As one can see from the analysis of the curves given in fig. 1 with an increase of value W the concentrated maximums are situated on a deeper depth. Therefore when $W = 0.3 \text{ J}$ a higher value of concentrate is almost on the surface, meanwhile when $W = 6.4 \text{ J}$ the dislocation of maximum is approximately $15 \mu\text{m}$ in the depth of the basic metal. However off the limits of undersurface layer, the dependence $C = f(x)$ for all the energy values W , can be approximated the exponential dependence on the depth of penetration both in basic metal and in the material the layer is made of. The depth of atom penetration and the thickness of the layer ($\gamma \sim 1.5$) changes ones with the position of the maximum with the increase of energy. It is worth mentioning that some increase of the depth of metal penetration $^{55,59}\text{Fe}$ around 10 % for molybdenum and 15 % for iron during the applying of molybdenum covering on iron. The slowdown of iron migration in steel compared to its migration in iron is caused by the presence of carbon atoms in the crystal bar of the material both in hard solution and in cementing analogical to the one that takes place during deforming caused by striking [4], meanwhile the decrease of the depth penetration in molybdenum covering when applied on steel is connected with simultaneous transfer of carbon atoms in it, which are placed in steel and the formation of carbide phases.

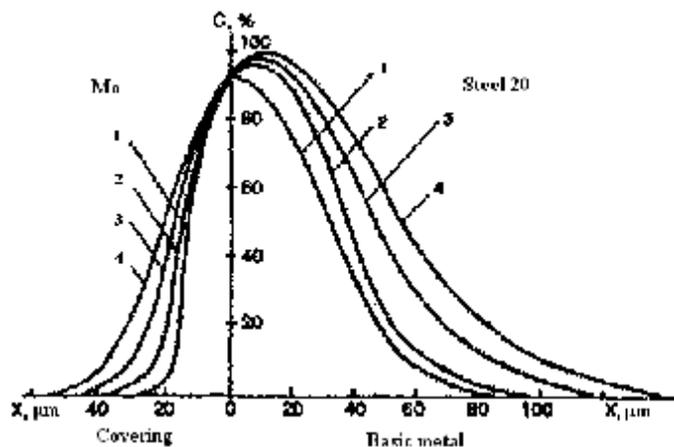


Fig. 1. Concentrated profiles of $^{55,59}\text{Fe}$ iron atoms distribution in steel and molybdenum after ESA with the energy W 0.3 J (1), 0.9 J (2), 3.14 J (3), 6.4 J (4)

Table 1
Phase structure of molybdenum layers on steel 20 being processed with ESA with different discharge energy W

W = 0.3 J			W = 0.9 J			W = 3.14 J			W = 6.4 J						
d/n, nm	(hkl)	Phase	I, %	d/n, nm	(hkl)	Phase	I, %	d/n, nm	(hkl)	Phase	I, %	d/n, nm	(hkl)	Phase	I, %
0.260	100	Mo ₂ C	1	0.260	100	Mo ₂ C	1	0.260	100	Mo ₂ C	1	0.260	100	Mo ₂ C	1
0.238	002 111	Mo ₂ C Mo ₂ N	1	0.238	002 111	Mo ₂ C Mo ₂ N	1	0.237	002 111	Mo ₂ C Mo ₂ N	1	0.237	002 111	Mo ₂ C Mo ₂ N	1
								0.028	011	Mo ₂ C	2	0.028	011	Mo ₂ C	2
0.222	110	Mo	100	0.222	110	Mo	100	0.222	110	Mo	100	0.222	110	Mo	100
				0.206	200	Mo ₂ N	5	0.205	200	Mo ₂ N	6	0.205	200	Mo ₂ N	7
0.202	110	Fe	20	0.202	110	Fe	5								
								0.166			3	0.166			3
0.157	200	Mo	30	0.157	200	Mo	30	0.157	200	Mo	30	0.157	200	Mo	30
				0.146	220	Mo ₂ N	3	0.146	220	Mo ₂ N	4	0.146	220	Mo ₂ N	4
0.143	200	Fe	5												
0.128	211	Mo	50	0.128	211	Mo	50	0.128	211	Mo	50	0.128	211	Mo	50
				0.124	311	Mo ₂ N	2	0.124	311	Mo ₂ N	1	0.124	311	Mo ₂ N	2
												0.119	211	α-Mo	1
0.117	211	Fe	10												
0.111	220	Mo	20	0.111	220	Mo	20	0.111	220	Mo	20	0.111	220	Mo	20
0.109	220	α-Mo	10	0.109	220	α-Mo	10	0.109	220	α-Mo	15	0.109	220	α-Mo	15
0.101	220	Fe	7.5												
0.990	310	Mo	50	0.990	310	Mo	50	0.990	310	Mo	50	0.990	310	Mo	50
0.930	310	α-Mo	10	0.930	310	α-Mo	10	0.930	310	α-Mo	15	0.930	310	α-Mo	25
0.911	222	Mo	40	0.911	222	Mo	40	0.911	222	Mo	40	0.911	222	Mo	40

X-Ray structural analysis of molybdenum coverings in steel 20 (table 1) showed that a diffusion zone with a greater number of phase components appears under the effect of ESA. Except pure iron and molybdenum, there are hard solutions of molybdenum in iron, iron in molybdenum and phases of penetration: carbides and nitrides of molybdenum. Once with the increase of the discharge energy, the thickness of the layer grows thicker proved by the decrease of the intensity of diffraction maximums of iron and considerably increases the quantity of molybdenum nitrides, while the quantity of carbides decreases (table 2). This difference can be caused by different mechanisms of phase formation. The appearance of nitrogen is connected with its claw from air during the process of ionization in the plasma of sparkling discharge, while the entering of carbon atoms is limited by its concentration in steel. Indeed, we can see the traces of Mo_2C during the processing in the same regime of samples made of steel 3 which contains a considerable smaller amount of carbon in the diffusion zone only at $W = 6.4 \text{ J}$.

Table 2

The influence of discharge energy on the redistribution of the phase content in Mo layer

Energy W, J	The phase content				
	Mo	$\alpha\text{-Fe}$	$\alpha\text{-Mo}$	Mo_2N	Mo_2N
	Relative concentration of carbon, at. %				
0.3	100	20	10	<1	<1
0.9	100	4	12	10	<1
3.14	100	0	15	15	<1
6.4	100	0	15	15	1

The diffraction maximums corresponding to this phase are at the level of the background when using less energy. The molybdenum carbides cannot be found using the X-Ray structural method during the interaction of molybdenum and iron.

The increase of the level of the discharge energy leads to a higher level of homogeneity of created phases. Thus, diffraction minimums are less washed away on the X-Ray photographs of the diffusion zone (fig. 2). We must pay attention to the fact that there are no oxides of both molybdenum and iron. Besides, there are no intermetallic phases neither in the layer nor in the transitional zone at $W = 6.4 \text{ J}$, in spite of their obligatory combination under similar conditions [5].

In order to define the possibility of intermetallids combinations such investigative methods were used that characterized by high sensibility, for example, the Mössbauer electronic spectroscopy method. Experiments on molybdenum-iron were held to exclude the possible influence of the carbon presence. This allowed to reveal a small quantity of unequal intermetallic phase $\text{Fe}_x\text{Mo}_{1-x}$ in the thin molybdenum layer. Its quantity, however, is not enough to reveal the symmetry and the contrasting with the intermetallic substance Fe_2Mo (λ -phase).

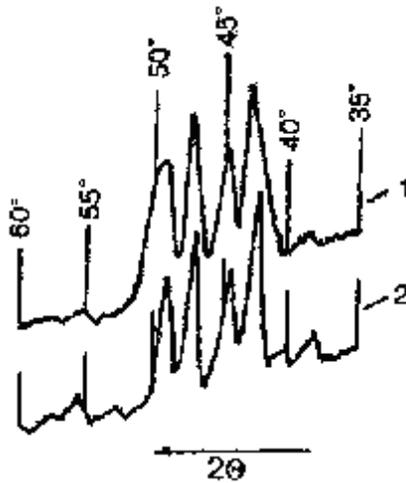


Fig. 2. Diffraction maximums of plain surfaces (100), (002), (011) of combination Mo_2C and (111) Mo_2N while processed with energy of 0.3 J (1) and 0.9 J (2)

Such phases appear when applying the iron layer on the monocrystal molybdenum. Thus, thick solutions with a similar content of the dissolved element, molybdenum and iron nitride and an intermetallic combination with the disturbance of the balanced stoichiometry $\text{Fe}_{1.9}\text{Mo}$ appear at the discharge energy $W = 6.4 \text{ J}$ (fig. 3).

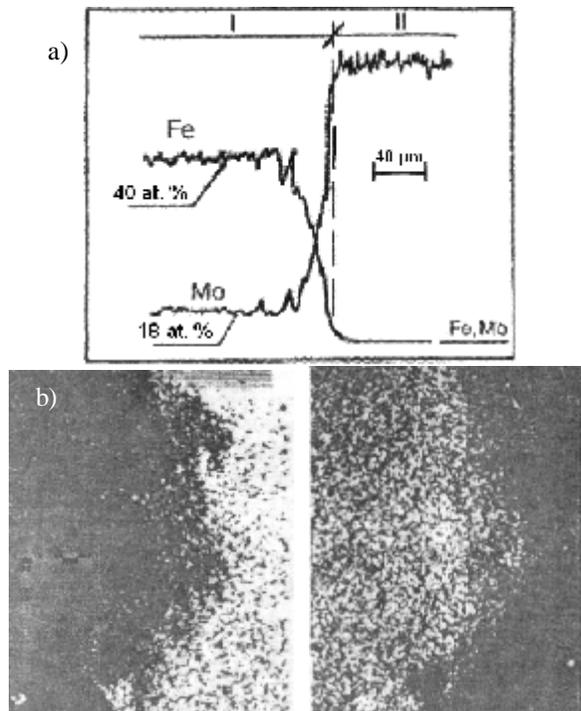


Fig. 3. The concentrated curves of iron and molybdenum distribution (a). Molybdenum and iron interaction zones at the reflected electrons in the iron (b) and molybdenum (c) radiation.

It should be mentioned that the carbide phases do not appear, as it happened in the case of the molybdenum and steel interaction, since the quantity of CO_2 in air is insignificant compared to the nitrogen, and there are no other ways of carbon atoms supplying in layer and base metal. Besides, the oxygen atoms are fixed in the layer, i.e. from the iron side. There is an average of 12 at. % of oxygen in the undersurface layer which is not associated with the oxides. It can be supposed that the oxygen is presented as a hard solution in the iron and in molybdenum solution in Fe- α . There are no oxygen atoms in the basic metal (molybdenum). This is similar to the case when molybdenum was covering, and iron and steel were the basic material.

The peculiarities of phase formation in this system in ESA conditions must be also mentioned. An intermetallic combination is formed in the iron hard solution in molybdenum and evolves from it into a molybdenum base to a considerable depth (up to 30 μm) as needles, placed normally towards the molybdenum sample (fig. 4).

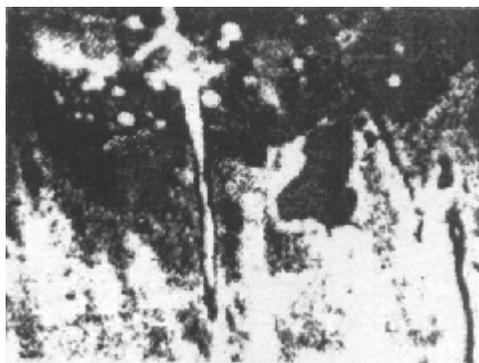


Fig. 4. The microstructure of the monocystal molybdenum with an iron layer, received using the ESA method and a 0.9 J energy

While processing thin pellicle layers of ^{57}Fe in the same regime (~ 1000 nm) on the monocystal molybdenum by means of molybdenum anode, hard solution of iron in molybdenum and intermetallic combination $\text{Fe}_x\text{Mo}_{1-x}$ appears on the surface, where $x < 0.66$. There is a hard molybdenum solution in α -Fe, as phases, their dimensions are up to 15 nm and they reach a depth of ~ 1500 nm.

Therefore, in the molybdenum layers on steel, due to the interaction of the layer materials and the basics with the light elements, a high dispersal phase of penetration forms, which contributes to hardening of the material, subject to ESA.

Thus, we can affirm that under the influence of sparkle discharge in the molybdenum-steel system, multiphased structure solutions, oversaturated with hard substitute solutions, oversaturated with hard penetrating solutions, penetrating phases and non-stoichiometric intermetallids are formed.

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CZU:

CERCETAREA INFLUENȚEI PROCESULUI DE ALIERE PRIN SCÎNTEI ELECTRICE ASUPRA STRUCTURII DE FAZĂ A ACOPERIRILOR DIN MOLIBDEN PE OȚEL 20

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