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A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S

Volume 60 2015 Issue 3

DOI: 10.1515/amm-2015-0274

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SELECTED PROPERTIES AND TRIBOLOGICAL WEAR ALLOYS Co-Cr-Mo AND Co-Cr-Mo-W USED IN DENTAL PROSTHETICS

WYBRANE WŁAŚCIWOŚCI ORAZ ZUŻYCIE TRIBOLOGICZNE STOPÓW, Co-Cr-Mo I Co-Cr-Mo-W STOSOWANYCH W PROTETYCE STOMATOLOGICZNEJ

The presented work provides the results of the abrasive wear resistance tests performed on Co-Cr-Mo and Co-Cr-Mo-W alloys with the use of the Miller's apparatus. The analyzed alloys underwent microstructure observations as well as hardness measurements, and the abraded surfaces of the examined materials were observed by means of electron scanning microscopy. The performed examinations made it possible to state that the Co-Cr alloys characterized in a high hardness, whereas the changes in the mass decrement were minimal, which proved a high abrasive wear resistance.

Keywords: Co-Cr alloys, wear, slurry abrasion test ("Miller test"), dental prosthetics

W prezentowanej pracy przedstawiono wyniki badań zużycia ściernego stopów, Co-Cr-Mo i Co-Cr-Mo-W przy użyciu aparatu Millera. Analizowane stopy poddano obserwacjom mikrostruktury, pomiarom twardości i mikrotwardości, a ścierane powierzchnie badanych materiałów obserwacji przy wykorzystaniu elektronowej mikroskopii skaningowej.

Przeprowadzone badania pozwoliły na stwierdzenie, że stopy, Co-Cr charakteryzowały się wysoką twardością i mikrotwardością, zaś zmiany ubytku masy były bardzo minimalne, co świadczy o wysokiej odporności na ścieranie.

1. Introduction

Human dentition is characteristic of the "system", which is heavily exposed to a variety of processes that may cause degradation. Due to this fact, materials used in dental prosthetics, except a good biocompatibility and high mechanical properties, should also have good tribological properties.

The used material should be selected in such a way so as the probability of its wear, degradation and the formation of cavities would be minimal. Cobalt alloys are included in the group of materials with a good biocompatibility [1÷3]. Their mechanical properties as well as corrosion resistance mainly depend on the chemical composition and structure, the latter being dependent on the type of the used technology and the production conditions [4]. Casting alloys from the Co-Cr group are mostly used in stomatology for the production of prosthetic implants, frame prostheses and metal reconstructions to be mounted under ceramic crowns [4, 5].

These alloys can be divided into two basic groups: those used in motor organ surgery and those applied in stomatology. The first group includes, due to their chemical composition, the casting alloys of the Vitallium type. They are Co-Cr-Mo alloys with the carbon content of up to 0.35% [6]. The chromium and molybdenum contents in the Vitallium alloys are selected in such a way so as the alloy matrix would be β-Co.

The presence of carbide-forming alloy elements accompanied by the presence of carbon caused the formation of $M_{23}C_6$ type carbides in these alloys during the thermal treatment [6÷8].

According to Taylor and Waterhaus [9], in the structure of these alloys, also primary M_7C_3 carbides are formed, whereas, according to other scientists, Clemow and Daniell [10], M_6C carbides are formed as well. Co-Cr-Mo alloys are very susceptible to reinforcement, and that is why the casting process involves the use of a precise technique – the lost wax method [6].

Another group of alloys on a cobalt matrix used in stomatology are Co-Cr-Mo-W alloys [6]. Their chemical composition also includes tungsten. Additionally, these alloys characterize in a lower thickness of the oxidized layer formed in the production process, which favours the creation of solid connections with the ceramics. Due to this fact, they are used for firing the ceramics directly on the metal or for acryl coating. Co-Cr-Mo-W alloys are assigned for the production of frame constructions, crowns and bridges [6, 8].

Considering the extensive use of the discussed alloys in the widely understood stomatological technology as well as the constant lack of data on their basic properties, the work

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TABLE 1

The chemical composition of tested materials

Trade name	Company name	Chemical composition, wt %					
		Co	Cr	Mo	W	Si	Other
Remanium 2001	Dentaurum	63	23	7.3	4.3	1.6	Mn, N
Wironit LA	Bego	63.5	29	5	-	1.2	Ta, N, Mn, C < 1,0
Colado CC	Heraeus	59	25.5	5.5	5.0	-	Ga (3.2), Nb, Fe, B < 1.0
Heraenium P	Ivoclar Vivadent	59	25	4.0	10.0	1.0	N, Mn (0.8)

attempts at evaluating the properties and abrasive wear under simulated "natural" working conditions.

The aim of the work was to compare selected properties and the abrasive wear of four cobalt alloys from the Co-Cr group, presented in Table 1, applied in dental prosthetics, as well as to point to an optimal variant regarding the wear resistance under assumed conditions.

2. Material and test methodology

The test material was constituted by four selected cobalt-based alloys used for the production of frame prostheses, combined prostheses, implants and metal substructures under ceramics. The chemical composition of the examined Co-Cr-Mo and Co-Cr-Mo-W alloys is presented in Table 1.

The test samples were cast by means of the lost wax method. The first stage of the process consisted in the preparation of wax models for each alloy, of a specified size: 25.4x12x(9÷11) mm (dimensions of the samples required to perform the abrasive tests with the use of the Miller's apparatus). The following stage included placing the wax models in a ring, into which a phosphate-based refractory was then cast. After the casting, the rings were placed in a pressure chamber and the pressure of 0.4 MPa was applied for 20 minutes, with the purpose of the proper bounding of the refractory. When the refractory had bounded, the formed crucible was placed in the furnace and the process of heating at the rate of 7°C/min began.

Two isothermal stops were made during the heating process: the first - at the temperature of 250°C for the time of 20 minutes, when the evaporation of the wax as well as of the water from the casting ring occurred, and the second - at the temperature of 600°C for the same time, that is 20 minutes, when the transformation of the silica took place.

The end of the process took place at the temperature of 950°C/20min, and next the casting process began with the use of the Vulcan 3-550 furnace. After casting, the samples were removed from the furnace and cooled outdoors. The following stage of the work was removing the refractory as well as mechanical sand blasting with the Ecoblast Kombi machine, granularity 200μm, pressure 0.6 MPa. The final stage of the sample preparation was mechanical removal of the feed channels.

The hardness measurement was performed using the Vickers method. The hardness was examined by means of the ZWICK/ZHU 187.5 hardness tester with the load of 98.7 N (HV10). The number of measurements in randomly selected areas of the sample was 10 directions x, y and z.

In order to observe the microstructure of the examined Co-Cr-Mo and Co-Cr-Mo-W alloys, 10x15x5 mm samples underwent a mechanical treatment, which consisted of the following consecutive processes: mechanical grinding with 400÷4000 gradation abrasive papers and mechanical polishing, which included the final stages of sample preparation. Each time when the gradation of the abrasive paper was changed, the samples were cleaned and rinsed in ethanol, in an ultrasound washer. The rinsing process was each time performed in 3 cycles and for 3 minutes. The polishing involved the use of a silicon oxide suspension (SiO). The processes of grinding and polishing were performed by means of a polishing-grinding machine by Struers. With the aim to reveal the microstructure of the examined material, the micro-sections were chemically etched with the use of an etching reagent: 1 part of HNO_3 + 3 parts of HCl. The micro-sections prepared in such a way were observed with the use of the LEICA DM 4000 light microscope.

The abrasive wear tests were conducted with the Miller's apparatus, which is used to examine the abrasive properties of metals and the abrasive wear resistance of construction materials. The device also makes it possible to perform comparative examinations of the abrasive wear resistance of different groups of alloys (cast steel, cast iron, composites) under the abrasion conditions: metal– SiC and water mixture, according to the method recommended by ASTM. A diagram of the machine's construction is included in Figure 1.

The working parts of the device are four slideways (9) for the mounting of the samples (6) with a weight (7), which provides a unit pressure on the sample of the order of 0,07 MPa, and the total load of the sample equaling 22.24 N.

The slideway with the sample performs a reciprocating movement in a U-shaped chute, which enables the downflow of the SiC + water/SiC + artificial saliva mixture onto the bottom of the chute after each stroke.

The rate of the sample's movement is constant and equals 0.254 m/s, whereas the frequency of the sample's movement equals 48 min^{-1}. The "Miller test" consists in performing at least three runs in a time not shorter than two hours, which constitute a series allowing the determination of the wear curve. However, it is recommended to perform a sixteen-hour series, which consists of four four-hour runs.

Due to the fact that the examined alloys have stomatological applications, an attempt was made at assimilating at least some of the natural conditions of the alloy's operation. And so, the water was replaced by an artificial saliva solution.

The abrasive tests were performed in a mixture of a SiC powder, mean granulation 10 microns, and artificial saliva.

The composition of the artificial saliva solution is given in Table 2 [11]. The contents of the particular elements of the artificial saliva are given per 1 liter of water. In the case of the examinations performed on the Co-Cr-Mo and Co-Cr-Mo-W alloys, the abrasion process included the following cycles: 2, 4, 6, 8, 12 and 16 hrs.

After each cycle, the samples were rinsed in an ultrasound washer and then weighed on the analytical balance RADWAG AS 220/C/2. The surfaces of the samples after the abrasion in the SiC+artificial saliva mixture were observed using of the HITACHI S-3500N microscope.

TABLE 2

Composition of artificial saliva [11]

Component	NaCl	KCl	KH_2PO_4	$NaHCO_3$	Na_2HPO_4	KSCN
Quantity [g/l]	0.70	1.2	0.20	1.50	0.26	0.33

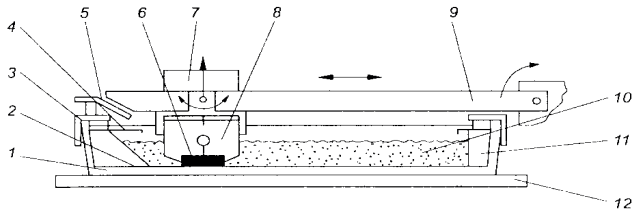

Fig.1. Miller's Machine (1- washer, 2- housing, 3- pressure bar, 4- protective plate, 5- lift arm, 6-sample, 7- load, 8- sample holder, 9- arm, 10- abrasive mass, 11- base) [12]

3. Test results

The broadly understood properties of the materials are a derivative of their structure. Due to this fact, first, an evaluation was performed of the microstructure of the alloys cast according to the procedure described above. The obtained results are presented in Figure 2 in the form of micro-structure images of the particular Co-Cr alloys.

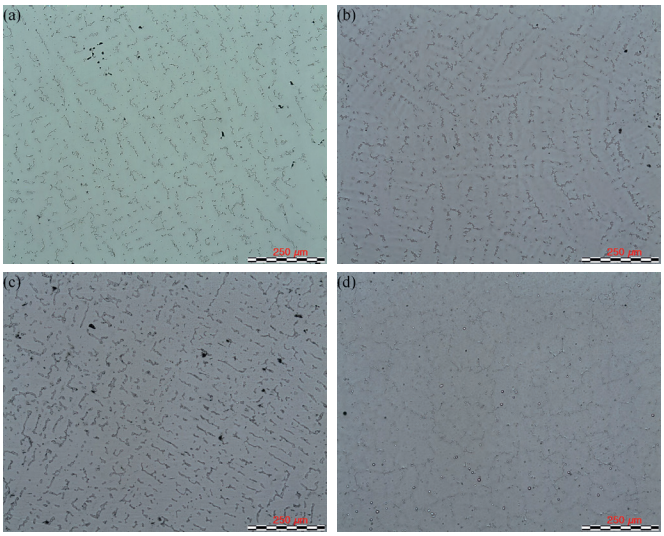

Fig. 2. Images of microstructures of Co-Cr-Mo and Co-Cr-Mo-W alloys: a) Remanium 2001, b) Wironit LA, c) Colado CC, d) Heraenium P after casting

The analyzed alloys characterize in a dendritic structure typical for cast alloys. The micro-structure of the cobalt alloys is not uniform and is formed by an austenitic matrix, which consists of a solid solution of cobalt and chromium in a dendritic core structure. On the basis of the literature data [6, 13], it was assumed that the main carbide precipitations which occur in this kind of alloys are phases of the $M_{23}C_6$ type carbides, distributed at the grain boundaries and in the interdendritic spacings, and they are the main reason for the material's reinforcement. Additionally, according to Taylor et al. [9], in casting cobalt alloys, one can also observe primary M_7C_3 carbides, and, according to Clemow, also M_6C [10].

Taking into account the microstructure observation results as well as the literature data on the possible chemical non-uniformities of the alloy, we performed HV10 hardness test. The aim of the examinations was to determine the hardness of the selected alloys after casting as well as the influence of the particular structural elements on the values of the obtained hardness number. The hardness tests were performed on three mutually perpendicular directions, *x, y* and *z*, where *x* was the casting direction.

Such an approach was chosen due to the high structural and chemical non-uniformity of the alloys as well as the necessity to verify whether the examined properties are isotropic in character or whether they are closely dependent on the selected measurement direction [14-16].

This information will have an extremely significant effect on the further scientific work, especially on the selection of the plane for the wet abrasion tests ("Miller test"). The determination of the anisotropic degree of the examined properties will also have an application character, e.g. allowing the prosthetists to select the appropriate fragment of the melt for the prosthesis element. On the basis of the obtained measurement results, the mean hardness, $\bar{x}$ and standard deviation of hardness (s_H) was calculated, and the obtained test results were statistically analyzed, with the assumption of t_α=2.262 for α=0.05 [17]. The test results are presented in Tables 3.

It is worth noting that the hardness of the alloys is not only connected with the carbon content in the alloy, but mostly with the carbide content, especially Cr_7C_3 – their shape, dispersion and distribution. In the case of the examined samples, the highest hardness value was exhibited by the Wironit LA alloy, whereas the lowest value – by the Colado CC alloy (Table 3). What is more, the obtained HV10 hardness results (Tab. 3) clearly prove the fact that, despite the distinct dendritic structure of all the examined alloys, the hardness is similar in the three selected perpendicular directions. In all the tested cases, the differences between the obtained values of the hardness number are below 10%.

That is why, in the further studies, it is not necessary to perform additional abrasion tests for the particular directions/planes. If the material is hard, it means that it also exhibits a high resistance to scratches and wear. The literature points to the fact that a high hardness of the alloy assures resistance to mechanical defects which can occur during certain procedures in orthodontic treatment [18÷22].

The further tests were performed on the Miller's apparatus, according to the procedure described above. Due

TABLE 3

The results of hardness measurements for the tested alloys in three orthogonal directions *x, y* and *z*

	Type alloy											
	Remanium 2001			Wironit LA			Colado CC			Heraenium P		
	Direction			Direction			Direction			Direction		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
$\bar{x}$	408.7	406.3	411.2	437.8	444.2	441.4	406.1	398.9	397.8	405.1	444.7	428.6
s_H	24.4	15.7	13.8	35.9	38.7	23.3	17.0	28.3	21.3	16.0	33.4	25.6

to the fact that no significant degree of hardness anisotropy was stated for the examined alloys, for further tests the surface perpendicular to the casting direction was selected. Table 4 presents the results of the performed tests of abrasive wear of the examined Co-Cr-Mo and Co-Cr-Mo-W alloys with the use of the Miller's apparatus, in the solution of SiC powder+artificial saliva. The analysis of the obtained abrasive wear test results showed that the lowest wear after 8 h of the process occurred in the case of the Remanium 2001 alloy (0.408 g), whereas the highest – in the case of the Heraenium P alloy (0.676 g). The mass decrements for the Wironit LA and Colado CC alloys equaled 0.535 g and 0.466 g, respectively. The following series of the "Miller test" showed that after 16 hours of abrasion, the mass decreased by 0.241 g for the Wironit LA alloy, this being the smallest mass decrement, whereas the highest one – 0.743 g – was recorded for the Heraenium P alloy. The mass of the Remanium 2001 and Colado CC alloys decreased by 0.377 g and 0.526 g, respectively.

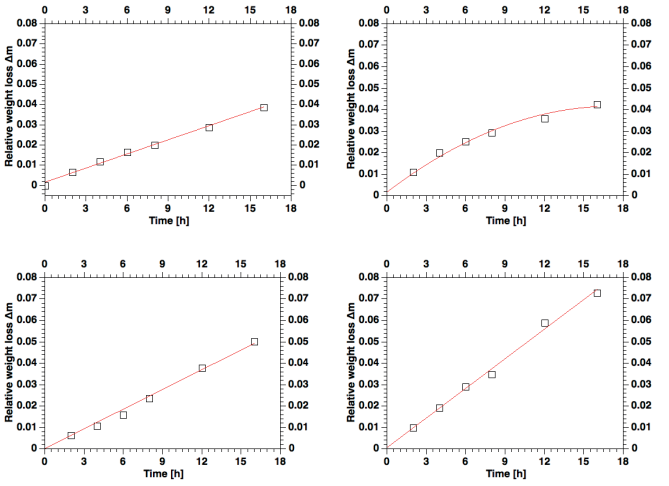

Fig. 3 The relative weight loss of the alloy subjected to abrasion tester using Miller's apparatus in the environment of SiC + artificial saliva: a) Remanium 2001, b) Wironit LA, c) Colado CC, d) Heraenium P

TABLE 4

The measurement results of abrasive wear alloys Co-Cr

Time abrasion [h]	Weight change [g]			
	Remanium 2001	Wironit LA	Colado CC	Heraenium P
0	20.349	18.298	19.749	19.473
2	20.213	18.097	19.626	19.282
4	20.108	17.934	19.536	19.098
6	20.012	17.839	19.436	18.909
8	19.941	17.763	19.283	18.797
12	19.761	17.639	19.002	18.327
16	19.564	17.522	18.757	18.054

With the aim to better understand the quantitative aspect of the abrasion process, the relative mass decrements were calculated from the equation (Eq. 1):

$$\Delta m = (m_o - m_k)/m_o \quad (1)$$

where: m_o – the initial mass of the sample, m_k – the mass of the sample after the given abrasion cycle. The dependences of the relative mass decrements on the test time of the particular alloys are included in Figure 3.

The analysis of the results presented in Figure 3 showed that, within the range of up to 8 hours, basically for all the examined cases, the values of the relative mass decrement were similar. At the same time, it was stated that the character of the changes was the same.

Within the range of up to 8 hours of abrasion, the results for all four alloys can be described by means of a straight line. Significant changes in the behaviour of the alloys were stated only after the period of 8 hours of the abrasion process was exceeded.

In particular, the behaviour of the Wironit LA alloy should be noted. It was observed that, for this alloy, as opposed to the remaining three, after the 8-hour test period is exceeded, the relative mass decrement begins to drop, reaching the value of about 0.04 for the time of 16 hours. However, on the other hand, this is the level which was observed also for the Remanium 2001 alloy. Still, the character of the changes in each case is different. In the case of the Remanium 2001 alloy, we observe a linear character of the relative mass decrement curve up to the time from practically the whole range, whereas, for the Wironit LA alloy, we observe a significant deviation from the rectilinearity within the range of 8–16 hours. This proves the occurrence of factors which positively influence the value of the abrasive wear of this alloy.

The analysis of the effects of the performed research was carried out also by way of observing the surface of the samples after each cycle using SEM. Figures 4 and 5 show selected micro-photographs of the surface after 8 and 16 test hours.

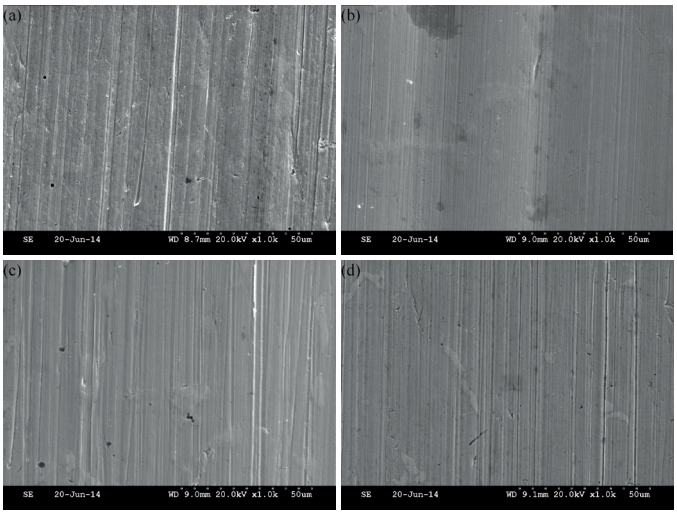

Fig. 4 Images of the surface of the tested alloys of the Co-Cr Miller's machine after 8 h: a) Remanium 2001, b) Wironit LA, c) Colado CC, d) Heraenium P

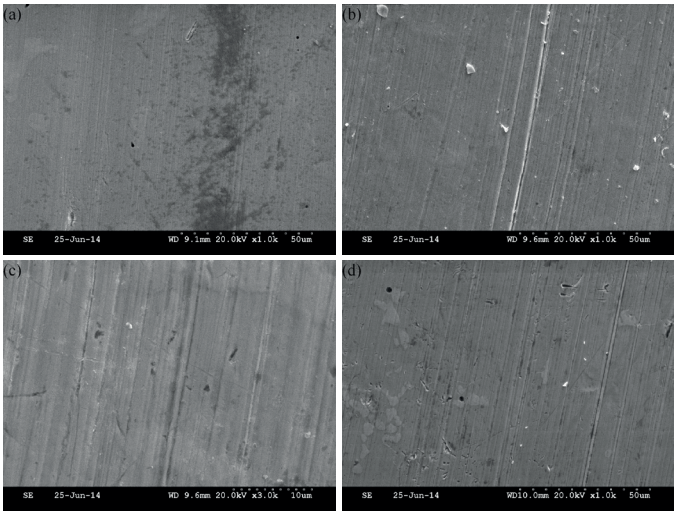

Fig. 5 Images of the surface of the tested alloys of the Co-Cr Miller's machine after 16 h: a) Remanium 2001, b) Wironit LA, c) Colado CC, d) Heraenium P

In the analysis of the abrasive wear of the Co-Cr alloys, during the tests by the Miller's method, it was stated that the basic abrasion mechanism was the process of micro-scratching of the surface. The shifting abrasive element (SiC powder + artificial saliva) created scratches as a result of the operation of hard carbide particles on the surface of the alloys, by way of partial shearing and shifting it to the sides.

However, it seems that this is not the only operating mechanism. Especially in the case of evaluating the micro-images of the surface of the Remanium 2001 (Fig. 4a), Heraenium P (Fig. 4d) and Colado (Fig. 4c) alloys, after 8 hours, one can also observe effects of a micro-ridging process. When the surface is observed after the test, it can clearly be seen that, in the case of the Remanium 2001 alloy (Fig. 5a), the process of micro-ridging does not occur anymore, and the main mechanism is micro-scratching. In the case of the remaining alloys, after 16 hours, it seems that the role of the micro-ridging significantly decreases, although one cannot unequivocally exclude its operation on the surface of the samples.

4. Summary

Metallic materials used in dental prosthetics characterize in different mechanical properties than those of ceramics, which is significant in the designing and producing of constructions made of these materials. Alloys applied in stomatology should characterize in the proper mechanical properties, especially a high yield point (mainly due to the possibility of exposure to high forces), the proper ductility, preventing fracture during the overbending procedure, as well as the proper hardness, which makes it easier for the dental technician to perform the mechanical (final) treatment of the ready element.

The mechanical properties of these alloys are not only dependent on the chemical composition but also on the applied production technique. The forming of ductility and strength is performed by means of the appropriate thermal treatment procedures.

The tribological properties of the Co-Cr-Mo and Co-Cr-Mo-W alloys used in dental prosthetics are very good. These alloys characterize in high hardness values, which provide them with a high abrasive wear resistance. Based on the survey, it was found that the feet have a hardness of about 400 HV10, which is identical to the planes differently oriented to the direction of casting. Additionally, they possess good tribological properties. This particularly refers to two alloys, that is Remanium 2001 and Wironit LA, for which the lowest values of the relative mass decrement has been recorded.

Taking into consideration the interesting results which has been obtained, as well as the scarcity of the literature data on and the demand from the stomatological sector for these alloys, it seems that it is advisable to continue the research in this field. One should particularly determine the effect of the change of the working environment, as well as the size of the abrasive elements and their character on the examined alloys. What is more, the determination of the effect of the carbide precipitates on the course of the abrasion process seems highly significant.

5. Conclusions

On the basis of the performed studies, it was stated that:

1. All the examined alloys characterize in a low degree of anisotropy of the hardness number, in three selected perpendicular directions, in relation to the casting direction. The obtained HV10 hardness values are within the range of 397÷444 HV.
2. The main mechanism operating during the tests was micro-scratching, whereas, in selected cases, it was accompanied, to a minor degree, by micro-ridging.
3. The lowest mass decrement value was recorded for the Remanium 2001 and Wironit LA alloys, although the character of the changes with test time for both alloys was similar only within the rage of up to 8 test hours. After this time, in the case of the Wironit LA alloy, we observed a significant deviation from the rectilinear character of the changes in the mass decrement, which was recorded for the Remanium 2001 alloy.
4. For the Colado CC and Heraenium P alloys, the observed changes in the mass decrement had practically the same character and values. The obtained differences between these two alloys equaled about 1%.

Acknowledgements

The work has been implemented within the framework of statutory research of AGH University of Science and Technology, contract No **11.11.110. 299 AGH**

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Received: 20 February 2015