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Influence of Cr and Co on hardness and corrosion resistance CoCrMo alloys used on dentures

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Properties

ABSTRACT

Purpose: The goal of the study is to try find the relationship between cobalt content on hardness and chromium content on corrosion resistance on the basis of base cobalt alloys CoCrMo used in prosthodontia.

Design/methodology/approach: To investigation was choose five base cobalt alloys with different concentration of cobalt and additions. Hardness test were obtained by use the microhardness FM ARS 9000 FUTURE TECH with load 1 kg. Structure observation was made after surface preparation by light microscope LEICA MEF4A with the magnification range 100-1000x. Corrosion resistance test were carried out at room temperature and use of the VoltaLab® PGP201 system for electrochemical tests. The examination were made in water center which simulated artificial saliva environment. The evaluation of pitting corrosion was realized by recording of anodic polarization curves with use the potentiodynamic methods.

Findings: The cobalt content in CoCrMo alloys in one of the possible parameters which influence on hardness. The highest value of hardness were obtain for alloy with the highest Co content. All of the research alloys characterized dendritic crystals in structure. Chromium content in one of the most important factor which influence on corrosion resistance, due to that alloy with the highest Cr content characterized the higher repassivation potential.

Practical implications: Research materials are used on dentures so it's demand that their characterized corrosion resistance and result of this work make up an information on what element should be pay attention in chemical composition of CoCrMo alloys.

Originality/value: The paper present influence of chemical composition especially cobalt and chromium, on the most important criteria CoCrMo alloys use on dentures.

Keywords: Biomaterials; Corrosion; CoCrMo alloys; Prosthodontia

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1. Introduction

Metals were used in dentistry for the hundreds years [1]. The first metal's materials used in stomatology was gold in foil form, used as loss and tooth decay filler. Unfortunately that materials couldn't be apply to customized crowns and bridges because of their low strength [2,3]. For that reasons to gold were start adding other elements. For many years on prosthetics reconstruction were used, in the first way, precious alloys base on gold, because of their biotolerance and good corrosion resistance. However for the sake of increase price the very valuable ore [4-6], used the precious alloys base on gold for prosthodontia were reduce which took effect in search different materials. Nowadays on a dental market are available many materials used to replace missing teeth, which are additionally division on materials group [7].

Metallic materials used in dentistry engineering could be classified due to content of precious metals in three groups like American Dental Association (ADA): high precious alloys, precious alloys and base alloys (Fig. 1) [3,8]. Because of the possible allergic interaction nickel on the human organism [1,5,9,10] the European Union in relevant directive and ADA propose to retired of alloys with that elements. One of the group which can substitute precious gold alloys, were nonprecious alloys based on cobalt with chromium [7]. Co-Cr-Mo alloys are actually found very wide in the prosthodontia used on implants, crown of a tooth, bridgework and full cast partial [3,7,11].

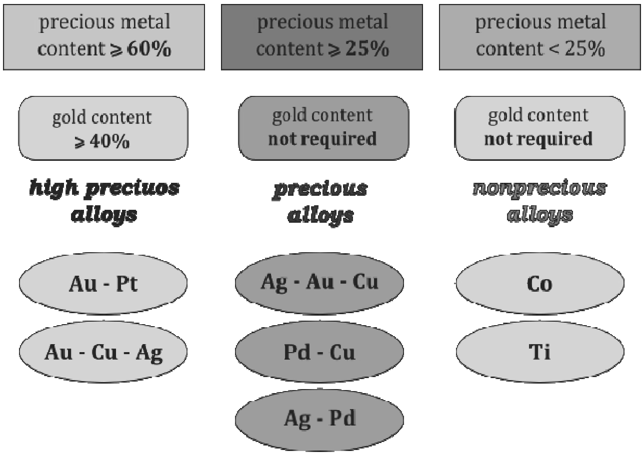


Fig. 1. ADA classification of metallic alloys used in dentistry engineering [3]

Fixed prosthesis, no matter the form, are introduces into human oral cavity on many years. After body implantation, user demand from prosthesis , they should all the time be resistance on stresses, characterized good hardness, biotolerance characterized and corrosion resistance in environment in which they works [12-14].

Corrosion resistance is one of the meaningful property because it's influence on possible allergy and other inflammation conditions in oral cavity environment [11,15]. It's also important value for almost all engineering materials for example in works [16-22, 27] about materials used in automotive industry.

Materials selection on dentures is usually connect with determined the corrosion resistance and some mechanical properties, because chosen metals must carried out that two criteria [19, 20]. Many scientists in their work about biomaterials, also about that use in prosthodontia, considered about anticorrosion protection and either criteria almost connected with mechanical properties like it's shown in [21] where are realized study about corrosion and tensile strength or in [22] which concerned influence of corrosion and hardness and also in [23] where authors determined corrosion, tensile strength and hardness.

On corrosion resistance has also influence surface preparation [24], so important is to take care during compare results of research and pay attention on way which samples were preparation.

Because of the many above alloys destination to use on dentures author decided to try find is there some relationship in CoCrMo alloys between chemical composition and corrosion resistance or influence on hardness.

2. Materials and methods

2.1. Materials

Materials used to testing were non precious alloys base on cobalt used in prosthodontia on crowns, bridgeworks and full cast partial. The experiment were carried out for five cobalt alloys about changing cobalt concentration and alloying addition, shows in Table 1.

Table 1.
Chemical composition of cobalt alloys used in hardness and corrosion resistance research

Material	Chemical composition, wt %					
	Co	Cr	Mo	W	Si	Other
Remanium 2000+	61	25	7	5	1.5	Mn, N < 1
Remanium 2001	63	23	7.3	4,6	1.6	Mn, N < 1
Remanium GM 380+	64.6	29	4.5	-	< 1	Mn, N, C < 1
Colado CC	59	25.5	5.5	5	-	Ga 3,2 Nb, Fe, B < 1
Wirobond LFC	33	30	5	-	< 2	Fe 29 Mn, N, C < 2

Materials were tests in delivery state. Samples were delivered as cylinders dimension was about 15 mm high and diameter was about 7.8 mm.

2.2. Research methodology

With the purpose of hardness tests, fronts of cylinders samples was grinding by SiC waterproof paper with granulation 220, 500 and 800 μm. Hardness research was realized by microhardness FM ARS 9000 FUTURE TECH in the 1 kg load used Vickers scale.

For testing materials was also realized structure observation on LEICA MEF4A light microscope with use normal light and polarisation and confocal microscope ZEISS LSM 5 Exciter with diode laser 405 nm. Before that test specimens was mount, next grinding by SiC paper about granulation from 220 µm do 1200 µm, polished with use the diamond suspension about 9 µm to 1 µm granulation and last operation was etched in HCl and HNO_3 mixture.

The corrosion resistance test were made in room temperature with use the VoltaLab® PGP 201 system for electrochemical tests. The examination were made in water center on composition presented in Table 2. Corrosion resistance research were carried out through polish standard PN-EN ISO 10271:2004 [25]. The standard shows methodology of electrochemical research for dental materials.

For each sample were made fresh electrolyte. Scheme of the test stand showed on Fig. 2. The range of measurement area was between 0.5 and 1.0 cm^2 as auxiliary electrode was use platinum electrode and as references electrode was use calomel (NEK) electrode.

First stage of the corrosion research was evaluate open circuit potential (E_{ocp}) after two hours soak samples in prepared water solution and then recording on testing stand the potential during 900 s. Second stage was evaluation the pitting corrosion by set the start potential 100 mV small than open circuit potential. Next start research corrosion resistance realized by recording the anodic polarization curves with the use of potentiodynamic method which was the base of evaluated the repassivation potential (E_{cp}).

Table 2.
Composition of water solution used in tests

Element	Content
Sodium carbohydrate $NaHCO_3$	4.2 g
Sodium chloride NaCl	0.5 g
Potassium carbonate K_2CO_3	0.2 g
Sodium nitrite $NaNO_2$	0.03 g
Distilled water	1 liter

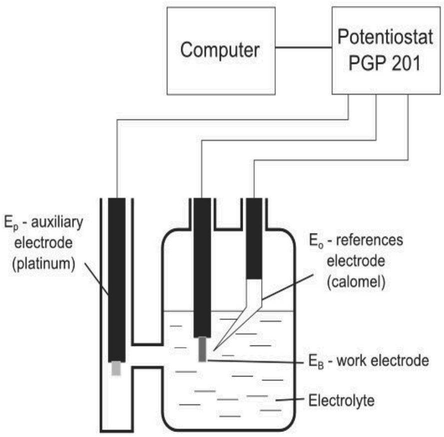


Fig. 2. Scheme of the corrosion resistance set

In order to calculate the corrosion current (i_{cor}), the Stern-Geary equation was used (1). Because it was not possible to evaluate Tafel's b_a and b_k coefficients, corrosion current was estimation using approximated Stern-Geary's equation (2).

$$i_{cor} = \frac{b_a \cdot b_k}{2{,}3(b_a + b_k)R_p} \quad (1)$$

$$i_{cor} = \frac{0{,}026}{R_p} \quad (2)$$

where:
b_a - slope coefficient of the anodic Tafel line
b_k - slope coefficient of the cathodic Tafel line
R_p - polarisation resistance [Ωcm^2]

3. Results and discussion

3.1. Hardness and structure results

Hardness results analysis for tested alloys allow to determined that Co content in CoCrMo alloys may influence on hardness. Increase the Co content in chemical compositions results in higher hardness, and that relationship was observed for four of five examinated alloys: Remanium 2000+, Remanium 2001, Remanium GM 380+ and Colado CC (Tab. 3). Relationship between cobalt content and hardness for that four alloys was shown on Fig. 3.

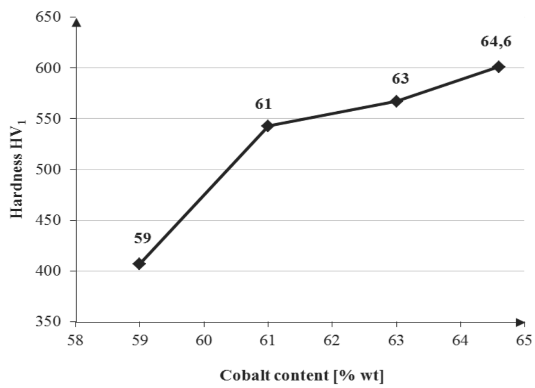


Fig. 3. Relationship between Co content and hardness in research CoCrMo alloys

Table 3.
Hardness results research CoCrMo alloys

Material	Hardness HV_1	Standard deviation
Remanium 2000+	543	± 20
Remanium 2001	567	± 14
Remanium GM 380+	601	± 16
Colado CC	407	± 15
Wirobond LFC	445	± 24

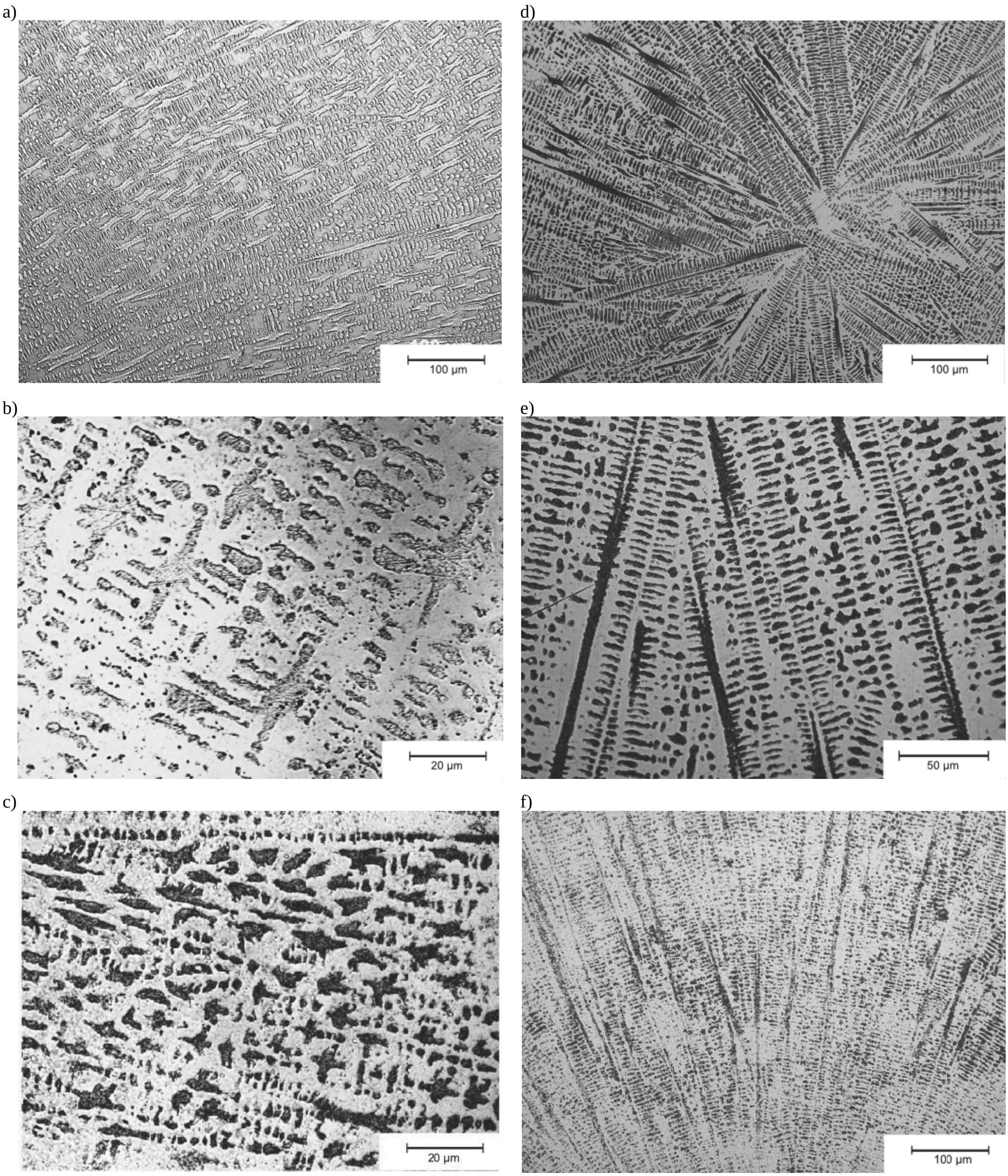


Fig. 4. Structure of research alloys with shown dendrites crystals, after etched in $HCl+HNO_3$: a) Remanium 2000+, polarisation light magnification 200x, b) Remanium 2001, confocal microscope magnification 500x, c) Remanium GM 380+, confocal microscope magnification 500x, d), e) Colado CC, magnification 200x, 500x, f) Wirobond LFC, magnification 200x

Exception of the shown relationship Co influence on hardness was occur for Wirobond LFC alloy about 33% Co which characterized higher hardness than Colado CC about 59% Co. To explain the difference must check the additions introduced to alloy, where is an information about 29 % of iron in chemical composition. Study about influence iron in CoCrMo alloys was realized in [26] where was explain effect of iron addition on plastic properties which decrease it. That effect is results by Fe action which stabilized Co phase structured, so it's the reason why Wirobond LFC about 33% of Co characterized higher value of hardness than Colado CC alloy about 59% of cobalt.

Structures of the CoCrMo alloys after microscope observation was compare and in results can be say that all research alloys characterized typical structures for non precious cobalt base, alloy matrix are solid solution crystallites of chromium, molybdenium and carbons in cobalt about face-centred cubic (fcc) and eutectic between crystals.

3.2. Corrosion resistance results

Open circuit potential was recording and saving potential in function of time for testing alloys. The E_{ocp} determine that the best corrosion resistance (potential), at water solution simulated environment in which works chosen materials, characterized alloy Wirobond LFC, next Colado CC and the worst present Remanium 2001 (Tab. 4). If higher open circuit potential than material characterized better anticorrosion protection (Fig. 5).

The results of pitting corrosion tests were recording and saving as anodic polarisation curves shown relation between changing potential in time and anodic current density (Fig. 6). Realized research of pitting corrosion gave an information about electrochemical parameters of alloys and allow to compare materials and characterized one about the best corrosion resistance in research environment.

Table 4.
Electrochemical parameters of the testing non precious cobalt alloys

Material	Open circuit potential E_{ocp}, mV	Average value of E_{ocp}, mV	Corrosion current i_{cor}, μA/cm^2	Repassivation potential E_{cp}, mV	Average value of E_{cp}, mV
Remanium 2000+	-397- -265	-333	0.039	631-632	631
Remanium 2001	-467- -370	-430	0.041	565-589	577
Remanium GM 380+	-151- -139	-145	0.005	604-620	611
Colado CC	-92- -69	-81	0.011	627-634	631
Wirobond LFC	-95- -34	-67	0.011	827-962	912

For this work was make an assumption that higher value of the repassivation potential (E_{cp}) means better corrosion resistance and the results of realized research suggested that Wirobond LFC characterized best anticorrosion protection because of E_{cp} range 820-955 mV and it's the alloy with the highest Cr concentration - 30%. The worst pitting corrosion protection was characterized alloy Remanium 2001 about E_{cp} range 560-584 mV and it's alloy with the lowest Cr concentration - 23% (Tab. 4).

Results of the pitting corrosion tests shown relationship between chromium concentration in the base cobalt alloys used in prosthodontia and anticorrosion protection. Higher Cr content results in higher repassivation potential and better corrosion resistance (Fig. 7).

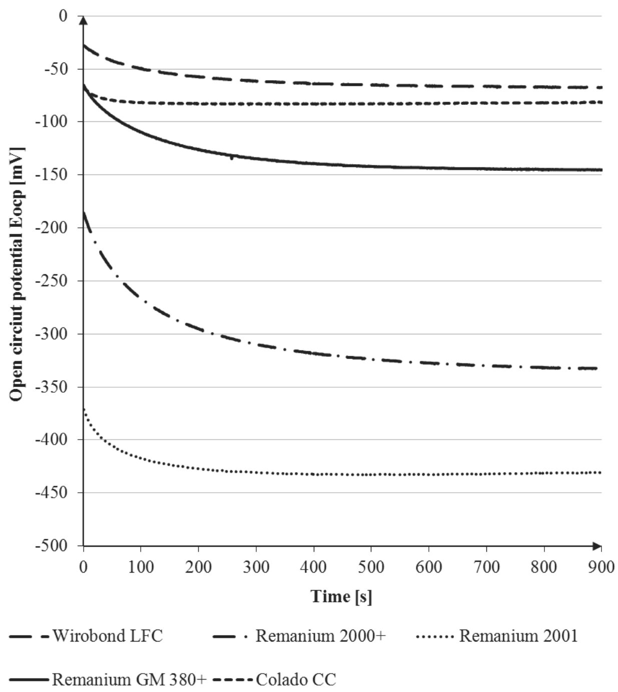


Fig. 5. Open circuit potential curves after 900s tests

4. Conclusions

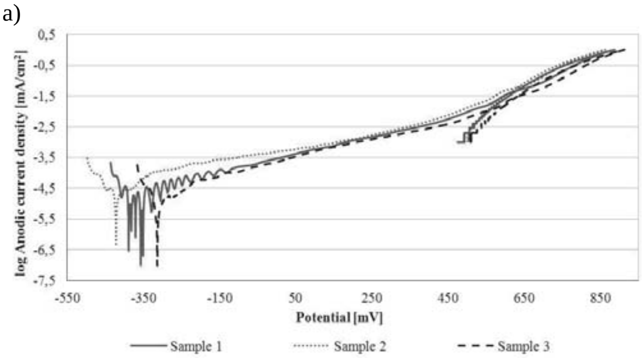
On the grounds of realized study and research was elaborate following conclusions:

- hardness and cobalt concentration may be connected by relationship, because it was observed that with increase Co concentration in research alloys hardness was also increased;
- the highest hardness of analysed alloys characterized Remanium GM 380+ (601 HV_1) with 64.6% Co and the lowest value of hardness was observed for Colado CC (407 HV_1) with 59% Co;
- meaningful influence on hardness in CoCrMo alloys has addition of 29% Fe for Wirobond LFC (30% Cr), what cause reduce of plasticity, because stabilized cobalt phase structure;
- there are exist a relationship between chromium concentration and corrosion resistance (repassivation potential), increase Cr

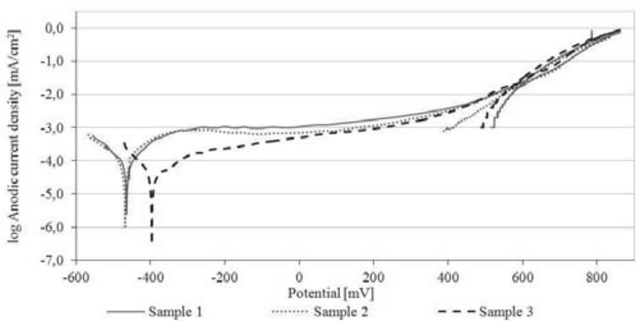
concentration in research alloys cause increase repassivation potential;

- the best corrosion resistance parameters characterized Wirobond LFC (E_{cp} = 912 mV) about 30% Cr and the lowest repassivation potential 577 mV characterized Remanium 2001 about 23% Cr.

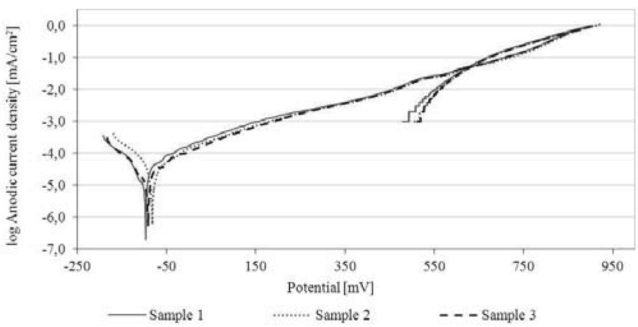
a)



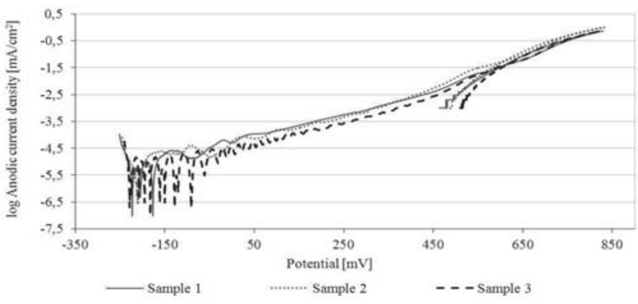
b)



c)



d)



e)

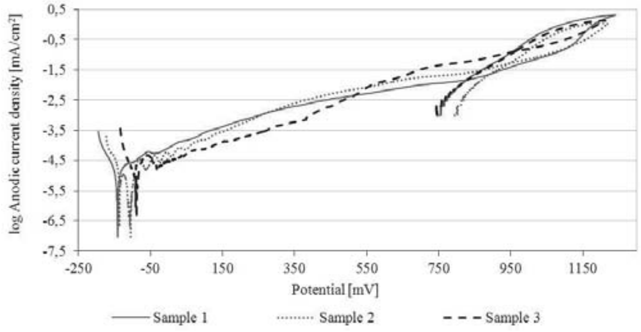


Fig. 6. Potentiodynamic curves of pitting corrosion for examinations alloys: a) Remanium 2000+, b) Remanium 2001, c) Colado CC, d) Remanium GM 380+, e) Wirobond LFC

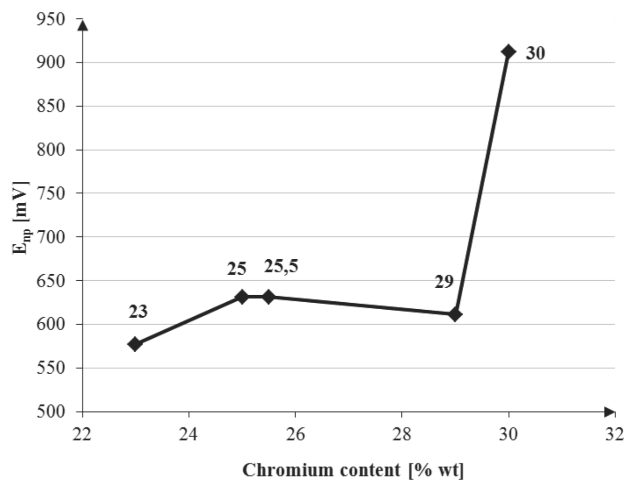


Fig. 7. Relationship between Cr content and repassivation potential in research CoCrMo alloys

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