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Effect of age hardening on corrosion resistance and hardness of CoCrMo alloys used in dental engineering

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ABSTRACT

Purpose: The goal of the study is to research the effect of various time of ageing on corrosion resistance, hardness and structures of Remanium 2000+ Co-Cr-Mo alloys used in prosthodontia.

Design/methodology/approach: To investigation was prepared mould, cast in 1430°C and realized the heat treatment: solutioning in 1250°C by 3 hours and then ageing in 850°C by 4, 8, 16 and 24 hours. Electrochemical corrosion examination were made in water center which simulated artificial saliva environment. The evaluation of breakdown potential was realized by recording of anodic polarization curves with use the potentiodynamic methods. Corrosion resistance test were carried out at room temperature and use of the VoltaLab® PGP201 system for electrochemical tests. Hardness test were obtained by use the microhardness FM ARS 9000 FUTURE TECH with load 1 kg. Structure observation was made after surface preparation: grinding, polishing and etching by light microscope LEICA MEF4A with the magnification 500x.

Findings: The age hardening for Co-Cr-Mo alloys is one of the possible method which effect in forming the hardness. The highest value of hardness were obtain for specimen which was ageing with the longer time. Research alloy characterized dendritic crystals in structure for all realized heat treated process. At specimen after the longer ageing was observed the most of discontinuous precipitation and stacking faults in compare with specimen ageing by 4 hours. The age hardening doesn't influenced much on electrochemical results and only the open circuit potential changed by decreased while increased ageing time. The values of breakdown potential and repassivation potential kept at a constant level.

Practical implications: Research material is used on dentures so it's demand that their characterized corrosion resistance and result of this work make up an information on what heat treatment parameters may be pay attention for CoCrMo alloys.

Originality/value: The paper present effect of age hardening especially the ageing time, on the most important criteria of CoCrMo alloys use in dental engineering.

Keywords: Biomaterials; Corrosion; CoCrMo alloys; Age hardening; Prosthodontia

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MATERIALS

1. Introduction

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 [1, 2].

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, used the precious alloys base on gold for prosthodontia were reduce which took effect in search different materials. One of the group which can substitute precious gold alloys, were nonprecious alloys based on cobalt with chromium. Co-Cr alloys are actually found very wide in the prosthodontia used on implants, crown of a tooth, bridgework and full cast partial [3, 4].

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. On the base of that criteria from availability alloys are made selection of materials to each application. As well in group of the materials oriented on prosthodontia is existing numerous representation of metals alloys about different chemical composition, properties and place of install the dentures [5, 6].

Obtain the advisable mechanical properties and corrosion resistance as one of the meaningful property because it's influence on possible allergy and other inflammation conditions in oral cavity environment [7, 8], may be possibility by use different ways: introducing to alloys additions or modify content of the main component like cobalt or chromium in Co-Cr-Mo alloys [9-11] or like for different materials for example light alloys [12] used in different branch of industry. From many research aim at improvement the properties may find the study on influence nickel and molybdenum in Co-Cr alloys on structure and corrosion resistance [9], work about change the properties depends on chromium and cobalt [9, 10]. In other work was studied the effect of the tungsten addition elements on the formation face center cubic phases in pure cobalt and how it influence on structure and try detect formed carbides [11]. Different possibility to form the properties is perform plastic forming [13, 14] or the heat treatment [15]. In the alloys selected to prosthodontia applications chemical composition and the group in which the alloys belong to, have a significant effect on properties (Fig. 1) not only mechanical but also for example corrosion resistance and other [1].

Structure and properties of the metal alloys quite often is formed by heat treatment. Usually heat treatment is realized for non precious alloys on cobalt base, used on dentures substrates because of their excellent mechanical properties and their quite good corrosion resistance. Alloys after casting are slow cooling in air with the casting mould, what may influence on their structure through forming big crystallites and in consequence it have an effect on properties final products (dentures). In order to prevent disadvantageous phenomenon were realized heat treatment, especially age hardening which allow on structure homogenizing and improve mechanical properties [16]. The ageing can induce significant improvement of the corrosion resistance It were prove that age hardening of Co-Cr-Mo alloys influence on structure, the numbers of carbides release in alloys with carbon additions and also on hardness and wear resistance [17-21].

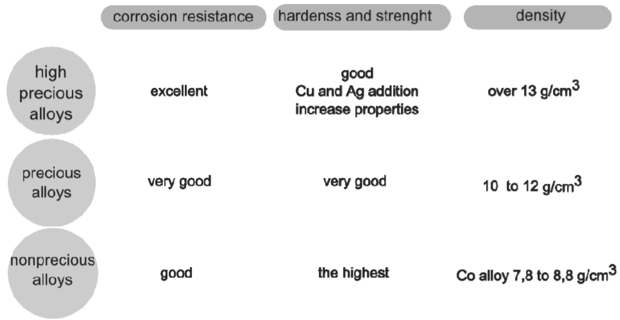

Fig. 1. Properties of metal alloys used in prosthodontia divide on three group [1]

Materials engineering researches used for prosthodontia increasingly are builds on computer aided systems to better predict the properties or behavior in cooperation with human tissues. That computers tools are mostly basis on finite element method and it's allow user to adjust the geometry with the states of stress and then recalculate the construction of dentures [22-25].

The aim of that work is to study the effect of age hardening on corrosion resistance and mechanical properties of one of the commercial Co-Cr-Mo alloys Remanium 2000+ used on dentures.

2. Material and methods

2.1. Material

Material used to testing was non precious commercial alloy Remanium 2000+ Dentaurum, base on cobalt used in prosthodontia on crowns, bridgeworks and full cast partial. The composition of cobalt and alloying additions and producer recommended properties are presented in Table 1.

Table 1.
Chemical composition and properties of Remanium 2000+ alloy used in studies

Element	Co	Cr	Mo	W	Si	Mn	N
Remanium 2000+	61	25	7	5	1.5	< 1	< 1
Properties	Density, g/cm^3	Hardness, HV$_5$	$R_{p0.2}$, MPa	A5, %	E, GPa	CTE, 10^{-6} K^{-1}	
Remanium 2000+	8.6	340	700	7	200	14.0	

Materials were delivered as cylinders dimension was about 15 mm high and diameter was about 7.8 mm.

2.2. Specimens and heat treatment

To study the age hardening effect were prepared specimens using centrifugal casting methods. To cast was necessity to construct the casting mould. For casting dental alloys the mould was prepared in lost-wax technique. At the beginning wax model was prepared as cylinders dimension samples about 11 mm high and diameter about 6.5-7.0 mm, by casting into silicone moulds (Figs. 2a,b), next wax model after prepared casting cone and the casting runner, were fixed to casting ring stand (Fig. 2c). The casting ring was line by band Hera to prepare a place for expansion of precision investment materials Hera Moldavest exact. Wax model with casting runner were sprinkled by Aurofilm Bego for reduce surface tension. Last stage in preparing mould was using a vacuum mixing unit to obtain investment material which fill the casting ring (Fig. 2d). Ready mould were put into preheating furnace to burn out the wax and heat before install in casting machine in conditions determined by the investment material: temperature 950°C and 0.5 hour. All used materials are typical apply in prosthodontia practice. Next stage was casting in centrifugal machine after melt the alloy samples by oxy-acetylene blowpipe at 1430°C. After casting process the mould was pull out and cooling in air then the mould was break, casting part removed and clean by sand spreader.

After cast all specimens was realized the heat treatment which combinable solutioning and ageing. The detail process are shown in Table 2. The solutioning was done in high temperature HT 1800 Furnace with application argon as protective atmosphere and cooling in water. The ageing was performed in Thermolyne 6000 Furnace and slow cooling in air.

Study the effect of age hardening on properties and on structure of the Co-Cr-Mo casting alloy Remanium 2000+, were made by following researches: electrochemical test (pitting corrosion resistance) and the Vickers hardness. In study was also realized microscopic observation of the structure after specimens preparation.

Table 2.
Solutioning and ageing parameters for study alloy

Heat treatment operation	Temperature, °C	Time, h	Cooling medium	Specimens marker
Solutioning	1250	3	Water - 25°C quenching	Re/1430/P
Ageing	850	4 8 16 24	Air cooling	Re/1430/4 Re/1430/8 Re/1430/16 Re/1430/24

Specimens for corrosion tests were grinding on 500 µm SiC paper, ultrasonic cleaning in acetone and then was determined test area on surface. To the hardness test specimens were prepared by grinding on 220, 500 and 800 µm SiC papers, to microscopic observation specimens were grinding on 220, 500, 800, 1200 µm SiC papers, then polishing with use the diamond suspension about 9 µm to 1 µm and last operation was etched in mixture of HCl, H_2SO_4 and HNO_3.

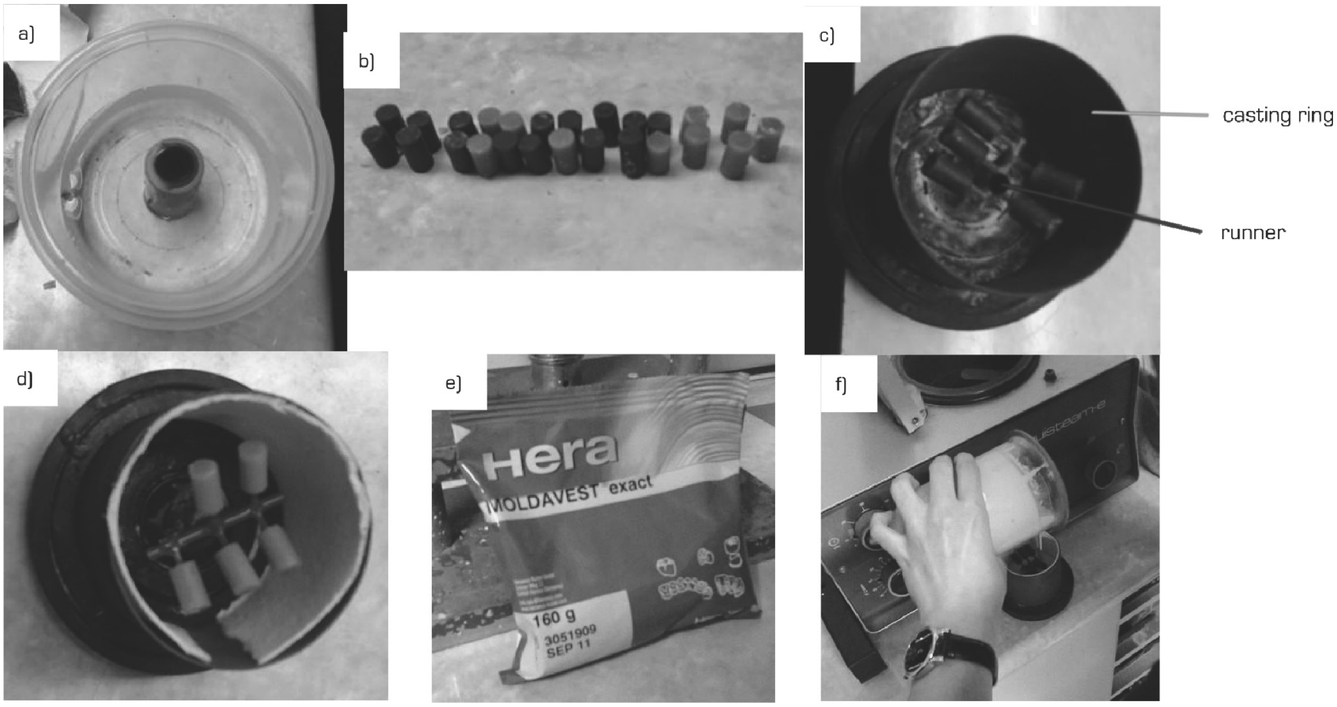

Fig. 2. Stages of preparing the mould to cast tests specimens: a) preparing the wax model by cast liquid wax into silicon mould placed in cold water, b) wax specimens after remove from silicon and cut, c) wax models with runners in casting ring, d) paper band install to better expansion of investment material, e) the investment materials to prepare the mould, f) fill the casting ring by investment material after vacuum mixing

2.3. Research methodology

The corrosion resistance test were conducted at room temperature with using the VoltaLab® PGP 201 system for electrochemical tests. The test was realized in an artificial saliva of the Fusayama type with composition presented in Table 3. For each sample were made fresh electrolyte. Scheme of the test stand showed in Fig. 3. 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 standard saturated calomel electrode (SCE).

Table. 3.
Composition of an artificial saliva by the Fusayama

Element	Content
NaCl	0.4 g/l
KCl	0.4 g/l
$NaH_2PO_4 \cdot H_2O$	0.69 g/l
$CaCl_2 \cdot H_2O$	0.79 g/l
Urea	1.0 g/l
Distilled water	1 l

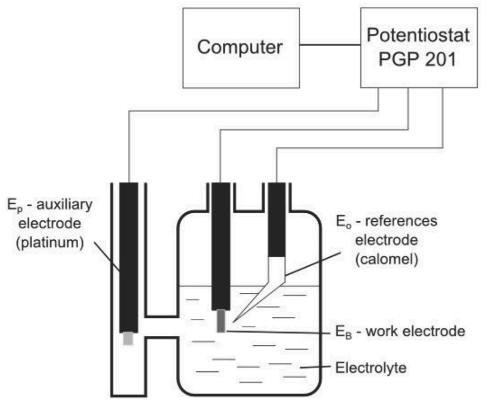

Fig. 3. Scheme of the corrosion resistance set to evaluate pitting resistance

Electrochemical corrosion research starts from evaluate open circuit potential (E_{ocp}) at non current conditions, samples were placed on two hours into prepared water solution and then the open circuit potential vs. time curves was recording on testing stand for 900 s. Second stage was evaluation the breakdown potential and recording the anodic polarization curves with the use of potentiodynamic method which was the base of evaluated the typical parameters and relationships of potential, current and time.

In order to calculate the corrosion current density (i_{cor}), the Stern-Geary equation was used (1). Because it was not possible to evaluate Tafel's b_a and b_k coefficients for each results, corrosion current was estimation using approximated Stern-Geary's equation (2), with assumption that $b_a = b_k = 0.12$ V·dec^{-1}.

$$i_{cor} = \frac{b_a \cdot b_k}{2.3(b_a + b_k)R_p} \quad (1)$$

$$i_{cor} = \frac{0.026}{R_p} \quad (2)$$

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.

In electrochemical corrosion examination were determined corrosion potential (open circuit potential – $E_{ocp,}$), corrosion current – i_{cor}, pitting potential – E_b and repassivation potential – E_{cp}.

With the purpose of hardness tests, fronts and back of the specimens were grinding. Hardness research was realized by microhardness FM ARS 9000 FUTURE TECH at the 1 kg load used Vickers scale.

In study effect of age hardening on structure was realized microscopic observation on LEICA MEF4A light microscope at bright field and the magnification was 500x.

3. Results and discussion

3.1. Corrosion resistance results

Open circuit potential was recording and saving potential in function of time for testing alloys (Fig. 4). The E_{ocp} determine that the best corrosion resistance (potential), at water solution simulated environment in which works chosen materials, characterized alloy after casting without heat treatment, near value characterized specimens after ageing by 16 hours. Results of research effect of the age treatment shown that increase the ageing time caused worse E_{ocp}. The worst open circuit potential characterized specimen after solutioning and ageing by 24 hours (Fig. 4). If higher open circuit potential than material characterized better anticorrosion protection.

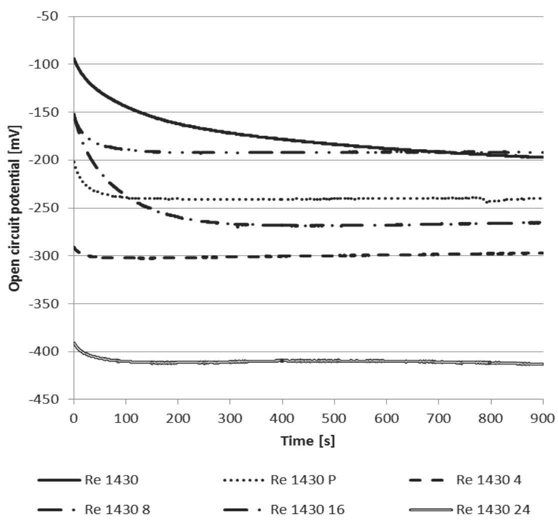

Fig. 4. Open circuit potential curves after 900 s tests

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. 5).

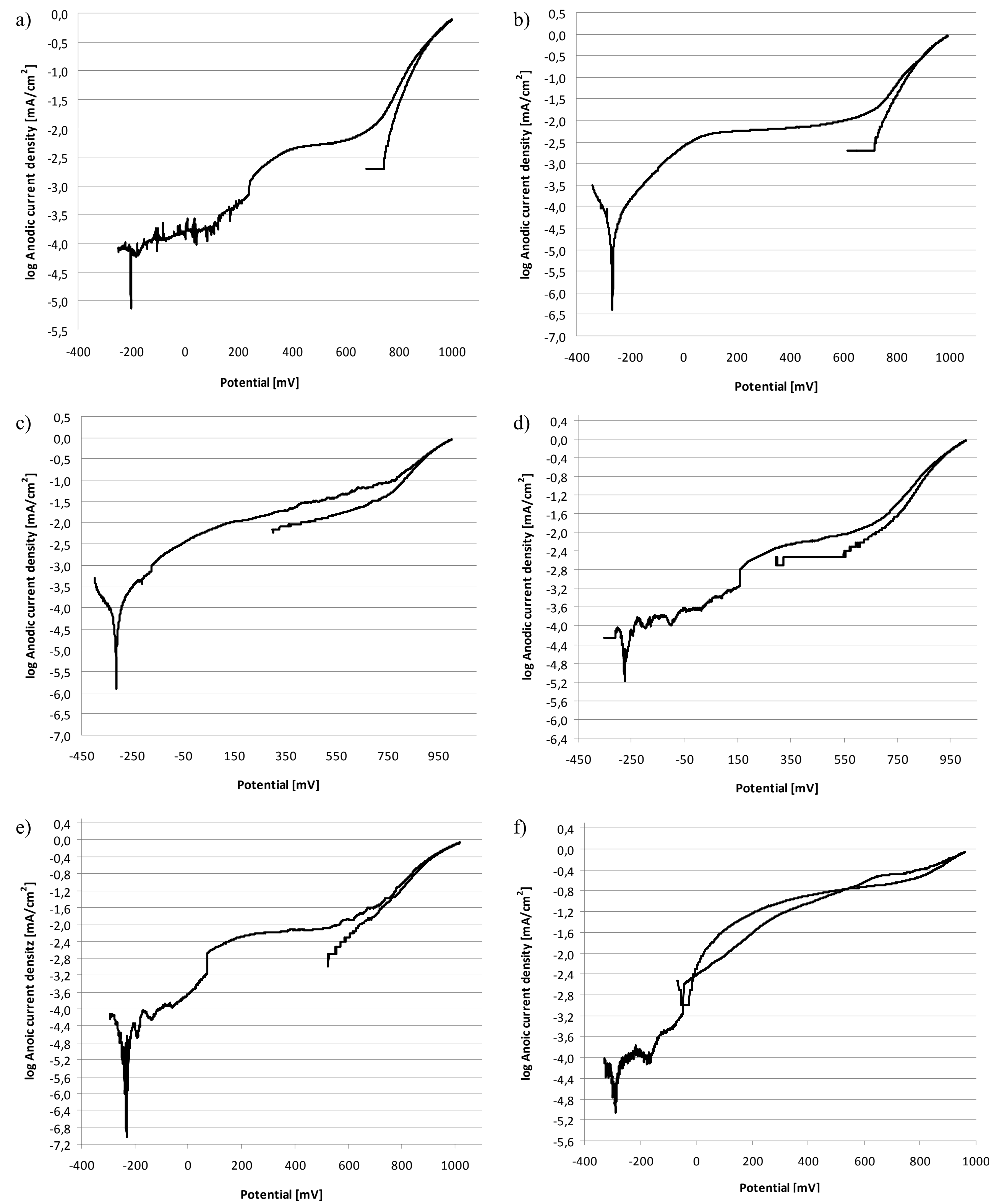

Fig. 5. Potentiodynamic curves of pitting corrosion alloy after different heat treatment conditions: a) casting stage, b) solutionized stage, c) solutionized and ageing by 4 h, d) solutionized and ageing by 8 h, e) solutionized and ageing by 16 h, f) solutionized and ageing by 24 h

Table 4.
Effect of the age hardening on electrochemical parameters of testing Remanium 2000+ cobalt alloys

Specimens	Corrosion potential E_{cor}, mV	Corrosion current density i_{cor}, µA/cm^2	Polarization resistance R_p, kΩcm^2	Breakown potential E_b, mV	Repassivation potential E_{cp}, mV
Re/1430	-202	0.002	11	838	929
Re/1430/P	-264	0.06	408	861	882
Re/1430/4	-327	0.12	215	845	941
Re/1430/8	-340	0.075	423	835	937
Re/1430/16	-266	0.035	453	833	937
Re/1430/24	-364	0.075	340	855	543

Realized research of pitting corrosion gave an information about electrochemical parameters of alloy and effect of the age hardening on anticorrosion (Table 4). For research was decided that the corrosion current (i_{cor}) and repassivation potential (E_{cp}) values were state the corrosion resistance studied material. Realized research suggested that Remanum 2000+ characterized best anticorrosion protection after solutioning and ageing by 16 hours because both parameters are high or the highest: E_{cp} = 937 mV and i_{cor} = 0.05 µA/cm^2 and. The worst pitting corrosion protection was characterized alloy Remanium 2000+ after solutioning and ageing by 24 hours: E_{cp} = 543 mV, i_{cor} = 0.1 µA/cm.

3.2. Hardness results and structure observation

Hardness results analysis for tested Co-Cr-Mo alloy for all age hardening stages allow to determined that increase time of the ageing effect on increase hardness. After solutioning hardness decrease to 358 HV_1 what is about 50% of value compared to cast sample hardness 671 HV_1 and during the time of ageing increase the hardness also increase from 358 HV_1 to reach 627 HV_1 so near the value of cast (Fig. 6). Although the highest hardness characterized alloy just after casting without any heat treatment (Table 5). That same characterized different alloy with carbon, where increase carbides influence on higher hardness [21].

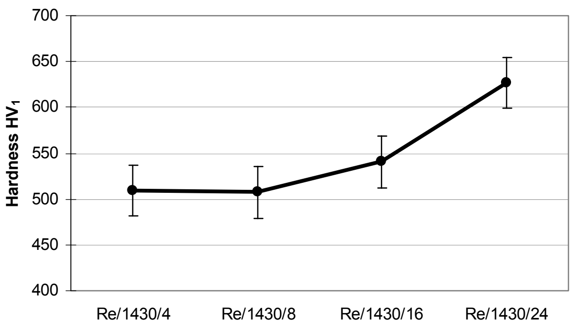

Fig. 6. Effect of the age hardening time on hardness Co-Cr-Mo

The light microscope structures observation of the Remanium 2000+ alloy for all age hardening stages are shown that all samples have similar two phases eutectic dendritic microstructure (Fig. 7). Effect of increasing the ageing time on structure was observed as appeared more stacking faults formation especially fr treated by 8 and more hours. The discontinuous lines find on structures that's possibility the discontinuous precipitation of carbides that same like in different works [17]. The structure is consists of dendrites - dark phase and interdendritic region - light phase.

Table 5.
Hardness results research Remanium 2000+ alloy

Specimens	Hardness HV_1	Standard deviation
Re/1430	671	± 9
Re/1430/P	358	± 14
Re/1430/4	510	± 66
Re/1430/8	507	± 42
Re/1430/16	541	± 25
Re/1430/24	627	± 19

4. Conclusions

On the grounds of realized study and research about effect of age hardening on alloy Remanium 2000+, was elaborate following conclusions:

- age hardening has effect on the corrosion resistance especially on the corrosion potential, because if longer ageing time then the potential was decreased, to reach value -364 mV in compare with the E_{ocp} = -202 mV after cast;
- the effect of ageing time on other electrochemical parameters like breakdown potential and repassivation potential wasn't performed, because pitting potential for ageing by 4, 8, 16 or 24 hours was on range 833-855 mV, an the repassivation potential after ageing behave that same reach the values from range 937-941 mV;
- the smallest repassivation potential 543 mV has characterized specimen after 24 h ageing;
- hardness of analysed alloy during realized age hardening after solutionized has increased with increase the process time and the higher hardness 627 HV_1 characterized specimen after ageing by 24 hours;
- effect of the ageing on structured was observed by increasing the discontinuous precipitation of stacking faults formation while longer time, and the most of discontinuous precipitation and faults was observed in specimen aged by 24 h.

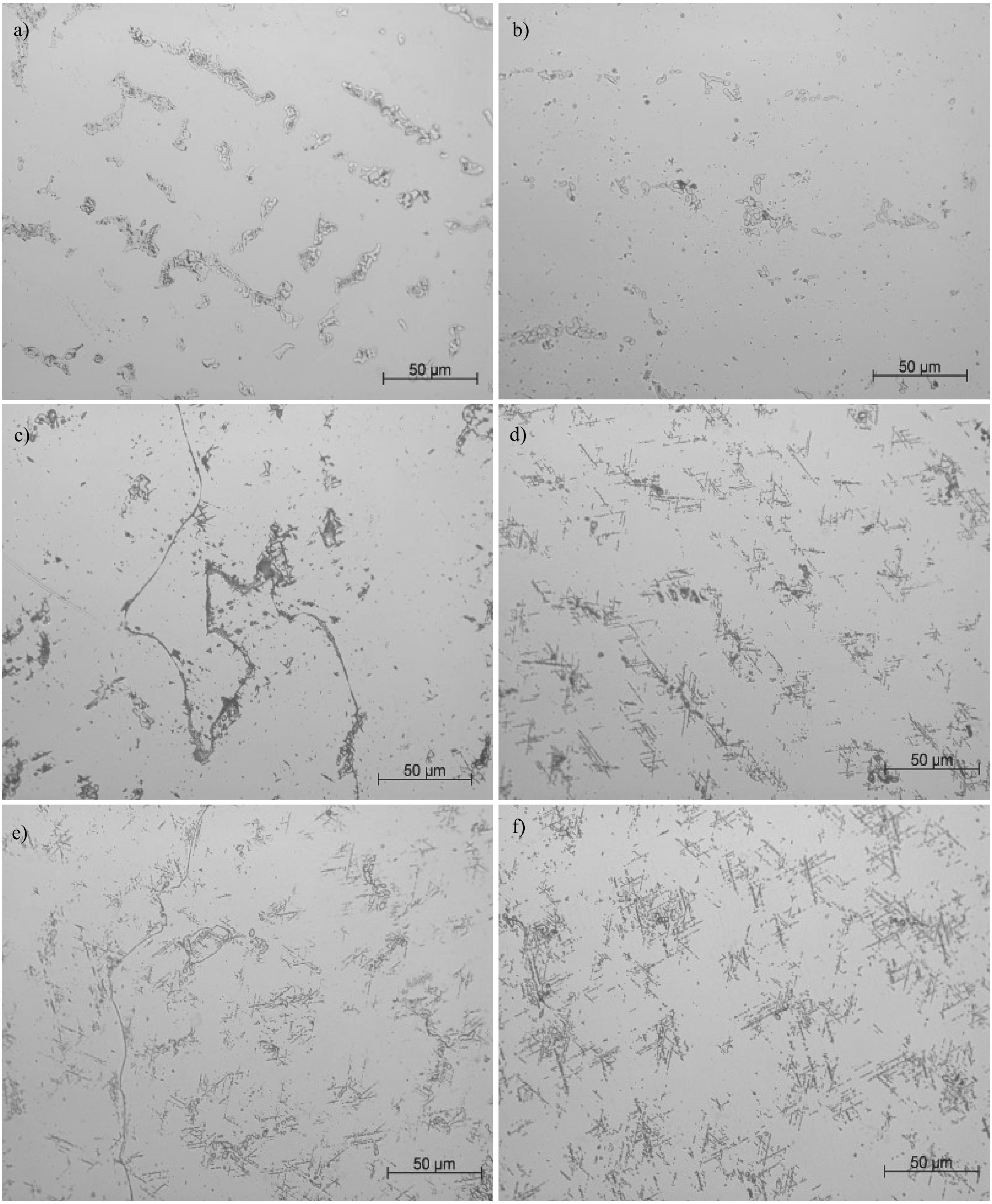

Fig. 7. Structure of research alloy in all age hardening stages, shown dendrites crystals, after etched in $HCl+H_2SO_4+HNO_3$: a) casting from 1430°C, b) solutioning 1250°C, c) ageing by 4 h, d) ageing by 8 h, e) ageing by 16 h, f) ageing by 24 h

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