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METAL ALLOYS WITH ANTIMICROBIAL PROPERTIES

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Abstract: *Biomaterials are usually non-magnetic, non-corrosive, resistant and durable materials, with a pleasant appearance and possibly recyclable. They are manufactured by clean and efficient technologies, from high quality raw materials, which have properties adapted to specific requirements. The paper presents research on the obtaining of biocompatible austenitic stainless-steel type that have been doped with chemical elements such as Cu, Ag and Ti, which are known for their beneficial effects in terms of inhibiting the ability of microbes and bacteria to proliferate. Following the microstructural analyses, it was observed that the simultaneous addition of these elements allows the grain refinement, with the effects of improving the mechanical properties.*

Key words: *antimicrobial, properties, microstructure, chemical composition, doping.*

1. INTRODUCTION

Alloys used in bioengineering require significantly improved physical and chemical properties compared to classical industrial alloys [1]. Most of the applications in which such alloys are used have clear requirements for the properties such as high oxidation and corrosion resistance, superior wear and fatigue resistance, high thermal stability and excellent electrocatalytic capacity [2–4]. Other fields that use alloys with special properties are the energy conversion and storage industry, the biomedical industry, the aerospace industry and the food industry [5]. Due to the increase in bacterial resistance to bactericides and antibiotics and the toxicity of many organic antimicrobial agents as well as allergic reactions, inorganic antimicrobial agents such as metallic nanoparticles containing Ag, Au, MgO, CuO, TiO2 and ZnO are continuously being developed with the aim of to control bacterial growth due to their durability, improving stability under severe processing conditions and safety [6–9]. Certain thin films prevent and reduce the spread of microbial organisms, including bacteria, fungi and viruses. They can be prepared from a variety of nanostructured materials, including metal nanoparticles, metal oxides, plant materials, enzymes, bacteriocins, and polymers [10–12]. Their antimicrobial mechanism varies mainly depending on the types of active agents from which the film is made [13–14]. Metal nanoparticles are among the widely reported materials with promising antimicrobial activity due to their small size and high surface-to-volume ratio, which gives them a relatively large reactive surface to interact with microbial molecules [15–16]. They can be easily complexed with other biomaterials to exert enhanced antibacterial activity. For example, thin films based on silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) have high antibacterial activity against various bacterial species [17–19].

An increasingly explored method, which ensures the long-term protection of metal components in direct contact with biological substances, are alloys doped with different chemical elements that develop antimicrobial activity [20–22]. The main chemical elements known to have bactericidal or fungicidal properties are Ag, Cu, Ti, Zn. The main mechanism by which metal-based thin films can inhibit microbial growth is through the release of ions such as Ag+, Zn2+, Au+, and Cu2+. These ions interact directly with the cell walls of microorganisms to create pores or holes that disrupt their normal functioning. In addition, they also form complexes with enzymes or other cellular components that can further inhibit biofilm growth or cause membrane damage and cell death. For example, it was found that silver ions can quickly penetrate the membranes of bacterial cells, which leads to the interruption of oxidative processes such as respiration and protein denaturation and then damage to the integrity of microbial cells. Copper is a metal known for its good antimicrobial activity, with a bactericidal efficacy of up to 99.9% [22].

The paper presents some experimental stainless-steel recipes obtained by electric arc melting in an inert atmosphere, using a VAR ABJ 900 installation. To obtain improved corrosion resistance and antimicrobial properties, elements such as Cu, Ag and Ti were added to the chemical composition, in different proportions. The effects produced by the simultaneous or individual addition of these chemical elements with antimicrobial properties on the microstructure of a biocompatible steel of type 316L, which constituted the basic matrix for the design of experimental doped alloy recipes, were analyzed.

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2. MATERIALS AND METHODS

2.1. Materials

To perform the experimental alloys calculation for stainless steels doped with Cu, Ti and Ag, standard chemical composition of an SS316L austenitic stainless steel was used. This steel is often used for the manufacture of current medical instrumentation. The chemical elements such as Cu, Ag and Ti were added in different proportions and combinations to analyze their effect, separately or in combination, on the microstructure, corrosion or biological behavior in different environments. Raw materials with advanced purity (more than 99.9%) were used to make the experimental alloys.

The projected chemical composition of experimental alloys with anti-microbial properties (wt.%) is shown in Table 1.

The total mass of each experimental alloy and the individual masses of the raw materials used, determined by weighing with a precision electronic balance (Kern analytical balance, with accuracy measurement of 0.001g) are shown in Table 1.

2.2. Metallurgical aggregate

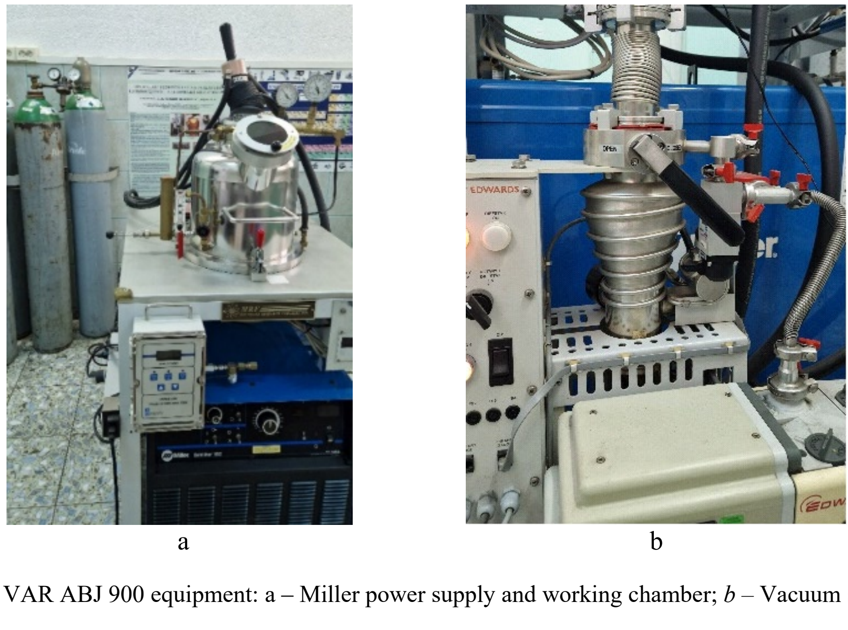
The metallurgical aggregate used to obtain the experimental alloys presented in this paper was the vacuum arc remelting equipment (RAV MRF ABJ 900, ERAMET Laboratory, SIM Faculty, UNSTPB, Fig. 1a). The vacuum pressure during arc melting, of more than 10 mm Hg, was provided by the vacuum system (Fig. 1b), consisting of Edwards preliminary pump and molecular vacuum pump. Melting took place under argon atmosphere at a pressure of 1.85 mbar. The vacuuming plant ensured a minimum throughput of 50 dm^3/h that allows avoided vaporization loss of high vapor pressure chemicals during melting.

The melting of raw materials process was realized by means of an electric arc primed between the metal charge placed on a high purity copper mold and a non-fusible tungsten electrode alloyed with 2% Th. The mold in which the raw materials were melted consists of two plates, one provided with alveoli with predetermined dimensions and the other connected to a water-cooling system, to ensure a low temperature of the plate and to avoid diffusion effects with the metallic melt. The chemical composition of the base materials is shown in Table 2.

Table 1

The mass of experimental alloys (g)

Alloy	Chemical elements proportional mass [g]	Initial total mass M_0 [g]	Final mass (after melting) M_1 [g]
10	Fe = 20.183; Mn = 1.34; Cr = 7.33; Ni = 3.33; Mo = 1; Cu = 0; Si = 0.167; Ti = 0; Ag = 0	33.34	33.037
11	Fe = 19.17; Mn = 1.33; Cr = 7.33; Ni = 3.33; Mo = 1; Cu = 1.08; Si = 0.16; Ti = 0; Ag = 0	33.40	33.39
22	Fe = 19.15; Mn = 1.35; Cr = 7.33; Ni = 3.33; Mo = 1; Cu = 1; Si = 0.17; Ti = 0.08; Ag = 0	33.41	32.795
33	Fe = 19.01; Mn = 1.34; Cr = 7.33; Ni = 3,33; Mo = 1; Cu = 1.17; Si = 0.17; Ti = 0; Ag = 0	33.49	33.336
44	Fe = 18.95; Mn = 1.34; Cr = 7.33; Ni = 3.33; Mo = 1; Cu = 1.17; Si = 0.167; Ti = 0.06; Ag = 0.034	33.38	33.337
55	Fe = 18.85; Mn = 1.34; Cr = 7.33; Ni = 3.33; Mo = 1; Cu = 1.34; Si = 0.17; Ti = 0; Ag = 0	33.36	33.30
66	Fe = 18.78; Mn = 1.34; Cr = 7.33; Ni = 3.33; Mo = 1; Cu = 1.34; Si = 0.17; Ti = 0.06; Ag = 0.05	33.40	33.318



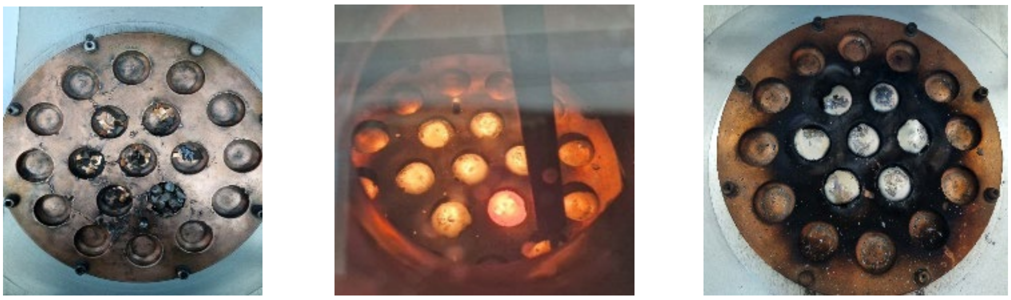
a b

Fig. 1. VAR ABJ 900 equipment: a – Miller power supply and working chamber; *b* – Vacuum system.

Table 2

Chemical composition of experimental alloys with antimicrobial properties (wt.%)

Sample	Cr	Ni	Mo	Mn	Si	Cu	Ti	Ag	Fe
0	22	10	3	4	0.5	0	0	0	Bal.
1	22	10	3	4	0.5	3	0	0	Bal.
2	22	10	3	4	0.5	3	0.1	0	Bal.
3	22	10	3	4	0.5	3.5	0	0	Bal.
4	22	10	3	4	0.5	3.5	0.1	0.1	Bal.
5	22	10	3	4	0.5	4	0	0	Bal.
6	22	10	3	4	0.5	4	0.1	0.1	Bal.



a b c

Fig. 2. Images of alloys during obtaining process.

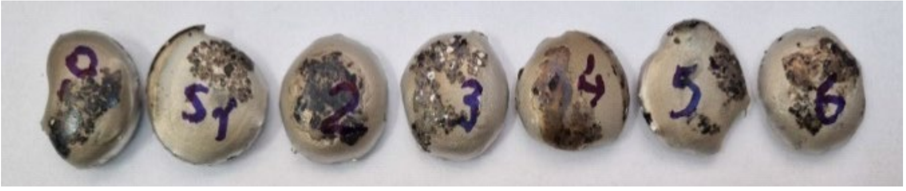


Fig. 3. Samples of experimental biocompatible stainless steels doped in different proportions with Cu, Ag and Ti.

The main stages of making the alloy in the VAR installation were:

- establishing the composition of the charge (the placement of the raw materials that make up the alloy recipe, depending on the melting temperature and the vaporization tendency, to avoid evaporation losses during melting in the electric arc (which develops temperatures above 3000 °C) (Fig. 2a).
- closing the working chamber and ensuring tightness.
- adjusting the vacuum values necessary for the alloying process (with the preliminary vacuum pump and then with the diffusion pump).
- flooding the working chamber with argon at a working pressure of 2 bar, to ensure the stable burning conditions of the electric arc and the protection of melts.
- ignition the electric arc between the solid raw material and the electrode tip, then maintaining and moving the arc across the surface of the alveoli filled with solid materials for their complete melting (Fig. 2b).
- rotating the samples over the opposite surface and re-melting three times on each side, to homogenization of the chemical composition.
- solidification of the melted alloy under argon atmosphere on the cooled copper plate until a temperature of 100 °C is reached (Fig. 2c).

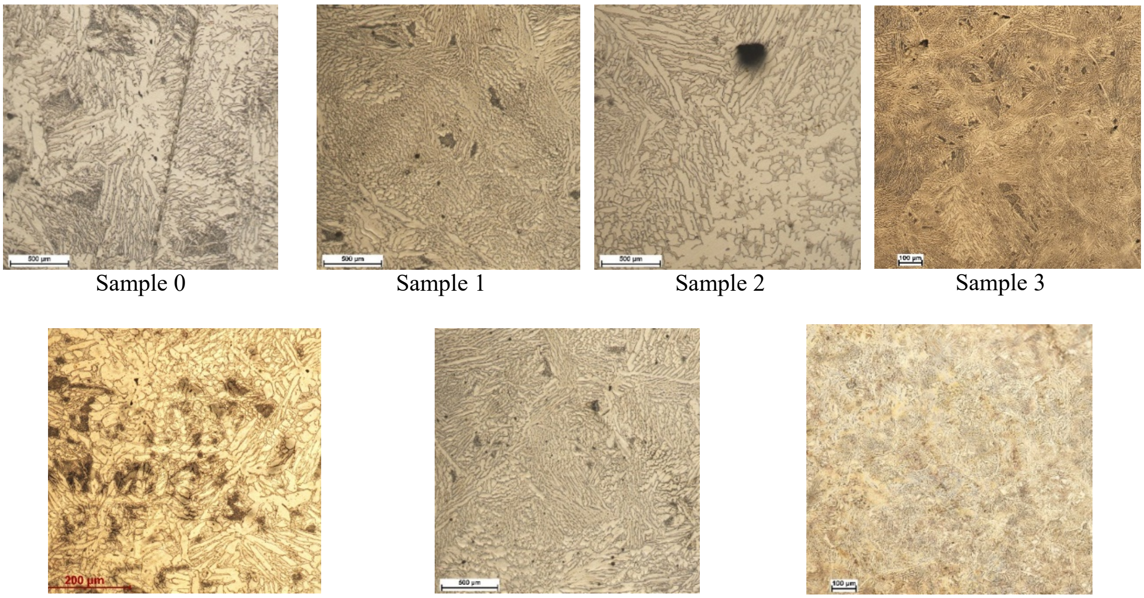
3. RESULTS AND DISCUSSION

3.1. Microstructure

After complete cooling, the obtained samples were coded to maintain the traceability, with codes ranging as follows: 0 (for undoped alloy) and 1 to 6 (for alloys doped with Cu, Ag and Ti) (Fig. 3).

The samples were machined for obtain flat surfaces, were sanded with abrasive papers (with successive grain sizes from 240 to 2400 grit) and polished with alpha alumina in suspension (grain sizes from 3 to 0.1 microns) on a felt textile support. All sanding and polishing operations were carried out under a softened water jet using specialized metallographic machines (Fig. 4).

Fig. 4. Samples sanded with abrasive materials.



Sample 0 Sample 1 Sample 2 Sample 3

Sample 4 Sample 5 Sample 6

Fig. 5. Optical microscopy images of experimental stainless steel samples doped with Cu, Ti and Ag.

After surface's preparation, the samples were washed with ethanol and then were etched using Kalling's reagent (2g $CuCl_2$; 40 ml HCl; 40 ml C_2H_6O), to reveal microstructural aspects. Before being examined with the optical microscope, the surfaces of the samples were washed again with deionized water and dried with warm air. The optical microscopy images for the 7 samples of the experimental alloys are presented in Fig. 5.

The experimental alloys were designed on the principle of ensuring the chemical composition of an austenitic high-alloyed steel, currently considered to be biocompatible. As a novelty, the designed alloys were doped with biocompatible elements such as Copper, Silver and Titanium in different concentrations.

For comparison, un experimental alloy without doping elements was also obtained. The term doping was used to emphasize the low concentration of the elements Cu, Ag and Ti, compared to the main elements from the stainless-steel metallic matrix, as Fe, Cr and Ni.

The maximum concentration of Cu doping element was used, of 3; 3.5 and 4 wt.% respectively.

Other samples doped with combinations of Cu + Ti, Cu + Ag, or with all 3 doping elements were also obtained. All microstructures of the experimental alloys were typical for cast alloys with dendritic appearance. A tendency of grain refinement was observed in the doped samples (1 to 6) compared to the control sample (0).

The microstructure of the experimental alloys was influenced by the doping elements. A grain refinement was observed when the three elements (Cu, Ag and Ti) was used together as doping elements.

5. CONCLUSION

The aim of the study was to obtain alloys to determine the effects of doping elements on corrosion behavior in simulated chemical or biological environments, as well as for ultra-thin layer deposition tests by concentrated energy methods to enhance biocompatibility properties.

This research demonstrated that biomaterials like doped stainless steels can be successfully obtained using Vacuum Arc Remelting Equipment.

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