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VERSATILITY OF NICKEL-ALUMINIUM BRONZES AS WEAR RESISTING MATERIALS

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ABSTRACT

The paper presents the results of experimental research regarding the establishing of some chemical positions of the nickel-aluminium bronzes used as monoblock and bimetallic bearings. The areas of the applications are discussed with reference to the working property required of these alloys. Normally a combination of several properties finally governs the selection of a particular material. The correlations between chemical compositions, structures and properties are analysed with a view to selecting the material for certain application. The wear resistance and the corrosion behavior into seawater of the nickel-aluminium bronzes with variable content of iron and manganese are studied.

KEYWORDS: nickel-aluminum bronzes, alloying elements, bimetal, wear applications, seawater corrosion

1. Introduction

The nickel-aluminum bronzes comprise a wide range of compositions by alloying with some specifically chosen elements (iron and manganese). Consequently there is a family of copper-based alloys with complex metallurgical structures that offer a combination of mechanical and chemical properties unmatched by any other alloy series.

This feature often makes nickel-aluminum bronzes the first choice (and sometimes the only logical choice) for applications. These attributes are: excellent strength, similar to that of low alloy steels; excellent corrosion resistance, especially in seawater and similar environments, where the alloys often outperform many stainless steels; favorable high temperature properties, for short or long term usage; good resistance to fatigue, ensuring a long service life; good resistance to creep, making the alloys useful at elevated temperatures; oxidation resistance, for exposure at elevated temperatures and in oxidizing environments; ease of casting and fabrication, when compared to many materials used for similar purposes; high hardness and wear resistance, providing excellent bearing properties in arduous applications; ductility, which, like that for all copper alloys, is not diminished at low temperatures; good weldability, making fabrication economical; readily machined, when compared with other high-duty alloys; low magnetic susceptibility, useful for many special applications; ready availability in cast or wrought forms [1, 2, 3].

The nickel-aluminum bronzes can be considered a versatile material. By selecting the elements content and their controlled added it can modify the properties. This is easier as than redesigning parts and modification of their fabrication technology. But for this it is necessary to correct knowledge of the working conditions for demanding applications. This is the most important criterion to follow when making a good material selection. This paper presents the results of several experimental studies for an optimum selection of the composition, the thermal treatment and the manufacturing method of the nickel-aluminium bronzes alloyed with iron and manganese, used as wear resisting materials. For each industrial application the material selection was based on the requirements for working conditions: friction conditions, forces and pressures, lubrication, corrosion conditions etc.

2. Constitution of nickel-aluminium bronze alloys and its influence on the properties

The nickel-aluminium copper alloys are a range of copper-based alloys in which aluminium is the primary alloying element (up to 14-15%). For obtaining the aluminium bronzes with excellent properties especially for marine applications the addition of nickel is important. Besides Ni and Al, the main alloying elements of the bronzes analysed include Mn and Fe that could also be added into nickel-aluminium bronzes to improve their properties. The content of each element added has an important influence on the structure and, as a result, on the properties [4, 5].

The microstructure of these bronzes is quite complicated, not only because of its multiple alloying elements, but also because several phase transformations could take place during their preparation (Figure 1)

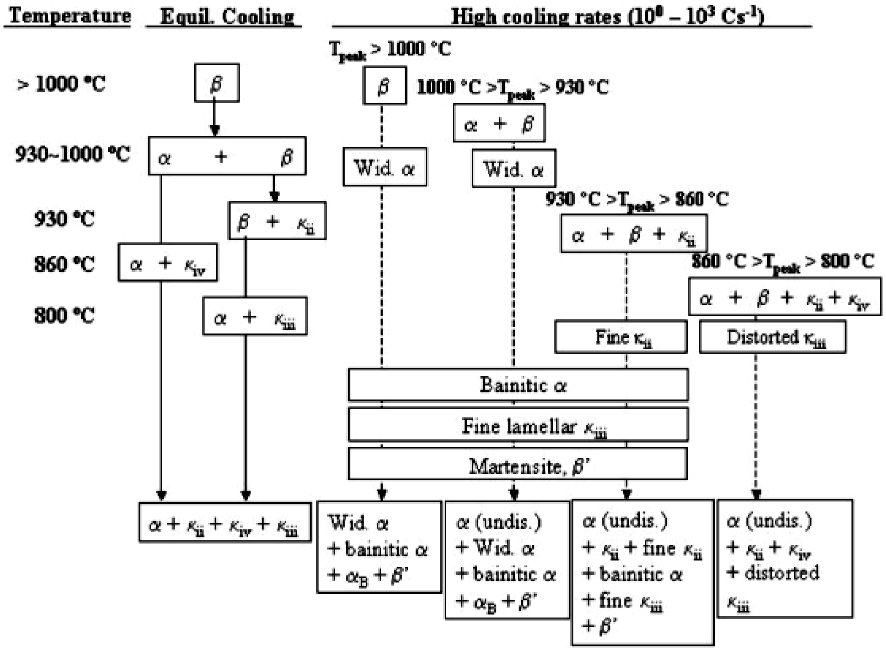


Fig. 1. *Transformation products of nickel-aluminium bronzes during cooling [6].*

Binary Cu-Al alloys (Figure 2a) containing less than 9.4 wt. % Al are single phase α alloys. The solidification commences with the formation of α dendrites.

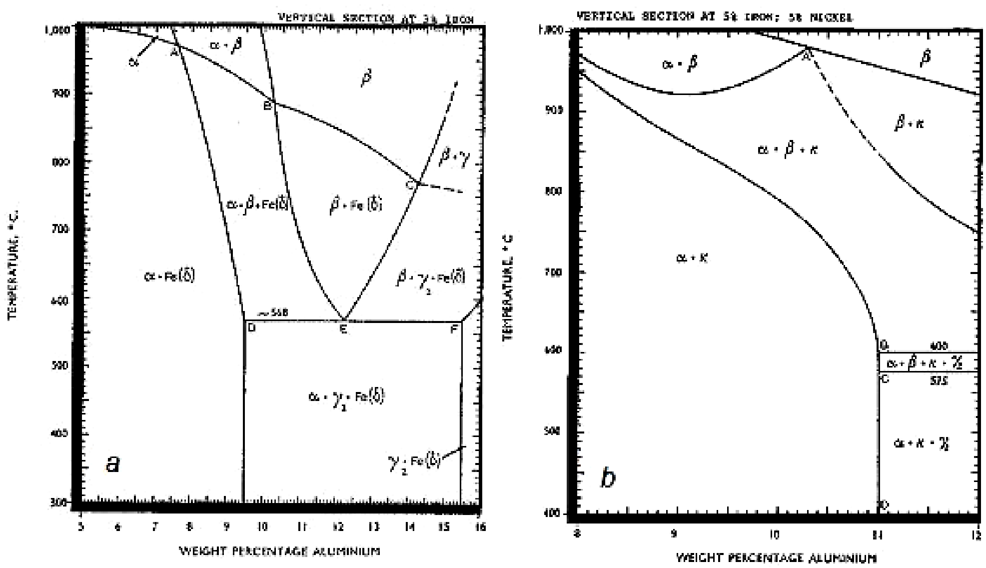


Fig. 2. *Equilibrium diagram of Cu-Al system (a) and a cross section of CuAlFeNiMn diagram at 5% Fe and 5%Ni (b). [2]*

The freezing range is short and so segregation is not pronounced and the alloy solidifies as a single phase.

Copper-aluminum alloys containing more that 9.4 wt. % Al solidify as a single-phase bcc β; under slow-cooling conditions, fcc α gradually forms from the β until the remaining β transforms to α + γ in a eutectoid reaction at about 570ºC. The γ phase corrodes preferentially due to its high Al content and its presence is thus deleterious.

Even greater strength and hardness is developed in alloys containing more than 10% Al. Such alloys are favored for specialized applications that require superior wear resistance. Other alloying elements also modify the structure and thereby increase strength and corrosion resistance: iron improves tensile strength and acts as a grain refiner; nickel improves yield stress and corrosion resistance and has a beneficial stabilizing effect on the metallurgical structure; manganese also performs a stabilizing function [7].

The addition of nickel and iron to copper-aluminum alloys extends the α phase field while effectively suppressing γ phase formation (Figure 2b) [2].

The mechanical properties of aluminum bronze depend primarily on the aluminum content and also on the varying proportions of secondary additions. The Ni and Fe additions have been found to considerably increase the mechanical properties of aluminium bronzes (especially give higher strength) through the formation, from both the α and the β, of complex intermetallic κ phases [8].

The alloy remains fully β upon cooling to about 1000ºC. Below this temperature α phase precipitates from the β with Widmanstätten morphology, followed by the nucleation of globular κ, which is nominally Fe_3Al, in the β. This phase is apparent in the micrograph of the cast alloy (Figure 3) and is often termed $κ_{ii}$. In Cu-Al-Ni-Fe alloys containing ≥ 5 wt. % Fe, an Fe_3Al phase forms with a dendrite morphology, which is usually termed $κ_i$. At about 850ºC, the solubility of Fe in the α is exceeded and fine κ precipitates begin to form; these fine precipitates are also nominally Fe_3Al and are usually termed $κ_{iv}$. Finally, at about 580ºC, a nickel-rich κ phase, $κ_{iii}$, forms from β. The α phase is an fcc equilibrium terminal solid solution with a lattice parameter a = 3.64 a eutectoid reaction giving lamellar α + κ. Proeutectoid κ may exhibit a globular morphology. The α phase is an fcc equilibrium terminal solid solution with a lattice parameter a = 3.64Å [15]. The Fe_3Al phases ($κ_i$, $κ_{ii}$ and $κ_{iv}$) have a DO_3 structure; the lattice parameter of $κ_{ii}$ is 5.71Å while that of $κ_{iv}$ is 5.77Å. The NiAl ($κ_{iii}$) phase exhibits a B_2 structure with a lattice parameter of 2.88 Å. Thus, fully ordered Fe_3Al ($κ_i$, $κ_{ii}$ and $κ_{iv}$) and NiAl ($κ_{iii}$) phases will have inter-atom spacing that differ by less than one percent.

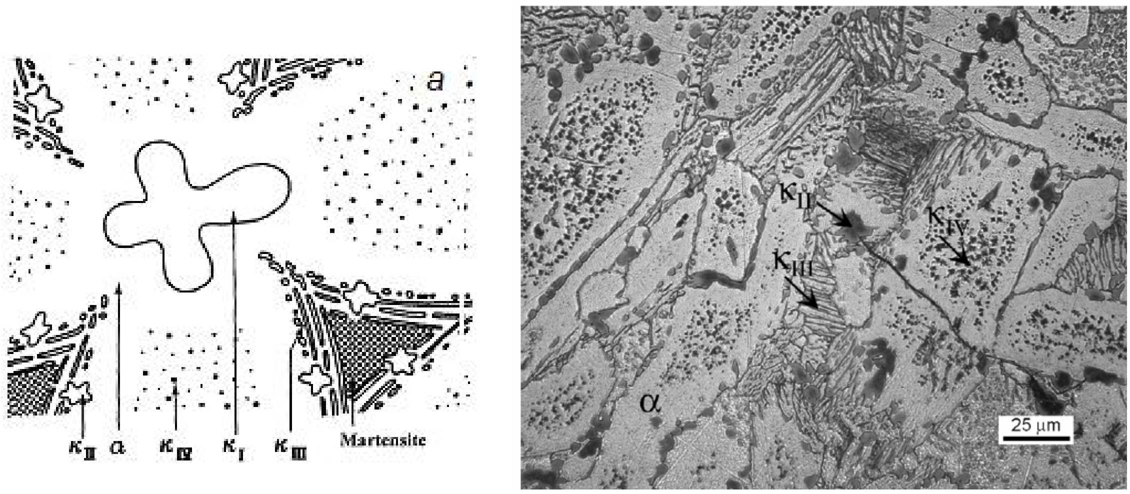


***Fig.3.** Microstructure of NAB specimens: a) schematic representation; b) optical micrograph of as-cast aluminium bronze (etched with ferric chloride and hydrochloric acid in ethanol) [8, 9].*

Iron acts as a grain refiner both during solidification and during slow cooling, and increases resistance and hardness: every Fe percentage in a bronze with aluminium leads to an increase of the mechanical resistance of the alloys with 2.8 daN/mm^2. The addition of nickel increases the mechanical characteristics, the antifriction and anticorrosion properties.

The nickel addition also increases compactness and high temperature resistance. The manganese increases resistance, plasticity and antifriction properties, but significantly decreases fluidity. In comparison with iron, manganese behaves as a stabilizer. It is dissolved in the solid solution and it doesn't provoke structural changes [8, 10].

3. Experimental research and industrial applications

In cast and wrought forms the literature recommends the nickel-aluminum bronzes for their excellent wear resistance. Metal-sprayed or welded overlay deposits of aluminum bronze on steel also provide effective wear-resistant surfaces. As a result these alloys can be used as bearing materials. They thrive on heavy loads, shocks and harsh working environments. In rotating applications, best results are usually achieved when running aluminum bronzes against hardened surfaces. When lubrication of sliding surfaces is less than ideal, aluminum bronzes are superior to ferrous materials [7, 11].

The research summarized in this paper were focused on the establishing of the optimum compositions of the bronzes as wear resisting materials for monoblock and bimetallic parts.

These were tested as bearing at the following industrial applications: steel mill, presses in rubber industry, manufacturing of the ferrites, offshore drilling equipments, and the parts for machine - building industry. Also the corrosion behaviour into marine media for the bimetals was analysed.

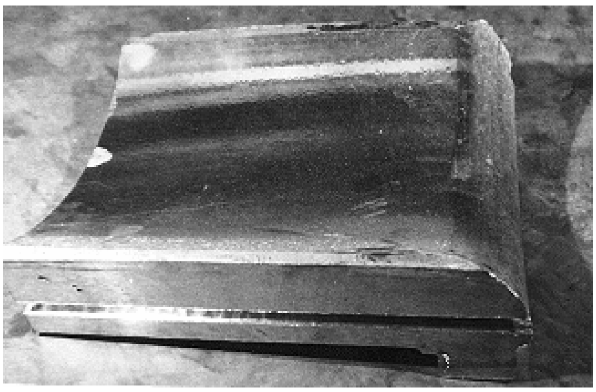
The experiments were based on the correlations between the chemical composition, structure, properties and manufacturing methods in accordance with a thorough knowledge of the working conditions for each application.

The conventional materials that were used to cast the steel mill bearings studied (Figure 4a) are tin bronzes (10 - 14 %Sn sometimes with Pb additions) [12, 13]. For their substitution a copper alloy of around 6% - 10% of aluminium with addition of nickel, iron and manganese was tested. After experimental study the following ranges of chemical compositions were tested for this application: 6.5 - 7.5 %Al; 1-1.5 %Ni, 1-1.5 %Fe%; 1 - 1.5 %Mn, Cu balance.

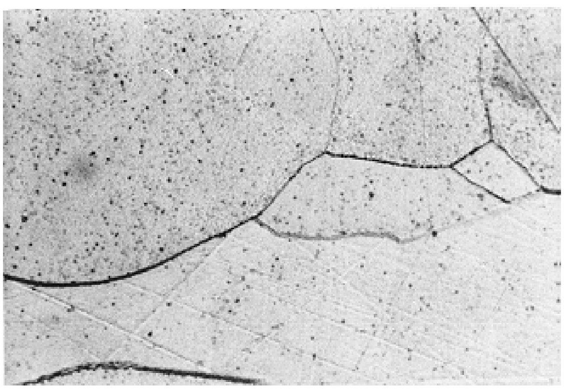
These ensure an optimum structure in accordance with required mechanical properties and specific working conditions (wear conditions and lubrication, forces, specific pressure, environmental media etc.). There are single phase α alloys. The solid solution α is the soft base and it ensures the plasticity of the mill bearing. The other alloying elements involved the development of the complex intermetallic κ phases.

These are incorporated and uniformly distributed as hard compounds in the soft base (solid solution α). A like structure ensures the properties for a good behavior in practical applications. Figure 4b show the microstructure of the aluminium bronze with 7.2 %Al, 1.2 %Ni, 1.2 %Fe, 1.32 %Mn, and Cu balance.

A crucible graphite furnace was used to make the alloy. Argon was blown into the melting bath to produce degasification: 0.2 Nm^3 at 0.3 – 0.5 daN/cm^2. Also charcoal as protective flux and respectively phosphor copper as deoxidizer were used. The alloy was casted at maximum 1150 ^{0}C [14, 15].



a.



b.

Fig. 4. *Mill bearing (400x600mm) (a) and optical micrograph of aluminium bronze alloyed with nickel, iron and manganese (b)*

The rubber industry is other industrial domain whe the utilization of the nickel-aluminium bronzes as wear resisting material was studied. The castings which were assembled into presses for tire vulcanization are exposed at clamping forces variable into range of 200-546x10^3 daN.

The composition of the experimental material is given in table 1 [16].

Table 1. *Composition (wt. %) of experimental bronzes for the rubber industry*

Al	**Ni**	**Fe**	**Mn**	**Sn**	**Pb**	**Cu**
7.90	2.50	5.84	1.50	-	-	bal.
5.58	1.30	4.60	1.50	-	-	bal.
10.00	1.20	5.24	2.10	-	-	bal.
8.85	4.00	5.6	1.5	-	-	bal.

The castings were heat-treated through annealing. The following parameters were recommended: heating rate ≤80^{0}C/h; tempering temperature 600^{0}C, treatment time 5 minute/mm; cooling in air. This treatment controls the coarseness of the κ precipitates and improves the mechanical properties.

For machine - building industry systems aboard ships and offshore platforms the unstandardized aluminium bronzes were casted as bars with diameters from 70 to 600 mm and machine worked to obtain parts used as bushings or bearings.

In other applications the nickel-aluminium bronzes were used to obtain bimetals because, most often than not, a single material cannot satisfy all of the working requirements in special conditions. For these applications the bimetals are recommended because they satisfy working conditions impossible for a single metallic material. In the cases analyzed the bimetals were obtained by deposition of bronze layers on steel support by a welding process. The high resistance to corrosion of the aluminium bronzes with nickel, manganese and iron, combined with their ability to carry heavy loads under friction conditions without excessive wear, makes them suitable for antifriction layers deposited on steel for bearings constructions.

This paper presents the results of the experimental research carried out to establish the corresponding chemical composition of the bronze and the cladding technology in accordance with a specific industrial application.

The first experimental bimetal obtained was subjected to high contact pressures. The parts named PATINA TPA 45 and CAMA 45 were components that were used into ferrites presses [17], characterized by a high hardness necessary for special working conditions: a good wear resistance at a specific contact pressure of min. 200 daN/mm^2 and a working speed of 60 m/min, high corrosion and abrasion resistance, a minimum wear loss at the end of the working time. Bronzes with variable compositions (Table 2) were deposed as multilayers on steel support (C≤0.25%). These are casted as bars with diameters of 4mm.

Table 2. *Bronzes with variable compositions and their adequate hardness*

Samples	**Chemical composition** (%wt)					**Hardness (HB)**
	Al	**Ni**	**Fe**	**Mn**	**Cu**	
1	7.8	-	3.5	-	bal.	178
2	9.5	4.5	4.6	0.8	bal.	214
3	10.6	3.7	4.2	0.9	bal.	230
4	11.2	4.6	4.8	1.0	bal.	275
5	14.7	4.1	4.4	1.1	bal.	338

Argon shielded arc welding (WIG welding) with the following parameters was the method applied: 20-30l/min for the inert gas flow; 200-250A for the welding current. It is seldom necessary to preheat the steel samples to higher than 150-200°C. Excessive preheat can lead to the heat-affected zone being excessive, with a greater volume of metal at risk of hot cracking and distortion problems. [7, 18].

In accordance with the properties required by the working conditions the following composition range was recommended: 11-12%Al, 4-5%Ni, 4-5%Fe, 0.8-1.2%Mn, Cu balance. In other applications the nickel-aluminium bronzes were tested as wear resistant material deposed on the cones for the drilling pipes used by petroleum exploitation industry (Figure 5). The cones were made by steel with ≤0.25%C, ~0.3%Mo and ~3.5%Ni [19, 20]. An important problem that arises is the service endurance of the bearings. The cones are usually subjected to high variable contact pressures on the sliding surface and to wear under improper lubrication. The nickel-aluminium bronze was tested for the substitution of the classical antifriction material AgMn15. The silver alloy is very expensive. The same welding method for cladded bronze was used. Only the welding current was different (120-150A). For selecting the material more factors were taken into consideration: the properties, the results of wear tests, the economical aspects (in this case the antifriction material AgMn15 is very expensive), etc.

Also the rules imposed for parts manufacturing were taken in consideration.

Fig. 5. *Steel cone of drilling rod and its section as support for bronze deposition.*

For the steel cones it is compulsory to apply the heat treatments after antifriction layers deposition: carbonitriding (at 950°C), double quenching (at 860^{0}C and 760 ^{0}C), and stress relieving (at 180^{0}C).

In order the microstructure of the antifriction material is highly influenced and the properties and the wear behaviour are modified. The behaviour to wear was tested on an Amsler stand.

As counter-sample the hard steel thermal treated to obtained 43HRC hardness was used. The wear results are given in Table 3.

Table 3. *Results of wear behaviour tested on Amsler stand*

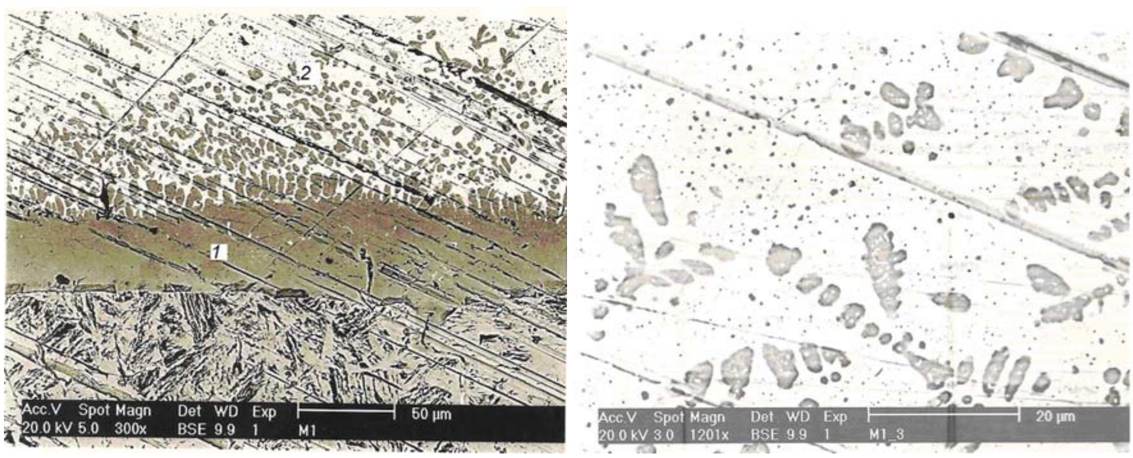
Antifriction material	**Working time**	**Friction coefficient**	**Working temperature**	**Wear of sample radius**
	[h]		[^{0}C]	[mm]
Nickel-aluminium bronze alloyed with iron and manganese	83	0.07-0.12	125-140	0.33

The heat affected zone and a transition zone are developed in the bimetal at steel-bronze interface. These were analized from the structural and the chemical composition points of view (Figure 6).

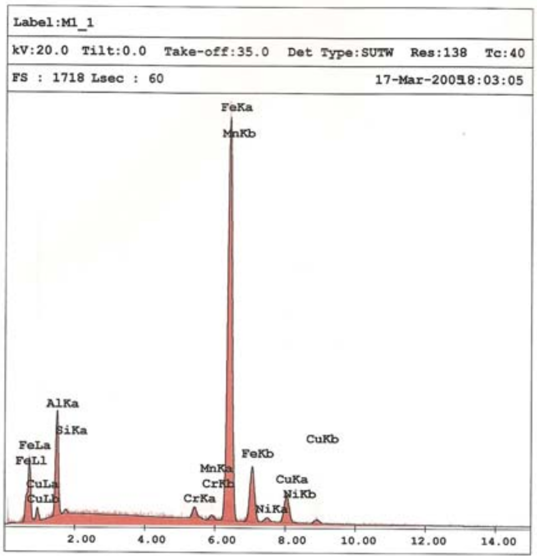
In other applications the nickel-aluminum bronzes work in marine environments. When exposed to sea water, aluminium bronze with controlled composition and structure shows a high corrosion resistance together with good resistance to heavy loads and friction conditions.

The electrolyte is not aggressive for the individual alloy [5, 10].

When the bronze and the steel as dissimilar alloys are in contact in the presence of an electrolyte (which may not be aggressive for individual metals when they are not coupled), an additional corrosion (named bimetallic corrosion) occurs (if the difference in the electrode potential is sufficiently large) [21-25]. Galvanic corrosion results from differences in composition or structure of the weld bronze and the parent steel. This may occur in the transition zone formed between the two alloys. In the case studied, the multilayer welding technology, and its parameters, may adversely affect corrosion resistance.

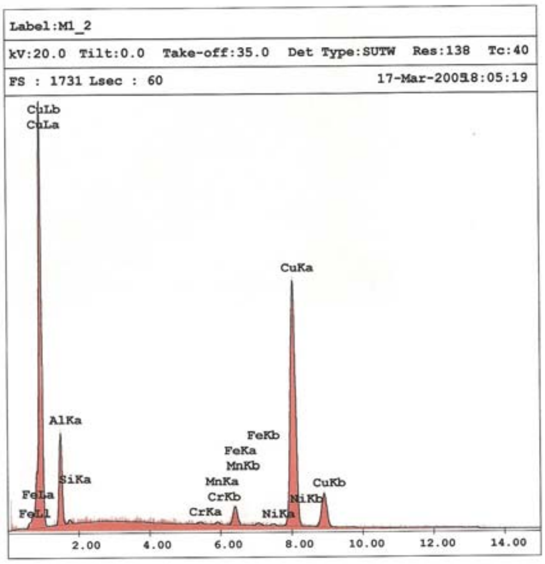


a. b.



Element	Wt %	At %	K-Ratio	Z	A	F
AlK	10.49	19.67	0.0369	1.0764	0.3267	1.0006
SiK	0.36	0.64	0.0016	1.1072	0.4007	1.0011
CrK	1.16	1.12	0.0138	0.9893	0.9843	1.2286
MnK	0.65	0.60	0.0063	0.9722	0.9920	1.0092
FeK	75.62	68.54	0.7560	0.9913	0.9953	1.0133
NiK	1.26	1.09	0.0115	1.0083	0.9051	1.0000
CuK	10.47	8.34	0.0931	0.9613	0.9248	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
FeL	28.72	1.28	2.46	22.38
CuL	6.37	2.03	5.88	3.13
AlK	54.82	5.98	1.84	9.16
SiK	2.33	8.07	17.84	0.29
CrK	7.87	7.23	6.38	1.09
MnK	3.12	5.17	11.92	0.60
FeK	322.98	4.53	0.72	71.25
NiK	3.53	4.10	10.09	0.86
CuK	23.80	3.50	2.83	6.80



Element	Wt %	At %	K-Ratio	Z	A	F
AlK	10.94	22.22	0.0320	1.0961	0.2673	1.0001
SiK	0.42	0.82	0.0016	1.1274	0.3368	1.0000
CrK	0.31	0.32	0.0033	1.0092	0.9698	1.0960
MnK	0.33	0.33	0.0037	0.9919	0.9807	1.1381
FeK	2.85	2.79	0.0344	1.0117	0.9878	1.2103
NiK	0.57	0.54	0.0059	1.0297	0.9931	1.0000
CuK	84.58	72.97	0.8278	0.9820	0.9966	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
FeL	6.41	1.47	5.65	4.37
CuL	208.20	2.17	0.90	96.09
AlK	47.58	4.00	1.95	11.90
SiK	2.35	5.12	15.01	0.46
CrK	1.87	5.60	18.90	0.33
MnK	1.83	5.47	19.03	0.34
FeK	14.70	4.88	3.89	3.01
NiK	1.80	4.03	17.32	0.45
CuK	211.53	3.73	0.90	56.66

c.

Fig. 6. *Microstructures of bimetal, x 400, 20 kV, BSE (back scattering electrons): a. transition area between bronze and steel; b. bronze in proximity of transition zone; c. EDAX analysis of points 1 and 2 into diffusion zone (according to fig. 6a) [20].*

There are several differences in composition or structure that affect resistance to corrosion: in the cladding made of several layers (deposited successively by multipass welding); between filler and parent metal; in the heat-affected zone adjacent to the weld. In the multipass welds, the relatively high temperature can induce tensions in the welded material, while in the heat affected zones of the basic material cracks may occur due to the combined effect of corrosion and stress.

These can be avoided by thermal treatment applied after welding [4, 5].

The immersion test of the bimetallic materials was carried out to investigate their corrosion resistance in saline water.

Experimental materials were cut into cylindrical specimens with diameters of 50mm [26].

For such systems the corrosion behaviour of the bimetal at the transition zone is important (Figure 7).

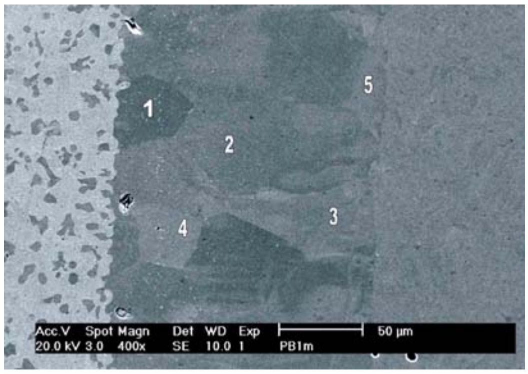


Fig. 7. *Transition area between bronze and steel 20 kV [26].*

The welding develops in this area the diffusion of the elements. The elements content vary on the depth of this zone (Table 4) and as a result selective corrosion phases were observed.

Table 4. *Variation of elements on the depth of transition zone [%wt] (points into depth of diffusion zone according to Fig. 4) [26].*

Elements	Points located into depth of diffusion zone				
	1	4	2	3	5
Al	6.73	6.31	5.90	4.16	1.02
Mn	1.27	1.43	1.20	0.96	1.21
Fe	82.41	83.51	85.84	87.48	93.59
Ni	4.40	4.20	3.47	2.92	3.11
Cu	5.18	4.54	3.58	4.48	1.07

The analysis of the transition zone after exposure to corrosion media put into evidence three subzones that have approximately equal thickness (Figure 8).

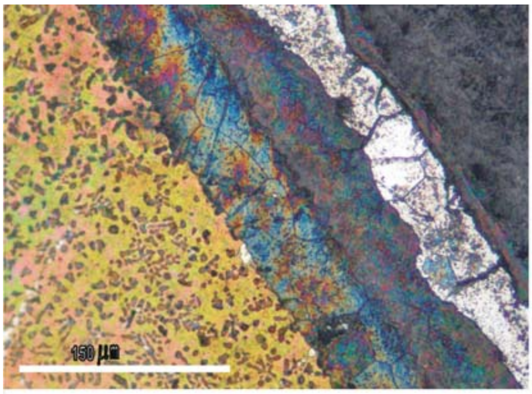


Fig. 8. *Microstructure of bronze-steel bimetal after 48 hours of exposure to sea water [26].*

In the first subzone (to bronze), as a result of copper diffusion and its limited solubility in solid solution, coarse separations of copper occurred. These are arranged to grain boundary and inside solid solution grains. In the next subzone (into central transition zone), the separation of copper was dispersed into solid solution grains as very fine and globular precipitates. In the third subzone (to steel) these copper precipitations do not show; probably copper is in a low concentration, not in excess, and it is fully dissolved in solid solution.

Therefore, the intensity of the corrosion process for these subzones is different.

The subzone adjacent to steel has a good resistance to corrosion, and stability at 3 week exposure to sea water (Figure 9).

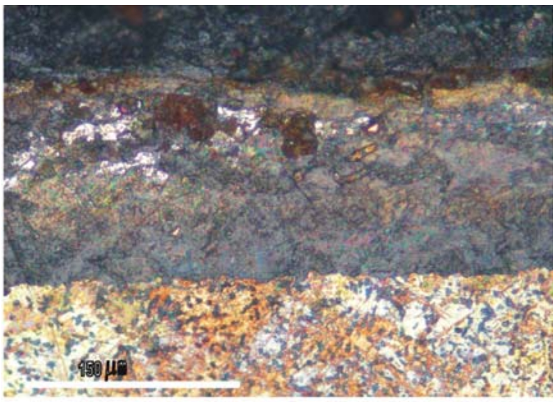


Fig. 9. *Microstructure of bronze-steel bimetal after 3 week exposure to sea water [26].*

The entire surface of this subzone is less corroded and uniform. An accelerated and deep corrosion is developed in the central subzone. In brief, the presence of heterogeneous structures (observed in the subzone close the bronze and the central subzone) enhances electrochemical corrosion.

The phases dispersed in the matrix of the solid solution are in contact and have such as behaviour of dissimilar metals available in contact under the corrosive environment (Figure 8). At the same time, close to the transition zone, heat-affected areas developed.

The uncontrolled thermal treatment is produced in both alloys, into certain depths of the bronze and steel, and was manifested by recrystallization of the phases and finishing of the grains (Figure 10).

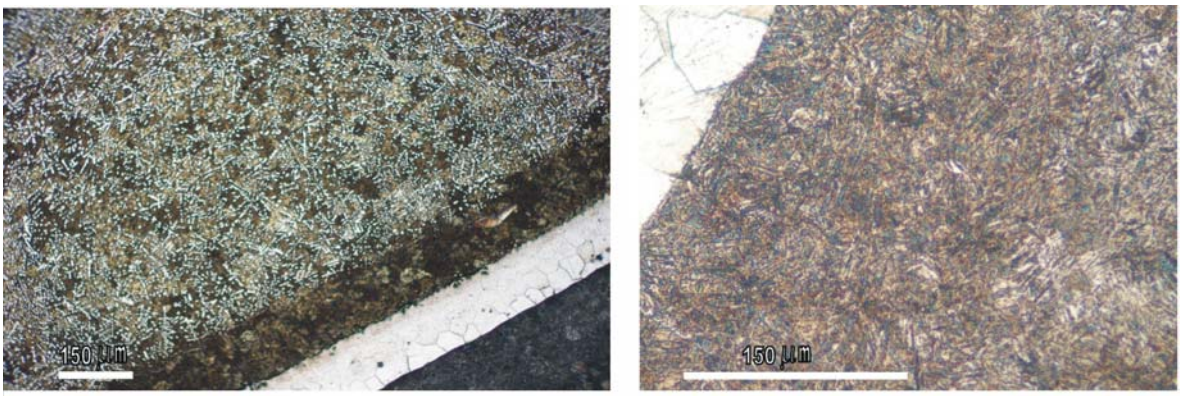


Fig. 10. *Microstructure of the bronze and steel after exposure to metallographic attack (without exposure to sea water) [26].*

Selective phase corrosion occurs in response to different electrochemical potentials between adjacent phases. Nickel-aluminium alloy develops a complex microstructure as indicated by the equilibrium phase diagram.

As a result, small variations in composition and heat treatment had a marked effect on the microstructure and hence the corrosion resistance. In accordance with the working conditions the dissimilar materials must be chosen to minimize the corrosion process.

Conclusions

The variety of combinations in terms of chemical composition and properties of the aluminium copper alloys alloyed with some important elements makes them extremely versatile, useful as wear resisting material in a large number of applications.

The aluminium bronze alloy with determined contents of nickel, manganese and iron is an excellent choice for applications involving heavy loads, adhesive wear, friction, abrasive wear and corrosion. In some applications the bearings as monoblock castings were recommended. For the antifrictions properties the chemical composition of bronzes was correlated with the microstructure. This ensures a soft phase hardened with compound uniformly distributed. In the cases analysed the selected aluminium content leads to obtaining a solid solution α as soft base.

The choice contents of nickel, iron and manganese develop those complex intermetallic κ phases that hardened the material.

Weld cladding was used to obtain a bimetal with good behaviour in working conditions specific to complex applications.

This technical solution involves the welding of an alloy layer on the other base alloy.

The processes taking place when the steel is plated with a non-ferrous alloy using the welding process are similar with the processes specific for a metallic bath formed through a metal melting in the welding zone with the contribution of both involved materials.

The solidification mechanism of added material which caused the formation of a transition structure characterized by variable composition and properties can be different. If the welding process is well done, the transition zone of the melted added material and the superheating based material is formed. The selection of the welding parameters and the heat treatments of bimetals minimize the risks associated of the transition bronze-steel zone.

A most important attention must be given to the additional corrosion process induced by dissimilar metal contacts immersed in an electrically conducting corrosive liquid.

The controlled association of bronze with steel provides systems which satisfy the requirements of mechanical properties associated with strong resistance to corrosion in marine environments.

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