COBEM 99
XV Congresso Brasileiro de Engenharia Mecânica
15th Brazilian Congress of Mechanical Engineering
22 - 26 de Novembro de 1999 / November 22 - 26, 1999 Águas de Lindóia, São Paulo,

ADDITION OF Mo AND W TO ALTERNATIVE THERMORESISTIVE ALLOYS BASED ON Fe-Al-Si-Nb.

Aparecido Carlos Gonçalves
Departmment of Mechanical Engineering, UNESP – Ilha Solteira Campus. Zip Code: 15385-000.
Ilha Solteira, S. P., Brazil.

Summary. *Industrial electric furnaces use thermo-resitance with special characteristics. These should possess a high value of electric resistance and support high temperatures.*

This article presents a study of alternative alloys to the commercial alloys using non strategic materials, which are abundant in Brazil and have reasonable prices. After some theoretical studies, alloys of the system Fe-Al-Si was prepared with approximately 5.5% of Al and 2% of Si. To this alloy system it was added 1.0% of Nb, three different amount of Mo for a series and three different amounts of W for another series.

A series of alloy specimen was obtained with 3, 5 and 7% of Mo and the other series with 3, 5 and 7% of W respectively. The alloys were melted in a vacuum induction furnace and powred in ingots. After that, it was forged to 1250^0C *and heat treated.*

In the tensile test at room temperature, all the alloys presented low ductility and in the tensile test at 850^0C *temperature all alloys presented satisfactory yield point. In the oxidation test for mass gain, except for the alloy with 7% of Mo, the alloys of the two series presented about the same resistance.*

Keywords: *Thermo-resistance, Alloys, Strategic materials.*

1. INTRODUCTION

The technique of industrial furnaces constructions has experienced, during last years, a strong and continuous development. Among them the electric resistance furnace occupies a privileged place, especially in the iron and steel industries as well as of chemical, ceramic and glass products industries. The reason of the growing use of industrial electric furnaces is based on the numerous advantages offered by the same ones.

The progresses in this field are essentially determined by the development of high electrical resistance materials (in order to have a small length of material) and heat resistant material. Besides that it is necessary that the materials have the smallest possible variation of electrical resistivity as function of temperature and have a high creep.

The properties of heating resistance alloy industrially used are summarized in the Table 1.

Table 1- Composition, electrical resistivity and maximum operation temperature for commercial heat resistance alloy (Smithells,1967).

Alloy	***Composition (% W)***	***Resistivivity ($\mu\Omega$.cm)***	***T_{max} (^oC)***
Constantan	Cu-55Ni	49	300
Manganin	Cu-12Mn-2Ni	43	300
Kumanal	Cu-10Ni-2Al	41	300
Nichrome / Brightray “B”	Ni-24Fe-16Cr	108,5	950
Brightray “F”	Fe-37Ni-18Cr-2Si	108	1000
Nichrome 4 / Brightray “C”	Ni-20Cr	107	1150-1250
Kanthal	Fe-20/30Cr-5Al	140	1150-1350

It can be seen in the Table 1 that heat resistance alloy are divided into two groups (King & Whittmore, 1979):

a) Cu based alloys,
b) Fe or Ni based alloys.

The maximum temperature of operation of the copper alloy is 300^0C, which limits its applications. On the other hand Fe or Ni based alloys can be used up to $950\text{-}1350^0$C temperature range. This permits a $300\text{-}800^0$C temperature range where also the Fe or Ni based alloy can be used . These applications are not economically viable. The purpose of present investigation is to develop a heat resistance alloy at a low cost using materials found abundantly in Brazil. Although resistance to oxidation at high temperature is a requirement of the alloy to be developed, the element Cr that gives this characteristic to the materials should be avoided in detriment of a cheaper alloy and non strategic elements. Ni should be avoided due to its high cost. The thermo electrical properties of the alloy will also be presented as a secondary objective.

2. BACKGROUND

Some works were carried out in order to substitute Ni partially by Mn in Fe-Cr-Ni (AISI 400) or Cr by Al in Fe-Cr-Mn stainless steel (Lillys & Gibson, 1968), but the complete substitution did not have a satisfactory result. No work on the alternative steels to the Fe-Cr-Ni alloy has been done lately. This lack of research is due to the relative abundance of Ni, Cr and accumulated technology along the years in Europe and in North America. (Morgan and Zackay, 1955) studied the Fe-Al system and concluded that the Fe-8% Al alloy is equivalent, in relation to the oxidation, to the type SAE 302 (UNS S30200) stainless steel. In these studies they mention that, as part of the experimental program of the scientific laboratory of the Ford Motors company, a ductile and non strategic Fe-Al alloy was developed with the name “Ferral”. That had excellent resistance to oxidation and could be manufactured by conventional methods.

The oxidation resistance of the Fe-Al alloy is shown in Figure 1, where the corrosion index was obtained by dividing the weight losses of each corroded tested alloy by weigh loss of the most resistant corrosion alloy for each temperature.

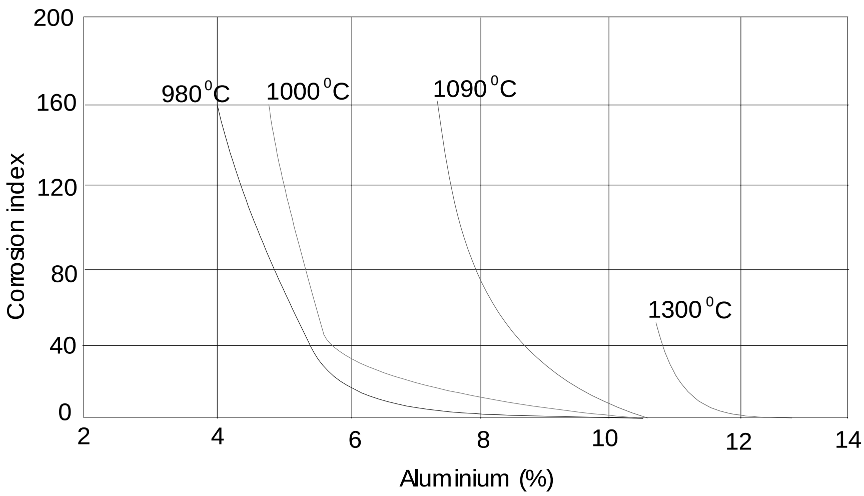

Figure 1 – Oxidation resistance of Fe-Al alloy as function of temperature (Morgan & Zackay, 1955).

The oxidation of the alloy varies with the aluminum amount and a larger amount than 8% is necessary to give a reasonable resistance to the oxidation in a temperature above 980^0C.

3. BEHAVIOR AND MECHANISM OF OXIDATION PROTECTION

The aluminum and the oxygen are strongly linked to each other and the crystalline structures of the aluminum oxide can be oriented in order to have an almost perfect combination and a considerable continuity of one phase to another. This results in a strong coherence between the aluminum oxide film and the metal.

With Al added to a steel the formation of the alumina (Al_2O_3) is facilitated due to the atmospheric oxygen. This alumina improves significantly the oxidation resistance. For such resistance to happen it is not necessary that the alumina be just in the combined form. It could be also the spinel (FeO Al_2O_3) (Shreir, 1976). Depending on the temperature the alumina presents different crystalline structure . Below 900^0C it is γ-Al_2O_3 and above 900^0C it is α-Al_2O_3. γ-phase presents the cubic structure while in the α-phase it is rhomboedric. The α-Al_2O_3 type is more protective, although it possesses larger cracking tendency and superficial peeling off (Shreir, 1976).

4. ALTERNATIVE ALLOYS BASED ON Fe-Al-Si

The interest in these Fe-Al-Si alloys originates from (Matsumoto, 1936) who investigated the magnetic properties of the Fe_3Al and Fe_3Si phases and developed an optimal soft "magnetic" alloy with the Fe + 5Al +1Si composition with the name "Sendust". This alloy also presents excellent corrosion and oxidation resistance at high temperatures. These properties are attributed to the formation of a thin Al_2O_3 impermeable film on the surface. The application of this alloy in the engineering is very limited because of its extreme brittness. So it is only used in melted form, for reatance and reles, point of poles and joint for magnet and for telephone diaphragms, all of them making use of its soft magnetic properties.

A more general study of the mechanical, electric and resistance to the oxidation properties of Fe-Al-Si alloy was done by (Schumatz & Zackay, 1959). They studied a series of alloy having 5, 7 and 9% of Al, with successive additions of 0.5, 1.5 and 2.5% Si. The results obtained are summarized in the Table 2 and indicate that, although 10 %Al can be added to the Fe without ductility loss, the presence of 2.5 Si in Fe-7Al or 1.5 Si in Fe-9Al results in total brittness of the material, while 2.5 Si in the Fe-5Al lowers the elongation from 50% to 3% (Justusson et al., 1957).

Table 2 – Mechanical and electric properties of Fe-Al-Si alloys

Alloy	σ_t ***(MPa)***	σ_e ***(MPa)***	***Elongation (%)***	***Resistivity (μΩ.cm)***
Fe-5Al	358	276	50	60
Fe-5Al-0,5Si	482	345	40	66
Fe-5Al-1,5Si	620	496	25	75
Fe-5Al-2,5Si	745	690	3	85
Fe-7Al	483	345	32	73
Fe-7Al-0,5Si	565	483	20	78
Fe-7Al-1,5Si	724	655	10	87
Fe-7Al-2,5Si	841	828	Weak	102
Fe-9Al	552	469	20	85
Fe-9Al-0,5Si	758	552	10	90
Fe-9Al-1,5Si	841	828	Weak	110

Thus, for practical purposes, and for the wire manufacturing, the amount of Si should not exceed 1.5%, while the maximum amount of aluminum is limited to 5%. Also the alloy should have a resistivity of about 80 μΩ.cm to compete with the commercial Cu alloy. According to Matsumoto (1936) the oxidation resistance of Fe-Al at 760^{0}C is significantly increased by the presence of Si. The alloy 5Al-1,5Si seemed to have the same visual superfice oxidation as for Fe-8Al alloy. In relation to the oxidation resistance the composition Fe-5Al-1.5Si should satisfy, in that way, the criteria of the present study that is leaning in the development of material of heat resistance for services up to 800^{0}C.

Schumatz & Sackay (1959) attributed the fragility of its alloy to the presence of intersticial elements. As these materials were prepared by vacuum melting, it is probable that the brittleness becomes more pronounced in alloys prepared by melt in air, using industrial techniques and materials of commercial purity. The requirement of preparation of alloy for vacuum melting, or of materials of high purity, increases significantly the cost of the unit and reduces its use for many industrial heat applications.

5. MATERIALS AND EXPERIMENTAL METHODS

Based on the theoretical studies made by (King & Whittemore, 1979) and based on the experimental results obtained by (Gomes, 1980) alloys based on Fe-5Al-2Si were studied. Starting from the matrix alloy, three alloy were prepared with different additions of Mo. These additions were about 3%, 5% and 7% to give a larger resistance to the heating oxidation and to increase the electrical resistivity of them. The alloy that presented better properties would be taken as being the best.

Also based on master alloy three composition were prepared with different additions of W in the same percentages, i. e., 3%, 5% and 7%. Here also, the alloy that presented better properties would be taken as being the best. To increase the electrical resistivity Nb was added to the materials with the main purpose of forming carbide avoiding, that way, the carbon effect on Mo and W to form carbide, since C has preferential effect on Nb. The table 3 presents the identification of each sample as well as its chemical compositions.

Table 3 – Chemical Composition of estudied alloys. Obs: Fe-balanced

Ident. (n^o)	***Si (%)***	***Nb(%)***	***Al(%)***	***Mo(%)***	***W(%)***
1	2	1	5	3	-----
2	2	1	5	5	-----
3	2	1	5	7	-----
4	2	1	5	-----	3
5	2	1	5	-----	5
6	2	1	5	-----	7

The material was vacuum melted and the ingots tops were cut off to remove the casting defects. It was tried to forge the ingots entirely, even so the reduction of the area was not gotten to the wanted value. To reach the desired cross section each ingots was longitudinally in equals parts. These parts were hot forged at 1200 ^{0}C with 50% area reduction. Before forging the ingots were pre-heated to 1250^{0}C in a oil furnace. During forging, the ingots were re-heated every time they became colder than a 1100 ^{0}C lower temperature. The following heat treatment was done for micrographical and hardness tests:

a) The bars were heat treated at 850^{0}C for 8 hours;
b) The furnace temperature was decreased to 600^{0}C and
c) The pieces were taken out of the oven and left at ambient atmosphere .

Four tensile tests specimens were prepared for each composition: two for room temperature test and two for hot testing. The chemical analysis, hardness and oxidation resistance tests were also conducted.

6. RESULTS AND DISCUSSIONS

The Table 4 presents the values of the chemical compositions of the materials studied and the Table 5 presents the hardness medium values with the respective standard deviations. For each material 5 measurement were taken.

Table 4 – Chemical analysis of specimens . Obs: Fe-balance.

Ident. (n^0)	***C (%)***	***Si (%)***	***Nb (%)***	***Al (%)***	***Mo (%)***	***W (%)***
1	0,005	2,16	1,01	6,11	3,13	----
2	0,006	1,98	1,02	5,51	5,17	----
3	0,007	1,83	1,10	5,69	7,14	----
4	0,010	1,70	1,04	5,86	----	3,23
5	0,011	1,69	1,04	5,71	----	5,17
6	0,011	1,86	1,00	5,60	----	7,20

Table 5 – Average hardness test values after hot forging.

Identification	***HRc – Load 150 kg***
1	27,0 ± 1,0
2	24,8 ± 1,2
3	25,2 ± 1,2
4	24,8 ± 1,1
5	25,0 ± 1,0
6	26,2 ± 1,0

Table 6 presents the average values (two samples for each composition) from the room temperature tensile test.

Table 6 – Mechanical properties values from tensile test at room temperatue.

Ident. (n^0)	***σ_R (MPa)***	***σ_E(MPa)***	***E(%)***	***R.A.(%)***
1	447,1	----	0	1,48
2	529,2	----	0	0,37
3	779,0	669	3,96	3,33
4	213,2	----	0	0,37
5	600,0	----	0	0,37
6	375,2	----	0	0,37

These results show that at room temperature all compositions identified as 1 to 6 are brittle. The alloy with Mo addition as the alloy with W addition showed the same brittleness characteristics of non ductility.

Table 7 presents the average values of two tensile tested samples at 850^0C temperature. Here significant variations were not observed in the values between one specimen and other for the same alloy.

Table 7 – Mechanical properties from tensile test at 850^0C.

Ident. (n^0)	***σ_R (MPa)***	***σ_E(MPa)***	***E(%)***	***R.A.(%)***
1	65,1	56,7	94,0	72,0
2	71,2	61,3	94,0	63,0
3	84,8	75,0	94,1	63,1
4	89,8	80,3	91,1	42,8
5	92,9	84,8	32,8	10,4
6	89,8	74,2	64,7	59,9

The Table 8 presents the average mass gain values for the 6 alloys varying the exposure times.

Table 8 – Average mass gain ($X10^{-7}$ g / mm^2) of test-specimens at 900^0C

T (h) / ***Ident. (n^0)***	***1***	***2***	***4***	***8***	***16***	***32***	***64***	***128***	***256***	***512***
1	3,21	3,74	4,17	4,25	4,79	5,40	7,02	9,31	13,89	18,34
2	18,45	20,46	21,05	21,34	22,04	22,25	23,20	24,52	26,48	29,58
3	83,75	97,37	113,12	128,63	133,93	137,50	139,61	142,0	142,29	144,77
4	3,05	3,40	3,50	3,60	3,82	4,50	5,61	8,12	11,42	15,33
5	4,58	5,01	5,20	5,42	5,55	5,96	7,03	8,62	11,35	15,55
6	6,16	6,93	7,55	8,34	8,95	9,31	10,20	12,01	14,40	17,47

The electrical resistivity for low temperatures was superior to 80 μΩ.cm.

The alloys percentage increase of the electric resistivity of the alloys from 50^0C up to 850^0C were respectively 46 for alloy 1; 53 for alloy 2; 53 for alloy 3; 51 for alloy 4; 48 for alloy 5 and 44 for alloy 6.

7. CONCLUSIONS

The addition of Mo and W increased the electrical resistivity increase and the variation of this electrical resistivity in a function of the temperature decreased satisfactorily in relation to the Fe-Al-Si alloy.

The alloys with Mo additions presented larger values of electrical resistivity compared to the others and the alloys with W additions presented a smaller percentage variation of the electric resistivity.

Optical and electronic metalographic analysis presented complex precipitate with amount of Mo and W highest than in solid solution in the matrix. The Mo and W rich precipitate formation, with matrix superior composition should affect the electrical resistivity percentage variation that, in this case, is superior to the required for the production of thermal resistors. The retention of these elements in the matrix would decrease this percentage.

The electrical resistivity analysis indicate the beginning of a transformation at 680^0C similar to the base alloy. A magnetic transformation, according to Fe balance diagrams analysis with the added elements, happens in higher temperatures.

The corrosion resistance for 850^0C is very superior to the existing standard required.

8. REFERENCE

GOMES, S.I.N. Resistência à oxidação de Ligas ferro-alumínio-silício. *Congresso Brasileiro de Engenharia e Ciências dos Materiais.* 4., Florianópolis, 1980. Proc. Florianópolis, UFSC, 1980, pp.685-693.

JUSTUSSON, W.; ZACKAY, V.F.; MORGAN, E.R. The Properties of iron aluminum alloys, *Transactions American Society for Metals*. V. 49, p. 905, 1957

KING, Hubert W.; WHITTEMORE, Carl R. *"Projetos de ligas de resistência de aquecimento"***.** São Carlos, 1979, 32p. (Project n^{o} 3677. Brazil)

LILLYS P.; GIBSON, R.C. In: SCHMATZ, D.J. Structure and properties of austenitic alloys containing aluminum and silicon. *Transaction American Society for Metals*. v.52, p.911-912, 1968.

MATSUMOTO, H. Science Reports. Tohuku Imperial University, p. 388, 1936.

MORGAN, E.R.; ZACKAY, V.F. Ductile iron aluminum alloys. *Metal Progress*. v.1, n.1, p.126-128, 1955

SCHUMATZ, D.J.; ZACKAY,V.F. Mechanical Properties of Fe-Al-Si alloys at room and elevated temperatures. *Transactions American Society for Metals*. V. 51, p.299-309, 1959

SHREIR, L.L. The oxidation resistance of low-alloy steels. In: *Corrosion***:** metal/environment reactions. 2 ed. London. Newnes Butterworths, 1976, v.1, p.7-13

SMITHELLS, C.J. *Metals reference book*.,4ed. London, Butterworths, 1967. V.3, p.749