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Composition Design Modeling and Experimental Verification of (Co Ni Al) Shape Memory Alloys

Abstract- The most important concepts to apply a shape memory alloy in many industrial applications is the composition design that controls the transformation temperatures. In this paper, two mathematical models were created to predict the transformation temperatures for poly-crystalline (Co-Ni-Al) alloys. The data that was depend on to find the relation between chemical composition and transformation temperatures were concluded from previous work and approved by preparing samples in investigation practically. Four different alloys were prepared to verify this relation. It was indicated that the best criteria that present the chemical composition is the (e/a) and make the alloy applicable for different applications. These suggested chemical compounds could be controlled and adjusted according to heat treatment time.

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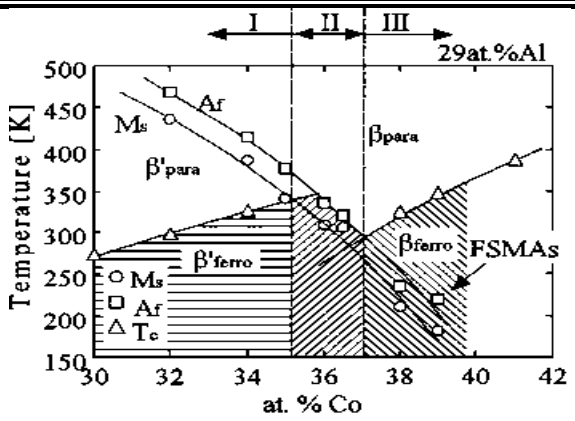
1. Introduction

Shape memory alloys was applied in a wide range of application especially in biomedical sensors and pipe coupling as in the petroleum industries where welding is not applicable. [1,2] A wide biomedical application also needed the SMA to be designed to work in a specific temperature within the range of the application like catheterization producers. [1]

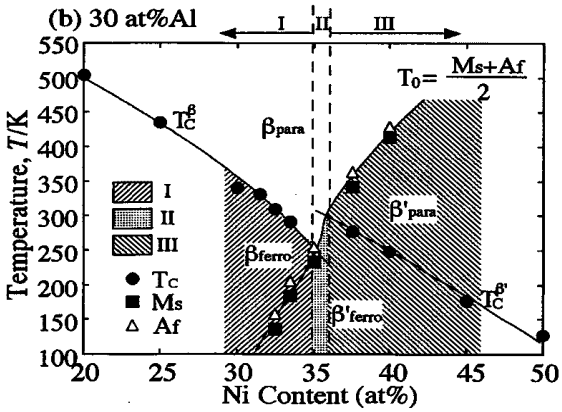
Co–Ni–Al alloys highly applicable FSMA and SMAs. These alloys are cheaper than other SMAs. This come from there composition. Where, these alloys include inexpensive elements in comparison with other SMAs. In addition to that the mechanical properties of this alloy are very notable. [3,4]

The behavior of this alloy could be a normal shape memory alloy that effected by temperature to remember its shape or by magnetic field in addition to temperature according to chemical composition where the cure temperature of this alloy will fix this property. Figure 1 (A) showed that the Co Ni Al of 29% Aluminum transformed to magnetic alloy when the Cure temperature below the transformation temperatures after increasing Cobalt atomic content more than 37% .[3,4]

According to Figure (1) it was indicated that the transformation temperatures highly effected by chemical composition of Co and Ni. Where, the To increase with Ni at.% and decrease with Co At.%. These effects taken place at fixed Al At.%.



(A) Ms & Af affacted by Co at.% for 29 at.% Al



(B) Ms & Af affacted by Ni at.% for 30 at.% Al

Figure 1 Composition dependence of the Curie temperature Tc, the martensitic transformation temperature Ms and the austenitic finishing temperature Af. The FSME can be observed in the hatched region. [3,4]

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The valance electron consecration factor (e/a) give an indication to the chemical composition by a group of researchers [7-10]. It was indicated that he the relation between the chemical composition and the transformations temperatures ranged from 7.58-7.66 and the martensitic transformation starting and austenitic ending temperatures increases in this range from (140-260)^{o}K (see Figure 2).

From Figure (2) It could be seen that the chemical composition effecting strongly on the transformation temperatures in comparison with heat treatment time. Where it could be concluded that Tc increases with an increase in the Co content and a decrease in the Al content. While, Ms decreases with an increase in both the Co and Al contents. [3,4]

The effect of e/a cannot be considered as a mathematical model because it could not be presented as a curve with a clear mathematical equation. This pushed the researches to find the criteria that put in consideration the changes in chemical composition for Co and Ni with a fixed Al at.%. as shown in Figure 3 [5,6]

The main preparation procedure of this alloy has been done with two steps which are melting and heat treatment. The heat treatment variables for this alloy is by heating to a temperature that make the alloy in the area of both (β + γ) area.[3,4,6]

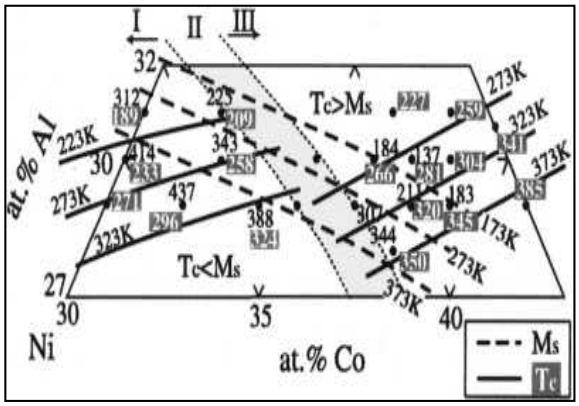

Figure 2: Composition dependence of the Curie temperature Tc and the martensitic transformation temperature Ms in the Co Ni Al ternary system. [3]

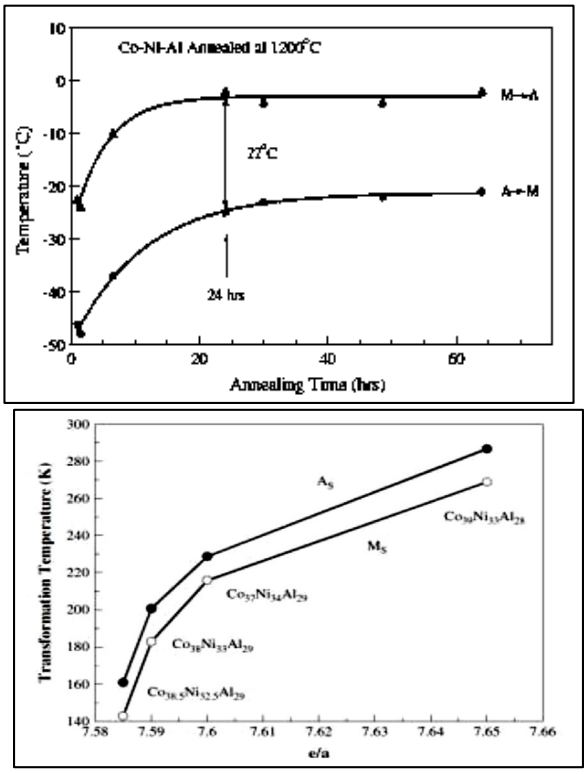

Figure 3: Valance electron concentration on starting transformation temperature for the melt-spin alloys in deferent compositions [6]

Figure 4 effect of annealing time at 1200^{o}C on transformation temperatures. [9]

The heat treatment temperature was 1200 ^{o}C. The time of heating was ranged from 1 to 24 hours [3,4,6-8] The researchers found that the transformation temperatures could be increased by increasing heat treatment time by 50 degrees. and further increase heat treatment time effect will be ineffective after 20 hours as shown in Figure (4).[9,10]

According to this figure it could be indicated that the transformation temperatures could be increased with about 25 ^{o}C in case of increasing the heat treatment time from 1 to 24 hours. [11, 12]

2. Experimental Work

Two main resources were selected to support our work with data. The manufacturing process of our samples are melted samples in different chemical compositions. The samples generally annealed for more than 12 hours and then quenched in ice water. As shown in Table (1). All samples have a fixed Al atomic content of 29%. The four transformations temperatures for these alloys for the two revers transformation from A to M shown in figure with two points presenting the starting (M_s and A_s) and final transformation temperatures

(M_f and A_f) have been presented finally with To which calculated according to Wiseman Equation $= \frac{Ms+As}{2}$

Four alloys have been prepared by mixing pure powders of the three components and the mixture finally pressed to a shape disks. These disks were melted with trips arc melting furnace under Argon to avoid oxidation. The alloys mounted in Argon gas filled tubes then heat treated for 12 hours at 1200 ^oC then quenched in ice water. Samples have been chemically analyzed by using EDAX by (FAI SEM). The Transformation Temperatures have been investigated by DSC Testing with (DSC 2000). All the results of DSC and e/a calculations listed in Table (1).

The e/a have been calculated by the summation of the number of free valance electrons multiplied by the element atomic content divided by the summation of the atomic weights of each component.

Many researchers prepared Co Ni Al alloy with different chemical compositions grouped according to the Al at.%. These composition with its transformation temperatures which presented as To. The transformation temperatures collected to all samples that heat treated for time to 20 hours.

Table 1: The prepared Samples DSC Results and (e/a) Calculations

Co%	Ni %	Al %	e/a	Ms ^oC	Mf ^oC	As ^oC	Af ^oC	To ^oC
36	35	29	7.61	65	47	65	101	83
35	36	29	7.62	60	37	80	110	85
34	37	29	7.63	104	80	150	175	139.5
34	37	29	7.63	115	105	121	140	127.5

3. Multiple Regression and Analysis

First group of samples was with Al at.% of 29%. This regression came with a linear equation taking Co at.% as a variable. The accuracy of the mathematical model indicated by calculating the errors squared root value. The accuracy of this model was about 93%.

The other group of samples was with Al at% of 30% gave the same type of model. These relations could not give a full picture about the chemical composition for the three elements.

According to above the (e/a) taken in mind while creating the mathematical models. And the second stage of this work. The mathematical model for e/a for both groups together give a low accuracy of 74%. As shown if Figure 5.

Table 2: Collected Samples Data from previous researches. According to figures 1,2,3 [3,4,6]

Co at.%	Ni at.%	Al at.%	e/a	To (C)
39	32	29	7.58	-71.5
38	33	29	7.59	-63
38	33	29	7.59	-50
37	34	29	7.6	-34
36.5	34.5	29	7.605	40.5
36	35	29	7.61	49.5
35	36	29	7.62	86
32	39	29	7.65	177
34	37	29	7.63	127
35	36	29	7.62	102
36	35	29	7.61	52
38	33	29	7.59	-48
34	37	29	7.63	128.5
35	36	29	7.62	135
37	34	29	7.6	35
39	32	29	7.58	-65
34	37	29	7.63	135
37	34	29	7.6	35
39	32	29	7.58	-65
32	39	29	7.65	253
34	37	29	7.63	163
35	36	29	7.62	118
36	35	29	7.61	65.5
38	33	29	7.59	-9.5
39	32	29	7.58	-39.5
38.5	32.5	29	7.585	-97
38	33	29	7.59	-57
37	34	29	7.6	-24.5
37	33	30	7.53	-65
38	32	30	7.52	-122
36.5	33.5	30	7.535	-72
35	35	30	7.55	-22
33	37	30	7.57	78
30	40	30	7.6	153

By applying the multiple regression with the two variables (e/a) and Al at.%. for each groups of samples alone. The accuracy give a high results of 98% for Al at.% 30 and 93% for Al at.% of 29 each group alone. Where the mathematical models for the two groups shown below in Equations No.1

for alloys with Al at%=30%& No.2 with Al at%=29%, with an Accuracy of 98.22% and 92.22% respectively.

To=-26127+3459 (e/a) (1)

To=-31894+4197 (e/a) (2)

But a full one relation need to be created as shown below note that all calculation done by using Minitab Ver. 17.

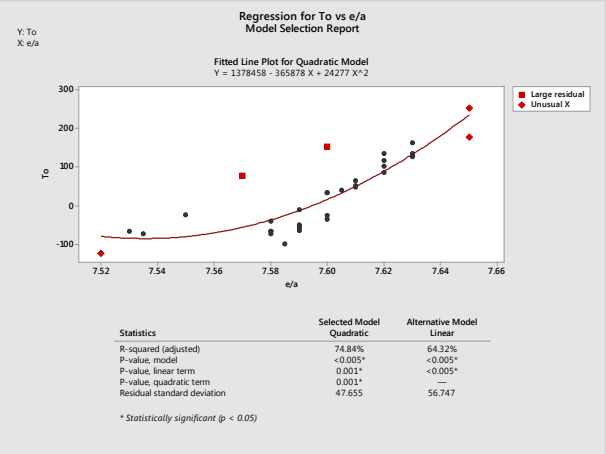

Figure 5: showing the low accuracy when the regression build on e/a ratio alone without taking the effect of Al at.% in consideration.

From figure (6) is could be seen that the e/a of Al at.% increasing increase the To. And the different change of e/a with Al content showing a different slop with two lines that can describe the low accuracy of the grouped Al Contents model where the accuracy was very low of about 76%. This will show why the researcher who depend on e/a alone without taking Al content in consideration could not conclude a mathematical model.

Figure (7) explain the dependence of the R-squared values on the Al and e/a. the Al showed a high dependency more that e/a. and showing the enhancement in accuracy after adding Al content to the model which increased to 95%.

The Total Model for both groups of Al at.% final mathematical model for this work is presented in equation no.3 below:

To=-228792 + 29523 (e/a) + 6756 (Al%) - 869 (e/a) (Al%) (3)

Testing Models showed that the calculated To from the suppurated groups for the experimental alloys more accurate and near to the investigated temperatures as presented in Table 3. These alloys laid in both magnetic and non-magnetics shape memory alloy area in the equilibrium diagrams shown in Figure 1.

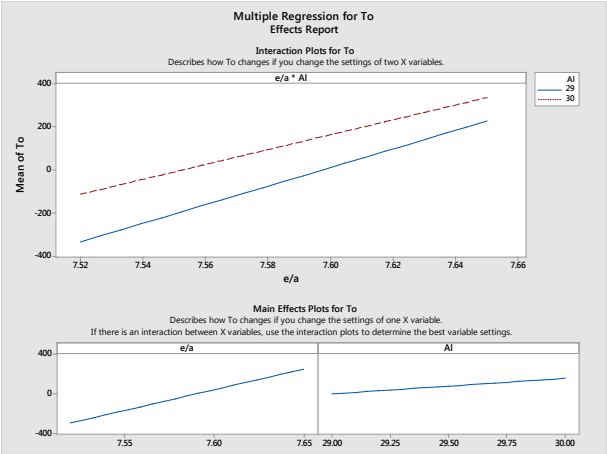

Figure 6: Showing the effect of Al Content and (e/a) ratio on To

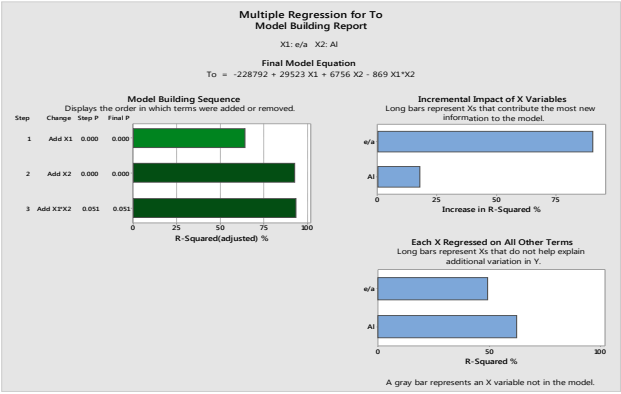

Figure 7: Showing the accuracy change when the model takes both e/a and Al at % as multiple variable in the equation.

Table 3: Compression between the real and calculated results for the two models.

Co %	Ni %	Al %	e/a	Exp.	Eq.1	Eq.2
36	35	29	7.61	83	45.17	22.42
35	36	29	7.62	85	87.14	65.64
34	37	29	7.63	139.5	129.11	108.86
34	37	29	7.63	127.5	129.11	108.86

According to that it could be proved that this mathematical model could be applied not only for the magnetics shape memory alloys region. [10]

According to that this alloy should be treated as groups according to the Al at% even in mathematical modeling.

4. Conclusion

1- The best way to design Co Ni Al alloys and compare between compositions is by fixing Al Content and change between Ni and Co.

2- The (e/a) electron valance ratio is not enough alone but the Al at.% need to be considered as a

criteria that could be depend on to design the chemical composition according to the transformations temperatures ranges needed for the application.

3- The heat treatment time can control and finally tune the transformation temperatures.

4- The relation could cover both Co Ni Al behavior as a magnetics and nonmagnetic shape memory alloy.

5- The best range to make the alloy applicable in biomedical sensing application or pipe coupling is between (7.605-7.610) with Al atomic of 29% this transformation temperature could be adjusted more by changing treatment time.

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