

Preparation and Characterization of Biomedical Ni-Co-Al Shape Memory Alloys

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ABSTRACT:

This research presents microstructural characterization of the Co Ni Al shape memory alloy with focus on understanding the significant properties as well as the relation between the physical properties and microstructure of this alloy. Melting technique were used to prepare Co Al Ni shape memory alloys, where scanning electron microscope, light optical microscopy and x-ray diffraction investigations showed that structure of this alloy is polycrystalline double phase (β and γ) structure, and it found that the grain size and phase fraction of β phase was ranged from 9 to 16 μm and (50-80) % respectively. It was found that by increasing the heat treatment time the phase fraction of hard β phase increased and phase fraction of ductile γ phase decreased, and consequently the grain size and the hardness of β phase increased. Differential Scanning Calorimeter results showed that transformation temperature decreased by increasing Al/Co, that Co content affected on transformation temperature. Tafel Curves showed the corrosion behavior in simulation body fluid, where the corrosion rate was ranged from 0.13 to 0.47 mpy and increased with each of increasing the annealing time and Co content, and from cyclic curves, the pitting corrosion possibility is not observed due to the formation of a protective layer that formed by Al element. According to these properties and behavior, it was found that this alloy could be a good choice to be used for biomedical applications, especially in surgical, catheter tools and medical instruments.

Keywords: Smart materials, Shape memory alloys, Nickel-Cobalt-Aluminum alloy, Biomaterial, Corrosion Behavior.

INTRODUCTION

Smart materials exhibit special properties that make them an attractive choice for industrial applications (e.g., aeronautical, biomedical, structural, and earthquake engineering) in many branches of engineering. Among different types of smart materials, shape memory alloys (SMAs) [1]. Shape memory alloys (SMA) are materials that have the ability to return to a former shape when subjected to an appropriate thermo mechanical procedure [2].

The cobalt alloys (close to the Co Ni Al stoichiometry) are the less known shape memory alloys. Such behavior is consequence of the martensitic transformation. The phase diagram of Co Ni

Al system was established and seems not to be complicated. The area with high content of cobalt contains just three phases. The A1 disordered fcc cobalt solid solution, B2 ordered phase and L12 ordered phase, which appears in high nickel alloys. This L12 phase is ordered superstructure of A1 phase. There was observed martensitic transformation of B2 phase into the tetragonal L10 phase. The described transformation kinetics is similar to Ni Al system [3]. Co Ni Al systems are considered as alternative materials to the well-known Ni Mn Ga or Ni Fe Ga alloys [4].

Oikawa et al. in 2001 and 2002, firstly developed the new group Co Ni (X) alloys. The phase equilibrium of these systems showed that the martensitic and magnetic phase transformations are in the β (B2) phase region of the Co Ni Ga and Co Ni Al systems [4]. Cobalt and nickel alloys are used for corrosion protection and for high temperature resistance, taking advantage of their high melting points and high strengths [5]. Recently the Co base alloys were widely used as an implant in different biomedical applications [6].

According to that, this alloy will be studied as an applicable alloy to be used in biomedical application and precisely as an interactive catheter tool. This work is aimed to produce a cheap components SMAs by an easy manufacturing process to produces a polycrystalline structure without need of additional costly mono directional processes, and study the effect of chemical composition and heat treatment time on the microstructure, mechanical properties, transformation temperature and corrosion behavior of Ni Co Al that prepared by melting technique.

Experimental Work

Polycrystalline Co-Ni-Al alloy ingot was prepared by using arc melting technique, where high purity powders of cobalt 99.9%, nickel 99.9%, and aluminum 99.5% were mixing and compacting as a tablet with a diameter of 8 mm, then melted under an argon environment in a water-cooled copper crucible. Three chemical composition in range Co (32-34 at. %), Ni (37-39 at. %) and Al (29 at. %) were chosen. The ingots was melted three times to ensure a good homogeneity. Next, the ingots were cut before annealing to treat each part of sample with different heat treatment. The heat treatment process was done by heating the quartz sealed samples to 1200 °C for different periods of time (1,3 and 5 hours) and then quenching the samples in ice water. Table (1) shows Chemical compositions of the three groups of alloys.

The microstructure and structural analyses were performed by applying several techniques, light optical microscopy (LOM), and scanning electron microscope (SEM) attached with energy dispersive x-ray (EDX) examination was used to reveal the microstructure and chemical composition of specimens. X-ray diffraction (XRD) was used to investigate the phases of melted samples. Differential Scanning Calorimeter (DSC) was used to assess transformation temperature of the prepared samples. And image analysis investigations were performed by using image J2X Software to analysis the area fraction of phases presented. Micro hardness testing was done by using a digital micro hardness tester type **HVS-1000 LARYEE**. MLab Multi Channel Potentiostats / Galvanostats device was used to investigate the corrosion behavior of specimens, where electrochemical measurements were made at 37 °C using a cell containing Ringer's solution which was prepared by the addition one tablet of RINGER tablets supplied by Merck KGaA Germany to 500 ml of distilled water, then the corrosion rate was determined by applying mils penetration per year (mpy) method.

Table (1) Chemical compositions of the three groups of alloys.

Sample	Groups	Alloy composition (at. %)		
		Co	Ni	Al
S1G1	Group 1 (G1) annealed 1 hour at 1200 °C and then quenched in ice water.	34	37	29
S2G1		33	38	29
S3G1		32	39	29
S1G3	Group 3 (G3) annealed 3 hours at 1200 °C and then quenched in ice water.	34	37	29
S2G3		33	38	29
S3G3		32	39	29
S1G5	Group 5 (G5) annealed 5 hours at 1200 °C and then quenched in ice water.	34	37	29
S2G5		33	38	29
S3G5		32	39	29

Three groups of samples were prepared in order to investigate the chemical analysis on different Co Ni Al alloy characteristics. The annealing times were different from group to another as shown in the Table (1). These times were selected to indicate the effect of annealing time and the different chemical compositions of alloys on the microstructure and the mechanical properties of these alloys, and the relation between the chemical composition and the resulted phases fractions, was also studied.

Results and Discussions

Microstructure Image Analysis and Phase Investigation

All the groups which have exceptional treatments were investigated. The investigations give a thought in regards to the influence of annealing time and chemical composition on the structure of these alloys. According to previous studies [7, 8 and 9], it is good recognized that the structure of this alloy mainly consists of two phases (β & γ). The β phase is hard and brittle and transforms from austenite (β) to martensite (β' or M) producing the shape memory alloy effect. And, the γ (G) phase is a ductile phase that is precipitated on the grain boundary of β or M grains or inside the grains (γ'). It found that, the chemical composition of β phase is near to the main alloy composition but with a little bit increase in Al content and decrease in Co content. The γ phase is rich with cobalt content and poor with Aluminum [10, 11].

A good example for this description could be seen clearly in Figure (1) and Figure (2) shows microstructure and XRD pattern of S2G5 sample. Table (2) shows the both ratios that were calculated according to the chemical composition of prepared alloy. This table also presents the β phase volume fractions, grain size in (μm) and the Vickers Microhardness for all samples, where the hardness reading were taken by using (9.8 N) load for each group of samples to give an overall value of hardness. It was observed that the hardness values differ from point to another because of the variation in phases that have different hardness values. The precipitation of the ductile γ phase presented the lowest hardness values. While, the martensite has the highest values of hardness, and the redundant β phase hardness values lied in between.

Table (2) Chemical composition, phases fraction areas, β phase grain size and microhardness results.

Samples	Alloy composition (at. %)				Image Analysis			Average Hardness
	Co	Ni	Al	Al\Co	β %	γ %	G.S. (μm)	
S1G1	34	37	29	0.853	78	22	15	334
S2G1	33	38	29	0.879	65	35	10.5	321
S3G1	32	39	29	0.906	50	50	11	304
S1G3	34	37	29	0.853	80	20	16.3	370
S2G3	33	38	29	0.879	72	28	11	326
S3G3	32	39	29	0.906	57	43	9	300
S1G5	34	37	29	0.853	75	25	18	390
S2G5	33	38	29	0.879	67	33	12.4	343
S3G5	32	39	29	0.906	60	40	10.5	312

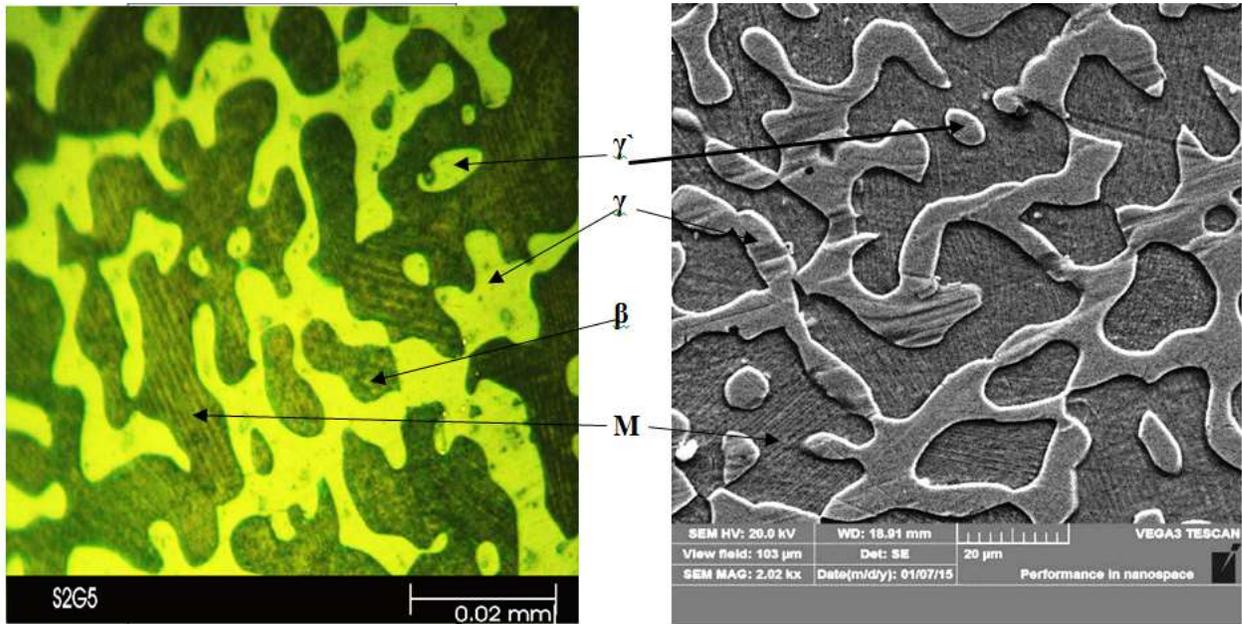


Figure (1) Microstructure of S2G5 sample represented all phases.

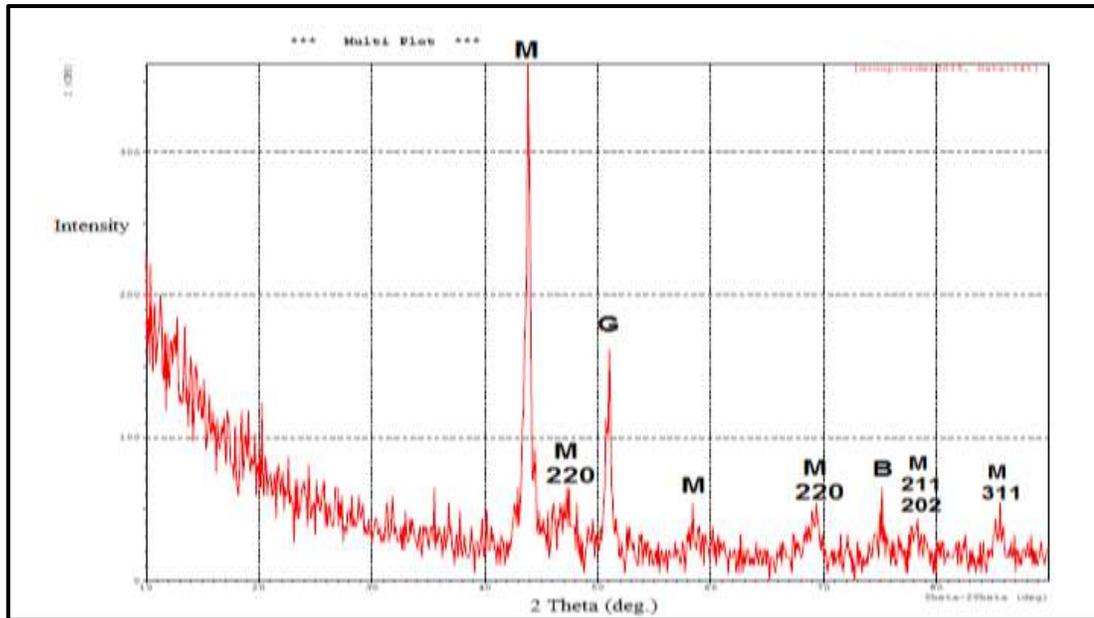


Figure (2) shows XRD pattern of S2G5 sample.

Figure (3) and (4) illustrate the effect of chemical composition on the microstructures of group (5). It was observed that the microstructure of (S1G5, S2G5, and S3G5) consist two phase ($\gamma+\beta$), where the volume fraction of β phase is about 75%, 67% and 60%, respectively, and the hardness range is (312-390) Hv. It was showed that the β phase fraction decreased by decreasing in Co content from S1G5 to S3G5, and normally the decrease in β phase fraction followed with a decrease in grain size and hardness, because the amount of transformed β phase will decrease and that effects on hardness values.

Where, the XRD analysis showed of S2G5 and S3G5 contained 3 peaks of martensite phase with different directions M (200), (220) and (311), while γ phase presented in two peaks G and G (002), and only two peaks referred to austenite phase (untransformed phase β), while in S1G5, the XRD chart presented the martensite phase with five directions, which indicated that content of Co effected on the amount of martensite phase (M or β'). This increased in martensite phase showed an increase in hardness values in different point.

Figure (5) reveal the effect of heat treatment time on the microstructure for same composition samples (S1G1, S1G3 and S1G5). According to samples image analysis, it was found that the β phase fraction increased by increasing annealing time and that will increase the grains sizes of β phase according to the homogenization that took place, and that gives a good explanation about the reason behind increasing the overall hardness. The grains growth has a dendritic shape and gathered with γ phase which get connected after long heat treatment with group (5).

The XRD patterns of S1G1 showed three peaks referred to martensite phase with different directions, and four peaks for γ and β phases, and by comparing with the XRD of S1G3 and S1G5, the peaks of M phase will increase to five peaks and peaks of γ , β phases decreased to two peaks.

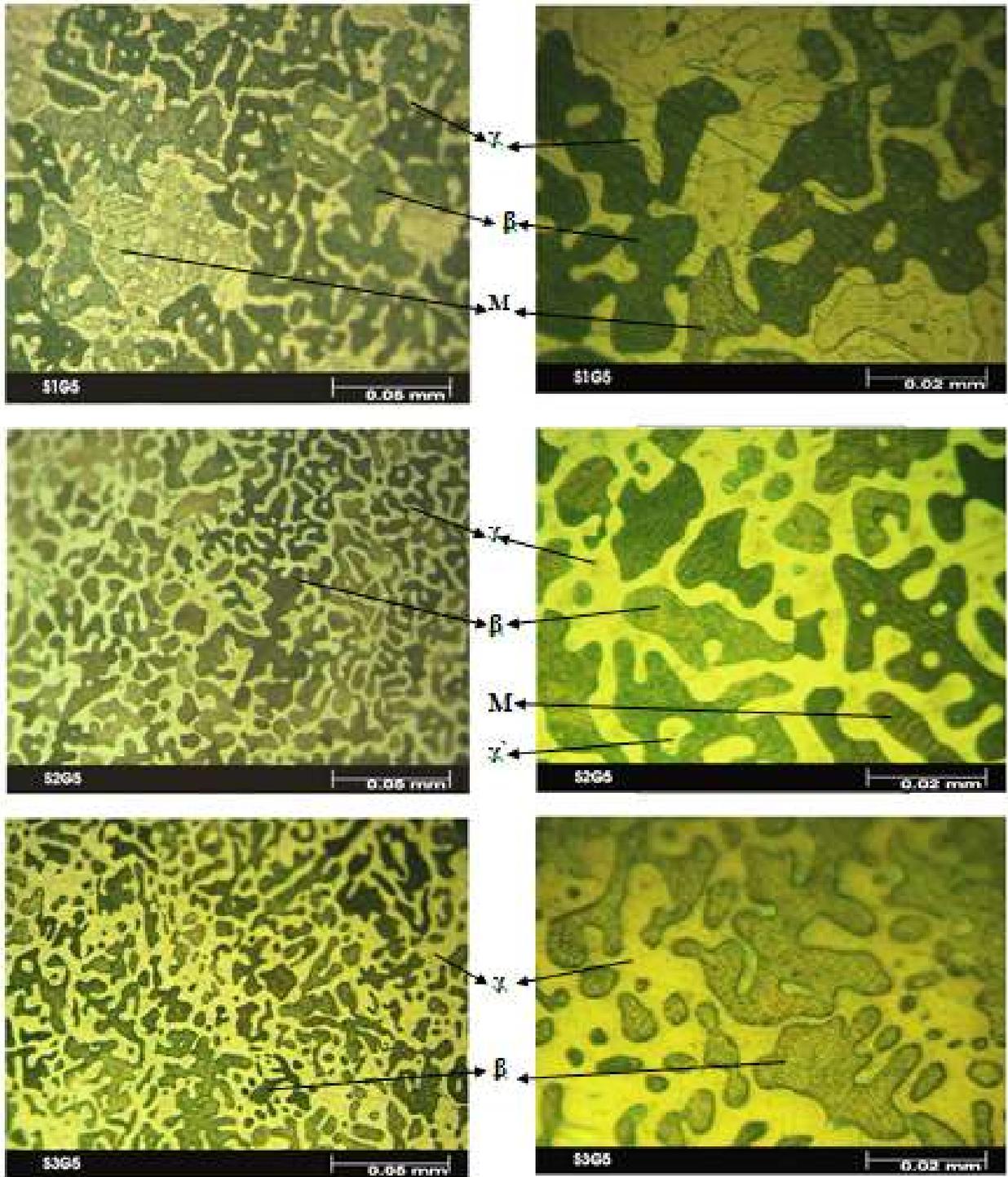


Figure (3) Microstructure image of group 5 (S1G5, S2G5 and S3G5) annealed for 5 hours.

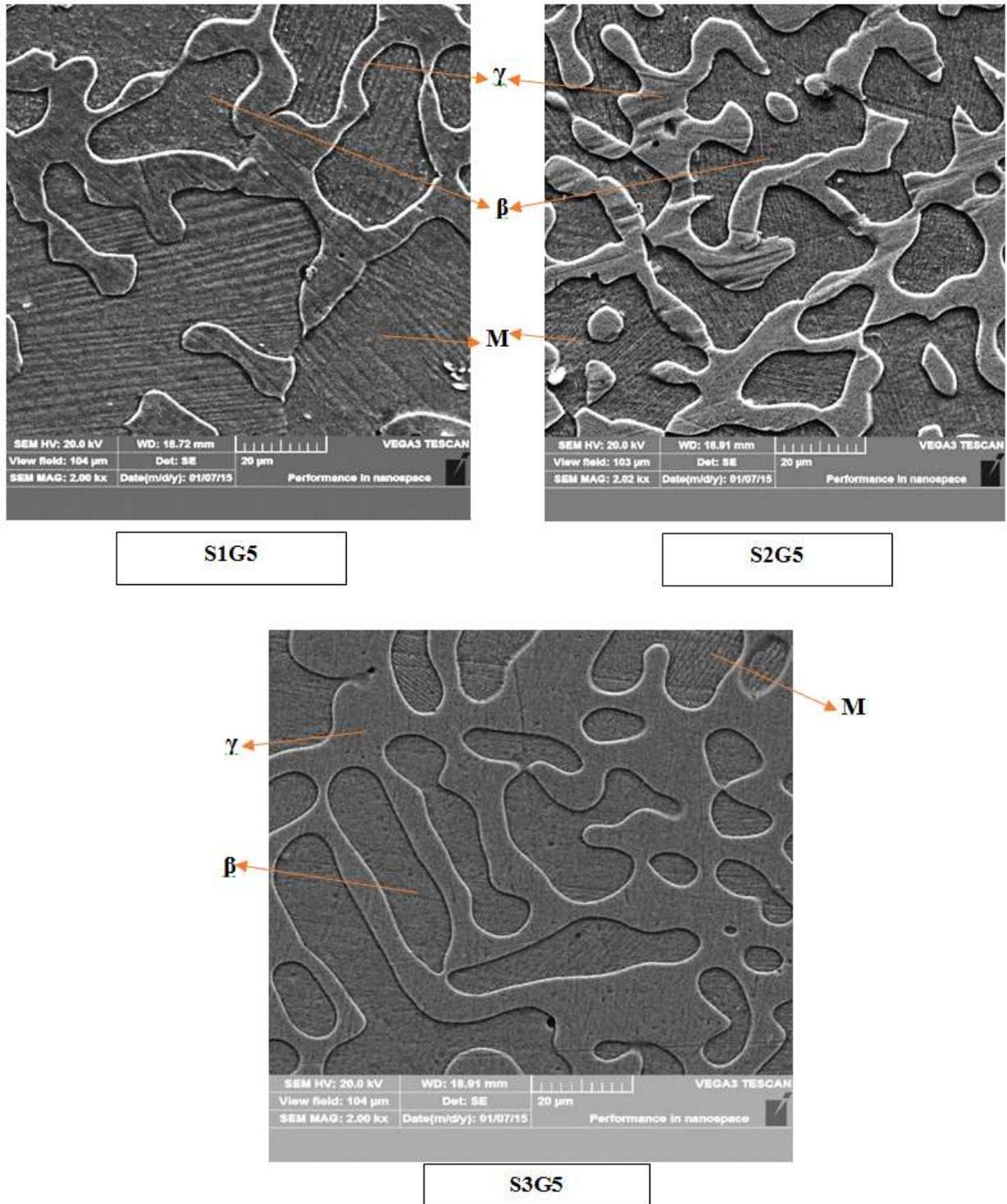


Figure (4) Microstructure image of group 5 (S1G5, S2G5 and S3G5) annealed for 5 hours.

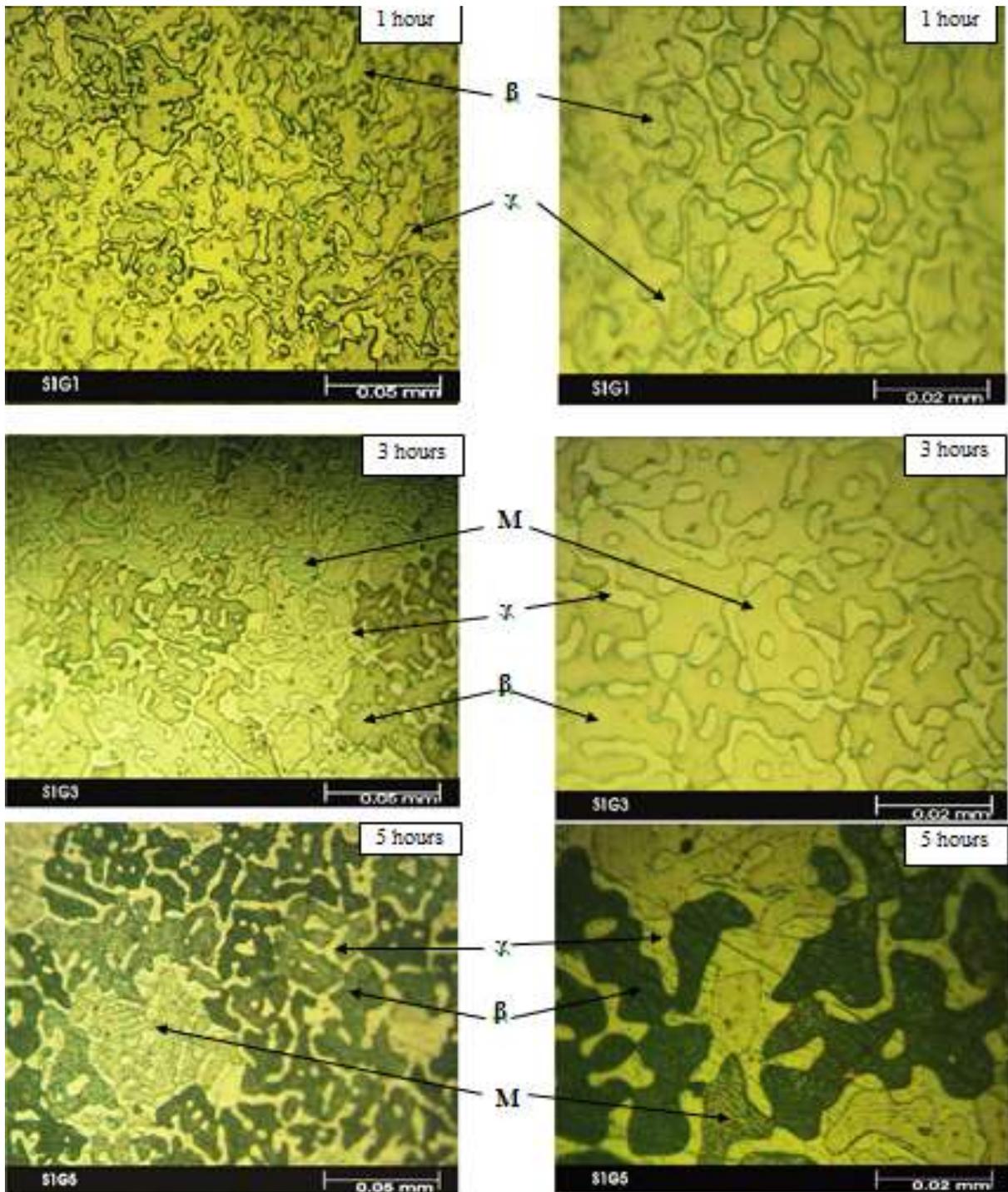
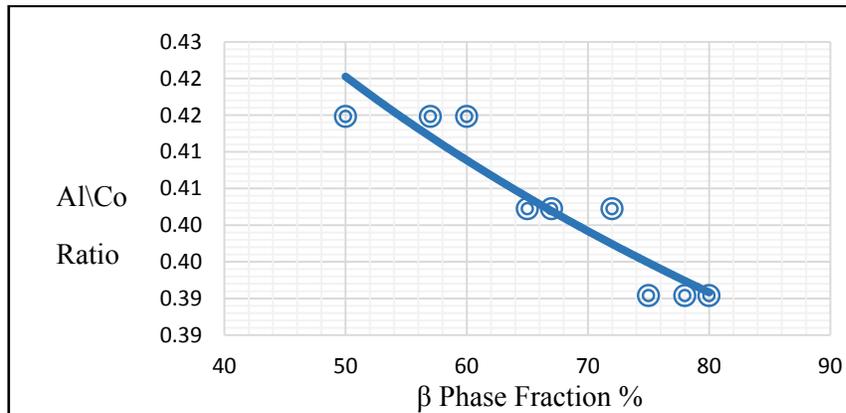


Figure (5) reveal the effect of heat treatment time on the microstructure for same composition samples (SIG1, SIG3 and SIG5).

Microstructure effect on properties

According to the results that are deduced from Table (2), it could be seen that the chemical composition is presented by the ratio (Al/Co), and the change in β grain size depends on the chemical composition. Where, according to the relation between (Al/Co) and the β volume fraction shown in Figure (6), the β volume fraction is increasing by decreasing (Al/Co) ratio depending on the Co content.



Figures (6) The relation between the chemical composition presented by (Al/Co) ratio on β volume fraction.

The contents of Co and Ni would effect on the amount of β phase if the Al content was fixed, and Figure (7 A) shows that the volume fraction of β phase is by the increase in Co content, while Ni content generally has an adverse effect on the volume fraction of β phase, where the amount of β phase decreases by increasing Ni content, as shown in Figure (7 B). The entire above relations approved to the relation that indicated by *Tanaka et al and Liu et al.* [9, 12].

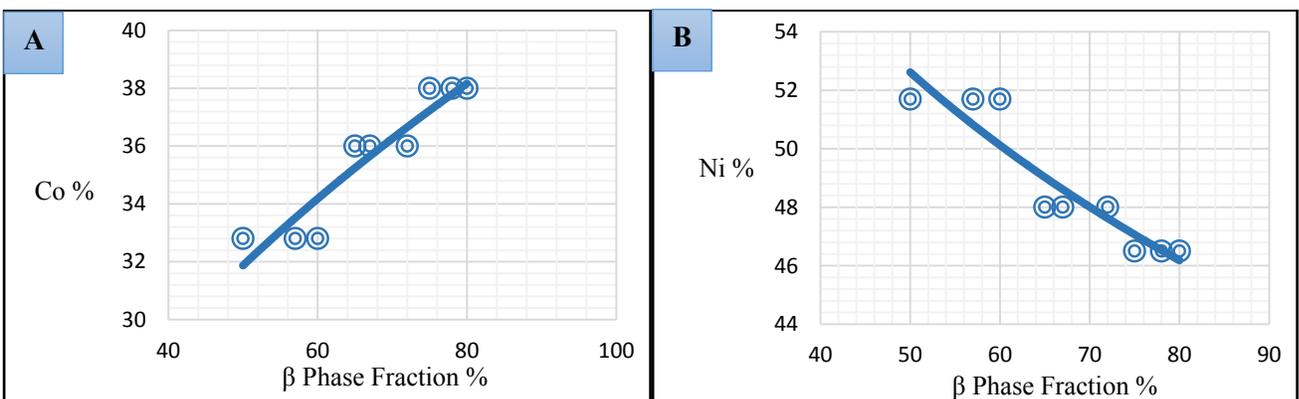


Figure (7) Relation between β volume fraction with (A) Co content and (B) Ni content.

As previously mentioned, the β phase has the high values of hardness, and therefore the hardness is increased by increasing the volume fraction of β phase because this increase is related

to a decrease in the γ ductile phase that precipitated on grains boundary of β phase, in another words, the increasing in γ phase generally decreased the hardness of these alloys, as shown in Figure (8 A). From Figure (8 B), the grain size of β phase has affected on the hardness values, where the increasing in grain size of β phase leads to increasing the hardness.

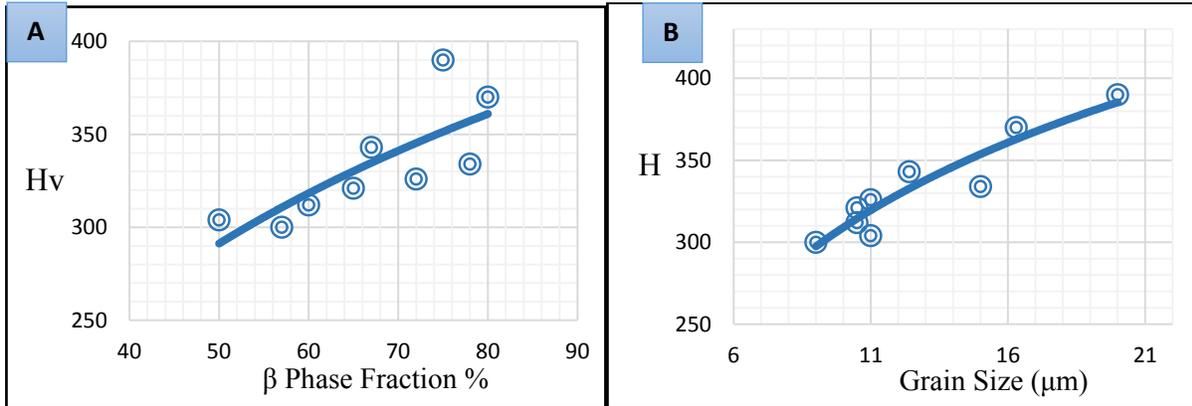


Figure (8) A)The effect of β % volume fraction on the hardness value, B)The effect of grain size on the hardness value.

Transformation Temperatures Investigations

The DSC results were presented by the four transformation temperatures as shown in Table (3), and the DSC charts are re-plotted as a way to calculate the four transformations temperatures for samples of AL29 group, as shown in Figures (9).

Table (3) Transformation Temperature of alloys at 29Al.

Sample	Alloyed Composition (at. %)				EDAX (β at. %)	Transformation Temperatures ($^{\circ}$ C)				
	Co	Ni	Al	Al/Co	Al/Co	A_s	A_f	M_s	M_f	T_o
S1G5	34	37	29	0.853	0.794	121	145	155	105	150
S2G5	33	38	29	0.878	0.876	77	97	83	69	90

The chemical composition of β phase was determined for the investigated alloys in order to calculate the Al/Co ratio in β phase which influences on the martensitic transformation temperatures. And by analyzing the DSC test results, it was found that by increasing the Co content, the transformation temperatures increased, and that agreed with some previous studies [12, 13], where they analyzed the composition of β phase to calculate Al/Co ratio in β phase in correlation with their M_s temperatures. Also it was found when Ni content decrease with increasing in Al content in β phase caused a decrease of martensitic transformation temperatures. According to the previous studies [7, 14 and 15], a relation between (Al/Co) and the transformation temperatures was found, these relations presented the effect of chemical composition of alloy on the transformation temperatures, and that could give a good indication for the approximated chemical composition that could produce SMAs working in the temperature range of application. For AL29 group samples,

DSC represented by to were appointed on the plot area of this relation between (Al/Co) and the transformation temperatures, it was found that these samples approved that the linear relations that were plotted represent the transformation temperatures according to the chemical composition for this alloy with Al atomic content 29% after annealing at 1200 °C for 5 hours and quenching in ice water. The transformation temperature presented in Table (2) gives a near temperature to the appropriate composition, but with an increase of about 50 °C, because the difference between the oriented samples and polycrystalline samples, according to previous work [15, 14].

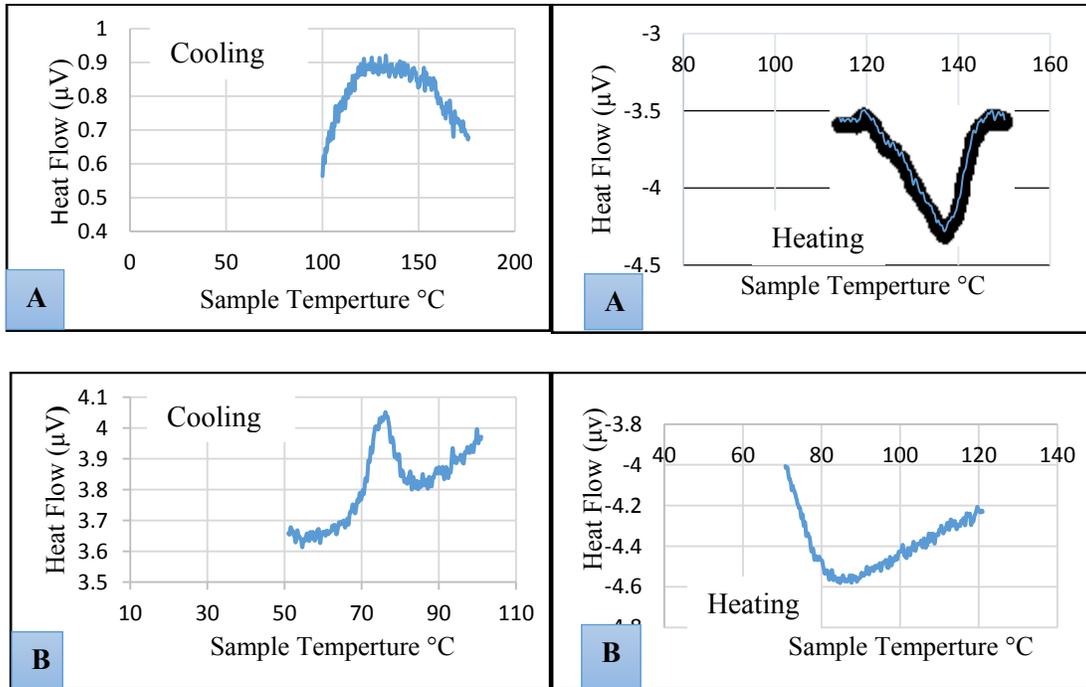


Figure (9) DSC curves of (A) S1G5, and (B) S2G5.

Corrosion Behavior

Tafel Corrosion Curves

After electrochemical investigation in simulated body fluid environment, the polarization curves of the three group of samples are shown in Figure (10). These figures indicate the anodic and cathodic regions in Ringer’s solution. At anodic sites, the dissolution of metals (Co, Ni, Al) takes place according to their potentials in galvanic series. While at cathodic sites, the reduction of oxygen can occur according to the following reaction:



The effect of chemical composition on the corrosion behavior will be discussed. Table (4) shows the data of corrosion, these data indicate that the samples S2 in each group has the lowest corrosion rates, while S1 and S3 samples have the higher corrosion rates.. In S2 samples, all aluminum was depleted in phases formed (β and γ) in alloys as shown in the optical microscopy and SEM inspections. In S1 samples, there is increment in Co content, while in S3 samples, there is

increment in nickel. Therefore, the S1 samples have corrosion rates higher than S3 samples because the potential of Co (- 0.277 V) is more active than Ni (- 0.25 V).

For different annealing times, the corrosion behavior of this alloy depends on β phase which transformed to martensite, where the corrosion rate increased with increasing the volume fraction area of transformed phase (β). It was found that, by increasing the heat treatment time the corrosion rate increased, because annealing for long time increases the amount of transformed phase (β) as shown in Figure (11). Through the cyclic curves and the microstructure image of samples after corrosion showed that β phase is acting as a cathode because of its chemical composition is rich with Al content that formed protective layer. Where found that the fraction area of β phase in the same sample that treated for 5 hours is larger than samples that treated for 1 and 3 hours.

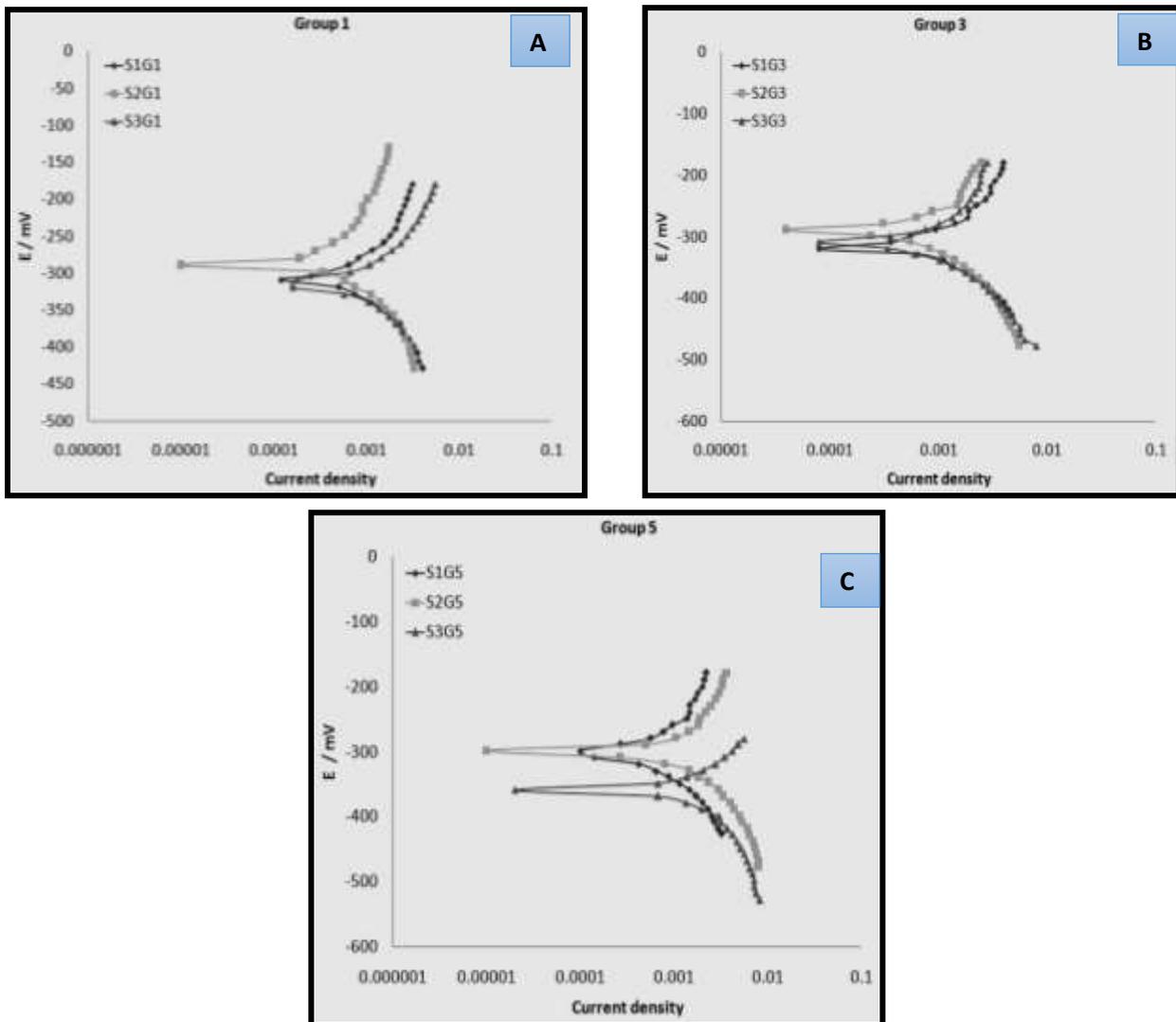


Figure (10) Tafel curves of samples, A) Group 1, B) Group 3, and C) Group 5.

Table (4) Corrosion parameters of samples in Ringer’s solution.

Samples	Annealing Time (H)	Alloyed Composition (at. %)			$E_{corr.}$ (mV)	$I_{corr.}$ ($\mu A/cm^2$)	C.R. (mpy)
		Co	Ni	Al			
S1G1	Group 1	34	37	29	-310	0.651	0.279
S2G1	Annealed at (1 h.)	33	38	29	-287.8	0.296	0.13
S3G1		32	39	29	-318	0.635	0.277
S1G3	Group 3	34	37	29	-321	0.793	0.34
S2G3	Annealed at (3 h.)	33	38	29	-290.3	0.411	0.173
S3G3		32	39	29	-310.3	0.652	0.28
S1G5	Group 5	34	37	29	-301.6	1.111	0.477
S2G5	Annealed at (5 h.)	33	38	29	-299.2	0.418	0.179
S3G5		32	39	29	-360	0.844	0.363

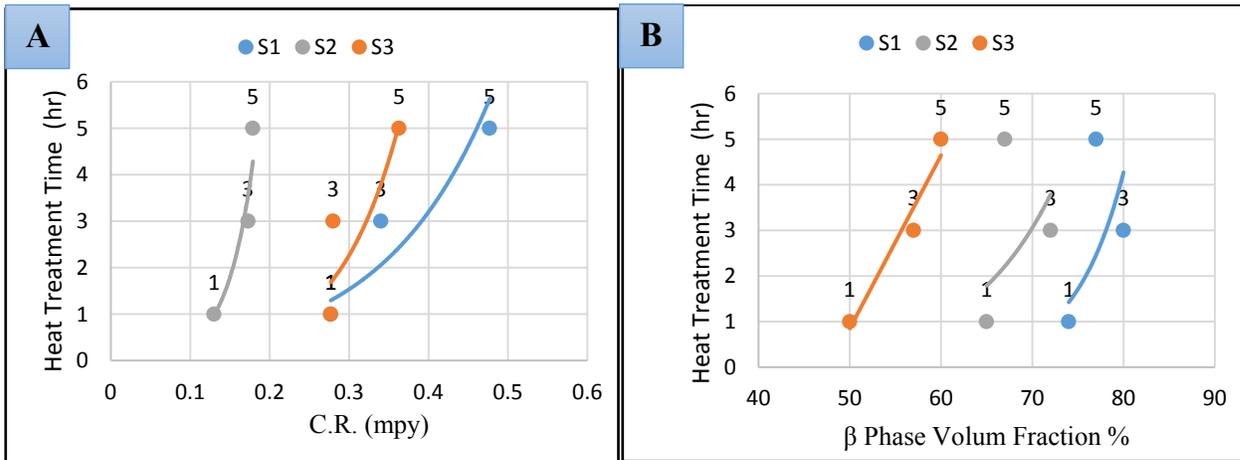


Figure (11) The relation between heat treatment time with, (A) Corrosion rate, and (B) β phase volume fraction.

Cyclic Corrosion Curve

Cyclic Polarization is a technique used to measure the pitting corrosion tendencies of a specimen in a given metal-solution system. The susceptibility to pitting corrosion is investigated by reversion the anodic polarization curve from the trans-passive area till the intersection point with the primary anodic polarization curve. The intersection point indicates to probability of pitting corrosion.

By investigating the cyclic curve shown in Figure (12), it was observed that the reversion of anodic polarization curve did not intersect with the primary anodic polarization curve, and that indicated there is no probability of pitting corrosion. And Figure (13) of microstructure image of sample after corrosion shows that the corrosion located at the grain boundary of β phase where γ phase presented, which indicated that γ phase acting as anode, and the corrosion type is an intergranular corrosion.

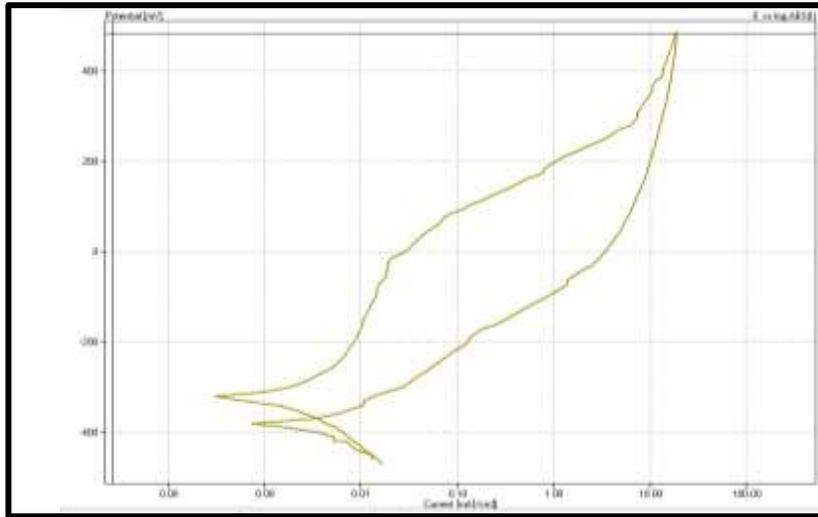


Figure (12) The cyclic corrosion curves of sample S3G3.

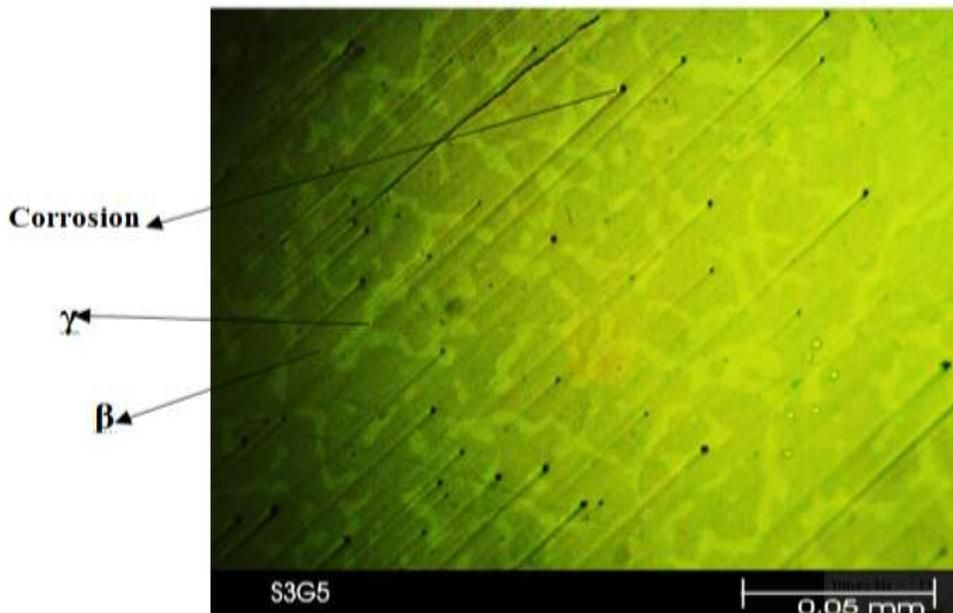


Figure (13) Microstructure image after corrosion test S3G3.

CONCLUSION

Based on the obtained results, the following conclusions are made:

- 1- The formed microstructure of melting technique samples composed basically of the two phases (γ , β), and the transformed β phase (M). Additional γ' phase precipitated inside the β phase.
- 2- The β phase fraction increased by increasing Co content while decreased with increasing Ni content. And by increasing (Al/Co) ratio, the volume fraction of β phase decreased and accordingly the grain size and hardness of β phase would decrease.
- 3- By increasing the heat treatment time, the β phase fraction increased and the amount of M phase presented also increased.
- 4- Transformation temperatures decrease by increasing the Al\ Co ratio.
- 5- The corrosion rate increased by increasing of Co content and the β phase volume fraction. No pitting corrosion occurred due to formation of a protective layer because the high Al concentration in β phase.

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