Comparative Study of Conventionally Sintered Co-Ni-Al Alloy With Spark Plasma Sintered Alloy

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Abstract:
Co-Ni-Al alloy samples were prepared by compacting the powdered alloy at various pressures in proper stoichiometric ratio and the high density compacted alloy was sintered at 673 K. The magnetic, mechanical properties, microstructure and phase analysis were studied and compared with that of spark plasma sintered (SPS) alloy. The sintered alloy exhibit martensitic twin variants with $\beta$ phase structure. Along with the diffused particle, few agglomerated clusters were observed on the topographic images. The magnetic and the mechanical studies of the test specimens were investigated using the vibrating sample magnetometer, pin on disk tribometer and universal testing machine respectively. The coercivity value and the ductility of the SPS alloy are higher than the same of the as-sintered alloy.

Keywords: Ferromagnetic shape memory alloy; $\beta+\gamma$ martensite phase; High ductility; Crystalline structure; Spark plasma sintering.

1. Introduction
In the development of sensors and actuators, more importance were given towards the ferromagnetic shape memory alloys (FSMA) due to its fast actuation mechanism and large strain when it was subjected to magnetic field [1]. The conventional thermo elastic shape memory alloys (SMAs) such as Ti-Ni alloys show the evidence of high value of strain but usually they have less actuation speed, which is limited by the heating/cooling rates. In the literature [2-6], various types of FSMA alloys were studied for phase transformation, structural and magnetic properties. In this paper, the Co-Ni-Al FSMA alloy has been studied, which is known for its high ductility, wide range of martensitic transformation temperature and phase transformation.

The chemical composition of the alloy, method of alloy preparation, thermal and mechanical pre-treatment, microstructure analysis, presence of stresses and ductile phase determine the martensitic transformation temperature of the alloy. In the literature [7-9], the Co-Ni-Al was studied by the method of casting, arc melting and bridgman method. For the present study, the Co-Ni-Al alloy samples were prepared by conventional sintering method and SPS method (Powder metallurgy technique), which are expected to yield high ductility. In

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order to obtain extremely dense, lesser amount of porous and well grained alloy in a short time period with relatively low sintering temperature and high rate of sintering, the spark plasma sintering method and the conventional sintering method were employed. It was reported [10] that FSMA alloys, namely, Ni-Mn-Ga, Cu-Ni-Al, and Ni-Ti that they lack in actuation mechanism due to their low ductility. However, in [11] the authors confirm that Co-Ni-Al has good ductility nature on account of its $\beta+\gamma$ phase structure by arc melting and casting method. Motivated by the results, the ductility property of Co-Ni-Al alloy has been studied by preparing the alloys using conventional sintering method. The stoichiometric composition of the alloy has been chosen as Co$_{38}$Ni$_{35}$Al$_{27}$ to achieve high recoverable strain with low symmetry variant.

In the paper [12], the spark plasma sintered Co-Ni-Al alloy was studied for its microstructure and phase transformation behaviour. The present study investigates the structural, morphological studies, mechanical and magnetic properties of the conventionally sintered alloys and the SPS sintered alloys.

2. Experimental details of Co$_{38}$Ni$_{35}$Al$_{27}$ alloy

The required raw materials Co, Ni and Al are procured with the purity level of 5N, mixed with appropriate stoichiometric proportion and grinded mechanically for two hours. Fig. 1 a,b shows the schematic drawing of the die, punches, and spacers that were used to process SPS sintered alloy and as-sintered Co$_{38}$Ni$_{35}$Al$_{27}$ alloy. The stoichiometric Co$_{38}$Ni$_{35}$Al$_{27}$ alloy powders were compacted to 10 mm, 30 mm and 65 mm disks using hydraulic press (Peeco Industries, Calcutta) at a constant ram rate of 1mm/min under varying pressures from 200 to 600 MPa. The compacted samples of 10, 30 and 65 mm diameter were then sintered at 673 K for a period of two hours in a tubular furnace with PID control. An argon flow of 100 ml per minute was purged to maintain the inert atmosphere. The highly compacted alloy, having green density of 4.479, sintered at 673 K has been studied further and they are compared with the SPS alloy. For the preparation of SPS alloy, the stoichiometric Co$_{38}$Ni$_{35}$Al$_{27}$ alloy powders were sintered to 20mm disks by SPS system at a pressure of 50 MPa with a heating rate of 150 °C/min to peak temperatures of 1000 °C with a dwell time of 5 minutes [12].

![Fig. 1. Schematic drawing of the die, punches, and spacers that were used to process the: a) SPS Co$_{38}$Ni$_{35}$Al$_{27}$ alloy, b) as-sintered Co$_{38}$Ni$_{35}$Al$_{27}$ alloy.](image-url)
The phase analysis and the crystalline nature of the alloy were studied by X-ray diffractometer technique. The morphological study was carried out by using Joel scanning electron microscope and Optical microscope. The magnetization loops of the alloy were obtained using Lakeshore 450 vibrating sample magnetometer (VSM). The wear resistance studies were taken using DUCOM pin on disk method. The stress strain curve of the alloys was carried out by tensile test using the Universal testing machine.

3. Results and discussion
3.1. Densification studies

The green densities of the as-sintered alloy samples were calculated by dimensional method and the percentage theoretical density was calculated by the rule of mixtures [13] which is tabulated in Tab I. Fig. 2 a,b show the graph of green densities and average densities of the as-compacted alloy of various compaction pressures. As the compaction pressure increases the green density of the Co$_{38}$Ni$_{35}$Al$_{27}$ alloy also increases. For 600 MPa pressure, the average green density of the as-compacted alloy was found to be 82.67%.

Tab. I Compaction pressure, specimen dimensions and green density of the Co$_{38}$Ni$_{35}$Al$_{27}$ alloy samples.

<table>
<thead>
<tr>
<th>Compacti on Pressure (MPa)</th>
<th>Dimensions (mm)</th>
<th>Mass (g)</th>
<th>Green density (g/cm$^3$)</th>
<th>Average green density (% TD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diameter</td>
<td>Thickness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>10.08</td>
<td>3.8</td>
<td>1.09</td>
<td>3.65</td>
</tr>
<tr>
<td>300</td>
<td>10.08</td>
<td>3.45</td>
<td>1.08</td>
<td>3.988</td>
</tr>
<tr>
<td>400</td>
<td>10.08</td>
<td>3.45</td>
<td>1.14</td>
<td>4.148</td>
</tr>
<tr>
<td>500</td>
<td>10.07</td>
<td>2.73</td>
<td>0.93</td>
<td>4.346</td>
</tr>
<tr>
<td>600</td>
<td>10.07</td>
<td>2.73</td>
<td>0.96</td>
<td>4.479</td>
</tr>
</tbody>
</table>

Fig. 2. (a), (b) Compaction pressure vs green density and average density of the as-compacted Co$_{38}$Ni$_{35}$Al$_{27}$ alloy.
3.2. Structural analysis

Fig. 3. X-ray diffraction pattern of the as-sintered Co$_{38}$Ni$_{35}$Al$_{27}$ alloy.

In Fig. 3, the XRD study of the as-sintered alloy is shown. The XRD pattern exhibits the high rate of polycrystalline cubic $\beta$ phase structure. Also it indicates that the Co$_{38}$Ni$_{35}$Al$_{27}$ alloy has favoured orientation towards $\beta$ (110) plane and similar peaks with high intensity, which are the characteristic of the Co-Ni-Al alloy and they correlate with the JCPDS data (file no- 654244) [14]. In the as-sintered alloy, along with the high intensity plane at (110), few more peaks are observed along $\gamma$(111), $\beta$(200), $\gamma$(200), $\gamma$(220) which indicate that the alloy is in martensite phase with cubic structure. From the peaks, in the SPS alloy [12] and in the as-sintered alloy, it has been observed that there is a minor shift of 0.2 degree in the lower angle side, which might have been caused by the internal stress present in the alloy. Z. H. Liu et al. [15] also examined two different super lattice peaks in addition to the fundamental peaks, which represent the cubic $\beta$ structure. The $\beta$ phase structure of the as-sintered Co-Ni-Al alloy is in uniform order, proving the austenite phase with the lattice parameter $a = 11.39$, which is similar to the SPS alloy [12]. The combination of $\beta$ phase and $\gamma$ phase of the as-sintered alloy is confirmed by their peak which shows that they have high ductility. The electron/atom ratio of the Co$_{38}$Ni$_{35}$Al$_{27}$ was calculated as 7.73.

3.3. Morphological analysis

Fig. 4 a-d show the microstructure of the as-sintered Co$_{38}$Ni$_{35}$Al$_{27}$ alloy. The fusion of $\beta$ phase and $\gamma$ phase structure of the as-sintered alloy is shown in the optical image Fig. 4 a, b where the $\gamma$ phase structure is seen in white patch of lines. During the sintering process, large rate of diffusion has been taken place in the compacted alloy. Also it is observed that the sintering temperature 673 K of the as-sintered alloy does not have any impact on densification factor; however, the sintering temperature may have little impact on the microstructure, phase structure and hardness of the sample [16]. The SEM image of the as-sintered alloy is shown in the Fig. 4 c, d. The morphological images show mild presence of oxidation during the process of sintering at 673 K [17]. By comparing the SEM image of the SPS alloy [12] with the as-sintered alloy, we find the presence of pores with agglomeration of particles, which is not large enough to prevent the grain growth. Also, due to the high densification rate of the as-sintered alloy, the grain growth might have merged the pores together to become a larger one. The $\gamma$ phase is known to improve the ductility of the brittle $\beta$
phase [18]. The lamellar microstructure in the SEM image shows that they are partly martensitic in the austenitic matrix. A similar type of microstructure was also reported by N. Scheerbaum et al [19].

![SEM images of the as-sintered Co<sub>38</sub>Ni<sub>35</sub>Al<sub>27</sub> alloy.](image)

**Fig. 4.** (a), (b) Optical micrographs of the as-sintered Co<sub>38</sub>Ni<sub>35</sub>Al<sub>27</sub> alloy; (c), (d) SEM images of the as-sintered Co<sub>38</sub>Ni<sub>35</sub>Al<sub>27</sub> alloy.

### 3.4. Magnetic studies

The M-H loops of the polycrystalline as-sintered and SPS Co<sub>38</sub>Ni<sub>35</sub>Al<sub>27</sub> alloys are given in Fig. 5 a, b. The hysteresis loop confirms that both polycrystalline alloys exhibit the soft ferromagnetic behaviour at room temperature. The coercivity of the SPS alloy was increased when it compared with the same of the as-sintered alloy. The magnetization of both alloys was not saturated even for the maximum applied field. This indicates that the sharp increase of high field magnetization is due to the large number of magnetic ions inside the domain walls. Similar observations were made by B. Rajini Kanth et.al for Co-Ni-Al thin films [20]. Fig. 5 shows that the magnetic domain walls reversible displacements of 180° have taken place for both kinds of sintered samples. Also the reversible rotation of the magnetic ions in both variants was confirmed which may be due to the sudden change in size and orientation of the ferromagnetic domains during the sintering process.

![M-H curves of the as-sintered and SPS Co<sub>38</sub>Ni<sub>35</sub>Al<sub>27</sub> alloy.](image)

**Fig. 5.** (a), (b) M-H curves of the as-sintered and SPS Co<sub>38</sub>Ni<sub>35</sub>Al<sub>27</sub> alloy.
3.5. Mechanical studies
3.5.1. Wear resistance studies

Fig. 6. (a) Wear resistance graph for the SPS alloy and insight graph shows the coefficient of friction of the SPS alloy; (b) wear resistance graph for the as-sintered alloy and insight graph shows the coefficient of friction of the as-sintered alloy.

Fig. 6 a shows the wear resistance graph of the SPS alloy and the insight graph shows the coefficient of friction of the SPS alloy. Fig. 6 b shows the wear resistance graph of the as-sintered alloy and the insight graph shows the coefficient of friction of the as-sintered alloy. The wear resistance studies for both test specimens have been carried out using DUCOM pin on disk tribometer instrument. The instrument rotational speed was 477 rpm and the wear track diameter (WTD) was kept at 80 mm. The test was conducted at the room temperature for the applied load of 50 mN for both as-sintered and SPS specimen. For the present study, in order to minimize the local temperature rise during the experiment, the wear test has been conducted at low speed with less load. While comparing the wear rate of the SPS specimen with the same of the compacted alloy, we find the wear rate of the SPS sample is less than the same of the as-compacted sample. It was observed that, in the beginning of the test, when the two surfaces are in contact, the sample surface adapts each other and undergoes plastic deformation with increased wear rate [21]. Later the wear rate becomes moderate with an increase in time period.

The coefficient of friction of an as-sintered alloy was maintained at around 0.3 up to 0.4 for 250 seconds. But for the SPS sample, the coefficient of friction was gradually increasing from 0.5 up to 1.2 for 250 seconds. It is observed that the coefficient of friction of the SPS sample is unstable with an increase in time period. Also the wear rate of the SPS sample initially increases and later it decreases gradually with an increase in time period. Fig. 7 a, b shows the optical microscopic images for the as-sintered and SPS alloys after the wear test was taken for the samples.

Fig. 7. (a) Optical microscopic image for the SPS alloy; (b) optical microscopic image for the as-sintered alloy after wear test was taken for the samples.
3.5.2. Tensile studies

![Stress-strain curves obtained by tensile test of the a) as-sintered Co\textsubscript{38}Ni\textsubscript{35}Al\textsubscript{27} alloy, b) SPS alloy.](image)

The tensile tests for both samples are conducted on universal testing machine (UTM) at the room temperature and the obtained stress-strain curves of the Co\textsubscript{38}Ni\textsubscript{35}Al\textsubscript{27} alloys are shown in the Fig. 8. Both samples prove its ductility; however the SPS sample curve shows that its ductility is higher than the same of the as-sintered alloy sample. Further, both samples may undergo permanent changes in its shape without any loss of its strength. Also the samples prove that the ductile property is uniform and dependable. In the low strain proportion limit of the curve, the material shows its elastic nature till 0.5 % of strain and obey Hooke’s law (stress is proportional to strain). As the strain is increased, the material shows the stress induced plastic nature of the specimen from 0.5 % up to 2.1 %. This non-linear curve, after drifting away from the proportion limit, indicates that the material undergoes a rearrangement of the internal molecular structure as the atoms have been moved to new equilibrium positions. Further for the SPS alloy sample with slight increase in strain, the tensile stress is increasing, which shows its high ductile nature. However, for the as-sintered alloy sample, there is no increase in the stress with increase in strain.

4. Conclusion

The polycrystalline Co-Ni-Al alloy samples have been prepared by conventional sintering technique, which are sintered at 673 K after grinding the powder for few hours. From the microstructure analysis, it is observed that the as-sintered alloy has the presence of pores with agglomeration of particles due to grain growth, whereas the SPS alloy has no evidence of pores with high density. Also the study shows high ductility by the confirmation of \(\beta+\gamma\) phase structure. The XRD study of both alloys reveals that they are in largely favoured martensite phase with cubic \(\beta\) phase structure. The SEM image shows that they are partially martensitic in the austenitic matrix. Both alloys exhibit soft ferromagnetic behaviour at the room temperature. The coercivity of the SPS alloy was found to have increased value when it compared with the same of the as-sintered alloy. The stress-strain curve of the SPS alloy sample shows that its ductility is higher than the same of the as-sintered alloy sample. The wear rate was moderate and the coefficient of the friction was unstable with an increase in time period for both samples. The wear resistance of the SPS alloy is higher than the same of the as-sintered alloy. The study shows that the Co\textsubscript{38}Ni\textsubscript{35}Al\textsubscript{27} alloys have good sign of actuation mechanism.
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5. References


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