Microstructure and Mechanical Properties of nano-Structured Ni-(92-x) wt.% Al–(x) wt. % Ce ribbon.

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Abstract-- The effect of Ce- addition on microstructure and mechanical properties of melt spun Ni –(92-x) wt. % Al –(x)wt. % Ce ribbon (x=1.2 and 4 wt.%) were investigated. Fcc- Al (γ-Al) is the main phase for all composition. By increases Ce-content some phases of orthorhombic Al₃Ni and hexagonal Al₃Ce were found. The lattice parameter of α-Al decreases by increasing Ce-content. Grain size of melt spun alloys, <D>, decreases while the dislocation density, ρ, increases with increasing Ce-content. Vickers hardness, HV, and Young’s modulus of compacted alloys decreases with increasing Ce-content. The effect of ball milling on microstructure and mechanical properties of ball milled Ni–90 wt. % Al–2 wt. % Ce powders were investigated.

Index Term-- Rare earth , RE, Transition metals, TM, Microstrain, Hardness

1. INTRODUCTION
A new family of aluminum based metallic glasses, recently discovered by two independent groups [1-4], show remarkably high tensile strength as well as good ductility. These metallic glasses are based on Al-TM- RE (TM= transition metals, RE= rare earths), containing 80-92 at. % aluminum. It has been reported that the tensile yield strength of these materials reaches as high as 800 Mpa in the amorphous state, and can be increased to 1500 Mpa by partial crystallization [5-9]. The partially crystallized metallic glass consists of nanoscale fcc-particles embedded in an amorphous matrix. The particle dispersion can be controlled by varying the cooling rate and the yield strength reaches a maximum with a particle volume fraction of approximately 20 % [5,6,8]. Nanostructured of these family obtained from melt spun amorphous ribbons have attracted much attention because of their excellent glass-forming abilities and their remarkable mechanical properties such as high tensile strength, hardness [10,11] and wear resistance [12]. Grain size below 5 nm cause Bragg peak line widths that are too broad for evaluation. For standard laboratory diffractometers, the upper grain size that can be evaluated is about 200 nm; otherwise, the line broadening is too small, but with 5 nm ≤ <D>, the nano-crystalline size region is covered, this explains the importance of X-ray line shape analysis for nano-crystalline materials.

This paper presents a detailed investigation of: (a) the effect of Ce- addition on structure and mechanical properties of melt spun Ni-(92-x) wt.% Al–(x) wt.% Ce ribbons (x=0.1, 2 and 4 wt.%), (b) the effect of milling time on structure and mechanical properties ball milled Ni-90 wt.% Al–2 wt.% Ce powders (τ=0, 12, 24, 48 and 72 h.).

2. EXPERIMENTAL TECHNIQUES

Master alloys of Ni –(92-x) wt.% Al -(x) wt.% Ce (x=0, 1, 2 and 4 wt.%) were prepared by induction melting of appropriate proportions of high-purity Al and Ni elements, together with Ce element supplied by Aldrich, inside alumina crucible under vacuum. Melt spinning experiments were carried out using circumferential wheel speeds in the range 12-47 m s⁻¹ under argon atmosphere. The resulting melt spun ribbons were typically 20 μm in thicknesses, 3 mm in width and 20-40 m in length. Melt spun Ni –90 wt.% Al -2 wt.% Ce alloys ball milled for different milling time (τ=0, 12, 24, 48 and 72 h.). The milling was performed under argon atmosphere in stainless steel vials with stainless steel balls.

X-ray diffraction (XRD) profiles from the melt spun ribbon and powders were recorded on a Philips diffractometer coupled with a Philips X-ray generator (PW 1730). The radiation used Cu Kα (λ= 0.154178 nm) at operating parameters 20 mA and 40 kV and step size 0.025° and scan speed 2° min⁻¹ in the range of 20 = 20⁻⁰. The X-ray line broadening of each reflection, were calculated by a computer software after automatic background removal, and Kα₂ stripping (stripping rate Kα₁/Kα₂= 0.56).

The mechanical properties of the compacted alloys were investigated by a special kind of continuous Vickers hardness test (Shimadzu Dynamic hardness tester). During the test a Vickers pyramid was pressed into the surface of the sample by a computer controlled hydraulic mechaical testing machine (MTS 810). During the loading period the Vickers pyramid penetrated into the surface of the sample at constant velocity and the same velocity was applied in the unloading period when the pyramid moved backwards. In the course of the test the load was registered as a function of the penetration depth.

3. RESULTS AND DISCUSSIONS

3.1-Microscopic density

Microscopic density, ρ, of melt spun Ni –(92-x) wt.% Al -(x) wt.% Ce (x=0, 1, 2 and 4 wt.%) ribbons were determined by using Archimedean technique and mixing rule calculation, respectively. The densities of pure Al, Ni and Ce used in the mixing rule calculation were 2.70 g/cm³, 8.908 g/cm³ and 6.770 g/cm³, respectively. The values the theoretical density, ρₜheor increases from 3.197 to 3.359 g/cm³, while the values of the experimental density, ρₑxp increases from 3.002 to 3.102 g/cm³ over range of studied. A comparison have been
hold between the values of $\rho_{\exp}$, and the values of $\rho_{\text{thr}}$. It was found that the values of $\rho_{\exp}$ was smaller than the values of $\rho_{\text{thr}}$. The values of $\rho_{\exp}$ were in the ranging from 92 to 94% of $\rho_{\text{thr}}$. This in a good agreement with the previous study[13], where the most previous studies on nano-material reported $\rho_{\exp}$ ranging from 60 to 97% of the respective $\rho_{\text{thr}}$. This was attributed to that the $\rho_{\text{thr}}$ was hold for the crystalline alloys but the $\rho_{\exp}$ for nanostructured alloys. It can also be postulated that, to some extent, the lower densities in nano materials are caused by large volume fraction of interfacial region.

3.2. Microstructure

3.2.1. The effect of composition

Fig. 1 shows the X-ray diffraction patterns of melt spun Ni-(92-x) wt.% Al -(x) wt.% Ce (x=0,1,2 and 4 wt.%) ribbons. It can be seen that the X-ray peaks characterized by five main Bragg’s peaks corresponds to (111), (200), (220), (311) and (222) refer to α-Al phase for all composition. With increasing the Ce- content (Ce=2 wt.%), α-Al and orthorhombic Al$_2$Ni phases were found. For (Ce=4 wt.%), α-Al phase, orthorhombic Al$_2$Ni and hexagonal Al$_3$Ce were formed. It can be seen also in Fig. 1, that, the Ce addition and ball milling exhibit a broadening of crystalline peak and decreases in intensity. This is attributed to the development of nano-crystals and internal lattice strain in the samples.

The lattice parameter, $a$, of α-Al were calculated as a function of Ce-content. By plotting the lattice parameter, $a_{\text{hkl}}$, calculated from the Bragg law’s against an extrapolating function $f(\Theta) \cdot [f(\Theta)=\frac{1}{2}(\cos^2\Theta + \sin\Theta \cos^2\Theta)]$ which hold quite accurately down to low value of $\Theta$ [14,15,16]. The results indicate that the values of $a$, for α-Al decreases with increasing Ce-content and has a value between 4.043 and 4.037 Å. These values are lower than lattice parameter of pure Al which is 4.0496 Å [17].

The change of $a$ with Ce-content provides additional insight into the mechanism of disordering process upon the composition.

The logarithm of the real part of the Fourier coefficients, $L_n A_l$, of different reflections of melt spun Ni-90 wt.% Al -2 wt.% Ce ribbons (as a represenation example of melt spun Ni-(92-x) wt.% Al -(x) wt.% Ce (x=0,1,2 and 4 wt. %)) and ball milled Ni-90 wt.% Al -2 wt.% Ce powders (ball milled for different milling time $t=0$, 12, 24, 48 and 72 h.) are plotted in Fig. 2, against $k^2$C at different values of L, according to modified Warren Averbach equation [14,18,19]

$$\ln L_n A_l=\ln A_{l0}-\rho (\pi b^2/2) L_n \ln (R/L) (k^2 C) + O(k^4 C^2)$$

(1)

Where $A_{l0}$ is size Fourier coefficient, $\rho$ is the dislocation density, $R_e$ is the effective outer cut-off radius, $b$ is the Burgers vector, $L$ is the Fourier length defined as $L_{\text{max}}$ [20], where $a_0=\lambda/2(\sin \Theta_2 - \sin \Theta_1)n$ are integers starting from zero and $(\Theta_2 - \Theta_1)$ is the angular range of the measured diffraction profile, $\kappa=2\sin \Theta_0/\lambda$, $C$ is the contrast factor of dislocation and O is the stands for higher order term in $k^2 C$.

The average contrast factor, C, of cubic system for edge, $C_{\text{edge}}$ and screw $C_{\text{screw}}$ dislocation can be determined according to the following equation [14,16,18,19]

$$C=\text{choo}(1-q\mathbf{f}^2)$$

(3)

where $C_{\text{choo}}$ is the average dislocation contrast factor for the h00 reflection, q is parameter dependence on the elastic constant and $H^2=(h^2+k^2+l^2)/((h^2+k^2+l^2)^2)$. For elastic constant of Al: $c_{11}=107$ Mpa, $c_{12}=60.8$ Mpa and $c_{44}=28.3$ Mpa[21]. The average values of dislocation contrast factor, C, corresponding to the (h00) reflection, $C_{\text{h00}}$ and dislocation character, q, for screw and edge dislocations in fcc-Al are listed in Table.

In Fig. 2 we can be observed for each particular L values, the values of $\ln A_l$ decreases with $k^2 C$ on a global scale, indicating the presence of lattice distortions. The linear behaviour of $\ln A_l$ as a function of $k^2 C$ indicating that the second order term in eq (1), can be neglected, i.e the correlation between the dislocation in the system is negligible. The intercepts of the fitted straight at $k=0$ yield the sequency of the $\ln A_l$. The slope of the fitted straight line M(L) is given by

$$M(L)=\rho (\pi b^2/2) L^2 \ln (R/L)$$

The size of Fourier coefficient, $A_{l0}$ are plotted versus the Fourier length L, for melt spun Ni-90 wt.% Al -2 wt.% Ce ribbons (as a representation example of melt spun Ni-(92-x) wt.% Al -(x) wt.% Ce (x=0,1,2 and 4 wt. %)). The area weighted average column length, $<L>_{\text{area}}$, is given by the tangent to small L values of $A_{l0}$ extrapolated to the x-axis, while the volume weighted average column length, $<L>_{\text{vol}}$, can be determined from the area under the curve of $A_{l0}$ against L.

Fig. 3 shows the variation of the expression $M(L)/L^2$ against $\ln L$ according to:

$$M(L)/L^2=\pi b^2/2 L^2 \rho \ln R_e - (\pi b^2/2) L^2 \rho \ln L$$

The slope of the fitted straight line yields the average dislocation density, $\rho$, while the outer cut-of radius $R_e$ can be determined from the intersection with the ordinate.

The detailed evaluation of the modified Warren Averbach procedures described above were applied for melt spin ribbons are listed in Tables I. It could be notice the values $<L>_{\text{area}}$ and $<L>_{\text{vol}}$ decreases with increasing Ce-content. The ratio of $<L>_{\text{vol}}/<L>_{\text{area}}$ varies between 1.49 and 1.78 for ribbons contain Ce-element which interval coincides fairly with results on nano crystalline Al powders, where the ratio of $<L>_{\text{vol}}/<L>_{\text{area}}$ for nano-crystalline Al powders varies between 1.4 and 1.75 [22]. The primarily obtained average column length of an ensemble of particles can be transformed into average grain sizes if all the crystallites in the sample have roughly the same shape[23,24], the standard assumption is a spherical shape, then

$$<D>_{\text{vol}}=4/3 <L>_{\text{vol}}$$

&

$$<D>_{\text{area}}=3/2 <L>_{\text{area}}$$

The values of $<D>_{\text{vol}}$ and $<D>_{\text{area}}$ of melt spin ribbons were listed in Table 1. They decreases with increasing Ce-content. The average values of dislocation density, $\rho$, increases from $10 \times 10^{-12}$ m$^{-2}$ for $x=0$ wt.% to $15 \times 10^{-12}$ m$^{-2}$ for $x=4$ wt.% while the average distance between the adjacent dislocation, $L_e=1/\rho^{1/2}$, decreases with increasing Ce-content. The average weighted averaged column length, $<L>_{\text{area}}$, is only by a factor of 1.36 larger than the average values of $L_e$, i.e individual nano-grains contain just a few dislocations. This is in a good
agreement with previous observations, according to which the second order term in modified Warren Averbach analysis, corresponding to the dislocation-dislocation interaction was negligible [19]. The values of the dislocation arrangement parameter, \( M = R_v \rho^{1/2} \), increases with increasing Ce content. Wilkens[25] has shown that the value of \( M \) gives the strength of the dipole character of dislocations. If \( M \) is small or large the dipole character and the screening of the displacements filed of the dislocations is strong or weak, respectively. At the same time, strong or weak correlation in the dislocation distribution, respectively. This means that the strength of the dipole character of dislocation for melt spun ribbons increases by increasing Ce content.

3-2.2. The effect milling time

The detailed evaluation of the modified Warren Averbach procedures described above were applied for ball milled Ni-90 wt.% Al-2 wt.% Ce powder for different milling time (\( \tau=0, 12, 24, 48 \) and 72 h) are listed in Table II. It could be notice the values \( <\gamma>_\text{area} \), \( <\gamma>_\text{vol} \) decreases with increasing Ce content. The ratio of \( <\gamma>_\text{vol}/<\gamma>_\text{area} \) were 1.5 for all milling times. The values of \( <\gamma>_\text{vol} \) decreases from 40.7 nm to 33.7 over the range of milling time. The average of dislocation density, \( \rho \), decreases 13x10\(^{-12}\) m\(^{-2}\) to 22x10\(^{-12}\) m\(^{-2}\) over range of milling time. Fig. 5 shows that the dislocation density, \( \rho \), varies inversely with the volume average grain size. Similar related was observed in the behavior dislocation density, varies inverse grain size in the case of nanocrystalline Al- powder[22], and root main square (rms) lattice strain versus inverse grain size in the case of nanocrystalline Fe powders[26,27]and on pd [28]. Tian and Atzmon [26] interpreted this phenomenon as a results of two independent effects. The first one is due to the grain size represents the strain resulting from the defects within the grain interior, and the second effects is proportional to specific grain boundary area and represents the strain resulting from grain boundaries. The average distance between the adjacent dislocation, \( L_v = 1/\rho^{1/2} \) decreases with increasing milling time. The area weighted averaged column length, \( <\gamma>_\text{area} \), is only by a factor of 1.37 larger than the average values of \( L_v \), i.e individual nano-grains contain just a few dislocations. The values of the dislocation arrangement parameter, \( M = R_v \rho^{1/2} \), increases with increasing milling time.

3-2.3. Mechanical properties

3-3.1. The effect of composition

Fig. 6 present experimental data ( loading versus displacement) for compacted melt spun Ni-90 wt.% Al-2 wt.% Ce ribbons (( as a represenation example ) of melt spun Ni-(92-x) wt.% Al -(x) wt.% Ce (x=0, 1, 2 and 4 wt. %) and ball milled Ni- 90 wt.% Al -2 wt.% Ce powder for different milling time (\( \tau=0, 12, 24, 48 \) and 72 h)). The difference in hardness of the samples are apparent from the large difference in the depth attained a maximum load. The investigated values of Vickers hardness, HV, of compacted melt spun Ni-(92-x) wt.% Al -(x) wt.% Ce ribbons were listed in Table I. The Vickers hardness decreases with increasing Ce content. The best fit line in fig. 7 describes the Hall-Petch dependence of microhardness on the grain size[14-16] for compacted ribbons a in the following form :

\[ HV_{0.01} = 1330 – 6705(<\gamma>_\text{vol})^{-0.5} \text{ (kg/mm}^2) \]

where \( HV_{0.01} \) is the Vickers hardness at 0.01 kg and \( <\gamma>_\text{vol} \) is the averaged grain volume size (nm). Apparently , in the present work the Hall-Petch relationship is characterized by a negative slope. According to Suryanarayana[29] the original Hall-Petch relationship was derived using the concept of dislocation pile-ups in individual grains. However, in nanocrystalline materials pile-ups cannot form when the grain size is less than a critical values \( d_c \). Then, negative Hall-Petch slope by an increase of volume fraction of amorphous phases with crystallite size decreases below \( d_c \) assuming that the composite rule of mixture for crystalline and amorphous phases is valid for microhardness. The hardness of our alloys is attributes mainly to the combination of solid solution hardness of \( \alpha \)-Al phase matrix by Ni and Ce. The reduction in hardness by increasing Ce content results from the loss of this solid solution hardening combined with coarsening of \( \alpha \)-Al cell size and forming \( \gamma \)-NiAl and \( \gamma \)-Cr phases. Then, negative Hall-Petch slope in the alloys under studied can be explain by increasing the volume fraction , both Ni and Ce are almost completely rejected from the \( \alpha \)-Al phase, and on Ce is enriched at the interface the rejected Ce atom are enriched at the interface and lead to increases the volume fraction. The effective elastic modulus, \( E_{\text{eff}} \) and Young’s modulus, \( E \), of compacted melt spun ribbons were calculated and listed in Table I. They decreases by increasing Ce content.

4. Conclusion

Microstructure and mechanical properties of Nano structured Ni-(92-x) wt.% Al -(x) wt.% Ce (x=0,1,2 and 4 wt. % ) ribbon were synthesis by melt spinning method were studied. The effect of Ce-content and milling time on the
microstructure and mechanical parameters were investigated from X-ray line broadening and Vickers hardness test

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REFERENCE


TABLE I

Microstructure mechanical parameters of melt spun Ni-(92-x) wt. % Al-(x) wt. % Ce ribbon as a function of Ce-content (x=0, 1, 2 and 4 wt. %)

<table>
<thead>
<tr>
<th>Ce. wt. %</th>
<th>&lt;L&gt; area (nm)</th>
<th>&lt;L&gt; vol. (nm)</th>
<th>&lt;D&gt; area (nm)</th>
<th>&lt;D&gt; vol. (nm)</th>
<th>ρx10^4 (kg/m²)</th>
<th>Lc (nm)</th>
<th>M</th>
<th>HV (kg/mm²)</th>
<th>Eeff (kg/mm²)</th>
<th>E (kg/mm²)</th>
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<tr>
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<td>35.3</td>
<td>55.9</td>
<td>10</td>
<td>32</td>
<td>3.95</td>
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<td>28.7</td>
<td>37.9</td>
<td>15</td>
<td>26</td>
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<td>0.99</td>
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TABLE II

Microstructure parameters of ball milled Ni-90wt. % Al-2 wt. % Ce powders as a function of τ (τ=12, 24, 48 and 72 h)

<table>
<thead>
<tr>
<th>τ (h)</th>
<th>&lt;L&gt; area (nm)</th>
<th>&lt;L&gt; vol. (nm)</th>
<th>&lt;D&gt; area (nm)</th>
<th>&lt;D&gt; vol. (nm)</th>
<th>ρx10^4 (kg/m²)</th>
<th>Lc (nm)</th>
<th>M</th>
<th>HV (kg/mm²)</th>
<th>Eeff (kg/mm²)</th>
<th>E (kg/mm²)</th>
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</thead>
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<td>30.8</td>
<td>30.6</td>
<td>42.7</td>
<td>13</td>
<td>28</td>
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<td>16</td>
<td>25</td>
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Fig. 1. X-ray diffraction patterns of melt spun Ni-(92-x) wt.% Al-(x) wt.% Ce ribbons (x=0, 1, 2, and 4 wt.%)

Fig. 2. The relation between Ln A_s and k²C/nm² at different values of L of melt spun Ni-90 wt.% Al-2 wt.% Ce ribbons (as a representation example of melt spun Ni-(92-x) wt.% Al-(x) wt.% Ce ribbons and ball milled Ni-90 wt.% Al-2 wt.% Ce powders for different milling time)
Fig. 3. (a) The relation between $A_s$ versus $L$ of melt spun Ni-90 wt.% Al-2 wt.% Ce ribbons (as a representation example of melt spun Ni –(92-x) wt.% Al -(x) wt.% Ce ribbons and ball milled Ni –90 wt.% Al-2 wt.% Ce powders for different milling time).

Fig. 4. The relation between $M(L)/L^2$ and $\ln L$ of melt spun Ni-90 wt.% Al-2 wt.% Ce ribbon (as a representation example of melt spun Ni –(92-x) wt.% Al -(x) wt.% Ce ribbons and ball milled Ni–90 wt.% Al-2 wt.% Ce powders for different time).
Fig. 5. The dislocation density varies inversely with the volume averaged grain size for ball milled Ni-90 wt.% Al-2 wt.% Ce powders at different milling time.

Fig. 6. The relation between load and depth for compacted mult spun Ni-90 wt.% Al-(2-x) wt.% Ce (as a representation example of melt spun Ni-(92-x) wt.% Al-(x) wt.% Ce ribbon and ball milled Ni-90 wt.% Al-2 wt.% Ce powders for different milling time.)
Fig. 7. The relation between VH and $\langle D \rangle^{0.5}$ for compacted melt spun Ni-(92-x) wt.% Al – (x) wt. % Ce (x=0, 1, 2, 3 and 4 wt. %) ribbons.

Fig. 8. The relation between VH and $\langle D \rangle^{0.5}$ for compacted ball milled Ni-90 wt.% Al – 2 wt.% Ce powders for different milling time.