Crystalline to Amorphous Phase Transition in Al-Ni-Co System during Mechanical Alloying

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The different transformation behavior towards amorphization observed during mechanical alloying of $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{100-x}\text{Zr}_x$ powder mixtures where $x=0$ to 4 at.% was characterized by means of X-ray diffraction patterns, scanning electron microscopy, differential scanning calorimetry and transmission electron microscopy. It was found that mechanical alloying of Al, Ni and Co elemental powders without Zr leads to the formation of nanocrystalline equilibrium phases fcc-Al solid solution and $(\text{Co}, \text{Ni})_2\text{Al}_3$ compound. Upon disordering the resulting phases it was concluded that amorphization cannot be obtained. The measured enthalpy stored ΔH_i during deformation was found less than 1 kJ/mol. Whereas, the crystalline to amorphous phase formation was observed when a few at.% of Zr was added into the Al-Ni-Co ternary system. The reasons seem to result from the fact that at the Al/Ni, Al/Co and Ni/Co the criteria for amorphization by solid state amorphization during mechanical alloying are not fulfilled, while at the Al/Zr, Ni/Zr and Co/Zr interfaces these criteria are satisfied and the amorphization is observed at an early stage of deformation. Increasing Zr substitution increases the thermal stability of the amorphous phase, which explains the complete amorphization for compositions containing Zr up to 4 at.%. The crystallization evolves in two stages: precipitation of Al phase dispersed in an amorphous matrix which crystallized in turn. The total exothermic heat ΔH_c released vary from 2.2 to 3.1 kJ/mol in going from 1 to 5 at.% Zr. The activation energy (E_a) and crystallization temperature (T_x) both increased with increasing Zr addition.

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I. Introduction

The phase formation by mechanical alloying (MA) of many binary systems with large negative enthalpy of mixing $\Delta H_{\text{mix}} < 0^{(1)(2)}$ or positive enthalpy of mixing $\Delta H_{\text{mix}} > 0^{(3)}$ are now rather well understood⁽⁴⁾⁽⁵⁾. However, little is known about the phase formation by MA in ternary, and quaternary systems⁽⁶⁾. The reasons seem to be in part the lack of thermodynamic data, and the chemical diffusion in multicomponent systems is far beyond the reach of any atomistic model, only a qualitative understanding of the diffusion in ternaries is available⁽⁷⁾. Recently, quantitative calculations have shown that the sharp concentration gradients occurring during diffusive mixing in binary systems facilitate the amorphization by reducing the driving force for crystallization, and the addition of an appropriate third element should improve further the metastability of the amorphous phase⁽⁵⁾. In the recent work, we have found that MA of the Al-Ni-Co system allows the formation of nanostructured equilibrium phases (with Al > 80 at.%), and the partial substitution by Zr or Ti in the composition range of 1 to 4 at.% Zr or Ti leads to the synthesis of amorphous single phase or amorphous matrix with a random distribution of fcc-Al nanograins⁽⁸⁾⁽⁹⁾. In the present study we deal with the morphology, structure, and mechanism of formation of $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{100-x}\text{Zr}_x$ amorphous alloys (where $x=0$ to 4 at.%) produced by MA process. Such systems are of interest for several reasons: First, they have good mechanical properties when compared to the

highest values of tensile strength and Vickers hardness observed in the case of Al-Y-Ni⁽¹⁰⁾, and Al-Ce-Ni (Al > 85 at.%) amorphous alloys containing homogeneously dispersed fcc-Al nanograins⁽¹¹⁾⁽¹²⁾.

Secondly, the leaching treatment of these Al-rich materials mechanically alloyed produces very porous Raney Nickel with high electrocatalytic activity, which is difficult to be obtained by conventional methods⁽¹³⁾. The last aim was to report the compositional dependences of crystallization temperature, enthalpy of crystallization, activation energy, and discuss the thermally activated return to equilibrium state.

II. Experimental Details

Elemental Al, Ni, Co, and Zr powders with a purity of 99.95% and a particle size in the range of 10 to 15 μm were mixed to give the desired average atomic composition $(\text{Al}_{88}\text{Ni}_8\text{Co}_4)_{100-x}\text{Zr}_x$ (where $x=0$ to 4 at.%). The powders were milled in stainless steel vials using a planetary machine (Fritsch/Pulverisette) with a ball-to-powder weight ratio of about 10:1. Milling was carried out under a purified argon atmosphere to prevent formation of oxides or nitrides. The loaded vial was sealed in dry argon after being evacuated to 1.333×10^{-2} Pa (10^{-4} torr) or better. The vial temperature was maintained near 308 K, and the long milling duration ranged from 50 to 400 h in the data presented below is due to the low speed rate (2 s^{-1}) selected for our experiments. Scanning-electron-microscopy X-ray fluorescence analysis was used to evaluate the degree of contamination by Fe, Cr impurities (see

Table 1 Chemical analysis of $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{100-x}\text{Zr}_x$ alloys prepared by MA.

Initial Compositions (at. %)	Milling time (h)	Fe	Cr	Al	Ni	Co	Zr
		(at. %)			(at. %)		
$\text{Al}_{88}\text{Ni}_8\text{Co}_4$	100 (EDX)*	0.42	—	87.64	7.95	3.99	0
	200 "	1.27	—	86.80	7.87	4.06	0
	400 (ICP)**	3.45	0.5	84.53	7.68	3.84	0
$\text{Al}_{86.24}\text{Ni}_{7.84}\text{Co}_{3.92}\text{Zr}_2$	100 (EDX)	0.51	—	85.79	7.79	3.89	2.02
	200 (ICP)	1.15	—	85.16	7.73	3.86	2.10
$\text{Al}_{85.36}\text{Ni}_{7.76}\text{Co}_{3.88}\text{Zr}_3$	100 (EDX)	0.48	—	84.86	7.71	3.85	3.10
	200 "	1.21	—	84.27	7.66	3.83	3.03
$\text{Al}_{84.48}\text{Ni}_{7.68}\text{Co}_{3.84}\text{Zr}_4$	100 (EDX)	0.52	—	83.92	7.62	3.80	4.11
	200 "	1.27	—	83.33	7.57	3.78	4.05
$\text{Al}_{83.6}\text{Ni}_{7.6}\text{Co}_{3.8}\text{Zr}_5$	100 (EDX)	0.55	—	83.01	7.54	3.77	5.13
	200 (ICP)	1.28	—	82.47	7.48	3.73	5.04

* X-ray fluorescence analysis (error within ± 2 at.%)

** Induction coupled plasma

Table 1), while the oxygen in the alloys was determined by the helium carrier fusion-thermal conductivity method, and found to be in the order of 0.21 and 0.32 at.% for powder mixtures milled for 200 and 400 h, respectively. Phases were identified by X-ray diffraction with $\theta/2\theta$ Rigaku diffractometer using $\text{Cu-K}\alpha$ radiation, and by transmission electron microscopy TEM operating at 200 kV (Jeol 2000 EX).

Thermal analysis was performed in Seiko differential scanning calorimeter DSC (model 220) at various heating rates/(0.17 to 0.67 K/s). Approximately 10 mg of milled powder were sealed hermetically in Al pan for each DSC run. Two to three DSC run data for each sample were used to estimate an average value of the kinetic parameters.

The base line was determined by repeating each run. Temperature and peak-area calibration was carried out with Zn, and In standards.

III. Results and Discussion

1. Structural evolution of $\text{Al}_{88}\text{Ni}_8\text{Co}_4$ ($X_{\text{Zr}}=0$) under MA

The MA of $\text{Al}_{88}\text{Ni}_8\text{Co}_4$ powders evolves in two stages,

i.e., agglomeration, and mixing reaction. During the agglomeration stage, the powder mixture tend to form large particles of the order of $30\text{ }\mu\text{m}$ as Al, Ni and Co are repeatedly flattened and welded by colliding balls. The morphology and the smooth appearance of the particles surface $\text{Al}_{88}\text{Ni}_8\text{Co}_4$ after 50 h of milling shown in the Fig. 1(a) is characteristic of ductile powders where the equilibrium between the fracture and welding is difficult to maintain. The scanning electron micrograph (SEM) of Fig. 1(b) reveals the cross-section of $\text{Al}_{88}\text{Ni}_8\text{Co}_4$ powders after 50 h, where the individual Ni and Co lamellae are from 1 to $3\text{ }\mu\text{m}$ thick. The harder, higher melting metals Ni, and Co break down into slice-type within the Al matrix. The energy-dispersive X-ray analysis (EDX) indicates that the grey regions of Fig. 1(b) contain Al, Ni, and Co, while the white lamellae are Ni and Co. For continuous milling, the elemental Al, Ni, and Co lines in the diffraction pattern broaden significantly and are reduced in intensity (see Fig. 2). Above 50 h the mixing reaction takes place and the Co peaks have completely disappeared. The Al solid solution and fcc-(Ni, Co) solid solution remain. As the intensity of the elemental X-ray lines is reduced the diffraction lines of the fcc-Al are slightly displaced compared to the Bragg peaks of the pure Al. The contraction of the lattice parameter of the Al solid

Fig. 1 Scanning electron micrographs of $\text{Al}_{88}\text{Ni}_8\text{Co}_4$ powders after 50 h of milling. (a) Surface topology, (b) Cross-section.

Fig. 2 Evolution of X-ray diffraction patterns of $\text{Al}_{88}\text{Ni}_8\text{Co}_4$ powders versus milling time and as annealed sample (bottom).

solution, which becomes exactly 0.17% lower indicates that interdiffusions reaction occurred, while no significant displacement of the fcc (Ni, Co) solid solution was detected. The reason seems to originate from the absence of difference between the atomic ratio of the Ni and Co. The progression of milling above 180 h allows the formation of new crystalline phase with a monoclinic symmetry $(\text{Co, Ni})_2\text{Al}_9$ (see Fig. 2). This indicates that true alloying takes place during milling. The fcc-Al and $(\text{Co, Ni})_2\text{Al}_9$ nanocrystalline phases are not a metastable phases. More evidence for this conclusion is from DSC measurements of sample milled 50, 200 and 400 h shown in Fig. 3 (the actual composition of the powders does not deviate significantly from the desired nominal composition as shown in Table 1. The composition milled 400 h contains 3.45 at.% of Fe due to wear debris. The dissolved amount of Fe has negative effect on the amorphization reaction. Raynor reports that the dissolution of Fe in the Al–Ni–Co system and for Ni/Co atomic ratio about 2 increases the volume fraction of the $(\text{Co, Ni})_2\text{Al}_9$ phase⁽¹⁴⁾. The sharp exothermic peak of powder milled 50 h corresponds to the formation of fcc-Al and $(\text{Co, Ni})_2\text{Al}_9$ phases from the reaction at 772 K of the pure lamellae of Ni, Co, and Al. The heat released during this reaction was estimated to be in the order of 8 kJ/mol. The DSC spectrum (bottom) of powder milled 200 or 400 h shows very broad two exothermic peaks, the total heat released was found less than 1 kJ/mol. The X-ray diffraction patterns of sample annealed from 400 to 573 K exhibit only peak sharpening. This suggests that these two broad peaks correspond to the annihilation of defects generated during deformation and grain growth. The milling in the case of $\text{Al}_{100-1.5x}\text{Ni}_x\text{Co}_{0.5x}$ powders (where $x=2$ to 8 at.%)

Fig. 3 DSC thermogram of $\text{Al}_{88}\text{Ni}_8\text{Co}_4$ powders as milled. 50 h (top) and 200 h, 400 h (bottom).

leads to the formation of equilibrium phases with high density of grain boundaries. Further grinding of the Al solid solution and $(\text{Co, Ni})_2\text{Al}_9$ compound ($x=8$ at.%) above 200 h does not lead to the formation of amorphous phase as evidenced by the TEM investigations (see Fig. 4). We have observed in going from 150 to 200 h of milling only a broadening of the X-ray diffraction lines and from 200 to 400 h no appreciable broadening was detected. The broadening is attributed to a refinement of the crystal size and an increase in atomic-level strain. To separate both effects we analyzed the peak broadening as function of scattering vector after correcting for instrumental broadening (for details⁽¹⁵⁾). The refinement seems to attain an ultimate grain size. The average grain size after 200 h determined from dark field viewgraph of Fig. 4 (obtained by the selection of the (111)-Al and (220)- $(\text{Co, Ni})_2\text{Al}_9$ reflections) is in the order of (16 ± 2) nm. From the deconvolution of the X-ray diffraction lines of fcc-Al we have also found that the grain size first decreases rapidly and saturates at steady-state value (the deconvolution of only the Al-Bragg peaks was selected, as this phase is the major phase for the compositions studied and allows more accurate data). The ultimate grain size depends on the composition of the elemental mixture powders. This is illustrated in Fig. 5, showing the measured average grain size obtained by ball milling for $\text{Al}_{100-1.5x}\text{Ni}_x\text{Co}_{0.5x}$ powders (where $x=0$ to 8 at.%) after 200 h of milling. Whereas, the grain size can be reduced to only (24 ± 2) nm for pure Al ($x=0$) (in agreement with values reported⁽¹⁶⁾), it decreases to values below 12 nm for pure Ni, Fe, and Co⁽¹⁷⁾. Thus the grain size of $\text{Al}_{100-1.5x}\text{Ni}_x\text{Co}_{0.5x}$ powders for compositions in the

Fig. 4 Bright and dark field electron micrographs and selected diffraction patterns of $\text{Al}_{88}\text{Ni}_8\text{Co}_4$ milled 200 h.

Fig. 5 Average grain size obtained by mechanical milling for $\text{Al}_{100-1.5x}\text{Ni}_x\text{Co}_{0.5x}$ powders after 200 h of milling vs Ni content.

range of $x=2$ to $x=8$ at. % is expected and found limited in the ranges of (24 ± 2) nm to (15 ± 2) nm. Moreover, the ultimate grain size scales with the melting point or the bulk modulus of the specific element⁽¹⁷⁾. Indeed, we have summarized in Table 2, the melting temperature T_m , calculated bulk modulus B , and measured average grain size L for $\text{Al}_{100-1.5x}\text{Ni}_x\text{Co}_{0.5x}$ powders mechanically deformed. Since, the bulk modulus B of $\text{Al}_{100-1.5x}\text{Ni}_x\text{Co}_{0.5x}$ powders $x > 0$ are not known. We have taken to calculate B , weighted average values based on the Vegard-law type behavior for B . It is seen in Table 2 that the general trend of decreasing grain size agrees with the trend observed when the melting temperature increases. The observed dependence of the grain size suggests that the recovery rate during the milling process correlate with the melting temperature. Thus preventing very small grain sizes for low melting alloys. However, the refinement of the grain size

Table 2 Measured melting point T_m , average grain size L and calculated bulk modulus B for $\text{Al}_{100-1.5x}\text{Ni}_x\text{Co}_{0.5x}$ powders after 200 h of milling and for pure elements.

Elements and alloys (at. %)	T_m/K	L/nm (from TEM)	B/GPa	References
Fe	1809	8 ± 3	170	(17)
Co	1768	14 ± 3	181	(17)
Ni	1726	12 ± 3	177	(16)(17)
Al	933	22 ± 2	75	(17)
$\text{Al}_{97}\text{Ni}_2\text{Co}_1$	927	20 ± 2	78	Present results
$\text{Al}_{94}\text{Ni}_4\text{Co}_2$	924	17 ± 2	81	"
$\text{Al}_{91}\text{Ni}_6\text{Co}_3$	920	18 ± 3	84	"
$\text{Al}_{88}\text{Ni}_8\text{Co}_4$	916	16 ± 2	87	"

is not a sufficient condition for subsequent amorphization. It is clear here that no amorphization occurs at the Al/Ni, Al/Co or Ni/Co interfaces. The amorphization if exists will be expected to originate from the defects introduced by disordering the Al and $(\text{Co}, \text{Ni})_2\text{Al}_9$ crystalline phases. Thus, the enthalpy stored by disordering will raise the Gibbs free energy above that of the amorphous state. The crystallization enthalpy measured for $\text{Al}_{88}\text{Ni}_8\text{Co}_4$ amorphous prepared by melt spinning was in the order of 4 kJ/mol, which is too high compared to the maximum enthalpy stored during MA of $\text{Al}_{88}\text{Ni}_8\text{Co}_4$ (0.5 kJ/mol). The difficulty for enthalpy storage is mainly due to higher recovery rate, further enhanced by the heat generated by the plastic work.

2. Crystalline to amorphous phase transition in $(\text{Al}_{88}\text{Ni}_8\text{Co}_4)_{100-x}\text{Zr}_x$ elemental powders during mechanical alloying

The substitution by Zr in the composition ranged from 1 to 4 at. % does not change the nature of the microstructure or the powders morphology observed in $\text{Al}_{88}\text{Ni}_8\text{Co}_4$ under deformation, i.e., slices of Ni, Co, and Zr dispersed randomly within Al matrix. This microstructure is always observed when one or more constituent elements present strongly different aptitudes for plastic deformation near room temperature (see Fig. 6(b) and (c)). The scanning electron micrograph of Fig. 6(a) reveals cross-section of $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{98}\text{Zr}_2$ agglomerates after 50 h of milling, where the Zr, Ni and Co harder components break down into increasingly needle-shaped particles leading to a slice-type microstructure. The EDX analysis indicates that the white slices are Zr element and the black layers are pure Al, while the grey regions contain a mixture of Al, Ni and Co. At this stage of deformation (50 h) the X-ray diffraction shows important amorphous fraction formed which appear clearly in regions I and II of Fig. 6(a). The region I is situated between Zr/Al/Zr interfaces and region II Zr/Al-Ni-Co interfaces. Furthermore, the X-ray diffraction patterns of Fig. 7 show the complete disappearance of the Co bragg peaks and the intensity of the pure Al, Ni and Zr elements are reduced and broad halo appears indicating growth of an amorphous phase upon reaction. For more than 100 h of milling the amorphous phase grows, while the crystalline Zr,

Fig. 6 Scanning electron micrograph of $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{98}\text{Zr}_2$ after 50 h of milling. (a) Cross-section, (b) Morphology, (c) microstructure.

Fig. 7 Evolution of X-ray diffraction patterns of $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{98}\text{Zr}_2$ as function of milling time.

Al, Ni are considerably reduced. Beyond 200 h, the XRD patterns show the disappearance of the pure Zr, while a small amount of Al and Ni remain, and with evidence of presence of new crystalline Bragg peaks. Before this stage is attained, amorphous single phase is concluded to be close to compositions more rich in Zr. Figure 8 shows the changes of the XRD spectra end-products as function of Zr substitution up to 4 at.% milled 200 h. In powder mixtures (where $X_{\text{Zr}} < 3$ at.%), the amorphization reaction ceases with some remaining pure Al and Ni. The increase of milling time above 200 h does not lead to a more complete reaction, but Bragg peaks of $(\text{Co}, \text{Ni})_2\text{Al}_9$ appeared.

It is interesting to mention that the minimum Zr con-

Fig. 8 X-ray diffraction spectra of $(\text{Al}_{88}\text{Ni}_8\text{Co}_4)_{100-x}\text{Zr}_x$ end-products ball milled 200 h.

tent to obtain a single amorphous phase by MA in (Al, Ni, Co)-Zr binary systems should be superior than 10 at.%⁽¹⁸⁾. In our case the transition from the synthesis of Al solid solution and $(\text{Co}, \text{Ni})_2\text{Al}_9$ to the amorphous phase with addition of Zr (for $1 < X_{\text{Zr}} < 4$ at.%) is not due to the extension of the amorphization range (induced by the raise in the pure component free Gibbs energies). Indeed, several authors have reported recently the formation of amorphous phase by MA in compositions close to $\text{Al}_{77}\text{Co}_{23}$ (in at.%): the formation first of $\text{Al}_{13}\text{Co}_4$ compound and under continuous milling to full amorphization by mechanical disordering the $\text{Al}_{13}\text{Co}_4$ compound⁽¹⁹⁾. This indicates that the thermodynamic and kinetic criteria for amorphization by solid state reaction is not fulfilled at the Al/Co interfaces. Hence, it seems that the amorphization observed in these quaternary systems is mainly due to the three factors:

(1) The following criteria:

- Fast diffusivities of one or more solute atom, which gives a characteristic reaction time for nucleation and growth of the amorphous phase which is shorter than that of the crystalline phases
- Negative heat of mixing in the amorphous alloy providing the necessary driving force for the reaction

are fulfilled at the Al/Zr, Ni/Zr and Co/Zr interfaces of the quaternary systems.

(2) The increase of the thermal stability of the amorphous phase with increasing Zr content (as detailed in Section III.4).

(3) The concentration gradients effect which is expected

to reduce the driving force for crystallization of compounds during at least the early stage of deformation (20 to 100 h)

3. Concentration gradients effect

The amorphization process during M.A. of $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{100-x}\text{Zr}_x$ quaternary systems can be described as the formation at first stage of needle-shape particles of Ni, Co and Zr dispersed within an Al matrix and then formation of amorphous phase upon milling at the interfaces (where the criteria mentioned above are satisfied), through fast diffusion of the small atom into the Zr host lattice. There are Al-Zr, Ni-Zr and Co-Zr effective interfaces leading to the synthesis of the amorphous phase. At the beginning of the mixing reaction the disappearance of the Co Bragg peaks together with an increase of the amorphous fraction suggests the diffusion of Co atoms into Zr grains. Soon afterwards, the Ni and Al have to cross the amorphous regions in order to react with the remaining Zr. Increasing the milling time, increases the amorphization degree.

During the growth of the amorphous phase at the effective interfaces (Al-Zr, Ni-Zr and Co-Zr) the formation of new crystalline phases has not been detected which is related to the concentration gradients effect established in the amorphous slices during the interdiffusions reaction (from 20 to 100 h of milling). These gradients can suppress the thermodynamic driving force for nucleation of crystalline phases as long as the thickness of the amorphous slices remains by deformation below a certain critical value X_c given by⁽²⁰⁾:

$$X_c = \frac{9\Delta C\sigma_{pc}\alpha^{1/2}}{\rho(2|\Delta G_{pc}|)^{3/2}} \quad (1)$$

where ΔC , σ_{pc} , α , ρ and ΔG_{pc} are the amorphous concentration range, interfacial energy, second derivative of the free Gibbs energy of the amorphous phase (free energy of the liquid phase extrapolated at milling temperature $T=400$ K) with respect to the concentration, atom density and the molar free energy of polymorphous crystallization, respectively. Using expression (1) available at initial stage of deformation, where the amorphous phase forms at the Al/Zr, Co/Zr and Ni/Zr binary interfaces. A qualitative estimation of X_c based on (the interfacial energies have been calculated following the same approximations as in Ref. (20)) the thermodata reported⁽²¹⁾⁽²²⁾ shows $X_c(\text{Ni-Zr}) > X_c(\text{Al-Zr}) > X_c(\text{Co-Zr})$. The lowest value found of X_c of (Co-Zr) is in the order of 20 nm. Above 100 h of milling time the microstructure changes from lamellae microstructure to an amorphous matrix with a dispersion of fcc-Al crystals and remaining Ni. In this case no effect of concentration gradients as shown on the TEM viewgraph of Fig. 9. At this advanced stage of deformation the progression of the amorphization is dominated by the increase of the thermal stability of the amorphous phase with increasing Zr content, and the full amorphization was observed for composition containing Zr up to 4 at.% as seen in Fig. 10.

Fig. 9 Bright and dark field electron micrographs and selected diffraction patterns of $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{96}\text{Zr}_4$ powders milled 120 h.

Fig. 10 Bright field electron micrographs and selected diffraction patterns of $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{96}\text{Zr}_4$ powders milled 200 h.

4. Thermal stability of $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{100-x}\text{Zr}_x$ amorphous alloys

During the reverse process to return to equilibrium the crystallization process takes place in all the compositions studied through two exothermic stages, i.e., precipitation of fcc-Al, and crystallization of the remaining amorphous phase and formation of $(\text{Co}, \text{Ni})_2\text{Al}_9$ and Al_3Zr compounds. This indicating that the crystallization reaction in $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{100-x}\text{Zr}_x$ amorphous alloys is a primary transformation. After heating through the second peak shown on the DSC spectrum (of $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{96}\text{Zr}_4$ amorphous alloy) of Fig. 11. X-ray diffraction, and electron diffraction patterns (not shown in the present report) show three phases: fcc-Al, monoclinic $(\text{Co}, \text{Ni})_2\text{Al}_9$, and tetragonal Al_3Zr . After heating through the first peak only diffraction Bragg peaks of the fcc-Al are present. The significant differences between $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{100-x}\text{Zr}_x$ amorphous alloys are illustrated in Fig. 12. The crystallization temperature T_x , the crystallization enthalpy ΔH_x , and the activation energy $E_a(T_p)$ increases with increasing Zr content. In going from 1 to 5 at.% Zr, the crystallization becomes almost 60 K higher, the activation energy two to three times larger, while the crystallization enthalpy vary from 2.2 to 3.1 kJ/mol.

Fig. 11 DSC thermogram of $(\text{Al}_{0.88}\text{Ni}_{0.08}\text{Co}_{0.04})_{96}\text{Zr}_4$ amorphous powders after 200 h of milling.

Fig. 12 Variation of the crystallization temperature, crystallization enthalpy and activation energy as function of Zr substitution.

IV. Conclusion

Mechanical alloying of Al-Ni-Co in the ranges of 4 to 8 at.% Ni, 2 to 4 at.% Co (for Ni to Co atomic ratio equal 2) and the crystalline to amorphous phase transition observed in the present study during partial substitution by Zr allows the followig interpretations:

(1) Absence of amorphization by solid state reaction at the Al/Ni, Ni/Co and Al/Co interfaces and continuous milling leads to the formation of fcc-Al and (Co,

Ni)₂Al₉ phases.

(2) The refinement of the fcc-Al, and (Co, Ni)₂Al₉ by disordering attains an ultimate grain size which is limited by the recovery rate, further enhanced by the heat generated during deformation.

(3) The maximum enthalpy stored by extensive deformation of fcc-Al, and (Co, Ni)₂Al₉ was in the order of 0.5 kJ/mol, which represent only 8% of the crystallization enthalpy measured on Al₈₈Ni₈Co₄ amorphous ribbons.

(4) Presence of amorphous fraction at the Al/Zr and Ni, Co/Zr interfaces, in addition to the disappearance of Co Bragg peaks at early stage of deformation. The amorphization goes to completion with increasing Zr substitution up to 4 at. %.

(5) Important increase of the thermal stability of the Al-based systems with increasing Zr. The crystallization temperature and activation energy become almost 150 K higher and two to three times larger, respectively in going from 0 to 5 at.% Zr.

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