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On the evolution of quasicrystalline and crystalline phases in rapidly quenched Al-Co–Cu–Ni alloy

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Abstract

The occurrence of stable decagonal quasicrystalline phase in Al–Co–Ni and Al–Cu–Co alloys through conventional solidification is well established. Earlier, we have studied the effect of Cu substitution in place of Co in the $Al_{70}Co_{15}Ni_{15}$ alloy. Here we report the structural/micro-structural changes with substitution of Cu for Ni in rapidly solidified Al–Co–Ni alloys. The melt spun ribbons have been characterized using X-ray diffractometry, scanning and transmission electron microscopy. With an increase in Cu content in the melt spun $Al_{70}Co_{15}Cu_xNi_{15-x}$ (x = 0–15 at.%) alloys, the relative amount of the decagonal phase decreased up to 10 at.% of Cu. At this composition, the quaternary alloy showed the co-existence of decagonal quasicrystal and superstructure of τ_3 vacancy ordered crystalline phases. The decagonal phase containing Cu showed more disordering than Al–Co–Ni alloys. The implication of the structural and microstructural changes due to Cu substitution in stable decagonal quasicrystals will be discussed.

Keywords: Quasicrystalline particle; Rapidly quenching; Al–Co–Cu–Ni alloy

1. Introduction

Quasicrystals are intriguing because they require one to reconsideration of all the basic concepts that have been developed for periodic crystal. After the discovery of icosahedral quasicrystals (IQC) by Shechtman et al. [1], many more alloy systems exhibiting various classes of quaiscrystal have been reported [2]. Among those the icosahedral and the decagonal phases have been studied most extensively. Icosahedral (I) phase is quasi-periodic in three dimensions with a point group of $m\bar{3}\bar{5}$, while the decagonal (D) phase is quasi-periodic in two and periodic in the other dimension, with point group 10/*mmm* [3]. The two stable classes of two-dimensional quasicrystal having decagonal symmetry are reported in Al–Co–Ni and Al–Co–Cu ternary systems [4]. The stable decagonal phases with composition of $Al_{65}Co_{15}Cu_{20}$ (numbers indicate at.%) and with different periodicities of ≈4, 8, 12 and 16 Å were reported by He et al. [5] and confirmed by Tsai et al. [6]. Grushko and Urban [7] studied the solidification behavior of D-$Al_{65}Co_{15}Cu_{20}$ and D-$Al_{65}Co_{20}Cu_{15}$ and found that the D phase melts incongruently. The Al–Co–Cu phase diagram and stability of the D phase were studied in detail by Grushko [8]. The other stable decagonal quasicrystals in $Al_{70}Co_{15}Ni_{15}$ system have been investigated by Tsai et al. [9]. The analysis of X-ray diffraction (XRD) results of $Al_{65}Co_{15}Cu_{20}$ has been shown to give rise to higher dimensional space group of $P10_5/mcm$, whereas $Al_{70}Co_{15}Ni_{15}$ belongs to the symmetry group of $P10/mmm$ [10]. A subtle change in their diffraction characteristics between the decagonal phases of $Al_{70}Co_{15}Ni_{15}$ and $Al_{65}Co_{15}Cu_{20}$ has been observed in an electron diffraction study by Edagawa et al. [11].

The question concerning the stability of decagonal quasicrystal and the underlying stabilization mechanism are not yet fully understood. Grushko et al. [12] have investigated the transition between the periodic and quasi-periodic structures of decagonal Al–Co–Ni alloy of as-cast and annealed condition. The effect of the Si substitution for the conformation of the stability of Al–Cu–Co decagonal phase has been studied [13]. Recently, the transition from decagonal to vacancy ordered phases (VOP) in $Al_{70}Co_{15-x}Cu_xNi_{15}$ alloy system have been investigated by Yadav et al. [14]. It is important to note that the possibility of the formation of different VOPs by changing the alloy composition

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has been discussed in details [15]. The substitution of elements for 3d transition metal atoms in $Al_{70-x}Co_{15}Cu_{x+y}Ni_{15-y}$ alloys leading to interesting structural variations has been reported by Pramanik et al. [16]. While deciding on the compositions of the alloys investigated here the stable decagonal phases, namely the $Al_{70}Co_{15}Ni_{15}$ and $Al_{70}Co_{15}Cu_{15}$ are considered. In the present investigation, we have substituted Ni with Cu in the stable decagonal phase $Al_{70}Co_{15}Cu_xNi_{15-x}$ gradually up to the composition $Al_{70}Co_{15}Cu_{15}$. The phase evolution under rapid solidification condition has been investigated in detail.

2. Experimental procedure

The alloy with nominal composition of $Al_{70}Cu_{15}Cu_xNi_{15-x}$ (x = 0, 2.5, 5.0, 7.5, 10 and 15 at.%) were prepared in an argon atmosphere by melting high purity Al (99.96%), Co (99.98%), Ni (99.96%) and Cu (99.99%) using an RF induction furnace. Rapid solidification processing (RSP) of the as-cast alloys were conducted by melt spinning on to a copper wheel rotating at a speed of ∼3600 rpm in an argon atmosphere. During the melt spinning, the entire apparatus was enclosed in a steel enclosure through which argon gas was made to flow continuously at pressure of 4.5 MPa so as to prevent oxidation of the ribbons after ejection from the nozzle. The thickness and width of the RSP ribbon were found to be ∼50 μm and ∼0.75–1.0 mm, respectively. The structural characterization was done by employing a Philips PW-1710, X-ray diffractometer with a graphite monochromator and Cu Kα radiation. For characterizing the surface features scanning electron microscope JEOL 840A W3 with a Kevex Sigma-II energy dispersive X-ray analyzer was employed. The ribbons were thinned using an electrolyte of 92% ethanol and 8% perchloric acid at −14 °C. Further structural and microstructural investigations of the sample were carried out using a Philips EM-CM-12 electron microscope, operating at a voltage of 100 kV.

3. Results and discussion

The surface morphology of the as-cast $Al_{70}Co_{15}Ni_{15}$ and $Al_{70}Co_{15}Cu_{15}$ alloys showed aggregates of decagonal needles, which have been reported earlier by Yadav et al. [17]. The elongated needle structure has been characterized by transmission electron microscopy (TEM) and identified as D phase. The D phase grows faster along the 10-fold direction compared to the other two directions. However, scanning electron microscopy (SEM) of other alloys containing Cu did not show any regular or symmetric morphology like decagonal rods, rather it showed highly irregular shapes. This can be attributed to the effect of Cu in the quaternary alloy during solidification.

Powder X-ray diffraction patterns of the $Al_{70}Co_{15}Cu_xNi_{15-x}$ (x = 0, 5, 10 and 15) alloys are shown in Fig. 1(a–d). After 5 at.% of Cu substitution (i.e. $Al_{70}Co_{15}Cu_5Ni_{10}$), there is a distinct peak broadening in X-ray diffraction pattern as exhibited by Fig. 1(b). After 10 at.% Cu substitution (i.e. $Al_{70}Co_{15}Cu_{10}Ni_5$) in Fig. 1(c) both the decagonal and crystalline phases start evolving. It may be discerned from Fig. 1 that 5 at.% of Cu in $Al_{70}Co_{15}Cu_5Ni_{10}$ alloy has a tendency to destabilize the decagonal phase by increasing the substitutional disorder. When the Cu concentration is further increased, the precipitation of a crystalline phase similar to Al_3Ni_2 type vacancy ordered phase occur and this phase co-exist with the Al–Co–Cu type decagonal phase (Fig. 1(c)). It is interesting to note that Mukhopadhyay et al. [18] have also observed an evolution of the microcrystalline B2 phases (related to Al_3Ni_2 phase) due to disordering in Al–Cu–Co–Si system while growing the single crystals of D phase.

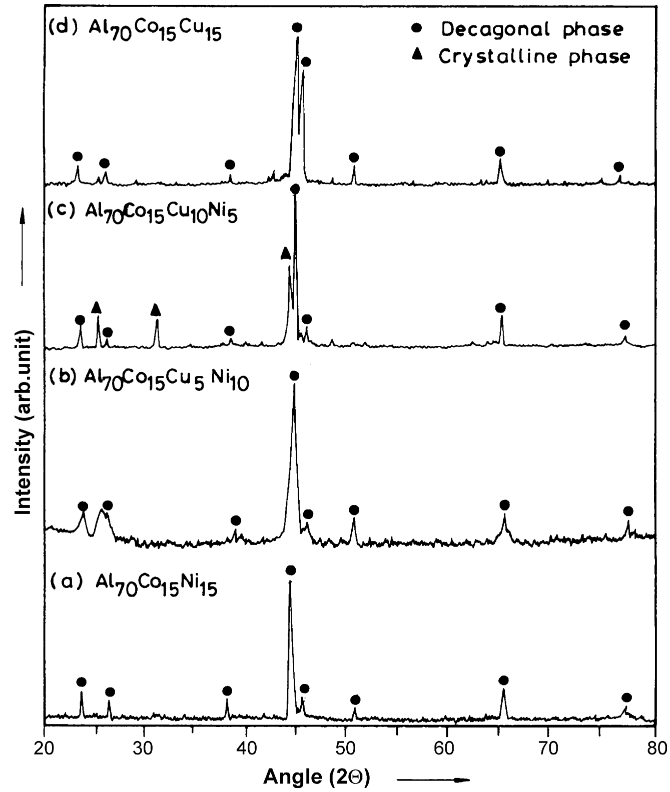

Fig. 1. (a–d) Powder X-ray diffraction (XRD) patterns of the $Al_{70}Co_{15}Cu_xNi_{15-x}$ (x = 0, 5, 10 and 15).

Fig. 2 shows the effect of Cu concentration on the full width at half-maximum (FWHM) for the radial scan of the $(1\,0\,\bar{2}\,\bar{2}\,0\,2)$ fundamental reflection (following the indexing scheme by Mukhopadhyay and Lord [19]) of $Al_{70}Co_{15}Cu_xNi_{15-x}$ (x = 0–15) alloys. Here the FWHM is found to increase with increasing Cu concentration up to 5 at.% (i.e. in $Al_{70}Co_{15}Cu_5Ni_{10}$ alloy). On further addition of Cu, FWHM is found to decrease due to the decomposition of the disordered D phases to vacancy ordered phase and decagonal phase. The increase in FWHM with Cu concentration can be understood in terms of introduction of homogenous strain field in the quasi-periodic and periodic decagonal planes. Such a strain field is characteristic of the quasicrystal structure just before the transformation/precipitations to the approximant phases [20]. It is evident from XRD that the precipitation of the crystalline phase occurs above the 5 at.% of Cu from where the decrease in FWHM of the XRD peak has started. It should be mentioned here that from XRD, we have estimated the quasilattice parameters a_R and c for $Al_{70}Co_{15}Cu_xNi_{15-x}$ (x = 0, 2.5, 5, 7.5, 10 and 15). The

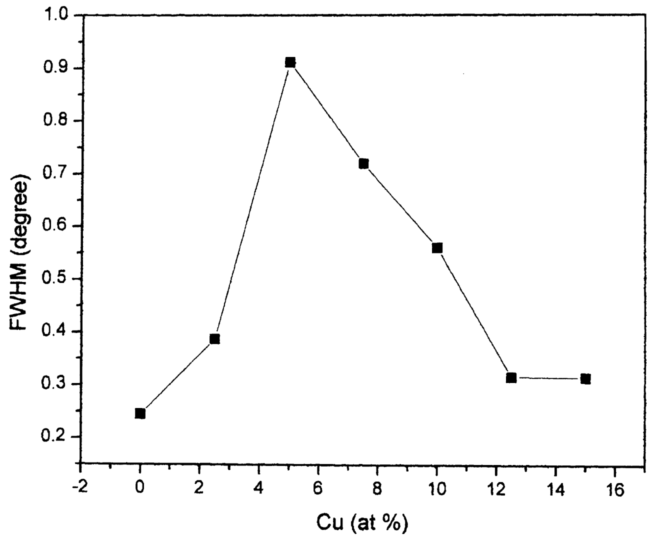

Fig. 2. Cu concentration dependence of the FWHM for the radial scans of the $(1\,0\,\bar{2}\,\bar{2}\,0\,2)$ fundamental reflection of $Al_{70}Co_{15}Cu_xNi_{15-x}$ (x = 0–15) alloys composition.

value of a_R for 5 at.% Cu is minimum in our case. The general trend of variation of a_R and c for these types of alloys is in conformity with the work reported by Steurer [21]. The values are shown in the Table 1 along with values of e/a ratio.

The selected area electron diffraction (SAD) patterns of $Al_{70}Co_{15}Ni_{15}$ and $Al_{70}Co_{15}Cu_5Ni_{10}$ RSP ribbons taken along the 10-fold direction are shown in Fig. 3. The diffraction spots in Fig. 3(a) are rather sharp and arranged at strictly fixed position. This also indicates that the phason strain causing the peak shift and splitting is not significant along the 10-fold axis of the decagonal phase. However, 10-fold pattern obtained from $Al_{70}Co_{15}Cu_5Ni_{10}$ alloy show ample variation in the intensities and position in Fig. 3(b) and diffuse pentagonal arrangement of spots can be seen in the plotted circle. Fig. 4(a–f) shows the A2D and J type two-fold patterns of these alloys, respectively (following the notation of Yan et al. [22]). The selected area electron diffraction patterns show the presence of streaking/diffuse row perpendicular to the periodic direction, as typified by the streaked diffraction rows shown in Fig. 4(b and e). It is very interesting to note that as we increase the Cu concentration in $Al_{70}Co_{15}Cu_xNi_{15-x}$ system, the streaking gets broader first and then gradually starts weakening. It remains very prominent at the composition of $Al_{70}Co_{15}Cu_5Ni_{10}$. This feature is evident in Fig. 4(b and e). The streaking can be explained in terms of the substitutinal disordering of Cu/Ni in quasi-periodic planes

Table 1
The a_R, c and e/a value with Cu concentration in $Al_{70}Co_{15}Cu_xNi_{15-x}$

Composition	a_R (Å)	c (Å)	e/a
$Al_{70}Co_{15}Ni_{15}$	4.00	4.00	1.73
$Al_{70}Co_{15}Cu_{2.5}Ni_{12.5}$	3.96	4.00	1.79
$Al_{70}Co_{15}Cu_5Ni_{10}$	3.80	4.03	1.83
$Al_{70}Co_{15}Cu_{7.5}Ni_{7.5}$	3.81	4.03	1.87
$Al_{70}Co_{15}Cu_{10}Ni_5$	3.82	4.03	1.91
$Al_{70}Co_{15}Cu_{15}$	3.82	4.03	1.99

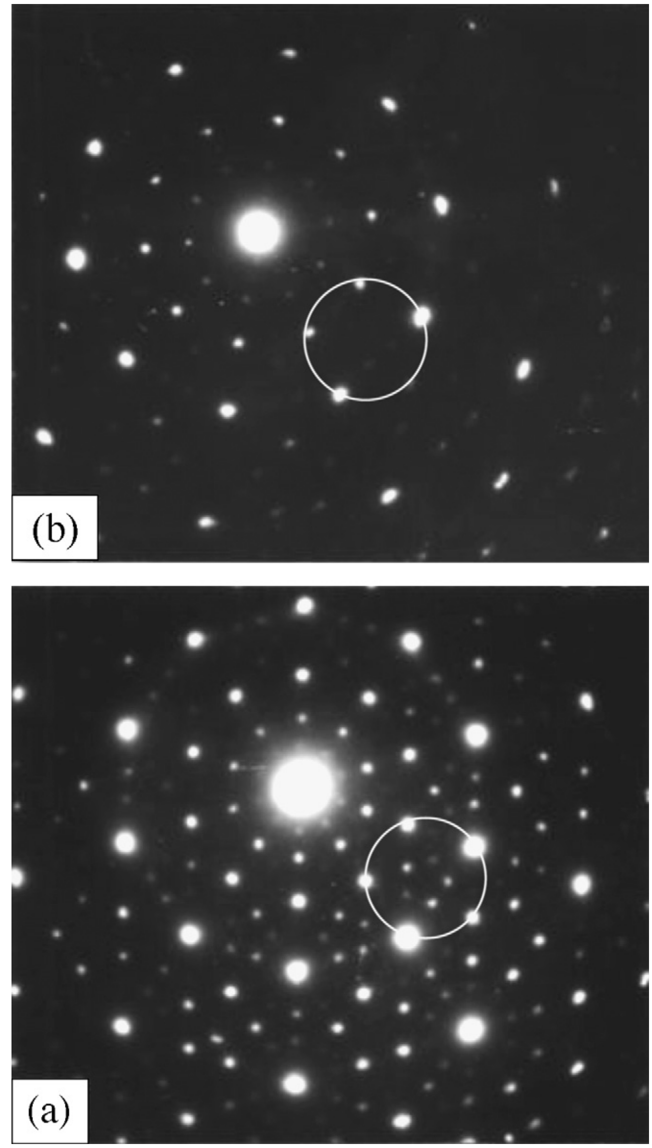

Fig. 3. (a and b) The selected area diffraction pattern of $Al_{70}Co_{15}$ Ni_{15} and $Al_{70}Co_{15}Cu_5Ni_{10}$ RSP ribbons taken along the 10-fold direction.

stacked along 10-fold axis. Similar features have been reported by Van Tendeloo et al. [23] and interpreted as due to disordering of pencil-like linear regions of the decagonal structure.

Fig. 5(a) shows the diffraction patterns from the alloy composition $Al_{70}Co_{15}Cu_{10}Ni_5$. The indexing of the SAD reveals the presence of super structure of τ_3 (vacancy ordered) phase, it may be noticed that (1 1 1) reciprocal vector corresponding to B2 phase has been divided into several divisions (Fig. 5(a)). This suggests that modulation of B2 phase along [1 1 1] direction has become six times of the parent phase (i.e. B2 phase). As we know, different τ phases are identified on the basis of the number of division made by Bragg peaks along [1 1 1] direction of B2 phase [24]. Therefore, the VOP in the present observation can be understood as the superstructure of τ_3 by doubling its unit cell. The details of the superstructure and its atomic ordering will be discussed elsewhere. Chattopadhyay et al. [24] first pointed out the possible link between the vacancy ordering and one-dimensional

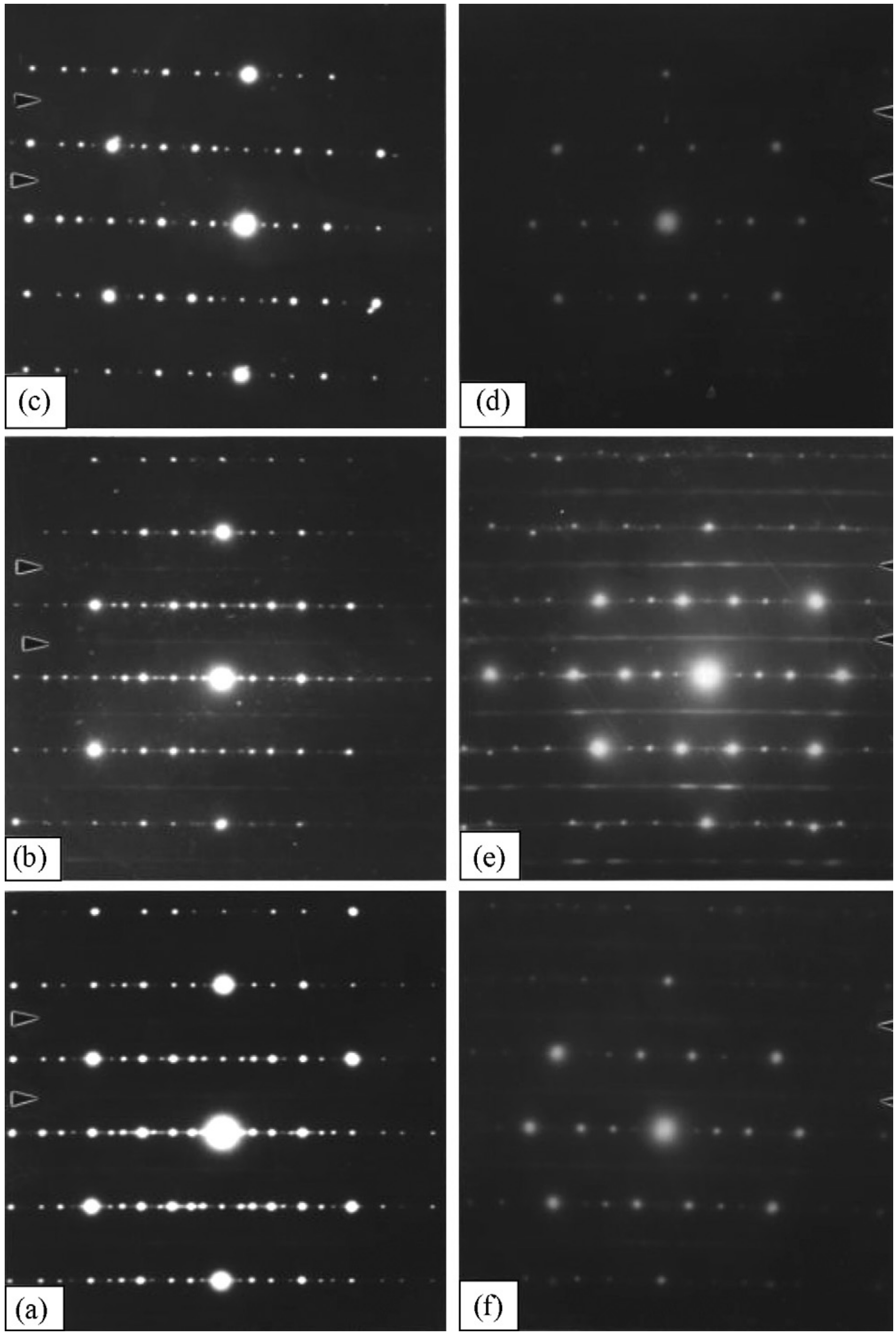

Fig. 4. The selected area electron diffraction patterns of melt spun ribbon of the $Al_{70}Cu_xNi_{15-x}$ ($x = 0$, 5 and 7.5) alloys. (a–c) The A2D and (d–f) J type two-fold patterns of these alloys.

quasi-periodicity. Thus, the formation of τ phase indicates the structural instability of D phase in the presence of Cu and Ni and the continuous transformation from D phase to crystalline approximant phase. The corresponding microstructure is shown in Fig. 5(b). The gray and white area has been identified as superstructure of τ_3 and decagonal phase, respectively. It can be noted that this is the first time that we have observed superstructure of τ_3 phase in Al–Cu–Co–Ni alloy system. It is interesting to notice that the microstructures exhibit good contact between the grains, and these grains are somewhat faceted. However, as the Cu concentration increase to 15 at.% it has been found (microstructure is not shown here) that the grains become almost entirely composed of the equiaxied D phase structures without the τ phases as mentioned above. This suggests that in absence of the Ni, the formation of τ phases appears to be difficult. Therefore, it can be understood that the formation of superstructure of τ_3 phases requires the compositional variation, which ultimately controls the *e*/*a* ratio of the alloy and in turn stabilizes the τ phases. The

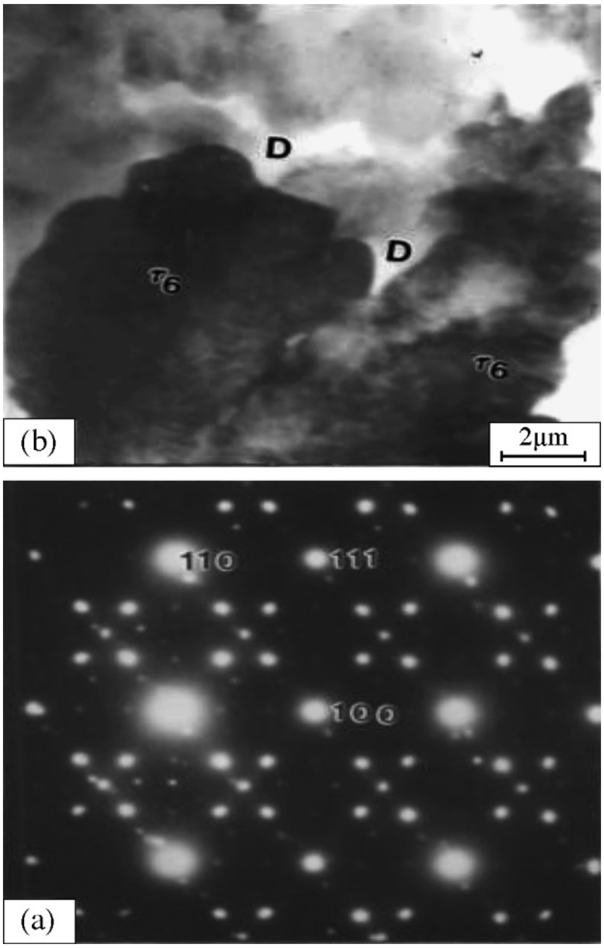

Fig. 5. (a) The diffraction patterns from the alloy composition $Al_{70}Co_{15}Cu_{10}Ni_5$ indicated the presence of τ phase. (b) The microstructure of superstructure of τ_3 and D phase.

stability of these phases at high temperature is being investigated through suitable heat treatment. This will help us to established phase equilibrium in these quaternary alloys and the role of *e*/*a* ratio on their stabilization.

4. Conclusions

After investigation of the $Al_{70}Co_{15}Cu_xNi_{15-x}$ alloys, the following conclusion can be drawn.

The presence of Cu up to 5 at.% causes maximum strain in quasilattice structure and on further addition of Cu, i.e. up to 10 at.% results in strain relaxation by giving rise to the formation of crystalline, τ and decagonal phases. The disordering due to Cu in the quaternary alloy is clearly established. This is reflected in the morphology of the as-cast microstructure as well as the rapidly solidified microstructure and structure of the alloys investigated here. The evolution of the superstructure of τ_3 phases, links the instability of decagonal phase containing Cu (10 at.%) and Ni (5 at.%). It is also clear that in the absence of Ni, the formation of τ phase is not favored due to the lack of appropriate *e*/*a* ratio, which appears crucial to stabilize the D and τ phases.

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