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Special Diffraction Effects in $Al_{70-x}Co_{15}Cu_{x+y}Ni_{15-y}$ Decagonal Alloys

A. K. PRAMANICK, R. K. MANDAL and G. V. S. SASTRY

Center of Advanced Study Department of Metallurgical Engineering Banaras Hindu University Varanasi-221 005, India

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Stable decagonal phases are observed to form in both as cast and rapid solidification condition in $Al_{70}Co_{15}Ni_{15}$ and $Al_{65}Co_{20}Cu_{15}$ alloys. The former shows diffraction spots and diffuse intensity at positions other than those of a decagonal phase in the 10-fold and 2-fold diffraction patterns. These compounds are stabilised at a specific e/a ratio. Therefore, quaternary alloys with general alloy composition $Al_{70-x}Co_{15}Cu_{x+y}Ni_{15-y}$ were prepared with varying e/a ratio. We present here the electron metallographic characterisation of the melt-spun ribbons of different alloy compositions. Changes observed during electron microscopic investigation include streaking and diffuse intensity around the spots and also the presence of totally diffuse rows in some cases. The consequence of the latter on the underlying structure is disorder in the decagonal phase. Owing to the presence of streaking in a 10-fold like zone in the $Al_{70}Co_{15}Cu_5Ni_{10}$ composition, symmetry breaking of 10-fold to a 2-fold Diagonal phase (222) occurs. Further, the presence of a type II superstructure is also observed in $Al_{68}Co_{15}Cu_{12}Ni_5$ composition.

1. Introduction:

The decagonal quasicrystalline (DQC) phase was first discovered in rapidly solidified alloys independently by Chattopadhayay et al. [1] and Bendersky [2]. It is commonly found to form in Aluminum based ternary Al-Mn-TM, Al-Cu-TM as well as binary Al-TM (where TM= Transition Metal) alloy systems. DQC is also reported in Zn-Mg-Dy [3], Fe-Nb [4] etc. A stable DQC is reported in Al-Co-Ni [5], Al-Cu-Co [6], Al-Pd-M (M= Mn, Fe, Ru, Os) [7,8] alloy systems. Among these stable alloy systems, $Al_{70}Co_{15}Ni_{15}$ (e/a=1.75) and $Al_{65}Co_{20}Cu_{15}$ (e/a= 1.89) have been widely discussed in the literature. These can be stabilised even at slow solidification rates.

X-ray diffraction results showed the presence and in some cases absence of 105 screw in the systems above [9,10]. Grushko and Urban brought out the comparisons among the DQC in stable ternary quasicrystals Al-Cu-Co, Al-Co-Ni, and Al-Fe-Ni [11]. Grushko et al. have discussed the superlattice ordering of $Al_{65}Co_{20}Cu_{15}$ with a variation of Cu content [12]. Edagawa et al. [13] pointed out superlattice ordering as decoration of weak intensities around the main reflections in electron diffraction patterns of $Al_{70}Co_{15}Ni_{15}$ in annealed condition. In contrast $Al_{65}Co_{20}Cu_{15}$ DQC does not show any superlattice ordering. Hiraga et al [14] found absence of superlattice ordering in the case of annealed samples of $Al_{70}Co_{15}Ni_{15}$. This superlattice ordering gives the possibility of order-disorder transition in ANC alloy system. Ritsch et al. [15] reported eight different structural modifications in their extensive investigation on the above system.

2. Experimental Details:

Alloys were melted in an induction furnace in an alumina crucible under flowing high purity Argon cover at around 1500 C.The coupling to the alumina crucible charge was enhanced through a graphite suscepter. Four-nine purity metals were used for the charge. Rapid solidification was done by using planar flow casting in inert atmosphere on a rotating Cu wheel of 15-cm diameter, rotating at a speed of 2200 rpm. Argon gas provided the inert atmosphere at the nozzle of the crucible and the ejecting gas pressure was around 4 kg/cm2. Transmission electron microscopy was carried out by JEOL 200CX microscope. Scanning electron microscopy was done by JEOL 840A microscope equipped with KEVEX SIGMA II EDX analyser.

3. Results and Discussion:

The electron to atom ratio is chosen as a basis for the selection of compositions of the quaternary alloys such that they remain within the end limits of ACC and ANC. Growth of decarods in all five alloy buttons and equivalence of their strong diffracting vector position in the X-ray diffraction pattern (i.e. 200000) with the calculated Fermi vector emphasizes the fact that the decagonal phase has got stabilised in all the alloys selected and melted.

Figure 1: The 2-fold patterns D (left) and P (right) for the alloys $Al_{69}Co_{15}Cu_{11}Ni_5$ (1st row), $Al_{68}Co_{15}Cu_{12}Ni_5$ (2nd) and $Al_{65}Co_{15}Cu_{10}Ni_{10}$ (3rd row).

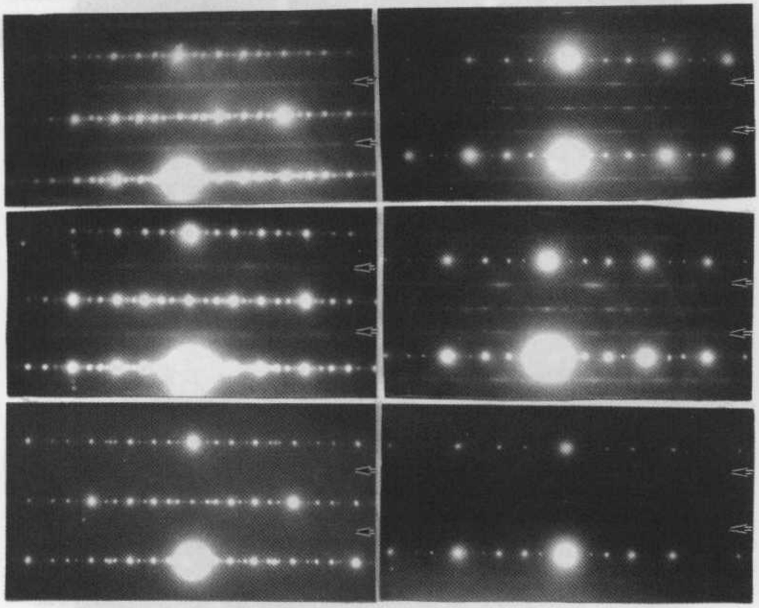


Figure 2: Presence of diffuse discs (marked by arrow) in the 10-fold pattern for the alloy $Al_{70}Co_{15}Cu_5Ni_{10}$.

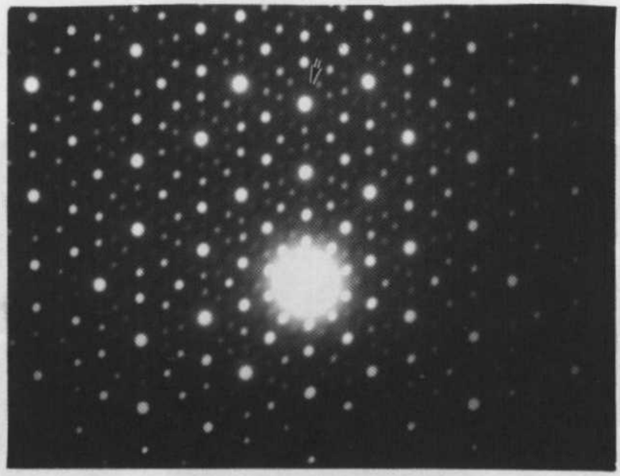
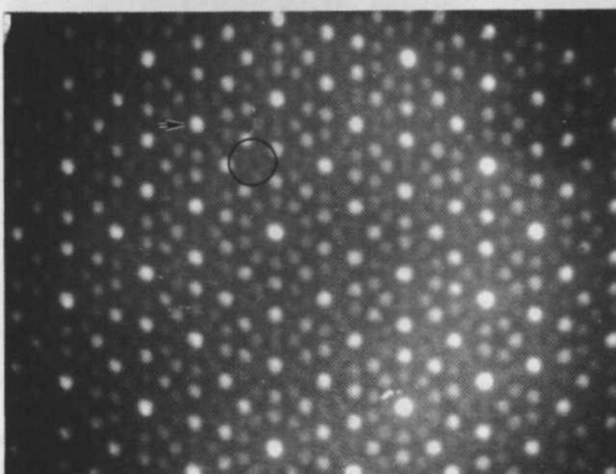


Figure 1 depicts the two distinct 2-fold patterns (D and P) for the compositions $Al_{69}Co_{15}Cu_{11}Ni_5$ (e/a=1.89), $Al_{68}Co_{15}Cu_{12}Ni_5$ (e/a=1.87) and $Al_{65}Co_{15}Cu_{10}Ni_{10}$ (e/a=1.73). The other 2-fold patterns for compositions $Al_{70}Co_{15}Cu_5Ni_{10}$ (e/a=1.83),
$Al_{68.85}Co_{15}Cu_{6.15}Ni_{10}$ (e/a=1.81) are reported in our earlier work [16]. The subtle difference in diffraction characteristics in terms of diffuse intensity and either partially or complete streaking intermittent rows have been summarised in the Table given in reference [16]. The 10-fold patterns obtained from these alloys show ample variation in the intensities and positions. The subtle differences between different alloys are of two types: one pertains to the presence of diffuse discs of intensity around each intense spot (Figure 2) (c.f. in the composition $Al_{70}Co_{15}Cu_5Ni_{10}$ and $Al_{65}Co_{15}Cu_{10}Ni_{10}$). The essential nature of SADP is similar to that reported by Grushko et al. [17]. The presence of those discs can be attributed to domain formation (≈ 5 nm in diameter) in the thin foils. Absence of such discs of the corresponding spots (P and D) in the 2-fold patterns indicated that these are pencil like in shape. Second one relates to the diffuse pentagons in the composition $Al_{68}Co_{15}Cu_{12}Ni_5$ (Figure 3). These are taken as a signature of type II superstructure [15]. However, some of the subtle features associated with type II order are not present in our pattern. Noteworthy point here is that

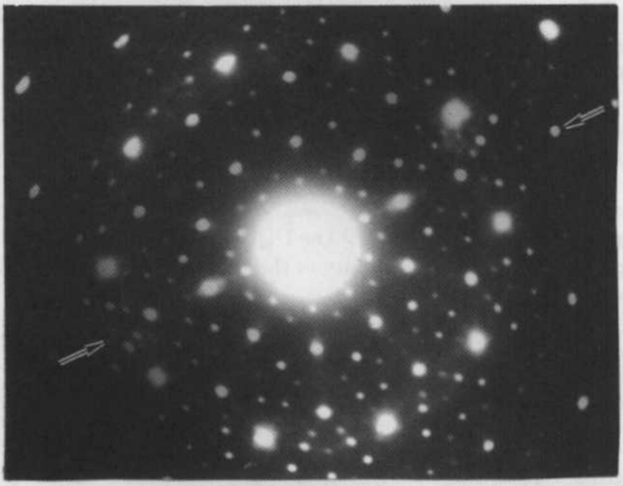
ordering to any degree is present in alloy composition that corresponds to e/a values far away from those of ANC phase, while the fundamental or intense spots are similar among themselves as well as to those observed in the case of ANC or ACC phases. Characteristic features of b-Ni obtained by Ritsch et al. [15] are also observed in the 10-fold patterns for our alloys. The most unexpected and important occurrence is the complete symmetry breaking from 10-fold symmetry as shown in the Figure 4 for the composition $Al_{70}Co_{15}Cu_5Ni_{10}$. The e/a value for this composition is 1.82 that is nearly mid value for the range of the e/a value selected for our study. It is important to note that only 2-fold symmetry is present in this apparent 10-fold pattern for this composition. Such symmetry breaking has occurred owing to the presence of streaks around the spots in a row marked with an arrow head in (Figure 4). The DQC solidifies as or transforms to a completely symmetry broken state of the Diagonal structure with (222) symmetry [18,19].

Figure 3: Diffuse Pentagons (circled), a characteristic feature of type II superstructure, observed in the alloy $Al_{68}Co_{15}Cu_{12}Ni_5$.



Energy dispersive x-ray analysis carried out for each of the alloys from different locations of a 'decarod' or from the different 'decarods' in the as cast alloy buttons confirmed the nominal composition of the alloys within the experimental errors. The diffuse intensity pentagons present at the

Figure 4: Complete symmetry breaking from 10-fold along the periodic direction to 2-fold in the case of $Al_{70}Co_{15}Cu_5Ni_{10}$.



arrowhead locations in (Figure 3) indicate that the type II superstructure is stabilised in the alloy $Al_{68}Co_{15}Cu_{12}Ni_5$ and has developed to some extent. Other diffuse intensity discs can be correlated to domain size effects. None of the patterns revealed any other types of ordering reported in the case of ANC

4. Conclusions:

We have reported the various structural characteristics of alloys of Al-Cu-Co-Ni systems. All the three compositions chosen for present work were selected based on the criteria of e/a values lying between the two compositions of stable DQCs $Al_{65}Co_{15}Cu_{20}$ and $Al_{70}Co_{15}Ni_{15}$. Alloys having e/a falling within the range for stable decagonal phases exhibit a type II superstructure. DQC b-Ni [15] characteristic has also been found in one of the alloys. We have observed the occurrence of Diagonal symmetry quasicrystal through symmetry breaking in $Al_{70}Co_{15}Cu_5Ni_{10}$ alloy.

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References

[1] K. Chattopadhyay, S. Ranganathan, G. N. Subbanna and N. Thangaraj, Scripta. Metall., 19, 767 (1985).
[2] L. Bendersky, Phys. Rev. Letts., 55, 1461 (1985).
[3] T. J. Sato, E. Abb, A. P. Tsai, Jpn J. Appl. Phys. 36, 1, 1088 (1997).
[4] A. Q. He, Q. B. Yang and H. Q. Ye, Phil. Mag. Letts. 61, 69 (1990).
[5] A. P. Tsai, A. Inoue and T. Masumoto, Mater. Trans. JIM, 30, 463 (1989).
[6] X. L. He, Z. Zhang, Y. K. Wu and K. H. Kho, J. Mater. Sci. Letts., 7, 1284 (1987).
[7] C. Beeli, H. U. Nissen and J. Robadey, Phil. Mag. Letts., 63, 87 (1987).
[8] A. P. Tsai, A. Innoue and T. Masumoto, Phil. Mag. Letts., 64, 163 (1991).
[9] W. Steurrer and K. H. Kuo, Acta. Cryst., B 46, 703 (1990).
[10] A. Yamamoto, K. Kato, T. Shibuya and S. Takeuchi, Phys. Rev. Letts. 65, 1603 (1990).
[11] B. Grushko and K. Urban, Phil. Mag. B, 79, 1063 (1994).
[12] B. Grushko, R. Wittman and K. Urban, Phil. Mag. Letts., 67, 25 (1993).
[13] K. Edagawa, M. Ishihara, K. Suzuki and S. Takeuchi, Phil. Mag. Lett., 66, 19 (1992).
[14] K. Hiraga, F. J. Lincon and W. Sun, Mater. Trans. Jpn. Inst. Metals, 32, 308 (1999).
[15] S. Ritsch, C. Beeli, H. U. Nissen, T. Gdecke, M. Scheffer and R. Lck, Phil. Mag. Lett., 78, 67 (1998).
[16] A. K. Pramanick, R. K. Mandal and G. V. S. Sastry (Accepted for publication in, Mat. Sci. and Engg. A, 2000.
[17] B. Grushko, D. Holland-Moritz, R. Wittmann, G. Wilde, J. of Alloy and Comp., 280, 215 (1998).
[18] R.K. Mandal, Ph. D Thesis (1990), Banaras Hindu University (India).
[19] S. Ranganathan, K. Chattopadhyay, Alok Singh and K. F. Kelton, J. of Mate. Sci 41, 195 (1997).