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Quasicrystals and related structures in Al–Ni–Co

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Abstract

A great number of crystalline intermetallics are formed in the Al-rich Al–Co and Al–Ni alloys. They are usually extended to the ternary compositions. In the range between $Al_{73}Co_{27}$ and $Al_{69}Ni_{31}$ decagonal quasicrystals are formed. Binary quasicrystals are metastable but are stabilized by the second transition metal. Periodic structures with pseudodecagonal symmetries were observed at compositions typical of those of quasicrystals. The variety of these structures is reviewed. © 1997 Elsevier Science S.A.

Keywords: Intermetallics; Quasicrystals; Al–Co–Ni

1. Introduction

Systematic investigation of aluminum-rich alloys containing transition metals (TMs) has led to an assumption that in the environment of a relatively higher-valency metal the TM atoms can absorb electrons from the structure as a whole in order to fill the vacancies in their atomic orbitals [1]. In Al-rich compounds containing one or two TMs the electron contribution of Al may be sufficient to saturate the vacant atomic orbitals of Mn, Fe, Co or Ni. The important role of electron absorption in the formation of Al–TM–(TM_1) intermetallics was suggested [1]. These compounds were usually found in the Al-rich parts of the corresponding phase diagrams where the effect should be strong.

Interest in these alloys increased after the discovery of quasiperiodic crystals (QCs), many of which are formed in Al-rich alloys with one or two TMs (for review see [2,3]). Among them Al–Ni–Co is one of the interesting systems exhibiting QCs in both binary Al–Co [4] and Al–Ni [5] where they are metastable phases. In ternary compositions the QCs are already thermodynamically stable [6–11]. A great number of periodic phases structurally related to QCs were also observed in Al–Ni–Co [8,11–18]. The complete Al–Ni–Co phase diagram has not been yet published, but partial information is available [8–11,17–19]. Equilibrium in binary Al–Ni [20,21] and in binary Al–Co [16,17] has been investigated. In this contribution we review the Al-rich phases formed in Al–Ni–Co.

2. Crystalline compounds

Both Al–Co and Al–Ni contain congruent equiatomic phases produced in the ternary space continuous range (Fig. 1) naturally separating the high-Al region from the rest of the phase diagram. Apart from this the binary Al–Co and Al–Ni alloy systems are very different. In the Al-rich range the Al–Co equilibrium phase diagram contains six crystalline phases [16,17]: Al_9Co_2, M-$Al_{13}Co_4$, O-$Al_{13}Co_4$, Y, Z and Al_5Co_2. In the Al-rich part of Al–Ni there are Al_3Ni, Al_3Ni_2 and Al_4Ni_3 [20,21]. Metastable Al_9Ni_2, isostructural with Al_9Co_2, was also observed [5]. The data for the phases are presented in Table 1.

All binary Al–Ni phases may contain a significant quantity of Co [8] (Fig. 1). Significant miscibility of Ni

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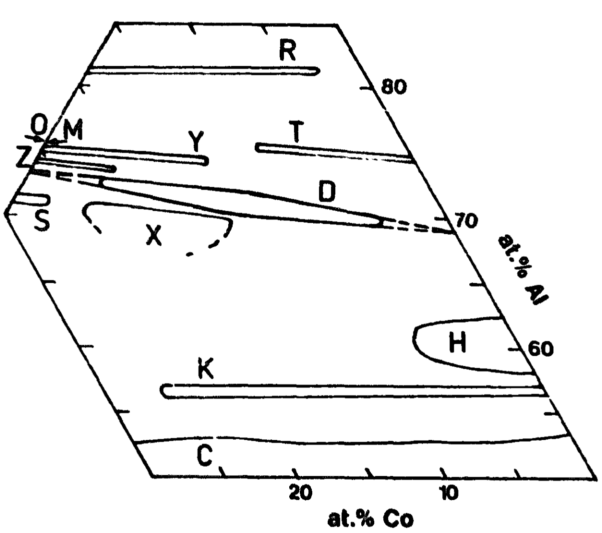

Fig. 1. Overall compositional ranges of the crystalline phases and the D-phase in Al–Ni–Co. The designations are as in Table 1.

was also observed in Al_9Co_2 and Al_5Co_2 [8], in the Y-phase [17] and in the Z-phase [18], but was very low in M-$Al_{13}Co_4$ and O-$Al_{13}Co_4$ [17,18]. The ternary compositions of Al_3Ni, Al_3Ni_2, Al_4Ni_3, Al_9Co_2, Y, Z and Al_5Co_2 were found to extend at approximately constant Al. Close to Al_5Co_2(Ni) a ternary crystalline phase designated X is reported [8,9,18] (Fig. 1; Table 1).

3. Decagonal phase(s)

Decagonal QC phase presents a structure which has tenfold symmetry in the quasiperiodic plane and is periodic along the direction perpendicular to this plane. In the following the Al–Co, Al–Ni and Al–Co–Ni decagonal phases are designated D-AC, D-AN and D-ANC, respectively. Their periodicities of approx. 0.4, 0.8, 1.2 and 1.6 nm in the specific direction were reported in rapidly solidified Al–Co and Al–Ni alloys containing 70–80 at.% Al [4,5]. In these experiments the lower periodicities were associated with the lower-Al compositions [4,5,7].

Table 1
Al–Ni–Co crystalline phases

Formula	Space group	Lattice parameters				Ref.
		a (nm)	b (nm)	c (nm)	β (°)	
R Al_9Co_2	$P2_1/a$	1.0149	0.6290	0.8557	142.4	[22]
O $Al_{13}Co_4$	$Pmn2_1$	1.2357	0.8159	1.4455	—	[13]
M $Al_{13}Co_4$	C2/m	1.5173	0.8109	1.2349	107.84	[24]
Y[a] $Al_{13}Co_4$	C2/m	1.7071	0.4099	0.7491	116.17	[14]
Z —	[b]	3.9840	0.8148	3.2230	107.97	[15]
S Al_5Co_2	$P6_3/mmc$	0.7658	—	0.7604	—	[16]
T Al_3Ni	Pnma	0.6618	0.7368	0.4814	—	[20]
H Al_3Ni_2	$P\bar{3}m1$	0.4034	—	0.4894	—	[20]
K Al_4Ni_3	Ia3d	1.1408	—	—	—	[21]
C AlCo	Pm3m	0.2855	—	—	—	[23]
X —	[c]	1.2129	0.4066	0.7646	105.88	[25]

[a] The diffraction pattern of the binary Y-phase [16] is slightly different from that of the ternary Y-phase [14]. It is argued [17] that this is because of the distortions of this high-temperature phase during cooling and that the small quantity of Ni stabilizes the phase at lower temperatures.

[b] Monoclinic (primitive and/or C-centered).

[c] C-centered monoclinic.

Binary D-AC of approx. 0.8 nm periodicity is formed close to 73 at.% Al [18,26]. Although it is metastable its solidification was even achieved from the carefully undercooled liquid in levitation experiments where the cooling rate after solidification was relatively low. The virtual melting temperature of the D-phase measured in these experiments was 1165°C which corresponds to the liquid-Al_5Co_2 region in the phase diagram. This temperature is approx. 20°C lower than the melting temperature of stable Al_5Co_2 and approx. 10°C higher than that of the stable Z-phase formed peritectically at 74.5 at.% Al [26]. The D-AC structure is stabilized by only a few atomic percent of Ni. The melting temperature of the D-phase decreases with the increase of the Ni content and reaches approx. 950°C at 24 at.% Ni. In contrast to D-AC, formation of D-AN is quite difficult even in splat-cooled samples [19]. The D-phase with a periodicity of approx. 0.4 nm was observed in the 75 at.% Al alloy [5,7], however, this structure is stabilized by only a few atomic percent of Co at approx. 70 at.% Al, which allowed us to suggest that its composition is close to $Al_{69}Ni_{31}$ [19]. Investigation of 70% Al alloy produced by splat-cooling confirmed formation of the D-phase.

No stabilization by the second TM was reported for the binary D-phases of higher periodicities. In the following we refer only to the D-phases formed along approx. $Al_{73}Co_{27}$–$Al_{69}Ni_{31}$. The lowest-Co stable D-phase was observed at approx. $Al_{70}Ni_{24.5}Co_{5.5}$ [17–19] and at the opposite side of the D-range the stable D-phase was observed in thermally annealed $Al_{73}Ni_5Co_{22}$ [19].

The diffraction patterns of D-AC and D-AN are similar but not identical [9–11,19]. The typical tenfold diffractogram of splat-cooled D-AC is shown in Fig. 2a while Fig. 2b shows the electronogram of stable $Al_{71}Ni_{24}Co_5$, which is similar to that observed in melt-spun Al–Ni alloys [7]. Strong reflections around the incident beam are arranged in the ten-spot rings, whose diameters increase with the factors of the golden mean ($\tau = 1.618$). These reflections are surrounded by weaker decorations varying with the phase composition. The detailed description of the diffraction patterns is outside the scope of this paper, for more information see [8–11,27,28].

The Al concentration of the D-phase decreases slightly with the decrease of Co and increase of Ni

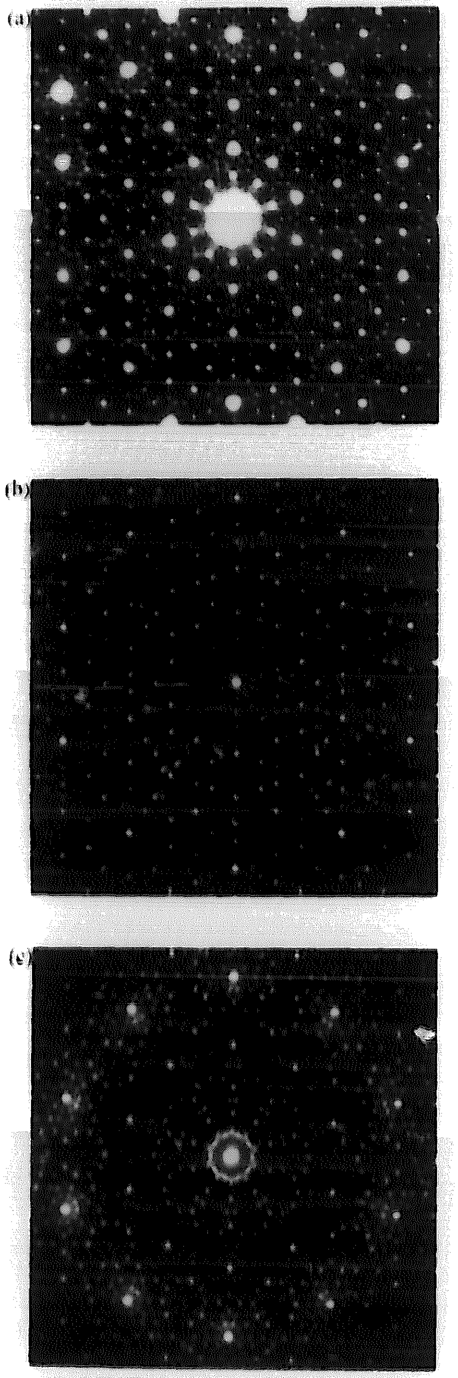

Fig. 2. Specific tenfold electron diffraction patterns of the D-phases of: splat-cooled $Al_{73}Co_{27}$ (a), $Al_{71}Ni_{24}Co_5$ annealed at 900°C (b) and $Al_{71}Ni_{14.5}Co_{14.5}$ annealed at 1000°C and then at 800°C (c).

(Fig. 1). Therefore it is plausible that the ternary compositions of the D-phases are obtained mainly by replacement between Co and Ni. The formation of structural vacancies is also suggested [29]. This produces disorder typical of the solid solutions. Diffuse scattering frequently observed in the diffractograms of the D-phases [30] may follow from this disorder. Diffraction patterns of low-Ni D-ANC are similar to that of D-AC and those of low-Co D-ANC are similar to that of D-AN. The results of the in-situ diffraction experiments [31] are in favor of the continuous high-temperature range between these limits where the diffraction properties of the D-phase change continuously. However, at lower temperatures and essentially ternary compositions specific diffraction patterns are observed which are different from those of D-AC and D-AN. This is associated with a superstructure ordering [9–11]. The typical tenfold diffractogram of D-ANC from the central part of its compositional region is shown in Fig. 2c.

4. Periodic pseudodecagonal structures

Apart from the 'normal' crystalline and quasiperiodic structures there are those exhibiting clear periodicity of the reflection positions, but not of their intensities. They have orthorhombic or monoclinic unit cells ($\beta \approx 108°$) with huge a and c lattice parameters. Several examples are shown in Fig. 3. In these electronograms the sets of 10 strong reflections are distributed, like in the D-phase, on the hierarchy of 'rings'. Their diameters are related by the ratios of τ in the D-phase and by ratios close to τ in the periodic structures. The powder X-ray diffractograms of these structures are also very similar to that of D-ANC but several reflections are split (Fig. 4).

This group of structures was observed in the range between approx. 5 and 17 at.% Ni in thermally annealed samples. Different single-phase structures were observed in the samples annealed typically at 800–900°C while the samples of the same compositions annealed at higher temperatures (depending on the composition) consisted of D-ANC. The thermal stability of these structures is unclear. Thus, $Al_{71}Ni_{14.5}Co_{14.5}$ annealed after solidification for 2350 h at 800°C exhibited a periodic structure as in Fig. 3b. On the other hand, if the material was first annealed at 1000°C in order to obtain the D-structure, it remained decagonal after the subsequent annealing at 800°C for 3100 h (Fig. 2c).

5. Distorted decagonal structures

Metastable QC-like structures were frequently observed in the samples solidified at moderate rates. They were revealed in Al–Co in the same compositional range where D-AC forms at higher cooling rates [18]. These structures resemble the D-phase even more than those presented in the previous section and were related in [15] to the so-called τ''-$Al_{13}Co_4$ family of structures. In Ni-containing compositions such structures were already observed in samples thermally annealed at elevated temperatures and subsequently quenched. We don't associate them with the high-temperature structures but with the distortions of the D-phase during cooling [10,18]. This is

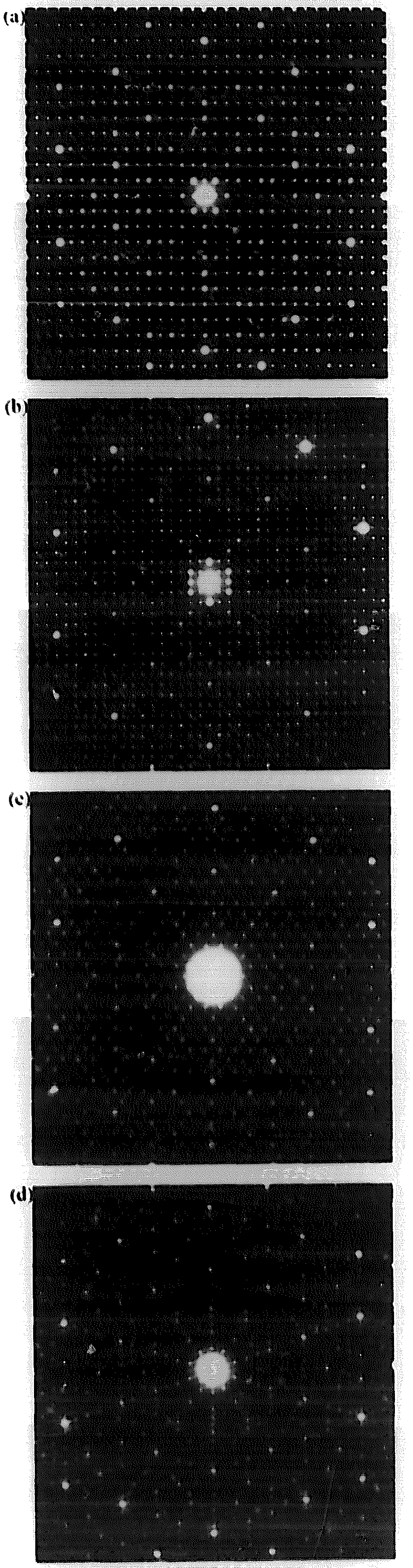

Fig. 3. Specific pseudo-tenfold electron diffraction patterns of orthorhombic (a,b) and monoclinic (c,d) phases observed in the thermally annealed alloys corresponding to the D-ANC compositional region. The lattice parameters of the structure presented in (d) are $a = 6.34$ nm, $b = 5.12$ nm, $\beta = 108°$. The scale is as in Fig. 2.

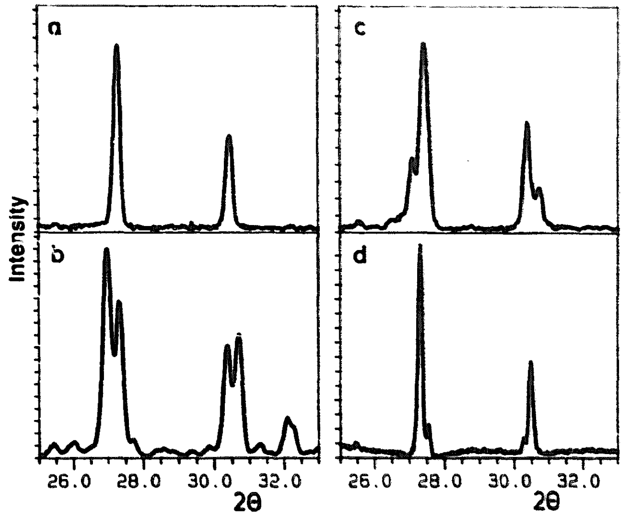

Fig. 4. Powder X-ray diffraction patterns typical of: D-ANC (a), Z (b), the periodic structure whose electron diffraction is shown in Fig. 3b (c) and that in Fig. 3c (d). Co radiation.

supported by the results of the in-situ experiments [31] where the periodic reflections observed at room temperature disappeared at elevated temperatures. In particular, the distortions may result in a one-dimensional quasiperiodicity demonstrated in [32].

6. Structural similarity between the phases

Tenfold rotational symmetry of the diffraction patterns observed in the D-phases is not compatible with periodicity. However, even a small deviation from the perfect symmetry allows periodic structures to be obtained. In Al–Ni–Co periodic phases with diffraction patterns resembling the D-phase are formed at the compositions close to or even the same as those of D-ANC. The similarity of diffraction patterns suggests the structural similarity of various crystalline phases to each other and to the D-phase. This can be demonstrated for M-$Al_{13}Co_4$, O-$Al_{13}Co_4$ and Y, whose atomic structures are known [13,14,27]. The [010] diffractogram of the 'normal' periodic O-$Al_{13}Co_4$ and M-$Al_{13}Co_4$ phases [12] already exhibit distorted tenfold arrangements of reflections (in [12] O-$Al_{13}Co_4$ is called Al_3Co). For illustration, in Fig. 5 we present the calculated diffractogram of O-$Al_{13}Co_4$.

The structures of M-$Al_{13}Co_4$ and O-$Al_{13}Co_4$ are built from flat and puckered atomic layers containing distorted fivefold arrangements of atoms and subsequently staked with approx. 0.2-nm spacing along the pseudodecagonal direction [13,14,27,33]. Although the structure of the Z-phase has not yet been determined, it is assumed that the simplest pentagonal structural block, being a part of M-$Al_{13}Co_4$, repeats in this more complicated phase in such a way that large pentagons

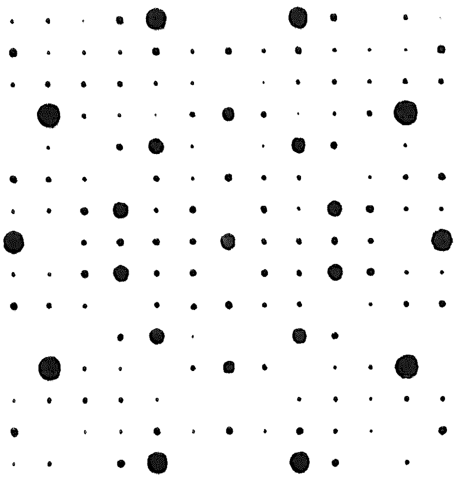

Fig. 5. The [010] electron diffractogram of O-$Al_{13}Co_4$ calculated from the atomic positions determined in [13] (kinematic approximation). The scale is as in Figs. 2 and 3.

are built from the six small pentagons of M-$Al_{13}Co_4$ [15]. In the model of D-ANC [27] the layered structure with similar, but perfectly symmetric elements is proposed. All species in the decagonal layers may be located at the geometrically equivalent nodes of a quasiperiodic net constructed from only two kinds of rhombi which have the same edges and angles of 36° and 72°, respectively. With the increase of the lattice parameters the structural similarity of a periodic phase to the D-phase should be more pronounced.

In Al–Co a clear tendency is observed for the formation of QCs and related periodic structures in a small compositional range close to Al_3Co, where five stable periodic phases and the metastable D-phase are formed. Analysis of the known structures and Monte Carlo simulations of hypothetical decagonal approximants have shown [33] that the atomic clusters typical of these structures and the links between the clusters are strongly favoured energetically. These phases should be close in free energy and small changes in composition and temperature should be sufficient to change the mutual stability of the phases [33].

Although the neighboring periodic Al–Co structures exhibit great similarity among themselves and to the D-phase, they differently incorporate a third element. Thus, Al_5Co_2, Y and Z may contain a significant quantity of Ni, but M-$Al_{13}Co_4$ and O-$Al_{13}Co_4$ may not. On the other hand, only M-$Al_{13}Co_4$ was found to exhibit a significant extension to the ternary compositions in Al–Cu–Co [34]. The D-phase exhibits a more 'flexible' substitution behavior i.e. it can contain both Ni and Cu. This may be because, in contrast to the crystalline phases, the positions of the different species in the D-structure are geometrically equivalent. This great 'flexibility' of the D-structure allows it to stabilize at ternary compositions, where the binary periodic compounds become unstable.

It is worth noting that similar phenomena were observed close to Al_3Fe, Al_3Mn–Al_6Mn and Al_4Cr–Al_7Cr, i.e. from Al–Cr to Al–Co the Al concentration of the corresponding compounds decreases. Such crystalline structures are not observed in Al–Ni where solidification of the D-phase is difficult to achieve. The suggested composition of D-AN is at still lower Al. While the Al concentration of D-ANC decreases slightly with the increase of Ni (decrease of Co) concentration, the electron to atom ratio at the high-Al limit of the D-region remains approx. 1.86 [10,19].

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