Investigation of room temperature ageing of powdered decagonal Al–Co–Ni

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Abstract

We report on long-term observations obtained from powder X-ray diffraction (XRD) measurements with milled Al–Co–Ni of decagonal structure at room temperature under ambient conditions. Several powder samples were prepared from different pieces of initially bulk polycrystalline $Al_{70.7}Co_{13.3}Ni_{16.0}$ by ball milling for a total period of 14 min. The as-milled samples were investigated without any intermediate annealing. While a number of them exhibited X-ray powder patterns without sharp reflections, the specimen in the focus of this report exhibited X-ray reflections, which could be unambiguously attributed to the decagonal structure. Evaluating the time-dependent course of integral intensity and position of the four strongest reflections we found evidence that, due to milling, order along the periodic direction is disturbed more than order within the quasiperiodic planes. In a first stage of room temperature ageing, order is restored within the first $\sim$100 h. In a second stage, quasiperiodic order recovers within the planes, which is probably caused by the relaxation of phason strains induced by the milling procedure. Fourier analysis of the XRD patterns yielded differences in the radial distribution function (RDF) at about 6 Å and less pronounced at 3 Å, indicating the preferred occupation of bond lengths between transition metal (TM = Co, Ni) atoms rather than pairs involving Al.
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1. Introduction

Starting point of the experiments described in this study was the indication of a phase transition in a powdered sample of $Al_{70.7}Co_{13.3}Ni_{16.0}$ at low temperatures [1]. Since there were no indications in the literature that this behaviour occurred in single crystalline material at comparable temperatures, the explanation was mainly based on the powder preparation procedure and the considerable impact of mechanical energy. After the milling process, the sample was not heat-treated (above room temperature), thereby implanted lattice defects could not anneal (relax) at a sufficient rate. Instead of annealing, the sample under investigation was cooled down to a temperature of 15 K, thereby freezing-in lattice defects, which are supposed to be implanted by the mechanical treatment. This gave rise for more detailed long-term investigation of the as-prepared sample at ambient conditions.

It is well-known from the literature, that by the impact of external energy—such as high-voltage electron irradiation, ion bombardment, scratching, high-energy ball milling or simply annealing—(metastable) quasicrystalline structures can be transformed to crystalline structures with a release of heat, evidencing an exothermic reaction. Up to date it is questioned whether quasicrystals represent equilibrium phases or not. Since they are grown from the melt they are considered as stable phases at least in the high temperature region. A number of (mostly ternary) quasicrystalline alloys such as Al–Co–Ni, Al–Co–Cu, Al–Pd–Mn, Al–Cu–Fe, etc. are re-

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garded to be stable in the entire range up to their melting temperature. However, some quasicrystalline phases relax to microcrystalline or approximant phases upon annealing. This has been reported for the pseudo-quaternary Al–Cu–Co(–Si) system by several authors (see, e.g. [2–4]). It proves difficult to classify a quasicrystalline alloy as stable or metastable since atomic diffusion is slow at ambient temperatures [5], thus equilibration by moderate annealing is hindered. As a way out, stimulating diffusion, Zhang and Urban [5] transformed an initially decagonal Al–Cu–Co(–Si) phase to a disordered B2 phase by electron irradiation, which is believed to be the equilibrium phase. The co-existence of either B2 or B2-based Al_3Ni_2 type vacancy ordered phase with the decagonal quasicrystalline phase has been observed in vapor deposited thin films [6]. In the same system during compression Kang and Dubois [7] observed the formation of a rhombohedral phase, whose atomic positions were similar to those in Al_3Ni_2. Wu et al. [8] discovered a disordered bcc phase in the Al–Cu–Fe system by means of scratching. Zhang et al. [9] have observed a disordered B2 phase when ion milling samples of decagonal structure of the Al–Cu–Co(–Si) system. The phase transformation was attributed to the preferential sputtering of Al during ion milling, causing a change of composition towards $Al_{50}TM_{50}$ and leading to the transformation, first to the disordered bcc phase and finally to the ordered B2 phase. The formation of a disordered B2 phase initiated by high-energy ball milling was observed in $Al_{65}Co_{15}Cu_{20}$ by Mukhopadhyay et al. [10]. Annealing at 600 °C led to an ordered B2 phase instead of the formation of a decagonal structure, suggesting that the decagonal phase is not the ground state but is stabilised by the entropy contribution to the free energy at high temperature.

2. Experimental

A polycrystalline bulk specimen of composition $Al_{70.7}Co_{13.3}Ni_{16.0}$ grown by the Czochralski method similar to Gille et al. [11] was cut into several pieces. They were then subjected to iterative milling in a ball mill (Vibrator E. Hammerschmidt, one steel ball of 9 mm diameter in a spherical cavity of 25 mm diameter, under ethanol) and sieved. The sample of the present report was obtained using seven cycles of milling for 2 min followed by sieving through sieves of 20 and 15 μm meshwork in ethanol. The fraction between 20 and 15 μm was extracted and only the particles of larger diameter were milled once more. The powder was fixed on a copper specimen holder with the aid of a viscous binder suspended in ethanol. The vaporisation of ethanol took about 42 h, defining the start of the first measurement.

Diffraction experiments were carried out using a D 5000 X-ray diffractometer (Siemens AG, X-ray tube with copper anode) working in Bragg-Brentano geometry. A scintillation detector was used for the Cu Kα radiation ($\lambda \approx 1.5418$ Å) extracted by a secondary crystal monochromator. The diffraction patterns were recorded within the range of scattering angles $2\theta = 10–138°$ (sampling time: 5 s per step, step width $\Delta 2\theta = 0.01°$). Thus, one scan took about 18 h. The ageing periods mentioned below refer to the starting time of the corresponding scan.

3. Results and discussion

After milling a number of samples exhibited no sharp reflections at all in the XRD patterns, but very broad reflections reminding of characteristics of amorphous structures rather than crystalline substances. In contrast to these results, the sample of the present report exhibited sharp reflections though parameters of the milling/sieving procedure were held constant. The observed reflections could be unambiguously attributed to the decagonal structure. It was subjected to ageing at ambient temperature and pressure for several days.

The most significant changes were observed with respect to the four strongest reflections 10000, $\bar{1}0\bar{1}\bar{1}1$, 00002 and $00\bar{1}\bar{1}1$. Fig. 1 depicts the corresponding sections of XRD patterns for six selected times of ageing.

Three experimental aspects should be emphasised. (i) There is a significant increase of intensity of the 00002 reflection with time of ageing, *t*. (ii) Integral intensities of 10000 and $\bar{1}0\bar{1}\bar{1}1$ reflection drop in the very beginning of RT ageing and are subject to a slight recovery after $t \sim 100$ h. The opposite behaviour is observed regarding the $00\bar{1}\bar{1}1$ reflection (Fig. 2). (iii) A significant shift to larger scattering angles is observed for the $\bar{1}0\bar{1}\bar{1}1$ reflection. The fluctuations of peak positions of the other reflections considered are within the error limits (Fig. 3).

Decagonal order is not destroyed by the rather short-term milling (compared with the long term milling of some 100 h as described in the literature [10]). However, the diffraction pattern of the as-milled sample indicates deviations from the ideal decagonal structure.

Observation (i) clearly indicates, that the periodicity along the *c*-direction is most disturbed by the mechanical treatment, suggesting an anisotropy of binding forces: binding within the planar decagonal ordered planes is stronger than between them. Long-range order in the periodic direction is restored after the release of stored energy (i.e. introduced by the milling) at the expense of order in the quasiperiodic plane within the first ~100 h. This can be seen from decreasing intensities of reflections corresponding to reciprocal lattice vectors with components in the quasiperiodic plane.

Afterwards an ordering process within the quasiperiodic plane sets in. The latter is probably caused by relaxation of a (linear) phason strain induced by ball milling for the following reason: the only one clearly detectable shift of peak position is observed for the $\bar{1}0\bar{1}\bar{1}1$ reflection which has the largest ratio $Q_\perp/Q_\parallel = 1.45$, ($Q_\perp = 2.694$ Å^{-1}, $Q_\parallel = 1.850$ Å^{-1}) of all the reflections in the XRD pattern ($Q_\perp/Q_\parallel$ (10000) = 1, $Q_\perp/Q_\parallel$ ($00\bar{1}\bar{1}1$) = 0.33 and $Q_\perp$ (00002) = 0).
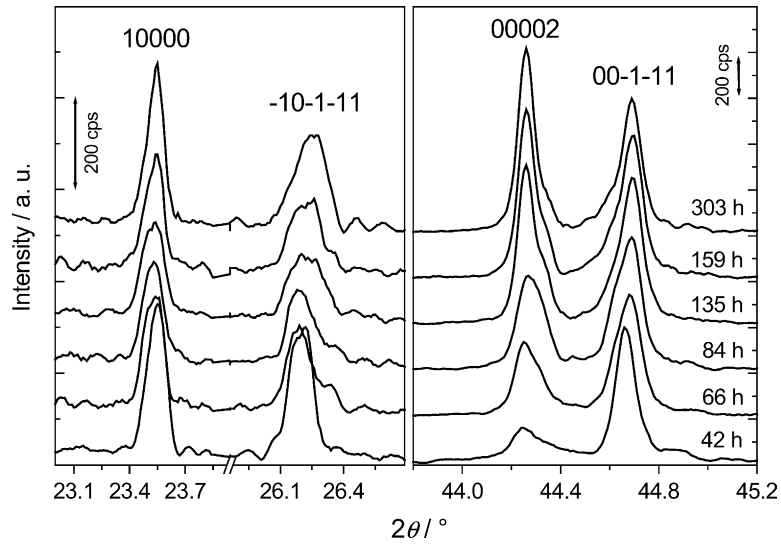
Fig. 1. Sections of as-measured XRD powder patterns (vertically shifted for better visual inspection) in the vicinity of strongest reflections for selected stages of room temperature ageing.

This becomes evident with respect to the definition of linear phason strains, which are attributed to shift the peak positions in physical space, $Q_{\parallel}$, while the magnitude of shift is directly proportional to $Q_{\perp}$. Two more indications of the presence of phason strain have been mentioned in refs. [1,12]: the deviations from the smooth overall course of thermal expansion coefficients in the vicinity of the low temperature phase transition at about 150 K and their non-zero values for the extrapolation $T \rightarrow 0$. The latter has been clearly evidenced by

Inaba et al. [13] who performed heat capacity measurements of perfect and phason-disordered icosahedral Al–Cu–Ru. While heat capacity $C_p(T)$ tended to zero in the first case it exhibited a non-zero intercept for the phason strained sample.

To find an explanation from the point of view of structure we performed a radial distribution function (RDF) analysis, i.e. a Fourier synthesis, of the measured X-ray powder pat-
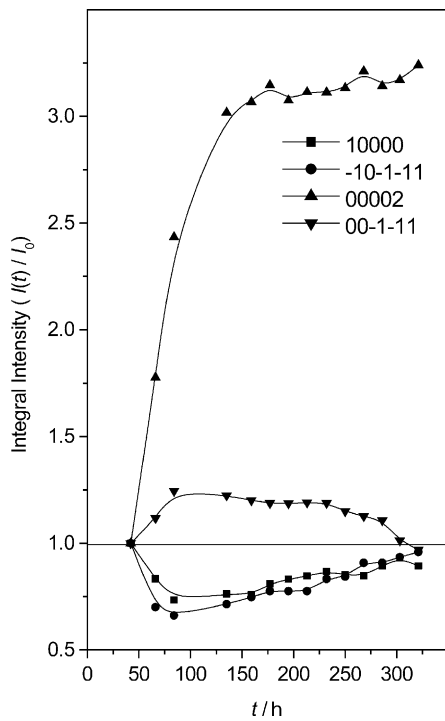

Fig. 2. Integral intensity vs. time of ageing, t, illustrating observations (i) and (ii).
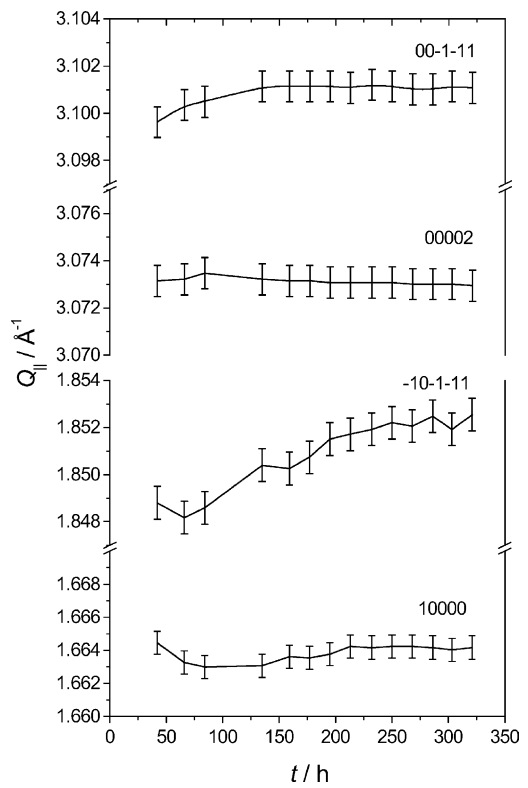

Fig. 3. The time-dependence of scattering vectors, $Q_{\parallel}$ (=$4\pi \sin\theta/\lambda$), reveals the significant shift of the $\bar{1}\,0\,\bar{1}\,\bar{1}\,1$ peak position.
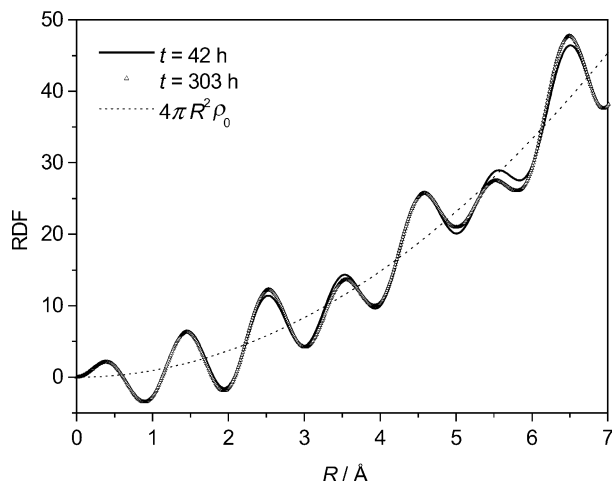
Fig. 4. Radial distribution function as derived from the diffraction patterns for the duration of room temperature ageing of 42 and 303 h. Note the changes between 5.4 and 6.6 Å (ρ_0 represents the average number of atoms per unit volume).

terns. The RDF analysis is widely used for a description of the averaged coordination at an atomic scale for substances lacking periodic long range order, above all amorphous materials.

Fig. 4 shows the computed RDF for the first ($t = 42$ h) and the last ($t = 303$ h) step of the investigation. The strongest changes are observed in the range of bond-lengths between 5.4 and 6.6 Å. While the number of interatomic distances at $R \approx 5.6$ Å are reduced the opposite holds for the occupied bond-lengths at $R \approx 6.4$ Å. A significantly smaller change of the PDF occurred at $R \approx 2.5$ Å which slightly increased on expense of the amplitude at $R \approx 3.5$ Å.

The modified Li/Steurer model [14–16] of structure provides bonds at 5.46, 5.55 and 5.63 Å, which represent Al–Al pairs and Al–transition metal (TM) pairs, only. In terms of diffraction their contribution to the scattered intensity is small, since it scales as the product of atomic scattering amplitudes involved in the bonds. Contrary to that, the bonds at 6.18, 6.30, (6.39–small occupancy) and 6.42 Å, which got more pronounced in the course of ageing, are inhibited by all three types of pair correlations, especially containing TM–TM bonds representing the largest scattering power by the product of their atomic scattering amplitudes.

From the observation outlined above, that long-range order in the periodic direction is restored preferentially, one could expect to find bonds aligned nearly parallel to the periodic axis. However, no tendency of this type can be recognised from the interatomic distances observed.

A significantly smaller change of the RDF occurred at $R \approx$ 2.5 Å, which slightly increased on expense of the amplitude at $R \approx 3.5$ Å. While the 2.5 Å wiggle corresponds to the bond lengths 2.45, 2.55 and 2.88 Å, the latter two of which include TM–TM pairs, the 3.5 Å wiggle arises from Al–Al correla-

tions at 3.18, 3.77 and 3.83 Å (including a small number of Al–TM bonds at 3.18 and 3.77 Å).

Regardless of the bond direction, we can conclude from both changes of the RDF data that TM–TM correlations are restored preferentially during ageing, i.e. on an atomic scale the impact of mechanical energy most probably leads to a displacement of TM positions of the quasicrystalline structure.

4. Conclusions

Short-term ball milling did not destroy the decagonal structure completely. However, the structure was disturbed significantly, preferentially its periodic component. Order was restored within the first ∼100 h of room temperature ageing. There are indications, that recovery of the quasiperiodic order within the planes of tenfold symmetry, which occurred in a second stage, is due to the relaxation of phason strains. Fourier analysis of the diffraction patterns indicated the preferred restoration of bond-lengths corresponding to TM–TM pairs.

Acknowledgements

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