

FORMATION AND STABILITY OF SINGLE-PHASE Al-Cu-Fe QUASICRYSTALS UNDER PRESSURE

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Abstract. Alloy powder with nominal composition $\text{Al}_{67}\text{Cu}_{23}\text{Fe}_{10}$ was prepared by ball-milling of elemental metallic powders. The as-milled powder consists mainly of a nanocrystalline Al(Cu,Fe) solid solution.

The structural phase transitions upon heating under different pressures were investigated by *in-situ* X-ray diffraction at the F2.1 beamline of DESY-HASYLAB (Hamburg, Germany), in order to establish a pressure-temperature phase diagram. A single-phase quasicrystalline powder was obtained upon heating above 800 °C, following a sequence of phase transitions at temperatures lower than 700 °C. The quasicrystalline phase was found to be stable upon quenching under pressure.

1. INTRODUCTION

Aluminium-copper-iron quasicrystals have a unique combination of physical, thermal and mechanical properties, such as low, electrical conductivity, low surface energy and coefficient of friction, absence of work hardening as well as high hardness and brittleness at room temperature [1]. Thus Al-Cu-Fe icosahedral QC (iQC) phases are suitable for several important applications for ex. as coatings [1,2], or as reinforcement particles in aluminium-based metal matrix composites [3]. Their friction properties and hardness makes them an interesting material for wear-resistant coatings, while their low thermal conductivity and their improved ductility above 750 °C make them suitable for thermal-barrier coatings. Their biocompatibility also allows their use as coatings on bone implants and prosthesis for biomedical applications [1].

The production of good quality quasicrystalline Al-Cu-Fe alloys on an industrial scale is still difficult, as the QC phase is stable only within a narrow composition domain [1-4]. Several previous studies provided evidence for the formation of QC phases upon adequate thermal treatment of $\text{Al}_{65}\text{Cu}_{23}\text{Fe}_{12}$ mechanically alloyed powders [5-8]. The formation of Al-Cu-Fe quasicrystals from atomized powders [9] or in cold-rolled multilayers [10] was also recently reported.

The objective of the present work is to investigate the formation and stability of iQC phases upon heat treatment of ball-milled Al-Cu-Fe nanopowders under different applied pressures, and to establish a pressure-temperature phase diagram that could be used for determining the process parameters to obtain quasicrystalline phases by sintering. The experimental method used for this study was *in-situ* X-ray diffraction using synchrotron radiation.

2. EXPERIMENTAL

2.1. Preparation of precursor materials by high-energy ball milling

Nanocrystalline precursor powders with nominal composition $\text{Al}_{67}\text{Cu}_{23}\text{Fe}_{10}$ were prepared by high-energy ball-milling using a planetary ball-mill Retsch PM-400. A slightly lower Fe content was chosen, as some Fe-contamination from the milling media is expected. Appropriate mixtures of elemental powders were placed into chromium-steel vials together with 10 mm- and 20 mm-diameter chromium-steel balls and ball-milled for 40 hours at 200 rotations per minute (rpm). The ball-to-powder mass ratio was chosen equal to 139/10. Hexane was added to prevent oxidation events. No other milling additives were employed in the present wet-milling experiments.

2.2. In-situ X-ray diffraction using synchrotron radiation

In-situ X-ray diffraction experiments in normal pressure conditions were performed in angular dispersive mode at the beamline B2 at the synchrotron facility DESY-HASYLAB (Hamburg, Germany). The high-resolution diffractometer at the B2 beamline was equipped with a semicircular image-plate detector allowing the fast acquisition of diffraction patterns [11]. The powder samples were mounted into 0.3 mm-diameter quartz capillaries and centered into a STOE high-temperature oven (max. temperature 900 °C).

High-pressure *in-situ* X-ray diffraction experiments were performed in energy-dispersive mode at the beamline F2.1 at DESY-HASYLAB. In the configuration used for our experiment, the high-temperature high pressure diffractometer F2-1 used a white X-ray beam and was equipped with an energy dispersive detector, allowing fast acquisition of the diffraction patterns at a fixed diffraction angle 2θ . Pressure and temperature were applied respectively by a multi-anvil press and an electric-current heating system. The powder sample was mounted into a specific sample environment consisting of an amor-

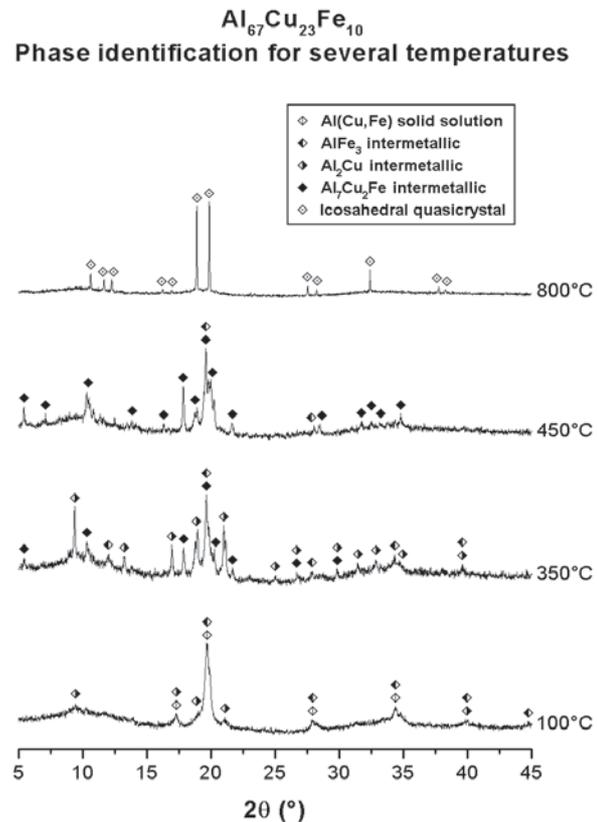
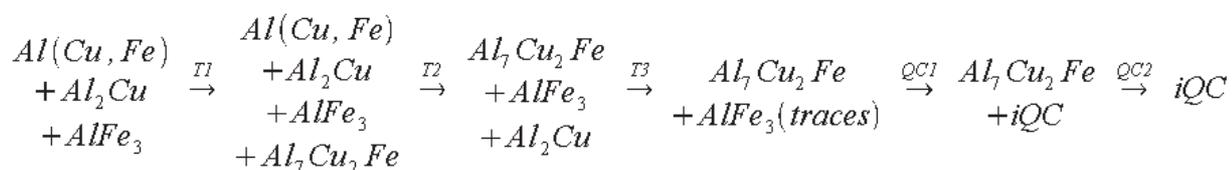


Fig. 1. Diffraction patterns obtained in normal pressure conditions at temperatures 100, 350, 450 and 800 °C, with indication of the present phases.

phous boron cubic container (external dimensions $8 \times 8 \times 8 \text{ mm}^3$), with graphite and copper ensuring electrical conduction for sample heating, and boron nitride for chemical isolation. Sodium chloride was used as a standard for pressure calibration. Temperature was monitored using a thermocouple embedded in the central boron nitride layer.

3. RESULTS AND DISCUSSION

Fig. 1 shows diffraction patterns obtained at ambient pressure for the temperatures 100, 350, 450 and 800 °C. At lowest temperatures, the Al-Cu-Fe powders consist of a nanocrystalline Al(Cu,Fe) solid solution, with small traces of crystalline intermetal-



Scheme

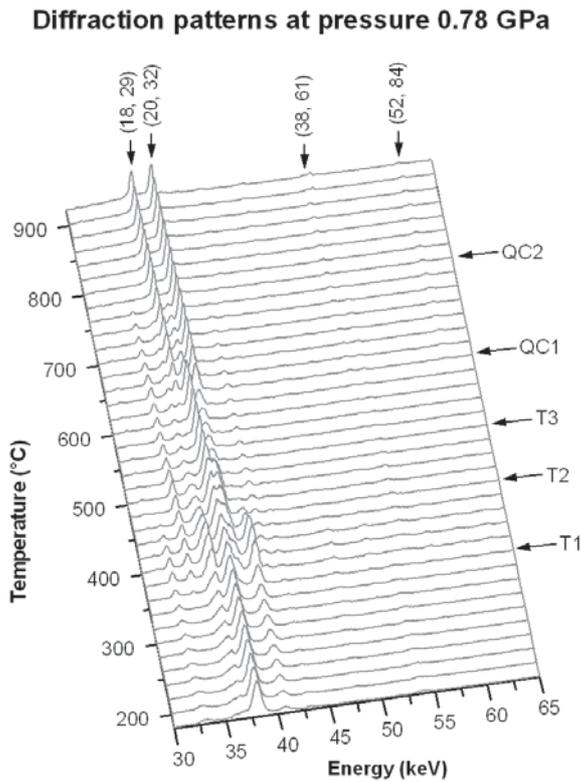


Fig. 2. Examples of diffraction patterns obtained by *in-situ* XRD at pressure 0.777 GPa; crystalline state phase transitions at temperatures T_1 , T_2 , T_3 ; icosahedral quasicrystalline phase (iQC) starts to form at temperature QC1; quasicrystal as single phase above temperature QC2; iQC phase is easily recognisable by intense peaks (18, 29) and (20, 32).

lic phases Al_2Cu and $AlFe_3$. The volume fraction of the intermetallics increases upon heating. A tetragonal Al_7Cu_2Fe phase starts to form at temperature T_1 and becomes dominant above temperature T_2 . At temperatures above T_3 , the sample mainly consists in tetragonal Al_7Cu_2Fe intermetallic phase, with possible traces of $AlFe_3$. The icosahedral quasicrystalline (iQC) phase starts to form at temperature QC1. At temperatures above QC2, the sample consists in a single iQC phase. The evolution of phases in the sample upon heating can be summarised in the scheme.

Fig. 2 illustrates the evolution of diffraction patterns of ball-milled $Al_{67}Cu_{23}Fe_{10}$ powder upon heating under an applied pressure of 0.78 GPa. At all investigated pressures, the samples undergo the same series of phase transitions observed during the experiments at ambient pressure [8] leading to the formation of single-phase icosahedral quasicrystalline phase. Phase transitions described above occur at temperatures noted T_1 , T_2 , T_3 , QC1, and QC2.

The transition temperatures at all investigated pressures as listed in Table 1 and shown in Fig. 3 were determined with an uncertainty of approximately $\pm 10^\circ C$ in temperature and ± 0.02 GPa in pressure. Apparently, increasing pressure has no significant influence on the phase transformation temperatures.

Phase transitions in such systems usually occur through grain nucleation and growth [12,13]. The

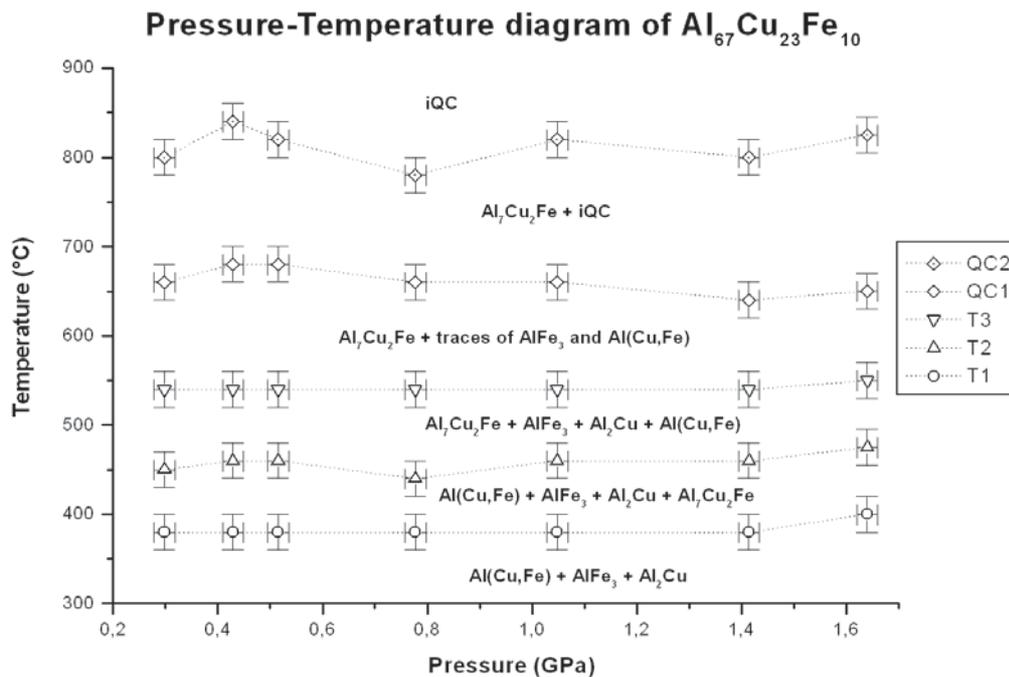


Fig. 3. Pressure-Temperature phase diagram of the $Al_{67}Cu_{23}Fe_{10}$ quasicrystalline alloy; the dot lines between experimental points are present as guide for the eye.

Table 1. Transition temperatures observed at different applied pressures; experiment at ambient pressure was performed at the beamline B2 of synchrotron facility DESY-HASYLAB (Hamburg, Germany); others were performed at the beamline F2.1.

Pressure (GPa)	Transition temperatures (°C)				
	T_1	T_2	T_3	QC1	QC2
Ambient	350	400	475	600	750
0.30	380	450	540	660	800
0.43	380	460	540	680	840
0.52	380	460	540	680	820
0.78	380	440	540	660	780
1.05	380	460	540	660	820
1.41	380	460	540	640	800
1.64	400	475	550	650	825

nucleation rate can be described by the formula $I=I_0/\exp[(\Delta G^*+Q_n)/k_B T]$, where I_0 and k_B are constants, ΔG^* is the energy barrier for nucleation and Q_n the activation energy for atomic diffusion across the interface of a nucleus [13]. Crystallisation and phase transitions are governed by two distinct mechanisms, i.e. nucleation and diffusion. Applied pressure influences these two processes by lower-

ing the energy barrier for nucleation and by increasing the energy necessary for atomic diffusion [12]. These two competing effects might in some cases compensate each other [14]. Such effects can occur in transformations involving quasicrystalline phases, which usually have low energy barriers for nucleation [13], nevertheless, in the present case, all phase transitions appear globally unaffected by pressure, which is unusual.

A quenching experiment was performed under an applied pressure of 0.45 GPa (Fig. 4). The sample was heated at relatively fast rate up to 650 °C in order to obtain a single iQC phase, and then quenched under pressure. The diffraction patterns after pressure-assisted quenching and pressure release demonstrate the retention of a major iQC phase (Fig. 4). This is promising with respect to the stabilization of the quasicrystalline phase by this procedure. The patterns in Fig. 4 index to a main quasicrystalline phase constituent with a small amount of residual $\beta(\text{Al,Fe})$ phase. However, the formation of crystalline approximant phases cannot be firmly excluded at this time [4]. Angular-dispersive high-pressure XRD experiments are planned to clarify this issue.

4. CONCLUSIONS

Phase transitions in mechanically alloyed $\text{Al}_{67}\text{Cu}_{23}\text{Fe}_{10}$ nanocrystalline powder were investigated by *in-situ* X-ray diffraction at different pressures upon heating. Under ambient pressure conditions, the sample undergoes a series of phase transitions starting at relatively low temperature with the formation of intermetallic phases Al_2Cu and AlFe_3 , and subsequently tetragonal $\text{Al}_7\text{Cu}_2\text{Fe}$, and finally the forma-

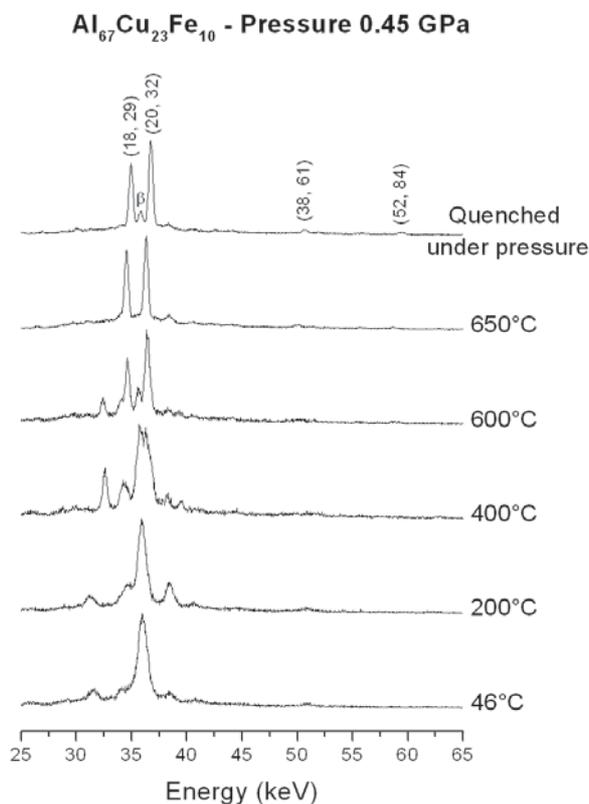


Fig. 4. Stabilisation of Al-Cu-Fe iQC phase upon quenching under pressure 0.45 GPa.

tion of a well-defined single iQC phase above 750–800 °C. The application of pressure does not modify the nature of the phase transitions taking place in the material, and does not affect the transition temperatures.

An experiment with quenching under a pressure of 0.45 GPa was performed in order to stabilise the iQC phase. The pattern after rapid cooling and pressure release could be indexed to a main quasicrystalline phase constituent with a small amount of residual β (Al,Fe) phase. However, the formation of crystalline approximant phases cannot be firmly excluded at present. Angular-dispersive high-pressure diffraction experiments are planned to clarify this issue.

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