THERMAL STABILITY OF Al-Cu-Fe QUASICRYSTALS PREPARED BY SHS METHOD

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Resume

Quasicrystal-containing materials are usually prepared by rapid solidification of the melt (e.g. by melt spinning) or mechanical alloying. In this work, the method using exothermic reactions between compressed metallic powders called SHS (Self-propagating High-temperature Synthesis) was tested. The microstructure and phase composition of the product was described in dependence on cooling regime from the reaction temperature. Thermal stability of prepared Al-Cu-Fe quasicrystals was studied by annealing at the temperatures of 300 and 500 °C.

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1. Introduction

Quasicrystals were discovered in 1982 by Daniel Schechtman, who was awarded by Nobel Prize in 2011 [1]. Before this date, scientists interested in crystallography thought that the crystals cannot have the 5-, 8-, 10- and 12-fold symmetry. The reason is that it is impossible to fill the space by such geometric objects using the translation symmetry common for crystals [1]. In the case of quasicrystals, these elements of symmetry are allowed, since filling of the space is possible by more complex operations, as represented in 2D by Penrose tilling [1], shown in Fig.1a.

Up to now, the quasicrystals were found in more than 100 alloy systems during rapid solidification, e.g. in aluminium alloys with transition metals (Fig.1b). In general, currently known quasicrystals can be divided to two groups – metastable quasicrystals, obtainable by rapid solidification only [2], and stable ones, which arise also during conventional solidification or after annealing [3]. The Al-Cu-Fe quasicrystals, which are investigated in this work, belong to more stable ones.

Reactive sintering was previously reported as a promising way of the preparation of many intermetallics (e.g. NiAl, NiTi, Ti_5Si_3) [4, 5]. This method comprises rapid heating of the compressed powder mixture. During heating, thermally-activated exothermic reactions occur. The released heat sustains and propagates further reaction through the body of the reactants. Therefore, this process is commonly called Self-propagating High-Temperature Synthesis (SHS) [6].

2. Experimental

Experimental materials containing Al-Cu-Fe quasicrystals were prepared by reactive sintering powder metallurgy concerning SHS reactions. The process consisted of blending of elemental powders of aluminium (particle size < 400 μm, 99.99 % purity), iron (particle size <

10 µm, 99.8 % purity) and copper (particle size <10 µm, purity >99.99 %) and uniaxial pressing at the laboratory temperature by a pressure of 260 MPa using LabTest 5.250SP1-VM universal loading machine. The powder mixture contained 63 at. % Al, 24 at. % Cu and 13 at. % Fe. Compressed powder mixtures were subjected to reactive sintering at 700°C for 15 min. Two cooling regimes from the reaction temperature were tested – air cooling and water quenching.

Samples were characterized by X-ray diffraction analysis (PANalytical X'Pert Pro diffractometer), microstructure observation (scanning electron microscope TESCAN VEGA 3 LMU with OXFORD Instruments INCA 350 EDS analyser) and Vickers hardness measurement (HV 5). To observe the microstructure, samples were ground, polished and etched using Kroll's reagent (10 ml HF, 5 ml HNO_3 and 85 ml H_2O). Area fraction (which is known to be approximately equal to the volume fraction) was measured by the ImageJ 1.46 image analysis software.

Thermal stability was studied by annealing at 300 and 500 °C for 4 – 40 h. After annealing, phase composition, microstructure and hardness (HV 5) were evaluated.

3. Results and Discussion

Phase composition of the material prepared by SHS in dependence on the cooling rate is shown in Fig.2. Both air- and water-cooled materials contain $Al_{60}Cu_{30}Fe_{10}$ quasicrystalline phase, $Al_{13}Fe_4$ (orthorombic, Bmmm), $CuAl_2$ (tetragonal, I4/mcm) and small amounts of unreacted iron, aluminium and copper. $Al_{60}Cu_{30}Fe_{10}$ quasicrystals are usually identified in rapidly solidified aluminium alloys prepared by melt spinning or melt atomization techniques. In this case, even air cooling was sufficient to produce this phase. The reason probably lies in the fact that the SHS reaction (probably connected with the formation of $CuAl_2$ phase) produces large amount of heat, leading to rapid increase of the sample's temperature far above 1000°C. It causes partial melting of the sample. Air or water cooling of this sample enables rapid solidification, resulting in the formation of non-equilibrium phases.

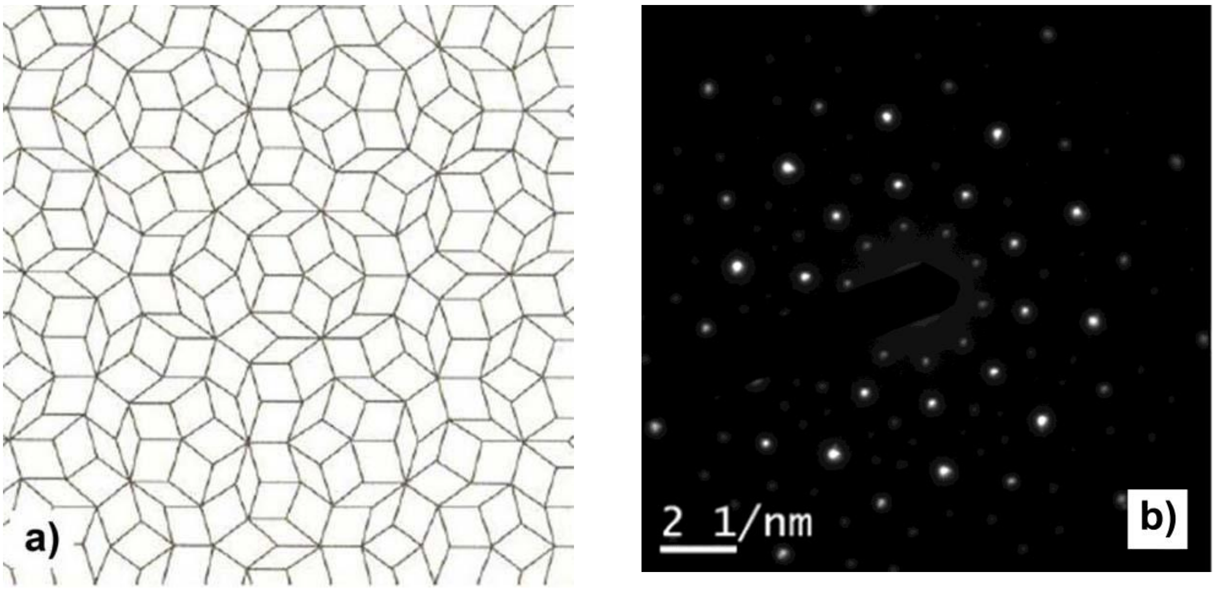

Fig. 1. a) Penrose tiling, b) diffraction pattern of Al-Cr-Fe quasicrystalline phase [1]

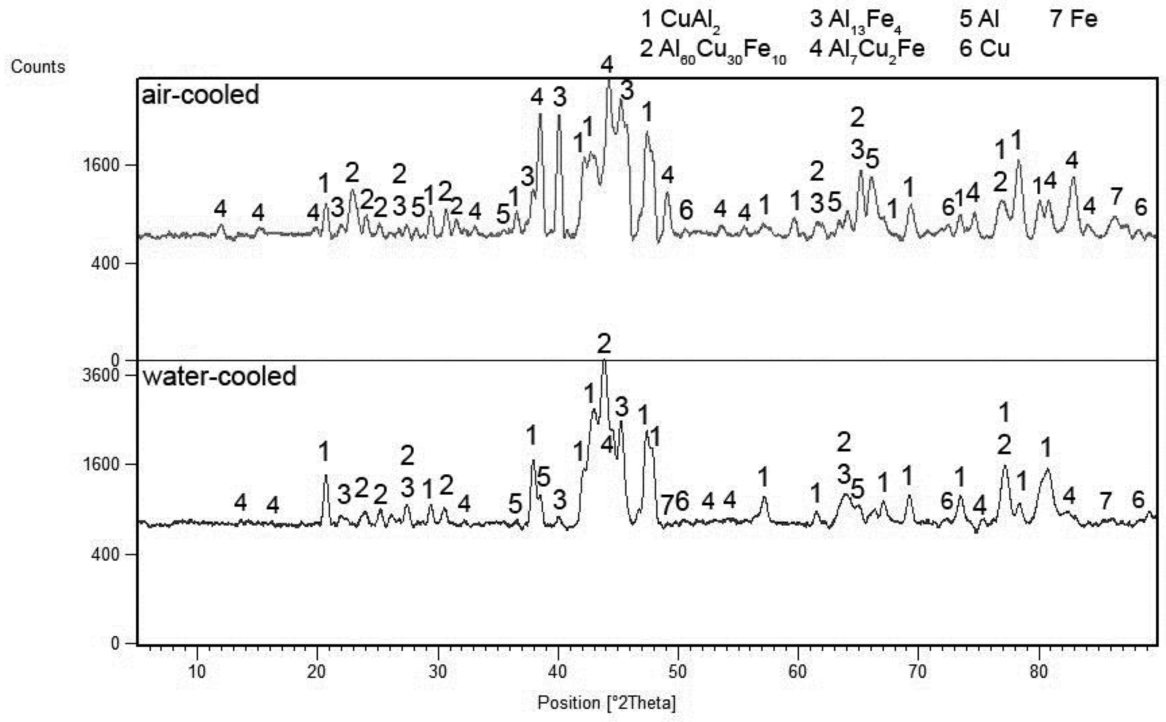

Fig. 2. XRD patterns of Al-Cu-Fe alloy prepared by SHS process followed by air cooling and water cooling

The difference between the air- and water-cooled samples lies in the volume fraction of quasicrystalline $Al_{60}Cu_{30}Fe_{10}$ and stable Al_7Cu_2Fe (tetragonal, P4/mnc). In the case of air-cooled material, the dominant phase is the stable Al_7Cu_2Fe, while in water-quenched one the quasicrystalline phase and $CuAl_2$ dominate. The difference of the volume fraction of $Al_{60}Cu_{30}Fe_{10}$ quasicrystalline phase between air- and water-cooled materials is clearly visible in Fig.3.

In fact, the darker grey areas are not the grains of quasicrystalline phase, but the clusters of its small particles with the other phase, probably $CuAl_2$, see Fig.4. The quasicrystalline $Al_{60}Cu_{30}Fe_{10}$ is probably the darker rounded phase in the cluster, while $CuAl_2$ is the lighter irregular one. This assumption is supported by the literature [7-11], where quasicrystals are reported as spherical particles. The area fraction of these quasicrystal-containing collonies was measured on the metallographic samples by image analysis. The water-quenched sample contains approx. 37 % of these areas, while in the air-cooled one it is only about 10 %. The hardness of the material is proportional to the content of the quasicrystalline phase, i.e. the water-quenched alloy achieves higher hardness than the air-cooled one, see Table 1. During annealing of the water-quenched material at 300°C, the hardness remains almost constant. On the other hand, annealing at 500°C reduces the hardness from approx. 430 HV 5 down to 370 HV 5. It indicates possible decomposition of the metastable phases and shows that this material probably has no ability of precipitation strengthening.

The conclusions made on the base of hardness measurements were confirmed by the observation of the microstructure after annealing at 300 and 500°C. In Fig.5a,b and Fig.6, no significant decomposition of the $Al_{60}Cu_{30}Fe_{10}$ can be observed after annealing at 300°C. On the other hand, annealing at 500°C leads to the coarsening of the $Al_{60}Cu_{30}Fe_{10}$ quasicrystal clusters and to their decomposition to Al_7Cu_2Fe and $CuAl_2$ stable phases (Fig. 5c,d and Fig. 6).

Table 1

Plasma spraying parameters

Sample	Hardness (HV 5)
air-cooled	316
water-cooled	436
water-cooled and annealed (300°C, 4h)	429
water-cooled and annealed (300°C, 40h)	425
water-cooled and annealed (500°C, 4h)	363
water-cooled and annealed (500°C, 40h)	373

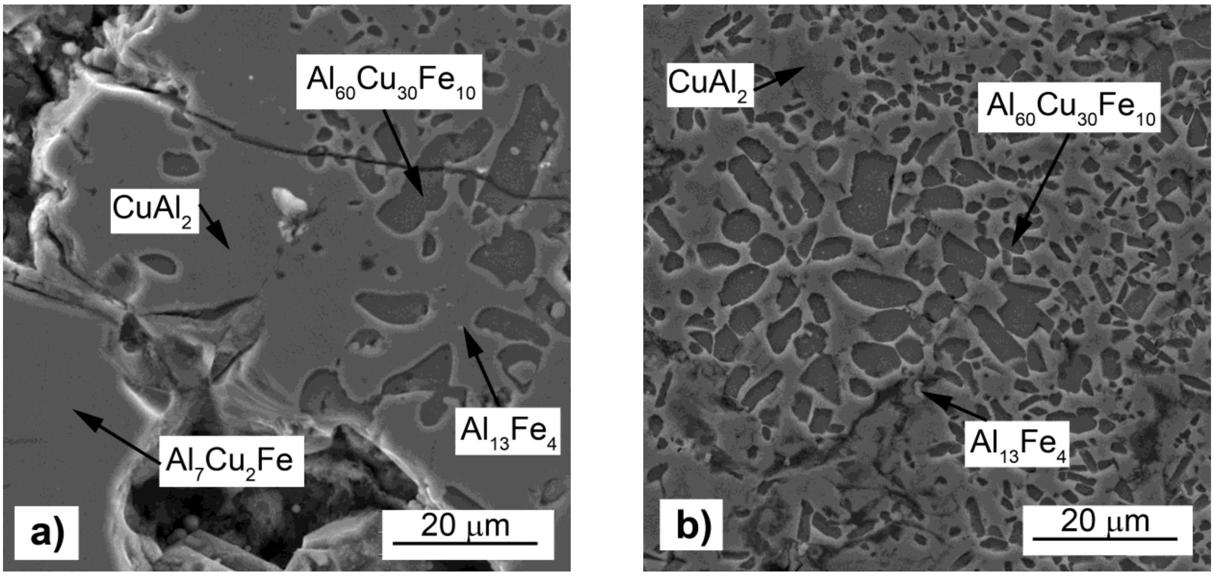

Fig. 3 Microstructure (SEM) of the material prepared by SHS and a) air cooling, b) water cooling

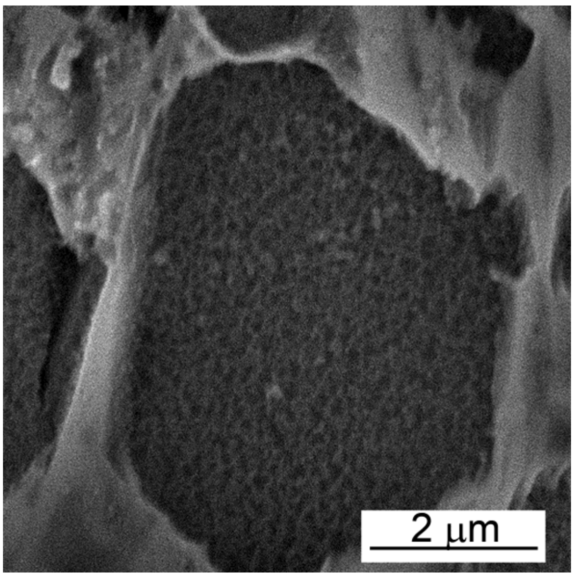

Fig. 4. Detail of the microstructure (SEM) of the material prepared by SHS and water cooling.

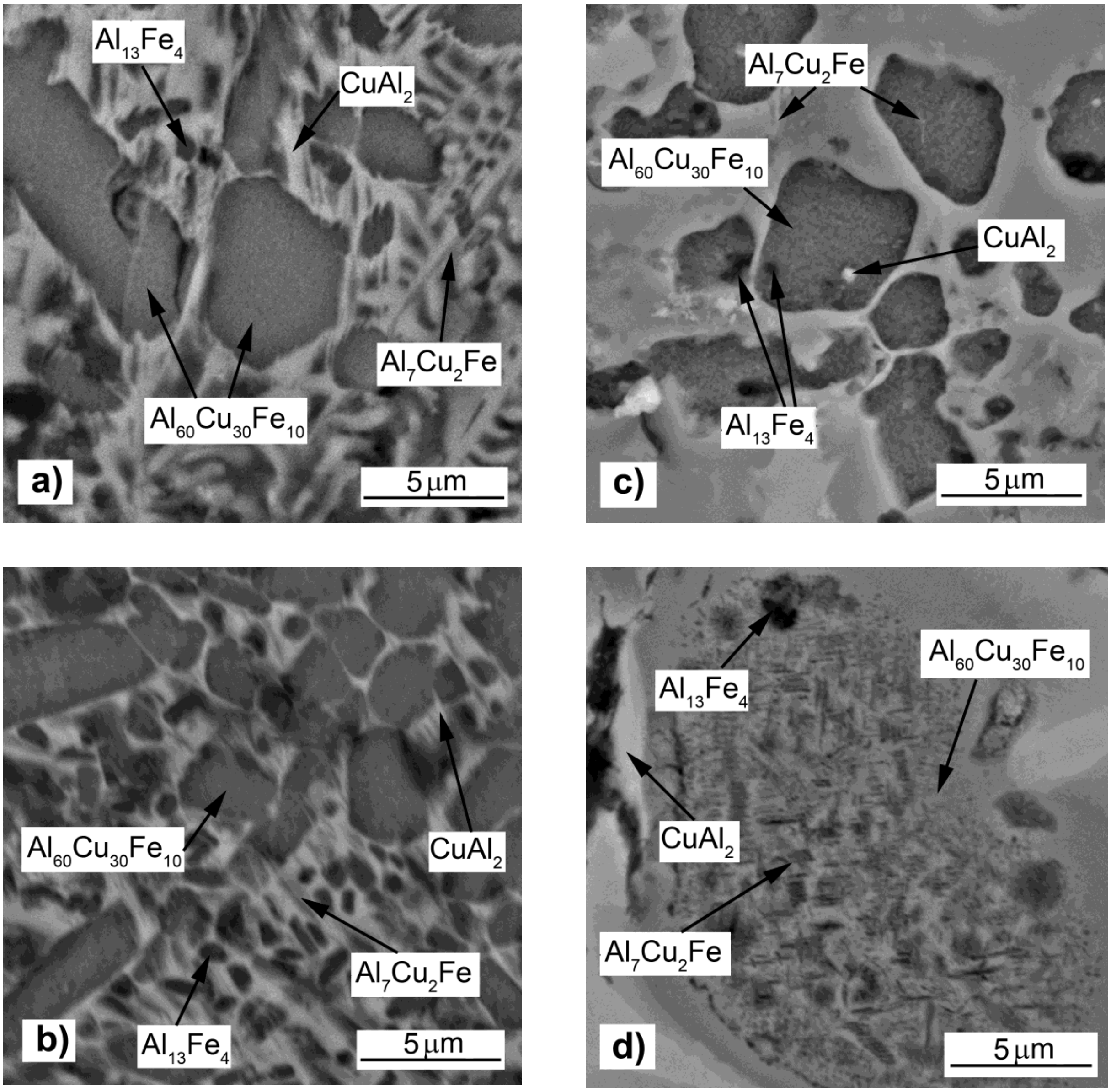

Fig. 5. Microstructure (SEM) of the material prepared by SHS and annealed at a) 300°C for 4 h, b) 300°C for 40 h, c) 500°C for 4 h and d) 500°C for 40 h

4. Conclusions

In this work, Al-Cu-Fe alloy containing quasicrystals was successfully prepared by a reactive sintering of Al, Cu and Fe elemental powders, followed by air- or water-cooling. Quenching in water was found to be more suitable, since it yields higher volume fraction of $Al_{60}Cu_{30}Fe_{10}$ quasicrystals. This simple technique does not require either rapid solidification techniques, such as melt spinning and melt atomization, or mechanical alloying, which are commonly used for this purpose. Due to high volume fraction of the $Al_{60}Cu_{30}Fe_{10}$ clusters and their size up to 20 µm, this material can serve as a model for the description of the behaviour of quasicrystals e.g. at elevated temperature or during deformation.

The thermal stability of $Al_{60}Cu_{30}Fe_{10}$ phase, which is reported as stable quasicrystal was tested at 300 and 500°C. No significant changes of this phase were observed at 300°C, while annealing at 500°C caused the continuous decomposition of the $Al_{60}Cu_{30}Fe_{10}$ quasicrystals to Al_7Cu_2Fe and $CuAl_2$ stable phases. This decomposition is connected with the hardness decrease.

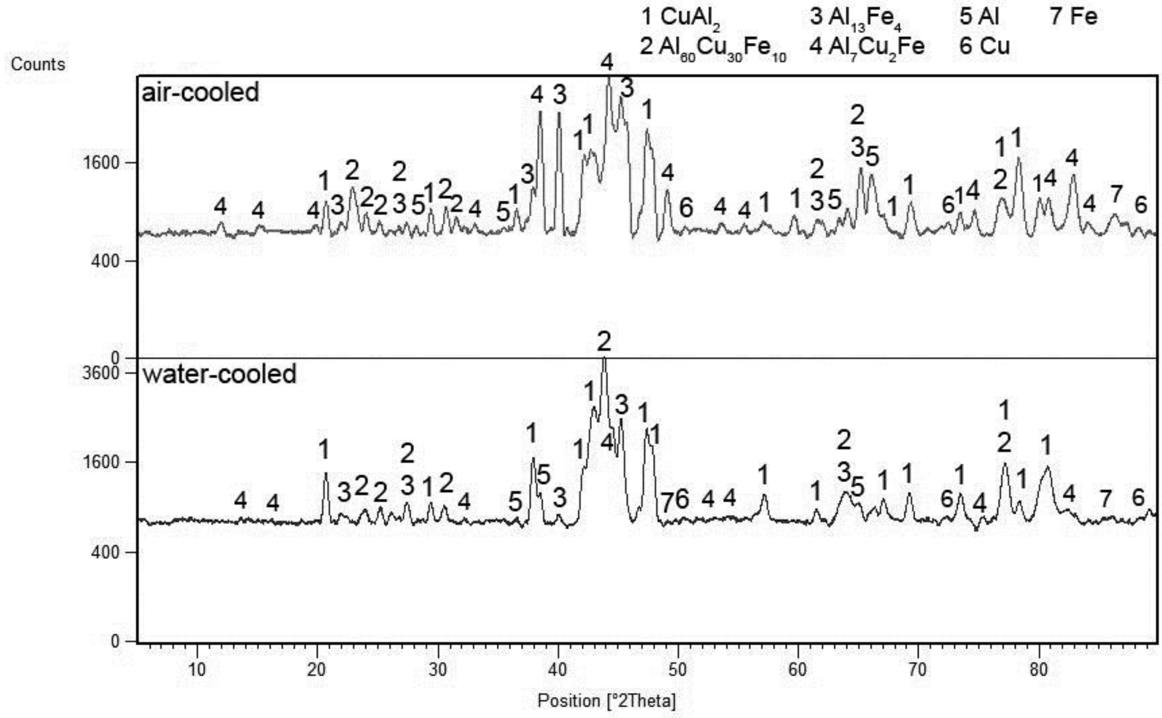

Fig. 6. XRD patterns of Al-Cu-Fe alloy prepared by SHS process followed by water cooling, annealed at 400 and 500°C for 4 and 40 h

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