Stable Quasicrystalline Phase in Al-Cu-Fe-Cr Coating Materials

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Transmission electron microscopy (TEM) studies have been carried out on magnetron-sputtered coatings in the Al-rich region of the Al-Cu-Fe-Cr quasicrystalline phase field, focusing on the composition that exhibited the best tribological performance among a group of sputtered coatings. The size of the particles in the as-deposited coating is around 10 nm. The TEM experiments on annealed coatings (450 °C for 6 hours + 400 °C for 7 hours) revealed that the material is composed of a decagonal quasicrystalline phase with a periodicity of 1.24 nm along the unique axis and a hexagonal crystalline phase, with $a = 2.48$ nm and $c = 1.24$ nm. These results show that a thermodynamically stable quasicrystalline phase exists in the Al-Cu-Fe-Cr alloy system, in addition to previously reported microcrystalline structures and orthorhombic and monoclinic approximants. The hexagonal phase is a crystalline approximant of the decagonal phase, structurally related to hexagonal crystalline phases previously reported in Al-Mn and Al-Cr-Ni quasicrystalline alloys.

I. INTRODUCTION

QUASICRYSTALS (QCs) exhibit rotational symmetries, which were previously believed to be forbidden in crystals. These extraordinary materials not only have unique structures, but also have unusual properties. Unlike conventional metallic materials, QCs exhibit high hardness and stiffness, but low electrical and thermal conductivity and exceptionally low fracture toughness. The QC materials are reported to exhibit a very low coefficient of friction, measured against diamond and steel counterfaces. This, together with their high hardness, suggests that QC materials may be valuable in tribological applications. The utilization of QC materials in bulk form is compromised by their low fracture toughness, which presents problems both in the manufacture of components and in service lifetimes. Materials with low fracture toughness may, however, be used in combination with more ductile materials. This is of particular interest for tribological applications, where the surface properties of QC materials (high hardness and low friction coefficient) may be combined with the bulk properties of conventional metals (high toughness and ductility) by means of a QC coating on a metallic substrate.

Dubois and his co-workers were the first to investigate the tribological properties of coatings, starting with the Al-Cu-Fe system and then extending to the Al-Cu-Fe-Cr system.[1,2,3] Their attention was focused on one potential application, the preparation of nonstick thermal-sprayed coatings on cookware. The Al-rich corner of the phase diagram of the Al-Cu-Fe-Cr system was explored for promising QC coating materials.[4,5] A metastable icosahedral phase was found in rapidly quenched samples, which transforms into the approximants of the decagonal phase upon annealing. The decagonal phase was formed within a certain cooling-rate limit. If the cooling rate was too high, the icosahedral phase formed, while slow solidification led to the formation of the crystalline approximants, including a microcrystalline (MC) structure with pseudo tenfold symmetry. Five polymorphous approximants have been observed, which belong to an orthorhombic and monoclinic system.[6] The MC structures are composed of different approximant components, thus leading to many kinds of MC structures.

The coating materials produced by thermal spraying (or hot-projection) techniques are metastable quasicrystals and (or transformed into) stable crystalline approximants and MC structures within the aforementioned composition range.[1–5] Their work shows that the approximant phases may have similar mechanical and thermal properties to the quasicrystalline phases. It is known that the formation of quasicrystalline phases depends on the control of composition and metallurgical processing (thermal history, deposition, and processing steps). In order to achieve even higher mechanical (physical and chemical) properties, it is important to tune the composition to look for stable quasicrystalline phases, which can be used as coatings.

A systematic study on the quasicrystal–related coating materials is being carried out in the Wear Sciences and Coating Group of Technology Assessment and Transfer, Inc. Magnetron-sputtered samples were found to have a comparatively low friction coefficient against a steel ball. The coating materials were deposited on different kinds of substrates, *e.g.*, Inconel and Si, and on both have virtually identical surface energies: 35.8 mJ/m^2 for the as-deposited and 34.3 mJ/m^2 for the annealed samples (results on mechanical properties will be published separately). Transmission electron microscopy (TEM) and electron diffraction (ED) experiments reveal that a thermodynamically stable decagonal quasicrystal, together with a new hexagonal approximant, exist in the annealed coating layer.

In this article, we present preliminary phase identification for these Al-Cu-Fe-Cr coating materials on Si substrates.

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II. EXPERIMENTAL

Coating samples (composition of $Al_{76.2}Cu_{3.9}Fe_{7.9}Cr_{10.5}O_{1.6}$ and Si substrate) prepared by magnetron sputter deposition were supplied by Technology Assessment and Transfer, Inc.; further details will be published elsewhere. The samples used in the TEM study were as-deposited Al-Cu-Fe-Cr and annealed Al-Cu-Fe-Cr on a (100) Si single substrate from the same deposition run. The Si wafer on which the as-deposited film was sputtered was broken in half. Half of the sample was annealed at 450 °C for 6 hours under an argon overpressure in a box furnace, with a subsequent anneal at 400 °C for 7 hours to assist grain growth. As-deposited coatings adhered well to the substrate. For the annealed samples, differential thermal expansion delaminated part of the annealed coating, but most of the coating adhered.

The sputtered samples were cut into 3 mm disks using an ultrasonic tool. Plan-view TEM samples were then prepared by mechanical grinding and polishing, dimpling, and final thinning to electron transparency with a GATAN precision ion polishing system. An Hitachi H8100 microscope was used for the TEM and ED experiments.

III. RESULTS AND DISCUSSION

A. *Coating Layers*

The morphology of the coating layer (plan view) in the as-deposited sample and in the annealed sample are shown in Figures 1(a) and (b), respectively. The particles form a dense layer covering the substrate. The size of the as-deposited particles is rather small (around 10 nm). In the annealed sample, the grains have grown to almost 20 to 30 times their size in the as-deposited sample. Figure 2 shows the Debye–Scherrer ED ring patterns from a large number of the particles/grains in the as-deposited sample (left-hand side) and the annealed sample (right-hand side). Due to grain growth in the annealed sample, the trace of the rings appears rougher and also is expanded in width. The spacing of rings 1, 3, and 4 remains the same from the as-deposited to the annealed samples, but the spacing of rings 2 and 5 changes. This indicates that in addition to grain growth, a phase transformation has also taken place. The ED experiments were carried out to identify the phases in the annealed material.

B. *Decagonal Quasicrystal Phase*

The Al-Cu-Fe-Cr quasicrystal–related coating materials have been confirmed to have unique mechanical properties (high hardness, low surface energy, and low friction coefficient). However, to date, there is no direct evidence for the existence of a decagonal quasicrystalline phase in Al-Cu-Fe-Cr thermal-spray-coated materials. As mentioned previously, five crystalline approximants have been identified, and a variant of microcrystalline structures exist which may have approximants as their components. In a review article,[7] it was speculated that within a certain composition range and possibly also within a limited temperature zone, there might exist a stable decagonal phase in this quaternary system. Does a thermodynamic stable decagonal quasicrystal phase exist in the Al-Cu-Fe-Cr alloy system? If it does exist, a further question will be, do coatings containing a higher percentage of quasicrystalline phase have better friction, wear, optical, thermal, and electronic properties? We will clarify here the first question.

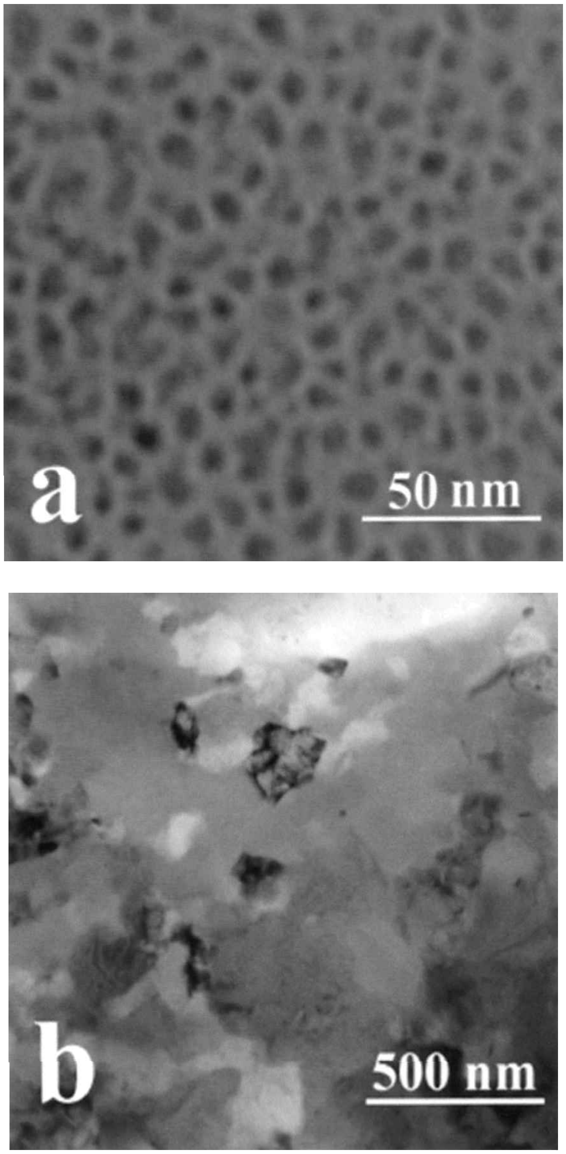

Fig. 1—Transmission electron micrographs of magnetron-sputtered Al-Cu-Fe-Cr films in the (*a*) as-deposited and (*b*) annealed films showing a large increase in the grain size as a result of the annealing.

A thermodynamically stable decagonal quasicrystal does exist in the Al-Cu-Fe-Cr alloy system, and is, in fact, the major phase in the annealed samples. The ED patterns in Figures 3(a) through (c) show the decagonal phase in the annealed Al-Cu-Fe-Cr film: Figure 3(a) shows the pseudo five axis, and Figures 3(b) and (c) show the twofold axes; the latter two are perpendicular to the tenfold axis and are referred to as the P and D patterns, respectively, in the literature. It should be mentioned that the unique axis of the decagonal quasicrystal appears to be parallel, or nearly so, to the coating surface, so the ED pattern of the tenfold axis is hard to find experimentally. According to the ED patterns in Figures 3(b) and (c), the periodicity of the decagonal quasicrystal phase along the tenfold axis is about 1.24 nm.

The structure of five crystalline approximants found in Al-Cu-Fe-Cr alloys may provide a hint to the structure of the Al-Cu-Fe-Cr decagonal phase. One of the approximants (referred as the O3 phase in Reference 6), with a composition of $Al_{61.3}Cu_{7.4}Fe_{11.1}Cr_{17.2}Si_3$,[8] is iso-structural to an Al_3Mn phase.[9,10] The structures of the other four Al-Cu-Fe-Cr approximants were interpreted in terms of structure motifs of the O3 phase.[6] The Al_3Mn phase, as an approximant of the Al-Mn decagonal phase, has been used to derive the structure of the Al-Mn decagonal phase.[11] We speculate that the Al-Cu-Fe-Cr decagonal phase is of the Al-Mn type.

C. *New Hexagonal Phase*

In addition to the decagonal quasicrystal phase, a hexagonal phase has also been observed in the annealed film. Figures 4(a) and (b) show ED patterns of the hexagonal phase: Figure 4(a) shows the sixfold [00.1] axis and Figure 4(b) shows the pseudo tenfold [11.0] axis. Lattice parameters determined from the ED patterns are $a = 2.48$ nm and $c = 1.24$ nm. A large number of hexagonal phases structurally related to the

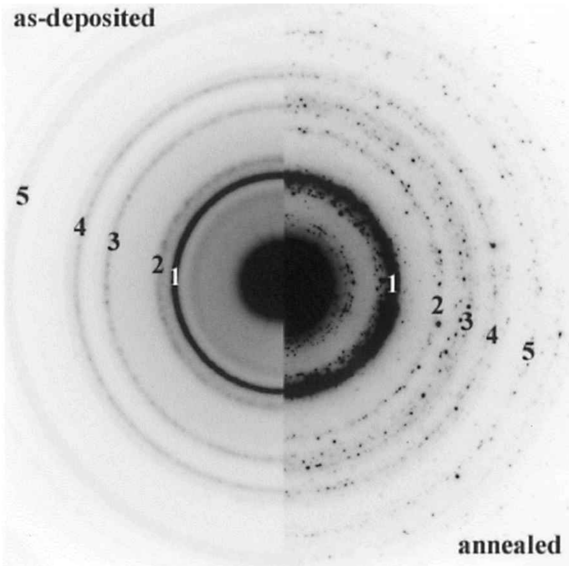

Fig. 2—Electron diffraction patterns of the magnetron-sputtered Al-Cu-Fe-Cr films in the as-deposited (left) and the annealed (right) conditions. Spacing changes in the two and five rings of the annealed film indicative of a phase transformation.

decagonal and/or icosahedral phases have been found in a variety of alloys, *e.g.*, μ-Al_4Mn,[12,13] μ-Al_4Cr,[14,15] β-AlMnSi,[16] Z-$Al_{59}Cu_5Li_{26}Mg_{10}$,[17] λ-Al_4Mn,[18,19] $Al_6Cr_{0.5}Ni_{0.5}$,[20] κ-AlCrNi,[21,22] ν-AlFeCr,[23,24] and Zn-Mg-RE.[25] Two of them, mentioned subsequently, are associated with the structure of the Al-Cu-Fe-Cr hexagonal phase.

A hexagonal metastable phase coexisting with a decagonal quasicrystal in a rapid-quenched $Al_6Cr_{0.5}Ni_{0.5}$ alloy was reported,[20] with lattice parameters of $a = 1.24$ nm and $c = 1.24$ nm. In some sixfold ED patterns of $Al_6Cr_{0.5}Ni_{0.5}$, weak diffraction spots were also observed at the midpositions of the original lattice, implying a doubling of the a parameter. Figure 5 shows the diffraction patterns for the Al-Cr-Ni hexagonal phase, which are similar to those of the decagonal phase. It is apparent that not only the lattice, but also the distribution of the diffraction intensities in the [00.1] and [11.0] patterns, are similar for the two hexagonal phases. These structural features indicate that the new hexagonal phase is a stable analog of the one in the $Al_6Cr_{0.5}Ni_{0.5}$ alloy. Thus, this is a crystalline approximant of the decagonal phase in the Al-Cu-Fe-Cr alloy system.

Pseudo fivefold ED patterns of the μ-Al_4Mn hexagonal phase were reported soon after the discovery of the Al-Mn icosahedral quasicrystal.[12] The structure of the μ-Al_4Mn phase was then determined by single-crystal X-ray diffraction.[13] One structural feature of the μ-Al_4Mn phase is that it does not contain a complete Mackay icosahedra (MI),* but there are areas where the atoms are arranged in part of an MI, with its center occupied by a Mn atom. The other feature of this phase is that it has a layer structure perpendicular to both the [00.1] and [10.0] axes. Detailed structural analysis[27] revealed a structural relationship between the μ-Al_4Mn phase, the Al_3Mn phase, and the Al-Mn decagonal quasicrystal. We speculate that the hexagonal phase in the Al-Cu-Fe-Cr alloy is structurally related to the μ-Al_4Mn one.

*Mackay icosahedra consists of the first two shells of the icosahedral shell packing, described by Mackay,[26] which is an important atom cluster for interpreting the structure of the Al-Mn icosahedral quasicrystal.

IV. SUMMARY

In summary, newly sputtered Al-Cu-Fe-Cr coatings have been examined by TEM. Particles in the as-deposited film are around 10 nm in diameter. During an annealing treatment, a phase transformation occurred along with a twentyfold to

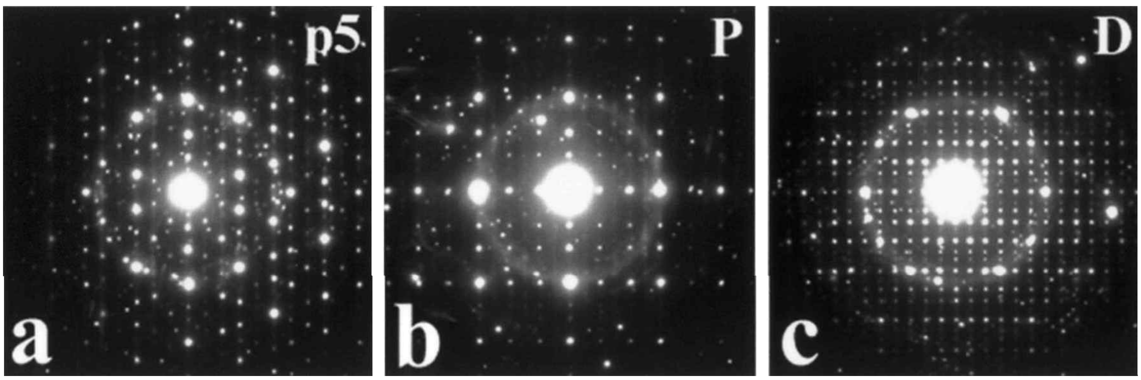

Fig. 3—Electron diffraction patterns of decagonal phase in the annealed coating: (*a*) pseudo five axis and (*b*) and (*c*) twofold axes; the latter two are perpendicular to the tenfold axis and are referred to as P and D patterns in the literature.

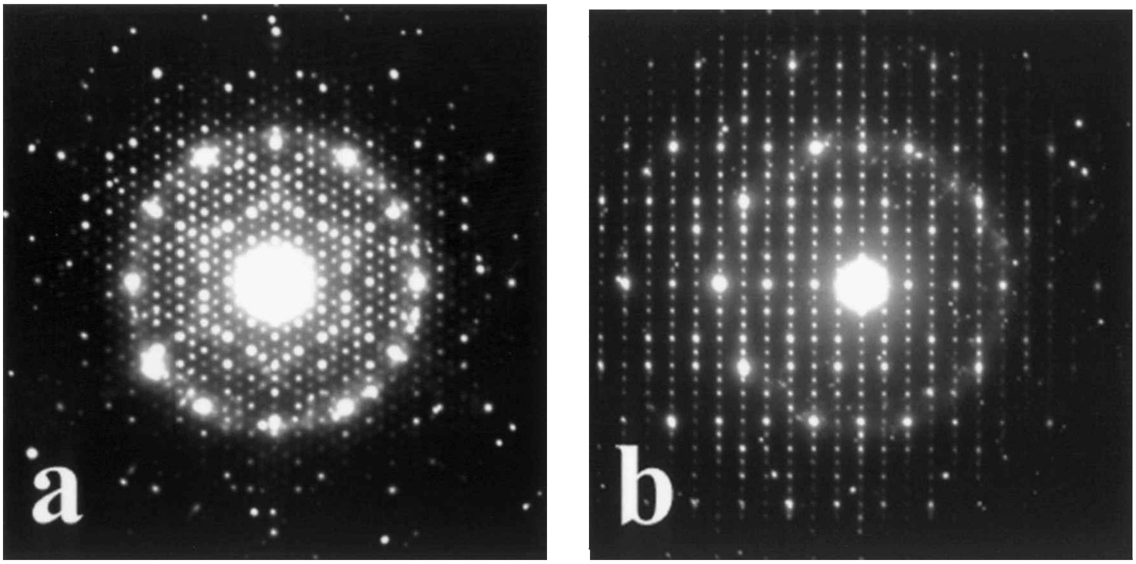

Fig. 4—Electron diffraction patterns of a hexagonal phase in the annealed coating: (*a*) sixfold [00.1] axis and (*b*) [11.0] axis with pseudo tenfold symmetry. This is a crystalline approximant of the decagonal phase in the Al-Cu-Fe-Cr system.

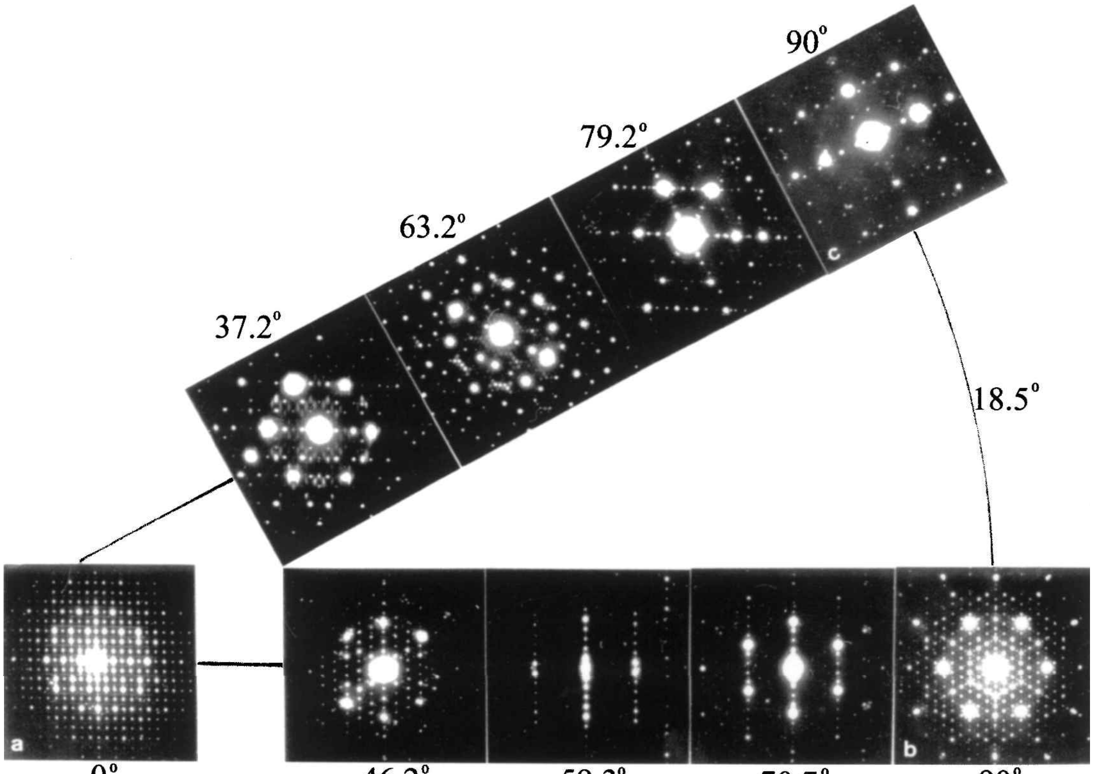

Fig. 5—Electron diffraction patterns of a metastable Al-Cr-Ni hexagonal phase, which is an isotypic structure with the hexagonal phase in the Al-Cu-Fe-Cr system. The patterns show similarity to the ED patterns of the decagonal phase, with respect to the strong diffraction spots.

thirtyfold increase in grain size. A thermodynamically stable decagonal quasicrystalline phase, with a periodicity of 1.24 nm along the unique axis and a hexagonal crystalline phase, with a = 2.48 nm and c = 1.24 nm, have been identified in the annealed coating film. The similarity of the ED patterns from the two phases indicates a orientational relationship between them: $[11.0]_{\text{Hexagonal}}$//tenfold axis and $[00.1]_{\text{Hexagonal}}$//twofold D axis.

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