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Quasicrystalline Thin Films, One Way to Follow in Quasicrystals

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ABSTRACT

Although the quasicrystal theory has allowed an enormous developing on the concepts of different fields of materials science and physics of the solid state, the quasicrystalline phases are lacking by now of a technical application. How can this problem be solved if most of the alloys which present these structures are, e. g., too fragil?. However, the quasicrystalline structures have been reported in thin films of some alloys, some times they are reported as presented during the amorphous-crystal transition and some others as presented in the as-obtained thin films. In this paper I present the cases of Al-Mn, Al-Cu-Co-Si and Bi-Mn thin films and discuss the possibility of find a technical application for these phases following the way the thin films indicate.

KEYWORDS

Quasicrystalline phases, Thin films, Electron microscopy

INTRODUCTION

Quasicrystalline phases are characterized by the occurrence of symmetry elements which are not allowed in the crystalline phases because they are inconsistent with their translational order. The discovery of the icosahedral phase, which is characterized by long-range icosahedral translational order (five-fold symmetry), by Shechtman et al. [1] in 1984, meant the beginning of several reports on quasicrystalline phases such as those whose structure presents either the eight-fold [2], twelve-fold [3] or ten-fold [4] symmetry. The phase whose structure presents the ten-fold symmetry is called "decagonal" and consists of a two-dimensional quasiperiodic array periodically stacked in the third axis, i.e. it is a bidimensional quasicrystalline array whereas the icosahedral phase represents the three-dimensional case. Comparatively speaking, the octagonal quasicrystalline phase (eight-fold symmetry) and the dodecagonal quasicrystalline phase (twelve-fold symmetry) have received less attention than the icosahedral and the decagonal phases, probably because of the scarce experimental data existing on them [5].

Although the basic question on where the atoms in these materials are remains unsolved, the quasicrystalline structures have represented a revolution in the crystallographical ideas, principally those which aim to describe the crystalline structure. Now is well accepted the five-fold symmetry as one of those ones which can describe the structure of some alloys. However, by now the most important problem the quasicrystalline phases are facing is their technical application. In this paper I present my idea on how this enigma could be solved.

The first method used to get the quasicrystalline phases was the rapid quenching using the melt spinning apparatus [1], whose velocity of solidification is of approximately 10^6 ^{0}K/sec.. However, now there are a considerable number of different methods, some of them use very slow solidification rates [6]. These methods open new roads in the study of these phases. The quasicrystalline phases have also been observed in thin films of aluminium-transition metal alloys [7,8]. Therefore, and this is the basis of the idea which I have mentioned

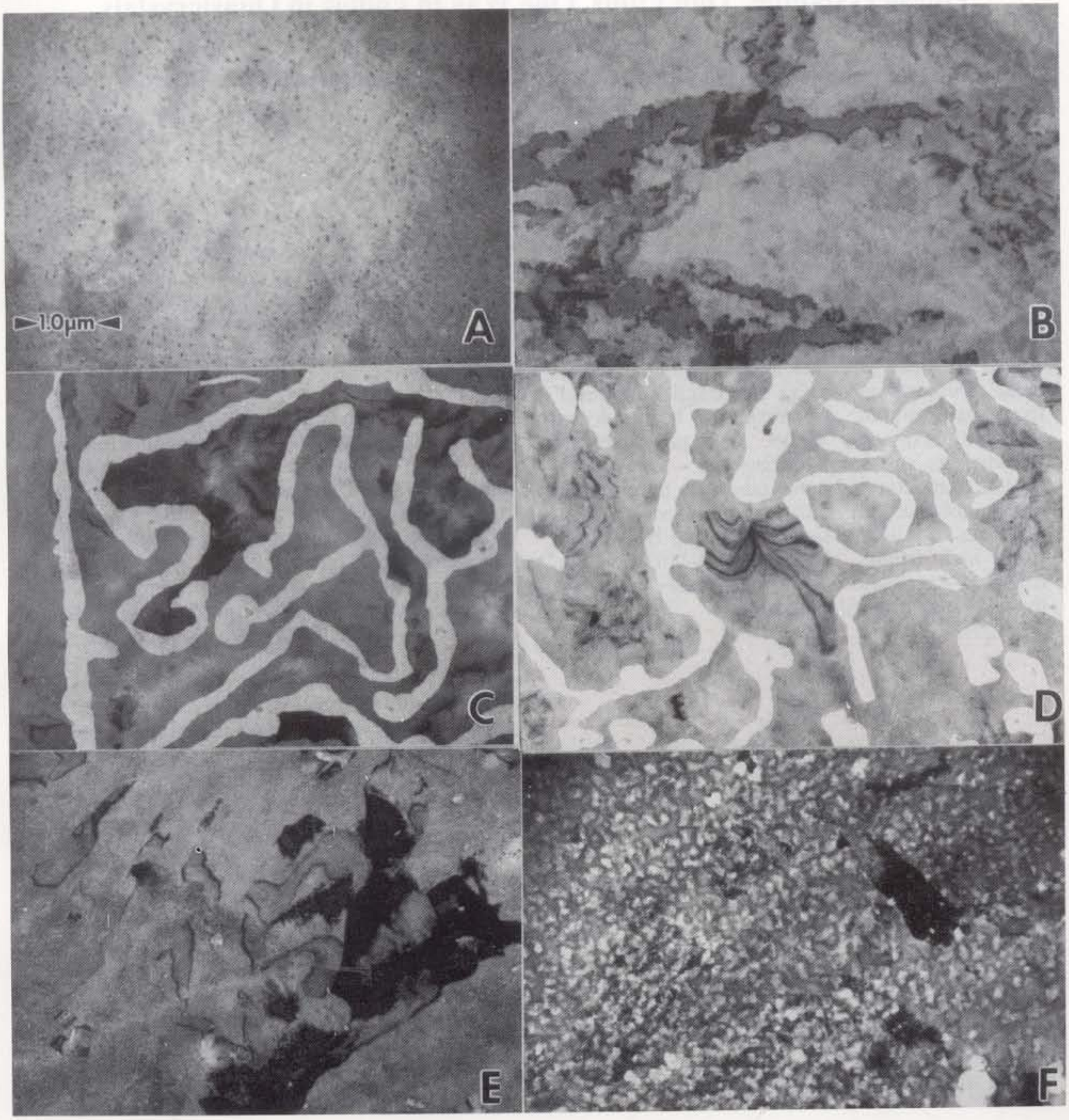

Figure 1. Sequence of the contrast changes observed when a Al-Mn thin film is heated in situ in the electron microscope. (A) at room temperature; (B) at 340 °C; (C) at 550 °C; (D) at 600 °C; (E) at 1660 °C; and (F) at 700 °C.

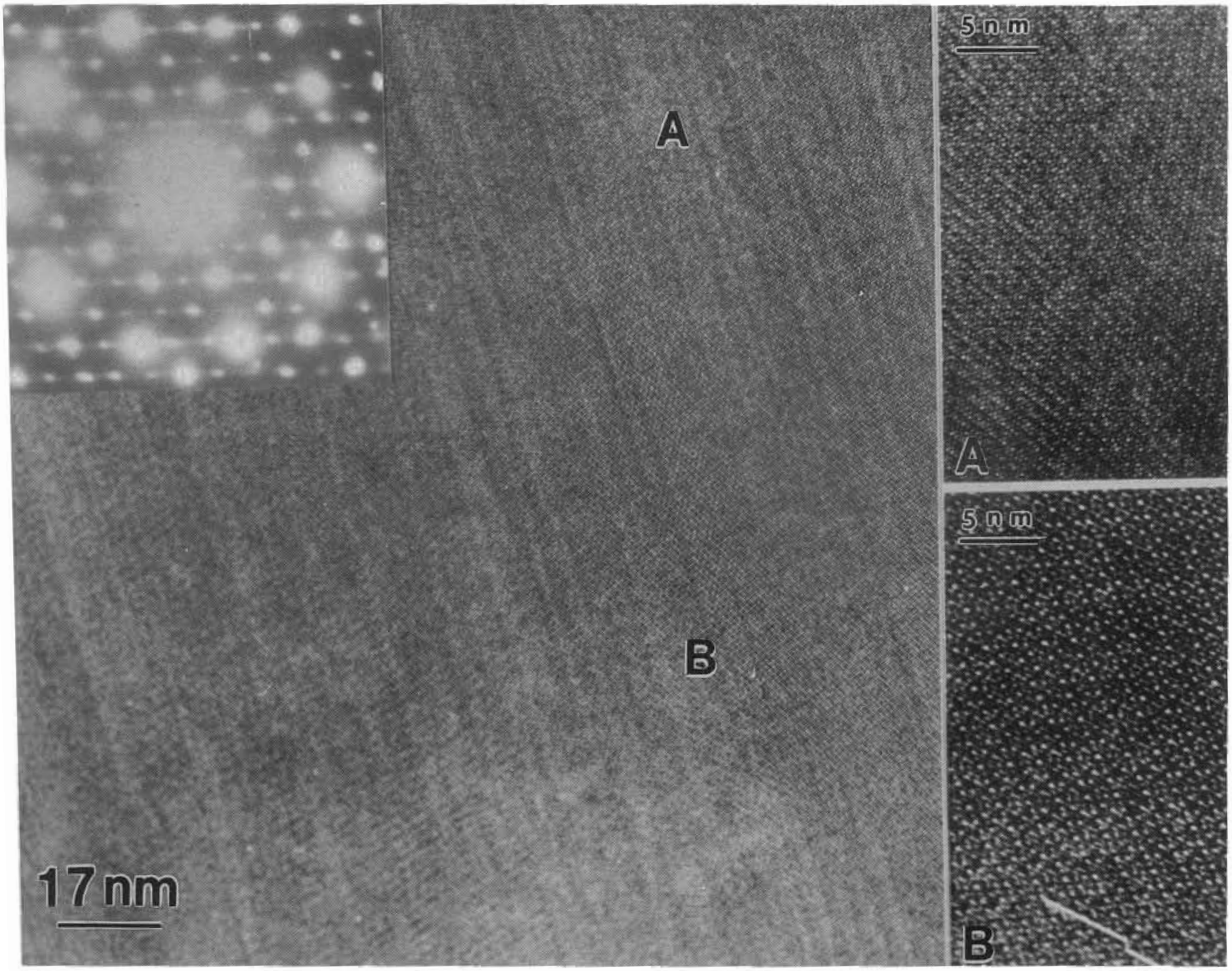

Figure 2. High resolution image of the decagonal quasicrystalline phase: (A) shows a higher magnification from zone A of the image which exhibits periodicity; (B) shows a higher magnification from zone B of the image which exhibits quasiperiodicity. The insert shows the selected area diffraction pattern of all the image; therefore, it is the result of the superposition of zones A and B.

before, the fact of having thin films with quasicrystalline structures opens the opportunities of finding some applications for these structures.

Up to now all the quasicrystalline structures observed in thin films coexist together with some metastable crystalline phases, some of them are the so-called rational approximant phases [5]. In this moment I am struggling with some experiments in order to get a homogeneous quasicrystalline structured thin film. In the present work I present my results which in this field I have reached.

EXPERIMENTAL PROCEDURE

Thin films which show quasicrystalline structure are relatively easy to produce. One method is to evaporate the alloy, which can either present or not quasicrystalline structures (but there is a sign of their existence), on an appropriate substrate and get the quasicrystalline structures by an after-deposition heating. Other method includes the evaporation of this alloy, or co-evaporation of their elements, on a cold substrate in order to get an amorphous structure. In this latter case the quasicrystalline structures are gotten during the amorphous-crystal transition phase by heating. This amorphous-crystal transition can be followed in-situ in the electron microscope [7,8]. For example, Csanady et al. [9] reported the formation of quasicrystalline phases in vapour-deposited films of transition metals; Lilienfeld et al. [10] have obtained these phases by conventional heat treatment of Al-Mn thin films; Knapp and Follstaedt [11] employed electron beam heating for producing them in Al-Mn and Al-Ru thin films; Urban et al. [12] reported the formation of quasicrystalline phases by thermal interdiffusion in thin films of Al-Mn; Kreinder et al. [13] reported the formation of these phases by sputter deposition of Al-Mn and Al-Mn-Si alloys; Barna et al. [14] have produced a multilayer films of Al-Mn and obtained the quasicristaline phases by interdiffusion of the Al and Mn layers during heating.

Commonly I use monocrystals of NaCl as substrate, therefore the thin films are easily separated by dissolving it in water. For the electron microscope observation and analysis, the thin films are supported on copper grids. The electron diffraction tilting experiments and chemical analysis are carry out using a JEOL 100CX analytical electron microscope which is equipped with a 60° goniometer and an energy-dispersive x-ray analyzer. For the in situ heating of the thin films a heating stage is used in this microscope. The high resolution observation is used a JEOL 4000EX electron microscope. Some of the images can be computer processed to enhance their contrast using an Innovion system on line with a 1178 VAX computer.

I have produced and observed thin films with quasicrystalline phases in different systems: Al-Mn [7,8], Al-Cu-Co-Si [15], and Bi-Mn [16]. Each of then have some particular experimental procedure but all include a thermal treatment. I am going to describe their experimental procedure in separate sections.

1. Al-Mn system

Al-Mn thin films with different compositions were produced by evaporation of powder of the $Al_{(1-x)}Mn_x$ alloys, x = 0.10, 0.14, 0.20, 0.25, 0.32. The NaCl substrates were held at either liquid N_2 or room temperatures in a 10^{-6} Torr vacuum. Thin films with thicknesses of 50 and 150 nm were studied. The goal in mind was to obtain thin films with an amorphous structure or with different crystalline grain size in order to study their influence on the evoluted phases during an in situ heating experiment in the electron microscope.

In general, images of the films were obtained at high temperatures. However, it was found that the structures formed at these temperatures remained quite stable on cooling the specimen, i. e., the processes occurring are not reversibles. Therefore, a double tilt stage was also used to characterize the developed structures and observed them by high resolution electron microscopy.

2. Al-Cu-Co-Si system

The $Al_{63}Cu_{20}Co_{15}Si_3$ alloy was produced as reported elsewhere [6]. Electron microscopy analysis has shown that the structure of this alloy is related with the decagonal quasicrystalline phase [17]. With powder of this alloy, thin films of 10 and 50 nm were produced by evaporation on NaCl substrates in a vacuum of 10^{-6} Torr and, afterwards, annealed at 400 and 900 °C for 1 h. The rise of the temperature was relatively rapid from room temperature to the required temperature (20 °C/min) and the temperature was kept constant there during the indicated period of time.

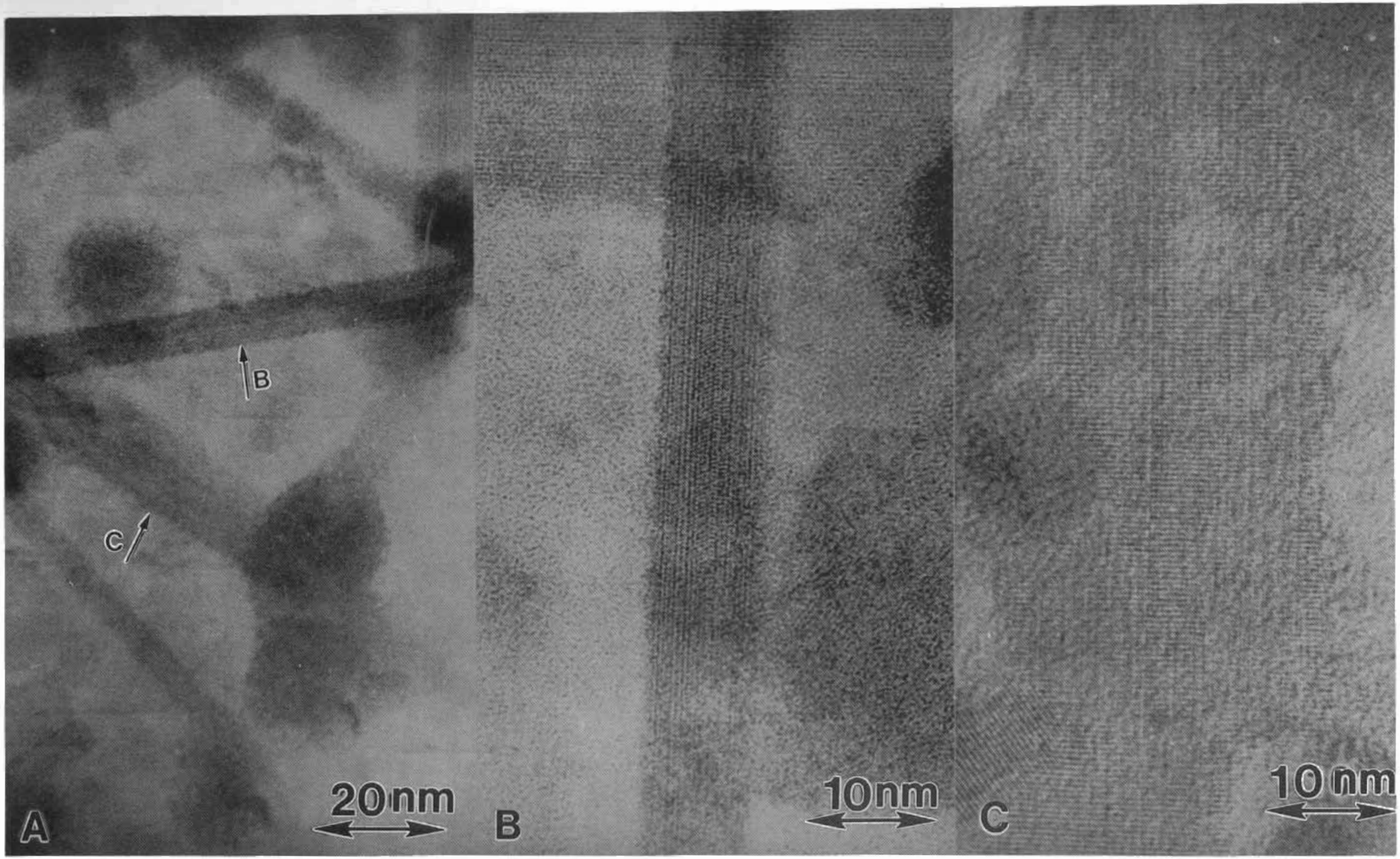

Figure 3. High resolution of the whiskers resulted when the as-obtained amorphous Al-Cu-Co-Si thin films are heated at 900 °C during 1h. The arrows in (A) indicate the whiskers shown in (B) and (C).

3. Mn-Bi system

These films were produced using a method of successive evaporation reported by Yoshida and Yamada [18]. A composite double-layer film was prepared by successive evaporation of one bismuth film first, with a thickness of 30 nm, followed by one manganese film, with a thickness of 20 nm. These evaporations were carried out on both NaCl and glass substrates in a vacuum of 10^{-6} Torr. Afterwards the substrate temperature was raised up to 270 °C and maintained there for long period of time.

RESULTS

All the obtained thin films, regardless of their thickness and before any annealing, exhibit an amorphous contrast. After annealing, the structure of the films change considerably, always it was found that the developed structure depends on the thickness of the film. When amorphous films with thickness of 50 nm or less are heating, only small particles are observed. This is, exist a critical thickness after which other structures different than particles are developed. All the results presented here were observed in films whose thickness were bigger than 50 nm.

1. Al-Mn system

When the amorphous thin films are heated in situ in the electron microscope several phenomena typical of a crystallization process are observed. Generally the process starts from a less-stable intermediate phase until the final equilibrium phase is reached. In this case some of the phases observed were Al_6Mn, Al_3Mn, Al_4Mn and the decagonal quasicrystalline phase. One set of the contrast changes observed during the evolution of this experiment is shown in Figure 1 and some observed phases and their temperature of appearance is shown in table 1. The decagonal quasicrystalline phase (Fig. 2) was always obtained at high temperatures, approximately 700 °C, after some phases such as Al_6Mn and Al_4Mn.

TABLE 1. Some of the phases observed in thin films of the Al-Mn system during a heating treatment

Temperature (° C)	Phases
370	Al_6Mn
550	Al_3Mn
650	Al_4Mn
700	Quasicrystalline phases
800	AlMn and diffuse scattering

2. Al-Cu-Co-Si system

When the obtained amorphous thin films are annealed at 900 °C for 1h, whiskers are observed (Fig. 3). The structure of these whiskers is the same as that of the decagonal phase, as both conventional an high resolution microscopy analyses showed. In Figure 4 the microdiffraction pattern from one whisker (Fig. 4a) together with the selected area diffraction pattern of the decagonal phase observed in the $Al_{62}Cu_{20}Co_{15}Si_3$ (Fig. 4b) are shown for comparison. Therefore, all the characteristics observed in the latter pattern, principally its proportionality with the irrational number τ, are observed in the former, except for the weak lines which represent a periodicity of 0.8 nm along the ten-fold axis. The relationship with the irrational number $\tau = (1+5^{1/2})/2$ is the most important characteristic of the decagonal and icosahedral quasicrystalline phases: the ratio of distances among the bright spots which form the aperiodicity in the diffraction pattern of these quasicrystalline phases is proportional to it.

3. Mn-Bi system

The dodecagonal quasicrystalline phase

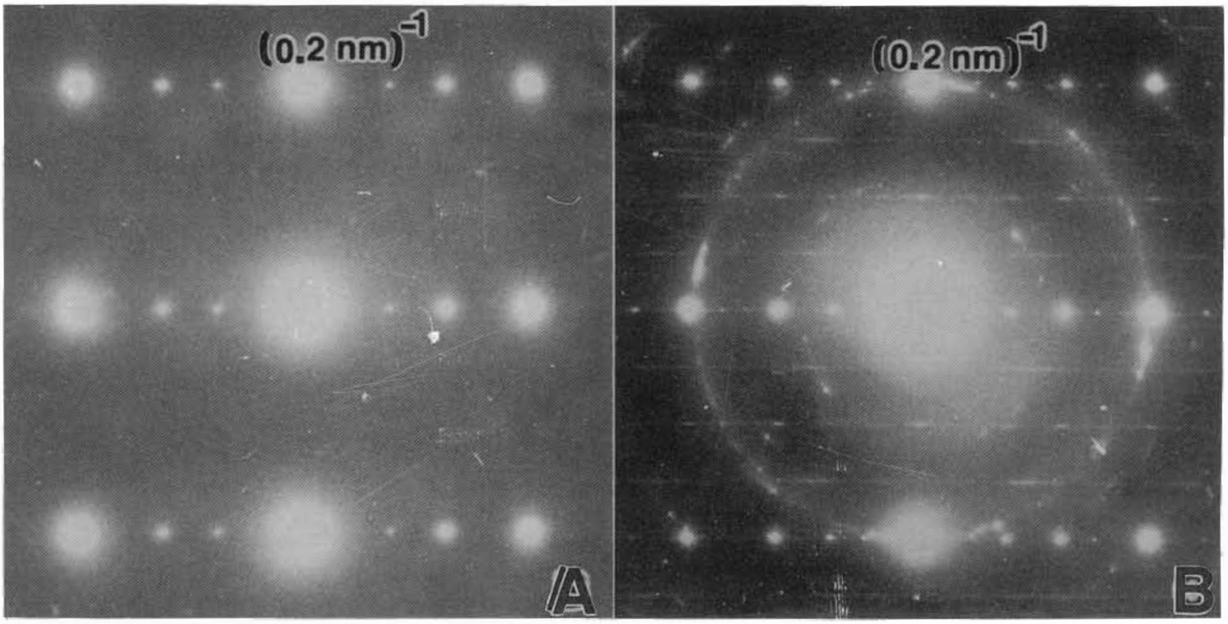

Figure 4. (A) Microdiffraction pattern from one of the whiskers shown in fig. 3. (B) Selected area diffraction pattern along one two-fold axis of the decagonal phase obtained in the $Al_{62}Cu_{20}Co_{15}Si_3$ alloy.

was observed after heating at 270 °C the thin films deposited on glass for 100 h... This is confirmed by the diffraction pattern shown in Figure 5 and its high resolution image shown in Figure 6. The high resolution (Fig. 6) shows several twelve-dot motifs which follow a pattern which can be associated with those ones found in some theoretical work on dodecagonal quasicrystalline lattices [19] (Fig. 7). The x-ray chemical analysis showed that its composition is approximately $BiMn_3$. The evolution from this quasicrystalline phase to its respective crystalline phase have been also analyzed.

DISCUSSION

As the results have shown, it is relatively easy to produce thin films with quasicrystalline structures using the method consisting on the heating of amorphous thin films of some alloys. The structural changes produced during this method represent a way to study the quasicrystalline and crystalline phases and their transitions, and also several material science topics, e. g. nucleation, growth, defects and grain boundaries. However the analysis of the optical, mechanical, and other properties of these films is by now not trivial because in most cases there are other structures coexisting with the quasicrytalline phases (Fig. 2). Some of these phases are the so-called rational approximant phases. It has been mentioned in the introduction of this paper that the situation of the quasicrystals is by now the searching of a technical application of these materials. I consider that the quasicrystalline thin films can play a very important role in this field because if we are able to produced them completely homogeneous, the next step, their characterization will be easily done. This is, after quasicrystalline thin films with the results which their optical, thermal, mechanical, and electrical analyses can be obtained and the searching of their application will be easier. The most important step in this objective is the obtention of a highly homogenous quasicrystalline thin film. Therefore, it is necessary to produce the quasicrystalline thin films having in mind this requirement. Among the thin films with quasicrystalline structure in this work presented, those observed in the Al-Mn system are the most probable to help in this goal. The quasicrystalline structure fill all the thin film plane, although together with others phases therefore is this system which will be studied the most in the search of the homogeneous quasicrystalline thin film and the technical application of the quasicrystals.

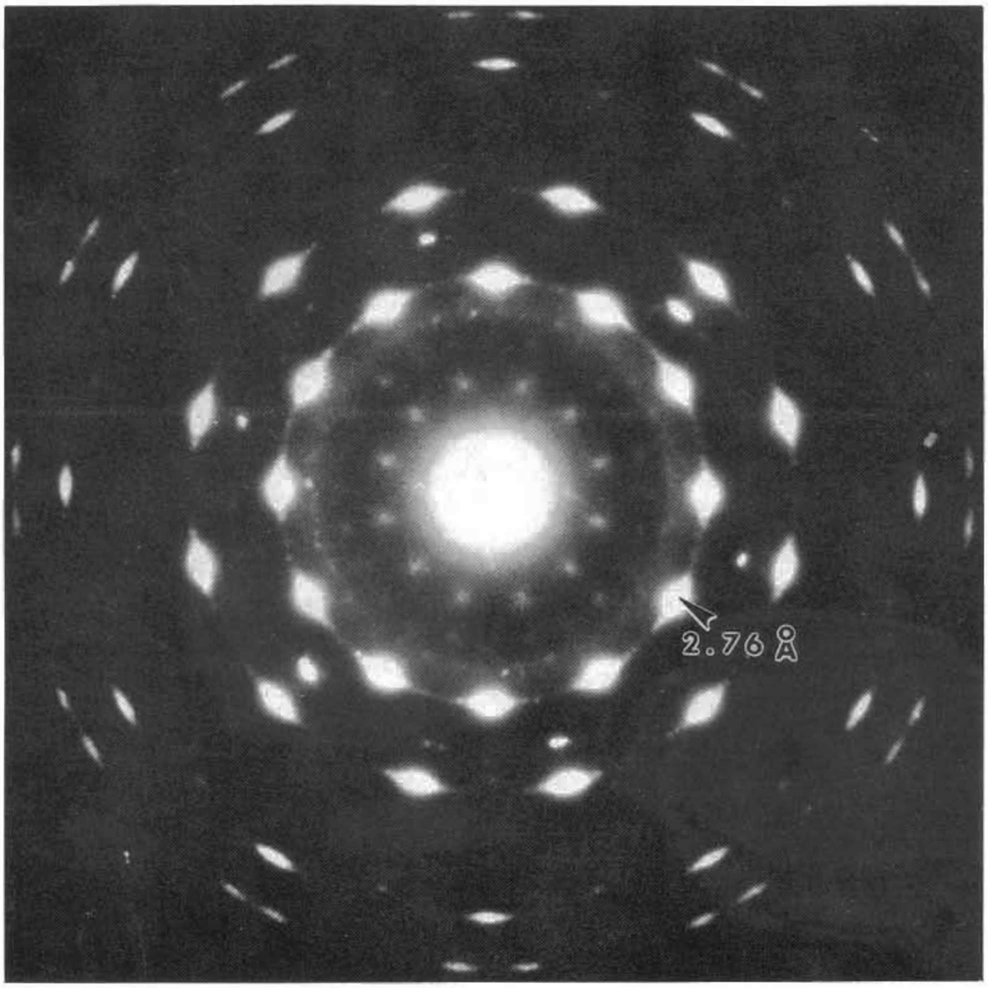

Figure 5. Selected area electron diffraction pattern from the Bi-Mn thin film evaporated on glass and heated at 270 °C for 100 h.

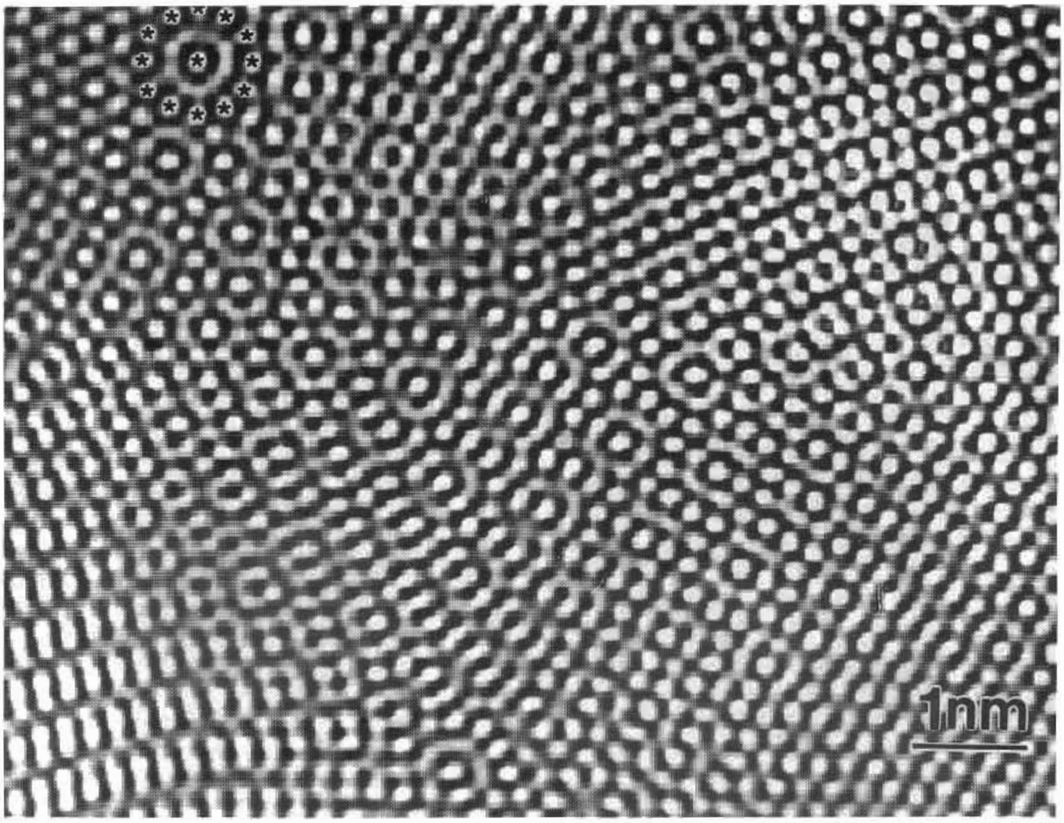

Figure 6. High resolution image of the dodecagonal phase observed in the Bi-Mn thin films. This image has been computer processed to enhance its contrast.

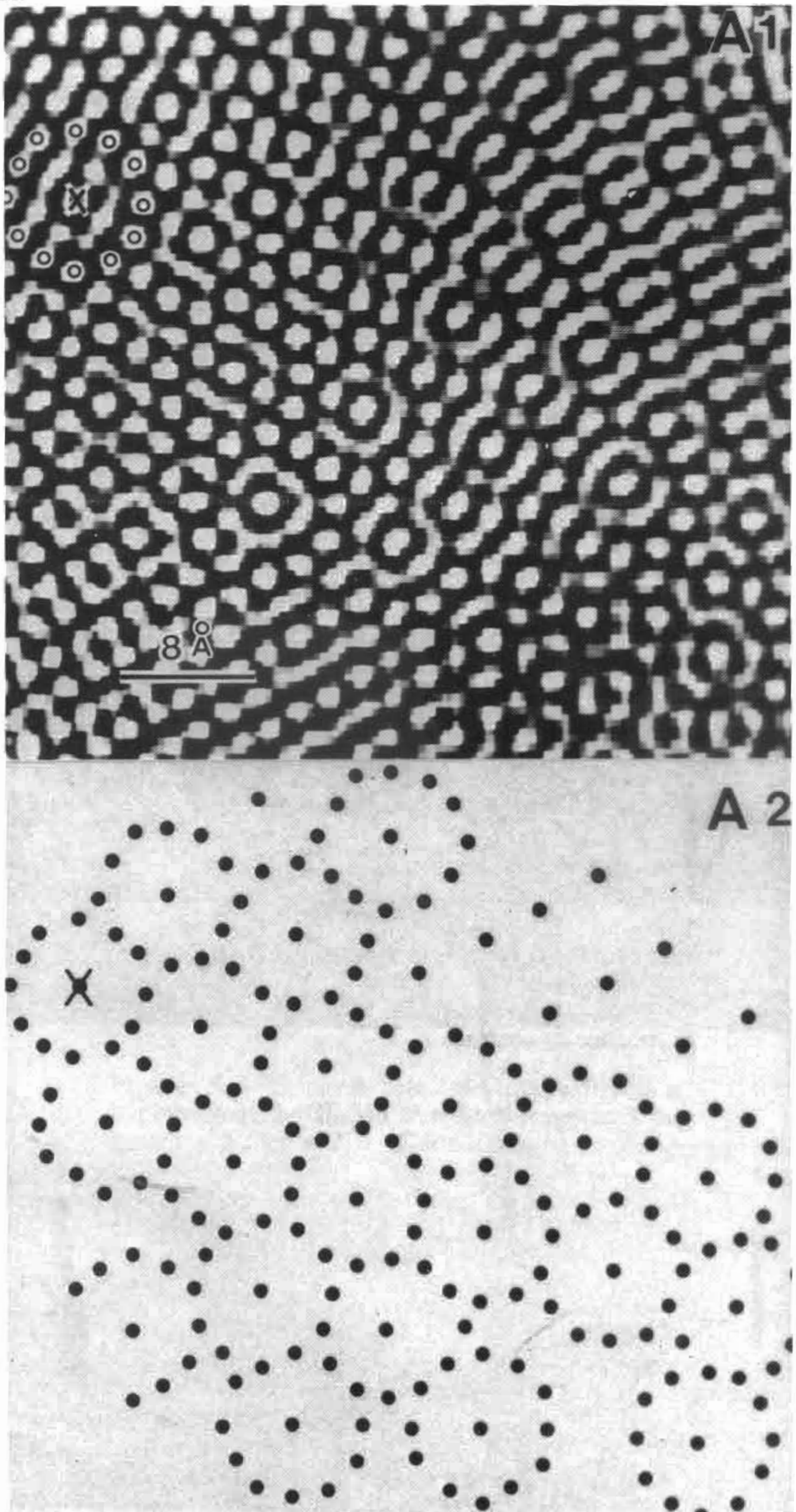

Figure 7. High resolution images where can be observed several twelve-fold motifs which follow a pattern very similar to those ones found theoretically [19]. In the bottom is shown a schematic representation of the twelve-fold motifs. The cross indicates the same motif both in the image and the representation.

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RESUMEN

La teoria de los cuasicristales ha permitido desarrollar los conceptos de la cristalografia y diferentes campos de la ciencia de los materiales y de la fisica del estado sólido. Sin embargo, hasta el momento no se ha encontrado una aplicación técnica de los materiales cuasicristalinos necesaria para consolidarlos como un gran descubrimiento de este siglo. ¿Cuál puede ser el camino a seguir para encontrar una aplicación de estos materiales?. Hay que tener muy presente que hasta el momento las aleaciones que presentan estos materiales son muy frágiles. Tomando en caso de que últimamente películas delgadas que presentan estructuras cuasicristalinas se pueden producir con relativa facilidad, en este artículo quiero presentar la alta posibilidad de encontrar una aplicación tecnológica de estos materiales suiguiendo el camino de la tecnología de las peliculas delgadas. Comentaré como ejemplo los casos de las películas delgadas de los sistemas Al-Mn, Al-Cu-Co-Si y Bi-Mn.

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