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**Atomic-scale electron microscopy and spectroscopy of AlMnPd quasicrystal**

E. Abe,<sup>a</sup> T. Seki,<sup>a</sup> H. Sawada,<sup>b</sup> E. Okunishi,<sup>b</sup> Y. Kondo,<sup>b</sup> K. Takayanagi,<sup>c</sup>  
<sup>a</sup>Dept. of Materials Science & Engineering, University of Tokyo.  
<sup>b</sup>JEOL Ltd. <sup>c</sup>Dept. of Condensed Matter Physics, Tokyo Institute of Technology. E-mail: abe@material.t.u-tokyo.ac.jp

Quasicrystals are aperiodically long-range ordered solids that exhibit rotational symmetries incompatible with conventional periodic lattice order. Their structure is often described according to a hyperspace crystallography, which interprets the quasicrystal as a periodic structure embedded in a hyperspace. This mathematical recipe enables to calculate the diffraction intensity of any quasicrystal model structures, and accordingly the quasicrystal structures can be determined by the x-ray diffraction analysis along the similar manner for periodic crystals.

Al-Mn-Pd alloys form a thermodynamically stable decagonal quasicrystal, a planar realization of the quasiperiodic order. Its structure had been intensively studied by single-quasicrystal X-ray diffraction [1], [2] and high-resolution phase-contrast electron microscopy [3], [4], which led to the established model structure that reasonably satisfies the both observations. In the present work, we have revisited the decagonal Al-Mn-Pd by aberration-corrected ultrahigh-resolution scanning transmission electron microscopy (STEM), and immediately find that the observed Z-contrast is significantly different from that expected from the existing model structures. The observed contrast cannot be reproduced by the simulation based on the model structure proposed by x-ray analysis [2], forcing to modify the local chemical order of Al/Mn/Pd. During the course of study, we particularly emphasize an effective use of electron energy-loss spectroscopy (EELS) at atomic-scale, which has been successful for identifying the Mn and Pd sites that are hardly distinguished based on the Z-contrast intensity alone. The present results strongly demonstrate that the direct observation of real-space atomic configurations is indispensable to determine the quasicrystal structure conclusively [5].

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**Effect of Ti addition on the hydrogen storage properties of nanoquasicrystal-glass composites in  $(Zr_{69.5}Al_{7.5}Cu_{12}Ni_{11})_{100-x}Ti_x$  alloys**

R.S.Tiwari, Devinder Singh, Rohit R Shahi, O.N.Srivastava *Hydrogen Energy Centre and Unit of Nano Science and Technology, Department of Physics, Banaras Hindu University, Varanasi, Uttar Pradesh-221005, (India)*. Email: rstiwari@yahoo.com

The high number of potential interstitial sites for hydrogen and the favourable hydrogen-metal chemistry make Zr-Al-Cu-Ni quasicrystalline alloys a promising material for the hydrogen storage applications [1]. The alloy  $Zr_{69.5}Al_{7.5}Cu_{12}Ni_{11}$  is of special interest for studying the influence of hydrogenation on the microstructure of these quasicrystalline alloys [2]. We have investigated the effect of Ti addition on the quasicrystalline phase formation and indentation

characteristics of  $Zr_{69.5}Al_{7.5}Cu_{12}Ni_{11}$  alloy [3]. The addition of Ti changes the morphology of quasicrystals. It is therefore imperative that a systematic examination of hydrogen storage properties in a given system is carried out.

In the present study, the hydrogen storage properties of  $(Zr_{69.5}Al_{7.5}Cu_{12}Ni_{11})_{100-x}Ti_x$  ( $x=0, 4$  and  $12$ ) nanoquasicrystal-glass composites have been investigated. The investigation will be focussed on the phase formation and microstructural changes with addition of Ti and their correlation with hydrogen storage properties of Zr-Al-Cu-Ni alloys. It has been found that the hydrogen uptake capacity and the absorption kinetics of the composites increase with addition of Ti. The hydrogen storage capacity is found to be 1.20 wt. %, 1.38 wt. % and 1.56 wt. % for the alloys with  $x=0, 4$  and  $12$  respectively. The increase in the hydrogen uptake capacity may be attributed to the grain refinement of quasicrystals resulting due to Ti addition. The hydrogen decomposition behavior of  $(Zr_{69.5}Al_{7.5}Cu_{12}Ni_{11})_{100-x}Ti_x$  ( $x=0, 4$  and  $12$ ) nanoquasicrystal-glass composites has been investigated by using temperature programmed desorption (TPD) experiment. The TPD experiments indicate that the addition of Ti reduces the maximum desorption temperature of hydrogenated ribbons.

The microstructural changes during hydrogenation have also been investigated. The structural characterization of the hydrogenated ribbons reveals an expansion of the quasilattice with hydrogenation. After hydrogenation, a broad hump along with weaker peaks in the X-ray diffraction pattern has been observed. Transmission Electron Microscopy (TEM) investigations exhibited microstructural changes during hydrogenation. It has been observed that microstructural and morphological changes alter the hydrogen storage properties of nanoquasicrystal-glass composites.

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**Ion beam analyses of Al(Si)-Cu-Fe approximant thin films**

Simon Olsson, Jens Jensen, Fredrik Eriksson and Lars Hultman<sup>a</sup>  
<sup>a</sup>Thin Film Physics Division, IFM, Linköping University, SE-581 83 Linköping, (Sweden). E-mail: simol@ifm.liu.se

Quasicrystalline materials exhibit properties that are very different from conventional metallic materials. They are metallic alloys, and show high hardness and stiffness but low electrical and thermal conductivity. The coefficient of friction and surface energy of the quasicrystalline materials are also very low [1]. Both structure and physical properties of a higher order approximant crystal are similar to those of a quasicrystal.

In this work, multilayered Al-Cu-Fe thin films have been deposited by triple-target unbalanced high vacuum magnetron sputtering onto Si substrates. The multilayer periods are ranging from  $\Lambda=2$  nm to  $\Lambda=400$  nm, with nominal layer thicknesses ratios of 7:2:1 to maintain a global chemical composition corresponding to the icosahedral quasicrystalline phase. The number of periods was varied from  $N=1$  to  $N=50$  with total film thicknesses up to 400 nm.

Isothermal annealing was performed on all samples for temperatures up to 800 °C using an in situ high-temperature X-ray diffraction (XRD) furnace. The composition of the multilayer sequences before and after annealing was investigated using time-of-flight elastic recoil detection analysis (ToF-ERDA) and Rutherford backscattering

spectrometry (RBS). In addition, supplementary compositional analysis was performed by energy dispersive X-ray (EDX) analysis, X-ray photoelectron spectroscopy (XPS) in combination with sputter depth profiling, and secondary ion mass spectrometry (ToF-SIMS) in dynamic mode.

It was found that the as-deposited Al/Cu/Fe layers on Si clearly has a multilayered structure. After annealing the individual layers diffused together creating a homogeneous film with an ~50 nm thick Al<sub>2</sub>O<sub>3</sub> surface oxide. Si started to diffuse into the film below 390 °C, during a substrate-film reaction. This caused a change in film composition preventing the quasicrystalline phase region to be reached, and instead the approximant Al<sub>55</sub>Si<sub>7</sub>Cu<sub>25.5</sub>Fe<sub>12.5</sub> together with other crystalline phases was formed in the temperature range 400 to 670 °C. The single approximant phase was obtained at 600 °C.

After 4 h annealing at 600 °C the film contained ~9 at% Si, corresponding well to the expected value of the approximant phase [2]. Even though the amount of Si in the films is found to slowly increase to ~13 at% during extended annealing (>100 h) the approximant phase was retained.

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### Structural transformation in Al-Fe-Cu-Mn one dimensional quasicrystals

T. P. Yadav,<sup>a</sup> N.K. Mukhopadhyay<sup>b</sup> and O. N. Srivastava<sup>a</sup>  
<sup>a</sup>Department of Physics, Banaras Hindu University, Varanasi-221 005 (India). <sup>b</sup>Department of Metallurgical Engineering, Institute of Technology, Banaras Hindu University, Varanasi-221 005, (India).  
 E-mail:yadavtp@gmail.com

The main objective of the proposed work would be to investigate into the transformation mechanism in one dimensional quasicrystal. The one dimensional quasicrystalline phases in Al<sub>70</sub>Cu<sub>20</sub>Fe<sub>2</sub>Mn<sub>8</sub> alloy have been synthesized by melting the individual elements using radio frequency induction furnace (18 kW) under continuous flow of argon gas into the silica tube. During melting process, water is circulated in the outer jacket around the silica tube to reduce the contamination of the alloy. The transformation behaviors of one dimensional quasicrystalline have been investigated during annealing (up to 900 °C) and mechanical milling (up to 100 hours). The transformation of one dimensional quasicrystalline phase to icosahedral as well as various disordered states have been observed in Al-Fe-Cu-Mn alloys during milling. The milling of pre-alloyed material was carried out a high-energy ball mill by varying milling time up to 100 h under liquid hexane medium and at various milling intensity. X-ray diffraction and transmission electron microscope were carried out for evaluating the lattice strain, lattice parameters and crystallite sizes of the mechanically milled samples. The evolution of nano icosahedral phases as well as crystalline phases was found to occur. The subsequent thermal treatment led to the structural ordering in the concerned phases. The implication of the evolution of various phases, their structural correlations and their relative stability will be discussed.

**Keywords:** quasicrystal, phase transformation, mechanical milling

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### Structural characterization of highly defective Al-Pd-Fe crystalline approximant

W. Sun, J. P. Wang, Z. Y. Liu, *Institute of Microstructure and Property of Advanced Materials, Beijing University of Technology 100 Pingle Yuan, Chao Yang District, Beijing 100124, (China)*. E-mail: weisun@bjut.edu.cn

Crystalline approximants, which are structurally related to their corresponding quasicrystals, belong to a class of structurally complex alloy phase. A crystalline approximant can have a quite large unit cell consisting of hundreds or even thousands of atoms. Due to its structural complexity, the structural defects in the crystalline approximant can be quite different in comparison with those in an ordinary crystalline phase with a small unit cell [1]. In general, a crystalline approximant contains the characteristic atom clusters which are of the same type as those in its corresponding quasicrystal. Therefore, in order to understand the intrinsic structure of the crystalline approximant and special structural defects in it, the characteristic arrangement of atom clusters has to be taken into account rather than a usual structural description in terms of unit cell. Existence of various special structural defects associated with wrong arrangements of atom clusters in hexagonal tiling structures of the  $\xi$ - and  $\xi'$ -phases in Al-Pd-Mn [2] and Al-Ni-Rh [3] systems has been reported. In the Al-Pd-Fe system, the crystalline approximant, corresponding to an Al-Pd-Fe decagonal quasicrystal with 1.6 nm periodicity, can have a kind of pentagonal tiling structure of atom clusters, which is more complex than the tiling structures of the  $\xi$ - and  $\xi'$ -phases. It is still an open question about whether any new defect can exist in the non-hexagonal tiling structure of atom clusters. In this study, a highly defective Al-Pd-Fe crystalline approximant which can accommodate new type of special structural defect (H-type) has been found in the as-cast and heat-treated Al<sub>75</sub>Pd<sub>15</sub>Fe<sub>10</sub> alloys. By means of high resolution electron microscopy (HREM), the highly complex defective structure in the Al-Pd-Fe crystalline approximant has been characterized.

Electron diffraction examinations show that the principal diffraction patterns of the Al-Pd-Fe crystalline approximant (E-phase) can be indexed as a  $\epsilon_{16}$ -phase. However the actual structure of the E-phase is far from an ideal  $\epsilon_{16}$ -structure, because of the extensive existence of wrong arrangement and series absence of atom clusters. The significant deterioration of long-range crystallinity for the as-cast E-phase can be attributed to the coexistence of microtwins and underdeveloped H-defects without regular shape. Strap-shaped H-defects have been observed in the Al<sub>75</sub>Pd<sub>15</sub>Fe<sub>10</sub> alloys subjected to high-temperature heat treatments (>900°C). HREM observations and imaging simulations reveal that those atom clusters observed in the H-defect area are of the same type as the atom clusters in the E-phase structure. The arrangement of atom clusters in the strap of H-defect is characterized by a  $\xi$ -phase-like hexagonal tiling whose edge length is  $\tau$  time larger than that of the hexagonal tiling of an Al-Pd-Fe  $\xi$ -phase. The formation of strap-shaped H-defects in the highly defective E-phase is associated with the rearrangement of atom clusters during high-temperature heat treatment. For the ill-formed atom clusters identified to exist in the E-phase, the possible atomic structural model has been proposed and discussed.

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