

# SYMPOSIUM LL

## LL: Quasicrystals

November 30 - December 3, 2003

### Chairs

**Esther Belin-Ferre**

LCPMR  
11 Pierre et Marie Curie  
Paris, Cedex 05, 75231 FRANCE  
33-1-4427-6620

**Michael Feuerbacher**

Forschungszentrum Juelich GmbH  
Institut fuer Mikrostrukturforschung  
Juelich, D-52425 GERMANY  
49-2461-612409

**Yasushi Ishii**

Chuo University  
Kasuga, Bunkyo-ku  
Tokyo, 112-8551 JAPAN  
81-3-3817-1780

**Dan Sordelet**

Ames Laboratory  
Iowa State University  
Ames, IA 50011  
515-294-4713

---

### Symposium Support

Saint-Gobain Ceramics & Plastics, Inc.  
Saint-Gobain Coating Solutions

Proceedings to be published in both book form and online  
(see *ONLINE PUBLICATIONS* at [www. mrs.org](http://www.mrs.org))  
as Volume 805  
of the Materials Research Society  
Proceedings Series

\* Invited paper

## TUTORIAL

**FT LL: Quasicrystals-Relationships Between Surface and Bulk Phenomena**  
Sunday, November 30, 2003  
1:00 PM - 5:00 PM  
Room 201 (Hynes)

The tutorial will cover recent advances in the basic surface science of quasicrystals and the way that this new knowledge relates to our understanding of the bulk materials. Specific topics are: a) atomic and electronic structure; b) role and nature of vacancies; c) role of clusters; and d) orientational relationships at interfaces. The tutorial will begin with an introductory talk on the general tools and principles of surface science as they relate to the work that has been done in the field of quasicrystals, e.g., gas flux and exposure; the value of using complementary techniques; the definition of a surface vs. the bulk; quantitative analysis; and typical information depths for electrons vs. photons.

### Instructors:

**Patricia A. Thiel**, Iowa State University  
**Ronan McGrath**, The University of Liverpool

SESSION LL1: Synthesis and Structure I  
Chairs: D. H. Kim and A. P. Tsai  
Monday Morning, December 1, 2003  
Fairfax A (Sheraton)

### 8:30 AM \*LL1.1

#### Search and synthesis of new family of quasicrystals.

Tsutomu Ishimasa, Graduate School of Engineering, Hokkaido Univ., Sapporo, Hokkaido, Japan.

Approximant crystals may be very important and useful to find new quasicrystal alloys. In the framework of the projection method, an approximant crystal can be understood as relational approximation of the corresponding quasicrystal. In the case of an icosahedral quasicrystal, an approximant includes a local atomic configuration or atomic cluster satisfying approximately the icosahedral symmetry. Bergman- and Mackay-type clusters are famous examples of atomic clusters. Recently, stimulated by the discovery of binary stable quasicrystals in Cd-Yb and Cd-Ca [1], a new type atomic cluster has been recognized, which we call here "Tsai-type" cluster. Common characteristics of this cluster is triple shells: in the case of cubic Zn17Sc3 approximant, for example, the cluster consists of the innermost dodecahedral shell of 20 Zn, the icosahedral shell of 12 Sc and the outermost icosidodecahedral shell of 30 Zn [2]. Tsai-type cluster can be found in variety of alloys, namely Be-, Cu-, Zn-, Ga-, Cd- and In-based alloys. Accordingly, there is a lot of possibility to find new quasicrystals with different base metals. In the present work, the Zn17Sc3 crystal was selected as a starting approximant. By replacing 5 at.% Zn with Mg, a P-type icosahedral quasicrystal was found at the alloy composition of Zn80Mg5Sc15 [3]. This quasicrystal is thermodynamically stable and has very high structural quality. Millimeter-sized single grains of the quasicrystal are formed by slow cooling from the melt. Furthermore, it is possible to replace Zn with Cu and Ga, which are two neighbors of Zn in the periodic table. The Cu48Ga34Mg3Sc15 quasicrystal is also thermodynamically stable. Substituting Ti for Sc, Zn84Mg9Ti7 quasicrystal was obtained. It is also possible to replace Sc with Yb. In this case Zn74Mg12Yb14 quasicrystal is formed. The latter two quasicrystals are considered to be metastable. These new quasicrystals have almost the same average valence electron concentration,  $e/a$ , ranging from 2.00 to 2.16. This fact indicates important role of Hume-Rothery mechanism for the stabilization of these quasicrystal structures. [1] A.P. Tsai, J.Q. Guo, E. Abe, H. Takakura and T.J. Sato, Nature 408 (2000) 537. [2] R. I. Andrusyak, B. YA. Kotur and V. E. Zavodnik, Kristallografiya 34 (1989) 996. [3] Y. Kaneko, Y. Arichika and T. Ishimasa, Phil. Mag. Lett. 81 (2001) 777.

### 9:00 AM LL1.2

**Structural Evolution of Cold Rolled Multi-layers in the Al-Cu-Fe Ternary System.** J. S. Park<sup>1</sup>, Eric Fleury<sup>1</sup>, J. H. Kim<sup>1</sup>, H. J. Chang<sup>1</sup>, W. T. Kim<sup>2</sup> and D. H. Kim<sup>1</sup>; <sup>1</sup>Department of Metallurgical Engineering, Center for Noncrystalline Materials, Seoul, South Korea; <sup>2</sup>Division of Applied Science, Chongju University, Chongju, South Korea.

The icosahedral phase formation and associated structural evolution in the Al-Cu-Fe ternary system have been examined through a novel process. Al-Cu-Fe samples have been produced from the repeated cold rolling and folding process of the Al, Cu and Fe elemental foils with a

target composition of Al<sub>62.5</sub>Cu<sub>25</sub>Fe<sub>12.5</sub> (at%). Upon early increments of the rolling and folding cycles, the elemental Fe foil was dispersed through the refined Al and Cu layers. When the rolling and folding step reached 40 cycles the Al<sub>2</sub>Cu phase has been observed, but no ternary phases were identified even though additional rolling and folding cycles were carried out. As it has been reported for mechanical alloying, the stable icosahedral phase could be obtained only after thermal annealing at 650 and 750°C. Thus, it is believed that the dissolution of the Al<sub>2</sub>Cu phase provides a critical step for the formation of the icosahedral phase. The phase evolution in Al-Cu-Fe during repeated cold rolling and folding process will be discussed in terms of the identification of the diffusion pathway associated with chemical potential variation during thermal annealing.

### 9:15 AM LL1.3

**Effect of Boron Substitution on the Formation and Stability of Decagonal Phase in Al-Cr-Fe Alloys.** Varsha Khare<sup>1</sup>, Conradin Beeli<sup>2</sup> and Jean-Marie Dubois<sup>1</sup>; <sup>1</sup>LSG2M, CNRS, Ecole des Mines, Nancy, France; <sup>2</sup>Laboratory of Solid State Physics, Swiss Federal Institute of Technology Zurich (ETH Zurich), Zurich, Switzerland.

Effect of substitution of minority elements e.g. Si, C, Be, etc on the formation and stability of icosahedral phase has been extensively studied but the effect of Boron substitution on the stabilization of quasicrystalline phase has been sparsely studied. The Al-Cr-Fe system, containing various approximant phases of decagonal phase, has been investigated with regard to the stabilization of quasicrystalline phase. Apart from size factor, some interesting aspects of Boron in metal are the motivations of the present study. One of the important factors is the free energy of intermediate phases influencing the homogeneity range of primary solid solution due to the formation of extended interstitial solid solution, which affects the electronic factor responsible for the stability of quasicrystalline phase. Yet another fact which can not be ignored regarding the substitution of boron is the formation of layered structures in many borides up to 3at% Boron. As decagonal structure has been established as a layered structure, thus it can be expected that Boron substitution will enhance the stability of decagonal phase. Along with various approximant phases a stable decagonal phase has been obtained in the system by small addition of Boron. The phases present in the as cast and sintered Al-Cr-Fe samples have been studied by differential thermal analysis, x-ray diffraction, transmission electron microscopy, scanning electron microscopy and microprobe analysis. Some salient features of the decagonal phase in terms of growth morphology, surface structure and orientation relationship with approximant structures have been presented. The effect of boron addition has also been outlined.

### 9:30 AM LL1.4

**Oxygen Effects on Quasicrystal Formation in Zr80Pt20 Melt Spun Ribbons.** Daniel Sordélet, Xiaoyun Yang, Elena Rozhkova, Matthew Besser and Matthew Kramer; Metal and Ceramic Sciences, Ames Laboratory, Ames, Iowa.

The as-quenched structure and devitrification behavior of Zr80Pt20 melt spun ribbons containing measured oxygen contents ranging from 184 to 4737 ppm mass were studied. Ribbons containing less than 500 ppm mass oxygen are fully crystallized and consist predominantly of a metastable ordered beta-Zr phase with significant solution of Pt. Increasing oxygen content to 1053 and 1547 ppm mass produces a transition to an apparently amorphous and to mixed amorphous and quasicrystalline structures, respectively. Samples with further oxygen additions of 2690 and 4737 ppm mass are comprised of quasicrystalline and crystalline phases in an amorphous matrix. The results from this study suggest a critical level of oxygen is required to promote glass formation in Zr80Pt20 melt spun ribbons produced at a specific quench rate.

### 9:45 AM LL1.5

**A Critical Link Between Amorphous Structure and Quasicrystal Formation in Zr-based Alloys.** Dean J Miller<sup>1</sup>, Z. Liu<sup>1</sup>, Xidong Chen<sup>1,2</sup>, Dan Sordélet<sup>3</sup>, Matt Kramer<sup>3</sup> and Cynthia Jenks<sup>3</sup>; <sup>1</sup>Argonne National Laboratory, Argonne, Illinois; <sup>2</sup>Department of Science and Mathematics, Cedarville University, Cedarville, Ohio; <sup>3</sup>Metal and Ceramic Sciences Program, Ames Laboratory, Ames, Illinois.

In this work, we have used fluctuation electron microscopy (FEM) to provide direct evidence of the role of medium-range order on the crystallization of amorphous Zr<sub>70</sub>Pd<sub>30</sub> alloys. It has been speculated widely that the degree of short- or medium-range order in amorphous Zr-based alloys plays an important role on crystallization behavior, with such order necessary to lead to crystallization of quasicrystalline phases. FEM is a direct probe of medium-range order and thus provides unique capability to probe amorphous structures. We have used FEM to probe medium range order in two Zr<sub>70</sub>Pd<sub>30</sub> amorphous alloys that exhibit very different crystallization behaviors. Amorphous Zr<sub>70</sub>Pd<sub>30</sub> alloys prepared by melt spinning form the metastable

quasicrystalline phase during devitrification whereas amorphous alloys prepared by mechanical milling do not. FEM reveals significant differences in the degree of medium-range order in these amorphous alloys, suggesting the critical role such order plays in crystallization, and these results and their implications will be discussed. This work was supported by the U.S. Department of Energy, Offices of Science and of Energy Efficiency and Renewable Energy, under contract #W-31-109-ENG-38 (ANL) and #W-7405-ENG-82 (Ames). Electron microscopy was carried out in the Electron Microscopy

#### 10:30 AM \*LL1.6

**Unique indexing scheme of decagonal phases based on a six dimensional model.** Rajiv Kumar Mandal, A.K. Pramanick, G.V.S. Sastry and S. lele; metallurgical engineering, banaras hindu university, varanasi, up, India.

Mandal and Lele(1989) have proposed a six dimensional model for the structural description of the decagonal phases. The integral linear combination of six basis vectors for indicating a physical vector in their model, however, leaves the problem of redundancy in indexing. While revisiting their model, we have noted that the condition of a null vector in physical space permits the formulation of unique indexing scheme both in physical reciprocal and direct spaces. We will demonstrate that our scheme, unlike all previously discussed ones, relies only on the information contained in the model. It will also be shown that diffracted spot having equivalent indices possesses identical intensity. This aspect, though equally important, has been totally ignored in the past. We shall substantiate our claim by taking examples from the known decagonal phases. We shall also present parity condition on indices that will be helpful in discussing subtle features of diffraction patterns.

#### 11:00 AM LL1.7

**Composition Rules of Quasicrystals.** Chuang Dong<sup>1,2</sup>, Jianbing Qiang<sup>1</sup>, Yingmin Wang<sup>1</sup> and Patricia Thiel<sup>2</sup>; <sup>1</sup>State Key Lab of Materials Modification & Department of Materials Engineering, Dalian University of Technology, Dalian, Liaoning, China; <sup>2</sup>Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa.

Some simple composition rules of binary and ternary quasicrystals are pointed out and are related to quasicrystal stabilization mechanisms. For a binary quasicrystal of the icosahedral glass type, the composition is mainly determined by topological close packing of the atoms in the basic 1st-shell icosahedron. A ternary quasicrystal is located at the crossing point of two kinds of specific lines in a ternary phase diagram, which we term  $e/a$ -constant and  $e/a$ -variant lines, respectively. The  $e/a$ -constant line reflects the common electronic structure shared by the quasicrystal and its  $e/a$ -constant approximants. The  $e/a$ -variant line, defined by linking the composition of a binary quasicrystal, an approximant, or a favorable icosahedron-forming composition, to the third element, implies the growth pathway of a basic cluster towards final quasicrystalline and crystalline phases along the line. These simple rules are general in quasicrystalline systems. Applications of these rules in two exemplary systems, Al-Ni-Fe and Zr-Ti-Ni, are presented.

#### 11:15 AM LL1.8

**The Stability of Icosahedral Cd-Yb.** Guenter Krauss<sup>1</sup>, Sofia Deloudi<sup>1</sup>, Andrea Steiner<sup>1</sup>, Walter Steurer<sup>1</sup>, Amy Ross<sup>2</sup> and Thomas Lograsso<sup>2</sup>; <sup>1</sup>Department of Materials, Laboratory of Crystallography, Zurich, Switzerland; <sup>2</sup>Ames Laboratory, Ames, Iowa.

What stabilizes quasicrystals? It is still an open question whether or not quasicrystals are entropy stabilized. In that case, the quasicrystalline state would be restricted to a high-temperature regime. The recently discovered icosahedral phase in the system Cd-Yb could be very valuable to answer this question. The intermetallic system Cd-Yb shows six binary line phases. One of them is the congruently melting stable icosahedral phase Cd<sub>5.7</sub>Yb, and another one is its cubic 1/1-approximant Cd<sub>6</sub>Yb. Since these phases are line phases chemical disorder can be excluded as essential entropic contribution. The stability of icosahedral Cd<sub>5.7</sub>Yb, was studied as a function of temperature and pressure. X-ray diffraction experiments were carried out on single-crystalline as well as polycrystalline samples in the temperature range 20 K ≤ T ≤ 900 K. High-pressure studies were performed up to 13 GPa. Inter alia, it was found that powders behave different from single crystals. Therefore, also the influence of mechanical stress on the icosahedral phase stability was investigated. Time-dependent structural changes at ambient as well as at elevated temperature were recorded after (high-energy) ball milling of the icosahedral phase at liquid nitrogen temperature. The results indicate a low-temperature instability of this binary quasicrystal.

#### 11:30 AM LL1.9

**First-Principles Study of Order-Disorder Transition of**

**Cd<sub>6</sub>Ca.** Kazuki Nozawa<sup>1</sup> and Yasushi Ishii<sup>2</sup>; <sup>1</sup>SORST, Japan Science and Technology Corporation, Kawaguchi, Saitama, Japan; <sup>2</sup>Department of Physics, Chuo University, Bunkyo-ku, Tokyo, Japan.

Cd<sub>6</sub>Ca is a cubic 1/1-approximant of the binary icosahedral quasicrystal Cd<sub>5.7</sub>Ca. The structure of Cd<sub>6</sub>Ca is described by bcc packing of four-layered atomic shells at room temperature. The innermost shell is a 4Cd tetrahedron, where the eight vertices of a cube are occupied with half occupancy. Recently, some anomaly in the temperature dependence of the electrical resistivity and the specific heat at 110 K were found in Cd<sub>6</sub>Yb[1, 2], and they seem to be an order-disorder transition originated in the orientational ordering of Cd tetrahedra. These anomalous behavior were also observed in Cd<sub>6</sub>Ca[1]. We perform first-principles structural optimization including 168 atoms in a cubic unit cell. Calculations are performed with a pseudo-potential technique and a plane-wave basis set. We will try to calculate the energy cost owing to different orientations of the tetrahedron at body center of the cubic unit cell. We will discuss an energetically favorable ordering of the central Cd tetrahedron and a relaxed structure of atomic shells for each ordering. [1] R. Tamura, Y. Murao, S. Takeuchi, M. Ichihara, M. Isobe and Y. Ueda, Jpn. J. Appl. Phys. **41**, L524(2002) [2] S. K. Dhar, A. Palenzona, P. Manfrinetti and S. M. Patalwar, J. Phys. Condens. Matter **14**, 517(2002)

#### 11:45 AM LL1.10

**Order-disorder transition in a Cd-Ca quasicrystal approximant.** Michael Widom<sup>1</sup> and Marek Mihalkovic<sup>2,1</sup>;

<sup>1</sup>Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania; <sup>2</sup>Institute of Physics, Slovakian Academy of Sciences, Bratislava, Slovakia.

The stable Cd-based icosahedral quasicrystals have cubic approximants of Pearson type cI184 based on body-centered-cubic packings of icosahedral clusters. For Cd-Ca (and also Cd-Yb) the inner-most cluster shell consists of a single tetrahedron which takes one of two possible orientations consistent with the cubic symmetry of the approximant. This tetrahedron orientation defines an Ising-like local state variable. First-principles total energy calculations determine the interaction energies between tetrahedra in adjoining clusters, which turn out to be antiferromagnetic in nature. Monte Carlo simulations of this BCC antiferromagnetic Ising model reveal an order-disorder transition at about T=100K, consistent with experimental observation.

#### SESSION LL2: Synthesis and Structure II

Chair: Cynthia Jenks

Monday Afternoon, December 1, 2003

Fairfax A (Sheraton)

#### 1:30 PM \*LL2.1

**Crystal chemistry and electronic structure of magnesium based Mackay icosahedron type approximants.** Guido Kreiner<sup>1</sup>,

Yuri Moguilevich<sup>1</sup>, Daniel Gruener<sup>1</sup>, Christian Kudla<sup>1</sup>, Julien Makongo<sup>1</sup> and Melanie Schaeppers<sup>2</sup>; <sup>1</sup>Inorganic Chemistry, Max-Planck-Institut fuer Chemische Physik fester Stoffe, Dresden, Germany; <sup>2</sup>Fortis GmbH, Witten, Germany.

In order to obtain reliable experimental information on the long-range order, the role of the valence electron concentration and the type of chemical disorder for Mackay icosahedron type quasicrystals approximant phases of binary and ternary Magnesium alloy systems have been investigated. Mg-Pd, Mg-Ag, Ga-Mg-Ag, Ga-Mg-Pd, Al-Mg-Pd and Ga-Mg-Zn alloys were prepared by melting mixtures of high-purity elements in cleaned tantalum crucibles. Loading and sealing by arc welding was performed under dry argon atmosphere. The Ta containers were encapsulated in evacuated and sealed quartz ampoules for appropriate heat treatments. For sample characterization we used chemical analysis, X-ray powder and single crystal diffraction, metallography, thermal analysis, SEM, EDS and WDS. Electronic structure calculations were carried out within the LMTO-ASA framework. An overview is presented on the crystal structures, homogeneity ranges and physical properties including the following intermetallic phases: Mg<sub>6</sub>Pd, Mg<sub>4</sub>Pd, Mg<sub>3</sub>Pd, Mg<sub>5</sub>Pd<sub>2</sub>, Mg<sub>2</sub>Pd, Ag<sub>17</sub>Mg<sub>54</sub>, Ag<sub>7</sub>Mg<sub>26</sub>, Ag<sub>4</sub>Mg, Ga<sub>12</sub>Mg<sub>11</sub>Ag<sub>6</sub>, Ga<sub>30</sub>-xMg<sub>32</sub>+xPd<sub>21</sub>-y, Ga<sub>15</sub>-x-yMg<sub>38</sub>+yPd<sub>13</sub>+x, and GaMg<sub>3</sub>Pd<sub>2</sub>. Most phases are complex intermetallic alloys having a high degree of icosahedral structural order, e.g., Mg<sub>6</sub>Pd, Mg<sub>4</sub>Pd, Ag<sub>17</sub>Mg<sub>54</sub>, Ag<sub>7</sub>Mg<sub>26</sub>, Ga<sub>30</sub>-xMg<sub>32</sub>+xPd<sub>21</sub>-y and Ga<sub>15</sub>-x-yMg<sub>38</sub>+yPd<sub>13</sub>+x with the Mackay icosahedron as fundamental structural unit. The phase and cluster stability and the long-range order display a strong dependency on the valence electron concentration and the type of chemical disorder.

#### 2:00 PM \*LL2.2

**Ab initio structure determination of quasicrystals via single**

**crystal x-ray diffraction.** Hiroyuki Takakura<sup>1</sup>, Akiji Yamamoto<sup>1</sup>, Marc De Boissieu<sup>2</sup>, Taku J Sato<sup>3</sup> and An Pang Tsai<sup>3</sup>; <sup>1</sup>Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Japan; <sup>2</sup>LTPCM/ENSEEG, Grenoble, France; <sup>3</sup>Materials Engineering Laboratory, National Institute for Materials Science, Tsukuba, Japan.

The standard approach for structure solution of ordinary crystals begins with solving the phase problem. We can take similar step in the case of quasicrystals nowadays. The low density elimination (LDE) method can solve the phase problem in quasicrystals, and provide electron density distribution of unit cell in higher-dimensional space. The LDE method is an ab initio phase determination method based on a simple density modification approach in the real space. Although, the reconstructed density might not be complete, because of limitation of the phase reconstruction procedure itself, the reconstructed density gives us information about location of occupation domains (ODs), and size and shape of them. Moreover, we can specify which OD contain heavy element. Local atomic shell structure, so-called cluster, can be directly found from a geometrical investigation of the reconstructed density, and this is less affected by quality of the density. With these knowledge, therefore, one can construct a reasonable ideal atomic model based on the cluster model for structure refinement. The reconstructed density can be verified in process of structure refinement, or more easily by comparing the local atomic shell structure with that of known approximant structures if appropriate approximant crystals exist. We applied the LDE method to solve several different types of icosahedral quasicrystals; Al-TM(TM=transition metal), Mg-Zn-RE(RE=rare earth) and Cd-Yb.

### 2:30 PM LL2.3

**Stability of quasicrystals in Al-Ca-Co, B-Th and B-Co-Ti systems.** Marek Mihalkovic<sup>1,2</sup> and Michael Widom<sup>1</sup>; <sup>1</sup>Dept of Physics, Carnegie Mellon Univ, Pittsburgh, Pennsylvania; <sup>2</sup>Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia.

We identify the Al<sub>8</sub>-Ca-Co<sub>2</sub> phase (pearson symbol oP44) as an approximant phase of a novel type of decagonal quasicrystal. Generalization of its structure leads to a family of quasicrystal approximant structures based on Hexagon-Boat-Star tiling geometry. Ab-initio total energy calculations indicate metastability of the model decagonal quasicrystal structure in this ternary system. The B<sub>4</sub>-Th (pearson symbol tP20) and B<sub>2</sub>-Co<sub>5</sub>-Ti<sub>3</sub> structures are classified as an approximant tilings of the dodecagonal quasicrystal, based on the geometry of the square-triangle tiling. Relative stabilities of a model quasicrystal approximant tilings, based on ab-initio total energy calculations, are reported.

### 2:45 PM LL2.4

**Simulation of Disorder in Decagonal Al-Co-Ni Quasicrystals.** Miroslav Kobas, Thomas Weber and Walter Steurer; Department of Materials, Laboratory for Crystallography, Zuerich, Switzerland.

The origin of quasicrystalline stability is a challenging and still unsolved question. There are two fundamentally different approaches: energy- or entropy-stabilization. Former would mean that quasicrystals are a ground state of matter, latter that they are purely high-temperature phases. A key in answering these questions comprises the evaluation of short- and long-range order correlations in quasicrystals as a function of temperature, which can be obtained from an analysis of the diffuse intensities. The decagonal quasicrystal with composition Al<sub>70</sub>Co<sub>12</sub>Ni<sub>18</sub>, the so-called Edagawa phase[1] is a superstructure of the nickel-rich basic decagonal Al-Co-Ni phase[2]. It shows an extraordinary richness of complex scattering, including sharp satellite reflections, as well as one-, two- and three-dimensional diffuse diffraction features. In the present studies, we focus on the diffuse features inside the Bragg layers. Disorder is simulated on different scales, ranging from pentagonal bi-pyramids having a diameter of about 6Å to clusters with 20Å diameter. The structural models of the clusters are based on electron microscopy studies[3]. Furthermore, thermal diffuse scattering (TDS) and phasonic diffuse scattering (PDS) are calculated in a five-dimensional description. TDS and PDS have been identified to constitute the major part of the experimental diffuse intensities inside the Bragg layers. The disordered structure is examined by translating TDS and PDS into three-dimensional structural information based on structural units like subclusters and clusters and correlations among themselves. [1] Edagawa, K., Echiara, M., Suzuki, K. & Takeuchi, S., *Phil.mag.Lett.*, **661**, 19-25 (1992). [2] Steurer, W., Haibach, T., Zhang, B., Kek, S. & Lück, R., *ActaCryst.B.*, **494**, 661-675 (1993). [3] Abe, E., Saitoh, K., Takakura, H., Tsai, A.P., Steinhardt, P.J. & Jeong, H.-C., *Phys.Rev.Lett.*, **8420**, 4609-4612 (2000).

SESSION LL3: Properties I – Transport Properties  
Chair: Ester Belin-Ferre  
Monday Afternoon, December 1, 2003  
Fairfax A (Sheraton)

### 3:30 PM \*LL3.1

**Hydrogen Diffusion in Quasicrystalline ZrCuNiAl.**

Janez Dolinsek and Tomaz Apih; Solid State Physics, J. Stefan Institute, Ljubljana, Slovenia.

A high number of tetrahedrally coordinated interstitial sites within the crystalline structure and the favorable hydrogen chemistry make the Zr- and Ti-based quasicrystals attractive as potential hydrogen-storage materials. An important property of a good hydrogen-storage material is fast hydrogen diffusion within the lattice. Out of many experimental techniques employed to study hydrogen diffusion in metal hydrides, the technique of NMR diffusion in a pulsed magnetic field gradient (PFG) has the advantage of giving direct, model-independent value of the diffusion constant D. The PFG method is suitable to detect diffusion coefficients in the range between 10<sup>-5</sup> and 10<sup>-8</sup> cm<sup>2</sup>/s and was successfully applied to simple-structure metal hydrides, like the elemental fcc PdHx and TiHx. A more complicated structure and/or structural and chemical disorders make the hydrogen diffusion in quasicrystals slower with D < 10<sup>-8</sup> cm<sup>2</sup>/s, which is below the limit of sensitivity of the PFG method. We present a direct determination of the hydrogen diffusion coefficient in the hydrogen-storage ZrCuNiAl quasicrystalline alloy by using a method of NMR diffusion in a static fringe field (SFF) of a superconducting magnet, which was not applied before to hydrogen-storage materials. The SFF method takes advantage of the ultrahigh static magnetic field gradient outside the superconducting magnet coil and extends the limit of sensitivity to D values down to 10<sup>-10</sup> cm<sup>2</sup>/s. The investigation included several Zr<sub>69.5</sub>Cu<sub>12</sub>Ni<sub>11</sub>Al<sub>7.5</sub> samples in various phases (quasicrystalline, approximant and amorphous) hydrogenated to different hydrogen-to-metal (H/M) ratios. The hydrogen diffusion constant was determined in the temperature range between 300 K and 440 K, where it exhibited thermally activated behavior with the values in the range 10<sup>-9</sup> cm<sup>2</sup>/s. The general trend of D is a significant decrease with increasing hydrogen-to-metal ratio H/M, owing to creation of defects in the lattice during hydrogen loading, whereas the actual alloy structure-the amorphous, icosahedral or approximant-plays only a minor role in the hydrogen diffusivity.

### 4:00 PM LL3.2

**Phononic Quasicrystals.** Daniel Sutter, Guenter Krauss and Walter Steurer; Department of Materials, ETH Zurich, Zurich, Switzerland.

Phononic crystals are to ultrasound what photonic crystals are to light and crystals are to X-rays. If the wave length is of the same order of magnitude as the typical distances between the objects in their ordered arrangement then the interaction is dominated by diffraction beside refraction. Depending on the spectral properties of the material band gaps open for certain frequencies. In special cases these gaps are omnidirectional. A huge amount of application driven research has been performed on photonic crystals, much less on phononic crystals and almost nothing on phononic quasicrystals. Phononic (quasi)crystals can act, for instance, as perfect reflectors, wave guides or lenses for (ultra)sound. Since the spectral properties of phononic crystals scale with the size of the system, possible applications span the range from thermal barriers (phonons with nanometer wave lengths) to earth-quake shock-wave (wave length of meters to kilometers) protectors. We present first experimental studies on one- and two-dimensional quasiperiodic phononic crystals. Our experiments have been performed with ultrasound (0.2 - 4 MHz) on phononic crystals and quasicrystals consisting of steel sheets (0.2 mm thick), cylinders (0.8 - 1.2 mm diameter) and balls (1 mm diameter) in water, for instance. The pros and cons of phononic quasicrystals will be discussed

### 4:15 PM LL3.3

**Thermoelectric properties of the Al-Mn-Re-Si 1/1-cubic approximant.**

Tsunehiro Takeuchi<sup>1</sup>, Toshio Otagiri<sup>2</sup>, Hiroki Sakagami<sup>2</sup>, Uichiro Mizutani<sup>2</sup> and Hirokazu Sato<sup>3</sup>; <sup>1</sup>Research Center for Advanced Waste and Emission Management, Nagoya University, Nagoya, Aichi-ken, Japan; <sup>2</sup>Department of Crystalline Materials Science, Nagoya University, Nagoya, Aichi-ken, Japan; <sup>3</sup>Department of Physics, Aichi University of Education, Kariya, Aichi-ken, Japan.

Icosahedral quasicrystal is one of the potential candidates for a new thermoelectric material because of its possession of the large thermoelectric power more than 50  $\mu$ V/K and low thermal conductivity as low as 1 W/K-m. The large electrical resistivity generally observed in the icosahedral quasicrystals, however, has prevented us to utilize it as a practical thermoelectric material. To overcome difficulty in reducing the electrical resistivity in the icosahedral quasicrystals, we employed in this study the

corresponding 1/1-cubic approximants rather than the quasicrystals themselves. The electrical resistivity, thermoelectric power, and thermal conductivity were measured on the  $\text{Al}_{71.6-x}(\text{Mn,Re})_{17.4}\text{Si}_x$  ( $7 < x < 12$ ) 1/1-cubic approximant. A large thermoelectric power exceeding  $40 \mu\text{V/K}$  and a low thermal conductivity less than  $1.2 \text{ W/K}\cdot\text{m}$  were observed for these 1/1-cubic approximants. The electrical resistivity in these approximants was kept below  $1,000 \mu\Omega\text{cm}$  at room temperature, that is more than one order smaller than that in the corresponding quasicrystals. As a result of the large thermoelectric power, the low thermal conductivity, and the low electrical resistivity, a large figure of merit  $ZT = 0.25$  is achieved for the  $\text{Al}_{71.6}\text{Re}_{17.4}\text{Si}_{11}$  1/1-cubic approximant at room temperature. LMTO-ASA band calculation on the reliable atomic structure refined by the synchrotron radiation Rietveld analysis was employed to precisely determine the electronic structure of the  $\text{Al}_{71.6-x}\text{Re}_{17.4}\text{Si}_x$  1/1-cubic approximant. We calculate the thermoelectric power using the electronic density of states thus determined and Boltzmann transport equation under the assumption of the energy independent group velocity and the energy independent mean free path over a small energy range of  $10 k_B T$  centered at the chemical potential. The calculated values of the thermoelectric power show fairly good agreement with the measured ones not only in the absolute value but also in their temperature dependence. The origin of the low thermal conductivity and low electrical resistivity are also discussed in terms of the atomic structure and the electronic structure. On the basis of the present experimental observations and numerical calculations, we show advantages in employing the 1/1-cubic approximants as a potential thermoelectric material over the corresponding icosahedral quasicrystals and even commercial thermoelectric materials.

#### 4:30 PM LL3.4

**Electrical properties of Cd-(Yb, Ca) quasicrystals and their approximants.** Ken Minoda, Ryuji Tamura and Shin Takeuchi; Department of Materials Science and Technology, Tokyo University of Science, Noda, Chiba, Japan.

The binary Cd-(Yb, Ca) quasicrystals and their approximants are considered to be free from chemical disorder. We have studied the electrical properties of these compounds in order to obtain insight into the intrinsic properties of the quasicrystal. As a result, we have found that the approximants  $\text{Cd}_6\text{Yb}$  and  $\text{Cd}_6\text{Ca}$  exhibit metallic behaviors such as positive temperature coefficient of the resistivity. By contrast, the quasicrystals  $\text{Cd}_5.7\text{Yb}$  and  $\text{Cd}_5.7\text{Ca}$  display a distinctive resistivity maximum at low temperature and negative temperature coefficients at higher temperatures, the latter of which being a common property of the ternary quasicrystals. The difference in the electronic transport between the quasicrystals and approximants means that the coherence length of the conduction electrons in the quasicrystals are longer than  $1.5 \text{ nm}$ , i.e., the lattice constant of the 1/1 approximants. The results of the specific heat, magnetic susceptibility on the binary compounds will be also demonstrated in comparison.

#### 4:45 PM LL3.5

**Path to Strong Insulating Transport Properties in Bulk AlPdRe Samples.** Ralph Lewis Rosenbaum<sup>1</sup>, Yuan-Liang Zhong<sup>2,3</sup> and Juhn-Jong Lin<sup>4</sup>; <sup>1</sup>School of Physics & Astronomy, Tel Aviv University, Ramat Aviv, Israel; <sup>2</sup>Department of Physics, National Tsing Hua University, Hsinchu, Taiwan; <sup>3</sup>Institute of Physics, Academia Sinica, Taipei; <sup>4</sup>Institute of Physics, National Chiao Tung University, Hsinchu, Taiwan.

Electronic transport measurements have been made on bulk icosahedral  $\text{Al}_{70}\text{Pd}_{22.5}\text{Re}_{7.5}$  quasicrystal (QCs) samples, having increasingly larger resistance temperature ratios,  $rT = R(4.2 \text{ K})/R(300 \text{ K})$ . Data were taken between  $0.23 \text{ K}$  to  $300 \text{ K}$  and in magnetic fields up to  $17.5 \text{ T}$ . Both the zero field resistivity and the magnetoresistance changed from metallic behavior to weakly insulating behavior to highly insulating behavior, as the resistance temperature ratios  $rT$  of the samples became larger. For the insulating samples, the resistivity  $r$  followed an inverse temperature power law  $r = a/T^z$  where  $0.3 < z < 1.2$  for increasingly insulating samples. The weakly insulating QC samples showed no saturation in the resistivity down to  $0.23 \text{ K}$ . In contrast, the highly insulating QC samples exhibited saturation behavior of the resistivity below  $4 \text{ K}$ . A simple model yielded a good fit to the highly insulating data. We acknowledge Prof. Shui-Tien Lin and Drs. Cheng-Ren Wang and Shr-Wen Wu of the National Cheng Kung University in Tainan, Taiwan, for providing us the QC samples. This work was partially supported by the Taiwan National Science Council to Profs. J. J. Lin and S. T. Lin. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by the NSF Cooperative Agreement No. DMR 9627035 and by the State of Florida.

#### 8:30 AM \*LL4.1

**Semiconducting Aluminum-Transition-Metal Quasicrystals.** Marian Krajci<sup>1,2</sup> and Juergen Hafner<sup>2</sup>; <sup>1</sup>Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia; <sup>2</sup>Center for Computational Materials Science, University of Vienna, Vienna, Austria.

We report on a class of icosahedral aluminum-transition-metal (Al-TM) alloys with a true semiconducting behavior. The existence of a semiconducting gap is found to depend critically on a particular kind of Al-TM ordering defined by a simple rule in a 6-dimensional superspace. Any deviation from this 6D order leads to the formation of strongly localized defect states in the gap. The structure of the semiconducting quasicrystals belongs to the face-center-icosahedral structural class, the same to which also icosahedral AlPdRe belongs. The description of the structure is based on a modified Katz-Gratias-Boudard model. We have calculated the electronic structure for series of quasicrystalline approximants. In the density of states of the 1/1 approximant with 128 atoms/unit cell relaxed with Hellmann-Feynman forces we have found a real gap at or close to the Fermi level. To get a semiconductor the critical band-filling is 648 electrons per cell. It can be achieved for several different stoichiometries. We investigated the semiconducting 1/1 approximants with various combinations of 3d, 4d and 5d transition-metals. The gap widens as a 3d or 4d metal is replaced by a 5d metal. Calculations for the 2/1 approximant with 544 atoms/cell show the persistence of the gap. The chemical composition for which semiconducting behavior is achieved varies in the sequence of the approximants, but the existence of the gap in the electronic spectrum persists in higher order approximants, provided the Al-TM ordering is respected. Icosahedral AlPdRe represents the quasiperiodic limit in this hierarchy of approximants. As substitutional defects which obviously exist in real samples of any quasicrystal lead to formation of localized states, a real sample of icosahedral AlPdRe turns out to be a semiconductor with a band-gap filled by localized states.

#### 9:00 AM LL4.2

**Chemical Bonding and Pseudogap in Cd- and Zn-based Compounds with Complex Hexagonal Structures.**

Yasushi Ishii<sup>1</sup>, Kazuki Nozawa<sup>2,1</sup> and Takeo Fujiwara<sup>3</sup>; <sup>1</sup>Department of Physics, Chuo University, Tokyo, Japan; <sup>2</sup>Japan Science and Technology Cooperation, Saitama, Japan; <sup>3</sup>Department of Applied Physics, University of Tokyo, Tokyo, Japan.

A pseudogap in the electronic density of states (DOS) is a universal feature of quasicrystals (QC) and approximant crystals. It is believed that origin of the pseudogap is primarily due to the Hume-Rothery (HR) mechanism. However, we showed that the HR mechanism does not play a principal role in the pseudogap formation for Cd- and Zn-based alloys, which are approximant phases of newly discovered QC, but the hybridization of the  $s$  states just above the Fermi level with a wide  $sp$  band is essential. In this paper, we shall examine mechanism of the pseudogap formation in other family of Zn- and Cd-based compounds; hexagonal Zn-Mg-Y and  $\text{Cd}_{13}\text{Y}_{13}$ . Although these compounds may not be interpreted as approximant crystals, they show very deep pseudogap near the Fermi level and considered to be stabilized electronically. We calculate the electronic structures of these compounds by first-principles methods and study bonding nature of the electronic wavefunctions. We will discuss further evidence of the non-HR mechanism of stabilization in Cd- and Zn-based systems.

#### 9:15 AM LL4.3

**Atomic Structure, Electronic States, and Stability of Icosahedral Quasicrystals.** Eeuwé Sieds Zijlstra and Shyamal K Bose; Department of Physics, Brock University, St. Catharines, Ontario, Canada.

Several existing models of icosahedral quasicrystals are improved upon and studied by ab initio electronic structure methods. The following approach is used to optimize the models: 1) Interchange of atoms in the existing (skeletal) models based on available knowledge of the local atomic environments, and 2) subsequent relaxation of the atomic positions using forces determined via first principles density functional methods. After minimizing the total energy, we investigate the ground state, chemical bonding, and the relation of the stability of the icosahedral quasicrystals to the pseudogap. We examine the validity of the concept of negative valence states of the transition metal atoms in quasicrystals as advanced by Friedel. We compare calculated results with available photo-emission, tunneling, Moessbauer, and nuclear quadrupole resonance spectroscopy data. Significant improvement with respect to the starting (skeletal) model is achieved in several cases. Our study comprises many of the

icosahedral quasicrystals and their approximants that have received much attention, such as the first quasicrystal i-AlMn, the first stable icosahedral quasicrystal i-AlCuFe, the i-AlPdMn and i-AlPdRe phases, and the new quasicrystals i-CdYb and i-CdCa.

#### 9:30 AM LL4.4

##### Electronic Structure of Al-Cr-Fe Intermetallics.

Belin-Ferre Esther<sup>1</sup>, Dankhazi Zoltan<sup>2</sup>, Fontaine Marie-Francoise<sup>1</sup>, Thirion Jean<sup>1</sup>, de Weerd Marie-Cecile<sup>3</sup> and Dubois Jean Marie<sup>3</sup>; <sup>1</sup>LCPMR UMR7614, Paris, France; <sup>2</sup>Solid state physics, Eotvos University, Budapest, Hungary; <sup>3</sup>LSG2M, EMN, Nancy, France.

It has been shown recently that wetting of quasicrystalline and related intermetallics surfaces by water differs from Al-Cu-Fe to Al-Cr-Fe compounds and depends on the densities of states at the Fermi level of the bulk specimens. Whereas the electronic structure of Al-Cu-Fe systems has been widely investigated, to the best of our knowledge no such data is available for Al-Cr-Cu alloys. This has motivated the present experimental study of the electronic structure of various Al-Cr-Fe samples all decagonal or approximants of the decagonal quasicrystalline compound. The paper will report the results obtained for the valence band of these systems as probed combining the X-ray emission and X-ray photoemission spectroscopy techniques. Emphasis will be on the hybridizations at the Fermi level and the electronic interactions between the two transition elements. Hospitality by the Institute for Solid State Physics of the Technical University of Vienna (Austria) and assistance by Dr. Herbert Mueller are warmly acknowledged.

#### 9:45 AM LL4.5

##### Photoemission spectroscopy of the Cd-based quasicrystals and approximants.

Ryuji Tamura<sup>1</sup>, Ken Minoda<sup>1</sup>, Chieko Aoki<sup>1</sup>, Shin Takeuchi<sup>1</sup>, Tsunehiro Takeuchi<sup>2</sup>, Takayuki Kiss<sup>3</sup>, Takayoshi Yokoya<sup>3</sup> and Shiku Shin<sup>3</sup>; <sup>1</sup>Department of Materials Science and Technology, Tokyo University of Science, Noda, Chiba, Japan; <sup>2</sup>Department of Crystalline Materials Science/ Department of Physics, Nagoya University, Nagoya, Aichi, Japan; <sup>3</sup>Institute for Solid State Physics, The university of Tokyo, Kashiwa, Chiba, Japan.

We have performed a series of photoemission (PE) experiments of the Cd-based quasicrystals and approximants, such as Cd-Yb, Cd-Ca, Cd-Y, etc., using high-resolution ultraviolet PE spectroscopy. As a result, we have observed a sharp Fermi edge in all the studied compounds, and also a distinctive intensity maximum just below the Fermi energy in the case of the Cd-Ca compounds. Comparison of the PE spectra with the calculated DOS implies that the maximum in the valence band PE spectra is partly due to hybridization between Cd sp and Ca d states. In order to obtain more insight into the origin of the maximum we performed resonant PE spectroscopy of the Cd-Ca quasicrystal across the Ca 2p-3d threshold, i.e., from 345 to 352 eV binding energy. The results show that the maximum in the on-resonance PE spectra is considerably enhanced as compared with the off-resonance PE spectra, indicating that the occurrence of the sp-d hybridization in the Cd-Ca quasicrystal. The results of other Cd-based compounds will be also demonstrated.

#### SESSION LL5: Properties III – Mechanical Properties I

Chair: H.-R. Trebin

Tuesday Morning, December 2, 2003

Fairfax A (Sheraton)

#### 10:30 AM \*LL5.1

##### Plasticity of icosahedral Al-Pd-Mn and Zn-Mg-Dy

**quasicrystals.** Marc Heggen, Michael Feuerbacher and Knut Urban; Institute of Solid State Physics, Research Centre Juelich, Juelich, Germany.

The plasticity of icosahedral Zn-Mg-Dy single-quasicrystals was investigated using uniaxial compression experiments at different strain rates and temperatures and by transmission electron microscopy. The evolution of the dislocation density with strain was determined and planar defects such as antiphase boundaries, stacking faults and phason defects were observed and characterized. The presence of antiphase boundaries, in particular, provides a deeper insight into the mechanism of dislocation motion, since they allow for an independent determination of the planes of motion. Plastic deformation was shown to be mainly governed by dislocation glide. A constitutive model describing the plasticity of icosahedral quasicrystals (Feuerbacher et al. 2001) was applied to icosahedral Al-Pd-Mn over a wide range of experimental deformation conditions. The model incorporates the evolution of two microstructural parameters: The first, as in crystals, is the dislocation density; the second is a quasicrystal-specific order parameter that accounts for deformation-induced disordering and thermally activated reordering of the quasicrystal structure. Significant strain-rate dependence was found which can be understood

by the interactive evolution of these two microstructural parameters. Feuerbacher, M., Schall, P., Estrin, Y., and Brechet, Y., (2001) Phil. Mag. Lett. 81, 473.

#### 11:00 AM LL5.2

##### Which Kind of Singularities Are Phason Defects and

**Dislocations in Quasicrystals?** Maurice Kleman, Laboratoire de Mineralogie-Cristallographie de Paris, Université Pierre-et-Marie-Curie, Paris, France.

The plastic deformation of quasicrystals (QC) is ruled by two types of singularities of the QC order, singularities of the phonon strain field, and singularities of the phason strain field. In the framework of the general topological theory of defects, both types of defects appear as distinct components of the same entity, called a disvocation. Each of them can also be given a description in terms of more classical concepts, within a detailed analysis of the Volterra process: (a)- the phonon singularity breaks some symmetry of translation, represented by its Burgers vector  $b_{\text{par}}$ ; it is akin to a perfect dislocation (b)- the phason singularities (there are many attached to each  $b_{\text{par}}$ -dislocation), that we call matching faults, are dipoles of dislocations whose Burgers vectors are of a special type; they do represent not only a particular symmetry of translation but also the class of local isomorphism of the QC. In fact, such dipoles, if they open up into loops, bound stacking faults. Thus a phason singularity is an imperfect dislocation. A mismatch is nothing else but an elementary matching fault. Relations between  $b_{\text{par}}$ , the shape of the dislocation, and the distribution of matching faults, will be discussed. M. Kleman Phasons and the Plastic Deformation of Quasicrystals, Eur. Phys. J., B31 (2003) 315-325 : Prolegomena to the Plastic Deformation of Quasicrystals Scripta Materialia., 49 (2003) 5-9

#### 11:15 AM LL5.3

##### Low Temperature Deformation Mechanisms of AlPdMn

##### Quasicrystals.

Michael Texier<sup>1</sup>, Anne Prout<sup>1</sup>, Joel Bonneville<sup>1</sup>, Jacques Rabier<sup>1</sup> and Patrick Cordier<sup>2</sup>; <sup>1</sup>Physics, University Of Poitiers, Chasseneuil Futuroscope, France; <sup>2</sup>Physics, University of Lille, Villeneuve d'Ascq, France.

AlPdMn quasicrystalline specimens are known to be drastically brittle at low and intermediate temperatures, while at high temperature they exhibit a plastic behaviour which has some similarity with superplasticity. In the ductile temperature regime, it has been established that plastic deformation takes place by dislocation motion. The high brittle-to-ductile transition temperature (BDTT) clearly suggests that diffusion processes are requisite to plastic flow, but the microscopic mechanism by which dislocations move in this non-periodic structure is still an open question. An arising question is therefore to know if conservative dislocation movement can be produced in this quasiperiodic structure. In the present work, we have used a multi-anvil technique with an anisotropic solid confining medium in order to investigate the plastic behaviour of AlPdMn specimens at temperatures far below their BDTT. The confining chamber has been designed to apply concomitantly large confining pressures and high uniaxial stresses. The drawback is that the uniaxial stress cannot be measured. Such a technique has been applied to plastically deform AlPdMn specimens with a confining pressure of 5 GPa at temperatures ranging from 293K up to 673K, that is, a temperature at which diffusion processes can be reasonably assumed to be negligible. The microstructures have been examined, prior to and after plastic deformation, with a JEOL 200CX microscope operating at 200 kV. Microstructural observations indicate that the deformation microstructure evolves with deformation temperature. At room temperature, strips with high dislocation densities are the dominant feature of the microstructure. A careful examination of the dislocations inside the strips indicates that they moved by a glide process. Few events of dislocation climb are as well observed. With increasing temperature, more and more dislocation climb events are observed. A climb multiplication mechanism is proposed to explain the observed dislocation geometrical configurations.

#### 11:30 AM LL5.4

##### Dislocation mechanisms in AlPdMn quasicrystal.

Frederic Mompou<sup>1</sup>, Michael Feuerbacher<sup>2</sup>, Lionel Bresson<sup>3</sup>, Denis Gratias<sup>2</sup> and Daniel Caillard<sup>1</sup>; <sup>1</sup>CEMES/CNRS, toulouse, France; <sup>2</sup>IFF, Jülich, Germany; <sup>3</sup>LEM/ONERA, Chatillon, France.

Most models of quasicrystal plasticity rely on dislocation glide movements controlled either by Peierls-type mechanisms or interaction with clusters. Previous investigations in as grown samples have shown evidence of pure climb. Here, we report new experiments carried out at low temperature, on Al-Pd-Mn single quasicrystalline grain deformed at high pressure under compression. TEM observations in samples deformed at 600 K reveal high density of dislocations trailing phason faults. Contrast analyses show extensive dislocation climb associated with two climb systems in perpendicular and parallel planes to the compression axis and trailing respectively

vacancies/interstitials phason faults. These results can be interpreted by a concerted climb mechanism with exchange of matter between the two dislocation systems. In deformed samples at room temperature, the deformation is heterogeneous and accommodated by non-planar defects. Dislocations have been observed at the head and emerging from these defects. TEM analyses show that dislocations at the head have Burgers vectors belonging almost to the plane of the defect with a near screw character. These results can be interpreted by crack healing associated with a mode III crack at the head while high stresses incompatibility far from it are released by emission of climbing dislocation. We report also in-situ heating and/or straining experiments. They show dislocations moving in 2-, 3- and 5-fold planes with straight segments in dense 2-fold directions. After cooling, contrast analyses lead to Burgers vectors perpendicular to the plane of motion. Annihilation and multiplication have also been observed in agreement with plasticity mechanism mediated by dislocation motion. Phason fault flags have been observed in the wake of moving dislocations as a fast retiling process indicates. The impossibility of glide has been experimentally observed when a dipole formed by climb do not annihilate in its glide plane. All these results confirm that climb is the unique mode of dislocation motion in AlPdMn at least at high temperature.

#### 11:45 AM LL5.5

**Plasticity of decagonal quasicrystals.** Peter Schall<sup>1,2</sup>, Michael Feuerbacher<sup>2</sup> and Knut Urban<sup>2</sup>; <sup>1</sup>DEAS, Harvard University, Cambridge, Massachusetts; <sup>2</sup>IFF, Forschungszentrum Juelich, Juelich, Germany.

Decagonal quasicrystals belong to the class of two-dimensional quasicrystals exhibiting quasiperiodic order in two spatial directions and periodic order along the third. Some physical properties of these materials are known to show anisotropic behavior. We have grown the decagonal phase in the Al-Ni-Co system in the form of large single quasicrystals. We have carried out compression experiments on the single quasicrystals in three different orientations: with the compression axis parallel to, under an angle of 45 degrees and perpendicular to the periodic axis. In addition we have performed a detailed characterization of the microstructure of deformed samples by transmission electron microscopy. The deformation experiments reveal a distinct anisotropic deformation behavior. In the microstructural studies we find that the periodic slip system is clearly favored over the quasiperiodic slip system.

SESSION LL6: Joint Session with MM4: Quasicrystals  
from Metallic Glasses  
Chairs: Ken Kelton and Dan Sordelet  
Tuesday Afternoon, December 2, 2003  
Republic B (Sheraton)

#### 1:30 PM \*LL6.1

**Icosahedral Transformation from Supercooled Liquid in Metal-Metal Type Bulk Glassy Alloys.** Akihisa Inoue, IMR, Tohoku Univ., Sendai, Miyagi, Japan.

Since the first syntheses of metal-metal type bulk glassy alloys without metalloid element in Mg-, lanthanide- and Zr-based alloy systems for several years between 1988 and 1990, we have developed a number of bulk glassy alloys in metal-metal and metal-metalloid systems. It is well known that these bulk glassy alloys exhibit unique engineering properties such as high strength, large elastic elongation, high corrosion resistance, good soft magnetic properties and Newtonian flow. We have also noticed that the metal-metal type bulk glassy alloys have unique heating-induced phase transformation in which primary crystallization phase consists only of big cube or icosahedral phase. It has also been reported that the precipitation of icosahedral phase occurs in Zr-, Hf- and Cu-based alloy systems containing special additional elements such as Ag, Pd, Pt, Au, Ti or Nb leading to nearly zero or positive heats of mixing against the other constituent elements. In addition, the icosahedral phase precipitates homogeneously at very high nucleation rates from their supercooled liquid and their grain size is as small as 5 to 20 nm. The precipitation of the icosahedral phase in the alloys containing the special elements has been interpreted to result from an increase in instability of supercooled liquid accompanied by an ease of nucleation of icosahedral phase through the introduction of weak bonding sites in the supercooled liquid structure consisting mainly of short-range icosahedral atomic configurations. The first aim of this paper is to review alloy systems in which the icosahedral phase precipitates during heating from supercooled liquid, kinetic behavior and microstructure for the precipitation of the icosahedral phase, and mechanical properties of icosahedral base alloys in the Zr-, Hf- and Cu-based alloys containing the special elements. The second is to investigate the reason for the role of the special elements in the precipitation of the icosahedral phase.

#### 2:00 PM \*LL6.2

**Quasicrystals and Related Phases in Multicomponent Alloy Systems.** J Eckert, U Kuehn, S Scudino and N Mattern; Institute of Metallic Materials, IFW Dresden, Dresden, Saxony, Germany.

(Nano-)quasicrystalline, amorphous and nanocrystalline multicomponent Al- and Zr-based alloys are attractive materials for advanced high-strength applications. Further property improvements are achievable by designing multiphase composite materials with optimized length-scale, volume fraction and intrinsic properties of the constituent phases. Such alloys can be synthesized by quenching from the melt or by solid state reaction using mechanical alloying / ball milling techniques. Many studies suggest a linkage between the short-range order of the amorphous phase and the formation of quasicrystals or other related complex intermetallic compounds. These suggestions are based on the idea that the liquid prior to vitrification contains icosahedral short-range order or clusters, which are retained in the glass upon quenching, and even may stabilize the glassy state/supercooled liquid. Moreover, there are speculations that solid state synthesis does not provide the opportunity to form the initial short-range order as proposed in liquid-to-solid processing routes. We have investigated single-phase alloys and multiphase composites containing different volume fractions of (quasi-)crystalline or amorphous phases with different length-scale of the constituent phases prepared by quenching from the liquid as well as by solid state reaction. Examples for the phase formation and the development of the microstructure under different processing conditions, the short-range order and for the thermal stability of the metastable alloys will be given, and critically discussed by considering the underlying thermodynamics and kinetics of metastable phase formation. Data for the mechanical behavior will be presented, revealing that in particular the properties of composite materials in quasicrystal-forming systems can be tuned within a wide range of strength and ductility as a function of volume fraction, size and morphology of the different phases.

#### 2:30 PM LL6.3

**Quasicrystal Formation in Zr-Based Metallic Glasses: Influence of Ag.** Lyudmila Lyubenova and Uwe Koster; Dept. Biochem. & Chem. Eng., University of Dortmund, Dortmund, Germany.

In the Zr-Cu-Ni-Al system one of the best bulk metallic glass forming alloys was found. But in a narrow concentration range around the composition of the best glass forming ability (e.g.,  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ) formation of quasicrystals either by primary or polymorphic reaction is known to proceed during annealing [1]. Exchange of Cu or Ni by other late transition elements was found to stabilize or deteriorate quasicrystal formation. The reason for such an influence on the formation of quasicrystals are not known as yet. Recent papers mention for example some evidence that the quasicrystals in these alloys are a hybrid of two structural elements, i.e. the tetragonal  $Zr_2Ni$  ( $Al_2Cu$ ) and the tetragonal  $Zr_2Cu$  ( $MoS_2$ ) structure, as well as the influence of a positive enthalpy of mixing for at least one of the interactions, namely that between TM and M. Whereas replacement of Cu by Ag is known to result in nanocrystallization of the quasicrystalline phase [2], small Ag additions in the range of 0.5 to 1 at.% reduces the number of nucleation sites significantly, thus allowing growth of rather large quasicrystals. This paper presents a detailed study on the influence of Ag additions on the formation of icosahedral quasicrystals. Combining electron microscopy with DSC as well as crystallization statistics allows the separation of the influence of Ag on the relevant crystallization parameter, for example the interfacial energy. Reasons for the observed behavior will be discussed in detail. The results may help to understand the ruling factors on the formation of quasicrystals in Zr-based glasses. [1] U.Köster, J.Meinhardt, S.Roos, H.Liebertz, Appl.Phys.Lett. **69** (1996), 179; [2] J.Saida, M.Matsushita, A.Inoue, Mater.Sci.Forum **360 – 362** (2001), 73.

#### 2:45 PM LL6.4

**Influence of Al on quasicrystal formation in Zr-Ti-Nb-Cu-Ni-Al metallic glasses.** S. Scudino<sup>1</sup>, J. Eckert<sup>1</sup>, U. Kuehn<sup>1</sup>, H. Breitzke<sup>2</sup>, K. Lueders<sup>2</sup> and L. Schultz<sup>1</sup>; <sup>1</sup>Institut fuer Metallische Werkstoffe, IFW Dresden, Dresden, Germany; <sup>2</sup>Fachbereich Physik, Freie Universitaet Berlin, Berlin, Germany.

Although Zr-based glassy alloys that form a metastable quasicrystalline phase upon partial devitrification have attracted much attention in the last years and several investigations have been performed, the knowledge regarding quasicrystal formation is still incomplete. In order to clarify the role of Al, an element often present in quasicrystal-forming Zr-based alloys, on the formation of quasicrystals, the devitrification of glassy ( $Zr_{61.62}Ti_{8.64}Nb_{2.7}Cu_{15.03}Ni_{12.01}$ )<sub>100-xAlx</sub> alloys with x = 0, 2.5, 5 and 7.5 at.% prepared by melt spinning was investigated. The crystallization

behavior was studied by isochronal and isothermal thermal analysis, x-ray diffraction and electron microscopy. The devitrification of the ribbons is characterized by the formation of a metastable quasicrystalline phase during the first stage of the crystallization process, followed by successive transformation into intermetallic compounds at higher temperatures even for the alloy with  $x = 0$ . Therefore, Al is not essential for quasicrystal formation in the present alloys. However, it affects the properties of the amorphous as well as of the quasicrystalline phase. In fact, with increasing Al content, the range of stability of the quasicrystalline phase decreases whereas the stability of the amorphous phase increases together with a slight increase of the supercooled liquid region. Thus, it is concluded that although the addition of Al improves the properties of the glassy phase, it has no beneficial effect on the formation of quasicrystals.

### 3:30 PM \*LL6.5

#### Topological and Chemical Short-Range Order in Undercooled and Stable Melts Forming Quasicrystals and Approximants.

Dirk Holland-Moritz<sup>1</sup>, Thomas Schenk<sup>1,4</sup>, Virginie Simonet<sup>2</sup> and Robert Bellissent<sup>3</sup>; <sup>1</sup>Institut fuer Raumsimulation, DLR, Koeln, Germany; <sup>2</sup>Laboratoire Louis Neel, Grenoble, France; <sup>3</sup>Centre d'Etudes Nucleaires, Grenoble, France; <sup>4</sup>European Synchrotron Radiation Facility, Grenoble, France.

It was suggested already in 1952 by Frank that an icosahedral short-range order should be energetically favored in undercooled melts of systems consisting of atoms of spherelike geometrical symmetry. This hypothesis was recently experimentally confirmed by diffraction experiments on stable and undercooled melts of pure metals. In this work systematic in-situ investigations on the short-range order of deeply undercooled liquids of alloys forming quasicrystalline and polytetrahedral phases by elastic neutron scattering are presented. For  $Al_{13}(Co,Fe)_4$  melts partial structure factors were determined which allow the analysis of both the topological and the chemical short-range order as a function of the temperature. These investigations indicate an icosahedral topological short-range order prevailing in the undercooled liquids which is accompanied by a pronounced chemical short-range order such that the first coordination shell around transition metal atoms consists preferentially of Al-atoms. An enhancement of the topological and the chemical short-range order is observed, if the temperature is decreased. The influence of this short-range order on the nucleation behavior of quasicrystalline phases in undercooled liquids is discussed.

### 4:00 PM \*LL6.6

#### Metastable States During Devitrification of Metallic Glasses.

Matthew J. Kramer<sup>1</sup>, Dan J. Sordelet<sup>1</sup> and Pete L. Lee<sup>2</sup>; <sup>1</sup>Ames Laboratory, Iowa State University, Ames, Iowa; <sup>2</sup>Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois.

High energy-high temperature X-ray diffraction was used to investigate the time-temperature transformations in the short-range order (SRO) of  $Zr_{70}Pd_{30}$  and  $Zr_{70}Pd_{20}Cu_{10}$  alloys produced by rapid solidification (RS) and mechanical milling (MM). The differences in the total scattering function  $S(Q)$  as a function of time at a temperature  $\sim 50$  K below the crystallization temperature were determined. After rapidly heating, diffraction data were taken at 5 min intervals for 180 min. The difference in the  $S(Q)/s$  over this time interval shown that both alloys undergo a structural relaxation prior to nucleation and growth. The RS alloys are shown to have SRO dominated by a random polyhedral configuration close to icosahedral symmetry. The MM samples have SRO to medium-range order (MRO) which is topologically similar to the  $MoSi_2$ -type structure (I4/mmm), but chemically closer to the  $Al_2Cu$ -type structure (I4/mcm). Reverse Monte Carlo (RMC) simulations of the experimentally measured atomic pair distributions were performed to identify the partial pair distributions and differences in local chemical ordering. At nucleation, the RS alloy is transformed to the icosahedral phase while the MM alloy forms the  $Al_2Cu$ -type structure. The differences in the transformation pathways between the RS and MM alloy can be understood in terms of the differences free energy of the SRO relative to the possible metastable structures. The work at Ames Laboratory was supported by the U.S. Dept. of Energy through Iowa State University under contract No. W-7405-ENG-82. The Midwest Universities Collaborative Access Team (MUCAT) sector at the APS is supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, through the Ames Laboratory under contract No. W-7405-Eng-82. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

### 4:30 PM LL6.7

#### Investigation by Transmission Electron Microscopy, EDX and EELS of Quasicrystal Phase in

$Zr_{46.75}Ti_{8.25}Ni_{10}Cu_{7.5}Be_{27.5}$  and  $Ti_{40}Zr_{25}Ni_{8}Cu_{9}Be_{18}$  Alloys: Effect of the Be in the Quasicrystal Formation.

Bertrand Van de Moortele<sup>1,2</sup>, Jean-Marc Pelletier<sup>1</sup>, Won Tae Kim<sup>3</sup>,

Thierry Epicier<sup>1</sup> and Jean-Louis Soubeyroux<sup>4</sup>; <sup>1</sup>GEMPPM, INSA de Lyon, Villeurbanne, France; <sup>2</sup>IPMC, EPFL, Lausanne, Switzerland; <sup>3</sup>Applied Science Division, Chongju University, Chongju, South Korea; <sup>4</sup>CRETA, CNRS, Grenoble, France.

Since the first observation of quasicrystal phase in a rapidly quenched Al-Mn alloy by Shechtman et al., many materials containing quasicrystals were discovered. In particular, quasicrystal could be observed in metallic glasses during devitrification. Such phases are metastable and disappear when temperature or time of ageing increases. It is well known that an increase of Be-content between from Vit1 (22.5% Be) to Vit4 (27.5 %Be) alloy leads to the formation of a quasicrystal phase during ageing. Also stable quasicrystalline phase has been reported to form during crystallization of an amorphous  $Ti_{40}Zr_{25}Ni_{8}Cu_{9}Be_{18}$ . In metallic glasses, the formation of quasicrystalline phase often takes place by a polymorphous transformation, i.e. that only a change of local order is necessary to go from the matrix to the quasicrystal. However very few chemical analyses have been performed on such phases to ensure that composition of these phases is similar to that of the amorphous matrix. The aim of this work is to compare the chemical evolution of two metallic glasses during crystallization with an emphasis of Be effect on the formation of quasicrystal. EDX and EELS analyses show that the quasicrystalline phase in the  $Zr_{46.75}Ti_{8.25}Ni_{10}Cu_{7.5}Be_{27.5}$  alloy (Vit4) does not contain Be, indicating that a chemical partitioning takes place during the precipitation. Measurements in the  $Ti_{40}Zr_{25}Ni_{8}Cu_{9}Be_{18}$  alloy indicate an important change in the composition. This influence of the Be content on the quasicrystal formation is discussed.

### 4:45 PM LL6.8

#### The micromechanism of amorphous-to-quasicrystalline transformation in a Zr-based bulk metallic glass.

Lin Liu<sup>1,2</sup>, K. C. Chan<sup>1</sup>, G. K. H. Pang<sup>3</sup> and K. Z. Baba-kishi<sup>3</sup>; <sup>1</sup>Department of Industrial and System Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong; <sup>2</sup>Department of materials Science and Engineering, Huazhong University of Science and technology, Wuhan, Hubei, China; <sup>3</sup>Department of Applied Physics, The Hong Kong Polytechnic University, Kowloon, Hong Kong.

A Zr-based bulk metallic glass with a diameter of 2 mm was successfully prepared by copper-mould casting. The phase transformation of the glass was investigated by x-ray diffraction (XRD), differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). It was found that the bulk metallic glass obtained exhibits two distinct exothermic reactions. The first one corresponds to the formation of quasicrystals from the amorphous phase, while the second reaction results from the formation of a stable intermetallic compound from the previously formed quasicrystals. In order to understand the micro-mechanism governing the amorphous-to-quasicrystalline transformation, high resolution TEM coupled with nano-scale EDX was employed to monitor the structural evolution of the glass with the increase of temperature. It was found that the amorphous-to-quasicrystalline transformation does not follow the traditional nucleation/growth mechanism. Instead, it undergoes a series of inter-processes with the formation of a set of metastable phases. The metastable phases are highly disordered and possess a high density of lattice defects, such as dislocations, stacking faults and nano-twins. The lattice ordering of the metastable phases gradually modified with the increase of temperature, and finally fell into the lattice array and symmetry of quasicrystal. EDS revealed that no change in the compositions was involved in the whole process of the phase transformation, suggesting that the amorphous-to-quasicrystalline transformation in the present bulk metallic glass is a non-polymorphous reaction, and the transformation seems to be governed by the lattice-self-modification.

SESSION LL7: Poster Session

Chair: Yasushi Ishii

Tuesday Evening, December 2, 2003

8:00 PM

Exhibition Hall D (Hynes)

### LL7.1

Novel Microstructures and Microstructural Evolution During Cladding and Remelting of Quasicrystal Forming AlCuFe on Pure Aluminium. Krishanu Biswas<sup>1</sup>, Rolf Galun<sup>2</sup>, Kamanio Chattopadhyay<sup>1</sup> and Barry L. Mordike<sup>2</sup>; <sup>1</sup>Metallurgy, Indian Institute of Science, Bangalore, Karnataka, India; <sup>2</sup>IWW, Technical University, Clausthal-Zellerfeld, Germany.

In an earlier work [1], we have shown that it is feasible to form quasicrystalline phases in clad and remelted layers prepared on aluminium substrate with a continuous wave CO<sub>2</sub> laser of 2.5 kW power. It has been found that the clad and remelted layers contained cracks and pores and the quasicrystalline phase content in the

microstructure was quite small as compared to the crystalline phases. In order to improve the quality of the clad layers as well as the quasicrystalline phase content, we have changed the process variables by using a higher power laser (5 kW). The higher power is necessary because the interaction of aluminium with CO<sub>2</sub> laser is weak. This paper deals with the detailed microstructural evolution during the laser processing. The experimental results suggest that this endeavor has been successful. The X-ray diffraction analysis indicates the presence of icosahedral phase along with aluminium monoclinic Al<sub>13</sub>Fe<sub>4</sub> and tetragonal CuAl<sub>2</sub> and aluminium. The optical microscopic examinations reveal the microstructural difference between the clad and remelted layers. The clad layers show two-layered microstructure. The first layer evolves through a regrowth from the substrate by cellular manner and then the cellular front breaks into dendritic triggered by heterogeneous nucleation of Al<sub>13</sub>Fe<sub>4</sub>. The second layer shows predominantly Al<sub>13</sub>Fe<sub>4</sub> dendrites. On the other hand, the remelting of clad layers leads to microstructural evolution with four distinctly different microstructural layers. The scanning electron microscopic examinations show the different growth morphologies of phases. The presence of ten-pointed star like as well as lath shaped morphology of Al<sub>13</sub>Fe<sub>4</sub> have been found in the clad and remelted layers. The transmission electron microscopic analysis reveals the phase morphologies and solidification path ways. The growth of icosahedral phase at the interface of long faulted Al<sub>13</sub>Fe<sub>4</sub> dendrites by conventional peritectic reaction between liquid and primary Al<sub>13</sub>Fe<sub>4</sub> is common. The independent nucleation of icosahedral phase has been found in the remelted layer. This clearly indicates the different levels of undercooling the liquid has undergone before the nucleation of the primary phase. The novel microstructures, like the formation of tetragonal omega phase with shell like morphology around the icosahedral phase and ten-pointed star like growth of icosahedral phase from a central icosahedral grain have been observed. [1] K. Chattopadhyay, K. Biswas, S. Bysakh, G. Phanikumar, A. Weishit, R. Galun and B.L. Mordike, MRS Proceedings, 2001, Vol. 643, pp.K15.3.1-K15.3.12

#### LL7.2

##### Atomic Short-Range Order in Al-Ni-Co Decagonal Quasicrystals.

Hiroshi Abe, Materials Science and Engineering, National Defense Academy, Yokosuka, Kanagawa, Japan.

Diffuse scattering from atomic short-range order (SRO) of decagonal quasicrystals was observed in samples quenched above transformation temperature. By quantitative measurements using anomalous X-ray scattering (three wave length method), SRO diffuse scattering was divided into three pair correlation function, that is, Al-Ni, Ni-Co and Al-Co. Furthermore, the calculated diffuse scattering is in good agreement with the experimental one, where SRO parameters are determined by Monte Carlo method.

#### LL7.3

##### Local Chemical Fluctuation-induced Structural Variations in Al<sub>72</sub>Ni<sub>20</sub>Co<sub>8</sub> Quasicrystals.

Yanfa Yan<sup>1</sup> and Stephen Pennycook<sup>2</sup>; <sup>1</sup>National Renewable Energy Laboratory, Golden, Colorado; <sup>2</sup>Oak Ridge National Laboratory, Oak Ridge, Tennessee.

We investigate local chemical fluctuation-induced structural variations in Al<sub>72</sub>Ni<sub>20</sub>Co<sub>8</sub> quasicrystals using first principles density-functional total-energy calculations. We find that local chemical fluctuation can cause large structural variations on the central rings of the 2nm clusters. The relationship between the structural variation and phason-related defects will be discussed.

#### LL7.4

##### Local Order in Single Grain Cd-Yb Icosahedral Phase.

Y. Q. Wu, M. J. Kramer and T. A. Lograsso; Metals and Ceramics Sciences, Ames Laboratory, Iowa State University, Ames, Iowa.

Bulk, single grains of the icosahedral Cd<sub>84</sub>Yb<sub>16</sub> quasicrystalline phase were examined by high resolution transmission electron microscopy (HRTEM). Foils for HRTEM were electron discharge machined from larger grains on the order of 0.75 cm<sup>3</sup> and mechanically thinned to ~200 μm then electropolished. Examination was performed along the two and five-fold axes of the primitive icosahedral structure. Through focal images were obtained and compared to cluster structure proposed by Tsai et al. Nature 408 (537) 2000 and the approximant based on the YCd<sub>6</sub> solved by A.C. Larson and D.T. Cromer, Acta Cryst. B, 27 (1875) 1971. Image reconstruction of the multiple through-focal series for both the two and five-fold axes are consistent with the local cluster structure of concentric polyhedra consisting of Cd tetrahedron (1/3 occupied icosahedron), Cd dodecahedron, Yb icosahedron and a Cd icosidodecahedron. Edge-sharing of the clusters can result in complete tiling of the 2-D projections. Simple matching rules are being investigated to construct a 3-D model.

#### LL7.5

##### Three-Dimensional Atomic Structure of Icosahedral Zn-Mg-Y

Quasicrystal. Seung-Tae Hong<sup>1</sup> and John D. Corbett<sup>2</sup>; <sup>1</sup>LG Chem, Taejeon, South Korea; <sup>2</sup>Chemistry, Iowa State University, Ames, Iowa.

We show for the first time that the novel three-dimensional atomic structure of a QC, that of Zn<sub>50</sub>Mg<sub>42</sub>Y<sub>8</sub> as an example, can be derived from single crystal X-ray diffraction data without assuming higher dimensionality. The data were collected with a CCD area detector. About 2200 reflections were measured with  $I > 0.003 I_{max}$ . The Cartesian coordinates were used for the reciprocal vectors on a Fourier map as fractional indices relative to the three orthogonal 2-fold axes in Ih symmetry. Assuming centrosymmetry of the QC, among a total of 45 shells of independent peaks, five of the stronger independent sets were selected for the initial Fourier transformation. All of the possible combination of phases,  $2^5=32$ , were tried to calculate electron density maps for volumes of  $10 \times 10 \times 10 \text{ \AA}^3$ , among which careful examination showed that only one sensible model was produced. The tentative phases for the other reflection sets were then obtained via an inverse Fourier transformation, and in turn, an electron density map was calculated by Fourier transformation, which gave only sharper peaks, and so on. The volume of interest was increased, and the routine was iterated directly to convergence. More than 27,805 atoms were eventually located within a sphere of ~50 Å radius. The atom types were assigned according to observed electron densities and the overall stoichiometry. The resulting three-dimensional model has a global icosahedral symmetry and consists of many isolated or interpenetrated icosahedral clusters, each of which is surrounded by a dodecahedron. The model also clearly reveals structural motifs as well as the relationships between them in real space. This approach provides a significantly simpler and more direct way to build a three dimensional structural model, consistent with the observed X-ray diffraction, the measured stoichiometry, and density.

#### LL7.6

##### Decagonal AlNiCo: Lattice gas Monte-Carlo on an over-sized atomic surface.

Siddhartha Naidu<sup>1</sup>, Mike Widom<sup>1</sup> and Marek Mihalkovic<sup>2,1</sup>; <sup>1</sup>Dept. of Physics, Carnegie-Mellon Univ., Pittsburgh, Pennsylvania; <sup>2</sup>Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia.

We investigate the structure of the high temperature decagonal quasicrystalline phase of Al<sub>72</sub>Ni<sub>20</sub>Co<sub>8</sub> using a lattice gas Monte-Carlo simulation. To avoid biasing the atomic surface structure an over dense site list with a large fraction of free sites was chosen which permitted the simulation to explore a larger region of perpendicular space. The occupancy on the atomic surface was expanded on harmonic functions to aid analysis and especially to account for the phason drift associated with the over-sized region of perpendicular space. In addition correlation functions of the structure were calculated in both perpendicular and parallel space. Special considerations associated with the over-dense site list and the large approximants used are explored. The results obtained are discussed and compared to experimental determinations of the structure of this phase.

#### LL7.7

##### Ti-Zr-Ni and Ti-Hf-Ni Quasicrystals and Approximants.

V. T. Huett, J J Hartzell and K F Kelton; Department of Physics, Washington University, Saint Louis, Missouri.

Zirconium and hafnium are the two most similar elements known, having almost identical size and chemistry. However, rapidly quenched samples of Ti<sub>45</sub>Zr<sub>38</sub>Ni<sub>17</sub> form quasicrystals, whereas rapidly quenched samples of Ti<sub>40</sub>Hf<sub>40</sub>Ni<sub>20</sub> form a high order 3/2 rational approximant to the quasicrystal. Further, the as-cast phases are different; Ti<sub>45</sub>Zr<sub>38</sub>Ni<sub>17</sub> cast samples form a C14 Laves phase, while Ti<sub>40</sub>Hf<sub>40</sub>Ni<sub>20</sub> cast samples form a Ti<sub>2</sub>Ni-type phase. Both alloys store large quantities of hydrogen, up to a hydrogen-to-metal atom ratio of 1.7. However, while gas phase charging of the Ti<sub>45</sub>Zr<sub>38</sub>Ni<sub>17</sub> quasicrystals always produces an irreversible hydride phase the hafnium 3/2 RA composition shows little to no hydride formation when charged at the lower hydrogenation temperatures. To investigate these differences the phases in as-cast and as-quenched Ti<sub>45</sub>Zr<sub>38-x</sub>Hf<sub>x</sub>Ni<sub>17</sub> alloys were systematically studied using x-ray and electron diffraction. New measurements of the equilibrium vapor pressure as a function of hydrogen concentration are also presented. These show a pressure plateau near 10 atm., a suitable range for possible hydrogen storage applications.

#### LL7.8

##### Coincident Lattice Sites between Cubic β-Zr(Pt) and an Isochemical Icosahedral Phase in Rapidly Solidified Zr<sub>80</sub>Pt<sub>20</sub> Alloys.

X. Y. Yang, M. J. Kramer, E. A. Rozhkova, M. F. Besser and D. J. Sordelet; Metal and Ceramic Sciences Program, Ames Laboratory, Ames, Iowa.

Coexistence of a bcc hyperstoichiometric β-Zr(Pt) (Im3m) superstructure and a primitive icosahedral phase (pi phase) in rapidly

solidified Zr80Pt20 alloys has been studied by transmission electron microscope (TEM). Results show that the two phases have a well-defined orientation relationship, good crystallographic match and nearly identical stoichiometry. Orientation relationship can be described as: two-fold axes of the pi phase are nearly parallel to  $\langle 110 \rangle$ ,  $\langle 111 \rangle$ ,  $\langle 112 \rangle$  and  $\langle 113 \rangle$  axes in  $\beta$ -Zr(Pt); similarly, five- and three-fold axes have comparable orientations to  $\langle 110 \rangle$  and  $\langle 113 \rangle$  axes and to  $\langle 111 \rangle$ ,  $\langle 115 \rangle$  and  $\langle 123 \rangle$  axes, respectively, in  $\beta$ -Zr(Pt). The common thing in all the observed orientation relationships is the registry between  $\{110\}$   $\beta$ -Zr planes and icosahedral  $\{211111\}$  five-fold or  $\{221001\}$  two-fold planes. The space group Im3m for bcc  $\beta$ -Zr(Pt) and the observed orientation relationship preclude  $\beta$ -Zr(Pt) as an approximant to the pi phase, even though they appear to have similar primary interplanar spacing of 0.25nm. Both  $\beta$ -Zr(Pt) and the pi phase are distorted,  $\beta$ -Zr(Pt) maintain a basic  $\beta$ -Zr Bravais lattice but with aperiodic superlattice. Morphologies and growth habit suggest that the pi phase forms first, followed by an easy nucleation of the  $\beta$ -Zr(Pt) on the surfaces of the pi phase. To the best of our knowledge, this is the first report on an epitaxial crystalline associated with i phase in rapidly solidified Zr80Pt20 alloys.

#### LL7.9

**Electrical Properties of Ag-In-(Yb,Ca) quasicrystals and their approximants.** Daisuke Tetsuka, Ryuji Tamura and Shin Takeuchi; Materials Science and Technology, Tokyo University of Science, Noda, Chiba, Japan.

The Ag-In-(Yb,Ca) quasicrystals discovered by Guo et al. are obtained by replacing Cd with equal amounts of Ag and In in the binary Cd-(Yb,Ca) quasicrystals. The ternary alloys are of a particular interest from a viewpoint of the influence of the chemical disorder upon the electronic transport. In this work, the electrical properties of Ag-In-(Yb,Ca) quasicrystals and approximants were investigated in order to gain insight into the influence of the replacement of Cd with Ag and In in the electronic transport. As a result, we have observed that the ternary approximant Ag-In-Yb exhibits negative temperature coefficient of the resistivity with a resistivity maximum at a low temperature, which is similar to that seen in the ternary Ag-In-Yb quasicrystal. The result is in striking contrast with the case of the binary Cd-Yb system where the approximant exhibits a positive temperature coefficient in the whole temperature region. Such a result may imply that the occurrence of the negative temperature coefficient of the resistivity is a consequence of the chemical disorder that might have been induced by the replacement of Cd with In and Ag.

#### LL7.10

Abstract Withdrawn

#### LL7.11

**Low Energy Surface Phonons of Decagonal and Icosahedral Quasicrystals Studied by Inelastic He Atom Scattering.**

Hem Raj Sharma<sup>1</sup>, Katharina J. Franke<sup>1</sup>, Wolfgang Theis<sup>1</sup>, Philipp Ebert<sup>3</sup>, Peter Gille<sup>2</sup> and Karl-heinz Rieder<sup>1</sup>; <sup>1</sup>Institut fuer Experimental physik, Freie Universitaet Berlin, Berlin, Germany; <sup>2</sup>Institut fuer Kristallographie und Angewandte Mineralogie, Ludwig-Maximilians-Universitaet Muenchen, Munich, Germany; <sup>3</sup>Institut fuer Festkoerperforschung, Forschungszentrum Juelich GmbH, Juelich, Germany.

With the successful preparation of high structural quality surfaces, it has been possible to measure low energy surface phonons (Rayleigh mode) of quasicrystals by He atom time of flight (TOF) technique. The tenfold surface of decagonal Al<sub>71.8</sub>Ni<sub>14.8</sub>Co<sub>13.4</sub> and the fivefold surface of icosahedral Al<sub>70.5</sub>Pd<sub>21</sub>Mn<sub>8.5</sub> are found to possess well-defined Rayleigh modes with isotropic sound velocities of about 3840 m/s and 3470 m/s, respectively. The observed sound velocities are in good agreement with calculations based on the respective bulk data. The experimental phonon dispersions exhibit Quasi-Brillouin centers located at strong Bragg peaks. On the tenfold surface, single phonon peaks are measurable up to a sample temperature of about 550°C without shift in position indicating that the sound velocity does not change appreciably up to this temperature. The phonon peak intensity decreases monotonically with wavevector and becomes non separable from the broad background intensity for wavevectors larger than 0.30 Å<sup>-1</sup>.

#### LL7.12

**A maximum density principle for surfaces of icosahedral and decagonal quasicrystals.** Zorka Papadopolos<sup>1</sup>, P. Pleasants<sup>2</sup>, G.

Kasner<sup>3</sup>, V. Fournee<sup>4</sup>, C. Jenks<sup>5</sup>, J. Ledieu<sup>6</sup> and R. McGrath<sup>6</sup>; <sup>1</sup>Inst. fuer Theoretische Physik, Univ. Tuebingen, Tuebingen, Germany; <sup>2</sup>Dept. of Mathematics, The Univ. of Queensland, Queensland 4072, Queensland, Australia; <sup>3</sup>Inst. fuer Theoretische Physik, Univ. Magdeburg, Magdeburg, Germany; <sup>4</sup>Center d'Ingenierie des Matriaux, Ecole des Mines de Nancy, Nancy, France; <sup>5</sup>Ames Lab., Iowa State University, Ames, Iowa; <sup>6</sup>Surface Sci. Res. Centre, The University of Liverpool, Liverpool, United Kingdom.

The surfaces of crystals correspond roughly to maximally dense planes of atoms in the bulk of the material, so-called bulk-terminations. Comparing theoretical models of quasicrystals with experimental results, we find that this correspondence breaks down and that surfaces parallel to the densest planes in the bulk are not the most stable. The correspondence can be restored by recognizing that there is a contribution to the surface not just from one geometrical plane but from a layer possibly containing more than one plane. We find that not only does the stability of surfaces in the principal directions match the density of the corresponding layer-like terminations but the detailed geometric appearance of the surfaces depends on the shape of the graph of the density of parallel layers as a function of position in coding space. We study in particular icosahedral Al-Pd-Mn [1] and decagonal Al-Cu-Co [2]. [1] Z. Papadopolos, P. Pleasants, G. Kasner, V. Fournee, T. Cai, C. Jenks, P. Thiel, J. Ledieu, and R. McGrath: A maximum density rule for surfaces of quasicrystals, preprint: cond-mat/0302335 [2] A.R. Kortan, Phys. Rev. Lett 64 (1990) 200

#### LL7.13

**Corrosion properties of quaternary Al-based quasicrystal thin films.** Michael S. Donley<sup>1</sup>, Alexander N. Khramov<sup>2</sup>, Linda S. Kasten<sup>3</sup>

and Seva Balbyshev<sup>2</sup>; <sup>1</sup>Nonmetallic Materials Division, Wright-Patterson AFB, WPAFB, Ohio; <sup>2</sup>Universal Technology Corp., Dayton, Ohio; <sup>3</sup>University of Dayton Research Institute, Dayton, Ohio.

Aluminum-based quasicrystals are insulator alloys composed of 70-80% of aluminum. Recent work has shown that thin film quasicrystal coatings have unique properties such as very high electrical and thermal resistivities, very low surface energy, and resistance to corrosion. However, there exists no comprehensive study on corrosion protection afforded by quasicrystal thin films and the mechanism of protection of various metal alloys. The corrosion related properties of Al-Co-Fe-Cr quasicrystal coatings have been investigated on AA2024 and AA7075 substrates. Quaternary Al-based quasicrystal thin films were investigated on aerospace Al alloys for corrosion protection applications. Results of microstructural and surface chemistry analyses of the quasicrystal films are presented. The thin film deposition parameters are discussed briefly. The corrosion protection properties of the films have been studied by potentiodynamic scan and electrochemical impedance spectroscopy. Morphology studies and electrochemical analysis of quasicrystal films have shown that quaternary Al-based quasicrystal thin films possess unique corrosion control properties. Corrosion properties were found to be a function of target composition, deposition parameters, and film's structural characteristics. High resistance to prolonged electrolyte attack makes these coatings strong candidates for corrosion protection surface treatment of aircraft Al alloys. These films can be utilized as conversion coatings for Al substrates or incorporated into a full coating system containing an organic primer and a topcoat.

#### LL7.14

**LEED Studies of the 10-Fold Surface of d-Al-Ni-Co and Xe Adsorption.** Nicola Ferralis<sup>1</sup>, Katarina Pussi<sup>2</sup>, Martin Gierer<sup>3</sup>, C. J.

Jenks<sup>4</sup>, I. R. Fisher<sup>4</sup>, M. Lindroos<sup>2</sup>, Ronan McGrath<sup>5</sup> and Renee D Diehl<sup>1</sup>; <sup>1</sup>Physics Dept and Materials Research Institute, Penn State University, University Park, Pennsylvania; <sup>2</sup>Physics Institute, Tampere University of Technology, Tampere, Finland; <sup>3</sup>Institut fuer Kristallographie und Mineralogie, Universitaet Muenchen, Muenchen, Germany; <sup>4</sup>Ames Laboratory, Iowa State University, Ames, Iowa; <sup>5</sup>Physics Dept and Surface Science Centre, University of Liverpool, Liverpool, United Kingdom.

A dynamical low-energy electron diffraction (LEED) study of the structure of the clean 10-fold surface of Al<sub>72</sub>Ni<sub>11</sub>Co<sub>17</sub> at 50 K indicates that the surface structure is consistent with a truncation of the bulk structure determined by x-ray diffraction [1]. This model consists of periodically stacked planes, each of which has a structure based on a Penrose tiling having 5-fold symmetry, with each plane rotated by  $\pi/5$  relative to the next, in an ABAB stacking sequence. LEED intensity data were measured over the energy range 20-450 eV. The calculational approach was similar to that used previously for icosahedral quasicrystal surfaces [2,3]. Aside from a small amount of surface relaxation in the top surface layers and some intraplanar rumpling, the best-fit structure is very similar to a bulk truncation. Xe adsorbed onto this surface produces a LEED pattern having 30-fold symmetry, indicative of close-packed Xe islands nucleating and growing in alignment with the quasicrystal structure. Adsorption isobars indicate that the growth is layer-by-layer for at least two layers, and that the hexagonal ordering first occurs upon adsorption of the second layer. The isosteric heat of adsorption for the monolayer was measured to be 247 meV. [1] W. Steurer, T. Haibach, B. Zhang, S. Kek, R. Lueck, Acta. Cryst. B 46 (1993) 661. [2] M. Gierer, M. A. Van Hove, A. I. Goldman, Z. Shen, S. -L. Chang, P. J. Pinhero, C. J. Jenks, J. W. Andereg, C. -M. Zhang and P. A. Thiel, Phys. Rev. B 57 (1998) 7628. [3] T. Cai, F. Shi, Z. Shen, M. Gierer, A. I. Goldman,

M. J. Kramer, C. J. Jenks, T. A. Lograsso, D. W. Delaney, P. A. Thiel and M. A. Van Hove, Surf. Sci. 495 (2001) 19.

#### **LL7.15**

##### **Surface Transformations of Quasicrystalline Al-Pd-Mn.**

Cynthia J. Jenks<sup>1</sup>, Amy R Ross<sup>1</sup>, Thomas A Lograsso<sup>1</sup>, Josh A Whaley<sup>2</sup> and Robert Bastasz<sup>2</sup>; <sup>1</sup>Ames Laboratory, Iowa State University, Ames, Iowa; <sup>2</sup>Sandia National Laboratories, Livermore, California.

Preferential sputtering, as is well-known, causes changes in the surface composition of multi-component materials. To reduce this effect while sputter cleaning surfaces of the quasicrystalline phase of Al-Pd-Mn, He ion bombardment in the energy range 0.5 to 3 keV is often used. The low mass of He helps to equalize momentum transfer to the alloy components. Even so, the topmost surface composition can be changed by just a small exposure to energetic He ions, which tends to preferentially remove Al from the surface. We have explored, using low energy ion scattering, how the structure of the Al-Pd-Mn surface is altered by various He ion sputtering and annealing treatments. The structure appears to be sensitive to small changes in composition and undergoes a number of interesting transformations upon subsequent annealing. In some cases a surface exhibiting 5-fold symmetry result while for others a surface with decagonal symmetry is produced. Evidence for a gradual transformation from crystalline to a seemingly quasicrystalline structure is presented.

SESSION LL8: Surfaces and Coatings  
Chairs: Ronan McGrath and Patricia Thiel  
Wednesday Morning, December 3, 2003  
Fairfax A (Sheraton)

#### **8:30 AM \*LL8.1**

**Self-assembly of Low Dimensional Aperiodic Structures on Quasicrystal Surfaces.** Ronan McGrath, Surface Science Research Centre and Department of Physics, The University of Liverpool, Liverpool, United Kingdom.

We have investigated the clean 5-fold surface of icosahedral i-Al-Pd-Mn using scanning tunnelling microscopy (STM). The surface has several topologies as a function of annealing temperature, and prolonged annealing at 970 K produces a surface which is atomically flat. Atomic resolution images of this surface of i-Al-Pd-Mn show the surface to be bulk-terminated, and we show that a Penrose tiling may be constructed on the surface which is consistent with experimental and mathematical models. The ten-fold surface of d-Al-Ni-Co has been also been imaged with high resolution. This surface also has several topologies depending on anneal temperature, and at 1125 K a flat surface is formed. We have shown using LEED and STM data that the surface is consistent with bulk models. The development of the ability to prepare high quality quasicrystal surfaces opens up the possibility of using these surfaces for the creation of overlayer systems with unusual symmetries. If such systems can be created, they are potentially of great interest as single element quasicrystals, which greatly simplifies the characterisation of their properties [1]. With this goal in mind, we have carried out an investigation into the formation of a Cu overlayer on the icosahedral surface of Al-Pd-Mn. Investigations on the AlPdMn system using STM and LEED reveal 2 different morphological growths. Up to 8 monolayers, a layer-by-layer growth appears. From 8 ML up to 20ML 3D island growth is observed (Stranski-Krastanov growth mode). Although layer-by-layer growth has been monitored closely by STM, atomic resolution is only obtained from the 4th to the 6th layer. A new quasicrystalline LEED pattern is also observed at this coverage. Within these layers, 5 sets of lines following the substrate directions have been observed. Within these lines 2 spacings have been measured, with a ratio close to the Golden Number. In addition the appearance of these lines follows the Fibonacci sequence. Although some atomic structure is still visible within the islands up to 20ML, the LEED pattern degrades beyond this point to finally vanish around 25ML. [1] R.McGrath, J. Ledieu, E.Cox, R.Diehl, J. Phys Cond. Matt. 14 (2002) R1-R26

#### **9:00 AM \*LL8.2**

##### **Quasicrystal as a Promising Supporter and Precursor.**

An-Pang Tsai and Satoshi Kameoka; National Institute for Materials Science, Tsukuba City, Japan.

Quasicrystals, a new form of ordered matter with forbidden symmetries and quasiperiodicity have been found in several alloy systems. Due to the quasi-periodicity, a quasicrystal is generally brittle and therefore not expected to be used as a structural material. Quasicrystalline powders of the thermodynamically stable Al-based alloys contain elements possessing catalytic activity, obtained readily by casting and crushing, are available commercially. We have developed a potential application of quasicrystal as a support(or

precursor) on which metallic and oxide nano-particles responsible for catalytic reactions are promoted by solution leaching. We performed steam-reforming of methanol ( $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$ ) on a number of Al-Cu based stable quasicrystals. The stable Al-Cu quasicrystals reveal high activity for steam-reforming of methanol, quoted in terms of production rate of  $\text{H}_2$  for the reaction, reaches 300 l/kg-min at 623K, being superior to the industrial catalyst. The high activity is ascribed to the formation of nanoparticles of Cu and Fe, and network structure of Al oxides on the surfaces due to preferential dissolution of Al upon leaching of the Al-Cu-Fe quasicrystal. The Fe particles are supposed to act as a barrier suppressing grain growth due to diffusion of Cu atoms. This is an indication that the quasicrystal has potential to be developed as a high temperature catalyst. The thermal stability of the quasicrystalline catalysts strongly rely on the leaching condition.

#### **9:30 AM LL8.3**

##### **Structure, Property and Metal Thin Film Growth on the Surface of the $\xi$ -Al<sub>77.5</sub>Pd<sub>19</sub>Mn<sub>3.5</sub> Approximant Crystal.**

V. Fournée<sup>1</sup>, J. A. Barrow<sup>2</sup>, M. Shimoda<sup>3</sup>, H.-R. Sharma<sup>3</sup>, A. R. Ross<sup>2</sup>, T. A. Lograsso<sup>2</sup>, A.-P. Tsai<sup>3</sup> and P. A. Thiel<sup>2</sup>; <sup>1</sup>LSG2M, CNRS UMR 7584, Nancy, France; <sup>2</sup>Department of Chemistry, Department of Materials Science and Engineering, Ames Laboratory, Iowa State University, Ames, Iowa; <sup>3</sup>National Institute for Material Science, Tsukuba, Japan.

Despite close similarity between quasicrystals and approximant phases, most surface science studies performed so far only deal with true quasiperiodic surfaces and not with approximant. Here we will describe the surface structure of the  $\xi$ -Al<sub>77.5</sub>Pd<sub>19</sub>Mn<sub>3.5</sub> approximant crystal, for which large single grains can now be produced. The surface perpendicular to the pseudo ten-fold axis is investigated by low-energy electron diffraction (LEED), x-ray photoemission diffraction (XPD) and scanning tunnelling microscopy (STM). Both the long-range and short-range order with pseudo-ten fold symmetry is evidenced by LEED and XPD. STM images reveal a terrace and step surface morphology, with details consistent with a bulk termination of the surface. The bulk structure of the  $\xi$  crystal can be described by a sequence of layers stacked along the pseudo ten-fold axis. It appears that the terraces are formed at specific layers. Furthermore, terraces are covered by decagonal rings of Al atoms strongly bounded at specific lattice sites. The rings must be formed during the surface reconstruction upon annealing and are pretty stable. They are identified as part of the pseudo-Mackay clusters from which the 3D structure can be constructed. Then we study the growth of a Pd thin film deposited by electron beam evaporation. Pd do not form a smooth film but rather 3D particles covering the  $\xi$  surface. Pd clusters do not coalesce with time and are relatively stable upon annealing up to 870 K. Clusters have homogeneous size and their average size increases slightly with film thickness, up to 3 nm in diameter at a coverage of 8 monolayers. The local electronic structure of the clusters is studied by scanning tunnelling spectroscopy and appears to be cluster-size dependent, with a transition from non-metal to metal with increasing cluster size. The formation of nano-sized Pd particles on top of the  $\xi$  surface in UHV is to be related to the formation of Pd particles at the surface of leached quasicrystalline Al-Pd-Mn powders, that exhibit an excellent catalytic activity. Our system artificially grown in UHV environment could be used as a model system to get a better understanding of the origin of this property. High catalytic activity may indeed be related to the peculiar electronic structure of the Pd nano-clusters.

#### **9:45 AM LL8.4**

##### **Nucleation and Growth of Metallic Films on Quasicrystalline**

**Al<sub>72</sub>Pd<sub>19.5</sub>Mn<sub>8.5</sub> Surfaces.** Falko Baier, J. A. Barrow and P. A. Thiel; Ames Laboratory, Ames, Iowa.

An atomistic understanding of the nucleation and growth of materials atop quasicrystalline surfaces is important for two reasons. First, it can provide a window on how quasicrystals form and propagate their unique structure. Second, this understanding may be a useful tool for growing 'artificial quasicrystals' in the form of pseudomorphic thin films atop quasicrystalline substrates. For the deposition of Al on the five-fold surface of icosahedral Al<sub>72</sub>Pd<sub>19.5</sub>Mn<sub>8.5</sub> different growth behaviors can be observed. Al atoms show smooth growth at low coverages ( $\leq 1$  ML), and rough growth at higher coverages. Also surface alloying can be observed, in which the step edges change drastically and terrace widths increase in a very narrow coverage regime around one monolayer. Also the time dependent behavior of the step edge structures for different coverage regimes up to a few monolayers was investigated to get information about the kinetics and diffusion processes on the terraces of icosahedral Al<sub>72</sub>Pd<sub>19.5</sub>Mn<sub>8.5</sub> independent of different Al coverages and deposition fluxes. We will compare these results to the nucleation and growth behavior of Ag on the 5-fold surface of icosahedral Al<sub>72</sub>Pd<sub>19.5</sub>Mn<sub>8.5</sub> [1], and studies of Al deposition on an icosahedral Al-Cu-Fe quasicrystal [2]. [1] V. Fournée, T. C. Cai, A. R. Ross, T. A. Lograsso, J. W. Evans, and P.

A. Thiel, *Phys.Rev B* **67** (2003), 033406. [2] T. C. Cai, J. Lediue, R. McGrath, V. Fournée, T. A. Lograsso, A. R. Ross, and P. A. Thiel, *Surf. Sci* **526** (2003), 115-120.

#### 10:30 AM \*LL8.5

**Oxidation of quasicrystals and related compounds and its influence on their industrial production and applications.** Gaetan Bonhomme<sup>1,2,3</sup>, Stephane Raffy<sup>3</sup>, Patrick Weisbecker<sup>2</sup>, Conradin Beeli<sup>4</sup> and Jean-Marie Dubois<sup>2</sup>; <sup>1</sup>Coating Solutions, Saint-Gobain NRDC, Northborough, Massachusetts; <sup>2</sup>Laboratoire de science et genie des materiaux et de metallurgie, ENS Mines Nancy, Nancy, France; <sup>3</sup>Coating Solutions, Saint-Gobain CREE, Cavaillon, France; <sup>4</sup>Laboratory of Solid State Physics, ETH, Zurich, Switzerland.

Saint-Gobain is part of a handful companies strongly committed to research and industrialization of quasicrystals and related compounds. Through close collaboration with the international academic community, especially with the Laboratory of Science & Engineering of Materials and Metallurgy (LSG2M) at Ecole des Mines Nancy, a number of results have been collected on the oxidation behavior of such a class of materials and its influence on industrial production and potential applications. Using a variety of characterization techniques, such as Thermo-Gravimetric Analysis (TGA), X-ray Diffraction (XRD), Atomic Force Microscopy (AFM), X-ray induced Photoelectron Spectroscopy (XPS), Laser ellipsometry and Transmission Electron Microscopy (TEM), the oxidation of samples of different quasicrystalline and approximant compositions (icosahedral i-AlCuFe, orthorhombic approximant O<sub>1</sub>-AlCuFeCr and several other new phases) has been studied in a relatively broad range of temperature (from room temperature up to 950°C). The results of such studies as well as their impact on the properties of these intermetallic alloys will be discussed.

#### 11:00 AM \*LL8.6

**Wetting and Fretting on Quasicrystals and Related Compounds.** Jean-Marie Dubois, LSG2M, EMN, Nancy, France.

Reduced wetting and fretting are two essential surface properties that to a large extent currently embody the technological potential of quasicrystalline coatings. By quasicrystalline compounds, one considers here the whole family of complex Al-(Cu or Pd)-(Fe, Cr or Mn) intermetallics, which comprises true quasicrystals, their approximants and some crystalline materials of related composition. Experimentally, wetting of quasicrystalline surfaces by water is largely reduced in comparison to conventional metal surfaces. Moreover, a clear correlation is observed between the reversible adhesion energy of water and the density of states at the Fermi energy. Such surfaces are necessarily oxidized. Results from recent experiments suggest that the oxide layer plays an essential role in explaining the observed behavior. A model is developed in order to interpret the data, assuming an image force coupling between the water dipoles and the conduction states in the substrate, through the oxide barrier. Our conclusions go beyond the unique wetting behavior of quasicrystals and challenge the historical theory of wetting on metallic surfaces. Similarly, friction and fretting are reduced on quasicrystals. Sharp minima in friction coefficients and adhesive forces, which occur with the quasicrystalline surface in contact with a metallic surface under high frequency, low amplitude motion, are observed at the position of the true quasicrystal in the phase diagram. In high vacuum, the friction coefficient measured in contact against hard-steel riders is characteristically smaller than the one measured against conventional metallic alloys (including steel). Observing that wear is nearly unexisting under such friction conditions, the experiment allows for the first time to derive a fair estimate of the true surface energy of quasicrystals and related complex metallic alloys. The present work was supported by a CNRS-NSF grant for international co-operative research under number 545 and AMTT programme funded by the EC under contract number HPR1-CT-1999-00024 of the "Improving Human Potential" framework.

#### 11:30 AM LL8.7

**Debye Temperature at the Fivefold and Threefold-Symmetry Surface of the Al-Pd-Mn Quasicrystal.** Rouven Luscher<sup>1</sup>, Thomas Fluckiger<sup>1</sup>, Mehmet Erbudak<sup>2</sup> and Ahmet Refik Kortan<sup>2</sup>; <sup>1</sup>Physics, ETHZ, Zurich, Switzerland; <sup>2</sup>OFS Labs, Murray Hill, New Jersey.

The surfaces of the icosahedral Al-Pd-Mn exhibit well-ordered low-energy electron diffraction patterns. According to the standard Debye theory, the temperature dependence of the specular-beam intensity is characteristic of the atomic mean-square vibrational amplitude normal to the surface and yields the surface Debye temperature. Remarkably, for the fivefold and the threefold symmetry surfaces, the logarithm of the relative intensity is linear in temperature up to approximately 500 K, suggesting the validity of the Debye model for quasicrystalline surfaces. We have determined first the temperature dependence of the specular Bragg-peak energy by recording I-V spectra for both surfaces at different temperatures. The

resulting shifts to lower energies are accounted for mainly by a lattice expansion perpendicular to the surface, suggesting a thermal expansion coefficient of the atomic layers as  $24.5 \times 10^{-6}/K$ , for both surfaces. Subsequently, from several measurements, a Debye temperature of  $298 \pm 7$  K is found at 43 eV beam energy for the pentagonal surface and  $301 \pm 10$  K at 61 eV for the threefold-symmetry surface, respectively. The pentagonal surface is known to be the most stable bulk termination, followed by the twofold and threefold symmetry surfaces. This, we evidenced by the microfacet formation of all three symmetry directions on the threefold surface. Even though the two surfaces possess a different morphology, the Debye temperature and hence the corresponding vibrational amplitude of surface atoms shows no significant difference. This implies that the atomic bonding forces characteristic of the local neighborhood of an atom are comparable for both surfaces. The similarity of our surface Debye temperatures to that of the bulk value, suggest that the vibrational modes of the bulk and the surface are also similar, supporting the structural bulk model that incorporates structural voids and thermal vacancies, as reported by various groups.

#### 11:45 AM LL8.8

**Ageing in Ambient Conditions of the Surface of an Approximant Phase in Al-Fe-Cr System: Modifications of the Chemical Structure of the Surface and Consequences on the Surface Properties.** Delphine Veys<sup>1</sup>, Patrick Weisbecker<sup>1</sup>,

Christophe Rapin<sup>2</sup>, Vincent Fourné<sup>1</sup> and Jean-Marie Dubois<sup>1</sup>; <sup>1</sup>LSG2M-Ecole des Mines, Nancy, France; <sup>2</sup>LCSM-Universite Henri Poincare, Nancy, France.

In most of the technological applications that have been suggested or which are already on the market, quasicrystalline materials would be used in the form of coatings or thin films. This allows to circumvent their inherent brittleness and to make use of their interesting surface properties such as low surface energy, low friction coefficient and high resistance to oxidation and corrosion. In the case of Al-based quasicrystals or approximant compounds, surface properties must be influenced by the presence of a native oxide overlayer covering the surface. We will present experimental results providing evidence that this "passive" layer actually evolves with time upon interaction with ambient air and that this ageing of the surface has a strong influence on its physical properties. The same sample was used for all experiments. It is an Al-Cr-Fe approximant crystal. First, elemental quantification and chemical state of the various elements present at the surface is monitored by core-level photoemission spectroscopy as a function of time of exposure to air of the sample surface. Second, X-ray reflectivity measurements are performed for a freshly polished surface and after ageing. The results are in favor of a multilayer structure of the extreme surface: the electronic density, the thickness of each layer and the roughness of each interface can be deduced from fitting the variation of the reflected beam intensity with incidence angle. By combining XPS and X-ray reflectivity, it is suggested that the surface can be modeled as the stacking of three different layers growing onto the substrate. The first layer consists of a thin oxide (mixed aluminum or chromium oxides) on top of the bulk matrix, on which a hydroxide layer develops slowly with time. The third layer is a contamination layer with a high carbon content in contact with the atmosphere. The thickness of the various layers evolves slowly with exposure to ambient atmosphere. This evolution of the surface chemistry influences some of its physical properties. For example, the contact angle of water droplets increases with time, i.e. the reversible adhesion energy of water on the surface decreases upon ageing. The electrochemical behavior of the samples is also investigated by measuring the corrosion potential. After ageing, the surface layer behaves like a pure capacitance, i.e. electrical charges can easily accumulate at the interfaces after a sufficiently long exposure to ambient air. This is something that is not observed for a freshly polished surface. Both observations could be related to a modification of the electrical properties of the overlayer, in relation to the chemical variations mentioned above.

SESSION LL9: Properties IV – Mechanical Properties II

Chair: Michael Feuerbacher

Wednesday Afternoon, December 3, 2003

Fairfax A (Sheraton)

#### 1:30 PM \*LL9.1

**Swift Heavy Ion Irradiation on Quasicrystals.** Ratnamala Chatterjee, Physics, Indian Institute of Technology(Delhi), New Delhi, India.

Irradiation of quasicrystalline materials with swift heavy ions (SHI) has now been studied for quite some time [1,2,3,4&5]. Electronic stopping power (electronic excitations in the target material) corresponding to the inelastic collisions between the incoming swift heavy ions and the electrons of the target material, is the dominant

mechanism by which SHI lose their energy. We would discuss the results of our investigations on the structural modifications and /or any related changes in electronic structure of quasicrystals that might arise from such electronic excitations in the system. For our studies we have chosen a very stable and well studied icosahedral Al-Cu-Fe quasicrystalline system generally in form of rapidly quenched ribbons. The experiments are performed in the pure electronic excitation regime. In this regime, we systematically deposit various ranges of energy ( $\sim 1.3 \text{ keV}/\text{Å}$  to  $4 \text{ keV}/\text{Å}$ ) in to the system, causing electronic excitations in them. The choice of ions generally was dependent on calculations based on Monte-Carlo simulations and some existing literature work on metals/metallic alloys. The samples were irradiated at fluences of a few  $10^{12}$  to a few  $10^{13}$  ions/cm<sup>2</sup> in order to ensure homogeneous irradiation. The effect of these electronic excitations on the electronic structure of the quasicrystals is analyzed by doing in-situ resistivity versus fluence and resistivity Vs temperature measurements. Ex-situ resistivity versus temperature and X-ray diffraction (XRD)/high resolution X-ray diffraction analysis were also made on the irradiated pieces in order to understand the effect of SHI irradiation on quasicrystals. [1] Ratnamala Chatterjee, D. Kanjilal and R. A. Dunlap, Nucl. Instr. and Meth. B, 156, 201 (1999). [2] R. Chatterjee, A. Kanjilal, U. Tiwari, J.M. Ramillon & A. Dunlop, Sol. State. Commun. 120, 289-293, 2001 [3] A. Kanjilal, R.N. Dutta and R. Chatterjee, Vacuum 68, 349-355, 2002. [4] Ratnamala Chatterjee & Alok Kanjilal, ICQ 8 Proceedings, submitted to special issue of J. Non-Crys. Solids, 2002 [5] G. Coddens, A. Dunlop, H. Dammak, Ratnamala Chatterjee, Y. Calvyarac, M. Quiquandon, E. Elkaim, M. Gailhanou and S. Rouziere accepted for publication in NIM B

#### 2:00 PM LL9.2

**From Crystalline to Glassy: Crack Propagation Modes in Decagonal Quasicrystals.** Christoph Rudhart<sup>1</sup>, Peter Gumbsch<sup>2,3</sup> and Hans-Rainer Trebin<sup>1</sup>; <sup>1</sup>Institut fuer Theoretische und Angewandte Physik, Universitaet Stuttgart, Stuttgart, Germany; <sup>2</sup>Institut fuer Zuverlaessigkeit von Bauteilen und Systemen, Universitaet Karlsruhe, Karlsruhe, Germany; <sup>3</sup>Fraunhofer Institut fuer Werkstoffmechanik, Freiburg, Germany.

Numerical experiments have been performed on the propagation of mode-I cracks in a twodimensional decagonal model quasicrystal. In particular, the dependence on temperature, applied load and underlying structure has been investigated. The samples are endowed with an atomically sharp crack and subsequently loaded by linear scaling of the displacement field. The response of the system is monitored by molecular dynamics simulations. The modes of propagation are strongly influenced by the structure of the atomic planes and by tightly bound decagonal clusters. For temperatures below 30 % of the melting temperature T<sub>m</sub> the crack velocity grows monotonically with the applied load. We observe that the crack follows the path of dislocations nucleated at its tip. The tightly bound clusters are circumvented by the crack which results in rough fracture surfaces. For temperatures above 30 % of T<sub>m</sub> the crack does not remain atomically sharp but is blunting spontaneously. As a result, it is not possible to obtain a stable initial condition. To deal with this problem we establish a linear temperature gradient along a strip. From the low temperature regime, where a sharp tip can be stabilized, the crack is driven into a region of elevated temperature. In the range of 70 % - 80 % T<sub>m</sub> the quasicrystal fails by nucleation, growth and coalescence of micro voids. This gradual, dislocation-free crack extension is caused by plastic deformation which is mediated by localized rearrangements comparable to so-called shear transformation zones in amorphous solids. In summary, at low temperatures the crack propagates along planes as in periodic crystals, whereas at high temperatures a glass like behaviour is dominant.

#### 2:15 PM LL9.3

**Cleavage Planes of Icosahedral Quasicrystals: A Molecular Dynamics Study.** Frohmut Roesch<sup>1</sup>, Christoph Rudhart<sup>1</sup>, Peter Gumbsch<sup>2</sup> and Hans-Rainer Trebin<sup>1</sup>; <sup>1</sup>Institut fuer Theoretische und Angewandte Physik, Universitaet Stuttgart, Stuttgart, Germany; <sup>2</sup>Institut fuer Zuverlaessigkeit von Bauteilen und Systemen, Universitaet Karlsruhe, Karlsruhe, Germany.

Fracture has been investigated of a three-dimensional model quasicrystal, the icosahedral binary tiling, with atoms interacting by Lennard-Jones potentials. By measuring the interface energy suitable fracture planes were selected perpendicular to five-, two- and pseudo-twofold axes, and atomically sharp seed cracks were implanted. Loads were applied in mode I. The crack propagation was studied by molecular dynamics close to T=0 K. Brittle fracture was observed, i.e. without dislocation emission, contrasting simulations in two-dimensional decagonal model systems. The cleavage planes turned out rough on the scale of the Bergman clusters. The cracks did not circumvent the clusters completely, but intersected them partially. Cluster intersections by the dynamic cracks, however, were much less pronounced than by the flat seed cracks. The resulting cleavage planes resemble those of cracked i-AlMnPd monitored by scanning tunneling

microscopy (Ph. Ebert et al., 1996, Phys.Rev.Lett. 77, 3827). There is a distinct anisotropy with respect to the in-plane propagation direction of the crack, apparently due to an interplay between the structure of the planes and that of the clusters. For example, in planes of fivefold symmetry, steps are produced by cracks moving along the pseudo-twofold direction, but not along the twofold direction. Autocorrelation functions manifest the rotational symmetry of the cleavage planes in a faint way.

#### 2:30 PM LL9.4

**As Cast Ti-Zr-Ni Quasicrystalline alloys with Excellent Mechanical Properties.** Jianbing Qiang<sup>1</sup>, yingming Wang<sup>1</sup>, Zhiwei Yu<sup>2</sup>, Cuimin Bao<sup>1</sup> and Chuang Dong<sup>1,3</sup>; <sup>1</sup>materials engineering, Dalian university of technology, Dalian, Liaoning Province, China; <sup>2</sup>the Institution of Metal and Technology, Dalian Maritime University, Dalian, Liaoning Province, China; <sup>3</sup>State Key Laboratory for Materials Modification by Laser, Ion and electron Beams, Dalian University of Technology, Dalian, Liaoning Province, China.

Bulk Ti-Zr-Ni quasicrystalline alloys were directly prepared by suction-casting in a water-cooled copper mould. The as-cast samples contain mainly an icosahedral quasicrystal (I), coexisting with minor  $\alpha$ -Ti/Zr and/or C14 laves phase. According to compression and indentation tests at room temperature, the I phase-based duplex alloy ( $\alpha$ -Ti/Zr+I) has a hardness of 5.5 GPa and a fracture strength over 1000 MPa, which is extremely high in comparison with Al-based quasicrystalline alloys. The Young's modulus is in the range of 23~36 GPa. In particular, the as-cast Ti60Zr25Ni15 alloy exhibits an elastic deformation capability of 4.2% under a monaxial compression, which is about 4 times as large as that of the Al-based quasicrystals and is even comparable with many Zr-based bulk metallic glasses. The quasi-cleavage fracture morphologies point to a brittle fracture mechanism.

#### 2:45 PM LL9.5

**Mechanical Spectroscopy of the Formation of Quasicrystalline Order in Rapidly Quenched Ti- and Zr-Based Alloys.** Hans-Rainer Sinning<sup>1</sup>, Igor S. Golovin<sup>1</sup> and Adrian Jianu<sup>2</sup>; <sup>1</sup>Institute for Materials, Technical University of Braunschweig, Braunschweig, Germany; <sup>2</sup>National Institute for Materials Physics, Bucharest, Romania.

In several rapidly quenched Ti-Zr-Ni(-Ag) and Zr(-Ti)-Cu-Ni-Al alloys forming icosahedral quasicrystals, the gradual development of quasicrystalline order was studied by means of mechanical spectroscopy (vibrating-reed technique), which includes the annealing behavior of both Young's modulus and mechanical loss spectra. In particular – since these alloys are known for their good hydrogen absorption properties – the Snoek-type relaxation peak of hydrogen was used as a probe to monitor changes in the polytetrahedral short-range order of the metal atoms. Depending on the initial structural state after rapid quenching (amorphous, nano-quasicrystalline or poly-quasicrystalline), different types of transformation and ordering behavior may be distinguished. Among those, the initially nano-quasicrystalline ("X-ray amorphous") states are characterized by the strongest relative changes of Young's modulus during annealing (examples: Ti<sub>48</sub>Zr<sub>38</sub>Ni<sub>17</sub>, Ti<sub>51</sub>Zr<sub>27</sub>Ni<sub>20</sub>Ag<sub>2</sub>). Surprisingly, an order-induced narrowing of the hydrogen relaxation peak is then found only in the later annealing stages where the irreversible increase in Young's modulus is already completed; apparently, these two properties are sensitive to completely different types of ordering processes. The narrowing of the hydrogen peak is more pronounced for initially larger grained, well-developed poly-quasicrystals (e.g., Ti<sub>41</sub>Zr<sub>42</sub>Ni<sub>17</sub> or Ti<sub>53</sub>Zr<sub>27</sub>Ni<sub>20</sub>), indicating that in these cases a higher degree of quasicrystalline order is reached within the grains. Quasicrystals of different compositions are characterized by considerable differences in position and width of the hydrogen relaxation peak, whereas these quantities are almost indistinguishable between amorphous and quasicrystalline phases of the same composition. These results might add some new aspects to our understanding and classification of cluster structures in both metallic glasses and icosahedral quasicrystals. Financial support by the DFG Priority Programme "Quasicrystals" (grant Nr. Si 408/8-1) is gratefully acknowledged.

SESSION LL10: Application and Hydrogen Storage  
Chair: Jean-Marie Dubois  
Wednesday Afternoon, December 3, 2003  
Fairfax A (Sheraton)

#### 3:30 PM \*LL10.1

**Potential Application of Quasicrystals as Thermoelectric Materials: A Phenomenological Approach.** Enrique Macia, Fisica de Materiales, Universidad Complutense de Madrid, Madrid, Spain.

The unusual behaviors reported for the electronic transport properties of quasicrystals (QCs) strongly suggest that quasicrystalline alloys should be properly located at the border line between metals and semiconductors. Thus, QCs bridge the gap between semiconducting materials and metallic ones, a very promising position in the quest for novel thermoelectric materials (TEMs). Furthermore, the thermal conductivity of QCs is unusually low for a metallic alloy. This property is particularly remarkable in the light of Slack's phonon-glass/electron-crystal proposal for promising TEMs. In this talk, we address the question regarding whether the purported anomalies in the transport properties of QCs may render them as promising materials for thermoelectric applications. Such a possibility has been recently discussed by considering a number of experimental results. Additional evidence on the potential of QCs as TEMs comes from theoretical considerations as well. In fact, by considering what electronic structure provides the largest possible thermoelectric figure of merit it was concluded that the best TEM is likely to be found among materials exhibiting a sharp singularity in the density of states (DOS) close to the Fermi level, and that the larger the DOS the smaller the figure of merit value. Quite interestingly the electronic structure of QCs satisfy these conditions in a natural way. In fact, the presence of a pronounced pseudogap at the Fermi level minimizes the background contribution, and the possible existence of fine features in the DOS increase the probability of finding a sharp peak located at the proper place. Inspired by these results, we present a theoretical prospective analysis on the possible use of QCs as potential TEMs by considering a suitable model for their electronic structure. In this way, we show that relatively high values of the figure of merit may be expected. We make an estimation on the suitability of different QCs, concluding that a systematic research of the icosahedral AlPd(Mn)Re system, aimed to improve the figure of merit values observed to date, would be appealing.

#### 4:00 PM LL10.2

##### **Thermophysical Properties of Quasicrystal-forming Ti-Zr-Ni Alloys.** Robert W. Hyers<sup>1</sup>, Richard C. Bradshaw<sup>1</sup>, Jan R. Rogers<sup>2</sup>,

Thomas J. Rathz<sup>3</sup>, Geun W. Lee<sup>4</sup>, Kenneth F. Kelton<sup>4</sup> and Anup K. Gangopadhyay<sup>4</sup>; <sup>1</sup>Mech and Ind Eng, University of Massachusetts Amherst, Amherst, Massachusetts; <sup>2</sup>SD46, NASA Marshall Space Flight Center, Huntsville, Alabama; <sup>3</sup>Center for Automation and Robotics, University of Alabama in Huntsville, Huntsville, Alabama; <sup>4</sup>Physics, Washington University, St. Louis, Missouri.

The field of quasicrystal research holds vast potential for the materials research community. To date, quasicrystal forming alloys have shown potential use in low friction coatings, thermal detection sensors and hydrogen storage. Because quasicrystals were discovered only within the last two decades, many fundamental material properties are still not known. Of particular interest in the quasicrystal field are thermophysical properties such as density, viscosity and surface tension. This information can be used for the processing and development of alloys, as well as fundamental research on phase selection in quasicrystal-forming alloys and nucleation and growth of quasicrystals. Using an electrostatic levitation technique, the viscosity and surface tension of undercooled molten quasicrystal-forming Ti-Zr-Ni alloys were measured. The viscosity is typical of glass-forming alloys of similar composition, but the surface tension shows an unexpected behavior. The surface tension decreases sharply in the same temperature range as the sudden decrease in specific heat observed by Lee, et al. [1]. This provides further evidence of a structural transition in the deeply undercooled liquid observed by synchrotron x-ray diffraction [2].

#### 4:15 PM LL10.3

##### **Electrodeposited Quasicrystalline Coatings for Non-stick Wear Resistant Cookware.** Zoran Minenovski<sup>1</sup>, Charles

Tennakoon<sup>1</sup>, Carl Nelson<sup>1</sup>, Rick Burns<sup>1</sup>, Daniel Sordelet<sup>2</sup>, Chad Haering<sup>3</sup> and Don Pickard<sup>3</sup>; <sup>1</sup>Lynntech, Inc., College Station, Texas; <sup>2</sup>Metal and Ceramic Sciences, Ames Laboratory, Ames, Iowa; <sup>3</sup>Biological Chemical Command, US Army Soldier Systems Center, Natick, Massachusetts.

The foremost problem with traditional non-stick cookware is their lack of durability. Scratching, flaking and peeling are all common to commercial and professional non-stick coatings, and preventing it requires great care to protect the coating from contact with metal utensils and abrasive cleaners. Lynntech, Inc has successfully researched and demonstrated a unique process for the manufacture of non-stick, wear resistant quasicrystalline (QC) coatings that utilize electrocodeposition of quasicrystalline powders. The purpose of this study was to optimize the physical-mechanical properties of the QC coatings through measuring contact angle, wear and friction, and corrosion resistance. All metal substrates were aluminum alloy Al-3004 and codeposition was performed in nickel plating solution using Al<sub>65</sub>Cu<sub>23</sub>Fe<sub>12</sub> QC powders. Contact angle experiments were done in accordance with ASTM C813-90 at Pennzoil-Quaker State and the average angle was 117.2° for electrocodeposited QC coatings,

which compares favorably to published data for Teflon<sup>®</sup> coatings (108° – 118°). Pin-on-disk tests were performed at Ames Laboratory using a 3/16th diameter 316 stainless steel pin with a load of 9.8 N and wear track radius 8.0 mm. It was determined during these tests that significant wear was produced on a non-coated control Al-3004 sample after 10 minutes in contrast electrocodeposited QC samples showed no visible wear scar after 120 minutes. Friction was monitored during wear tests and QC coated samples had a coefficient of friction as low as 0.01 and average value of 0.05. Salt spray exposure corrosion tests were performed at ITI Anticorrosion and electrocodeposited QC coated coupons passed the ASTM B117 standard 168 hour salt spray test. Lynntech's electrocodeposited quasicrystalline coatings withstand high temperatures and exhibit low wear and low-friction characteristics making them ideal for cookware, as well as various other technological applications such as bearings, landing gear and engine parts, where thermal and mechanical conditions are prime importance.

#### 4:30 PM LL10.4

##### **Synthesis of Quasicrystal Phases by Mechanical Alloying of Ti<sub>45-x</sub>Zr<sub>38-x</sub>Ni<sub>17</sub> (0 ≤ x ≤ 16) Powder Mixtures, and Their Hydrogen Storage Properties.** Akito Takasaki<sup>1</sup>, Naoki Imai<sup>2</sup> and Kenneth F. Kelton<sup>3</sup>; <sup>1</sup>Department of Mechanical Engineering, Shibaura Institute of Technology, Saitama, Saitama, Japan; <sup>2</sup>Graduate School, Shibaura Institute of Technology, Saitama, Saitama, Japan; <sup>3</sup>Department of Physics, Washington University, St. Louis, Missouri.

We have previously reported that a Ti<sub>45</sub>Zr<sub>38</sub>Ni<sub>17</sub> icosahedral (i) quasicrystal phase produced by mechanical alloying (MA) could store about 60 at% hydrogen ([H]/[M] ≈ 1.5), indicating its potential as new hydrogen-storage material. In this study, MA of Ti<sub>45-x</sub>Zr<sub>38-x</sub>Ni<sub>17</sub> (0 ≤ x ≤ 16) elemental powders was performed to investigate the possibility of the i-phase formation. Their hydrogen storage properties were also measured and compared with those of the Ti<sub>45</sub>Zr<sub>38</sub>Ni<sub>17</sub> i-phase, and the effect of substitution of zirconium with titanium was discussed. As same as the Ti<sub>45</sub>Zr<sub>38</sub>Ni<sub>17</sub> powder mixtures, MA formed amorphous phases directly, and subsequent annealing at 833 K produced the i-phase and the Ti<sub>2</sub>Ni-type crystal phase for all powders in this study. The α-titanium was also produced in titanium-rich powders after annealing. The quasilattice constant of the i-phase and the lattice parameter of the Ti<sub>2</sub>Ni type crystal (fcc) decreased linearly as titanium concentration in the powder increased. The maximum hydrogen concentration that could be loaded in the annealed powders after electrochemical hydrogen charging was about 63 at% ([H]/[M] ≈ 1.7). No chemical compositional dependence on the maximum hydrogen concentration was observed. Hydrogen desorption temperatures, measured by thermal desorption spectroscopy equipped with a quadrupole mass analyzer, increased with increasing titanium concentration in the powder.

#### 4:45 PM LL10.5

##### **The Evolution of Short-Range Order in Ti-Hf-Ni Alloys with Hydrogenation.** Anne Sadoc<sup>1,2</sup>, Van T. Huett<sup>3</sup> and Kenneth F. Kelton<sup>3</sup>; <sup>1</sup>LPMS, Université de Cergy-Pontoise, Cergy-Pontoise Cedex, France; <sup>2</sup>LURE, Centre Universitaire Paris-Sud, Orsay, France; <sup>3</sup>Department of Physics, Washington University, Saint Louis, Missouri.

Ti-based quasicrystals and related crystals have a large capacity for hydrogen storage [1], presumably due to the large number of tetrahedral sites in their structure, which are favorable to occupation by hydrogen. Ti-Zr-Ni and Ti-Hf-Ni quasicrystals can absorb up to two hydrogen atoms for each metallic atom, making them candidates for hydrogen storage materials. The short-range order in 3/2 crystal approximant and amorphous Ti-Hf-Ni alloys was determined by EXAFS experiments, and compared to that obtained previously in Ti-Zr-Ni alloys [2, 3]. The alloys were loaded to different hydrogen-to-metal ratios (H/M) between 0 and 1.7 in order to follow the evolution of the local structure with hydrogenation. In the non-hydrogenated alloys, the local atomic structure in the Ti-Hf-Ni 3/2 crystal approximant is similar to that in the Ti-Zr-Ni alloys, icosahedral quasicrystal or 1/1 approximant, even around the Zr and Hf atoms. However, it is somewhat different in amorphous Ti-Hf-Ni alloys. After hydrogenation, drastic changes are observed in the local structure, with modifications of the atomic distances and an increase of the disorder. In the Ti-Zr-Ni alloys, a general increase in all of the mean nearest-neighbor distances was found, except for the Zr-Ni (or Ni-Zr) ones, which leads to a remarkable inversion of the atomic sub-shells of titanium and nickel in the first environment of zirconium atoms near H/M = 1. Preliminary results of the EXAFS analysis show similar tendencies in the 3/2 Ti-Hf-Ni phases. 1. Kelton, K.F. and Gibbons, P.C., MRS Bull., 22, 69 (1997). 2. Sadoc, A., Kim, J.Y. and Kelton, K.F., Phil. Mag. A, 79, 2763 (1999) and 81, 2911 (2001). 3. Sadoc, A., Huett V.T. and Kelton, K.F., J. Phys. Cond. Matter 14, 6413 (2002).