Available online at www.sciencedirect.com
SCIENCE DIRECT®
Surface Science 583 (2005) 4–15
SURFACE SCIENCE
www.elsevier.com/locate/susc

Step structure on the fivefold Al–Pd–Mn quasicrystal surface, and on related surfaces

J. Ledieu [a], E.J. Cox [a], R. McGrath [a], N.V. Richardson [b], Q. Chen [b], V. Fournée [c,1], T.A. Lograsso [c], A.R. Ross [c], K.J. Caspersen [c,2], B. Unal [c], J.W. Evans [c], P.A. Thiel [c,*]

[a] *Surface Science Research Centre, The University of Liverpool, Liverpool L69 3BX, United Kingdom*
[b] *School of Chemistry, University of St. Andrews, North Haugh KY16 9ST, United Kingdom*
[c] *Departments of Chemistry, Materials Science and Engineering, and Mathematics, and Ames Laboratory, Iowa State University, Ames, IA 50011, USA*

Received 11 October 2004; accepted for publication 8 February 2005
Available online 2 March 2005

Abstract

We compare step morphologies on surfaces of Al-rich metallic alloys, both quasicrystalline and crystalline. We present evidence that the *large-scale* step structure observed on Al-rich quasicrystals after quenching to room temperature reflects equilibrium structure at an elevated temperature. These steps are relatively rough, i.e., have high diffusivity, compared to those on crystalline surfaces. For the fivefold quasicrystal surface, step diffusivity increases as step height decreases, but this trend is not obeyed in a broader comparison between quasicrystals and crystals. On a *shorter scale*, the steps on Al-rich alloys tend to exhibit local facets (short linear segments), with different facet lengths, a feature which could develop during quenching to room temperature. Facets are shortest and most difficult to identify for the fivefold quasicrystal surface.

Keywords: Equilibrium thermodynamics and statistical mechanics; Scanning tunneling microscopy (STM); Step formation and bunching; Alloys; Stepped single crystal surfaces

1. Introduction

Quasicrystals are *non-periodic* intermetallics possessing long-range order. Their existence poses a fundamental question for the scientific community: whether and how their properties—often

* Corresponding author. Tel.: +1 5152948985; fax: +1 5152944709.
E-mail address: thiel@ameslab.gov (P.A. Thiel).
[1] Present address: Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544.
[2] Present address: LSG2M, CNRS-UMR 7584, Parc de Saurupt, F-54042 Nancy, France.

0039-6028/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2005.02.012

unusual—can be understood within the contextual framework established for *periodic* and well-ordered materials. This paper deals with one such property, a specific aspect of surface morphology—step roughness. We show that this aspect of the surface morphology is indeed unusual, when compared qualitatively with other materials.

The clean quasicrystalline surfaces that have been described most extensively in the literature are the tenfold (10f) surface of decagonal (d-) Al–Co–Ni, and the fivefold (5f) surfaces of icosahedral (i-) Al–Pd–Mn and Al–Cu–Fe. We first review the general picture of the fivefold (5f) Al–Pd–Mn surface, a main topic of this paper.

It is well-established that this surface can be prepared in a terrace-step morphology. Furthermore, consensus has emerged that the terraces are bulk-terminated, except for some interplanar relaxations. The terraces represent self-similar terminations consisting of two close-lying atomic planes (separated by less than 0.5 Å), with a high combined density. These conclusions are based upon data from both diffraction techniques [1–7], and scanning tunneling microscopy (STM) [1–3,8–12].

The steps, which are the focus of the present paper, have also generated interest, for two reasons. First, the predominant steps are of three different heights whose values are related, not by a simple integer, but by an irrational number, the Golden Mean, $\tau = 2\cos(\pi/5) = (1 + \sqrt{5})/2 = 1.618\ldots$ The values are: 2.4 Å (S-type), 4.1 Å (M-type) and 6.6 Å (L-type) [1,2,8,13]. Of these, the S-type is usually least common. Second, the structure of the steps within the surface plane is unusual, compared with crystalline materials. The steps often meander and intersect, to the extent that a mesoscopic step orientation cannot be defined. (The meandering nature has also been noted on the 10f surface of d-Al–Co–Ni [14].) This meandering nature is quite different, qualitatively, than conventional metals or semiconductors, where long, straight steps (or slowly curving steps in the presence of impurity pinning) are often obtained on vicinal samples of single crystals.

Twofold (2f) surfaces of the Al-rich icosahedral alloys are not as well understood, although there is evidence from LEED [9] and from STM [15] that they are also bulk-terminated. The most common step heights, found in STM, are 2.4, 3.6, 6.2, 9.5, and 15.8 Å [15].

In this paper, we compare (qualitatively) the steps on the 5f and 2f quasicrystalline surfaces of i-Al–Pd–Mn, and the steps on a close approximant phase, the so-called ξ'-phase. Compositionally, the quasicrystal can be described as $Al_{72}Pd_{19.5}Mn_{8.5}$ whereas the approximant is $Al_{77.5}Pd_{19}Mn_{3.5}$. (Broadly speaking, an approximant is a material having both chemical and structural similarity to a quasicrystal [16].) We choose to study the pseudo-tenfold (p-10f) surface of the ξ'-phase, for which we have already reported and analyzed the fine structure of the terraces, and the step heights [17]. In contrast to the quasicrystal, the steps on the ξ' surface are all the same height, 8.07 ± 0.16 Å. This equals half the period along the p-10f axis. Hence, these steps are about one-third taller than the L-type steps on the 5f quasicrystal surface. Furthermore, comparison is made with step morphology on Al(1 1 1), which has a single step height of 2.35 Å and which can be considered a simple chemical model of the Al-rich intermetallics.

All of our observations of step structure are made at room temperature, after the surface has been heated above 900 K and cooled to 300 K. Because no step motion is observed at room temperature, it is certain that the step structure reported here is not actually equilibrated at the observation temperature. Furthermore, there is evidence that long-range mass transport does not occur below 500 K [18,19]. It is reasonable to expect that the same limit applies to the approximant. Hence, the steps form and lock or freeze into position between 900 and 500 K, during cooling.

An explanation of sample preparation—particularly the annealing and cooling sequence that immediately precedes measurement in ultrahigh vacuum—is especially germane in light of step equilibration issues, and this is given in Section 2. In Section 3, we present qualitative comparisons between step morphologies on the quasicrystal, and step structures on related surfaces. In Section 4, we extract the effective step diffusivity of the M- and L-type steps on the 5f surface of quasicrystalline Al–Pd–Mn from one specific dataset. In Section 5, we discuss the observations.