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# Bulk Single Crystal Growth and Sample Surface Preparation of Catalytic NaAu<sub>2</sub>

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#### Abstract

Here in we have grown bulk single crystals of NaAu<sub>2</sub> for the first time to enable surface studies on the nature of the (111) bulk surface. This intermetallic compound exhibits surprisingly high catalytic activity for CO oxidation, a benchmark reaction. Theory predicts NaAu<sub>2</sub> to be the most thermodynamically stable composition in the Na-Au binary phase diagram and NaAu<sub>2</sub> has been seen to preferentially form in experiments containing Na and Au which supports this prediction. The (111) surface was also predicted to be the most stable and is nearly bulk-terminated making single crystal samples prepared with this crystallographic orientation a fitting choice. The crystal quality and surface composition of the metallographically prepared surface was determined by x-ray diffraction methods in addition to optical and electron microscopy.

Keywords: Bridgman, single crystal growth, (111) catalytic surface, sample surface characterization, intermetallic NaAu<sub>2</sub>

# 1. Introduction

Intermetallic compounds are of increasing interest as possible catalysts due to their stability and their potential to be inexpensive alternatives to precious metals such as Pt or Pd for reactions that are of both industrial and environmental importance. CO oxidation (CO +  $1/2O_2 \rightarrow CO_2$ ) on Pt-group metal surfaces is often viewed as an ideal reaction for fundamental investigations of heterogeneous catalysis.[1] This reaction features many of the fundamental steps involved in a typical heterogeneous catalytic system: molecular adsorption/desorption of reactants (CO  $\leftrightarrow$  CO<sub>ads</sub>), dissociative adsorption of a reactant (O<sub>2</sub>  $\rightarrow$  2O<sub>ads</sub>), surface reaction (CO<sub>ads</sub> + O<sub>ads</sub>  $\rightarrow$  CO<sub>2</sub>) and reaction inhibition/surface poisoning (oxide formation).

It has been known for many years that the preparation of active catalysts with copper and silver requires the metal to be well dispersed on a support.[2] Hence, it should not be a surprise that while bulk Au is noble, when it is deposited as nanoparticles on a

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metal oxide surface, it exhibits enhanced catalytic activity for CO oxidation at subambient temperature[3-5]. It is the combination of Au and the metal oxide that generates surprisingly high catalytic activity for CO oxidation as neither alone is active. And not only did early experimental demonstrations show that gold was not just an exceptional catalyst; for CO oxidation and ethyne hydrochlorination, it was shown to be, by far, the best.[2] A review by Daniel et. al.[6] relates the importance of the Au substrate and reactant interface makeup. The geometry of the Au environment, the Au particle size, and proximity and strength of interaction with the substrate are all factors in the rate of CO oxidation observed.[2] Gold intermetallics are favorable for this reason since their structure is inherently homogeneous with ordered vacancies (either actual vacancies or spacer atoms that may fulfill the role of the substrate[6] in facilitating the oxidation) and fixed gold coordination number as defined by the crystal structure. In comparison, a deposited Au layer contains a myriad of structures and particle sizes[2] that can be loosely controlled by deposition conditions but which always contain a mix of catalytic sites ranging from ideal to mediocre. As well, this surface can change both in composition and structure under reaction conditions[7]. Intermetallic surfaces can remain stable under these same conditions, which is likely due to their high formation enthalpies[8].

Activation energy differences at the catalyst surface, when the Au atom's environment is changed, is also a consideration. Xiao *et.al.*[9] point out that when Na and Au join to make an intermetallic compound, the constituent atoms' electronic structures are modified which alters the binding energies of surface adsorbates and thus changes the catalytic properties. Experimentally they tested NaAu<sub>2</sub>, Au and NaOH-coated Au and found NaAu<sub>2</sub> active for CO oxidation but not the latter two which supports the idea that the environment of the atoms in the intermetallic is unique. Their density functional theory (DFT) calculations further support this by showing that energy barriers to CO and O<sub>2</sub> adsorption, as well and intermediate species formation, in almost all cases has a lower energy barrier on NaAu<sub>2</sub> (111) compared to Au(221). Their calculations also predict that certain site configurations are preferred by different adsorbents and intermediates. The repetitious and ordered nature of the intermetallic surface means even coverage and a predictable arrangement of adsorbent species, which in this case, appears to be the advantage over other surfaces also containing Na and Au.

We have chosen to study the gold intermetallic Na-Au because it adapts a cubic Laves phase structure (MgCu2-type; space group Fd-3m). The (111) surface contains triangles and hexagons of Au atoms which would be related to Au (111) but with ordered vacancies. Also, it has a relatively high melting point and fairly low vapor pressure, which are important in ultra-high vacuum (UHV) conditions like those commonly used in surface characterization. Sarmiento-Pérez *et al.*<sup>[10]</sup> showed that NaAu<sub>2</sub> is the most stable binary in the Na-Au system using the *ab initio* minima hopping

structural prediction method which was substantiated by DFT.[10] Kwolek *et al.*[11] showed that the (111) surface, which is expected to be most stable among the low-index faces, is nearly bulk-terminated in its clean state. Single crystals are advantageous because their surfaces usually exhibit a terrace-step morphology, in which the atomic arrangement on the terraces and the step heights can be compared with bulk structure.<sup>[12]</sup> Kwolek was the first to characterize the bulk surface of NaAu<sub>2</sub>, although a closely-related system had been investigated by Barth *et al.*[13] Barth *et al.* studied Na film deposited on Au(111) and found that the surface reconstructed as Na and Au interdiffused to form films and multilayers of NaAu<sub>2</sub> which exhibited a (111) surface orientation commensurate with the underlying Au after heating the samples (with sufficiently high Na coverages) to temperatures ranging from 300 to 600K. Other groups[8, 14] discovered NaAu<sub>2</sub> as a product when a voltage was applied to Au in the proximity of Na, also validating this intermetallic's stability over other Na-Au binaries.

Our goal is to create a bulk surface that can be modeled, and its surface characterized for comparison to the model, to provide insight and understanding of the excellent catalytic activity. The first step in meeting this goal was growing a single crystal of NaAu<sub>2</sub> of sufficient size and quality for surface studies. In this paper we describe the growth and characterization of single crystalline, Bridgman grown NaAu<sub>2</sub>. Laue back reflection, metallography, powder x-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS) capability were used to evaluate the phase purity and quality of the crystal growth. Laue and XRD were used to evaluate surface quality of the crystallographically oriented samples.

# 2. Material and Methods

The Bridgman method of crystal growth was chosen after taking into consideration that NaAu<sub>2</sub> contains a reactive component (Na) with a high vapor pressure and therefore should be sealed in a crucible, and it melts congruently at 1002°C. While tantalum is not normally the first choice of crucible material for either Na or Au, it was chosen mainly for its weldability thereby affording control over the internal environment. Tantalum is also easily fabricated and it was formed to the shape and size crucible desired for optimal crystal growth by the Bridgman method. The crucible was acid etched in a solution of hydrofluoric acid-nitric acid-water in the ratio 2:4:4 to clean the surface and remove any oxide layer that could be a source of contamination of the alloy. The crucible was then sonicated, rinsed with methanol, and dried. The pure elements were loaded into the crucible, in appropriate quantities, in a glovebox. The Na, being soft and ductile, was packed in first in the bottom of the crucible. In this way the Na made good thermal contact with the bottom of the tantalum, thereby avoiding any melting during welding of the tantalum crucible. An arc melted and dropcast rod of Au, slightly smaller in diameter than the crucible, was placed on top of the sodium. A

tantalum cap was press fit onto the top of the crucible, with approximately ¼ inch head space above the contents. Then it was loaded into a gas tight jig with a transparent top so that it could be transferred to a laser welder, without exposure to air, where it was welded under vacuum.

Following sealing of the tantalum crucible, the elements were pre-alloyed in the tantalum crucible during multiple heating runs in an atmosphere controlled resistance furnace. The sealed crucible was heated above the melting point of gold ( $T_M = 1065$ °C) and allowed to cool to room temperature. The melting treatment was conducted twice more, flipping the crucible end for end between heating cycles to ensure good mixing. The sample was then loaded into a Bridgman style resistance furnace where it was heated to 1000°C under vacuum. Next the furnace ch amber was backfilled with argon gas to a pressure of 40 psi so in the event of crucible failure, there was a positive pressure to reduce evaporation of Na for the protection of the furnace. The sample was further heated to 1200°C and held for 1 hour for fu rther homogenization before withdrawing the crucible from the heat zone at a rate of 5 mm/hr.

Upon removal of the crucible from the furnace, the crucible could not be machined off as it had become embrittled and had become chemically bound to the alloy, see results and discussion. A slow speed diamond saw was used to cut off the top of the crystal growth near the meniscus; however, it was obvious from the cracking and chipping of the crystal that the abrasiveness of the diamond saw was too severe and all additional cuts were made by electrical discharge machining (EDM). Even utilizing low cutting power, some cracks still developed and small chips of crystal broke off, limiting the size of sample that could be harvested. Sonication in methanol was found to be the best way to remove the cutting fluid, but this also caused the sample to break up so care was taken to immediately remove the sample from the sonicator when it was adequately clean.

A cross-section of the crystal growth was vacuum mounted in epoxy to help keep it intact during metallographic preparation of the surface. The polished surface was carbon coated in order to reduce charging and was evaluated on a JEOL 5910LV or FEI Quanta SEM with EDS capability for phase purity and compositional variations. The choice of SEM was based on instrument availability considerations only. Electron micrographs were compared to optical imagery and found equivalent and so the latter are not shown here.

Independently, phase purity and identification of the alloy were also conducted using XRD on a PANalytical X'Pert Pro system. Later this same instrument was used to run  $\theta$ - $\theta$  scans on the surface of the oriented sample to determine the near surface composition after various treatments. The actual penetration depth of the x-rays was not calculated here, but in general the penetration depth of x-rays is on the order of a

few microns. The ingot was crystallographically oriented to within ± 0.25° by back reflection Laue using a PANalytical PW1830 generator with Photonic Science camera. Plates approximately 2 x 3 x 10 mm<sup>3</sup> with the face corresponding to the (111) plane were cut by EDM from the ingot. Final orientation and metallographic surface preparation was done using a Southbay Tech Model 170 multi-axis sample holder. After orientation the sample was first dry ground on silicon carbide paper that had been lightly coated with wax to reduce the depth of deformation of this soft material, on a Southbay Tech lapping machine. Slow speeds were used with no pressure added to the sample. Polishing was accomplished using alumina in water on velvet lightly coated with liquid dish soap. One micron alumina was the finest particle size used. Attempts to use finer particles or colloidal silica suspensions on a vibrometer gave unsatisfactory results. Samples were washed with soap and water and briefly sonicated between steps. The sharpness of the spots in x-ray diffraction Laue photos at a working distance of 100mm was used to qualitatively measure surface and crystal quality during the polishing process. Rocking curve data was collected on a Bruker AXS D8 Advance system.

Subsequent *in situ* cleaning was done to remove residual damage from the mechanical polishing as well as oxidation. The details of this subsequent cleaning are described by Kwolek[11] but is mentioned here because not only are the techniques in this paper useful for preparing the initial sample surface, they were also found useful to renew or reset the surface later on. During the study by Kwolek to determine the boundary conditions to reliably produce a clean surface by Ar ion sputtering and/or annealing in UHV suitable for the target goal of catalysis observation, the surface received damage. Herein it is collectively referred to as sputter-annealing.

# 3. Results and Discussion

SEM micrographs taken of the crucible-alloy interface, see Fig. 1a, show that a reaction layer has formed and that cracks develop between this reaction layer and the bulk alloy such that they are easily separated. The thin light colored layer next to the crucible is Au<sub>0.75</sub>Ta<sub>3.25</sub> and the darker, irregularly shaped layer next to the alloy is Ta with small amounts of Au and sometimes Na dissolved into it. It is not clear why the phase with higher Au content has formed farthest from the Au source. These phases are only seen at the crucible-alloy interface. A second phase of slightly Na-rich NaTa, see Fig. 1b, is seen in the bulk of the crystal. The black phase around the edges of the NaTa inclusion is much higher in Na content and readily oxidizes. These inclusions are not typical and were not seen in the prepared samples. All phases can also be seen and distinguished optically making visual surface quality checks easy and convenient. Optical images are not shown here as they were not significantly different from the SEM images in visual separation of the phases. Chemical analysis by EDS showed the bulk composition to

be homogeneous and of the nominal composition, leading to the conclusion that proportional amounts of Au are lost to the crucible-alloy interface and Na to the NaTa inclusions. X-ray diffraction was also used for phase identification as well as for crystallographic orientation and surface quality characterization. Figure 2a shows an XRD pattern of powder ground from the bulk NaAu<sub>2</sub> crystal growth for phase identification. All peaks can be accounted for by the theoretical pattern for cubic NaAu<sub>2</sub> indicating that if any of the second phase seen by SEM is present in the powder, it is less than the detection limit which is typically 3% by volume for XRD. A single crystal face, cut from this ingot with the (111) plane exposed, produces the back reflection Laue pattern shown in Fig. 2c where only peaks that meet the condition h=k=l are present. The same surface after repeated sputter/low-temperature anneal cycles (below 450K) or a one-time high temperature anneal (above 500K) produces only peaks associated with cubic Au powder, see Fig. 2b, indicating that Na migrates to the surface and is lost by thermal evaporation. The remaining Au atoms rearrange resulting in loss of the (111) long range order. However, surface characterization techniques that only penetrate a few atom layers deep such as LEED, XPD and STM, as opposed to XRD technique which has a typical penetration depth on the order of micrometers, show that the top surface layers of Au have a (111) structure[11]. The driving force behind the development of a polycrystalline-like layer sandwiched between two like oriented layers is not considered here but is likely due to differences in energy between surface and bulk atomic positions. This damage can easily be removed and bulk termination restored by re-polishing the sample as evidenced by Fig. 2c showing the Na depletion to be depth limited. The sputter-annealed surfaces had a noticeably decreased luster and bore small scratches from handling. Because of the variability of the damage that each sample received, it was not feasible to ensure damage removal caused by the experiment itself or from handling if the depth of the removal was fixed, therefore, the depth of material removal was determined visually rather than by a prescribed amount. In general, each surface was regenerated by starting with a fine SiC grit paper and grinding until the surface was uniform in appearance and then repolished to a brilliant, mirror-like finish. In addition to appearance, surface quality and restoration was monitored by x-ray diffraction which is described below.

Information about the near surface condition can be interpreted from the Laue back reflection photos based on overall spot shape, clarity and degree of splitting. Figure 3 is a Laue pattern from a polished (111) surface demonstrating its 3-fold symmetry. The background variation is from the camera set up and is independent of the sample. Here the spots are round with no streaking, clearly discernable from the background and make a clear pattern, and each spot consists of a tight cluster of several spots. The first two qualifiers indicate that this is a high quality crystalline sample and the last indicates discrete mosaic blocks with maximum misorientation less than 2 degrees based on the width of the clusters. The spot size can be affected by such things as x-ray tube

parameters, tube age and stability, and length of exposure so this is a qualitative approximation. When the sample becomes irreversibly damaged from sputterannealing the intensity and clarity of the spots is greatly reduced from what is seen here. Renewal of the surface through re-polishing can be qualitatively monitored by viewing Laue images taken during the polishing sequence. When the intensity, quality and number of spots no longer changes with additional polishing time the sample is considered ready for the final surface preparation which takes place in the UHV chamber itself, described elsewhere[11]. Spot splitting in the Laue photos was not uncommon and varied in extent across a sample's surface. The evidence of mosaic spread was not apparent in the data collected by surface techniques LEED, XPD and STM[11], which had similar sampling areas but less surface penetration. To better quantify the spot splitting seen in Laue back reflection, a rocking curve measurement was performed about the (222) reflection at 20 degrees theta, Fig 4. Maintaining the oriented surface horizontal, the sample was rotated 0, 45 and 90 degrees about phi. During each measurement phi was held constant while the sample was rocked in theta. Variation between the scans demonstrates that several mosaic blocks, or domains, are included in the area irradiated and that different domains are cross-sectioned as the sample is rotated. The appearance of peak clusters is analogous to the spot clusters in the Laue photo with approximately 1/3 the volume irradiated shifted to lower theta in two of the Phi orientations. The variation in mosaic spread at these three sample positions is between 0.3 and 1.4 theta at approximately full width half maximum (FWHM). It is possible that the comparatively large mosaic spread seen by x-ray diffraction is coming from layers below the surface that were distorted during coarse grinding or handling that were not completely removed during subsequent grinding and polishing steps. These subsurface layers may be far enough below the free surface that they are not detected by the techniques that only penetrate a few atom layers. The term distorted is used here rather than deformed as the sides of the peaks are sharp and the peaks appear to be merely shifted from the expected value. Since most samples were further processed by sputter-annealing, it is also possible that the distorted layers were improved before collecting data by the surface sensitive techniques. Also as can be seen in Fig 4, the orientation of the sample in Phi changes the outcome and so there is a sampling dependency. In any case, the discrete domains consist of highly crystalline material that is seemingly more cohesive in the top surface layers, than in deeper surface layers, which provides a surface with a consistent atomic environment at which to carry out the catalytic bench mark reactions.

# 4. Conclusions

Single crystal NaAu<sub>2</sub> has been grown for the first time and has been characterized using XRD and Laue diffraction, as well as optical and electron microscopy and found to be of high quality suitable for surface science studies using traditional surface probes.

Crucible-alloy interactions, when Ta is the crucible material, are largely kept to the interface and the small amount of second phase that makes it into the bulk as Na-Ta can be seen optically thereby making it easy to avoid by grinding the sample a little deeper or shifting the sample so that the second phase is not in the measurement area. Changes in the surface chemistry and crystallographic nature of the surface due to annealing above 450K or excessive sputter-anneal cycles in UHV can be tracked using XRD and Laue diffraction. It has been demonstrated that the stoichiometry and long range atomic order of the surface can be restored by repolishing the sample which removes the altered, damaged surface layer. These well characterized samples provide an excellent substrate with which to study the catalytic activity of NaAu<sub>2</sub> alloy.

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Figure 1. Scanning electron microscope (SEM) micrographs a) crucible-alloy interface - JEOL 5910LV, b) nontypical second phase in the bulk - FEI Quanta. Overall the bulk is phase pure with the crucible-alloy reaction layer being confined to the interface and the NaTa inclusions shown in b) being unevenly and sparsely distributed. The use of different SEMs was based on equipment availability consideration only.



Figure 2. Two theta x-ray diffraction scans with hkl values for the phase listed in the upper right corner of each pane. a) powder pattern of bulk crystal, b) (111) single crystal after sputteranneal conditions that depleted surface Na causing rearrangement of the remaining Au atoms, c) the same sample after re-polishing, bulk termination is restored. Peaks marked with an asterisk come from the sample holder.



Figure 3. Laue back reflection image of an as-polished  $NaAu_2$  (111) surface. Sample to detector distance = 100mm. Background variation is from the camera set up.



Figure 4. Rocking curve of  $NaAu_2$  (222) peak; same sample location as Laue photo in Figure 3. Mosaic spread varies with Phi between 0.3° theta for 90 Ph i and 1.4° theta for 0 Phi. Color online.

#### **Figure Captions**

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# <u>Highlights</u>

Bulk crystal growth of NaAu<sub>2</sub> by a modified Bridgman method; centimeter size grains.

Preparation of bulk terminated (111) surface by metallographic techniques.

Bulk (111) termination renewed by metallographic technique after surface degradation.

Surface quality characterization by x-ray techniques and electron microscopy.