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Reaction-induced surface reconstruction of silver in contact with zirconium

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In the case of solid state diffusion between two metals the effect of the initial surfaces of the metals on the intermetallic compounds (IMC) formation is not well understood, particularly when the surfaces are not flat and the contact time is relatively short. Here we demonstrate that in the case of Ag/Zr couple the early stage of IMCs formation starts at the Ag/Zr contact points and is the place of complex surface reconstruction of Ag in direct connection to the reaction/diffusion at these Ag-Zr contact points. The effect of incomplete contact has been studied by micromachining a regular pattern on the Zr surface prior to interdiffusion experiments. The nucleation and growth of $AgZr_2$ and AgZr occurred along the contact points and led to silver surface reconstruction with the formation of preferential {111} and {100} surface facets. A mechanism explaining this new phenomenon is developed based on the minimisation of Gibbs energy and the diffusion rates of both Ag and Zr atoms.

1. Introduction

The solid state diffusion between two metals is a common process used in industrial situations such as diffusion bonding [1,2]. This process leads sometimes to the formation of intermetallic compound layers (IMCs). The nucleation and growth of these IMC layers are of interest since these intermetallic compounds provide a good bond between the metals but are generally brittle and may lead to failure in the final product.

Silver is a metal of interest for many industries including dentistry where silver is alloyed with mercury for amalgams [3–5], microelectronics for interconnections [6–9] and the nuclear industry where silver is used to make control rods in nuclear reactors thanks to the capability of silver to absorb free neutrons [10,11]. Moreover, the catalytic properties of silver are widely used by the chemical industry for the epoxidation of ethylene or the partial oxidation of methanol to formaldehyde [12–14]. Recently, an increased interest has been observed for silver substrates textured for the growth of high temperature superconductors [15–17]. Finally, the anti-microbial activity of silver has been explored for (bio-) nano-technologies [18–20].

In many applications silver will be in contact with another metal at elevated temperatures and solid state diffusion will occur. The first stages in this process however will be dominated by the degree of contact and surface properties of the two components. However, when silver is heated to $T > 873$ K, the surface undergoes profound morphological changes and this will be operative over the elevated conditions required for solid state bonding. These morphological changes in silver surfaces are often termed "thermal etching" and have been extensively studied since the early 20th century [21–23].

The etching of silver includes grain-boundary grooving [24], etch pitting [25,26] and faceting [27] and can be induced by temperature −thermal etching− and/or by reaction −catalytic etching [28,29]. The mechanisms of Ag surface reconstruction can be described from a thermodynamic point of view, the driving force being the minimisation of the total Gibbs energy [30]. However, the kinetics of silver atom evaporation also has to be taken into account especially when dealing with heat treatments under vacuum [31,32]. Multiple parameters can impact both the etching of silver and the lowest temperature at which it may be observed. In addition to time and temperature, the presence of oxygen in the atmosphere surrounding the silver surface is known to promote the faceting and grain-boundary grooving [27,29]. Considerable work has been carried out to understand the key role of adsorbed oxygen and subsurface oxygen on these morphology changes during catalytic reactions [13,14,33–35].

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In order to understand the impact of etching and reaction on the surface of silver at elevated temperature, we have studied the contact reaction between solid silver and zirconium.

The silver/zirconium system was first described by Karlsson in 1952 [36], with two non-stoichiometric intermetallic compounds (IMCs) AgZr and $AgZr_3$. However, the most recent studies based on theoretical [37,38] and experimental [39,40] investigations contested this early study, and nowadays two stoichiometric IMCs are generally accepted: tetragonal AgZr and $AgZr_2$, with Strukturbericht Symbol B11 and $C11_b$, respectively. In Ag-Zr couples Taguchi & Iijima [39] found that in the Ag/Zr couple the diffusion flux of Ag atoms is greater than that of Zr atoms, which corroborates the multiple results of self-diffusion measurements of Ag tracers in bulk Zr [41–43].

One can assume that contact reaction at high temperature between silver and zirconium will then lead to the formation of two IMCs, AgZr and $AgZr_2$. However, no evidence of silver surface reconstruction in Ag-Zr diffusion couples has been reported in the literature yet [39,40]. This is quite understandable as the study of solid state diffusion between a couple of materials is generally carried out by using *(i)* laboratory-polished surfaces, *(ii)* similar sample size, *(iii)* high applied pressure between the two materials (screw), *(iv)* long diffusion time and *(v)* by characterising only the cross-section of the interface.

Nevertheless, in many industrial situations not all of these conditions are generally fulfilled. For example, materials are generally not polished, therefore the surface roughness can be high. Also, in some cases the force applied between two materials can be small and/or non-uniform, compared to a diffusion couple pressed by screws. Finally, edge effects are not taken into account in diffusion couples, although they can be important for industrial geometries.

The purpose of this paper is to demonstrate the relationship between the contact reaction of silver and zirconium at elevated temperature with thermal etching and morphological changes on the silver surface.

2. Experimental

The experimental part of this study is based upon vacuum annealing experiments of Ag/Zr couples. The influence of the contact itself has been investigated by using patterned zirconium and polished silver, as described below.

2.1. Material preparation

10×8 mm coupons of polycrystalline (grain size 20 μm) rolled and annealed silver sheets of 0.5 mm thickness and with a purity of 99.99% were used for this study. The main impurities of silver sheets are oxygen (20–27 wtppm), lead (14 wtppm) and copper (13 wtppm), and the description of silver sheets processing can be found elsewhere [44]. In order to remove any damage and contamination coming from the rolling process, the surface of the silver coupons was polished as follows: firstly coupons were ground using SiC papers down to 2000 grit size. Silver samples were then polished using diamond suspensions of 6 μm, 3 μm, 1 μm and finally 0.25 μm. After polishing, silver samples were cleaned using an ultrasonic bath of different alcohols in order to remove dusts and organic pollutants.

In order to study the effect of point contact on the Ag/Zr diffusion couple, zirconium samples were patterned with an array of 1 μm-high ridges spaced every 120 μm. This patterning was performed as follows. A $150 \times 150 \times 1$ mm zirconium sheet supplied by Goodfellow© (purity of 99.2% – main impurities: hafnium 2500 wtppm and oxygen 1000 wtppm; grain size 10–20 μm) was fixed on a rotating stage, while a fine tip engraved the zirconium surface. The Zr sheet was then removed and cut into $12 \times 2 \times 1$ mm rods with the machining marks approximately perpendicular to the 12 and 1 mm axes. Dust and organic pollutants from the machining process were finally removed using a cleaning process consisting of ultrasonic baths with different alcohols. Fig. 1 shows SEM images of the patterned Zr surface where ridges are easily recognisable.

For comparison, some zirconium samples were also polished prior to Ag/Zr couple annealing. The polishing process of zirconium samples was made of a first grinding step using SiC papers down to 4000 grit size. A second polishing step using a mixture of a suspension of silica particles (OP-S, Struers) diluted in deionized water and hydrogen peroxide with a volumetric ratio 5:6:1. This final polishing step was carried out on a MD-Chem pad (Struers©) for 2 h.

2.2. Annealing experiments

Once prepared, the Ag and Zr samples were set in a stainless steel holder and pressed by screws. The pieces were arranged such that one rod of Zr was held tightly against the Ag coupon with the machined Zr surface in contact with the polished Ag surface (the final rolling direction of the silver sheet was arranged to be 45° from the direction of Zr machining marks to ensure an ability to detect their influence). This arrangement did not always allow a perfectly parallel approach of the two surfaces and fortuitously this allowed insight into the reaction as it developed. Annealing experiments of the Ag/Zr couples were performed in a hot-wall alumina tube furnace equipped upstream with a gas panel and downstream with a pumping system. The furnace had a type-K thermocouple directly inserted in the hot zone of the furnace. Before reaching the working pressure of 1 Pa, the furnace was filled with argon (99.998%) then purged twice. Heat treatment experiments were then carried out at different temperatures (from 673 to 1073 K) and for different dwell times (from 1 min to 96 h). The heating ramp rate was fixed at 20 K min^{-1}.

After annealing, the Ag/Zr couples were cooled-down slowly (over 5 h). Samples were examined in two configurations. *(i)* Some samples were studied in cross-section, similar to the standard method used in the study of reactive diffusion, soldering and brazing. This involved mounting in cold resin and polishing with diamond solutions to reveal the Ag-IMC-Zr cross-sections. This configuration was particularly suitable for classical polished Ag/polished Zr couples. *(ii)* For other samples, a technique was developed to detach the Ag and Zr sheets after the heat treatment and to study their surfaces directly. This technique was possible here because in most cases the polished Ag & patterned Zr couples were not or only slightly bonded in the experimental conditions studied here (Ag & patterned Zr sheets were detached manually, while a screw was used to separate polished Ag & polished Zr). This configuration was found to be useful at revealing the contact reaction mechanisms. The different surfaces and interfaces were then

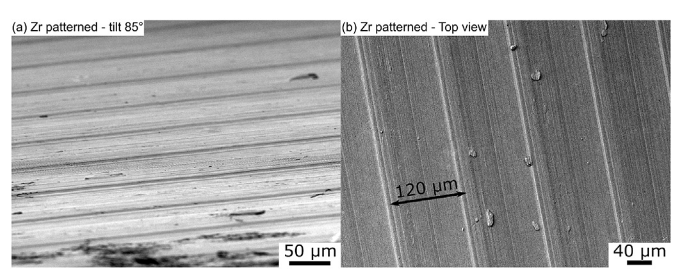

Fig. 1. SEM images of the surface of zirconium patterned with an array of 1 μm-high ridges spaced every 120 μm. (a) tilt 85°. (b) Top view.