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ASPECTS OF PERIODIC LAYER FORMATION IN Co_2Si/Zn DIFFUSION COUPLES

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Introduction

Periodic layer formation during solid state reactions was discovered in the beginning of the eighties (1). During the last decade several other authors made mention of this phenomenon (2,3,4,5) and different explanations have been put forward (6,7,8), none of which are completely satisfactory. In this paper we present our observations on reactions of Co_2Si with solid zinc. Apart from some common features with other systems showing periodic layer formation, there are some peculiar differences which deserve attention. Especially, the appearance of a pattern in a plane perpendicular to the diffusion direction is discussed. The pattern is similar to loops of dislocation emerging from a Bardeen-Herring source.

Experimental

Co_2Si was prepared by arc-melting the proper amounts of the pure elements into a polycrystalline bar of 12 mm diameter. The bar was annealed at 1000°C for homogenization. Slices of 2 mm thickness (to be used as a couple half, also called the substrate) were cut from the bar. Pure (99.9%) zinc was used as the other couple half.

The couple halves were placed in an alumina pressure bar and held together by the pressure of a metal spring. The diffusion couples were annealed at 390°C for various times in a horizontal tube furnace in a He atmosphere.

The couples were allowed to cool to room temperature, cut with a slow-speed saw and prepared for microscopical examination by standard metallographic techniques. Cross-sections were taken both perpendicular and parallel to the diffusion direction. Quenching of a couple produced the same results.

Light microscopy and SEM with quantitative analysis (EDS) were used in investigating the cross-sections.

Experimental Results

Morphology

The reaction zone consists of a number of cells with different morphologies (fig. 1). Some are regular and consist of parallel alternating layers (dark bands are slightly wavy), others are irregular but a certain kind of periodicity can still be observed.

The band spacing (or "wavelength") changes from cell to cell. It varies from 3.6 μm (minimum) up to 20 μm. Band width and -spacing occur in different proportions. In some zones we found a spacing of 4.4 μm with a band of 0.8 μm (ratio 5.5), in others a 9.0 μm spacing with a 1.0 μm wide band (ratio 9.0). With the minimum spacing a band width of 0.5-0.6 μm occurs (ratio 6.5). In each cell the spacing is nearly constant. The zones which have the smallest spacings are invariably the widest, i.e. they have grown fastest.

Along the zinc-side and extending over the complete zone there is always a very tiny band present. This we assume the first band to be formed.

Polarized light microscopy shows that cells of different morphology form on different grains of the orthorhombic (9) cobaltsilicide.

After etching with 2% nital the fine structure of the thin bands is revealed. They consist of small round grains, packed closely together in a matrix phase (fig. 2). The matrix phase consists of grains up to 5 μm diameter.

Cracks extending from the silicide to the zinc are observed after polishing (viz. fig. 1). They result from cooling. Frequently we find pieces of partly reacted Co_2Si inside the reaction layer.

A surprising morphology was observed when a Co_2Si/Zn couple was sectioned perpendicular to the diffusion direction (fig. 3). The cross-section was taken close to the zinc-side of the couple. The image resembles the dislocation loops which emerge from a Bardeen-Herring source. To our knowledge, this kind of pattern formation has not been observed before in solid state systems.

Several of these cross-sections have been taken throughout the reaction zones of different couples. In general very chaotic patterns of dark bands in a light matrix phase are observed. The regular bands that we see in the "side view" are thus obviously not dense planes of grains, but rather a cross-section of apparently random patterns, which seem to form from periodically. In the "top view" we can distinguish the grain boundaries of the underlying Co_2Si substrate. Different patterns are formed on different grains. The pattern of fig. 3 has only been observed in some rare cases. Sometimes remains or parts of circles are observed.

From those observations it is clear that the morphology of the reaction zone is strongly dependent on the crystallographic orientation of the Co_2Si. No quantitative relationship has been established yet.

Phase Equilibria/Composition

The ternary Co-Si-Zn phase diagram has not been extensively investigated but a cross-section at 395°C was tentatively described by Osinski (6). No ternary compounds are present, so the system consists of five intermediate cobalt-zinc binaries and four intermediate cobalt-silicon binaries. The silicon-zinc system is a simple eutectic with no intermediate compounds or solid solutions. Silicon is only slightly soluble in the cobalt-zinc binaries (up to 1 at.-%) and zinc is only slightly soluble in the cobalt-silicon binaries.

Quantitative analysis was performed by EDS. In the Co_2Si/Zn couples three reaction products have been found: γ_1 (11.0 < at.-% Co < 12.8) at the Co_2Si side, γ_2 (7.2 < at.-% Co < 8.7) at the zinc side and CoSi. The latter is present as small grains inside either γ_1 or γ_2. During the reaction of Zn with Co_2Si one mole of CoSi and one mole of γ_2 are formed according to: 13 Zn + Co_2Si = $CoZn_{13}$ (γ_2) + CoSi. The molar volume ratio $V_m(\gamma_2):V_m(CoSi)$ is 9.2. The observation of different ratios in the diffusion couples supports our observation that the bands are not single-phase. The mixture of CoSi and γ_1 or γ_2 makes up the dark bands in fig. 1. The lighter zones are γ_1 or γ_2 compounds with some CoSi.

Kinetics

The growth velocity of the reaction zone differs from cell to cell. As a measure of the growth rate we took the widest layer present in any investigated couple. This is always the zone with the smallest band spacing (about 4 μm), thus having the largest number of bands. The measurements are presented in fig. 4. The growth is parabolic with time, indicating diffusion controlled kinetics. There seems to be an incubation period, the reason of which is not clear. The measured points can be fit to a straight line $d^2 = k.t - A$, with $k = 4128(\pm 106)$ $\mu m^2.h^{-1}$ and $A = 16768(\pm 56511)$ μm^2.

We did not observe a Kirkendall-plane in the couples, but earlier experiments in the related Fe-Zn (10) and Fe-Si-Zn systems have shown zinc to have a much higher mobility compared to the other components.

Discussion

Crystallographic Dependence of Growth

Both growth velocity and morphology of the reaction layer are dependent on the orientation of the Co_2Si grains in the substrate. Co_2Si is orthorhombic, hence its properties are anisotropic. This can affect the reaction in the following way:

The crystals at the surface present different faces to the zinc. Those faces differ in surface energy and nucleation of a new phase is influenced. Since we found the reaction to be diffusion controlled (in some parts, perhaps not in all) nucleation problems do not play a major role. Moreover, the small band present along the zinc-side indicates that growth of all the cells starts at the same time. However, newly nucleated product phases may show preferential orientation of growth (i.e. texture) if they are not cubic. The diffusion of zinc through reaction product layers is rate-determining. If the various cells in the reaction layer posess different textures, the reaction rate can be different in different cells of the reaction layer.

Appearance of Loops

The pattern which is shown in fig. 3 is a top view of the reaction layer. The pattern is very similar to dislocation loops emerging from a Bardeen-Herring source (11). In the Bardeen-Herring mechanism dislocations are multiplied by climb. We suggest that macroscopic deformation loops, which are a result of the action of what we call a "super Bardeen-Herring source", are present in the Co_2Si. The source could be a result from the arc-melting procedure, whereby the rapid cooling introduces all kinds of imperfections into the lattice. A long stretch of dislocation line, possibly resulting from stacking faults, is running parallel to the Co_2Si surface. We have observed the presence of stacking faults in Co_2Si by etching the material. A section of the line is pinned. It extends over a length of about 30 μm (fig. 3). The subsequent heat treatment then could cause the source to expand by climb, curing the missing planes, and form several rings of deformed Co_2Si, the distance between the loops ranging from 20 μm up to 45 μm. Macroscopic dislocation spirals with comparable spacing have been observed in silicon (see, e.g. (12)). When this faulted Co_2Si is joined with zinc and annealed we suggest that when a Co-Zn phase nucleates, the remaining Co and Si are segregated out of the growing Co-Zn phase and precipitate as CoSi on the dislocation loops, i.e. the dislocation loops are covered by small CoSi-nuclei. In the course of reaction those nuclei grow out to macroscopic particles, decorating the places where used to be the dislocation loops.

Because of the polycrystalline nature of the substrate we can only observe this pattern in its purest form in some rare cases. Unfavorable orientations of the substrate grains and/or differently oriented dislocations will probably lead to the chaotic patterns that we commonly observe in cross-sections perpendicular to the diffusion direction.

Periodic Layer Formation

The mechanism of periodic layer formation has been debated by several authors. At present, the arguments point out two possible mechanisms, but the experimental evidence is scarce and verification is difficult.

The first model was proposed by Osinski (6) and considers the periodic build-up and release of stresses at the substrate/product silicide interface. The model is however only qualitative and supported by up til now non-reproducible experimental evidence.

The second model was proposed by Kao and Chang (8) and considers periodic thermodynamic instability of the substrate/product interface with subsequent new nucleation of the reaction layer. Although more quantitative, their model does not consider the possibility of two-phase layers. The bands in the periodic layered morphology are always observed to be two-phase.

For both models it is difficult to see how they can be used to explain the phenomena found in the Co_2Si/Zn system as described in this paper. We are setting up a series of critical experiments in various systems in which the periodic layer growth has been observed to find a predictive model to describe the phenomena.

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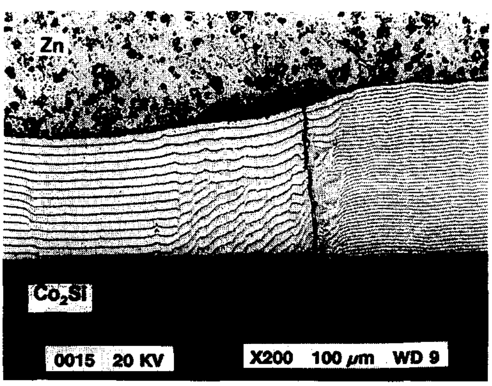

Figure 1. Reaction zone of a Co_2Si/Zn diffusion couple, annealed for 28 hours at 390°C (BEI).

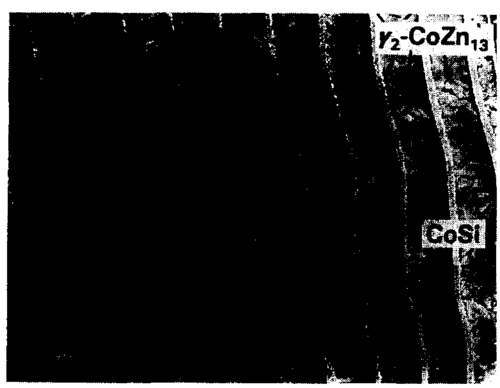

Figure 2. Etched reaction layer, revealing the small grains of CoSi packed into bands. Grain structure of $CoZn_{13}$ is also revealed (SEI).

Figure 3. Cross-section of reaction layer perpendicular to the diffusion direction (BEI).

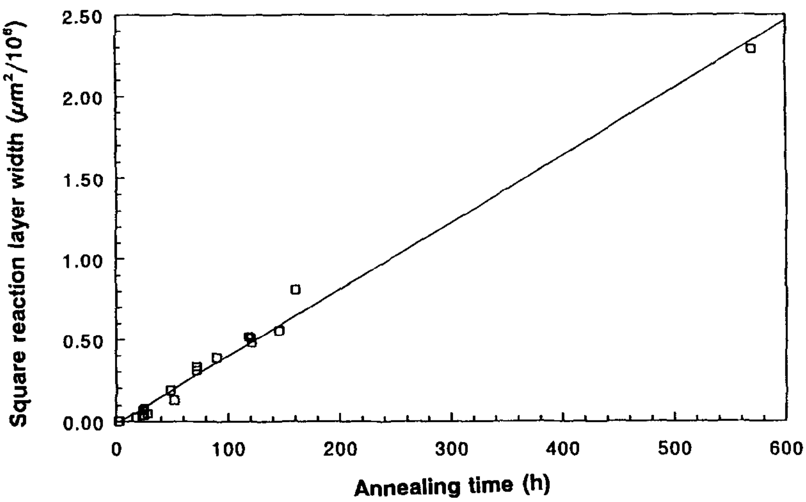

Figure 4. Square reaction layer width of Co_2Si/Zn diffusion couples at 390°C as a function of annealing time