Ordered bcc phases in a Cu-Pd-Mg hydrogen separation membrane alloy

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Abstract

Surface poisoning and corrosion are shown to be the most significant degradation mechanisms acting on the hydrogen membrane materials at elevated temperatures in synthesis gas derived from coal. Among other metallic dense membrane materials, Cu-Pd alloys have demonstrated promise for being resistant against these degradation mechanisms. Also, it has been shown that Cu-Pd compositions containing ordered bcc (B2) crystal structure exhibit high hydrogen permeability. Magnesium was one of the elements that were found to extend the stability of the B2 phase field in Cu-Pd to higher temperatures. High-temperature XRD, SEM and TEM were utilized to characterize the structure of a Cu-43Pd-5.6Mg (in atomic percent) alloy. Two ordered phases with the same crystal structure (B2), but with different chemical compositions, were identified in the alloy. Transition temperature from these ordered bcc phases to the disordered fcc phase was significantly increased by addition of Mg compared to the binary Cu-48Pd alloy.

Keywords: Hydrogen separation membranes, Cu-Pd alloys, Microstructure, High-temperature XRD

Introduction

To produce high purity hydrogen fuel from coal, hydrogen gas has to be extracted from synthesis gas (syngas), a product of coal gasification. Using gas separation membranes is one way to achieve this goal. The U.S. Department of Energy has established a set of performance targets for hydrogen separation membranes for the syngas applications in its Hydrogen from Coal program [1]. Although a variety of hydrogen separation membrane materials exist today, none of them are shown to be suitable for employment in contaminant laden syngas at elevated temperatures. Surface poisoning and corrosion are shown to be the most significant degradation mechanisms acting on the membrane materials at elevated temperatures in gases containing carbon dioxide, carbon monoxide, water vapor, and impurities such as hydrogen sulfide, arsenic, selenium, and mercury. Among other metallic dense

membrane materials, Cu-Pd alloys have demonstrated promise for being resistant against these degradation mechanisms [2-4].

The Cu-Pd binary system contains an ordered bcc (B2) phase field from about 35 at% Pd to 47 at% Pd at temperatures lower than 400°C [5]. The critical point of the B2 phase is at 598°C for a composition of 40 at% Pd. It has been shown that Cu-Pd compositions containing ordered bcc (B2) crystal structures exhibit hydrogen permeance comparable to pure palladium [6]. In the Cu-Pd membranes with primarily B2 phase, the superior hydrogen flux increases up to temperatures at which the alloy transforms primarily into a disordered fcc structure where a sharp drop in flux occurs.

The present authors have postulated that the enlargement of the B2 phase field in the Cu-Pd system by addition of ternary elements can be beneficial due to the evidence presented above. Magnesium was one of the elements that were predicted to hold the potential for stabilizing the B2 phase using first principles density functional theory (DFT) calculations [7]. The motivation of the present work is to verify by experiment the theoretical predictions.

Experimental Procedure

A 40 gram button of an alloy with an aim composition of $\text{Cu}_8\text{Pd}_7\text{Mg}$ (The DFT calculations were based on a B2 supercell of 16 atoms where one Mg atom is substituted for a Pd atom [7]) was prepared on a water-cooled copper hearth in a vacuum arc furnace back-filled with argon using high purity elemental materials. The button was melted three times to ensure homogeneity. Furthermore, the button was subjected to a homogenization heat treatment at 950°C for 72 hours. Bulk samples for microstructural characterization were held at 400°C for 21 days to approach equilibrium and then were furnace-cooled to room temperature. One sample was annealed at 400°C for one week and then quenched into cold water to determine whether there was a difference in microstructure when it was furnace-cooled or water-quenched. All heat treatments were carried out in a tube furnace with flow of high purity argon.

Wavelength dispersive x-ray fluorescence spectroscopy (WDXRF) (Rigaku, ZSX Primus II) was used for the chemical analysis. Standard Cu-Zn alloys (NBS 1101 and NBS 1103) were used for calibrating the WDXRF. The phase identification was done using x-ray diffraction (XRD) (Rigaku, Ultima III with a high temperature stage). Cu K_α characteristic radiation was used to scan a 2θ range of 25° to 55° at each temperature from 580°C to 920°C in 20°C increments. A bulk specimen with a polished surface was heated in a high temperature stage in vacuum at a rate of 2°C/min and was held for 15 minutes at temperature before each scan. All x-ray scans were conducted at a rate of 0.5° per minute at the increments of 0.02°. The XRD patterns were indexed using the ICDD PDF-4+ database [8]. PeakFit peak separation and analysis software [9] was used to reveal the hidden peaks.

Microstructure was characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Scanning electron microscopes (JEOL JSM-7000F FEM and FEI Inspect F50 with Oxford INCA Microanalysis) were used to obtain compositional contrast images in back-scattered electron mode and microchemical data. TEM samples were prepared by mechanical polishing and ion milling, where the samples were cooled using liquid nitrogen during the ion-milling process. Diffraction

contrast imaging, electron diffraction, high resolution TEM imaging and microchemical analysis were performed at room temperature in a JEOL 2100 equipped with a LaB₆ electron source and X-ray Energy Dispersive Spectrometry (XEDS).

Results

The chemical composition of the Cu-Pd-Mg alloy was analyzed using XRF and was, in mass percent, 40.9 Cu and 1.7 Mg with a balance of Pd (51.4 Cu, 5.6 Mg, 43.0 Pd in at.%). The XRF analysis of a sample from the button was done after the homogenization and equilibration heat treatments were carried out.

XRD spectra obtained at various temperatures between 580°C and 920°C were plotted in Figure 1. At temperatures lower than 680°C, the XRD spectra suggested a single phase of an ordered bcc (B2) structure. However, a peak separation analysis of the individual XRD spectra, acquired at lower temperatures, revealed multiple peaks for each set of reflections from the B2 phase planes, as illustrated in Figure 2. Although the (100) and (111) diffraction peaks of the B2 phase possessed this feature, it was more evident in the (110) peak. The double feature appeared as a primary peak with a right shoulder on the location of the (110) peak at the room temperature spectrum (Figure 2). The peaks on the XRD spectra at the elevated temperatures were shifted slightly to the left compared to the room temperature spectrum due to thermal expansion of the lattice. In addition, the shoulder on the right of the (110) peak became more pronounced. As the temperature increased to 620°C, the right shoulder became the dominant peak. It was clear that there were two peaks at this narrow 2 θ range. One was at 42.58°, corresponding to a d(110)-spacing of 0.2125 nm, and another was at 42.98°, corresponding to a d(110)-spacing of 0.2103 nm, at room temperature.

At 680°C, the first indication of the fcc phase was recorded as reflections from the (111) crystal plane. As the temperature increased above 680°C, the volume fraction of the fcc phase increased while the volume fraction of the B2 phase decreased. At 880°C, the B2 phase disappeared except for a very small fraction that persisted up to 920°C, as indicated by a small (110) peak. At temperatures higher than 680°C, the (110) peak with the larger d-spacing disappeared as the fcc (111) peak began to grow (shown in Figure 2). At 700°C and above, the XRD spectra exhibited one B2 (110) peak. This peak got smaller while the fcc (111) peak grew larger as the temperature increased above 700°C.

Temperature dependence of the lattice parameter of the bcc and fcc phases, as determined from the XRD spectra, is demonstrated in Figure 3. Two lattice parameters for the B2 phase were calculated from the two (110) peaks discussed above. The difference between the two lattice parameters at room temperature is 2.66×10^{-3} nm.

A general view of the microstructure of the Cu-Pd-Mg alloy is shown in a backscattered electron image in Figure 4a. Large matrix grains (in the order of 100 μ m) were decorated with smaller, disc-shaped grains. Although the large grains appeared in a variety of contrast on the BSE images, the disc-shaped grains were observed with a uniform contrast. A larger magnification BSE image, shown in Figure 4b, indicates the location of the spots where the microchemical analysis on this particular area of interest was done using EDS. The results of this analysis are given in Table 1. The EDS analysis was repeated on

four other areas of interest on the sample with very similar results. As shown in the table, the two phases had distinctly different compositions. The disc shaped grains contained less magnesium compared to the large grains. They also had lower palladium content. In addition, the images clearly show that the volume fraction of the disc-shaped phase was less than the large grained phase. The contrast difference among the large grains in Figure 4 was not due to the compositional difference as the microchemical analysis done on spots 4, 5 and 6 indicated similar compositions for these grains with varying contrast.

An interface region between the two phases, one with high Mg content (R1) and one with low Mg content (R2), was investigated using TEM, as shown in Figure 5. Regardless of the difference in composition, the two regions presented the same diffraction patterns, as shown in the inset of Figure 5. The small lattice parameter difference between the two phases was not revealed by the conventional electron diffraction. Interestingly, one set of satellite spots, mainly along the (100) planes, were present in the diffraction patterns from both the R1 and R2 regions. The satellite spots indicated the existence of a local compositional modulation in the R1 and R2 regions. Such compositional modulation was clearly evident in the high-resolution TEM images and the corresponding power spectrum, as shown in Figure 6. The modulated structures were mainly along one set of (100) planes, indicated by the arrows. The modulation period was about 4 times the interplanar spacing of (100) plane of the matrix phase with the B2 structure. The high resolution TEM image in Figure 7 also indicated the random distribution of the modulated structures. In the regions with the modulated structures, such as framed area C in Figure 7, the existence of modulation was accompanied by the weak satellite spots shown in the corresponding spectrum. By contrast, in the regions without modulation, such as the framed area A and B shown in the images, there were no satellite spots shown in the Fast Fourier Transformation (FFT) spectrum. In addition to the R1 and R2 regions both with B2 structures and randomly distributed modulated regions, but different Mg content, no additional crystal phase was found under TEM. This TEM result is consistent with the XRD results presented previously.

In order to check whether there was a difference between the observed microstructure cooled in the furnace from 400°C and quenched from 400°C, a sample was annealed at 400°C for 1 week and quenched into cold water. The microstructure of the samples that were water-quenched and furnace-cooled was very similar in terms of morphology, size and volume fraction of the two B2 phases.

Discussion

Comparison of the results from the XRD, SEM and TEM analyses points to the existence of two ordered phases with the same crystal structure, but different chemical compositions below 680°C. These two phases have the B2 crystal structure with slightly different lattice parameters. At room temperature, most of the volume of the Cu-43Pd-5.6Mg alloy is taken up by the B2 structure with a lattice parameter of 0.3000 nm. This phase appears as large grains in the microstructure. It is palladium rich with increased magnesium content. Based on these results, this phase is designated as PdMg in this paper since it is essentially the B2 phase that is present in the binary Pd-Mg system. It has a very large Cu solubility of about 41 at% at 400°C with Cu substituting for Mg since the Pd content is fairly close to its stoichiometric 50 at%. The other B2 phase has a lattice parameter of 0.2974 nm at room temperature.

Morphology of this phase is quite different and appears in the SEM images as disc-shaped individual particles in the matrix of PdMg. It has a small Mg solubility of about 1 at% at 400°C. Based on the results, this phase is designated as CuPd in this paper since it is essentially the B2 phase that is present in the Cu-Pd binary system.

CuPd is the minor phase up to approximately 600°C until its volume fraction increases with the temperature and becomes the major phase above 600°C, as indicated by the XRD spectra in Figure 2. Conversely, the PdMg phase diminishes with increasing temperature and completely disappears at 680°C. Its final disappearance coincides with the first appearance of the fcc phase. Since the diminishing of the PdMg phase begins at lower temperatures than that at which the fcc phase first appears, the PdMg phase must transform gradually into the CuPd phase as the temperature increases to 680°C. Although this transformation does not require a change in crystal structure (both phases have the B2 structure), it requires a significant amount of diffusion of all three elements between the two phases.

Note that the B2 phase that is stable above 680°C (see Figure 2) has a lattice parameter slightly larger than the B2 CuPd phase below 680°C. This increase is more than can be accounted for by thermal expansion. This discontinuity in the lattice parameter of B2 CuPd phase at about 680-700 °C could be due to several possible reasons. The most likely reason is the relaxation of a highly stressed B2 structure with the first appearance of the fcc phase with smaller molar volume, creating space for the B2 phase to expand. The second reason is the formation of a new B2 phase out of a ternary invariant reaction ($\text{B2 CuPd} + \text{B2 PdMg} \rightarrow \text{fcc} + \text{B2}$). This new B2 phase has a slightly larger Mg solubility than B2 CuPd at low temperatures and thus its lattice parameter is slightly larger. The third reason is that, although B2 CuPd disappears in the Cu-Pd binary system above 600°C, its small solubility for Mg may stabilize it in the ternary and cause formation of an island of B2-CuPd in a sea of the fcc phase. The fourth reason is an error due to the uncertainty in the peak splitting analysis.

The first explanation is favored because it also supports the events taking place at the lower and higher temperatures. At temperatures between 580°C and 680°C, the XRD data show that there is a decrease in volume fraction of the PdMg-B2 phase and an increase in volume fraction of the CuPd-B2 phase. Since there is no other phase observed at these temperatures, it is concluded that the PdMg-B2 transforms into CuPd-B2. This means that an increase in the Pd and Mg content of the CuPd-B2 phase should take place. The increase in the Pd and Mg content must cause an increase in the lattice parameter since both of these elements have an atomic size larger than Cu. However, the XRD data does not show an increase in the lattice parameter of the CuPd-B2 phase beyond what is already expected from thermal expansion. Since there is no transformation taking place between room temperature and 580°C, it is assumed that the increase in lattice parameter between these temperatures is due solely to thermal expansion. The increase in the lattice parameter from 580°C to 660°C follows the same slope indicating no increase in the lattice parameter additional to that due to thermal expansion. Therefore, this transformation must cause internal compressive stress in the CuPd-B2 structure. This is the stress that is relieved when the fcc phase with a smaller molar volume first appears at 700°C causing a sudden increase in the lattice parameter of the CuPd-B2 phase.

If the structure of the CuPd-B2 phase does not expand despite the increase in its Pd and Mg content between 580°C and 660°C and develops internal stresses instead, space created because of the molar volume difference between the PdMg and CuPd phases as the PdMg diminishes must be filled by some process. In addition to a possible slight change in the dimensions of the alloy piece, an expansion of the unit cell of the remaining PdMg-B2 phase can compensate for this difference. Although this is a small change in the lattice parameter, there is an indication that the XRD data can account for this expansion in the unit cell of the remaining PdMg-B2 phase, as shown in the inset of Figure 3. If a straight trend line between the lattice parameter data at room temperature and 600°C represents the thermal expansion, a straight trend line drawn on the PdMg-B2 data between 600°C and 680°C has a larger slope and the difference in the slopes must represent an expansion additional to the thermal expansion. This additional expansion in the lattice parameter of the remaining PdMg phase may be due to the enrichment in Pd and Mg as a fraction of it transforms to CuPd. Therefore, it is concluded that the PdMg → CuPd transformation between 580°C and 680°C causes an increase in concentration of Pd and Mg in both the product (CuPd) and the remaining parent (PdMg) phases. While the enrichment of Pd and Mg in the remaining PdMg phase results in an expansion in the lattice, it does not cause a change in the lattice parameter of CuPd but creates internal compressive stress which is relieved with the appearance of the fcc phase.

At temperatures higher than 700°C, increase in the volume fraction of the fcc phase causes an increase in the lattice parameter of the remaining CuPd-B2 phase as indicated with an increased slope of the trend line. In other words, the rate of increase in the lattice parameter of the CuPd-B2 phase above 700°C is due to a combination of thermal expansion and expansion in response to an increase in the volume fraction of a more closely packed fcc structure.

The uncertainty of the binary Mg-Pd phase diagram adds to the complexity of the Cu-Mg-Pd ternary phase diagram. For example, an early assessment [10] shows that B2 PdMg decomposes at 700°C. This temperature coincides with the temperature at which the B2 PdMg disappears in the Cu-Pd-Mg in the present study. However, a recent assessment [11] shows that binary B2 PdMg decomposes at 1003°C.

Despite the ambiguities at high temperatures, the current Cu-43Pd-5.6Mg alloy is composed completely of two ordered bcc (B2) phases, namely CuPd and PdMg, at low temperatures. It has a bcc+fcc region between 680°C and about 900°C where the ordered bcc phase is CuPd. However, the fact that the XRD data at each temperature was collected after a 15 minute hold at temperature should be taken into account. Although this hold time is probably sufficient above 700°C, it may be too short for the transformations to reach completion at lower temperatures. Therefore, caution should be exercised when dealing with the reported temperatures for the transformations from the PdMg-B2 phase to the CuPd-B2 phase and B2 to fcc at intermediate temperatures. Despite these difficulties, there is a significant enhancement in the stability temperature limit of the B2 phases in the Mg containing alloy over the binary B2 Cu-48Pd compound. The binary alloy contains two phases (B2+fcc) at room temperature [6]. Increasing the temperature increases the fraction of the fcc Cu(Pd) solid solution. At about 540°C, the binary alloy becomes completely fcc. The addition of 5.6 at.% Mg to replace Pd in the binary alloy positions the alloy between the two B2 phase fields at low temperatures and pushes the transition temperature to fcc higher by 260°C.

This finding may have significant implications for the hydrogen separation membrane applications for these alloys. As shown earlier [5], hydrogen separation membranes made of Cu-Pd alloys containing B2 structure perform better (higher hydrogen flux) than the Cu-Pd alloys with fcc structure. A sharp drop in hydrogen flux through these membranes is observed when the transition from B2 to fcc takes place. Therefore, expanding the compositional and temperature range of the B2 phase field of the Cu-Pd alloys by adding Mg may significantly improve the performance of these alloys as hydrogen separation membranes.

Conclusions

Two ordered B2 phases with different compositions have been identified in the Cu-43Pd-5.6Mg alloy below 680°C. One is the binary CuPd compound with a small Mg solubility, and the other is the binary PdMg compound with a very large Cu solubility. These two phases have slightly different lattice parameters.

The alloy has a bcc+fcc region between 680°C and approximately 900°C. This is a significant increase in transition temperatures over those in the Cu-48Pd binary alloy. Expanding the compositional and temperature range of the B2 phase field of the Cu-Pd alloys by adding Mg may significantly improve the performance of these alloys as hydrogen separation membranes.

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Highlights

1. Two ordered B2 phases with different compositions have been identified in the Cu-43Pd-5.6Mg alloy below 680°C. One is the binary CuPd compound with a small Mg solubility, and the other is the binary PdMg compound with a very large Cu solubility.
2. The alloy has a bcc+fcc region between 680°C and approximately 900°C. This is a significant increase in transition temperatures over those in the Cu-48Pd binary alloy.
3. Expanding the compositional and temperature range of the B2 phase field of the Cu-Pd alloys by adding Mg may significantly improve the performance of these alloys as hydrogen separation membranes.
4. A local compositional modulation in the B2 phases was identified. The satellite spots on the TEM diffraction patterns indicated the existence of the modulation.

Table 1. Microchemical analysis (EDS) of the phases in the micrograph on Figure 4b. Elements are given in atomic percent.

Spot	Pd	Cu	Mg
1	43.2	56.0	0.8
2	43.7	55.3	1.0
3	43.1	56.0	0.9
4	48.9	41.3	9.8
5	50.1	40.5	9.4
6	49.5	42.1	8.4

Figure 1
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Figure 3
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Figure Captions

Figure 1. High-temperature XRD spectra of the experimental Cu-Pd-Mg alloy.

Figure 2. XRD spectra enlarged over the 2θ of 40° - 44° illustrating the evolution of the overlapping B2 (110) peaks (existing only below 700°C) and the fcc (111) peak as the temperature is increased. The spectrum at room temperature is also included.

Figure 3. Lattice parameters of the phases as a function of temperature as determined from the XRD analysis.

Figure 4. Back-scattered electron images of the microstructure of the Cu-Pd-Mg alloy. A general view (a) and disc shaped second phase in darker contrast (b). The markers indicate the locations of the microchemical analysis (Table 1).

Figure 5 . TEM image with corresponding SADPs.

Figure 6. High-resolution TEM image and corresponding FFT spectrum taken from R1 in Fig 5.

Figure 7. High-resolution TEM image showing non-uniform distribution of the compositionally modulated regions and corresponding FFT spectra.