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Quantitative explanation of the enhancement of surface mobility of the metallic glass $Pd_{40}Cu_{30}Ni_{10}P_{20}$ by the Coupling Model

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ABSTRACT

Surface diffusion coefficient $D_s(T)$ measured for the canonical metallic glass, $Pd_{40}Cu_{30}Ni_{10}P_{20}$, by the method of surface-grating decay was found to be more than eight orders of magnitude larger than the bulk diffusion coefficient. So far no theory has attempted to account quantitatively for this spectacular enhancement of diffusion at the surface. The objective of the research reported in this paper is the application of the Coupling Model (CM) to predict the size of the surface diffusion found in $Pd_{40}Cu_{30}Ni_{10}P_{20}$. The prediction compares well with the size of the enhancement obtained by experiment. There is yet another prediction of the CM, which is $D_s(T)$ having the same Arrhenius activation energy as the bulk diffusion coefficient D_V^{Co} of the tracer ^{57}Co atoms in the same metallic glass. This prediction is also verified by the experimental data, and it provides additional support of the theoretical explanation of the enhancement of diffusion at the surface. A successful application of the CM to account for the decoupling of diffusion coefficient of P from that of Pd in the bulk of a similar metallic glass, $Pd_{43}Cu_{27}Ni_{10}P_{20}$, is recalled because the physics involved therein is similar to the present problem.

1. Introduction

Surface diffusion coefficient $D_s(T)$ of the canonical metallic glass, $Pd_{40}Cu_{30}Ni_{10}P_{20}$ (Pd40) was measured at temperatures below the bulk glass transition temperature $T_g = 566$ K by Cao et al. [1] using the method of surface-grating decay. However, the bulk diffusion constant $D_v(T)$ of this metallic glass had never been measured before. Therefore the actual enhancement of mobility at the surface determined by the ratio $D_s(T)/D_v(T)$ has not been determined. Cao et al. were forced to use, as substitute of $D_v(T)$, the bulk $D_V^{Pd}(T)$ of Pd of a different metallic glass, $Pd_{43}Cu_{27}Ni_{10}P_{20}$ (Pd43) measured at temperatures above its $T_g = 582$ K. Moreover, the Arrhenius temperature dependence of $D_V^{Pd}(T)$ of Pd43 above $T_g = 582$ K was extrapolated down to 519 K, and the extrapolated values were used to determine the enhancement of surface mobility of Pd40. The large difference in T_g of 16° between Pd43 and Pd40 makes the size of the enhancement determined in the manner by Cao et al. uncertain. Therefore it is necessary to take into consideration of the higher $T_g = 582$ K of Pd43 than 566 K of Pd40 before its $D_V^{Pd}(T)$ can be used to represent $D_V^{Pd}(T)$ of Pd40 and obtain accurate enhancement of surface mobility. This is one of the purpose of this paper.

After obtaining accurate value of the ratio $D_s(T)/D_v(T)$ below $T_g = 566$ K for Pd40, naturally the next step is to explain the enhancement quantitatively by theory. This had not been done by Cao et al. or anyone else, and is the main purpose of the research reported in this paper. Previously, the Coupling Model (CM) was applied successfully to explain quantitatively the surface mobility enhancement of a molecular glass-former [2]. We apply again the CM to predict the surface diffusion enhancement of Pd40, as well as the temperature dependence of $D_s(T)$, and compare with the experimental data. We make it absolutely clear that the analysis of data and the theoretical results of this paper are entirely new, and had not been given before by Cao et al. [1]. The only thing we have taken from Cao et al. are the $D_s(T)$ data measured by them. Hence, reported in this paper are new research with results making scientific advance.

2. Resolving the problem due to absence of $D_V^{Pd}(T)$ of $Pd_{40}Cu_{30}Ni_{10}P_{20}$

Measurements of surface diffusion of the canonical metallic glass, $Pd_{40}Cu_{30}Ni_{10}P_{20}$ (Pd40) were made by Cao et al. [1] using the surface grating method. Two-dimensional gratings with different wavelengths, λ, were created and the decay of surface grating was monitored. Mullins [3] showed that for a sinusoidal grating, the grating amplitude h decays exponentially, $h = h_0 \exp(-Kt)$, where the decay constant K is given as a polynomial of $q = 2\pi/\lambda$ by $K = Fq + Aq^2 + Dq^3 + Bq^4$. The coefficients F, A, D, and B have been given before by Cao et al.[1] and will not be duplicated here except the surface-diffusion term, $Bq^4 = D_s\gamma\Omega^2\nu q^4/kT$, from which the surface diffusion coefficient D_s was determined. In this

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term, γ is the surface tension, Ω the molecular volume, v is the number of atoms per unit area of surface. The values of $D_s(T)$ were deduced from the measured decay constant K at a number of temperatures T below the bulk $T_g = 566$ K of the metallic glass [1], but they were not presented explicitly and instead given in a plot of log$K$ vs. T (see Fig. 2d in Cao et al.). Also data of the bulk diffusion coefficient D_V^{Co} of Co (as substitute for D_v^P of P) in Pd40 measured by Zöllmer et al. [4] at temperatures above and below $T_g = 566$ K were also presented in the plot of log$K$ vs. T instead of a plot of logD_V^{Co} vs. T.

Bartsch et al. [5] showed the Stokes-Einstein relation holds for Pd in the bulk of a related metallic glass, $Pd_{43}Cu_{27}Ni_{10}P_{20}$ (Pd43), over 14 orders of magnitude of its $D_V^{Pd}(T)$ and temperatures down to about 592 K, which is 10 degrees above $T_g = 582$ K. This justifies that $D_v(T)$ is the same as $D_V^{Pd}(T)$, and hence the ratio $D_s/D_V^{Pd}(T)$ gives the enhancement of surface mobility in Pd43, and in the similar Pd-based metallic glasses $Pd_{40}Cu_{30}Ni_{10}P_{20}$ (Pd40). The smaller components, Co, Ni and P, are faster and are decoupled from Pd. The decoupling increases with decreasing temperature reaching about 4 orders of magnitude at 592 K.

To determine the enhancement of surface diffusion in Pd40, the bulk diffusion coefficient $D_V^{Pd}(T)$ of Pd in Pd40 are needed, but unfortunately so far it has not been measured. Available instead is the bulk diffusion coefficient $D_V^{Pd}(T)$ of $Pd_{43}Cu_{27}Ni_{10}P_{20}$ (Pd43) but only at temperatures above its $T_g = 582$ K from the work of Bartsch et al. [5]. Thus the best Cao et al. [1] could do in determining the ratio $D_s(T_g)/D_V^{Pd}(T_g)$ for Pd40 is to use $D_V^{Pd}(T_g)$ of Pd43 by assuming it is the same as that of Pd40. This assumption may be unjustified in view of the large difference of 16° between the T_g's of Pd43 and Pd40. In the next section we reanalyze the available data to give a more realistic values of $D_V^{Pd}(T)$ for Pd40 from that of Pd43, after having taken into consideration of the large difference in their T_gs.

3. New determination of the enhancement of surface diffusion coefficient for Pd40

To proceed, we show first all the data that are available for reconsideration and reanalysis in Fig. 1. These are the $D_s(T)$ data of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ (Pd40) measured by surface grating decay below the bulk $T_g = 566$ K together with D_V^{Co} of the tracer ^{57}Co atoms (pale blue close diamonds) measured by Zöllmer et al. [4] in the same material above and below $T_g = 566$ K. These values of D_V^{Co} are taken as approximately the same as D_v^P in accord with that found by Bartsch et al. [5] above T_g. In addition we have the $D_V^{Pd}(T)$ data of Pd (black close inverted triangles), and $D_V^{Co} \approx D_v^P$ of $Pd_{43}Cu_{27}Ni_{10}P_{20}$ (Pd43) measured by Bartsch et al., all at temperatures above $T_g = 582$ K. The line straddling the data of $D_V^{Pd}(T)$ is a reproduction of that drawn by Bartsch et al. The brown stars are D_V^{Co} of the tracer ^{57}Co atoms in Pd43 measured by Zöllmer et al. [4].

From the figure it is clear that the data of $D_s(T)$ measured by grating decay and $D_V^{Pd}(T)$ are not available at any common temperature. The best one can do is to extrapolate the apparently Arrhenius T-dependence of $D_s(T)$ of Pd40 to $T_g = 566$ K, and compare with $D_V^{Pd}(T)$ of Pd43 somehow extrapolated also to the same temperature of $T_g = 566$ K. However due to the significant larger $T_g = 582$ K of Pd43, its $D_V^{Pd}(T)$ cannot be identified with that of Pd40. This is forewarned by the difference in the values of D_V^{Co} (green closed squares) and D_v^P (blue closed triangles) found in Pd43 by Bartsch et al. [5] than D_V^{Co} in Pd40 (pale blue close diamonds) by Zöllmer et al. [4], which can be seen by inspection of Fig. 1. Notwithstanding, we can still use the $D_V^{Pd}(T)$ data of Pd43 for $D_V^{Pd}(T)$ of Pd40 after scaling reciprocal temperature (x-axis of Fig. 1) by the factor, 582/566, the ratio of their glass transition temperatures. This operation is justified by the isochronal condition at T_g that $D_V^{Pd}(T_g)$ or viscosity has the same value.

The T_g-scaled D_V^{Co} and D_v^P data of Pd43 shown in Fig. 2 now also have their values in good agreement respectively with those of Pd40, which in turn provides some assurance that after the T_g-scaling the $D_V^{Pd}(T)$ of Pd43 can be taken as $D_V^{Pd}(T)$ of Pd40. The line drawn by Bartsch et al. after being scaled in the same way, now appears as a parallel line on top. Its intersection with the orange vertical line located at 1000/566 K^{-1} determines the value of $D_V^{Pd}(T_g)$ for Pd40. The length of the orange line gives the size of the enhancement of diffusion, log$[D_s(T_g)/D_V^{Pd}(T_g)]$, of 8.5 decades at the surface of $Pd_{40}Cu_{30}Ni_{10}P_{20}$. The exact size may deviate somewhat from this value due to the extrapolation

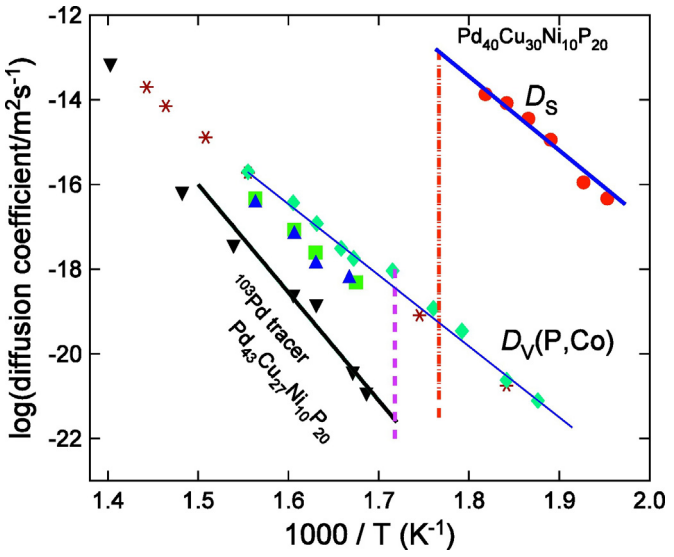

Fig. 1. Surface diffusion coefficients $D_s(T)$ of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ (red close circles) and the fit to the Arrhenius T-dependence (blue line) from Cao et al. [1]. Bulk tracer diffusion coefficients D_V^{Co} of Co (pale blue close diamonds) of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ from Zöllmer et al. [4]. The bulk tracer diffusion coefficients of $Pd_{43}Cu_{27}Ni_{10}P_{20}$, $D_V^{Pd}(T)$ of Pd (black close inverted triangles), $D_v^P$of P (blue closed triangles), and D_V^{Co} of Co (green closed squares) are from Bartsch et al. [5]. The brown stars are D_V^{Co} of Co of $Pd_{43}Cu_{27}Ni_{10}P_{20}$ from Zöllmer et al. [4]. The two vertical lines (from left to right) indicate the values of 1000/T for $T = 582$ K and 566 K, the T_gs of the two metallic glasses. The thick black line is the same as that drawn by Bartsch et al. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

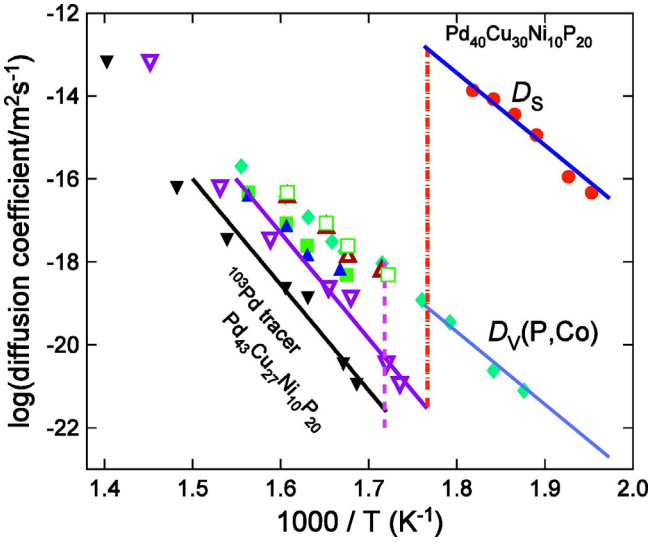

Fig. 2. All closed symbols and lines are the same as in Fig. 1 for $Pd_{40}Cu_{30}Ni_{10}P_{20}$ and represent the same quantities. Open symbols are new. They represent the bulk tracer diffusion coefficients, $D_V^{Pd}(T)$ (purple open inverted triangles and the purple line), D_v^P (open brown triangles), and $D_V^{Co}(T)$ (open green squares)) of $Pd_{43}Cu_{27}Ni_{10}P_{20}$ from Bartsch et al. [5] after temperatures are scaled by the ratio of the two glass transition temperatures (see text). The pale blue line placed near the data of D_V^{Co} of Co (pale blue close diamonds) in $Pd_{40}Cu_{30}Ni_{10}P_{20}$ from Zöllmer et al. [4] has exactly the same slope as the blue line above it, showing that $D_V^{Co} \approx D_v^P$ have the same activation energy as $D_s(T)$. The length of the orange line gives an estimate of the enhancement of surface diffusion at $T_g = 566$ K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)