

Diffusion in amorphous and crystalline Cu–Ti studied by the muon spin relaxation technique

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Abstract

Muon spin relaxation measurements have been carried out on Cu–Ti alloys with the aim of investigating the diffusional properties of hydrogen in crystalline and amorphous structures. Muon diffusion has been studied in samples both with and without hydrogen. In the amorphous alloys, muon diffusion could not be described by a single Arrhenius process. The muon spin relaxation results for the amorphous samples compared favourably with existing proton diffusion parameters obtained by NMR.

1. Introduction

Cu–Ti, like many other binary metal alloys, is of interest due to its hydrogen storage properties. In particular, the claim that an amorphous alloy absorbs much higher hydrogen concentrations than a polycrystalline alloy [1] has attracted much attention. This might indicate that the limiting hydrogen concentration is determined by the availability of diffusion paths for the hydrogen rather than by electronic properties.

An investigation with the muon spin relaxation (μ SR) technique [2] was initiated with the aim of examining diffusion processes in samples with and without hydrogen to supplement the data in existence from other techniques. A unique contribution of μ SR is the ability to study diffusion in the absence of hydrogen; that is, diffusive motion of muons may be examined directly using the motional narrowing of the dipolar linewidth from surrounding lattice nuclei. It is also possible to implant muons into a hydrided lattice to study hydrogen motion using the μ SR technique. In the presence of a sufficiently high hydrogen concentration, the motion of the muon can be blocked by

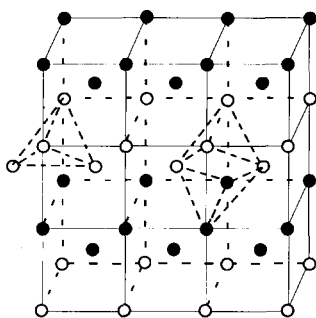


Fig. 1. The CuTi structure: ●, copper; ○, titanium. The unit cell is displayed twice showing the Ti_4 and the Cu_2Ti_4 sites.

neighbouring hydrogen atoms so that the muon is unable to move until a neighbouring site is vacated [3]. Experiments using this inhibited muon motion to trace hydrogen diffusion reveal information about the jump rates of both the muon and the hydrogen.

Few metallic glasses have been investigated using the μ SR technique. One early study was on $Cu_{10}Zr_7$ which was measured in both amorphous and crystalline form [4]; the surprising result was that diffusion in the two samples was the same. Subsequently crystalline and amorphous samples of Cu–Ti [5] and Zr–Ni [6, 7] have been studied with various hydrogen concentrations. In these experiments, considerable differences were observed between diffusion in the amorphous and crystalline materials. A metallic glass of $Ni_{35}Ti_{65}$ saturated with hydrogen has also been measured [8].

In this paper, some of the Cu–Ti data previously reported in preliminary form [5] have been subjected to a complete analysis. New data are presented on two unhydrided samples measured in zero magnetic field. These recent studies have higher statistics and required smaller correction for muons stopping in the sample holder.

Figure 1 shows the CuTi structure. It consists of alternating double layers of copper and titanium. The endothermic nature of the H–Cu interaction implies that the most favourable sites are Ti_4 tetrahedra (*i.e.* tetrahedral sites with four titanium nearest neighbours) and measurements on amorphous $CuTiH_x$ showed that the next most likely site to be populated is the octahedral Cu_2Ti_4 site [9, 10]. In these metallic glass alloys, substantial short-range chemical order usually exists. Thus, in spite of the absence of long-range order, it is still possible to discuss which types of site are occupied although there is considerable spread in the nearest-neighbour distances [10].

2. Experimental details

The samples contained equal amounts of copper and titanium. A polycrystalline sample (c-CuTi) took the form of a nugget of 27 mm diameter.

An amorphous alloy (a-CuTi) was produced by the melt spinning technique and a disc 40 mm in diameter was made by compacting the resultant ribbon. A description of the method used for the preparation and characterization of these glassy metal hydrides is given by Libowitz and Maeland [11, 12]. It should be noted that some texture is usually obtained in samples prepared by melt spinning and, as mentioned above, these amorphous alloys generally exhibit considerable short-range order [13]. The amorphous sample was hydrided by pressure loading and the concentration of the amorphous sample was determined to be a-CuTiH_{1.44} which is ideal for comparison with measurements reported in the literature.

A crystalline hydride was also prepared [14]; however, the exceedingly high concentration obtained through repeated loading indicated that phase segregation had occurred. The measurements made on these samples are presented elsewhere [15].

The μ SR technique (*e.g.* see ref. 2) is based on the implantation of a muon and the examination of its subsequent decay. As the positive muon is essentially a light isotope of hydrogen ($I=1/2$, $m_\mu=0.11 m_p$), samples without hydrogen may be studied with a view to understanding how an isolated proton might diffuse in the dilute limit. In concentrated hydrides the muon can be effectively blocked by the surrounding hydrogen atoms such that it is unable to move until a hydrogen atom jumps vacating a site (*e.g.* see refs. 3, 16 and 17). In this way muons can be used to trace the motion of hydrogen.

The measurements presented here were made both in zero field (less than 0.01 mT) and in an applied transverse field (2.2 mT). The relative merits of these two experimental modes may be summarized as follows. In transverse field, the muon spins precess at the Larmor frequency, the amplitude of the precession being modulated according to the environment of the muons and their dynamic behaviour. Thus a measurement of the resultant rate of the muon spin depolarization gives information on the position and behaviour of the muon. Zero-field measurements enable smaller depolarization rates to be measured than transverse field due to the enhanced dipolar linewidth and, in addition, there is a greater sensitivity to slow dynamics in this mode. The spectra do, however, require careful normalization when measuring in zero field.

The two unhydrided samples were both measured in zero and transverse applied field at the ISIS pulsed muon source at the Rutherford Appleton Laboratory. The amorphous hydride was studied in the interval 15–340 K at ISIS in transverse field. At temperatures not much higher than this, phase segregation begins to take place in the hydrided metallic glass which would have considerably complicated the interpretation of the data [18, 19]. The transverse field experiments have been presented elsewhere; however, the hydride data have been subjected to reanalysis using a dynamic 'Abragam' function [2] as discussed in the next section and are presented here with the zero-field data.

3. Results

3.1. Crystalline and amorphous CuTi

Typical zero-field spectra measured at comparable temperatures are shown in Fig. 2 for the crystalline and amorphous binary alloys. At the lowest temperatures, there is no substantial difference in the depolarization rates; however, the two higher-temperature spectra reveal that a marked change had taken place in the crystalline material. To examine the temperature dependence of the depolarization rate all spectra were initially fitted with a single gaussian function: $G(t) = \exp(-\sigma^2 t^2)$ where σ is the depolarization rate. The result is shown in Fig. 3. It is clear that the onset of motional narrowing takes place at a lower temperature in the crystalline sample than in the amorphous one, and that the temperature dependence differs greatly.

In general, it is a straightforward matter to calculate the expected depolarization rate by summing the contributions from the surrounding dipoles under the assumption that the muon is static at a certain site. As the nuclear moments of copper and titanium differ and the titanium moment is so dilute, the determination of which type of site is occupied in a crystalline sample should be easy. Furthermore, it is well established that muons have a tendency

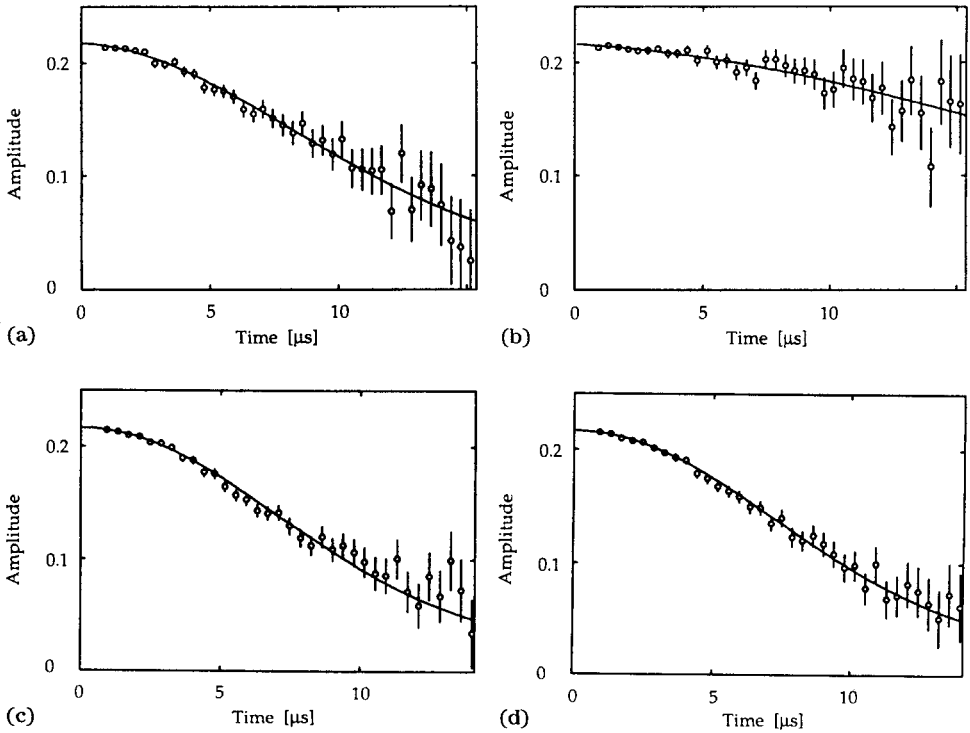


Fig. 2. μ SR spectra for crystalline and amorphous samples of CuTi measured in zero field at comparable temperatures: (a) c-CuTi, 18 K; (b) c-CuTi, 96 K; (c) a-CuTi, 18 K; (d) a-CuTi, 97 K.

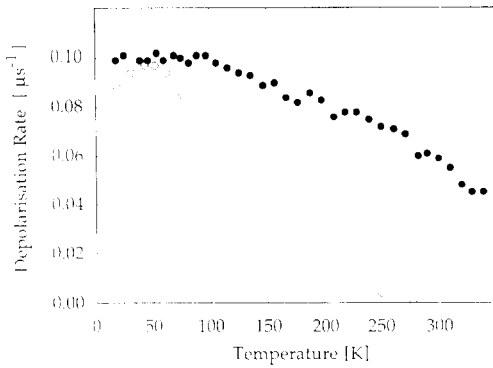


Fig. 3. The temperature dependence of the muon depolarization rate for c-CuTi (○) and a-CuTi (●). The fits were made with a gaussian function.

to occupy the same interstitial sites as hydrogen and that hydrogen in CuTi preferentially occupies Ti_4 tetrahedra (see Fig. 1). The value calculated for a point-like muon occupying a Ti_4 site in unhydrided crystalline CuTi measured in zero field was $0.097 \mu s^{-1}$ (*c.f.* $0.13 \mu s^{-1}$ for a muon in a Cu_2Ti_4 site). The experimental value at low temperatures (see Fig. 3) was about $0.10 \mu s^{-1}$ for both the crystalline and amorphous alloys in good agreement with this.

A fit of the zero-field data using a dynamic Kubo–Toyabe function [20] enables muon jump rates and activation energies to be obtained. In this case a fixed value of $0.097 \mu s^{-1}$ was used for the static depolarization rate σ_0 in crystalline CuTi and an activation energy of $0.031(4)$ eV was found by fitting an Arrhenius function to the rates in the motional narrowing regime (Fig. 4). The amorphous alloy was better fitted using a higher depolarization rate ($\sigma_0 = 0.12 \mu s^{-1}$) indicating that not all of the muons were completely static even at 18 K. This is supported by the analysis: the rate varies slowly with temperature in the lowest temperature range.

A single Arrhenius process is inadequate to fit the data in the amorphous alloy (Fig. 4). The best fit is obtained using three processes in which case the activation energies are $0.016(2)$, $0.030(2)$ and $0.112(3)$ eV. A reasonable fit is also found by using just two rates in which case the activation energies are $0.021(1)$ and $0.107(4)$ eV. The errors quoted are probably underestimated as they are determined from fits to the data in a given temperature interval. The activation energies obtained and the temperature intervals in which they are applicable are listed in Table 1.

3.2. Amorphous copper titanium hydride

The metallic glass hydride a-CuTiH_{1.44}, was measured in a transverse applied field of 2.2 mT. In comparison with the unhydrided alloys, a considerably increased depolarization rate σ was obtained due to the strong contribution from the hydrogen to the dipolar sum. As with the unhydrided samples, the data have been analysed both with a gaussian function and

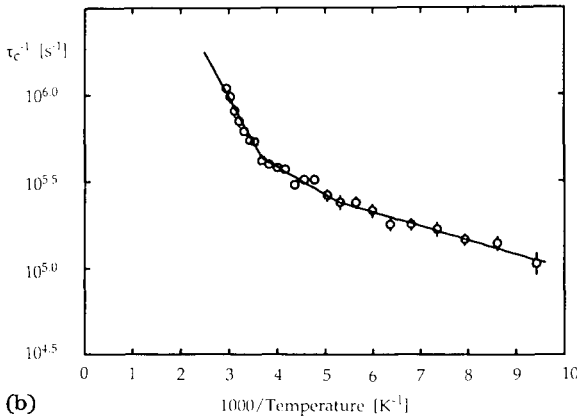
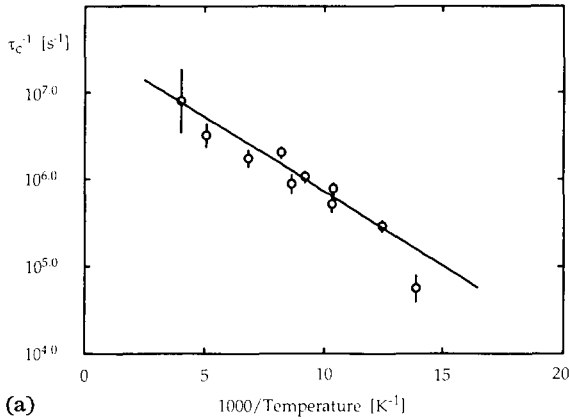


Fig. 4. Arrhenius plots for (a) c-CuTi and (b) a-CuTi.

with a dynamic function [2]; the result of fits to the former is displayed in Fig. 5.

Several distinct processes are evident (Fig. 6), with some motional narrowing occurring even at the lowest temperatures. A comparison between the amorphous samples with and without hydrogen (Figs. 3 and 5) reveals a remarkably similar temperature dependence.

The measured low-temperature depolarization rate in a-CuTiH_{1.44} is 0.22 (1) μs^{-1} (see Fig. 5). Unfortunately, a realistic calculation of the static depolarization rate is difficult to make for this intermediate concentration as the occupation of tetrahedral and octahedral sites is unknown for both the muon and the hydrogen. At high hydrogen concentrations, other sites are filled: no evidence has been found of hydrogen occupying other types of tetrahedra; instead the octahedral Cu₂Ti₄ site starts to be filled [9, 24]. Thus calculations have been made for the depolarization rate of a static muon in CuTiH_x assuming that the lattice is crystalline and taking no account of lattice expansion. Estimations were made for $x=1.0$ and 2.0 assuming that both muons and hydrogen occupy the same site, a tetrahedral site in

TABLE 1

The activation energies obtained for muons in CuTi and the temperature intervals in which they dominate, with results for proton diffusion obtained by NMR

Technique	Sample	Activation energy (eV)	Temperature interval (K)	Ref.
μ SR	c-CuTi	0.031(4)	70–250	
	a-CuTi	0.016(2)	90–190	
		0.030(2)	190–270	
		0.112(3)	270–400	
	a-CuTiH _{1.44}	0.019(5)	110–190	
		0.049(5)	190–260	
		0.127(4)	260–340	
NMR	c-CuTiH _{0.94}	0.87(3)	360–560	[21]
	a-CuTiH _{1.4}	0.09	150–207	[21]
		0.185	208–357	
		0.45	357–410	
	a-CuTi(H,D) _{1.4}	0.18	(230–312)	[22]
	a-CuTiH _{1.3}	0.18	(230–312)	[22]
	a-CuTiH _{1.7}	0.055	Below 230	[22]
		0.19	230–312	
	a-CuTi(D,H) _{1.4}	0.055	Below 270	[23]
		0.18	390–270	

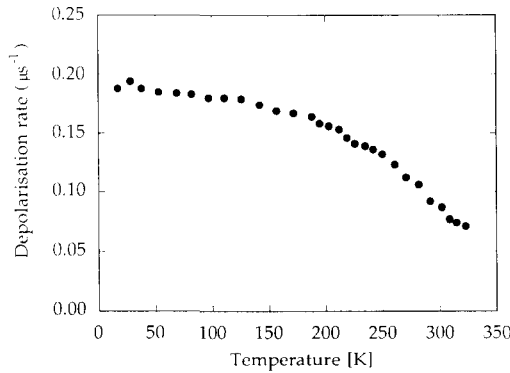


Fig. 5. The temperature dependence of the muon depolarization rate for a-CuTiH_{1.44}. The spectra were fitted with a gaussian function.

the former case and in the latter an octahedral one; the values obtained were $0.17 \mu s^{-1}$ and $0.24 \mu s^{-1}$ respectively for transverse field. A comparison with the calculated values shows that, as anticipated, the measured depolarization rate at low temperatures lies between the values expected for $x=1.0$ and 2.0 . In Fig. 6, the derived jump times are plotted as a function of inverse temperature for the amorphous hydride. Again better fits to the data using the dynamic function were obtained with a slightly higher σ_0 of $0.25 \mu s^{-1}$. Four distinct temperature intervals have been identified in the

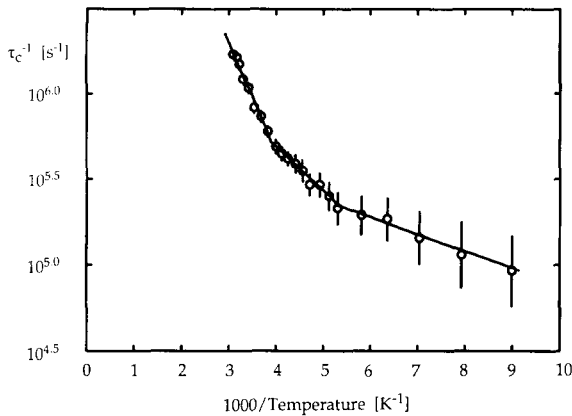


Fig. 6. Arrhenius plot for a-CuTiH_{1.44}.

amorphous alloy (the lowest temperature range is not shown). These and the corresponding activation energies are displayed in Table 1.

4. Discussion

The trends in the temperature dependence of the diffusion processes in amorphous alloys with and without hydrogen are remarkably similar as witnessed by the extracted values for the activation energies and temperature intervals (see Table 1). In addition to the μ SR data, the results from several NMR measurements taken from the literature [21–23] are listed in this table. Clearly the qualitative agreement is good; several well-defined temperature intervals have been identified using both techniques and activation energies obtained for the amorphous hydride. As is usually the case, the values obtained for hydrogen diffusion from μ SR lie somewhat below those from NMR [3, 16, 17].

In the amorphous samples, a comparison between the two μ SR measurements reveals that the diffusion processes must be related. The temperature intervals are almost identical; it is only the activation energies which differ slightly. Astonishing is the lower derived jump rate for the solitary muon in a-CuTi than for the muon in a-CuTiH_{1.44}. This demonstrates that the hydrogen serves to *enhance* the muon diffusion by a factor of 2–3 in the amorphous alloy. The presence of hydrogen must expand the lattice, giving rise to more facile muon motion.

In the amorphous alloys, uninterrupted double layers (see Fig. 1) cannot exist over more than a few lattice distances; therefore the variety of activated processes probably reflects a number of different diffusion paths. Several activation energies and temperature intervals have also been seen in NMR measurements. A comparison between the μ SR measurements and the proton diffusion studies enables the following assignment to be made. Below 190 K, the motion is due to slow muon diffusion; in the intervals above this, the

hydrogen is also mobile. It is known that, in α -CuTiH_x above about 370 K, irreversible phase segregation occurs [18, 19]; thus our measurements ceased at 340 K, giving no temperature overlap with the NMR measurements.

The distinct changeover from a process with one activation energy to another must imply that in some way one process supersedes the other. Similar pronounced breaks have been observed previously in amorphous CuTi measured by NMR [24]. In contrast, in zirconium nickel hydrides [7] measured with μ SR and zirconium palladium hydrides measured with NMR [21] the changeover between the two processes is seen as a smooth transition in the temperature interval in which both processes contribute. Thus it is deduced that in the present case the sharp transition between processes is attributable to the structure of CuTi. This is probably also the case in the metallic glass Ni₃₅Ti₆₅ where a break between two activated processes is seen at about 220 K [8].

The strong similarity between the hydrogen diffusion results and those presented here for α -CuTi suggests that the tunnelling effects normally dominant in muon diffusion are essentially absent in the amorphous material. This would imply that the muon and hydrogen diffuse by the same mechanism, which is not generally the case in pure metals [25].

At the lowest temperatures measured, μ SR measurements reveal that there is a process taking place which is characterized by an extremely low activation energy in the amorphous alloys. This has not been observed in the crystalline samples, nor, to our knowledge, has it been mentioned in the literature. The energy concerned is approximately 0.002 eV. The origin of this effect could either be muons thermalizing in one site and hopping to another of lower energy, or the amorphicity leading to a distribution in nearest neighbours and therefore to the existence of some easy diffusion paths, perhaps between just two sites. The same effect has been observed by μ SR in amorphous ZrNiH₄ but not in the corresponding crystalline sample [7] which supports the latter interpretation.

5. Conclusions

Various CuTi samples have been investigated and substantial differences have been seen between the activation energies and the number of distinct diffusional processes taking place in amorphous and crystalline materials. In crystalline CuTi, rapid diffusion (*i.e.* jump rates higher than 10^6 s^{-1}) occurred at relatively low temperatures (*i.e.* above 90 K) whilst in the amorphous sample, although some slow motion was observed at lower temperatures, the onset of long-range diffusion took place at a noticeably higher temperature. The results obtained for the amorphous alloys with and without hydrogen were almost identical.

In the amorphous alloys, the diffusion processes for muons and for hydrogen (as measured by NMR) were found to be extremely similar, indicating that μ SR gives direct information on the motion of the hydrogen.

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