Search for positron localization near transition-metal solutes of negative effective charge in Ni and Cu

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Abstract

Results of an early (1973) angular correlation (ACAR) study of dilute (0.5 at.%) Cu based alloys by a Japanese group were interpreted in terms of an attraction of e^+ by transition metal solutes of effective negative charge. Doppler Broadening (DB) measurements reveal no such an effect for Cu(Mn) and Cu(Ni) solid solutions as well as for Ni alloys with 3d, 4d and 5d transition metal solutes (0.1 to 1.5 at.%) i.e. no evidence of e^+ localization near these impurities is seen. Our results strongly suggest that the ACAR results are due to the metallurgical state of the samples. In contrast, significant DB lineshape parameter variations, observed for our Ni(Zr) alloys, are attributed to positron trapping in and near Ni_5Zr precipitates. Our DB results for a series of Ni(Au) alloys are understood in terms of a combination of the effect of an overall lattice expansion and a positron preference for clusters of Au atoms. The above comparison between DB and ACAR results is supported by our 'spin polarized' DB results for a (001) Ni single crystal which resemble those obtained by other groups using a 'spin polarized' 2D-ACAR technique.

Introduction

Friedel, making use of the concept of virtual bound states (VBS's), first explained the interesting magnetic properties of Ni - transition metal alloys in terms of the screening of substitutional impurities in Ni [1]. The positive muon (μ^+) and the positron (e^+), both of which predominantly probe interstitial sites, have been used to test predicted forms of impurity screening in dilute series of Nickel-transition metal alloys (of concentration ranging from 0.1 to 1.5 at %, with: Ti, V, Cr, Mn, Fe Co, Cu, Zr, Nb, Mo, Pd, Hf, Ta, W, Pt or Au). Results of a previous positive muon spin rotation (μ^+ SR) study [2] of the magnetic properties of these alloys, while clearly reflecting the emergence of VBS's, do not conclusively demonstrate the existence of a probe localization near solutes.

The possibility of such an attraction occurring for e^+ , whose wave function is relatively more extended, lead us to conduct Doppler Broadening (DB) studies both with and without an applied magnetic field.

The annihilation of a e^+ with an e^- in metals results almost exclusively in the emission of two γ rays having the same total energy and momentum as the e^-/e^+ pair. The two experimental techniques of interest here are DB, which consists of the measurement of the energy distribution of γ , and ACAR (or Angular Correlation of Annihilation Radiation), the measurement of the angular correlation between emitted γ . In both cases information about material properties may be inferred from the form of the distribution. For a recent review of positron annihilation techniques see Trifflhäuser [3]. In practice, e^+ are injected into the sample to be studied by putting it in contact with a radioactive source, here $^{22}\text{NaCl}$.

Most e^+ emitted from the source penetrate to depths of the order of hundreds of μm in metals and rapidly come into thermal equilibrium. Since the kinetic energies of most e^- in metals are greater than those of thermalized e^+ the form of measured DB and ACAR distributions reflects principally the electronic contribution. As a first approximation, one can consider that the greater the deviation from the centre of the distribution, the more tightly bound the electronic state. While limited in energy resolution by the detector, the DB technique permits the rapid acquisition of data. Due to the difficulty of directly relating the form of a measured distribution to material properties, comparative measurements are made. In the present DB study of dilute Ni and Cu based alloys, DB 'lineshapes' of alloy samples are compared to those of samples of the corresponding pure base material.

We begin by discussing our DB results for Cu and Ni based solid solutions in terms of a possible e^+ localization near solutes. For the Ni alloys, we then consider the annihilation of e^+ in defects, in and around precipitates and finally clusters of Au atoms.

Results and discussion

Search for e^+ localization near solutes in Cu and Ni

In alloys with a sufficiently low defect concentration, positively charged e^+ are in delocalized states which are concentrated in the interstitial regions. While it is generally accepted that e^+ density may be greater in precipitates and regions rich in the more attractive of the two constituents of a binary substitutional alloy [4], little convincing evidence of a preferential annihilation of e^+ near solutes exists.

Fig. 1 Schematic representation of DB results and their comparison with the simulation of results to be expected from the ACAR measurements of Doyama et al. a) Simulation procedure: Starting from the deconvoluted P+G (Parabola+Gaussian) model fit of Debowska et al [6] to pure polycrystalline Cu, simulations of Doyama's ACAR and our DB distributions are produced by convolution with the corresponding resolution functions (assumed to be Gaussian). b) DB results for solid solutions Cu(Mn) (0.5 at.%), Cu(Ni) (0.25 at.%) and 0.5 at.% Cu(Co) alloys all fall within the shaded band about zero representing our long term reproducibility (0.25%). The diagonal line represents simulated DB results corresponding to the variations in $R=N(0\text{mrad})/N(10\text{mrad})$ observed by Doyama et al (assuming that changes induced by solutes effects predominantly the width of the G component).

Results of an early ACAR study by Doyama et al [5] of dilute (0.5 at %) Cu(M) alloys (M: Cr, Fe, Co, Ni and Ge) were interpreted in terms of an attraction of the e^+ by solutes of effective negative charge, $\Delta Z_{\text{Cu(M)}} = Z_{\text{M}} - Z_{\text{Cu}} < 0$ (Z , the atomic number). They found that the ratio of peak to wing count rates of angular distributions, $R = N(0\text{mrad})/N(10\text{mrad})$, decreased in proportion to ΔZ . This decrease was understood in terms of an increasing overlap of e^+ density with more tightly bound electronic states of d character.

Homogeneous solid solutions of Cu(Mn), not considered by Doyama, as well as Cu(Ni) were prepared in an attempt to reproduce the above results using our DB system (for experimental details see [7]). The form of DB spectra are characterized by the lineshape parameters S and W , being the integral of counts over regions near the peak and in the wings respectively. As can be seen in Fig. 1a, their combination S/W is analogous to Doyama's ACAR ratio R . S/W values for these alloys, shown in Fig. 1b, do not vary with respect to pure Cu values by more than the long term reproducibility, 0.25%. In order to estimate relative changes in our S/W parameter to be expected from Doyama's results, DB spectra were simulated as shown schematically in Fig. 1a. Relative changes in S/W expected from simulated DB alloy spectra are an order of magnitude larger than our long term reproducibility. Consequently, an effect of the magnitude observed by Doyama should have been measurable with DB. Indeed, the fact that Cr, Fe and Co are known to precipitate in Cu casts some doubt on the metallurgical state of Doyama's samples and on his hypothesis that ΔZ , in an ideal solid solution, is the driving force behind the observed behaviour. In analogy with the ACAR results of Doyama et al for dilute Cu alloys a decrease in the parameter S/W with respect to the pure Ni value might be expected for solutes of effective negative charge, $\Delta Z < 0$. Our Ni alloy results [7], shown schematically in Fig. 2 for 3d, 4d and 5d transition metal solutes, indicate no such decrease in DB lineshape parameters S/W .

Fig. 2 Relative changes in S/W (per unit concentration alloying element) for all the dilute Ni alloys as a function of the effective charge ΔZ . Long term reproducibility is indicated by the shaded bands. Note that only values above these bands were observed.

The increases observed for Ni(Zr) and Ni(Au) series will be considered below. The lack of a Doyama-like decrease for solutes to the left of Ni, strengthened by virtue of the number (3 to 6) of different concentrations considered for each binary system, strongly suggests that a variation of this kind, if it exists, is smaller than our long term reproducibility. No evidence of e^+ localization near transition metal impurities in Ni and Cu alloys is found.

In Fig. 3a) our results for 5 Ni(Co) alloy samples are shown. We attribute this 'Doyama-like' decrease in S/W to superficial damage introduced during handling of the previously annealed Ni and Ni(Co) samples. The explanation lies in the extreme sensitivity of the technique to the presence of 'open volume' defects such as dislocations and vacancies. Due to their positive charge, e^+ are attracted by and localize in regions of lower than average ionic density. Their annihilation with the more weakly bound e^- found there, give rise to increased S and S/W parameters with respect to the undamaged case. Upon subsequent annealing, relative changes in S/W values observed for the Ni(Co) alloys disappeared. For the Ni and Ni(Co) samples it is reasonable to assume that the lower the concentration the more susceptible the sample to superficial damage, whence the apparent decrease in S/W.

Fig. 3 a) 'Doyama-like' DB behaviour for superficially damaged Ni(Co) alloys samples. Upon subsequent annealing, absolute S/W and S values, particularly for the pure Ni sample, decrease to the level of 1.5 at.% alloy value. b) Increases in S parameters observed for Ni(Zr) alloys containing semi-coherent Ni_5Zr precipitates and for Ni(Au) alloys, for which there exists lattice expansion and clustering of Au atoms. These results do not change upon subsequent annealing. The error bars shown in both cases are purely statistical and lines in b) are visual aids.

Positron trapping at precipitates

As shown in Fig. 3b, S parameters increase for Ni(Zr) alloys by up to 1% for the most concentrated Ni(Zr) alloy. Previous X-ray diffraction measurements clearly indicate the presence of precipitates of Ni_5Zr in the Ni(Zr) samples and TEM show equilateral triangle shaped ($0.1\mu m$ on side) semi-coherent inclusions [8]. A e^+ work function, estimated to be significantly greater in Ni than in the Ni_5Zr phase, indicates that e^+ may be trapped in the precipitates [7]. The possibility also exists that a substantial fraction of e^+ annihilate at precipitate-bulk interfaces. Irrespective of the nature of the trapping centres, the observed increasing trend of the annihilation rate is consistent with the fact that the mean free path of a thermalized e^+ in Ni is just becoming comparable, for the most concentrated Ni(Zr) alloy, with an average inter-trap distance of $0.25\mu m$ estimated from the TEM observations.

Effect of lattice expansion and clustering

As shown in Fig. 3b an increase in S was observed for the Ni(Au) alloys. The reproducibility of our results after successive anneals and chemical polishes suggests that a bulk effect is responsible. From the equilibrium phase diagram [9] it is seen that Au remains in solution at 300°C up to 2 at.%. Due to the presence of a miscibility gap it is possible that some clustering of Au atoms exists, especially in the more concentrated alloys. However, neither μ +SR [2] nor saturation magnetic moment [10] show any deviation from expected linear behaviour that might suggest that there exist important nonuniformities in the distribution of Au atoms. Lattice parameter increases linearly with Au concentration by 0.22 %/at.% [8]. In an expanding lattice, e^+ become progressively more localized in the growing interstitial regions, thereby resulting in an increasing S . The fact that S does not increase linearly may be explained by a strong positron affinity for clusters of Au atoms in these alloys.

Calculations [11] predict a slightly larger positron affinity for pure Au than for pure Ni. If volumes of Au atoms in the alloys are greater than that in pure Au, as implied by our observed positive deviation from Vegard's law behaviour [12], this positron affinity is expected to be greater still. Similarly, in an ACAR study of Li(Mg) alloys, Stott and Kubica [4], not able to account theoretically for their results, were led to conclude that e^+ localize in the more attractive Li clusters.

Comparison of DB and ACAR results.

In order to establish the validity of the comparison of our DB results with the ACAR results of Doyama et al [5] we have carried out an applied magnetic field ('spin polarized') DB measurement on a Ni (001) single crystal along the [100] direction [12], using a system similar to that of Seeger et al [13]. As shown in Fig. 4, our DB result compares favourably with the spin polarized (much higher resolution) 2D-ACAR result of Genoud et al [14], thus supporting the comparison between DB and ACAR results made above for Cu alloys.

Fig. 4 Comparison of our 'spin polarized' DB results to the 2D ACAR results of Genoud et al. for a Ni (001) single crystals along the [100] direction. In both cases data are represented as the difference between 2 spectra acquired with an applied magnetic field directed along and opposite to the flight direction of incoming e^+ . Error bars, shown for our DB results, are purely statistical. The differences in amplitude is due to the poorer resolution and e^+ polarization in our case.

Conclusions

Our DB results show no evidence of e^+ localization near transition metal solutes of effective negative charge in Cu and Ni of the kind suggested by the Cu alloy ACAR results of Doyama et al [4]. Such an effect, if it exists, is smaller than the reproducibility of our measurements. Indeed, relative changes in S/W expected from simulated DB Cu alloy spectra are an order of magnitude larger than our DB results.

A localization/trapping of e^+ in Ni(Zr) alloys was observed which increases with Zr, or equivalently, Ni₅Zr precipitate volume concentration. Lineshape narrowing observed for the Ni(Au) alloys is understood in terms of a combination of the effect of the overall lattice expansion and a positron preference for clusters of Au atoms. Finally, our spin polarized DB result for a Ni (001) single crystal which compares favourably with the spin polarized 2D-ACAR result of Genoud et al [14], supports the above comparison of DB and ACAR results for the Cu alloys.

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