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IN DILUTE AlFe ALLOYS

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NMR STUDY OF METALLURGICAL EFFECTS IN DILUTE AlFe ALLOYS

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ABSTRACT

The NMR of ^{27}Al nuclei in cold-rolled and annealed very dilute Al:Fe alloys has been investigated. Line broadening due to dislocation pinning by the impurities is the dominant effect in cold-rolled samples. Analysis of the NMR spectra measured on the homogeneous solid solution and on the precipitated alloy permits an evaluating of the parameters of the precipitated system. The role played by metallurgical effects in the NMR results for dilute alloys is discussed.

РЕЗЮМЕ

Были измерены спектры ЯМР ядер ^{27}Al в холодно-прокатных и отожженных, сильно разбавленных сплавах Al-Fe . В спектрах холодно-прокатных образцов преобладает расширение линий вследствие фиксации примесями. Анализ спектров, измеренных в однородных твердых растворах и в осажденном сплаве делает возможной оценку параметров осажденной системы. Было изучено влияние металлургической обработки на ЯМР спектры слабых сплавов.

KIVONAT

A ^{27}Al magok NMR spektrumát vizsgáltuk hidegen hengerelt és hőkezelt híg AlFe ötvözetekben. A hidegen hengerelt mintákban a szennyezéseken fennakadt diszlokációk hatására fellépő jelkiszélesedés a domináns effektus. A homogén oldatban és a precipitált ötvözetben mért spektrum elemzése útján a precipitált rendszer paramétereit határozhatók meg. A metallurgiai effektusok hatását tárgyaljuk híg ötvözetek NMR vizsgálata esetén.

I. INTRODUCTION

The electronic structures of 3d transition impurities in Al-based alloys have been extensively studied in recent years. The macroscopic parameters /e.g. the temperature dependence of the impurity resistivity in AlMn and AlCr alloys [1]/ are well interpreted in terms of the available theoretical models [2]. Nuclear magnetic resonance offers one of the microscopic methods which can furnish detailed information about both the charge and the spin density distributions around the impurities through the quadrupole effect [3] and the Knight shift [4] of the matrix nuclei. On the other hand, the susceptibility localised at the impurity site [5] can be measured by taking the NMR signal of the impurity nucleus.

Structural problems however, e.g. the low solubility in Al or dislocation impurity interactions, may influence the results considerably. It seems therefore of interest to find out what role such "metallurgical" effects play in the NMR investigations of the dilute alloy problem.

In spite of the sensitivity of the method there is a scarcity of papers dealing with these sorts of problems. The usefulness of the NMR method for the study of precipitation processes was shown by the measurements of Rowland [6] and Pavlowskaya [7] on high concentration alloys annealed under different conditions. The second moment of the ^{27}Al NMR signal was related by Faulkner [8] to the dislocation density determined by the measurement of stored energy, and Tompa [9] has established a relationship between recrystallization processes and the anisotropy of the NMR spectrum.

II. EFFECT OF IMPURITIES AND LATTICE DEFECTS ON THE NMR SPECTRUM

The cubic symmetry of the crystalline electric field in cubic metals is destroyed by impurities and lattice defects, which produce an electric field gradient at the sites of the neighbour matrix nuclei. The resulting quadrupole effect leads to a decrease in the line intensity and to a broadening of the spectrum.

It is usually assumed that in the presence of impurities the Al nuclei do not contribute to the resonance signal, if they experience a

field gradient higher than a critical value q_0 , while at the sites where $q < q_0$ they make a full contribution. Thus, the NMR signal amplitude $|3|$ /defined as the peak-to-peak value of the derivative/ of an alloy of given concentration can be described in the case of randomly distributed impurities as

$$I = I_0 / 1-c/n \quad /1/$$

where I_0 is the signal amplitude of the pure metal, c is the impurity concentration and n is the so-called "wipe-out number" characterizing the nature of the perturbation. In Al-based alloys the first-order quadrupole effect dominates at low impurity concentrations, and eq. /1/ applies to the satellite transitions only, while the central transition is taken to be unchanged. The all-or-nothing model is obviously a crude approximation, as it does not take into account the broadening of the resonance line caused by the contribution from the matrix atoms lying in a region where the values of q are near q_0 . The broadening of the line, however, is not very pronounced because of the rather strong radial dependence of the perturbation.

It has to be noted that in the case of non-magnetic transition impurities the dominant effect seems to be the perturbation of the electron charge density around the impurity [3] /charge effect/ whereas the effect of the lattice distortion due to the different size of the impurity [10] /size effect/ is apparently negligible in comparison.

Since eq. /1/ describes the NMR signal intensity at a given impurity concentration for homogeneously distributed impurities, it can not hold if precipitation takes place in the alloy. As a simplified picture we assume that the precipitation process results in a "matrix" with a relatively lower impurity concentration and in a precipitated phase with a higher concentration of impurity atoms. In order to evaluate the parameters of both the "matrix" and the precipitate, two parameters of the resonance signal, the amplitude and the second moment, can be utilized. Since the impurities are at a relatively high concentration in the precipitate, it can be assumed that the Al nuclei of the precipitate experience a higher field gradient than the critical value q_0 and thus do not contribute to the resonance signal. The impurity concentration of the "matrix" can be evaluated from the measured second moment by comparison with that measured in the homogeneous state. If the impurity concentration is known, the amplitude of the signal gives the number of Al atoms in the matrix /comparing it with the amplitude for the homogeneous alloy at the same concentration/. From these parameters we can evaluate the number and concen-

tration of the Al atoms in the precipitated phase. /In principle, the integrated intensity of the resonance signal yields the exact number of the contribution atoms. It is, however, difficult to measure the intensity to high accuracy and thus it is more convenient to use the signal amplitude for precipitate analysis in alloys with low impurity concentration./

It has to be noted, however, that the impurity concentration of the precipitate thus estimated is much lower than that evaluated for the equivalent phase from X-ray diffraction or other experiments. This is due to the definition of the precipitate used in this approximation. In fact, the actual precipitated zone - like an impurity - produces a field gradient that is higher than the value of q_0 at the surrounding matrix nuclei. This effect can be taken into account by assuming a "cloud" of given radius in the estimation of the precipitate parameters.

The perturbation around dislocations, which is less distance dependent [11], causes a marked broadening of the resonance line [8] and an increase in the second moment, roughly proportional to the dislocation density. The broadening of the line leads, of course, to a decrease in the signal amplitude, similarly to the impurity effect. In the evaluation of our experimental data on cold-rolled samples the second moment versus dislocation density curve measured by Faulkner and Ham [8] on Al foils with known deformations was used as reference.

III. EXPERIMENTAL CONDITIONS AND RESULTS

The measurements were performed at room temperature with the spectrometer described in [12]. A magnetic field varying from 5 to 9 kGauss was applied with a modulation amplitude $H_m = 2.0$ Oe. Samples of nearly identical volume were used under the same experimental conditions. The signal-to-noise ratio was of the order of 100. For the intensity measurements the ^{63}Cu signal from copper foils was used as reference.

The samples were prepared from high impurity /6 N/ aluminium and the Fe concentration, determined by spectroscopic analysis, was 2, 15, 100 and 150 at. ppm. /The solubility limit at 600°C , as determined by the resistivity method, is about 180 at ppm./ For details of the preparation and analysis see [13]. All samples were rolled to $20\ \mu$ to avoid the skin effect and prepared for the NMR measurements in three different ways: a/ only cold-rolled reduction about 99%; b/ annealed at 420°C for a week then slowly cooled; c/ annealed at 610°C for 1 hour and quenched in water. The measured electrical resistivity showed nearly complete precipitation after annealing at 420°C , and a homogeneous distribution of impurities after an-

nealing at 610°C. After annealing at 610°C the impurity resistivity measured at 77°K was proportional to the concentration, except for the 150 ppm. sample, for which - assuming linearity - an effective impurity concentration of 130 ppm. was found.

The measured values of the peak-to-peak amplitude and the second moment corrected for modulation broadening are shown in Figs. 1 and 2, respectively. The orientation dependence of the second moment after annealing indicated a nearly monocrystalline structure in the pure aluminium and in the sample with low Fe concentration [14]. The values given in the figures are averages obtained by taking into account the single crystal behaviour.

The samples with higher impurity concentrations /100 and 150 at ppm Fe/ showed approximately isotropic behaviour. The line-width was 7.8 gauss in the annealed samples and within the experimental error it did not vary with concentration. The measured values were found to be independent of the applied magnetic field.

IV. DISCUSSION

The experimental results for the differently treated samples will be discussed separately.

a/ Cold-rolled samples

After cold-rolling a marked intensity reduction and line broadening is observed with increasing impurity concentrations. This suggests the importance of the dislocation-impurity interaction mechanism. It is well known that pure aluminium self-anneals at room temperature and that cold-rolling does not influence the resonance signal after the dislocation annealing process has been completed [6]. The measurements were performed a few days after cold-rolling, in a state of equilibrium dislocation density. /It is of interest to note that in an Al:Ta alloy measured immediately after cold-rolling a line broadening independent of concentration was observed with an excess second moment of about 10 gauss² [15]. / The dislocation density evaluated from the excess second moment by making use of Faulkner's curve [8] was found to be $2 \cdot 10^8$, $5 \cdot 10^9$ and $6 \cdot 10^9$ cm⁻² as the Fe concentration increased. This non-linear dependence on the concentration is probably due to a change in the dislocation-impurity interaction mechanism. In fact, such a change was observed to occur below a critical value of the impurity concentration in Al-based alloys [16] and the present data suggest that this critical concentration lies in the range from 20 to 100 ppm.

This critical concentration seems to affect the recrystallisation process too; as mentioned in section 2, in samples with low Fe concentration a monocrystalline, while at higher Fe concentrations a polycrystalline, structure was obtained. This indicates that in the first case recrystallization is the dominant process and in the second polygonization.

b/ Annealing at 610°C

In the samples annealed at and quenched from 610°C the resistivity measurements showed that the impurity distribution was homogeneous. The signal amplitude decreases nearly linearly with increasing Fe concentrations /Fig. 1/ and the first-order quadrupole wipe-out number evaluated from the log plot of the data yields $n = 1700 \pm 10\%$, if we accept the concentrations determined by resistivity measurements and $n = 1500$ for the concentrations determined by spectroscopic analysis. This is a rather high value as compared to those obtained for non-magnetic transition impurities /e.g. $n = 98$ for AlZn alloys/, and is of the same order of magnitude as the values measured for other transition metal impurities [17]. Since it is important for the discussion of the data measured in the precipitated state, it is of interest to note that this wipe-out number is equivalent to the number of Al-atoms around an impurity in a sphere of a radius of 6 lattice constants.

The large wipe-out number can be interpreted in terms of the Anderson model [18]. The field gradient caused by the impurity is of the form $q = \beta \alpha \cos(2k_r r + \psi) r^{-3}$, where the amplitude α and the phase factor ψ depend on the phase shift of the electrons scattered by the impurity potential, with β , the so-called enhancement factor, determined by the properties of the host metal [17]. In the case of non-magnetic transition impurities the dominant contribution arises from the $\ell = 2$ phase shift $\eta_2 = \frac{N\pi}{10}$, where in Fe the number of the 3d electrons $N = 3$, and the oscillation amplitude $\alpha = 4.05$ [17]. It has been shown [19] that in a refined version of the all-or-nothing model for copper alloys the oscillation amplitude is proportional to the wipe-out number and that this version holds for Al alloys, too. Since the computed oscillation amplitude α is 0,3 for AlZn alloys [20], the similar wipe-out number to oscillation amplitude ratios in the two alloys support the validity of the Friedel-Anderson picture.

c/ Annealing at 420°C

The precipitation of a large fraction of the Fe content after annealing at 420°C has been observed by several authors [21]. The differences between the data reported for the degree of precipitation and the

composition of the precipitated phase are probably due to the different experimental methods used.

A marked change was observed in the signal amplitude and in the second moment as compared to the samples annealed at 610°C. The linear concentration dependence of both parameters shows that the degree of precipitation is roughly proportional to the impurity concentration. Considering now only the sample with 100 ppm Fe, the comparison of its excess second moment /relative to the second moment of pure aluminium/ with the values measured on the homogeneous state gives for the impurity concentration of the matrix 20 at. ppm, in good agreement with the resistivity data. By comparing the measured signal amplitude with that obtained for the same Fe concentration in homogeneous solid solution, the relative numbers of the Al atoms in the matrix and in the precipitate can be estimated as about 96% and 4%, respectively. It is to be noted that we have to take into account the difference of the signal amplitude and second moment of the slowly cooled and quenched pure Al, and the parameters were determined from the relative amplitude and second moment change. This means a Fe concentration of 0.3 at. % in the precipitate. On the other hand, the composition of the precipitate is expected to be Fe₃Al or FeAl [21], and therefore the low concentration obtained from the experimental data is evidence of the importance of the "wipe-out cloud" around the precipitate. The majority of the Al-atoms supposed to be in the precipitate are in these clouds, the radius of which must be of the order of 10 atomic distances /the number of Al nuclei perturbed by the precipitate must be somewhat greater than the number perturbed by a single impurity atom/. The radius of the precipitated grain is much smaller than that of the cloud; it probably equals a few lattice constants. This confirms the opinion that the low diffusion constant of iron in aluminium leads to the formation of fine precipitated grains, as observed by transmission electron microscopy [21].

It is of interest to note that for pure Al the value of the second moment measured on the sample slowly cooled from 420°C is lower than that of the sample quenched from 610°C. The difference can be attributed to the effect of the vacancies frozen in as a result of quenching. This effect of the vacancies is similar to that of the impurity atoms and is expected to appear also in the alloys, however, it cannot be separated from the effect of the impurities.

V. CONCLUSIONS

The present experiments have shown that the NMR parameters are markedly affected by the metallurgical conditions under which the samples

are prepared. It is therefore important to prepare well defined alloys for the experimental investigations. The dislocation pinning produces an effect which is proportional to the impurity concentration and it affects the signal amplitude in about the same measure as the impurity. Moreover, the data suggest that in the experiments reported as supporting the Anderson model [17], the effect of precipitation played an important role. Recent NMR measurements on Al Cr and Al Mn alloys [22] have shown that at room temperature the wipe-out number around manganese impurities is smaller than that around iron or chromium. This behaviour is connected with the nearly magnetic properties of the Mn impurities in aluminium causing a temperature-dependent oscillation amplitude [23] similar to the effect observed in resistivity measurements [1].

As regards the application of NMR to solving metallurgical problems, the method seems to be useful for studying the precipitation processes. The properties of the "matrix" in a precipitated alloy can be well determined and a rough estimation of the parameters of the precipitated phase is also possible. The dislocation density also can be evaluated from the pronounced changes of the second moment and thus it is expected to yield information on the interactions between the impurity atoms and the dislocations. Because of the low concentrations used in the present study the results are mostly of a qualitative nature only, but the data are thought to be of interest for comparison with those obtained by other methods.

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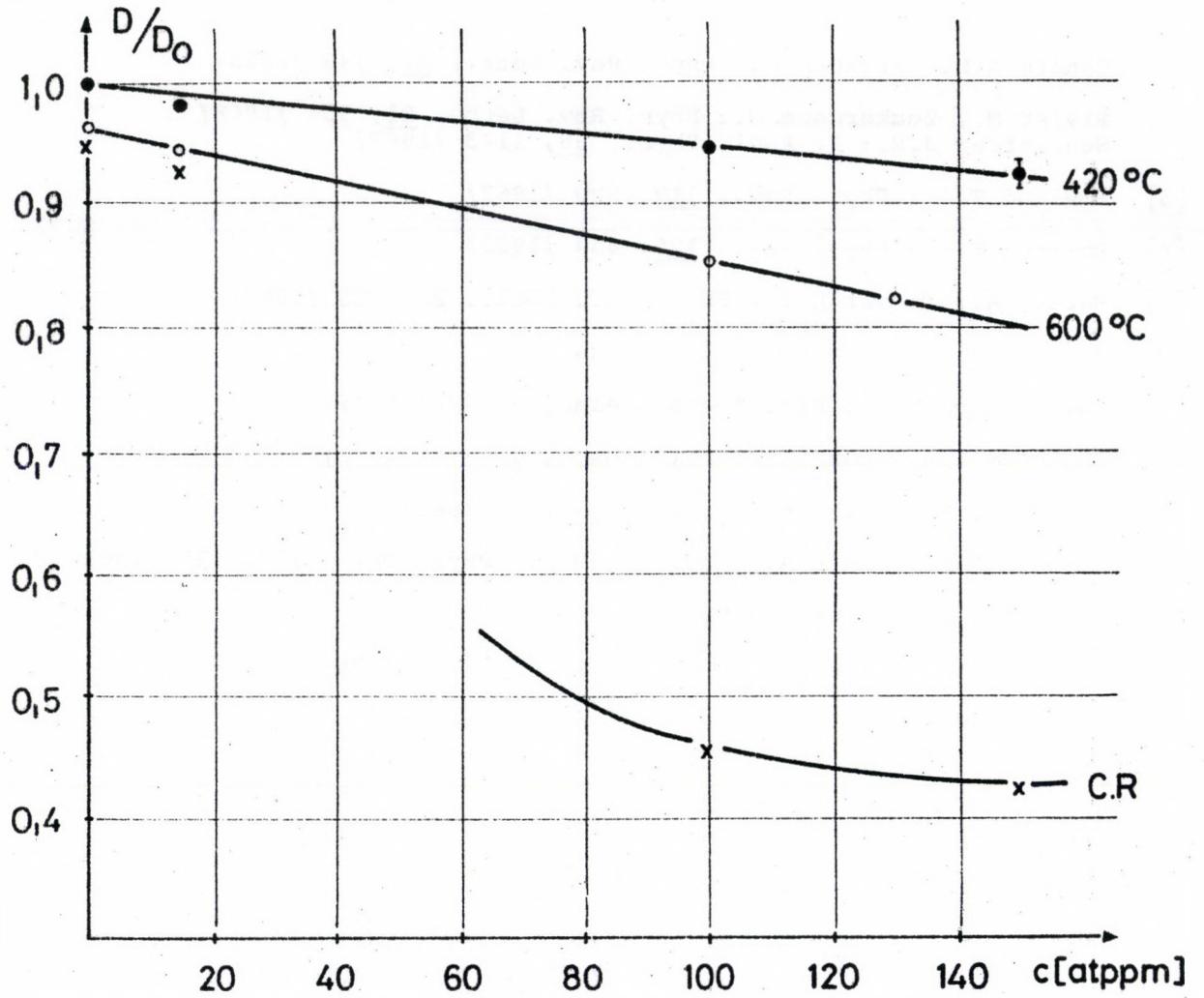


Fig. 1
Peak-to-peak amplitude of the ^{27}Al absorption derivative as
function of Fe concentration

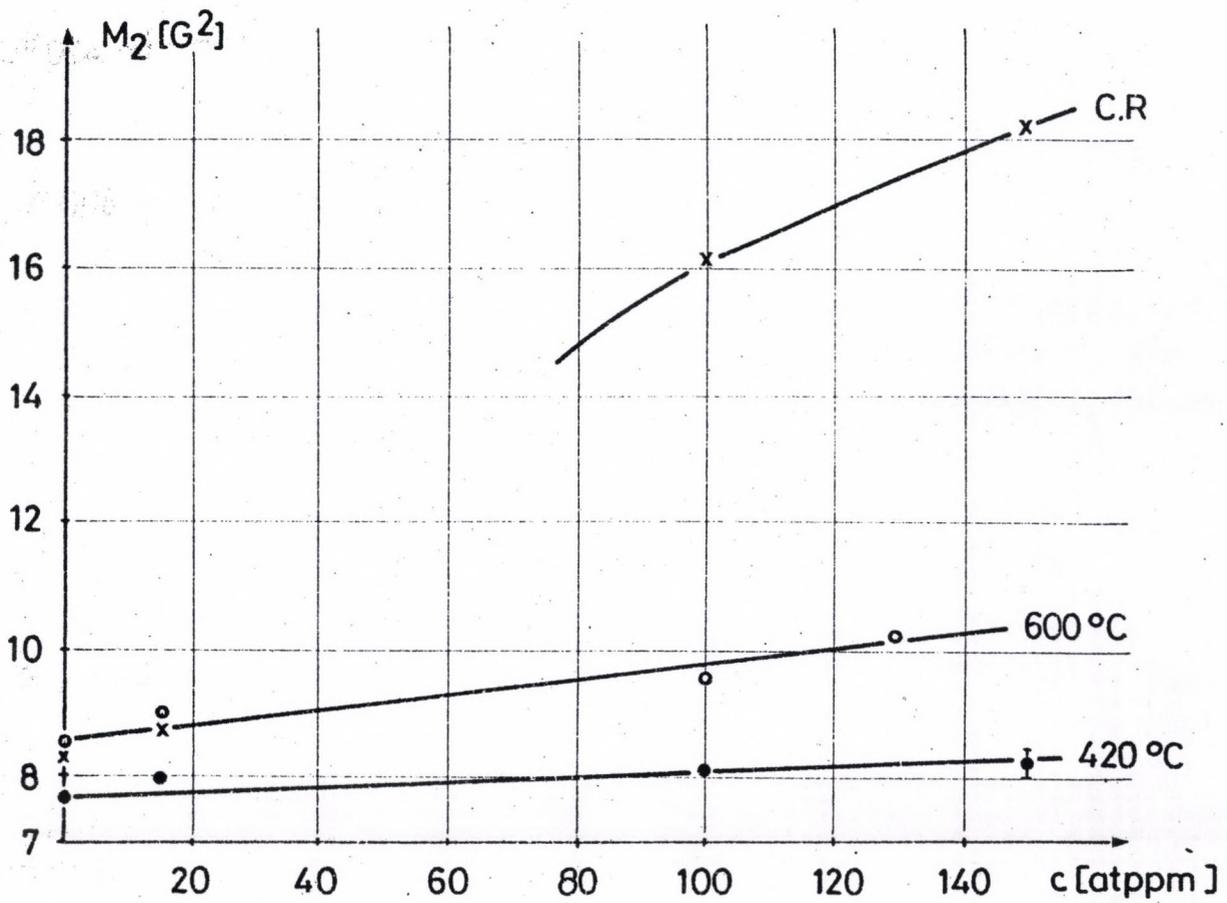


Fig. 2

Second moment of the ^{27}Al signal as a function of Fe concentration

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