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An NMR study on the mechanochemical interaction between Al and Ti in metals and hydrogels

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Abstract

^{27}Al-NMR was measured for mechanically milled Al–Ti mixtures and $Al(OH)_3$–$TiO_2 \cdot nH_2O$ hydrogels. In the Al–Ti systems, the peak of the spectrum shifted towards a higher magnetic field. This indicates the transfer of valence electrons from Al to Ti atom sites. Asymmetric broadening of the ^{27}Al-NMR spectra in the hydrogel systems after milling suggests the interaction between AlO_6 and TiO_6 polyhedra. This leads to an electronic configuration similar to that of Al_2TiO_5.

Keywords: Mechanical alloying; Intermetallic compounds; Mechanochemical interaction

1. Introduction

Incipient interaction between dissimilar species decisively dominates the mechanisms of complex formation under the influence of mechanical stress in mechanical alloying processes [1]. We have compared those processes for metal, oxide and hydrogel systems [2]. One of the most important conclusions is that the rate of complex formation is the highest in the hydrogel system. Moreover, the crystalline phase, Al_2TiO_5, which cannot be obtained by conventional heating, is produced by heating the preliminarily milled mixture. In the present study, we concentrate on the simultaneous amorphization and complex formation in the metal and the hydrous gel systems. We exclude the oxide system because the amorphization is not completed [2].

Since the complex formation should be accompanied by a change in the electronic structure, we measure solid-state ^{27}Al-NMR in order to examine whether and to what extent chemical interaction takes place, and accordingly, the mechanisms of complex formation via a mechanical route.

2. Experimental

2.1. Preparation of samples

Aluminum (Nihon Keikinzoku, particle size between 53 μm and 74 μm) and titanium (Osaka Titanium, particle size less than 10 μm) were mixed in a molar ratio of 2:1. The metal mixture was milled in an argon atmosphere by a rod-mill, comprising 10 pieces of stainless steel rods of 10 mm diameter and 190 mm length in a stainless steel cylindrical container of 105 mm diameter.

An arc-melt method was also employed for comparison to obtain alloys with the same molar ratio of metal powders, i.e. Al/Ti = 2/1.

Hydrogels were synthesized by mixing respective aqueous solutions, i.e. 0.025 M $AlCl_3 \cdot 6H_2O$ or $TiCl_4$ and 0.5 M NH_3 (aq.) at 283 K. The precipitates were washed several times in deionized water, filtered and dried at 323 K under 1.3 kPa. The gels were crushed down to particles smaller than 200 mesh (< 74 μm), dried again at 373 K and milled together in air in an

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agate vessel with eight pieces of 10 mm agate balls in a laboratory vibration mill (Glen Creston).

Calcination was carried out in a dry air flow (200 $cm^3 min^{-1}$) at a constant rate of heating, 10 K min^{-1}, up to 1573 K. After holding the temperature at 1573 K for 1 h, the calcined samples were air-quenched.

2.2. Characterization

For the observation of ^{27}Al-NMR signals of Al–Ti systems, a phase-coherent pulsed NMR spectrometer was used. Resonance spectra were obtained at room temperature, by plotting the spinecho amplitude with a box-car integrator as a function of the external magnetic field. The external magnetic field was swept in the narrow range by changing the current through modulation coils at a fixed magnetic field of a superconducting solenoid.

^{27}Al-NMR spectra of the hydrogel mixtures were also obtained at room temperature using a spectrometer (JEOL, EX-270) with a solid-state high-resolution unit (JEOL, ESH-27-T6) by a magic-angle spinning (MAS) technique.

3. Results and discussion

3.1. Amorphization of mechanically alloyed Al–Ti systems

Fig. 1 shows the X-ray diffraction patterns of the mixed metal systems. Generally, they show the gradual amorphization as usual. After milling for 50 h, major agglomeration took place. The size of the agglomerates exceeded 5 mm. After milling for 200 h, the inner wall of the container was coated with mixed metals.

In the X-ray diffractograms obtained from these mixed metals, the diffraction peaks specific to aluminum or titanium were not detected, indicating substantial amorphization and alloying, as shown in Fig. 1, spectrum (d). In order to check the coating effect of the container, the starting mixture was charged in the container with a coated inner wall and newly milled for 200 h. This sample, to be denoted as "200 'h", was less amorphized, as is shown in Fig. 1, spectrum (c). On rod-milling for more than 400 h, the grains became finer than 100 μm.

3.2. NMR spectra of the mechanically alloyed metal system

Fig. 2 shows ^{27}Al-NMR spectra for the milled metal mixture. The magnetic field on the abscissa in Fig. 2 refers to the relative value. The 0 G field in Fig. 2 corresponds to the absolute value of 61394 G.

It is to be noted that a longer milling period made the peak shift towards a higher magnetic field. This Knight shift change indicates the decrease in the charge density of the Al atom sites, suggesting the loss of valence electrons of Al. Since the peak shift took place in the presence of Ti in the milled mixture, the electron loss must be counter-balanced by the electron gain of the coexisting Ti atoms. It is plausible to consider that the s–p electrons of Al atoms transfer to the empty 3d band of Ti atoms.

In Fig. 3, the Knight shift is plotted against the milling time. The continuous and monotonous decrease in the Knight shift indicates that the amorphization progresses with the enhancement of atomic interaction between Al and Ti, without having any critical phenomena. The Knight shift of the non-milled sample

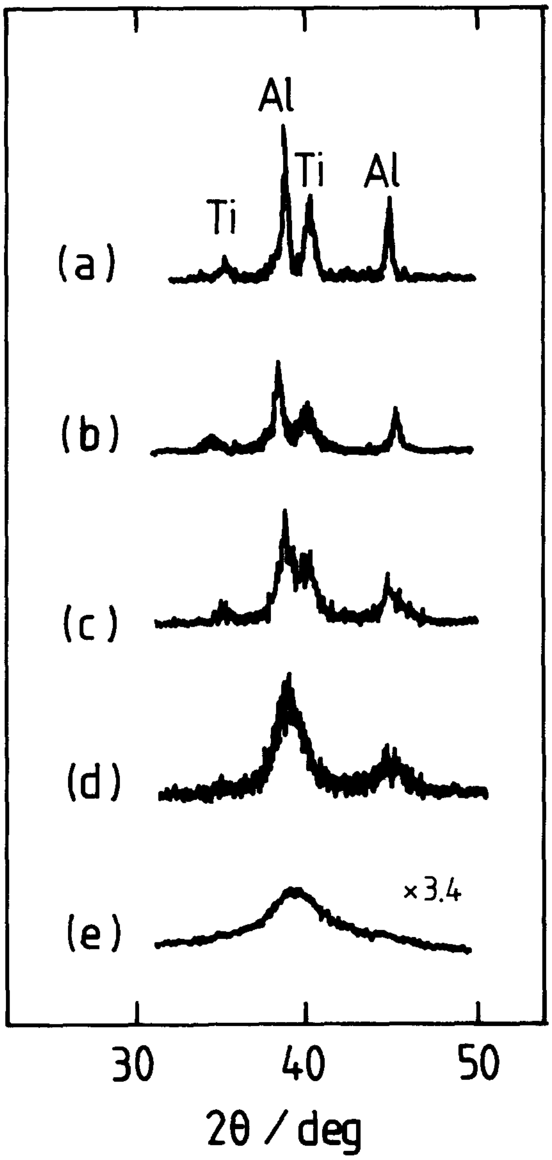

Fig. 1. XRD profiles of Al–Ti mixtures milled for: (a) 50 h; (b) 100 h; (c) 200 'h; (d) 200 h; and (e) 400 h.

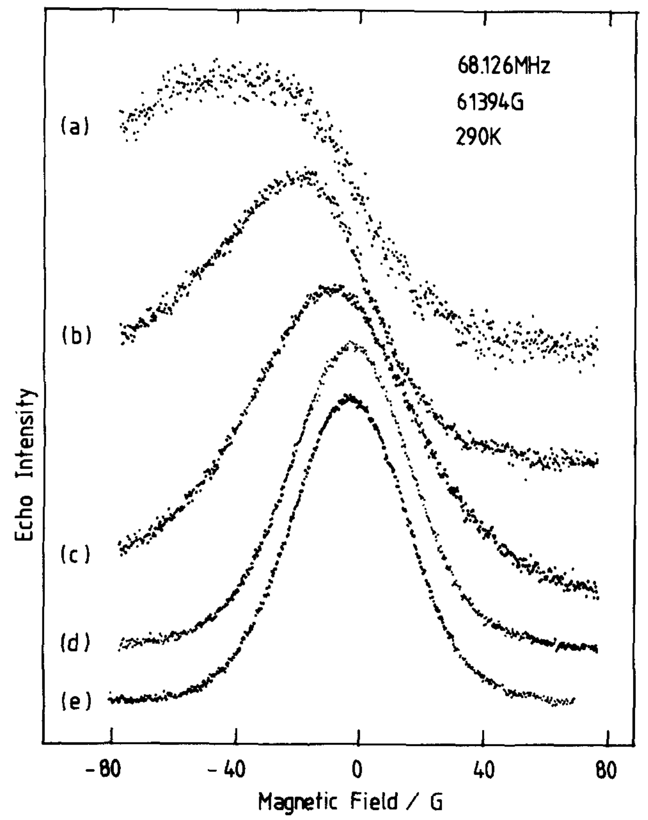

Fig. 2. ^{27}Al-NMR spectra of Al–Ti mixtures milled for: (a) 100 h; (b) 200 'h; (c) 200 h; (d) 400 h; and (e) 800 h, obtained at 68.126 MHz and at 290 K. The magnetic field zero on the abscissa is relative to the absolute value 61394 G.

was 0.164%, being equal to the reported value of the pure metallic Al [3]. After milling for more than 200 h, the Knight shift became stationary at about 0.04% and the line width of the NMR spectra became narrow, as shown in Fig. 2.

In order to examine the physical meaning of the stationary value of the Knight shift of 0.04%, an arc-melted alloy of the nominal atomic ratio Al_2Ti was prepared for comparison. The XRD profile of the arc-melted alloy showed the peaks characteristic of AlTi. The NMR line profile of this alloy was bimodal, as shown in Fig. 4. This indicates that Al atoms occupy two different crystallographic sites in the arc-melted alloy. One of the peaks at around zero relative magnetic field (the Knight shift of 0.04%) agrees with that of the atomic site for the mechanically milled Al–Ti mixture. The other one, observed at the relative magnetic field of −15 G (the higher Knight shift), corresponds to the atomic site in the metal mixtures with shorter milling time. The NMR spectrum with the latter peak must be attributed to the excess of Al over stoichiometric AlTi. Excess Al atoms replace the Ti sites of AlTi (crystallographically $L1_0$) up to relatively stable Al_3Ti ($D0_{22}$) [4,5]. Since such replacement could be done without breaking the parent fcc lattice, it cannot be distinguished by the conventional X-ray diffractometry. The NMR line width of the mechanically alloyed metal mixture is broader than those of the two different crystallographic sites in the arc-melted alloy. Therefore, Ti atoms are considered to be randomly distributed around Al atoms in the mechanically alloyed metal mixture.

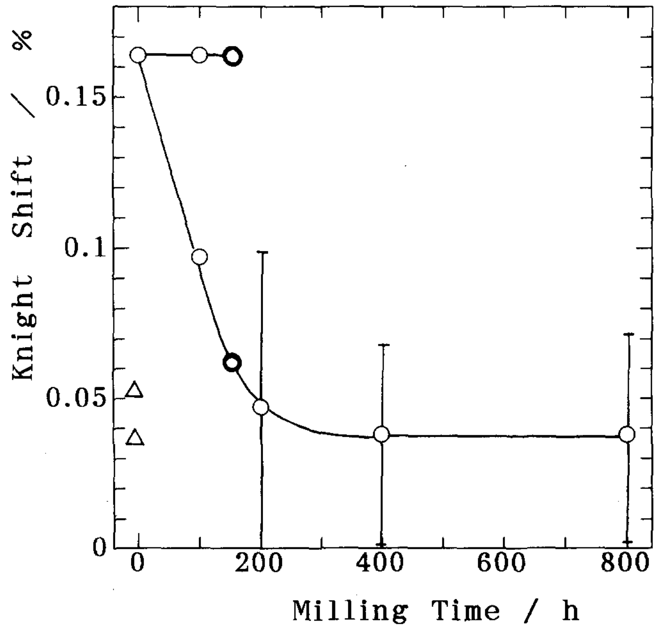

Fig. 3. Knight shifts of milled Al–Ti mixtures (circles) and arc-melted Al–Ti (triangles) at 290 K. Thicker circles are the Knight shifts of the sample milled for 200 'h. The vertical bars show the height width of each peak.

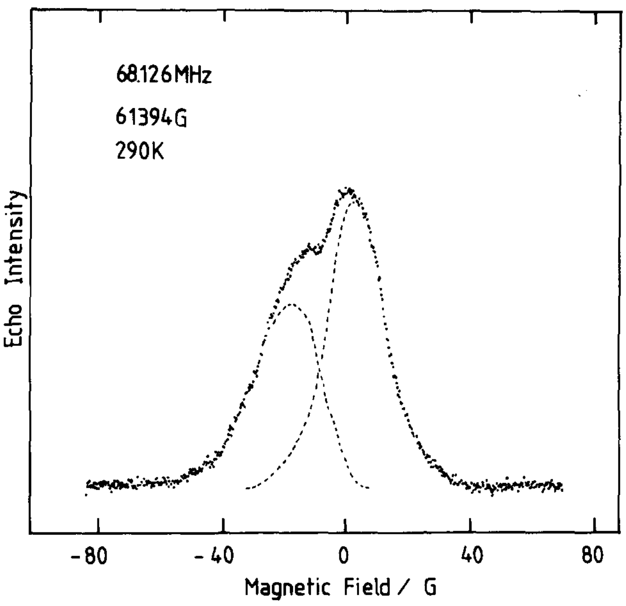

Fig. 4. ^{27}Al-NMR spectrum of the arc-melted Al–Ti, obtained at 68.126 MHz and at 290 K. The magnetic field zero on the abscissa is relative to the absolute value 61394 G.

Further characteristics of the mechanical alloying processes were examined by detailed analysis of the NMR spectra. In the spectra of the samples milled for 100 h and 200 'h, there is a shoulder at a lower magnetic value than the top peaks, as shown at the relative magnetic field of −32 G in Fig. 5, and at −49 G in Fig. 6. The knight shifts of these shoulders are both 0.164%, being assigned to the pure metallic Al. No distinctive peak shift indicates no change of charge density during milling. A slight difference in the location of the shoulder between Figs. 5 and 6 is simply attributed to the difference in the radio frequency. The presence of such a shoulder demonstrates that the complex is formed locally at the areas where the local mechanical stress exceeds a critical point, while some Al powders remain in the unreacted state owing to insufficient stresses. It is therefore concluded that the local environment of Al atoms is more diverse in the mechanically alloyed mixture than in the arc-melted alloy. Some Al atoms of the mechanically alloyed mixture are located at some Ti atom sites of the equimolar compound, AlTi, because of chemical and topological disorder. These features are typical for mechanically alloyed metals.

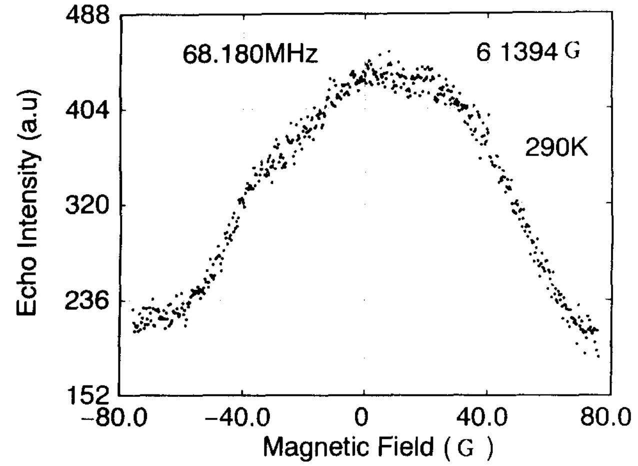

Fig. 5. ^{27}Al-NMR spectrum of an Al–Ti mixture milled for 100 h, obtained at 68.18O MHz and at 290 K. The magnetic field zero on the abscissa is relative to the absolute value 61394 G.

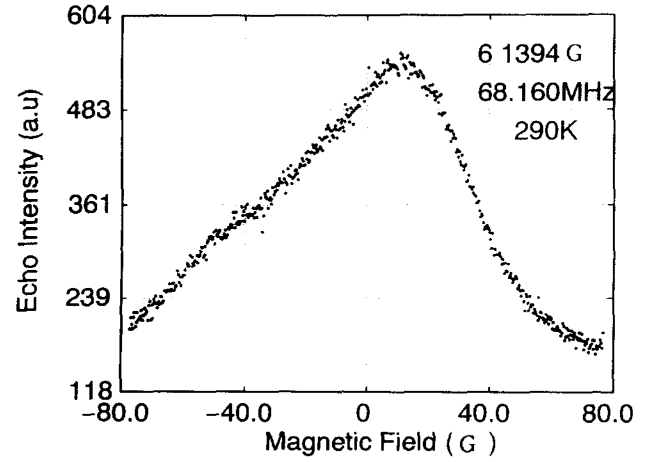

Fig. 6. ^{27}Al-NMR spectrum of an Al–Ti mixture milled for 200 'h, obtained at 68.16O MHz and at 290 K. The magnetic field zero on the abscissa is relative to the absolute value 61394 G.

3.3. NMR spectra of the hydrogel mixture

Before milling, the MAS–NMR spectrum of $Al(OH)_3$–TiO_2 mixed gel is symmetrical at the chemical shift of 0 ppm, relative to the signal obtained from $Al(NO_3)_3$ aqueous solution, as shown in Fig. 7, spectrum (b). This result agrees with that of the initial $Al(OH)_3$ hydrogel (Fig. 7, spectrum (a)).

After milling, the line shape became asymmetric with a tailing at the lower frequency side, as shown in Fig. 7, spectrum (c). This feature is similar to the spectrum obtained for the well-crystallized Al_2TiO_5, prepared by heating the milled mixture up to 1573 K and held for 1 h in air, as shown in Fig. 7, spectrum (d). Jager et al. [6] and Stebbins et al. [7] have also

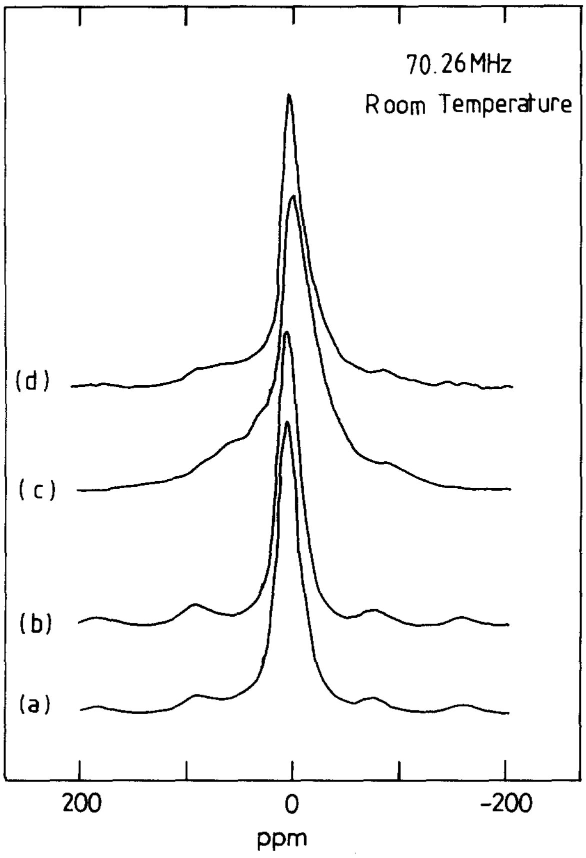

Fig. 7. MAS–^{27}Al-NMR spectra of (a) $Al(OH)_3$ hydrogel and mixtures of $Al(OH)_3$–TiO_2 hydrogel (b) before milling, (c) milled for 30 h, and (d) Al_2TiO_5 prepared by heating a 30 h-milled mixture up to 1573 K and held at 1573 K for 1 h in air. The chemical shift on the abscissa is relative to the resonance of the standard sample, $Al(NO_3)_3$.

reported this peculiar spectrum for Al_2TiO_5. It is therefore clear that the AlO_6 and TiO_6 polyhedra were mixed together, leading to an electronic configuration similar to that of Al_2TiO_5. This implies that the chemical bonding, Al–O–Ti, has been formed during a milling process.

3.4. Comparison of the NMR spectra of metal and hydrogel systems

We have already reported that longer milling results in the larger fraction of Al_2TiO_5 in the products after heating up to 1573 K for both the metal and hydrogel systems [1]. The present NMR measurements demonstrate that the reason is not only the matter of the particle size, but also the charge transfer and the redistribution of electrons leading to the formation of the new bonding, Al–Ti or Al–O–Ti, during the mechanical treatment.

The process of the incipient interaction is dissimilar between the metal and the hydrogel systems. The direct electron transfer is the initial process of interaction in the metal system. In the hydrogel mixture, on the other hand, the mixing of metal–oxygen polyhedra is the incipient process of their interaction.

It is worthwhile mentioning that better homogenization and simultaneous long-range ordering take place with the subsequent thermal treatment. The latter process is quite common in the metal and the hydrogel systems in spite of the different incipient interaction mechanisms.

4. Conclusion

Processes of complex formation between metallic Al and Ti as well as alumina and titania hydrogels are experimentally verified either by the Knight shift of ^{27}Al-NMR for metallic systems or the change in the line profile of MAS-^{27}Al-NMR for the hydrogel system. The Knight-shift value at the stationary state for the metallic system after prolonged milling is almost the same as that of the arc-melted alloy, which is free from any mechanical stresses. On prolonged milling, the signals from metallic Al disappear indicating completion of the alloying. In the hydrogel systems, the incipient interaction is the intimate mixing of AlO_6 and TiO_6 polyhedra, leading to an electronic configuration similar to that of Al_2TiO_5.

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