JOURNAL OF CATALYSIS 8, 189–196 (1967)

Solid Solution Formation in the $TiCl_3$-$AlCl_3$ System

E. G. M. TORNQVIST, J. T. RICHARDSON, Z. W. WILCHINSKY, AND R. W. LOONEY

From the Esso Research and Engineering Company, Linden, New Jersey

Received January 27, 1967

Solid solutions of $TiCl_3$ and $AlCl_3$ can be formed either directly by a cocrystallization reaction or by ball milling mixtures of $TiCl_3$ and $AlCl_3$ powers. The following evidence has been obtained for the presence of solid solutions: (a) X-ray diffraction shows only one phase which is isomorphous with $TiCl_3$; (b) the lattice parameters vary in a systematic manner with change in composition; (c) $AlCl_3$ cannot be easily sublimed from these preparations; and (d) the magnetic susceptibility dependence on temperature is the same for the ball-milled mixtures as for the cocrystallized preparations, but distinctly different from the nonmilled mixtures.

INTRODUCTION

Several years ago, it was discovered in our laboratories that crystalline substances having the composition $TiCl_3 \cdot nAlCl_3$, where n need not be a rational number, have attractive properties as catalyst components for polymerizing ethylene, propylene, and other α-olefins (*1–4*). A variety of methods were developed for preparing these materials, primarily by aluminum (*1*, *2*, *3*) and alkylaluminum reduction of $TiCl_4$ (*4*). It was found that these compounds could be made to contain only one crystalline phase (*1*), and that the structure of this phase could be varied by changes in the synthesis conditions (*2*, *4*) to be isomorphous with those three $TiCl_3$ modifications which were later designated the alpha, beta, and gamma forms by Natta (*5*, *6*, *7*). It was also found that intense grinding of the alpha and gamma forms, which have ordered layer lattice structures, results in the formation of a material having disordered stacking of the layers. This type of structure was considered a separate crystalline modification and called the delta form by Natta (*6*, *7*). The following discussion will be concerned exclusively with the three layer-lattice modifications, i.e., the alpha, gamma, and delta forms of $TiCl_3 \cdot nAlCl_3$.

The structures can be represented by layers of atoms on a hexagonal lattice. In the alpha form, the chlorine layers are in hexagonal close pack sequence (ABAB - - -) whereas, in the gamma form, they are in the cubic close pack sequence (ABCABC - - - -). In either form the metal atoms are in interstitial positions in sixfold coordination. Furthermore, the interstitial metal sites are located between alternate chlorine layers, e.g., first and second, third and fourth. This structure can be considered as composed of stacking of double layers, each consisting of two chlorine layers bonded together by interstitial metal atoms (*6*).

When either of these forms are cold-worked as, for example, by ball milling (*3*), sliding can take place at the interfaces between pairs of chlorine layers which are not directly held together by metal atoms. This leads to stacking disorder which causes both the alpha and the gamma forms to approach the same disordered structure, the so-called delta form, upon extensive grinding. An even simpler method of preparing δ-$TiCl_3 \cdot nAlCl_3$ was found in our laboratories when it was discovered that intense grinding of any layer lattice type $TiCl_3$ with $AlCl_3$ causes cocrystallization and formation of the corresponding delta form (*8*). This opened

up the possibility of studying more thoroughly the compositional limits within which cocrystallization can be accomplished as well as the properties of such cocrystalline materials. For this investigation two series of δ-$TiCl_3 \cdot nAlCl_3$ preparations were made by intensely grinding together the two components. The properties of each preparation were then determined in experiments involving: (1) atmospheric pressure propylene polymerization, (2) vacuum sublimation, (5) magnetic susceptibility measurement, and (4) X-ray diffraction analysis.

Experimental

Since $TiCl_3$ and $AlCl_3$ react readily with a variety of substances including moisture and air, the samples were maintained at all times in an inert environment.

Preparation of δ-$TiCl_3 \cdot nAlCl_3$ samples. δ-$TiCl_3 \cdot nAlCl_3$ preparations were made by two methods, one involving ball milling in a 1/2 gallon stainless steel jar for 7 days with 5/8-inch chrome alloy steel balls and the other milling for 30 min in a vibratory mill having a 1/4-oz size jar. In the former case, the pure chemicals were charged to the jar directly as received, while in the latter they were first individually ball-milled in the larger jar. This additional step was not absolutely essential for obtaining good cocrystallization, but it made certain that a homogeneous product was obtained.

To secure equal treatment for the various compositions, close to the same total charges were used for each type of equipment, viz. about 400 g in the 1/2 gallon jar and 1 g in the 1/4 oz-jar. In addition, a separate experiment was carried out in a quart ball mill jar in which 75 g of γ-$TiCl_3 \cdot 0.33AlCl_3$ were milled for a total of 4 days with small samples being taken at intervals throughout the milling.

Polymerization of propylene. The δ-$TiCl_3 \cdot nAlCl_3$ samples were used together with $AlEt_3$ as catalysts for polymerizing propylene at atmospheric pressure in xylene diluent. The procedure was essentially the same as has been described previously by Tornqvist and Langer for ball-milled $TiCl_3 \cdot nAlCl_3$ preparations, i.e., 2.5 mmoles $TiCl_3$ in 1 liter of xylene at 75°C for 1 hr, usually at a (total Al)/Ti ratio of 2 (*2*, *3*).

Vacuum sublimation of $AlCl_3$. Unmilled and ball-milled samples (25 or 50 g) of $TiCl_3 \cdot nAlCl_3$ components were subjected to vacuum sublimation for 4 hr at 4 mm Hg and at temperatures between 180° and 450°C. The heating was carried out in a 25-mm OD Pyrex tube which was inserted in a Heavy Duty combustion tube furnace. The amount of sublimed material was determined from both the weight loss of the material in the sublimation tube and the weight of sublimed material collected in a Dry-Ice-cooled receiver.

Magnetic susceptibility measurements. The magnetic susceptibilities were determined in an automatic susceptibility apparatus as described by Richardson and Beauxis (*9*). A known amount of each sample was sealed under a nitrogen atmosphere in spherical Pyrex containers and the susceptibility–temperature relationship was recorded over the temperature range −196° to 25°C. Field dependence checks were made for ferromagnetic impurities, so that corrections could be made where necessary. The susceptibilities are reported on a per gram of titanium basis by making corrections for the diamagnetic contributions of other constituent atoms.

X-Ray diffraction. Conventional diffractomer traces were made of the powder samples for crystalline phase determination and crystal size measurement by the line-broadening method. Separate traces were made for lattice parameter measurements.

For convenience of comparing the lattice parameters for the various samples, the measurements were referred to the system of hexagonal axes used for α-$TiCl_3$ (*10*).

Because of the layer stacking disorder, lattice distortion, and small crystal size produced by ball milling to obtain the delta modification, it was not possible to use a back reflection technique for measuring the lattice parameters. In fact, the only diffraction lines available for measurement were the fundamental {300} and {003} lines occurring at diffraction angles 2θ in the region of 52° and 15° with Cu radiation. Because of this rather unfavorable situation

for carrying out lattice parameter measurements, a procedure was adopted using internal standards; KCl and P_2O_5 were chosen for this purpose.

Ball-milled KCl, subsequently heated at 500°C to drive off moisture and to relieve internal strains, was used as a primary standard. When used as an internal standard, the positions of its diffraction lines, calculated from its lattice parameter 6.2931 Å (*11*, *12*), served as calibration points in a diffractometer pattern of the unknown. In this manner, the position of the {300} line for the milled mixture was measured, using the {222} line of KCl. For samples of nonmilled α-$TiCl_3$ and α-$TiCl_3$·0.33$AlCl_3$ the measurements were also extended to the back reflection region, and precise values of the lattice parameters a and c were determined by a least-squares method (*13*). For measuring the {003} lines of the milled mixtures, the two lines of P_2O_5, having d values 5.380 and 5.180 ± 0.003 Å were used. These d values were determined from a mixture of P_2O_5 and nonmilled α-$TiCl_3$, the latter serving in this case as an internal standard.

In the measurements with the diffractometer, the scanning rate was 1/8° in 2θ per minute and the recorder chart presentation was 4 inches per degree. These conditions permitted reading the peak positions to within 0.005° for the standards and to within about 0.01° to 0.02° for the milled samples. During the measurements, the room temperature was 26° ± 2°C.

The precision of the determinations varied with the experimental conditions and procedures. For the determination of the lattice parameters for α-$TiCl_3$ and α-$TiCl_3$·0.33 $AlCl_3$ by the least-squares method, the standard deviation is about 0.0005 Å for a and 0.002 A for c. From measurements on a single line, the estimated standard deviation for the corrected parameters are 0.002 Å for a and 0.02 to 0.04 Å for c. The effect of the temperature fluctuation is probably insignificant.

Results

Three of the methods used for studying the cocrystallization resulting from intense grinding, viz., vacuum sublimation, magnetic susceptibility measurement, and X-ray diffraction analysis, yielded direct proof for this phenomenon, while the polymerization studies yielded only indirect proof from comparison with the activity of ball milled $TiCl_3$·$n$$AlCl_3$ components which were cocrystalline as a consequence of their method of preparation.

Polymerization of propylene. The great increase in catalyst activity which occurs when $AlCl_3$ is cocrystallized with $TiCl_3$ was first demonstrated in two series of polymerization experiments involving unmilled and ball-milled samples of $TiCl_3$, $TiCl_3$ + 0.33 $AlCl_3$ (mixture, in case of milling, components milled separately under standard conditions), and cocrystalline $TiCl_3$·0.33 $AlCl_3$. The results reported in Table 1 clearly show

TABLE 1
Cocrystalline $TiCl_3$·0. 33 $AlCl_3$ Is Different from and Superior to Pure $TiCl_3$ or $TiCl_3$-$AlCl_3$ Mixtures[a]

Catalyst			
Composition	Ball milling time, (days)	Polymerization temp. (°C)	Polymerization rate (g/mmole Ti/hr)
α-$TiCl_3$	0	80°	0.64
α-$TiCl_3$ + 0.33 $AlCl_3$	0	80°	0.56
α-$TiCl_3$·0.33 $AlCl_3$	0	80°	4.4
δ-$TiCl_3$	6	75°	11.8
δ-$TiCl_3$ + 0.33 $AlCl_3$	6[b]	75°	15.4
δ-$TiCl_3$·0.33 $AlCl_3$	4	75°	46.3

[a] Xylene diluent; $AlEt_3$ activator; Al/Ti = 2.
[b] Components milled separately and then mixed.

the greatly superior polymerization activity of the cocrystalline solid.

The polymerization activity of ball-milled $TiCl_3$·$n$$AlCl_3$ mixtures was studied in a similar manner. The data reported in Fig. 1 show how the activity of such mixtures increases rapidly with the $AlCl_3$ content up to about 20 mole % $AlCl_3$, i.e., n = 0.25, and then rapidly decreases almost to zero at 50 mole % $AlCl_3$. Since at least part of the $AlCl_3$ in the solid component reacts with $AlEt_3$ according to the equation

$$2AlEt_3 + AlCl_3 \rightarrow 3AlEt_2Cl \quad (1)$$

addition of a quantity of $AlEt_3$ corresponding to ($AlCl_3$ + $AlEt_3$)($TiCl_3$ = 2 leaves little

or no free $AlEt_3$ to act as a catalyst component when the solid component is rich in $AlCl_3$. For this reason some experiments were also carried out with $AlEt_3/TiCl_3 = 1$ after complete reaction according to Eq. (1) had

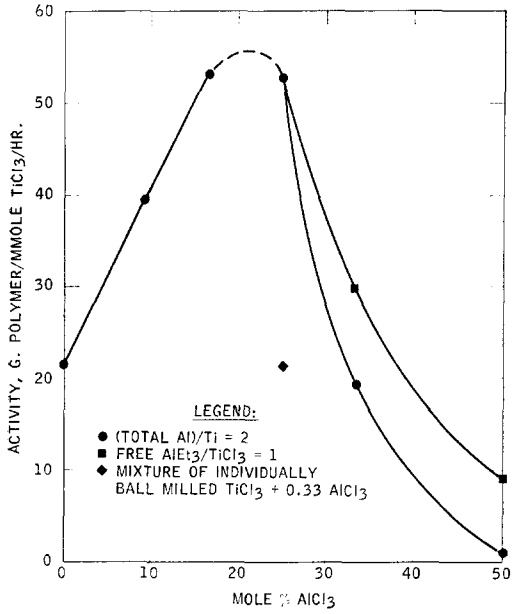

FIG. 1. The cocrystallization of $TiCl_3$ and $AlCl_3$ during milling influences catalyst activity.

taken place. This amount of $AlEt_3$ addition, which for $TiCl_3 \cdot 0.33AlCl_3$ is identical to the one giving (total Al)/($TiCl_3$ = 2, resulted in better polymer yields with the $AlCl_3$-rich catalysts, but even so the decrease in activity with increasing $AlCl_3$ content is quite striking.

It is readily recognized that these polymerization activities are very similar to those obtained with originally cocrystalline ball-milled $TiCl_3 \cdot nAlCl_3$ components as reported in Table 1. This in combination with the fact that mixtures made up from individually ball-milled components give only the activity of pure $TiCl_3$ strongly indicates that cocrystallization has taken place during the milling.

Sublimation experiments. The data presented in Table 2 clearly show that it is much more difficult to remove the $AlCl_3$ from originally cocrystalline $TiCl_3 \cdot 0.33AlCl_3$ preparations and from ball-milled $TiCl_3 + 0.33AlCl_3$ mixtures than from such mixtures made by simply shaking the two components together. Thus essentially all $AlCl_3$ is easily removed at 180°C from shaken mixtures, whereas 450°C is required for complete $AlCl_3$ removal from cocrystalline $TiCl_3 \cdot 0.33AlCl_3$ components even if they are in a finely divided ball-milled form. The ball-milled $TiCl_3 \cdot 0.33AlCl_3$ mixtures give off most of their $AlCl_3$ at a somewhat lower temperature, about 350°C, but show about the same stability as the originally cocrystalline preparations at 250°C. This difference could be the result of a somewhat incomplete cocrystallization, i.e., inhomogeneous composition, or of a smaller crystallite size in these intensely milled mixtures. The fact that the complete removal of $AlCl_3$ from these very finely divided powders requires such high temperatures leaves no doubt, however, that most or all of the $AlCl_3$ is so intimately associated with the $TiCl_3$ that it cannot be considered present as an individual species.

Magnetic susceptibility measurements. The magnetic susceptibility-temperature curves for various ratios of $TiCl_3$ and $AlCl_3$ ball-milled together are shown in Fig. 2. Also

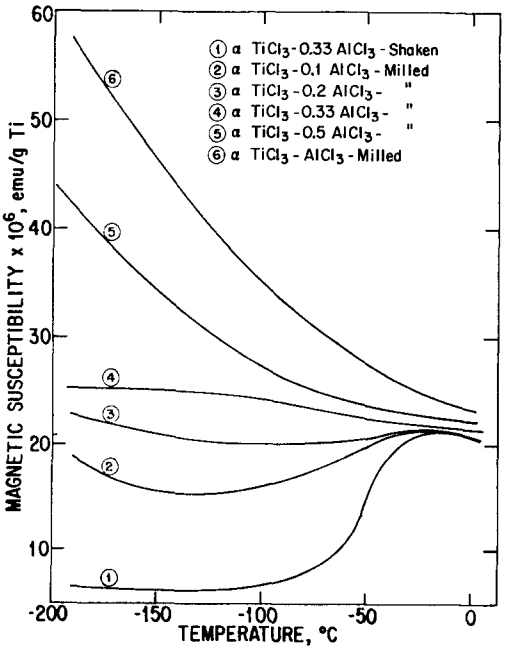

FIG. 2. Magnetic susceptibility of $TiCl_3$-$AlCl_3$ mixtures.

TABLE 2

VACUUM SUBLIMATION SHOWS THAT COCRYSTALLINE $TiCl_3$–0.33$AlCl_3$ PREPARATIONS ARE DIFFERENT FROM PURE $TiCl_3$ OR $TiCl_3$–0.33$AlCl_3$ MIXTURES[a]

Sample Composition: / Method of preparation:	$TiCl_3$[b]		$TiCl_3$–0.33 $AlCl_3$[c]			
	H_2 reduction		Al reduction		Mixed by ball milling	Mixed by shaking
Treatment:	None	Ball milling	None	Ball milling (71.5)[d]		(71.3)
	Material lost (%)					
$AlCl_3$[e] at (°C)						
180°	—	—	—	—	—	19.8
200°	—	—	—	—	6.4	—
250°	—	—	—	13.0	11.0	20.2
350°	—	—	12.4	13.8	20.2	20.4[f]
450°	—	—	—	21.5	—	—
$TiCl_4$ at (°C)						
180°	—	—	—	—	—	1.8 (69.5)
200°	—	—	—	—	1.2 (69.9)	—
250°	—	—	—	<3 (69.6)	1.2 (69.7)	3.4
350°	4.4[g]	4.6 (68.3)	10.7 (68.6)	8.0 (68.8)	3.6 (68.2)	3.4[f]
450°	6.4[g] (70.0)[d]	8.3 (69.6)	—	20.1[h] (64.3)	—	—

[a] 5 mm Hg, 4 hr.

[b] Should contain 69.1% Cl, originally the alpha form.

[c] Should contain 71.5% Cl, originally the alpha form.

[d] Values in parentheses give chlorine contents of the original samples or residues.

[e] The $TiCl_3$–0.33 $AlCl_3$ preparations should contain 22.2% $AlCl_3$.

[f] Sublimed at 300°C.

[g] Only partly consisting of $TiCl_4$.

[h] Analyzed 74.3% Cl, compared to 74.8% Cl for $TiCl_4$ and 79.8% Cl for $AlCl_3$.

curve 1 in this figure shows the susceptibility for a 75 mole % α-$TiCl_3$–25 mole % $AlCl_3$ mixture merely shaken together. It should be noted that this curve is typical of α-$TiCl_3$ diluted with a diamagnetic material, in this case $AlCl_3$. Curve 4 shows the dramatic change in the magnetic properties of this same mixture when it is subjected to ball milling rather than shaking. This result in itself shows that a different solid phase is now present. It is also interesting that curve 4 is similar to the curve obtained for a solid produced by reducing $TiCl_4$ with the stoichiometric amount of Al metal and having the composition $TiCl_3$·0.33$AlCl_3$. This indicates that there is a similar atomic arrangement of the Ti^{3+} and Al^{3+} ions in the Cl^- matrix in both cases. The other curves in Fig. 2 show the progressive change in the magnetic properties of the solid phase with increasing $AlCl_3$ in the $TiCl_3$ during the ball-milling operation.

X-Ray diffraction. Indications of solid solution from lattice parameter shifts for the alpha modification of $TiCl_3$·0.33$AlCl_3$ were noticed during early work in our laboratories and were later independently established and reported by Natta *et al.* (7). In the present paper, lattice parameter measurements of higher precision have been obtained for the alpha, gamma, and delta crystalline modifications and in particular, for a wide range of compositions of the delta form prepared by ball milling α-$TiCl_3$ with $AlCl_3$.

Blends of δ-$TiCl_3$ with $AlCl_3$ were prepared in the various proportions listed in Table 3. Before milling the blends, the {300} peaks for the individual components were present on the diffractometer traces. However, after

TABLE 3
LATTICE PARAMETER AND CRYSTAL SIZE MEASUREMENTS

Type of material	$AlCl_3$ (mole %)	Crystal size (Å)		Lattice parameters, (Å)			
				Uncorrected		Corrected	
		From {300} line	From {003} line	a	c	a	c
Ball-milled $TiCl_3$ and $AlCl_3$	0	52	69	6.136	18.01	6.168	17.73
	10.0	59	78	6.140	17.94	6.168	17.69
	15.0	59	80	6.140	17.91	6.169	17.70
	20.0	63	83	6.136	17.89	6.162	17.68
	25.0	46	59	6.106	18.02	6.142	17.67
	28.9	68	70	6.115	17.87	6.139	17.59
	33.3	70	64	6.103	17.89	6.127	17.59
	36.8	73	72	6.099	17.89	6.122	17.63
	50.0	95	112	6.067	17.80	6.084	17.62
	75.0	117	99	5.996	17.75	6.013	17.57
	100	200	155	5.913	17.69	5.921	17.58
Ball-milled α-$TiCl_3$·0.33 $AlCl_3$	25	74	106	6.118	17.78	6.140	17.63
Ball-milled α-$TiCl_3$·0.33 $AlCl_3$	25	—	—	—	—	6.142[a]	17.62[a]
Not milled							
α-$TiCl_3$	0	>1000	>1000	6.1581	17.617	6.1581	17.617
α-$TiCl_3$·0.33$AlCl_3$	25	>1000	>1000	6.1417	17.618	6.1417	17.618
γ-$TiCl_3$·0.33$AlCl_3$	25	155	460	6.131	17.65	6.142	17.62
$AlCl_3$	100	>1000	>1000	5.922	17.57	5.922	17.57

[a] Extrapolated data of Fig. 4.

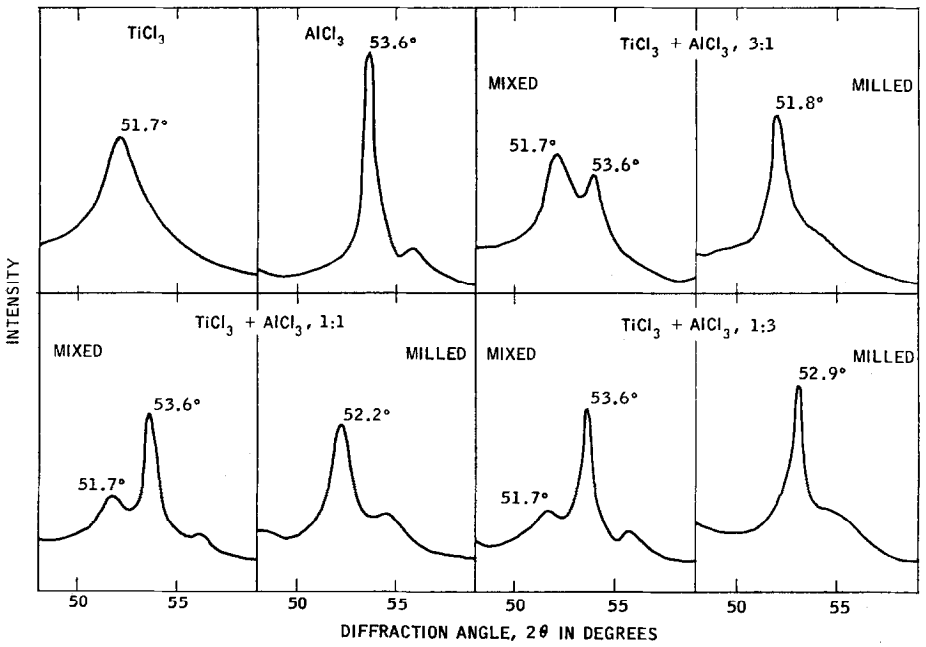

FIG. 3. X-Ray diffractometer scans of {300} lines for $TiCl_3$-$AlCl_3$ blends.

milling, only one peak was observed. Several representative cases are shown in Fig. 3. This indicates the transformation of the two separate phases into a new phase. A similar behavior was not observed for the {003} peaks since these peaks for the blends were not resolved. The diffraction patterns of all the ball-milled mixtures were quite similar to the ball-milled $TiCl_3$ signifying a set of structures isomorphous with δ-$TiCl_3$.

It was observed that the lattice parameters of the $TiCl_3$-$AlCl_3$ system varied with crystallite size. As the crystallite size decreased, the a parameter decreased and c increased. These effects were quite large and in many cases greater than the shifts in lattice parameters due to variations in composition. This had to be accounted for in the determination of the desired relationship between composition and lattice parameters. To make this correction, a series of samples was made by subjecting a γ-$TiCl_3 \cdot 0.33AlCl_3$ preparation to various degrees of milling and the dependence of a and c on crystallite size was determined. It was found that a correlated rather well with the reciprocal of the crystallite size measured from broadening of the {300} line. Similarly c correlated with the reciprocal of the crystallite size measured for the {003} line. These relationships are shown in Fig. 4. By extrapolating the curves to reciprocal crystal size of zero, i.e., infinite crystal size, values of the parameters free of the crystal size effect are obtained.

As it was impractical to obtain the data to construct similar curves for the ball-milled mixtures, the curves of Fig. 4 were used to correct all the lattice parameters to infinite crystal size. For the purpose of making this correction, it was assumed that the reduction of crystal size affected the lattice parameters to the same extent for all the ball-milled samples. Then for a measured crystal dimension, the algebraic difference from the respective curve to the dashed line was determined. This difference was added to the uncorrected value of the lattice parameter to give the value corrected to infinite crystal size. For the a parameter the correction was positive while for the c parameter it was negative.

Measurements of crystal size and lattice

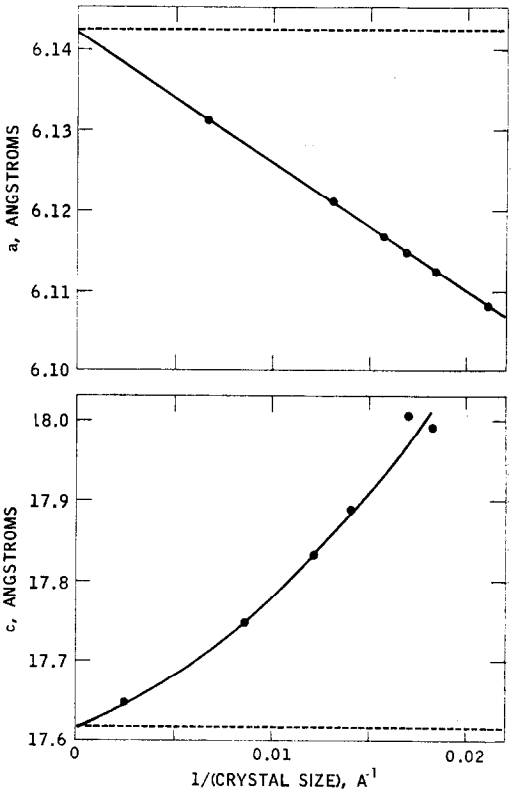

FIG. 4. Variation of lattice parameters with crystal dimensions. Data are for δ-$TiCl_3 \cdot 0.33$ $AlCl_3$ prepared by subjecting γ-$TiCl_3 \cdot 0.33$ $AlCl_3$ to varying amount of ball milling.

parameters carried out for the milled mixtures and also for α- and γ-$TiCl_3 \cdot 0.33AlCl_3$ prepared by the reduction of $TiCl_4$ with Al are summarized in Table 3. The corrected lattice parameters for the milled mixtures are shown plotted versus composition in Fig. 5.

The change in the a parameter with composition for this isomorphous series clearly indicates the presence of solid solutions. Furthermore, the absence of discontinuities in the plot indicates that solid solutions can be formed over the entire range of composition. The dependence of c on composition supports the preceding conclusions; however, the trend for c is not as well defined primarily because of the lower precision for the measurement of this parameter.

Measurements of higher precision carried out for α-$TiCl_3$ and α-$TiCl_3 \cdot 0.33AlCl_3$ showed a smaller value of a in α-$TiCl_3 \cdot 0.33AlCl_3$ by

about 0.26% and no significant change for *c*. The results for the *c* parameter are in agreement with those of Natta (7); however, Natta reported a much larger contraction for *a*—about 1.3%. The shift we found in *a* for α-$TiCl_3$·0.33$AlCl_3$ (well within the experimental accuracy) is considered strong evidence for the presence of a solid solution.

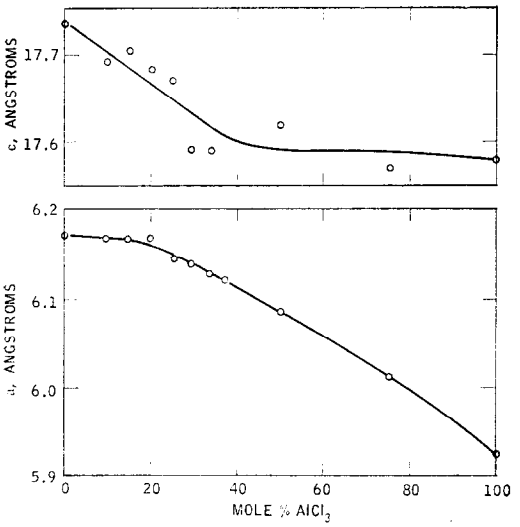

FIG. 5. Lattice parameters, corrected to infinite crystal size, for various compositions of ball-milled mixtures.

When this material is ball-milled, the solid solution should be retained in the delta modification. Furthermore, the delta modification formed from milling α-$TiCl_3$·0.33 $AlCl_3$ or the α-$TiCl_3$ + 0.33$AlCl_3$ mixture should have the same lattice parameters. The results in Table 3 bear this out within the accuracy of the data.

It is also of interest to note in Table 3 that *a* and *c* (corrected), for the alpha form of $TiCl_3$·0.33$AlCl_3$ have the same values, within the experimental accuracy, as the respective parameters for the gamma form. This is not surprising, considering the minor differences in structure of the two modifications.

CONCLUSIONS

From the foregoing discussion we conclude that ball milling the powder mixtures of $TiCl_3$ and $AlCl_3$ produced solid solutions having structures isomorphous with δ-$TiCl_3$. Such solid solutions can be formed over a very wide range of composition, presumably for any proportion of the two constituents.

REFERENCES

1. TORNQVIST, E., SEELBACH, C. W., AND LANGER, A. W., JR., U. S. Patent 3,128,252, April 7, 1964; Australian Patent 224,150, Sept. 26, 1957; and Italian Patent 575,133, April 1, 1958.
2. TORNQVIST, E., AND LANGER, A. W., JR., U. S. Patent 3,032,513, May 1, 1962.
3. TORNQVIST, E., AND LANGER, A. W., JR., U. S. Patent 3,032,510, May 1, 1962.
4. LANGER, A. W., JR., AND TORNQVIST, E., U. S. Patent 3,032,511, May 1, 1962.
5. NATTA, G., CORRADINI, P., AND ALLEGRA, G., *Atti Accad. Nazl. Lincei* **26**, 155 (1959).
6. NATTA, G., CORRADINI, P., AND ALLEGRA, G., *J. Polymer Sci.* **51**, 399 (1961).
7. NATTA, G., *Chem. Ind.* **42**, 1207 (1960).
8. TORNQVIST, E., AND LANGER, A. W., JR., U. S. Patent 3,130,003, April 21, 1964; French Patent 1,284,787, Jan. 8, 1962.
9. RICHARDSON, J. T., AND BEAUXIS, J. O., *Rev. Sci. Instr.* **34**, 877 (1963).
10. KLEMM, W., AND KROSE, E., *Z. Anorg. Chem.* **353**, 209 (1947).
11. SWANSON, H. E., AND TATGE, E., J. C. Fel. Reports, Natl. Bur. Std. (U. S.) (1950).
12. American Society for the Testing of Materials, "X-Ray Powder Data Card File" (1962).
13. AZAROFF, L. V., AND BUERGER, M. J., "The Powder Method in X-Ray Crystallography," Chap. 15. McGraw-Hill, New York, 1958.