cular fluorine were computed from sample mass, measured before and after reaction for a known time interval. For F_2, the apparent reaction probability (ratio of the Al removal rate to twice the F_2 flux at ambient F_2 pressure and specimen temperature) was $\epsilon_a(F_2/Al) = 0.006$. This value was unchanged over a twofold increase in the total pressure, as expected if gas phase mass transport does not limit the rate of reaction.

The heat transfer measurements show the gas temperature at the sample to nearly equal the sample temperature. However, reaction rate measurements show the reactant concentration at the sample to remain near its ambient value. This difference between heat and mass transfer effects is due to differences in the intrinsic rates of heat transfer and chemical reaction, governed by the thermal accommodation coefficient which is large and the reaction probability which is small. Under other conditions, external diffusion limitations may occur, depending on the prevailing values of the specimen diameter, reaction probability, convective mass transfer coefficient, and reactant diffusion coefficient.[11]

The kinetic studies described above meet design restrictions that need not be imposed on other applications of the technique. For example, the study of high temperature gas/solid or gas/liquid equilibria, phase changes (*via* cooling curves), and extreme temperature property measurements[12] do not require small sample size and low reactor pressures. On the other hand, the ability to work with small sam-

ples speeds thermal and chemical equilibration and low reactor pressures minimize the absolute concentration of gaseous impurities. Also, since only the sample of interest is heated, corrosion problems are avoided and heat dissipation is minimized. Work is presently in progress to extend the method to high temperature studies of nonmetallic solids and liquids *via* CO_2 laser heating of levitated specimens.

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Manufacture of TiAl by Extrusion of Blended Elemental Powders

ROBERT E. SCHAFRIK

Of all the titanium alloys proposed for extended high temperature applications, those based on the ordered intermetallic compound, TiAl, seem to have the most promise.[1,2] Needless to say, the obstacle which has precluded advanced development of TiAl is its minimal ductility at temperatures less than about 700°C. The brittleness of TiAl suggests that powder metallurgy techniques would be useful in the manufacture of the product. To date, this has been done using prealloyed powders. However, the use of prealloyed powders has several disadvantages. First, the melting, casting and powder forming processes each introduce impurities in the alloy. Also, since the titanium refining process produces sponge, which is easily convertible to powder, the practice of melt-

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ing sponge only to reform powder seems unnecessarily costly.

This investigation was an attempt to determine if TiAl could be manufactured directly from a mixture of the elemental powders of titanium and aluminum. The process variables which were partially investigated in this study were: presintering conditions, heat treating conditions, and the effect of extrusion conditions on the mechanical properties of the product. The properties of TiAl manufactured from the elemental powder mixture were compared to those of TiAl manufactured from prealloyed powders.

The powders which were used were readily available laboratory grade powders. The chemical analysis is shown in Table I. The powders were air-dried in an oven at 105°C for 4 h, seived through 140 mesh screen, and then mixed in a Spex Mill Mixer. Cylindrical extrusion billets of Ti-6Al-4V were utilized as the extrusion can. These billets were nominally 7.5 cm diam by 12.7 cm long, with a 4.0 to 5.0 cm hole in the center. Premixed powder was pressed into the billet to 10,000 K_g using an Instron Testing machine. Powder was added and pressed until the billet was full. The billets then were given a heat treatment to react the powders prior to additional processing.

Pressed compacts of the elemental powder mixture were heated in vacuo for various times at 650°C to determine the reaction kinetics. A sigmoidal time-temperature curve was developed using semiquantitative

X-ray analysis. It was found that the reaction of the powders to TiAl proceeds through an intermediate step in which the intermetallic compound TiAl$_3$ exists. Fig. 1 depicts this semiquantitative time-temperature curve. Note that the reaction was completed at 650°C after 72 h. Also, a compact of the elemental powders was found to have been completely reacted to TiAl after 2 h at 993°C without evidence of residual molten aluminum. It was this high temperature, short time, heat treatment which was selected for the powder-filled billets.

A total of four extrusions were attempted. The extrusion parameters and the results are summarized in Table II. The extrusions were accomplished on a high speed (15 ips) 700 Ton horizontal extrusion press. All extrusions were direct extrusions at a die temperature of 500°F. Prior to the actual extrusion, the billets were consolidated in the press by a blind die extrusion. This procedure increased the powder density from about 50 pct of theoretical to greater than 90 pct.

The first extrusion was very poor. A macrophotograph is shown in Fig. 2(a). Obviously, good consolidation during the extrusion operation was not achieved. The next extrusion was performed at a substantially higher temperature. Although this was not a successful extrusion, it was an improvement, as can be seen in Fig. 2(b). The fourth extrusion was unsuccessful
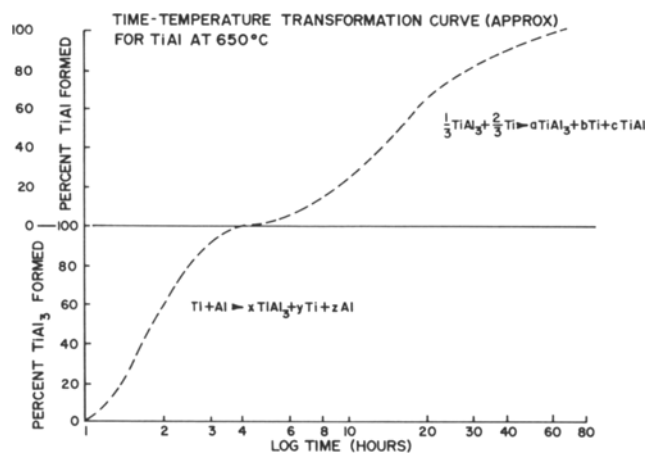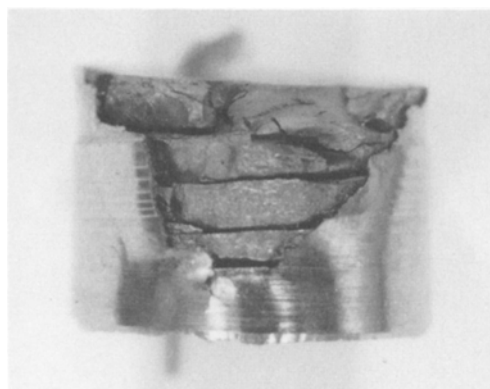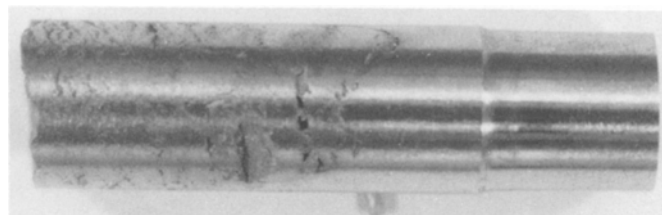

Fig. 1—Estimated time-temperature transformation curve for Ti + Al → TiAl at 650°C.

(a)

(b)

Fig. 2—(a) Extrusion Run 1 product; (b) Extrusion Run 2 product.

Table I. Analysis of Titanium and Aluminum Powder

|	Titanium Powder	Aluminum Powder
Aluminum	*	—
Copper	0.002	0.003
Titanium	—	*
Iron	0.20	0.10
Magnesium	0.01	0.001
Chromium	0.001	0.005
Silicon	0.01	0.03
Nickel	0.05	0.001
Calcium	0.20	<0.001
Maganese	0.02	0.01
Tin	0.005	<0.002
Zirconium	0.30	<0.002
Tantalum	<0.02	<0.002
Molybdenum	0.005	<0.001
Zinc	<0.003	<0.01

*Not analyzed.

Table II. Extrusion Summary

| Extrusion	Heat Treatment	Consolidation Temperature, °C	Extrusion Ratio	Pressed Powder Diameter, cm	Extrusion Temperature, °C	Product Density, Pct Theoretical	Comments
1	8 h at 982°C	1316	9:1	4	1316	96 to 99	Severe dogboning and severe lamination of product.
2	8 h at 982°C	1399	9:1	4	1399	91.5 to 99.6	Moderate dogboning and some lamination of product. Many microcracks and regions of inadequate flow
3	3.5 h at 1000°C	1427	16:1	5	1427	99⁺	Best extrusion. Some dogboning and regions of asymmetric flow
4	6.5 h at 640°C	1316	9:1	4	1427	99⁺	Excessive flow resulting in interspersion of billet material with product.

Table III. Summary Mechanical Test Data

Temperature, °C	Remarks	Elastic Modulus, Gn/m²	0.2 Pct Yield Strength, MN/m²	UTS, MN/m²	Fracture Stress, MN/m²	Elongation, Pct	Reduction in Area, Pct
25	Tension	192	–	–	214	0	0
	Compression	167	462	–	–	–	–
800	Tension	150	312	–	339	0.25	7.3
900	Tension	158	241	314	–	15.6	14.2

Note: Cross-head speed was 0.25 mm/min (0.01 in./min).
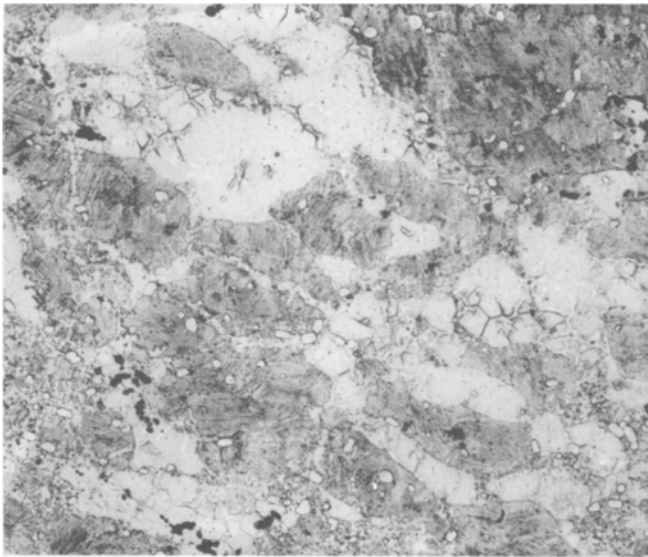
(a)
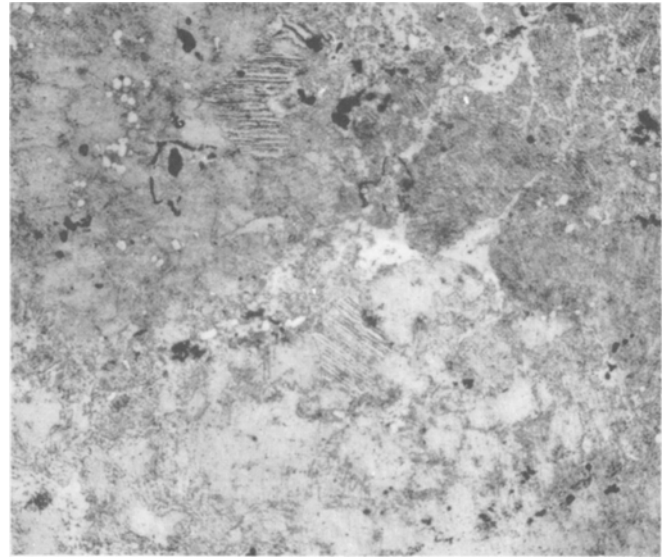
(b)

Fig. 3—(a) Photomicrograph of as-extruded product from Extrusion Run 3, magnification 230 times, Kroll's etch. See text for description of microconstituents; (b) photomicrograph of Extrusion Run 3 product after homogenization at 1300°C for 3 to 5 h in vacuo, magnification 230 times, Kroll's etch. See text for description of microconstituents.

in that the extruded product flowed more than expected, resulting in a small product diameter with a star-shaped cross-section.

Only the product from the third extrusion was suitable for the manufacture of tensile specimens. However, as indicated in Fig. 3(a), the microstructure was inhomogeneous. An homogenization treatment at 1300°C for 3.5 h in a 3×10^{-5} μm vacuum was given the specimens. Fig. 3(b) shows the resulting homogenized microstructure. Note that the material is two-phase, the overall composition being Ti-35.5 wt pct Al. The lamellar regions are TiAl + Ti$_3$Al, the angular particles are Ti$_3$Al, and the large single phase grains are TiAl. The dark areas are mixtures of titanium and aluminum oxides. The oxygen content was determined to be 0.71 wt pct and the nitrogen content 0.675 wt pct.

Preparation of the mechanical test specimens and the mechanical testing equipment and procedures were the same as reported for previous work.[2] A summary of the mechanical test data is shown in Table III. These data are comparable to that obtained from specimens extruded from prealloyed powder.[2] Especially significant are the high elastic moduli measured on the elemental powder extrusions at 800°C and 900°C. This enhancement of the modulus is attributed to saturation of the TiAl by oxygen. It has been determined that the solubility of O$_2$ in TiAl is between

1500 ppm and 2300 ppm.[3] The chemical analysis of the Extrusion Run 3 product indicated 7100 ppm. Also the formation of oxides, as evidenced by Fig. 3, substantiates the fact that the matrix was saturated with oxygen. The higher yield strength of the elemental powder extrusions is, thus, most likely due to solid solution strengthening effects.

In summary, TiAl was successfully manufactured from mixtures of the elemental powders. The process is not, however, without problems. A method of reducing the pickup of atmospheric gases must be found, and the extrusion process must be made more reproducible.

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Investigation of a Sinter Process for Extraction of Al₂O₃ From Coal Wastes

KENNETH P. GOODBOY

Sinter processes in the aluminum industry involve high temperature reaction of aluminous ores to form soluble Al₂O₃ compounds. The sinters are leached to extract Al₂O₃ and the leach liquors are subsequently treated to precipitate Al₂O₃ in purified form. In practice, rapid reaction during sintering, rapid leaching and high extraction (recovery of Al₂O₃ from the ore) are desirable. This paper is concerned primarily with sinter reaction chemistry for extraction of Al₂O₃ from high ash coal waste from a coal beneficiation plant.

All sinter processes for Al₂O₃ recovery are similar in that limestone is added to the beneficiated ore to react at high temperatures with SiO_2 to form dicalcium silicate ($2CaO \cdot SiO_2$) and CO_2.

$$2CaCO_3 + SiO_2 = 2CaO \cdot SiO_2 + 2CO_2. \qquad [1]$$

Once $2CaO \cdot SiO_2$ is formed, the Al₂O₃ is then available to react with a compound that will make it soluble in H₂O or leachable by Na₂CO₃ solution. Initially in our investigation, the lime sinter process, which has been extensively investigated as a means of extracting Al₂O₃ from clay, was considered a viable means of rendering the Al₂O₃ soluble from coal wastes.
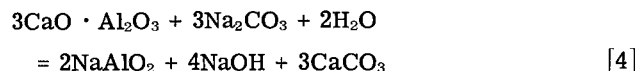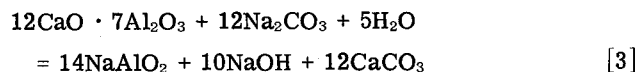
Lime Sinter Process. The aluminous ore in the lime sinter process is reacted with limestone at approximately 1350°C to form $12CaO \cdot 7Al_2O_3$ ($C_{12}A_7$), $2CaO \cdot SiO_2$ and CO_2.

$$12CaCO_3 + 7Al_2O_3 = 12CaO \cdot 7Al_2O_3 + 12CO_2. \qquad [2]$$
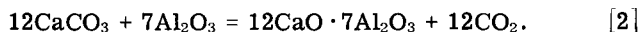
$C_{12}A_7$ is the desired calcium aluminate phase because it is the most readily solubilized and yields the highest percent Al₂O₃ recovery,[1,2] but some difficulty can occur in controlling the composition of the sinter so that $C_{12}A_7$ is formed.

If not enough limestone is present in the sinter mix, gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) will form. Al₂O₃ cannot be leached from this compound by H₂O or Na₂CO₃ solution. With enough limestone not to form $2CaO \cdot Al_2O_3 \cdot SiO_2$ but not enough for $C_{12}A_7$, $CaO \cdot Al_2O_3$ can form. On the other hand, if too much limestone is added, $3CaO \cdot Al_2O_3$ can form. Neither $CaO \cdot Al_2O_3$ nor $3CaO \cdot Al_2O_3$ leach as well as $C_{12}A_7$. The lower extraction values are due to precipitation of insoluble hydrates

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of calcium aluminate as shown by X-ray analysis of the leach residues.[1,2] The calcium aluminate leaching reactions are as follows:

$$12CaO \cdot 7Al_2O_3 + 12Na_2CO_3 + 5H_2O$$
$$= 14NaAlO_2 + 10NaOH + 12CaCO_3 \qquad [3]$$

$$3CaO \cdot Al_2O_3 + 3Na_2CO_3 + 2H_2O$$
$$= 2NaAlO_2 + 4NaOH + 3CaCO_3 \qquad [4]$$

$$CaO \cdot Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CaCO_3. \qquad [5]$$

With knowledge of lime sinter technology, coal waste/limestone sinters were prepared and leached with Na₂CO₃. The Al₂O₃ was readily soluble, but the X-ray analysis of the sinters showed not $C_{12}A_7$ but an entirely different compound, calcium sulphoaluminate ($4CaO \cdot 3Al_2O_3 \cdot SO_3$, abbreviated $C_4A_3\bar{S}$). Since $C_4A_3\bar{S}$ leached readily, we immediately conducted a more thorough investigation of proper sintering conditions.

New Sinter Process- Coal Waste/Limestone Sinters. Coal waste was sintered with five different amounts of limestone at temperatures from 1000 to 1400°C in an oxidizing atmosphere. The chemical analyses of the sinters are given in Table II.

The samples were then leached under the conditions of Table III.

The extraction data are presented in Table IV and in Fig. 1. Each curve in Fig. 1 has specified the theoretical CaO content based on the sinter analysis of Table II in order to form $2CaO \cdot SiO_2$, $C_4A_3\bar{S}$ and CaSO₄. The

Table I. Order of Reaction Products with Increasing Limestone Addition

Compound	Formula
Calcium Sulfate	CaSO₄
Dicalcium Silicate	2CaO·SiO₂
Gehlenite	2CaO·Al₂O₃·SiO₂
Monocalcium Aluminate	CaO·Al₂O₃
C₁₂A₇	12CaO·7Al₂O₃
Tricalcium Aluminate	3CaO·Al₂O₃

Table II. Chemical Analysis of Coal Waste/Limestone Sinters

Pct Theoretical CaO in Sinter*	Chemical Analysis, Pct					
	Al₂O₃	SiO₂	CaO	Fe₂O₃	MgO	SO₃
76	16.5	25.5	44.6	5.30	1.45	5.30
82	15.7	24.4	46.5	4.35	1.52	5.48
101	14.1	21.2	50.8	3.28	1.52	5.49
110	12.9	19.8	51.7	4.20	1.40	5.62
122	12.3	18.8	54.1	4.80	1.69	5.59

*For 2CaO·SiO₂, $C_4A_3\bar{S}$ and CaSO₄. Average sinter analysis for all temperatures.

Table III. Leaching Conditions of All Sinters

Size of ground sinter	=	−149 μ
Weight of sinter	=	10 g
Leaching solution volume	=	100 cc
Weight of Na₂CO₃ in solution	=	3 pct
Leaching temperature	=	50°C
Leaching time	=	30 min