

The Alloying of Titanium Aluminides with Ruthenium

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Titanium is ductile in pure form but hardens considerably on alloying. Titanium alloys have excellent physical and chemical properties, being resistant to oxidation and corrosion in most dilute corrosive environments, including sea water, resulting in their widespread application in chemical plants, oil platforms, underwater engineering and medicine. Furthermore, with a low density of $4.5 \times 10^3 \text{ kg/m}^3$ and strengths well in excess of 1000 MPa, coupled with good creep resistance, certain titanium alloys have found extensive use in the aerospace industry.

The physical metallurgy and alloying behaviour of titanium is, however, rather complex due to its allotropy, involving a h.c.p. crystal structure (α) below 882.5°C and a b.c.c. crystal structure (β) above this temperature. Alloying elements may dissolve preferentially in α -titanium (α -stabilisers), in β -titanium (β -stabilisers) or in both (neutral), thereby increasing the stability range of these phases. They may also form compounds with titanium. Accordingly, titanium alloys are classed as α -alloys (predominantly α phase), β -alloys and so on, each group having its own characteristic properties. Alpha and near alpha titanium alloys (containing additional small amounts of β -stabilisers) have very good creep resistance, high strength and good weldability. Beta titanium alloys have poor creep resistance, but good workability and formability. It is evident that a combination of useful properties can be achieved in an $\alpha + \beta$ alloy. Indeed one of the first aerospace alloys developed in the 1950s was an $\alpha + \beta$ alloy, Ti-6Al-4V (weight per cent), also known in the United Kingdom as IMI318. Capable of operating up to about 350°C, IMI318 is the most widely used of the titanium alloys in aerospace applications.

Over the past 40 years advances in aircraft jet-engine technology have resulted in more

efficient and powerful engines operating at increasingly higher temperatures, in order to achieve more thrust. The most advanced titanium alloys today are near- α alloys, such as IMI829 (Ti-5.5Al-3.5Sn-3Zr-1Nb-0.25Mo-0.25Si), capable of operating at 550 to 580°C. Above 600°C, however, their oxidation resistance becomes inadequate and they suffer from creep and general metallurgical instability. Future generations of jet-engines will require alloys capable of operating at even higher temperatures, beyond the limit of the conventional alloys currently available. The titanium aluminides, Ti_3Al (α_2) and TiAl (γ), are ordered intermetallic compounds with excellent oxidation resistance and mechanical properties at temperatures up to about 900°C, offering considerable potential in this context. They are, however, brittle at room temperature and most of the research during the past 10 to 15 years has concentrated on overcoming this brittleness. An obvious way to improve ductility is by alloying, with the aim of refining the microstructure and reducing the slip length by producing a second phase dispersion. In this context, β -stabilising elements such as molybdenum, niobium and vanadium have been used to produce aluminide + β structures, with some improvements in ductility, but most workers have ignored the effects of non-conventional β -stabilising elements.

The platinum group metals show extensive solid solubilities in β -titanium. In the past, elements such as palladium have been added to titanium-aluminium, titanium-chromium, titanium-molybdenum and various ternary titanium-aluminium based alloys to enhance their low temperature corrosion properties in aqueous environments (1, 2). IMI260 and IMI262, containing 0.2 weight per cent palladium, are the recommended materials for

use below 200°C in chemically reducing environments (3). Studies have shown that it is economically feasible to platinum ion plate some aerospace alloys such as AMS4975, IMI685 and IMI829 in order to increase their operating temperature (4, 5).

Previous work on the titanium-aluminium-ruthenium system (6) showed the presence of a ternary compound in the system, but lacked detailed experimental measurements. The present research was initiated in order to examine the effect of ruthenium on the structure and properties of titanium 17 to 37 atomic per cent aluminium alloys, mainly by establishing the details of constitution and phase equilibria in this section of the titanium-aluminium-ruthenium system.

Experimental Procedure

Alloy preparation and heat treatment entailed precautionary measures to minimise atmospheric contamination, in view of the known effect of impurities on titanium alloys (7, 8). The alloys listed in Table I were prepared by argon arc melting the constituents by a non-consumable tungsten electrode. Prior to melting, the furnace was evacuated and flushed several times with pure argon to reduce contamination. Weight losses after melting were around 0.2 per cent. Alloys, in the form of finger shaped ingots, were wrapped in molybdenum foil, sealed in quartz capsules containing argon and homogenised at 1250°C for 24 hours. Subsequent heat treatments were carried out at 1100 and 1050°C for 24 hours, 950°C for 96 hours and 870 and 770°C for 186 hours. All heat treatments were terminated by breaking the quartz capsules under water, in order to achieve rapid quenching while avoiding atmospheric contamination.

All the alloys were examined by light microscopy, scanning (SEM) and transmission (TEM) electron microscopy and X-ray diffraction. Elemental analysis was carried out using X-ray energy dispersive spectroscopy (EDS) of both thin foils and bulk samples. The former were prepared in a twin jet electropolishing apparatus employing a 10 to 12 per cent sulphuric

Alloy number	Composition, atomic per cent		
	Ti	Al	Ru
1	Balance	18	—
2	"	17	1
3	"	18	2
4	"	18	5
5	"	25	—
6	"	24	1
7	"	23	5
8	"	37	—
9	"	37	1
10	"	37	5
11	"	33	29
12	"	60	18

acid in methanol electrolyte at -25 to -35°C. X-ray diffraction of bulk samples, powders and extracted particles was also carried out.

Mechanical testing, consisting of compression and tensile tests, was carried out on all the alloys. Selected alloys were isothermally forged at 1100°C to approximately 50 per cent reduction in thickness, before ageing at 770°C. Tensile testing of the forged samples was carried out at 20, 650 and 800°C.

Results and Discussion

Alloys Based on Ti₃Al

Composition 17 to 25 atomic per cent Aluminium

Quenching alloys containing 1 to 2 per cent ruthenium from the high temperature β -titanium field results in transformation of b.c.c. β -titanium to martensite, see Figure 1. The martensite is hexagonal in alloys with 1 per cent ruthenium but orthorhombic in alloys with 2 per cent ruthenium. In alloys based on the stoichiometric Ti₃Al composition (25 atomic per cent aluminium), the hexagonal martensite contains small ordered domains, shown in Figure 2, with DO₁₉ type crystal structure. The finger shaped domains show a positive concentration gradient of ruthenium away from the central rib of the martensite plates, suggesting the involvement of a diffusional growth element

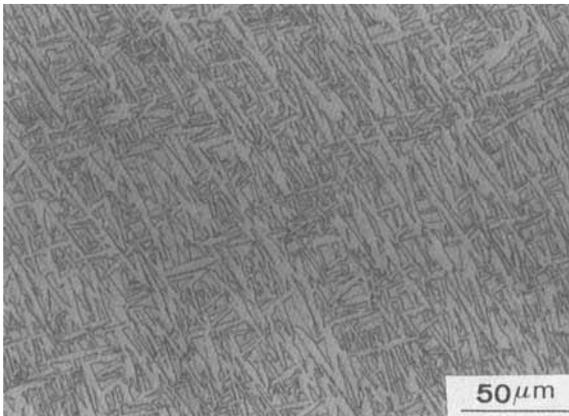


Fig. 1 Quenching a Ti-24Al-1Ru alloy from 1250°C results in the transformation of b.c.c. β -titanium to martensite, light micrograph

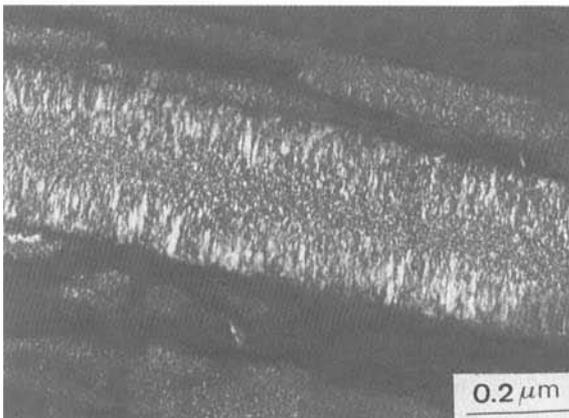


Fig. 2 The ordered finger shaped domains that occur in Ti-24Al-1Ru martensite have a positive concentration gradient of ruthenium away from the central rib of the martensite plates, dark field TEM micrograph



Fig. 3 Fine scale $\alpha_2 + \beta$ structures occur in Ti-18Al-5Ru quenched from a temperature of 950°C; an α_2 region is indicated on this SEM micrograph

coupled with initial martensitic transformations in these alloys.

The tempering behaviour of the martensitic structures in these titanium-aluminium-ruthenium alloys is similar to that of other titanium alloys containing β -stabilising

elements (9). In short, orthorhombic martensite reverts to β before precipitating low temperature equilibrium α or α_2 phases, whereas such transformation occurs without reversion in hexagonal martensite, depending on the tempering temperature. Details of solid

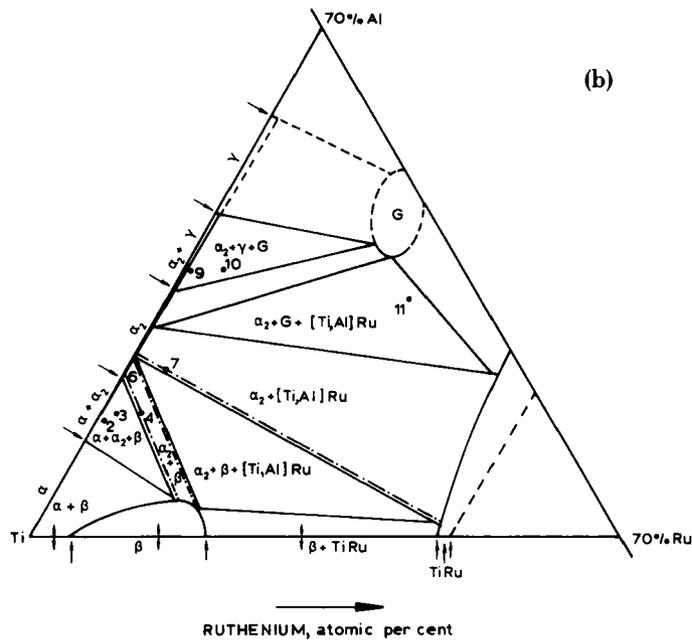
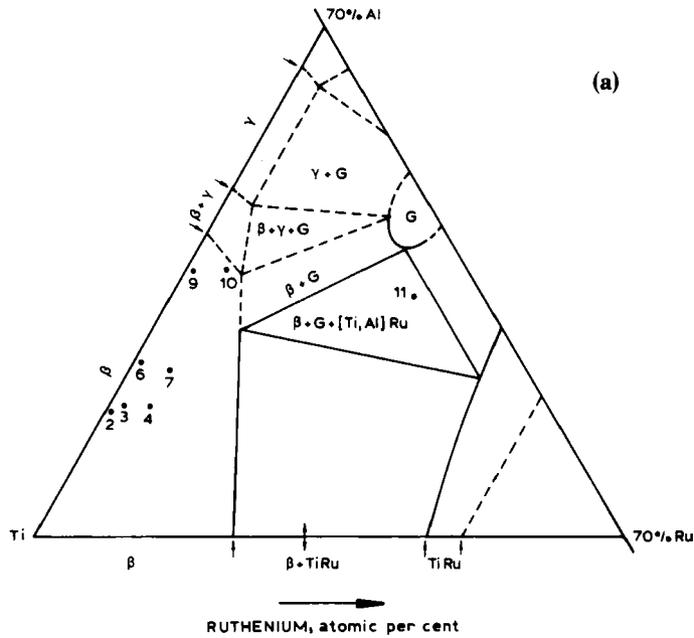


Fig. 4 Partial isothermal sections of the titanium-aluminum-ruthenium system at a temperature of: (a) 1250°C, (b) 770°C. The numbers refer to the alloys listed in Table 1

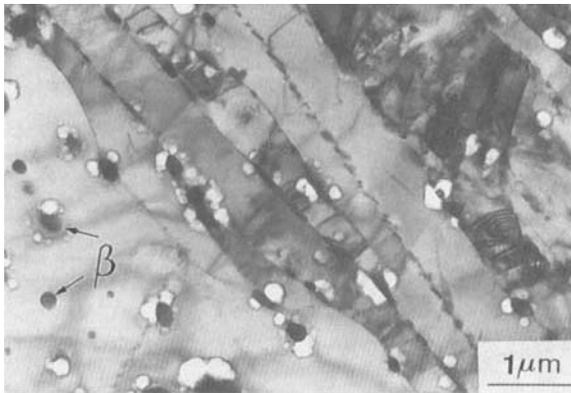


Fig. 5 Equilibrium β phase particles are indicated in the α_2 matrix, in Ti-24Al-1Ru, quenched from a temperature of 770°C, TEM micrograph (tensile tested alloy)

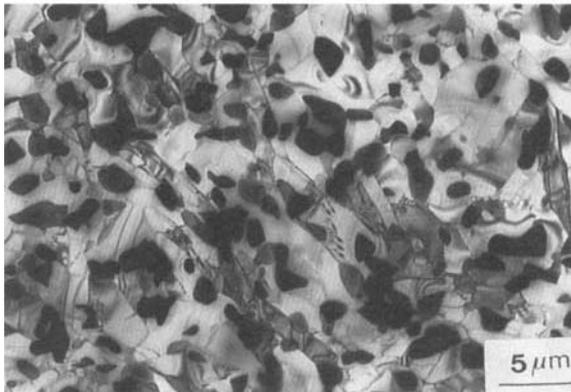


Fig. 6 [Ti,Al]Ru particles occur in an α_2 matrix, in Ti-23Al-5Ru, quenched from a temperature of 870°C, TEM micrograph

state transformations in titanium-aluminium-ruthenium alloys have been published (10).

The beta phase can be retained at room temperature in alloys containing 5 per cent ruthenium by rapid quenching. Ageing of these alloys at 770 to 950°C results in the precipitation from the beta phase of α , α_2 and/or [Ti,Al]Ru. The latter is a ternary phase based on a solid solution of TiRu and AlRu, in which aluminium and titanium atoms can substitute for each other (6). Ageing in most alloys, however, results in fine scale $\alpha_2 + \beta$ or $\alpha + \alpha_2 + \beta$ structures, shown in Figure 3, as can be seen from the partial isothermal sections determined in this work for the titanium-aluminium-ruthenium system at 1250°C and 770°C, and illustrated here in Figures 4(a) and 4(b), respectively. These diagrams serve to show the major constitutional features of this system, namely the extent of the $\alpha_2 + \beta$ field and the presence of two ternary phases, [Ti,Al]Ru and G-phase

(see below). The ternary sections were plotted from phase composition data obtained by EDS analysis of thin foils. For the binary sides, the titanium-aluminium and titanium-ruthenium assessed diagrams by Murray (11, 12) and the aluminium-ruthenium diagram according to Shunk (13) were used.

An important feature of the titanium-aluminium-ruthenium system is the low solubility of ruthenium ($< \sim 1$ per cent) in α -titanium and the titanium aluminides, as evident in the phase diagram of Figure 4(b). The rejection of ruthenium atoms from α , or the aluminides, gives rise to an enriched β phase formation. Thus alloys with as little as 1 per cent ruthenium, contain equilibrium β phase at 770°C, Figure 5. Higher levels of ruthenium and aluminium result in the formation of [Ti,Al]Ru, as in the Ti-23Al-5Ru alloy, shown in Figure 6. Generally, higher levels of aluminium promote compound formation in

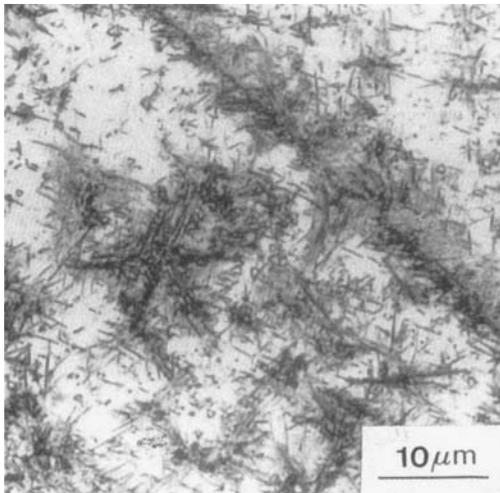
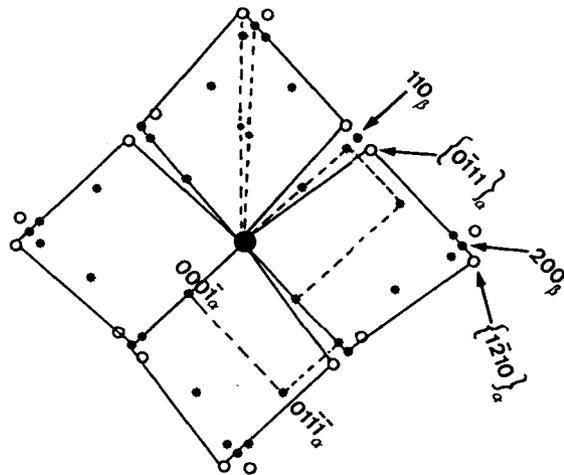


Fig. 7 The light micrograph of partially retained β phase in a Ti-37Al-5Ru alloy quenched from a temperature of 1250°C is supplemented by an electron diffraction pattern and key, showing the Burger's type transformation



these alloys, as in the case of the 37 atomic per cent aluminium alloy series, considered below.

Alloys Based on TiAl

Composition 37 atomic per cent Aluminium

Investigations of the martensitic transformations in these alloys revealed similar behaviour to that of lower aluminium content alloys, after quenching from the high temperature β field. Quenching of the Ti-37Al-5Ru alloy from 1250°C, however, resulted in only a partial retention of the β phase, see Figure 7. In comparison with lower aluminium alloys (17 to 25 per cent), where 5 per cent ruthenium is sufficient to cause complete retention of β , the Ti-37Al-5Ru alloy with partially retained β

demonstrates the α -stabilising effect of aluminium. This is also consistent with the fact that the M_s increases with the aluminium content in titanium-aluminium alloys (14).

The microstructure and equilibria in these alloys are significantly affected by the presence of a ternary compound, the G-phase, in this region of the system. The G-phase is one of a group of compounds with the $\text{Th}_6\text{Mn}_{23}$ type structure, based on b.c.c., and isotropic with $\text{Mg}_6\text{Cu}_{16}\text{Si}_7$, as described by Dwight (15). It is involved in equilibria with α_2 , γ , and $[\text{Ti,Al}]\text{Ru}$, as indicated in Figure 4(b). In the Ti-37Al-1Ru alloy, the G-phase is present as very small oval particles in equiaxed TiAl (γ) grains, as shown in Figure 8. The G-phase is, however, very brittle and its presence as large

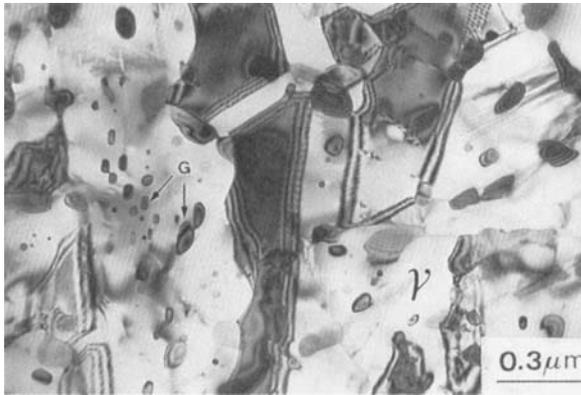


Fig. 8 G-phase particles are indicated in a TiAl matrix, in Ti-37Al-1Ru quenched from a temperature of 770°C, TEM micrograph (tensile tested alloy)

particles in the Ti-37Al-5Ru alloy caused severe embrittlement. Despite this, the compressive plasticity of the Ti-37Al-1Ru alloy showed marked improvement in comparison with the binary Ti-37Al alloy.

The data collected in Table II were obtained from a limited amount of mechanical testing of these alloys, and show considerable improvement in ductility and strength for two alloys, namely Ti-24Al-1Ru and Ti-37Al-1Ru. These alloys consist of fine scale microstructures containing small β or G-phase particles in α_2 or $\alpha_2 + \gamma$ matrix (Figures 5 and 8), after ageing at 770°C. Although room temperature ductility is absent in tension, the results of high

temperature tensile testing and sustained high temperature strengths of these alloys has clearly emphasised the potential of ruthenium as an important alloying addition to the Ti₃Al and TiAl based alloys. The mechanical testing results given in Table II represent average values of strength and strain obtained by testing two or more alloys in similar conditions.

Acknowledgements

This research was supported by a Science and Engineering Research Council Case Award, in collaboration with the Johnson Matthey Technology Centre. Isothermal forging and tensile testing of the alloys were carried out by Dr S. Kerry of the Royal Aerospace Establishment.

Alloy composition, atomic per cent	Test temperature, °C	Compressive strength, MPa	Compressive strain, per cent	Tensile strength, MPa	Tensile strain, per cent
Ti-17Al-1Ru	20	1782	4.6	—	—
Ti-18Al-2Ru	20	1716	1.7	—	—
Ti-18Al-5Ru	20	1825	0.6	—	—
Ti-24Al-1Ru*	20	2037	11.5	772	0
	650**	—	—	595	0
	800**	—	—	651	<1
Ti-23Al-5Ru	20	1625	0	—	—
Ti-37Al-1Ru*	20	2249	14.2	807	0
	650**	—	—	748	5.7
	800**	—	—	491	1.5
Ti-37Al-5Ru	20	—	0	—	—

*Alloys tested in tension at Royal Aerospace Establishment; ** only tested in tension

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Platinum 1989

The latest annual survey of commercial aspects of the six platinum group metals was published by Johnson Matthey during May. Compiled with the assistance of many people in the platinum-producing and platinum-using industries throughout the world, "Platinum 1989" first summarises the events that affected the supply, demand and use of platinum and palladium, and to a lesser extent rhodium, iridium, osmium and ruthenium during 1988, before going on to consider the outlook for 1989, and the years beyond.

For the second successive year supplies of primary platinum exceeded three million ounces troy, but demand was again greater than this and the deficit had to be met by metal withdrawn from stocks. Interestingly, Japanese imports jumped by no less than thirty per cent, compared with the record amount purchased in the previous year, to 67.5 tonnes, this being equivalent to 68 per cent of the primary supplies available to the Western World. The Japanese investment and jewellery markets were both of major importance during 1988, the latter absorbing just over one million ounces troy. A most interesting eight page section of the survey is devoted to the use of platinum in jewellery, a topic generally not considered in *Platinum Metals Review*; this includes a brief outline of the main technical features

of the metal that ensure its position in the highest-value sector of the market.

The perceived future demand for platinum metals in the European autocatalyst market was also highlighted. The European Commission has now reacted to growing concern about air quality, and the damage caused by emissions from motor vehicle engines. Thus the usage of the metals is expected to rise steadily over the next three years, as emission control catalytic converters become standard equipment on cars in Western Europe. Autocatalyst manufacture is already the largest application for platinum, taking 1.325 million ounces troy in 1988, and although the metal being recovered from scrapped converters is increasing, it amounted to only 160,000 ounces troy during the year under review.

Another notable feature of the past year was again the record demand for palladium resulting from increased use in both electronics and dental applications.

Readers of *Platinum Metals Review* who do not have ready access to "Platinum 1989", and who believe they would benefit from receipt of this comprehensive survey of the commercial aspects of the platinum metals should send their requests for a copy to the editor: Mr F. John Smith, Johnson Matthey P.L.C., New Garden House, 78 Hatton Garden, London EC1N 8JP.