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Alloy and process development of TiAl

XINHUA WU, D. HU, M. H. LORETTO
IRC in Materials, The University of Birmingham, Edgbaston B15 2TT, UK
E-mail: X.WU.1@bham.ac.uk
E-mail: M.H.Loretto@bham.ac.uk

The development of cast TiAl-based components for the automotive industry and the possibility of wrought components for applications in gas turbines are clear indications that these alloys are maturing as materials for engineering components. There are however problems in the cost of manufacture and in the properties of these alloys. In this paper it is argued that recent developments, which have resulted in a totally new microstructure, taken together with improved casting technology, open the way for wider application of these alloys. The new microstructure has been obtained by tempering massively transformed TiAl alloys so that a highly convoluted fine scale microstructure is obtained by simply heat treating cast samples. This fine microstructure can thus be obtained in cast components, without the need to add boron and problems associated with the extreme plastic anisotropy of fully lamellar samples are also eliminated.

1. Introduction

Following the early work [1] there has been a major effort aimed at developing TiAl-based alloys because they have a density about one half that of Ni-based alloys and they retain their strength up to about 800°C. It has been argued that if these alloys could be manufactured so that an acceptable balance could be obtained between their high and low temperature properties they would be used widely in automotive applications and in gas turbines. The problems in meeting these requirements are essentially twofold. Firstly and the aspect which is germane to the topic of this edition of Journal of Material Science, the TiAl-based alloys are made up of two and sometimes three, strongly ordered phases; alpha 2 (Ti_3Al), gamma (TiAl) and a B2 phase if sufficient beta stabilisers (such as W) are added. Neither of the two dominant ordered phases (Ti_3Al and TiAl) is ductile so that the alloys have limited ductility. Secondly, the processing of these alloys is notoriously difficult and expensive. Thus forging is commonly done isothermally, which is slow and expensive; extrusion requires canning to avoid excessive oxidation and to limit cracking and if cast products are made the reactions between the crucible and mould with the molten alloys lead to problems. The refractories CaO and Y_2O_3 are the only ceramic materials to use as moulds. Y_2O_3 is expensive and CaO tends to take up water and carbon dioxide from the atmosphere and special precautions have to be taken if this material is to be used.

The aim of this paper is to describe some recent developments in alloy development coupled with improved processing, which it will be argued provide a turning point in the use of TiAl-based alloys. In order to appreciate the significance of this recent work a short review will be presented of the current situation concerning the properties of TiAl-based alloys which are being considered for use in gas turbines and are already in limited use in the automotive industry. This discussion will consider the microstructures of these ordered alloys, since it is only by microstructural manipulation that these intrinsically brittle ordered alloys can be made into useful engineering components. Additionally and intimately linked to the properties and microstructure, the current processing routes which are used will be outlined. Finally the recent work, which has used all of the previous work as a foundation will be presented. The development of a reliable, cost-effective process route will be described and the alloy development, undertaken in parallel will be explained.

2. Properties and microstructure of TiAl-based alloys

The origin of the microstructures which have been extensively investigated in a wide range of TiAl-based alloys can be easily understood from a consideration of a generic phase diagram. This is shown in Fig. 1 where the important regions from the present viewpoint are the high temperature alpha (hcp) phase field and the (alpha + gamma (fct)) phase field. Two distinct microstructures can be formed, fully lamellar and duplex by appropriate processing.

If samples containing above about 45 at.% Al are cooled reasonable slowly from the alpha phase field i.e., either furnace cooled or cooled directly as a casting, the alpha phase transforms into lamellar alpha + gamma as indicated in Fig. 2. In this case the gamma is precipitated on the (0001) plane in the alpha and a "fully lamellar" structure is obtained. The original grain size in the alpha phase field determines the colony size of

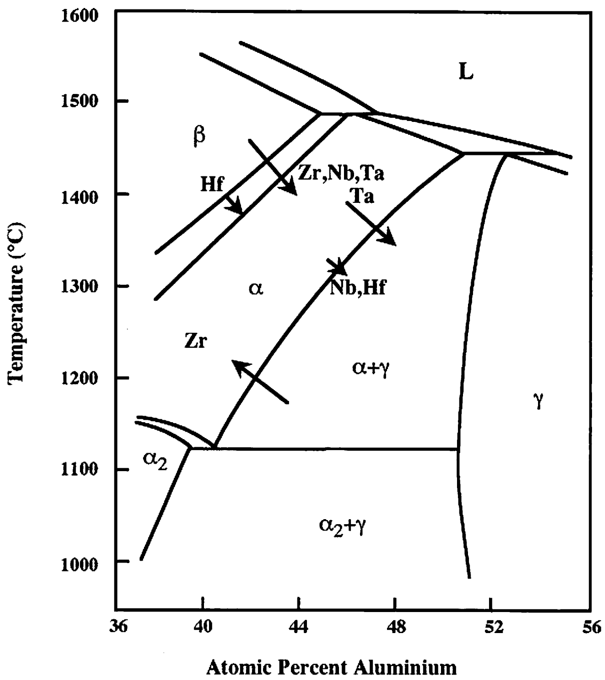


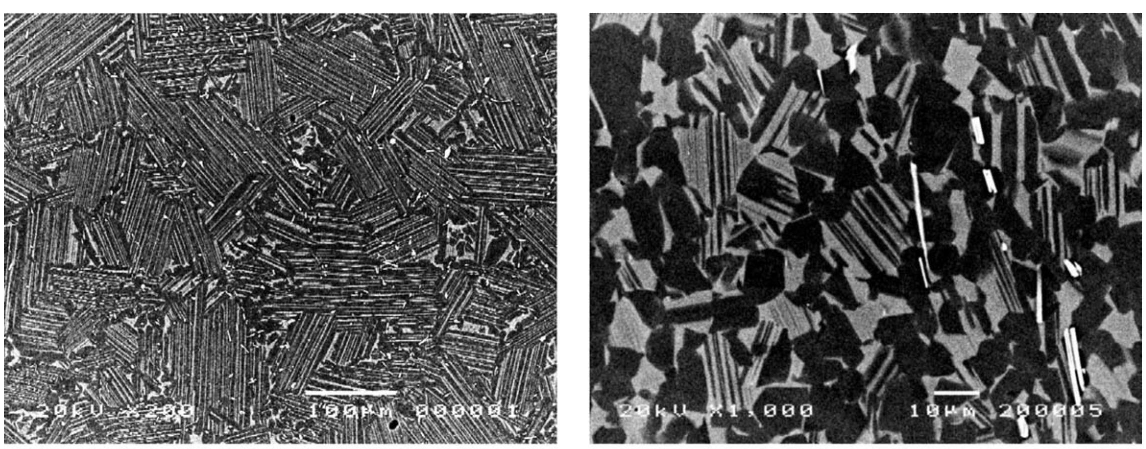
Figure 1 Schematic of central part of the Ti-Al binary phase diagram. The arrows indicate the direction in which phase boundaries are moved by alloying additions. The length of each arrow is an indication of the relative movement of the phase boundaries for the different elements.

the lamellar structure, since the lamellae delineate the (0001) within each grain, as illustrated in Fig. 2a. At about 1200°C the alpha phase orders to alpha 2 through a eutectoid transformation and a lamellar structure is formed consisting of this very strong ordered phase, Ti_3Al, and the weaker gamma, TiAl. Some of the lamellae boundaries separate alpha 2 and gamma and others separate twinned (or pseudo-twinned) gamma. The grain size in the fully lamellar samples can be several hundred microns, but (as discussed below) is strongly influenced by the Al content and by the other alloying additions and can be significantly reduced by addition of boron.

If samples are thermomechanically processed in the two phase (alpha + gamma) phase field then a duplex structure is formed. This duplex structure, illustrated in Fig. 2b, contains discrete grains of gamma, and lamellae grains. The gamma is formed during processing and lamellar grains are formed from alpha on cooling from the hot working temperature. The balance between the amount of gamma and the volume fraction of lamellar grains is determined by the temperature at which the samples are hot worked; the higher the temperature of hot working the higher the volume fraction of lamellar grains. The alpha again transforms to alpha 2 on cooling through the eutectoid temperature. The grain size in this structure, typically 10–20 μm, is usually considerably smaller than that of fully lamellar samples because recrystallisation takes place during hot working.

If samples are hot worked just above the alpha transus (i.e., totally within the high temperature alpha phase field) it is possible to produce very fine grained fully lamellar samples which have very small lamellar spacings [2]. Alloys processed in this way are very strong (room temperature tensile strengths above 1000 MPa can be achieved) but the very fine lamellae are not stable over long times at high temperatures. Similarly very fine grained duplex samples can be obtained by extensive working very close to the alpha transus.

The grain size in TiAl-based alloys can also be refined by adding boron at levels below 1 at.% and in the case of an alloy such as Ti44Al8Nb1B the presence of boron results typically in an as-cast grain size of about 50 μm. The ability to refine the grain size is a strong function of the Al-content and is also influenced by ternary additions as illustrated in Fig. 3. Because boron is virtually insoluble in the solid TiAl, the borides which are formed (either TiB_2 or TiB depending upon the alloy composition) pin grain boundaries during any subsequent thermo-mechanical processing and in this case the grain size is about 70 μm in Ti44Al8Nb1B. The decrease in grain size in cast alloys is important in increasing the hot workability of the alloys (hot working also breaks up the borides) but the presence of the borides in cast samples, which can be over 100 μm in length, can lead to early fracture. The slower the cooling rate the larger the borides and the more prone the samples are to premature failure. This is particularly important in the more highly alloyed TiAl alloys, since the borides formed are (TiM)B, where for example M can be W, Ta or Nb. In such alloys the volume fraction



(a) (b)

Figure 2 Secondary scanning electron micrographs of (a) fully lamellar and (b) duplex Ti-44Al-8Nb-1B.

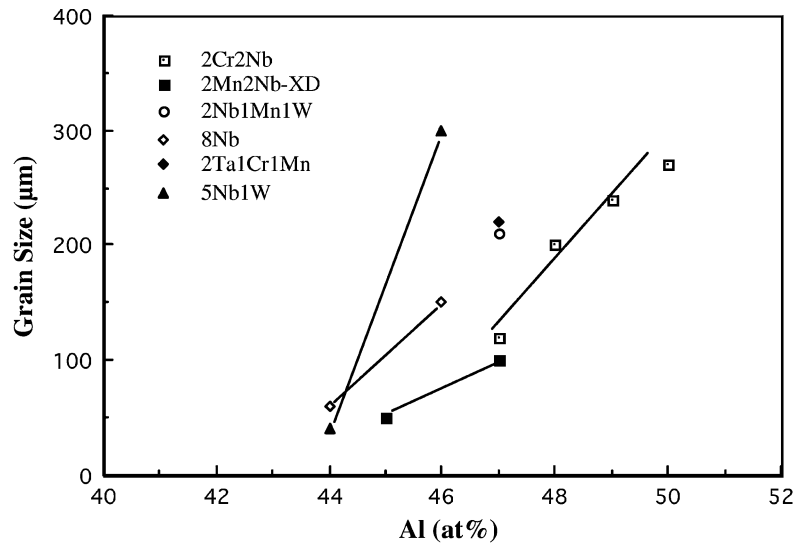


Figure 3 As-cast lamellar grain size against Al content for various cast TiAl alloys.

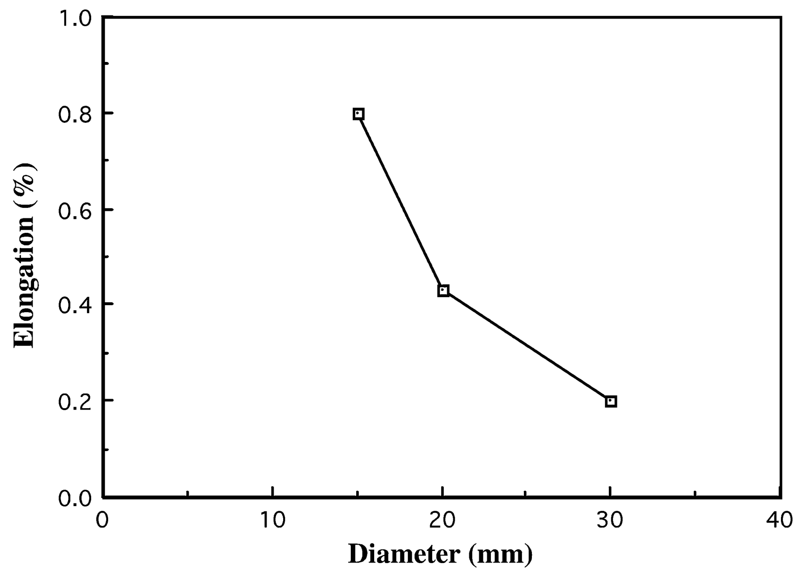


Figure 4 Showing the effect of cast bar size on ductility in Ti46Al8Nb1B (after Ref. [3]).

of borides is higher and they tend to form long thin borides which have a tendency to clump together [3]. Fig. 4 illustrates the dependence of ductility on diameter of cast bars in which the borides are larger for the larger diameter bars [3].

Generally for typical samples it is considered that the fully lamellar samples possess the best balance of properties. Thus their high temperature strength, their fracture toughness and the growth rate of fatigue cracks are superior to those of duplex samples, although the room temperature ductility is better in duplex samples, where values of 2–3% can be routinely obtained.

A group of high Nb content alloys, termed TNB, have been developed recently as duplex alloys, which after extensive thermomechanical processing give a balance of properties which are viewed as better than those so far obtained with fully lamellar samples [4]. This has been achieved by adding small amounts of C which dramatically improves the creep strength, the usual weakness of fine grained duplex samples. The properties of these alloys are among the best available, but if strengths above about 1000 MPa are required the room temperature ductility drops to about 0.5%.

Recent work has shown [5, 6] that the plastic anisotropy, which is characteristic of the lamellae [7] in lamellar samples, gives rise to considerable pre-yield plasticity and thus to pre-yield cracking. The cracking has been detected using acoustic emission [5] and the presence of cracks associated with the acoustic signals confirmed using optical microscopy. The yield strength of lamellae vary by nearly an order of magnitude [7], with soft lamellae (those at about 45° to the stress axis) yielding at about 100 MPa and hard crystals (those with boundaries at 90° to the stress axis)yielding at over 800 MPa.

Clearly in a polycrystalline sample the soft grains will yield at stresses well below the macroscopic 0.2% proof stress and it has been shown that in Ti44Al8Nb1B pre-yield cracking occurs at stresses of about 400–500 MPa, well below the yield stress of 625 MPa. No such pre-yield cracking is observed in duplex samples. The shapes of the stress-strain curves for duplex and

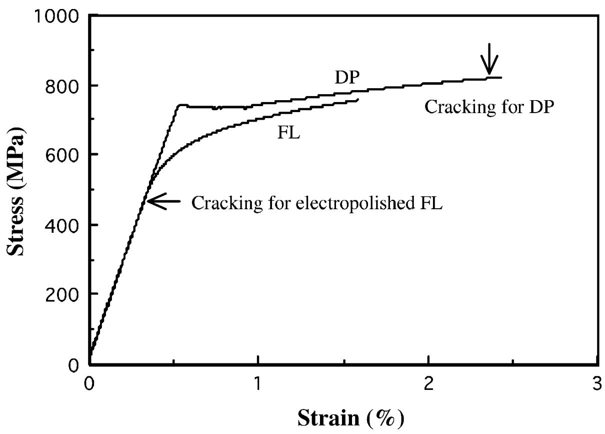


Figure 5 Typical stress strain curves for samples of Ti44Al8Nb1B. DP indicates duplex microstructure and FL, fully lamellar. Note the obvious deviation from linear relation for the FL curve well below the stress corresponding to the 0.2% proof stress (see text).

lamellae samples are very different, as can be seen in Fig. 5, where the deviation from linearity of the lamellar sample has been shown by loading /unloading experiments to be due to plastic deformation. This pre-yielding and pre-yield cracking results in a fatigue limit of about 400 MPa in Ti44Al8Nb1B which is only about 60% of the 0.2% proof stress. This is a much lower value than is found in weaker TiAl alloys (such as Ti48Al2Nb2Cr) where the fatigue limit is above 90% of the proof stress. It has been argued that this reduction in fatigue limit with respect to the yield strength is associated with the fact that the fracture strength is not significantly changed by the alloying additions which give rise to the increased yield strength [6].

Pre-yield cracking has been interpreted [6] in terms of the pile-up stresses induced by the dislocations and the magnitude of these stresses is clearly controlled by the difficulty of transmitting dislocations into adjacent grains (unless the lamellae in adjacent grains are close to parallel) and by the grain size. In smaller grains the pileups will be limited in length and hence the stresses correspondingly reduced. Hence no pre-yield cracking is observed in duplex samples, which not only have a smaller grain size but the adjacent grains are commonly relatively soft gamma grains so that slip can be easily transmitted and the stresses relieved.

On the basis of the work summarised above it appears that duplex samples suffer from poor creep and fatigue crack growth properties with the exception of the latest TNB alloy which requires extensive thermomechanical processing if optimum properties are to be obtained. Typical grain-refined fully lamellar samples show pre-yield cracking associated with plastic anisotropy and show a large scatter in ductility in cast samples, associated with the presence of borides. There appears to be a problem therefore with both types of microstructure which have been investigated so extensively over the last ten or so years.

3. Processing of TiAl-based alloys

Two different approaches have been used recently for the production of TiAl components; thermomechanical processing (of ingot material and of powder) and the production of shaped castings.

As noted above TNB alloys are produced as finished components after extensive extrusion followed by forging. This, together with the additions of C allows a very fine microstructure to be obtained provided that the extrusion conditions, the forging and heat treatment conditions are all tightly controlled [8]. This approach is currently being developed for the production of compressor blades for engine testing in a European programme, but it is clear that this is a very expensive processing route. A great deal of work has been undertaken using gas-atomised powder which is consolidated and subsequently processed to produce sheet. It has been found that gas-entrapment leads to problems for sheet production but further work is underway using powder route to produce discs [9]. This route is being investigated because of the problems associated with the segregation present in the large ingots which are required to produce the large diameter discs. All of the thermomechanical process routes which are appropriate for TiAl alloys are expensive, but for components such as discs it appears that forging, perhaps coupled with the use of powder starting material is the only process which is capable of providing the reliability required for such large components.

In the case of automotive components thermomechanical processing is being used to produce exhaust valves for formula-one cars [10], where cost is perhaps of secondary importance.

Cast products are already being used for turbochargers in top of the line cars in Japan and it appears that this market is set to grow when turbochargers are produced for diesels [11]. The casting technology used employs counter gravity casting in conjunction with a cold wall furnace. This was the first application of TiAl-based alloys to the automotive industry and although no data are available concerning failures during service a turbocharger is not a critical component. If it were to fail the effect would be simply a loss in the response of the engine rather than a catastrophic failure which would occur if fracture of an exhaust valve occurred. Thus although this is a very important example of the potential of TiAl-based alloys it is not perhaps a technology that can be immediately applied to gas turbines or to more demanding applications in automotive engines. The alloy used for the turbochargers was chosen in part for its resistance to the environment which was more important than high strength and thus the quality of the castings may also not be a central issue.

Many attempts have been made to produce low pressure turbine blades for gas turbines using casting, but the high failure rate has led to this programme being discontinued [12].

On the basis of the above brief review it appears that the processing of TiAl-based alloys to produce reliable, highly stressed engineering components can be done only if thermomechanical processing is used. This approach has been followed successfully to produce sheet for some applications in gas turbines [13] and if the market can stand the cost of this route then further applications will follow.

As noted above the problem with the casting route is that if conventional grain refined samples are used the borides which are inevitably present lead to a large scatter in ductility. If grain refined samples are not used the ductility is typically well below 0.5% and the scatter of properties in thin sections is unacceptable since it is the minimum values that are relevant, not the average.

In the following section, recent work which has overcome these problems will be presented.

4. Alloy and process development for TiAl-based components

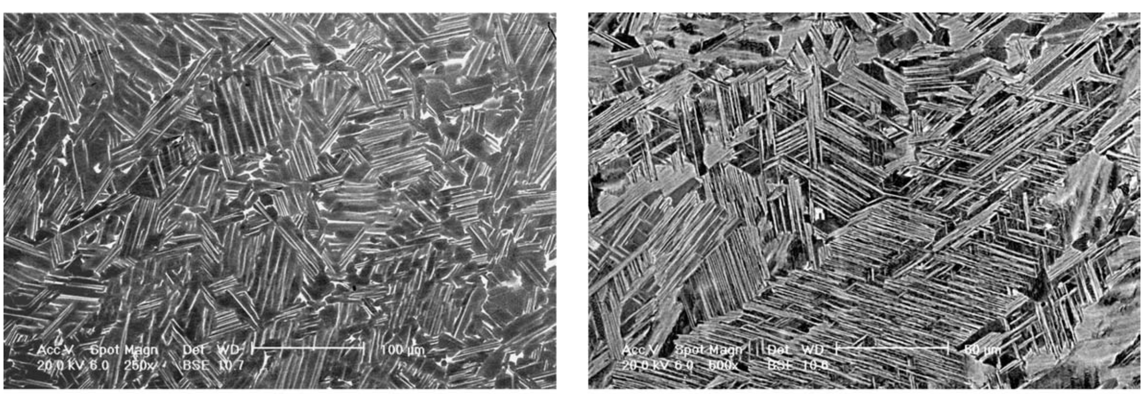
The fully lamellar structure is formed by precipitation of gamma within the hexagonal alpha and this means that the resultant microstructure reflects the fact that there is only one type of plane, (0001), in each grain that can nucleate the gamma. The length of the lamellae reflects the grain size of the alpha phase and thus any grain growth that takes place in the high temperature phase is retained in the final structure. Thus castings will generally tend to have a large colony size ($>100\ \mu$m), unless this is controlled by using boron additions and similarly when heat treating forgings in the alpha phase field grain growth will occur unless borides are present. As noted above coarse colonies will lead to pre-yield cracking and even in the case of forged samples of alloys such as Ti44Al8Nb1B pre-yield cracking is observed well below the 0.2% proof stress, because the grain size is large—about 70 μm. The situation is even worse for higher Al-content alloys where boron is less effective.

Since the origin of the problem in the fully lamellar samples lies in the fact that the structure is plastically anisotropic, because it inherits the anisotropy of the hexagonal alpha phase, it is clearly worth investigating alternative ways of transforming the high temperature phase. It is well known that alpha will transform massively when it is cooled at an appropriate rate [14, 15]. Since heavily dislocated gamma is formed, subsequent tempering in the two phase (alpha + gamma) phase field will result in precipitation of alpha within this massively transformed gamma. Since gamma is face centred tetragonal, with a c/a ratio close to one, there are four {111} planes on which alpha can precipitate and furthermore nucleation will be on a scale determined by the high defect density in the massively transformed sample. Hence the resultant microstructure will not show the same anisotropy as that which characterises the fully lamellar structure and the scale of the microstructure will be small because of the role of crystal defects in nucleating alpha.

An example of a sample of Ti46Al8Nb transformed in this way is shown in Fig. 6a. This sample was oil quenched from 1360°C and then tempered at 1320°C and it is clear that it is no longer possible to define the initial alpha grain size and that a very convoluted microstructure has been developed as would be expected from the above argument. Fig. 6b shows the microstructure obtained in Ti48Al2Nb2Cr after oil quenching from 1380°C (a higher temperature than used for Ti46Al8Nb s required because of the higher Al content) and tempering at 1320°C. Again a complex fine scale microstructure is formed. TEM reveals a very complex structure in these tempered alloys [16].

The room temperature tensile properties of Ti48Al2Nb2Cr treated in this way are shown in the Table I and it is clear that this simple heat treatment produces better properties than those obtained by forging and heat treating to produce a fully lamellar structure. Also shown in the table are the tensile properties in a forged, heat treated fully lamellar structure of the same alloy with addition of boron. Whilst the ductility is comparable with that in the tempered, boron-free sample the yield stress and the UTS are considerably lower. The work hardening observed is also far higher in the convoluted sample. The convoluted microstructure, formed by using the massively transformed structure as a precursor, is unlikely to show pre-yield cracking because the randomly oriented structure is expected to show an isotropic response to the applied stress. On that basis the fatigue limit could be a larger fraction of the yield stress but these measurements have not yet been done.

The "hardenability" of individual TiAl-based alloys will need to be determined in order to define the maximum diameter samples which can be transformed massively. It is known that the Al content has to be greater than about 45 at.% for the massive transformation to take place [15] but the influence of various alloying elements on this transformation needs to be further investigated.



(a) (b)

Figure 6 Secondary electron micrographs of (a) Ti46Al8Nb and (b) Ti 48Al2Nb2Cr after tempering massively transformed samples.

TABLE I Properties of cast and thermomechanically processed Ti48Al2Nb2Cr

Treatment	0.2% proof stress (MPa)	UTS (MPa)	% Ductility
Forged + 1380°C/1 h/FC	312	347	0.5
1380°C/1 h OQ + 1320°C/1 h/AC	425	622	1.3
Forged + 1380°C/1 h/FC 1 at.%B added	345	445	1.4

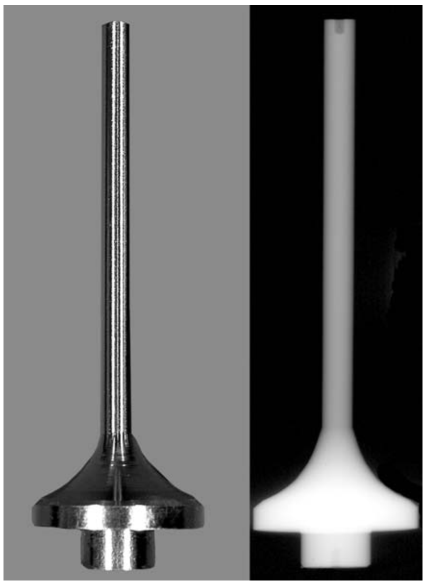


Figure 7 Photograph of roughly machined exhaust valve made at IMR, Shenyang [17] and the corresponding X-ray radiograph which shows no obvious porosity.

In parallel with the work aimed at producing improved casting alloys the casting process itself has been improved recently. In joint work between the IRC and the IMR (Institute of Metals Research, Chinese Academy of Sciences) at Shenyang [17] it has been shown that using CaO crucibles (which allow superheats of about 180°C to be obtained) in conjunction with centrifugal casting it is possible to produce components with no obvious porosity. An example of a roughly machined cast automotive valve together with an X-ray radiograph of the valve is shown in Fig. 7 and the valve appears to be pore-free Subsequent HIPping does not lead to any surface dimpling associated with the collapse of pores.

This process is now used routinely in the Institute of Metal Research(IMR), Chinese Academy of Sciences and many hundreds of valves have been made with a high success rate [17]. In addition to this approach, work in the IRC using a cold wall induction furnace, which allows only 60°C superheat, in conjunction with counter-gravity casting can lead to the production of pore-free components. This approach is not yet as reproducible as that developed in IMR but work is underway, using real time X-ray observations to optimise the mould filling.

5. Conclusions

1. Tempering of massively transformed samples of TiAl alloys can yield properties in cast samples which are comparable with those found in thermomechanically processed samples.

2. Improved casting can produce selected components which are free of obvious casting defects.

Acknowledgements

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