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(54) Title: TITANIUM ALUMINIDE BASED ALLOY

(57) **Abrégé/Abstract:**

The invention concerns alloys made through the use of melting and powdered metallurgical techniques on the basis of titanium aluminides with an alloy composition of Ti-z Al-y Nb where $44.5 \text{ Atom \%} \leq z \leq 47 \text{ Atom \%}$, $44.5 \text{ Atom \%} \leq z \leq 45.5 \text{ Atom \%}$, and $5 \text{ Atom \%} \leq y \leq 10 \text{ Atom \%}$ with possibly the addition of B and/or C at a content between 0.05 Atom % and 0.8 Atom %. Said alloy is characterized in that it contains a molybdenum (Mo) content ranging between 0.1 Atom % to 3.0 Atom %.



Abstract

The invention concerns alloys made through the use of melting and powdered metallurgical techniques on the basis of titanium aluminides with an alloy composition of Ti-z Al-y Nb where $44.5 \text{ Atom \%} \leq z \leq 47 \text{ Atom \%}$, $44.5 \text{ Atom \%} \leq z \leq 45.5 \text{ Atom \%}$, and $5 \text{ Atom \%} \leq y \leq 10 \text{ Atom \%}$ with possibly the addition of B and/or C at a content between 0.05 Atom % and 0.8 Atom %. Said alloy is characterized in that it contains a molybdenum (Mo) content ranging between 0.1 Atom % to 3.0 Atom %.

TITANIUM ALUMINIDE BASED ALLOY

Field of the Invention

The invention concerns alloys made through the use of melting and powdered metallurgical techniques on the basis of titanium aluminides with an alloy composition of Ti-z Al-y Nb where $44.5 \text{ Atom \%} \leq z \leq 47 \text{ Atom \%}$, especially where $44.5 \text{ Atom \%} \leq z \leq 45.5 \text{ Atom \%}$, and $5 \text{ Atom \%} \leq y \leq 10 \text{ Atom \%}$ with possibly the addition of B and/or C at a content between 0.05 Atom % and 0.8 Atom %.

Background of the Invention

Titanium aluminide alloys have properties which make those alloys highly suitable for use as light weight work materials, especially for high temperature applications. For industrial practice those alloys are of special interest which are based on an intermetallic phase γ -(TiAl) with tetragonal structure and along with the majority phase γ -(TiAl) also contain minority portions of the intermetallic phase α_2 (Ti₃Al) with hexagonal structure. These γ -titanium aluminide alloys distinguish themselves by properties such lightweight (3.85-4.2 g/cm³), high elastic modulus, high strength and creep resistance up to 700°C, which makes them attractive as work materials for moving parts at high operating temperatures. Examples of such uses are for turbine blades in aircraft engines and in stationary gas turbines, engine valves and hot gas ventilators.

In the technically important area of alloys with aluminum content between 45 Atom % and 49 Atom% there appears during the solidification of the melt and during the subsequent cooling a series of phase changes. The solidification can take place either entirely by way of β -mixed crystal cubic space centered structure (high temperature phase) or in two peritectic reactions in which α -mixed crystals with hexagonal structure and the γ -phase participate.

It is further known that the element niobium (Nb) leads to an increase in strength, creep resistance, oxidation resistance and also ductility. With the element boron which is practically insoluble in the γ -phase a fine graining can be achieved both in the cast condition and also after reshaping with subsequent heat treatment in the α -region. An

increased portion of the β -phase in the structure as a result of low aluminum content and high concentration of β -stabilizing elements can lead to a coarse dispersion of this phase and to an impairment of the mechanical properties.

The mechanical properties of γ -titanium aluminide alloys are, as to their deformation and break behaviors, but also because of the structural anisotropy of the preferred use of laminated structures or duplex-structures, strongly anisotropic. For a desired use of structure and texture in the making of components from titanium aluminides, casting methods, different powdered metal metallurgies and reshaping processes as well as combinations of these manufacturing methods are useable.

From the publication of Y-W. Kim and D. M. Dimiduk in "Structural Intermetallics 1997", editors M. V. Nathanael, R. Darolia, C.T. Liu, P.L. Martin, D. B. Miracle, R. Wagner, M. Yamaguchi, TMS, Warrendale PA, 1996, page 531 it is known that in the course of different development programs the effect of a large number of alloying elements with respect to constitution, structural tuning in different manufacturing processes and individual properties have been investigated. The discovered relationships are thereby similarly complex as for the case with the other structured metals, for example, steels and can only be summarized by rules which are limited and of very general form. Therefore certain mixtures can have exceptional combinations of properties.

A titanium aluminide alloy is known from EP1 015 605 B1 which has a structural and chemically homogenous structure. In this case the majority phases γ (TiAl) and α_2 (Ti₃Al) are separated into a fine dispersion. The disclosed titanium aluminide alloy with an aluminum content of 45 Atom% distinguishes itself by exceptionally good mechanical properties and high temperature properties.

A general problem of all titanium aluminide alloys is their low ductility. For a long time one has not succeeded in improving the pre-given high brittleness and low damage tolerance of titanium aluminide alloys arising from the nature of the intermetallic phases (compare "Structural Intermetallics 1997", page 531, see above). For many of the above mentioned uses indeed plastic fracture elongations of $\geq 1\%$ are sufficient. For the making of turbines and motors however it is necessary that this minimum amount of

ductility be guaranteed in industrial manufacturing throughout large batch numbers. Since the ductility is sensitively dependent on structure in industrial manufacturing processes it is extremely difficult to assuredly obtain a highly homogenous structural configuration. For high tensile strength alloys a maximum tolerable defect size, for example the maximum grain or lamina colony size, is very small so that for such alloys a very high structural homogeneity is desirable. This homogeneity can however, because of the unavoidable fluctuation of the alloying mixture from, for example ± 0.5 Atom % in aluminum content, only be reached with difficulty.

At the present time of the many possible structural types of γ -titanium aluminide alloys only lamellar and so called duplex structures are taken into consideration for high temperature uses. Upon the cooling from the single phase region the α -mixed crystals first appear while plates of the γ -phase crystallographically become oriented and separate from the α -mixed crystals.

Compared to this, duplex structures consisting of lamina colonies and γ -grains arise when the material has been heated into the second phase area $\alpha + \gamma$. Then upon cooling the α -grains lying in the second phase area again change into two phased lamina colonies. Above all, coarse structural components exist in γ -titanium aluminide alloys since during the running through of the α -area large α -grains are formed. This can indeed happen during the solidification when large stalk crystals of the α -phase are formed from the melt. Accordingly as much as possible the single phase area of the α -mixed crystals must be avoided during processing. Since in practice however fluctuations in the composition and processing temperatures appear and thereby locally vary the constitution in work pieces, the formation of large lamina colonies is not to be prevented.

Proceeding from this state of the art the present invention has as its object the making available of a titanium aluminide alloy with a fine and homogeneous structural morphology, as to which alloy the variations of the alloy composition as well as unavoidable temperature fluctuations which appear during manufacturing processes of industrial practice have hardly any or no significant effect on the homogeneity of the alloy, and especially without having to make any basic changes in the manufacturing

processes. Therefore a further object of the invention is to make available a structural component consisting of a homogenous alloy.

Summary of the Invention

This object is solved by means of an alloy based on titanium aluminide made through the use of melting and powdered metallurgical technologies with an alloy composition of Ti-z Al-y Nb where $44.5 \text{ Atom \%} \leq z \leq 47 \text{ Atom \%}$, especially where $44.5 \text{ Atom \%} \leq z \leq 45.5 \text{ Atom \%}$, and $5 \text{ Atom \%} \leq y \leq 10 \text{ Atom \%}$, which is further formed in that this alloy contains molybdenum (Mo) in the range of between 0.1 Atom % to 3.0 Atom%. The remainder of the alloy is made up of Ti (titanium).

Investigations have shown that the alloying of molybdenum with titanium aluminide having a niobium portion usually results in an alloy for which the β -phase is not stable over the entire temperature region, and therefore in a customary process procedure such as extrusion the remainder of the high temperature β -phase dissolves, and a better structural homogeneity of the alloy is obtained. In this way over the entire temperature range relevant to the before mentioned manufacturing process a portion of the volume of the β -phase without grain coarseness is realized. This type of alloy according to the invention therefore, because of the fine and very uniform dispersion of the β -phase, has a homogenous structure with high strength values.

Therefore an alloy is presented by the invention which is suitable as a lightweight work material for high temperature applications, such as for turbines blades or engine and turbine components. The alloy of the invention is made through the use of casting metallurgy, melting metallurgy or powdered metal metallurgy methods or by the use of these methods in combination with reshaping techniques.

Above all in the case of Ti-(44.5 Atom % to 45.5 Atom %) Al – (5 Atom % to 10 Atom %) Nb the addition of molybdenum at a content of about 1.0 Atom % to 3.0 Atom % leads to good microstructures with a high structural homogeneity.

Moreover an alloy according to the invention has a composition of Ti-z Al-y Nb-x B where $44.5 \text{ Atom \%} \leq z \leq 47 \text{ Atom \%}$, especially where $44.5 \text{ Atom \%} \leq z \leq 45.5 \text{ Atom \%}$, $5 \text{ Atom \%} \leq y \leq 10 \text{ Atom \%}$ and $0.05 \text{ Atom \%} \leq x \leq 0.8 \text{ Atom \%}$, or a

composition of Ti-z Al-y Nb-w C where $44.5 \text{ Atom \%} \leq z \leq 47 \text{ Atom \%}$, especially where $44.5 \text{ Atom \%} \leq z \leq 45.5 \text{ Atom \%}$, $5 \text{ Atom \%} \leq y \leq 10 \text{ Atom \%}$ and $0.05 \text{ Atom \%} \leq w \leq 0.8 \text{ Atom \%}$, each of which alloys contains molybdenum (Mo) in the region of between 0.1 Atom % to 3 Atom %, especially in the region of between 0.5 Atom % to 3 Atom %.

Alternatively the alloy is made up of Ti-z Al-y Nb-x B-w C where $44.5 \text{ Atom \%} \leq z \leq 47 \text{ Atom \%}$, especially where $44.5 \text{ Atom \%} \leq z \leq 45.5 \text{ Atom \%}$, $5 \text{ Atom \%} \leq y \leq 10 \text{ Atom \%}$, $0.05 \text{ Atom \%} \leq x \leq 0.8 \text{ Atom \%}$ and $0.05 \text{ Atom \%} \leq w \leq 0.8 \text{ Atom \%}$ and additionally of molybdenum in the region of between 0.1 Atom % to 3 Atom %.

By means of the given alloying and the corresponding alloying proportions high strength γ -titanium aluminum alloys with a fine dispersion of the β -phase are created for a wide range of processing temperature.

In the case of the present invention the strived for structural stability and process security are thereby achieved in that the appearance of single phase regions are avoided over the entire temperature region traversed in the manufacturing processes and upon use, by the aimed for inclusion of the cubic space centered β -phase. Principally the β -phase appears as the high temperature phase for all technical titanium aluminum alloys at temperatures $\geq 1350^\circ\text{C}$.

From the literature it is known that this phase can be stabilized at low temperatures by different elements such as Mo, W, Nb, Cr, Mn, and V. The special problem with the alloying of these elements exists however in that the β -stabilizing elements have to be very accurately tuned to the Al content. Moreover in the case of the addition of these elements undesirable exchange effects appear which lead to higher portions of the β -phase and to a coarse dispersion of this phase. Such a constitution is most disadvantageous for the mechanical properties. Further, the properties of the β -phase are dependent on the alloying elements and their composition. Especially the constitution must be so chosen so that a precipitation of the brittle ω -phase from the β -phase must be substantially avoided. Because of this relationship an alloying composition is presented whereby for the mechanical properties an optimum composition and dispersion of the β -phase can be realized for a wide region of processing temperatures. At the same time the best possible strength properties are achieved.

According to a preferred form of the invention the alloy likewise contains boron, preferably with a boron content in the alloy in the area of from 0.05 Atom % to 0.8 Atom %. The addition of boron leads advantageously to the formation of stable precipitates which likewise contribute to the mechanical hardening of the alloy and to the stabilization of the structure.

The object of the invention is further solved by a construction component made from an alloy of the invention. To avoid repetition reference is made to the previous exposition.

Brief Description of the Drawings

In the following the invention, without limitation to the general thought of the invention, is described by way of exemplary embodiments with reference to the accompanying schematic drawings, to which in regard to publication reference is made for all details of the invention not more closely explained in the text. The drawings are:

Fig.1 shows a raster electron microscope picture of a cast block having an alloying of Ti-45Al-8Nb-0.2C (Atom %);

Fig. 2a to 2c each shows a picture of the structure in an alloy of Ti-45Al-8Nb-0.2C (Atom %) taken by a raster electron microscope after different processing steps;

Fig. 3a and 3b each shows a picture of the structure in an alloy of the invention of Ti-45Al-Nb-2 Mo (Atom %) after different processing steps, and

Fig. 4 is a diagram with tension-elongation curves resulting from tests of the alloy Ti-45Al-5Nb-2 Mo (Atom %).

Detailed Description

Fig. 1 shows two pictures of a structure in a cast block made of the alloy Ti-45Al-8Nb-0.2 C (Atom %). The pictures as well as the further pictures in the following figures were taken by means of back scattered electrons in a raster electron microscope.

The structure (Fig.1) shows lamina colonies of the α_2 -phase and the γ -phase, which originate from former γ -lamina. The former γ -lamina are separated by stripes of

bright pictured grains of β -phase or B2-phase. The α -lamina next formed in the β - α -conversion decay upon further cooling into α_2 -lamina and γ -lamina.

In figures 2a to 2c two further pictures of the structure of the alloy Ti-45Al-8Nb-0.2C taken in the raster electron microscope and after different processing steps are shown. Fig. 2a shows the structure after extrusion at 1230°C. The extrusion direction runs horizontally. The structure shows grains of the α_2 - and β -phase, with the cubic space centered β -phase having vanished.

Fig. 2b shows the structure of the alloy after the extrusion at 1230°C and a further forging step at 1100 °C. This structure shows grains of the α_2 - and γ -phase and a few α_2/γ lamina colonies.

In Fig. 2c is shown the structure of the alloy after extrusion at 1230°C and a subsequent heat processing at 1330 °C. This structure exhibits likewise grains of the α_2 - and γ -phase. The picture shows a fully laminar structure with lamina of the α_2 - and γ -phase. The lamina colony size has a value of about 200 μ m, with colonies also appearing which are clearly larger than 200 μ m.

As in the structure illustrated in Fig. 2a, also in the structures illustrated in Figs. 2b and 2c the cubic space centered phase does not appear. So the β -phase in this temperature range with a heat processing after the extrusion is thermodynamically not stable.

In Figures 3a and 3b are illustrated raster electron microscope pictures of the structure of an alloy in accordance with the invention. Proceeding from an alloy of Ti-45Al-5Nb the alloying agent molybdenum was added at 2Atom%. This starting alloy Ti-45Al-5Nb-2Mo is based on a composition as described in European Patent EP 1 015 650 B1.

Figs. 3a and 3b show the structure of this alloy of the invention after an extrusion at 1250°C and a subsequent heat treatment at 1030°C (Fig 3a) as well as observed at 1270°C (Fig 3b).

The structure of Fig. 3a exhibits grains of the α_2 -phase, the γ -phase and the brightly pictured β -phase, with the latter being arranged in strips. The structure in Fig. 3b

shows lamina colonies of α_2 -and γ -phases as well as grains of the brightly pictured β -phase, which again have precipitated from the γ -phase.

The structures of Fig. 3a and 3b are fine, very homogenous and show uniform distribution of the β -phase. After the heat treatment of 1030°C a globular structure is presented, with it having grains of β -phase in strips parallel to the extrusion direction, while the material heat treated at 1270°C exhibits a very homogenous, fully lamellar structure with uniformly distributed β -grains (Fig 3b).

The colony size of the alloy Ti-45Al-5Nb-2Mo has a value of between 20 to 30 μm and is therefore at least about 5 times smaller than in the fully laminar structure of γ -titanium aluminide alloy. Moreover, in the β -phase the γ -phase has been eliminated so that the β -grains are very finely subdivided. Therefore, in summary, a very fine and homogenous structure has been achieved.

Tests have shown that this fine and homogenous structure morphology after heat treatment is present for the entire high temperature range up to 1320°C. The structures show clearly that over the entire temperature range relevant for the manufacturing processes a sufficient volume of the β -phase is provided and the grain growth is effectively suppressed.

In tension tests carried out on the material which was heat treated at 1030°C, at room temperature a stretch limit of 867 MPa, a tensile strength of 816 MPa and a plastic elongation at rupture at 1.8% were measured.

Fig. 4 shows measured tension-elongation curves from test of the alloy Ti-45Al-5Nb-2Mo in tension tests. The test material was extruded at 1250°C and subsequently subjected to a heat treatment for two hours at 1030°C and was then subjected to an oven cooling. The curves taken at 700°C and 900°C show that the alloy is suitable for many high temperature applications. By the alloying of a small amount of molybdenum a very uniform microstructure in the alloy is achieved so that this alloy can be well used as a high temperature work material.

Moreover in Fig. 4 the results of a tension test at room temperature (25°C) on the material of the invention is illustrated, with the tension σ in MPa being shown against the elongation ϵ in %. Thereby an elongation limit increase was found which otherwise up to

now has not been observed for γ -titanium aluminide alloys. This represents an indication of an especially fine and homogenous structure. The elongation limit increase indicates that the material can react to local tensions by plastic flow, which is very beneficial for ductility and damage resistance.

The homogeneity of the alloy of the invention in the region of relevant processing temperatures is not dependent on technically unavoidable fluctuations of the temperature or of the composition.

The titanium aluminide alloys of the invention are made through the use of metallurgical casting or powdered metal techniques. For example, the alloys of the invention can be processed by hot forging, hot pressing and hot extrusion and hot rolling.

The invention offers the advantage that despite the fluctuations of the alloying composition appearing with the industrial finishing and unavoidable processing requirements as previously, a titanium aluminide alloy with very uniform microstructure and high strength has been made available.

The titanium aluminide alloy of the invention achieve high strength up to a temperature in the region of 700°C to 800°C as well as good room temperature ductility. Therefore the alloys are suitable for numerous areas of application and can for example be used for highly loaded components or as titanium aluminide alloys for exceptionally high temperatures.

What is claimed is:

1. An alloy made on the basis of titanium aluminide through the use of melting and powdered metallurgical techniques the alloy comprising $44.5 \text{ atom } \% \leq \text{Al} \leq 47 \text{ atom } \%$, and $5 \text{ atom } \% \leq \text{Nb} \leq 10 \text{ atom } \%$, and the alloy containing molybdenum (Mo) in between 0.1 atom % to 3 atom % and defining a β -phase present up to a temperature of about 1,320°C.
2. An alloy as defined by claim 1 wherein $44.5 \text{ atom } \% \leq \text{Al} \leq 45.5 \text{ atom } \%$.
3. An alloy on the basis of titanium aluminide made with the use of melting and powdered metallurgical techniques the alloy comprising $44.5 \text{ atom } \% \leq \text{Al} \leq 47 \text{ atom } \%$, $5 \text{ atom } \% \leq \text{Nb} \leq 10 \text{ atom } \%$, and $0.05 \text{ atom } \% \leq \text{B} \leq 0.8 \text{ atom } \%$, and wherein the alloy contains molybdenum (Mo) in the region of between 0.1 atom % to 3 atom %, and defining a β -phase present up to a temperature of about 1,320°C.
4. An alloy as defined by claim 3 wherein $44.5 \text{ atom } \% \leq \text{Al} \leq 45.5 \text{ atom } \%$.
5. An alloy on the basis of titanium aluminide made with the use of melting and powdered metallurgical techniques the alloy comprising $44.5 \text{ atom } \% \leq \text{Al} \leq 47 \text{ atom } \%$, $5 \text{ atom } \% \leq \text{Nb} \leq 10 \text{ atom } \%$, and $0.05 \text{ atom } \% \leq \text{C} \leq 0.8 \text{ atom } \%$, and wherein the alloy contains molybdenum (Mo) in the region of between 0.1 atom % to 3 atom %, and defining a β -phase present up to a temperature of about 1,320°C.
6. An alloy as defined by claim 5 wherein $44.5 \text{ atom } \% \leq \text{Al} \leq 45.5 \text{ atom } \%$.
7. An alloy as defined by claim 5 wherein the alloy contains molybdenum in the region of between 0.5 atom % to 3 atom %.

8. An alloy on the basis of titanium aluminide made with the use of melting and powdered metallurgical techniques the alloy comprising $44.5 \text{ atom \%} \leq \text{Al} \leq 47 \text{ atom \%}$, $5 \text{ atom \%} \leq \text{Nb} \leq 10 \text{ atom \%}$, $0.05 \text{ atom \%} \leq \text{B} \leq 0.8 \text{ atom \%}$ and $0.05 \text{ atom \%} \leq \text{C} \leq 0.8 \text{ atom \%}$, and wherein the alloy contains molybdenum (Mo) in the region of between 0.1 atom % to 3 atom % and defining a β -phase present up to a temperature of about 1,320°C.
9. An alloy as defined by claim 8 wherein $44.5 \text{ atom \%} \leq \text{Al} \leq 45.5 \text{ atom \%}$.
10. A construction component made from an alloy according to one of claim 1 or 2.
11. A construction component made from an alloy according to one of claim 3 or 4.
12. A construction component made from an alloy according to one of claim 5 to 7.
13. A construction component made from an alloy according to one of claim 8 or 9.

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Figures: _____

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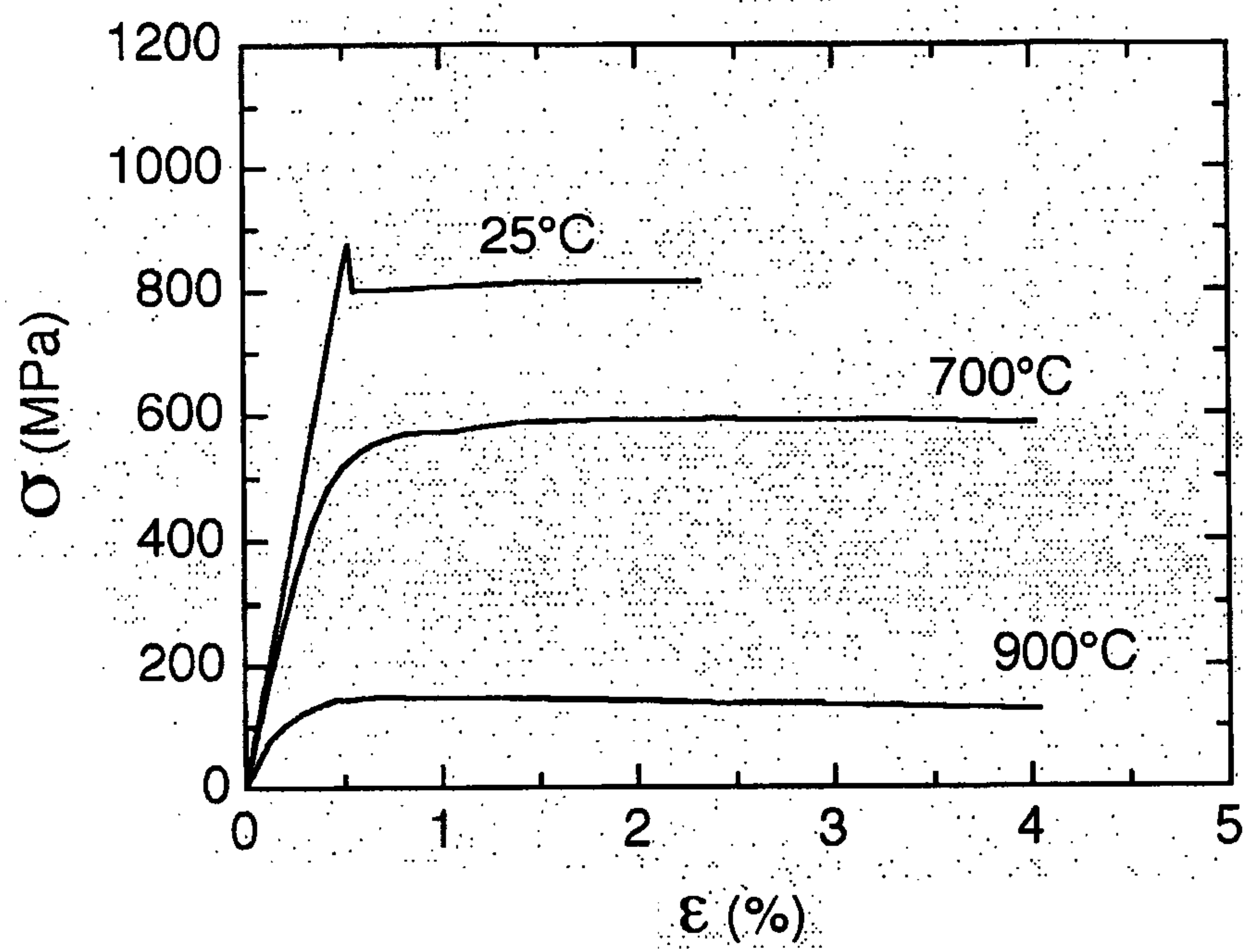


FIG. 4