Obtaining of Ti-Al alloy powder from TiO₂ - Al₂O₃ oxides by Ca or Mg co-reduction

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Abstract

In this paper the results of a study concerning the possibility of obtaining Ti-Al alloy powder by Ca or Mg co-reduction of titanium and aluminum oxides mixture realized at 1247 K during 7.2 to 129.6 Ks in primary vacuum.

The reducing metal evaporation is very important, especially in presence of vacuum. The losses have been reduced by using large particles of reducing metal and a compacted mixture. In these conditions the calcium has shown a better results. The product obtained after milling and lixiviation, is a Ti-Al alloy powder constituted from TiAl, Ti₃Al intermetallics and α-Ti solid solution with 0.9% oxygen minimal content after a holding time of 129.6 Ks.

Resume

Nous présentons les résultats d'une étude sur les possibilités d'obtention d'une poudre préalliée de l'alliage Ti-AL, par co-réduction séparement au Ca et au Mg, des mélanges d'oxydes de titane et d'aluminium, réalisée à 1247 K pendant 7,2 à 129,6 Ks, sous vide primaire.

L'évaporaation du métal reducteur, normalement trés importante surtout en présence du vide, a été sensiblement diminuée grâce à l'utilisation de grosses particules et au compactage du mélange sous forme de pastilles poreuses. Dans ces conditions le Ca s'est révélé le plus approprie à la réduction.

Aprés broyage et lixiviation la poudre est constituée d'un mélange d'intermétalliques TiAl, Ti₃Al et de Tiα, avec une teneur minimale d'oxygène de 0,9 % mass. , pour 129,6 Ks de maintien isotherme.

1. Introduction

The growing interest given by many laboratories and research studies to the Ti Alloys of Ti-Al system is justified by its intermetallic specific properties [1,2] such as its excellent metallic properties and its good resistance to oxidation at high temperature.

It is in the aeronautic construction and design where materials with low density, high strength and better resistance to hot oxidation are used. These materials often carried out by sintering could replace titanium classic alloys [2]. Among potential applications of these alloys, turbine vanes and rotors, outlets and coatings of parts working at high temperature. Because of complexity of obtaining

Ti alloys by fusion, it is in the alloy powder that they are likely to give good results.

Suzuki R.O and others [3] have developed a powder preparation technique without passing by the constituents classical fusion. This technique is based on calcium reduction of TiO₂ – Al₂O₃ oxide mixtures between 1173 and 1273 K. Reducing metal choice is justified by many considerations such as a formation of a low free energy of Ca oxide, absence of Ca-Ti-Al alloy, a relatively reduced speed at low temperature, easy elimination of CaO and finally a reasonable cost.

A fine powder constituted from TiAl and Ti$_3$Al intermetallic mixture was obtained with 0.9% weight of residual oxygen content, after a holding

time of 7.2 Ks and can reach 0.7% if reduction is extended.

The purpose of this work is to study the possibility of obtaining Ti-Al alloy powder from TiO$_2$ - Al$_2$O$_3$ by Ca or Mg reduction when the experiment is carried out in primary va cuum

2. Experiment

The initial mixture constituents, with respectively their chemical characteristics and grain size composition are given as follows: Al$_2$O$_3$ (99.8% < 63 µm); TiO$_2$ (98.5% < 63 µm); Ca (98%, 1500 to 3500µm); Mg (99.00%, 100 to 150 µm).

The reduction is realized on the basis of the following weight ratios: Al$_2$O$_3$/TiO$_2$ = 0.5 and M oxide/M reducing = 0.25. These two values have been chosen to allow a formation of powder rich in titanium and to compensate reducing metal losses by evaporation. Oxides were calcined during 14.4 Ks at 1173 K, after the introduction of the reducing metal, they have been subjected to homogenization in a ball mixer during 18.8 Ks.

Cylindrical porous of 20 mm diameter and 15 mm height were compacted by unilateral compression of 400 Mpa. The samples have an open porosity favorable to capillary diffusion of the reducing metal in gaseous phase. Concerning the reduction, samples were loaded in stainless steel nacelles and arranged in a tube of alumina in which a primary vacuum is maintained during the processing cycle.

Furnace temperature is controlled by a thermocouple Pt-Rh 6%, Pt-Rh 30% introduced directly in the nacelle. The reduction is made according to the following cycle: heating to 18 K/mn, maintaining at 1247 K during reduction time varying between 7.2 Ks to 128,6 Ks and its cooling speed 7 K/mn.

The evaporation weight losses is estimated by weighing before and after the reduction, this will help to find reducing metal efficiency. The final product is a porous conglomerate disintegrated in a ball mixer. The obtained powder is then leached in a solution at 35% of acetic acid during 1.8 Ks so as to eliminate the oxide of the reducing element.

The contents in Ti, Al and the residual rates of oxygen and calcium after lixiviation of the powder have been estimated respectively by EDAX and LECO TC336 analyzer, then confirmed by humid way.

The X-ray diffraction was used to identify phases, particles morphology is determined by scanning microscopy (MEB) Philips XL30.

3. Results and discussion

The realization of reduction in primary vacuum accelerates evaporation process and consequently increases the reducing metal losses. The preliminary test results given in fig.1, illustrate clearly these losses.
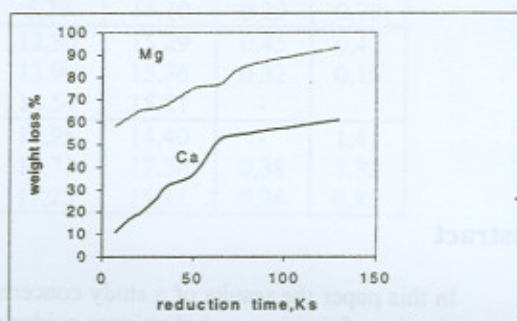

Fig.1. Influence of reduction time on reducing metal weight losses

The study was carried out only with calcium as it can be noticed from Fig.1 that, the best results are recorded in the presence of Ca. The Mg have excessive losses and vapors condensation in less hot furnace zones making difficult any manipulation.

The reaction result is a porous conglomerate of Ti-Al powder particles, CaO, CaO$_2$ and residues of non reduced oxides. After the choice of milling time , the reduction process is estimated by determining weight content of residual oxygen in function of isothermal time at 1247 K fig.2.
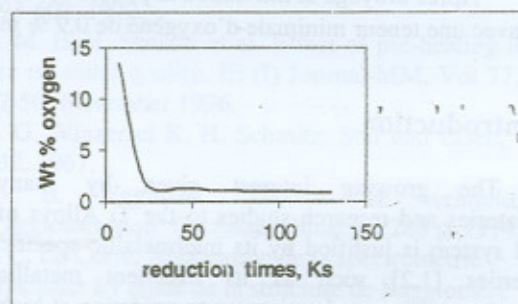

Fig.2. Influence of reduction time on oxygen residual content

It can be observed that, oxygen content is in the order of 13% after 7.2 Ks, 2.1% after 21.6 Ks and 1% after 79.2 Ks. The minimum oxygen content is 0.9% reached after 126.6 Ks. These purification

difficulties are related to CaO isolation and non reduced residues oxides following the intermetallic particles sintering.
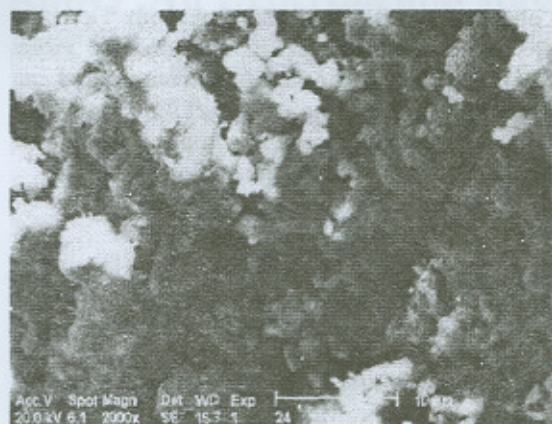

Fig.3. Scanning electron microgragh of TiAl alloy powder after reduction by calcium at 1247 K during 7.2 Ks and milling during 1.8 Ks

Fig.3. shows the final product morphology after a milling of 1.8 Ks and lixiviation. It can be noted that particles are sintered in conglomerate form due to the extended holding time. This hypothesis is confirmed by the results of EDAX analysis which gives relatively high contents of Ca in samples exceeding 5% weight, especially during short holding. This is explained by the unfinished consumption of the reducing metal which remains in heaps of TiAl alloy particles. These observations are in agreement with the results obtained by Suzuki R.O and others [4,5].

The particles structure needs more milling to insure their disintegration and grain size composition

favorable to lixiviation. The minimal content of recorded residual Ca after 7.2 Ks is in the order of 0.8 – 1.0% as mentioned in the chemical analysis by humid way. Grains less than 67µm that predominate the grain size composition. Tests have showed that, by increasing milling time the powder quality is improved, especially when the holding time is extended. The presence of Ti_3Al in a large quantity favors particles division.

Samples analysis by X-rays show that powder resulted from oxides co-reduction is constituted from TiAl and Ti_3Al intermetallic mixtures, α-Ti solid solution and oxide residues. However, Al/Ti ratio change in function of time reduction (see table below).

Table1. Influence of isotherm holding time on Al/Ti ratio and on alloy powder composition

Time reduction, Ks	Al/Ti ratio	Identified phase
7.2	1.080	TiAl*, Ti_3Al
21.6	0.140	TiAl*, Ti_3Al, Ti-α
64.8	0.060	TiAl, Ti_3Al, Ti-α
72.0	0.040	TiAl, Ti_3Al, Ti-α
86.4	0.029	TiAl, Ti_3Al*, Ti-α
129.6	0.029	TiAl, Ti_3Al*, Ti-α

* Maximal intensity

The extended holding time explained by powder being rich in titanium and the passage of TiAl to Ti_3Al. The comparison of the results obtained by diffraction reveals this tendency Fig.4.

O TiAl (111)
* Ti3Al (401)

a - 43.2 Ks
b - 50.4 Ks
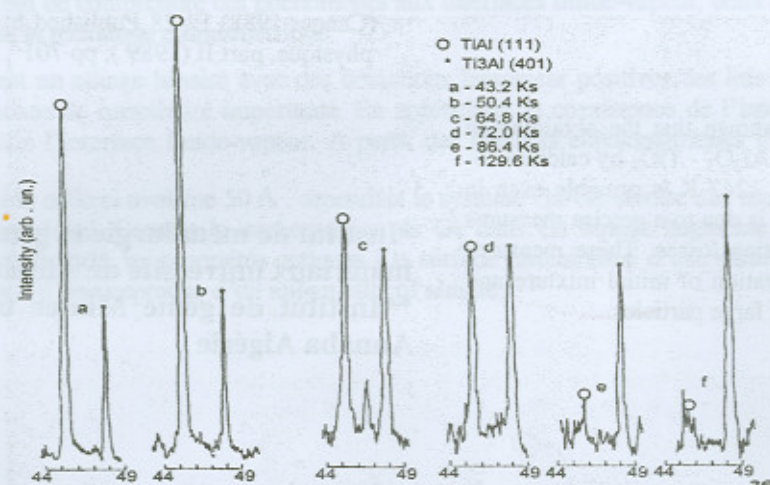c - 64.8 Ks
d - 72.0 Ks
e - 86.4 Ks
f - 129.6 Ks

Fig.4. diffraction rays intensity evolution in function of reduction time

constituent for short holding times, on the other hand, Ti_3Al rich in titanium, predominates powder composition from 86.4 Ks where, TiAl ray disappears. It can concludes that powder qualitative evolution is made according to the following steps:
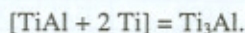
Simultaneous formation of Ti and Al free atoms

$$[2\ TiO_2 + Al_2O_3] + 7\ Ca = 2\ [Ti + Al] + 7\ CaO$$
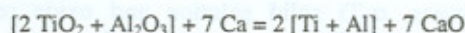
Titanium and Aluminum combined together to form TiAl

$$[Ti + Al] = TiAl$$

As the weight ratio $Al_2O_3/TiO_2 = 0.5$, the formation of a composite rich in titanium is preferred. Therefore, there is an extended isotherm holding time of tetragonal TiAl to hexagonal compact phase Ti_3Al.

$$[TiAl + 2\ Ti] = Ti_3Al.$$

One also notes the presence of α-Ti practically in all samples.

These results show the possibilities of obtaining Ti-Al alloy powder from TiO_2 - Al_2O_3 by Ca reduction in primary vacuum. The powder composition is similar to that obtained by Suzuki and others where, the reduction was realized in an atmosphere rich in vapor of calcium [3].

4. Conclusion

This study has shown that the obtaining of Ti-Al alloy powder from Al_2O_3 - TiO_2 by calcium co-reduction from oxides at 1247 K is possible even in primary vacuum and that is due to a precise measures which minimize evaporation losses. These measures are preliminary agglomeration of initial mixture and the use of Ca in a form of large particles.

The TiAl intermetallic is the main The obtained powder is constituted from TiAl and Ti_3Al intermetallics and α-Ti solid solution with oxygen minimal content of 0.9%. Its composition can be modified by changing Al_2O_3/TiO_2 ratio and reduction time. Its grain size composition can be improved by milling time optimization.

5. References

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