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Effect of TiH_2 in the preparation of MMC Ti based with TiC reinforcement

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ABSTRACT

Many studies were carried out on the elaboration Metal Matrix Composites (MMCs) and a wide variety of process is reported in the bibliography. For titanium based MMC, the basis material for these elaboration techniques mainly consists of atomized titanium powder.

In this work a titanium hydride powder is used to elaborate Ti/TiC MMC. Although an additional dehydrogenation operation is required a significant decrease of the sintering temperature is expected with this basis powder. In this context, the behavior of titanium hydride powder mixed with 0, 10 and 20 vol.% TiC reinforcement is studied during densification by free sintering. The effects of particle size, temperature and rate of sintering reinforcement are discussed. The comparison of the TiH_2 process with Ti HDH (Hydride Dehydride) and atomized Ti mixture is made with 10 vol.% reinforcement. The results indicate that the sintering temperature is lowered and the final densities achieved are higher if the hydride is used. Interactions between dehydrogenation and sintering mechanisms clearly appear for the higher sintering temperature rate (10 °C/min) and need specific attention to prevent porosity nucleation through hydrogen entrapment.

1. Introduction

The MMC exhibits high mechanical properties Young modulus and Yield stress and are for these reasons good material candidates for aeronautic structure lightening. Due to the large amount of interfaces they contain, a specific attention is to be given to the establishment of the chemical link between the matrix and reinforcement particles. Post processing operations such as CIC are very often employed to decrease the concentration of residual defects such as porosity.

Although many elaboration techniques of Metal Matrix Composites (MMCs) are reported in the bibliography [1–4] the sintering process is very promising. Indeed powder metallurgy enables the development of MMC with titanium matrix and the use of densification techniques like free sintering, HIP, hot extrusion, and SPS. The powder mixture enables the proportions of reinforcements such as TiC, TiB and TiB_2 to be varied, but also the matrix powder component [5]. For titanium matrix MMC, the basis material for these elaboration techniques mainly consists of atomized titanium powder. Unfortunately, the titanium (eventually titanium alloy) powder exhibits a poor ability to the treatments such as milling. Indeed, during milling the formation of aggregates due to the high reactivity of titanium creates a limitation to refinement of the initial powder. Such a refinement may promote the decrease of sintering temperatures and enables to limit microstructure evolutions during the MMC elaboration [6]. In this context the use of titanium hydride powder [7] may provide an opportunity for such refinement. The titanium hydride has a brittle behavior, and undergoes significant and fast particle size reduction by mechanical grinding [8]. In general the fine particles are easier to densify by free sintering and lead to higher density level [9]. Furthermore they lead to lower grain size in the titanium matrix and thus improve the mechanical characteristics. However, TiH_2 requires a stage of dehydrogenation which needs to be well controlled. This step determines the final material in terms of density, microstructure and purity (O_2 and H_2) [8]. In order to control dehydrogenation and shrinkage this paper deals with two grain size grades of titanium hydride powders (d_{50} = 5 and 20 μm) mixed with 0, 10 and 20 vol.% TiC. The effect of sintering temperature (between 800 and 1375 °C) is also studied on the MMC Ti + 10 vol.% TiC. Finally these results are compared to reference samples obtained respectively by:

– The sintering of a reference atomized Ti [6] with a reinforcement volume fraction of 10% TiC.

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– The process called HDH for Hydride Dehydride (dehydrogenation before mixing and after grinding), reported in the literature [10].

2. Experimental procedures

2.1. Initial powders

Titanium hydride powders (AG Materials) for this study, are available with the following mean size: d_{50} = 5 μm and 20 μm. The "reference" atomized Ti powder mean size is d_{50} = 70 μm, ("Electrode-Induction melting Gas Atomization" manufacturing process: EIGA) [6]. The titanium carbide particles are finer: d_{50} = 2.6 μm. The particle size distributions of the powders determined in an isopropanol medium (Malvern instruments, Mastersizer 2000) are given in Table 1 and particle morphologies are shown Fig. 6. The composition values provided by the supplier are summarized in Table 2: the oxygen content is higher for powders d_{50} = 5 μm and for the reinforcement particles. The densities retained for this work are as follows: 4.90 g/cm^3 for TiH_2, 4.50 g/cm^3 for Ti and 4.80 g/cm^3, for TiC.

2.2. Raw material preparation

Table 3 shows the mass fraction values of TiC and TiH_2 for each mixture. These proportions expressed in vol.% are given before and after heat treatment. The proportions are chosen according to the titanium volumes expected after dehydrogenation. Due to the dehydrogenation process during the heat treatment an evolution of the theoretical density of the material is observed. The density of TiH_2 and Ti are used respectively to calculate the relative density before and after heat treatment.

The preparation of the mixtures with 0, 10 and 20 vol.% reinforcement (Table 3) is carried out in ethanol suspension (70% dry matter/30% ethanol) with an organic binder (1.5% PVB and 1.5% PEG) in order to improve the quality (integrity and mechanical cohesion) of the pellet obtained by shaping. De-binding is included in the thermal treatment: the de-binding process occurs below 350 °C with a heating rate of 2 °C/min, a dwell time of 60 min is applied to secure the complete process. 8 mm diameter pellets are pressed at 400 MPa and 12 mm pellets at 600 MPa by uniaxial pressing (pressing device, anvil and die, mounted on an Instron testing machine). The density of the cylinders containing 0, 10 and 20 vol.% TiC, was measured geometrically, and founded to be between 72% and 82% of the theoretical density (%TD) except value reported of 67% for the Ti HDH 10 vol.% TiC. Indeed dehydrogenation of the powders before the shaping maybe limits the compaction ability of these mixtures.

Reference samples were elaborated through the following routes:

– Atomized titanium powder mixed with 10 vol.% TiC (Ti 10 vol.% TiC) is prepared in ethanol with 0.5% PVB/PEG. The shaping of the pellets is obtained through similar conditions.
– Mixture (TiH_2 20 μm) 10 vol.% TiC dehydrogenated at 800 °C for 60 min before and mixed with the organic binder before the shaping operation. This mixture is called Ti HDH 10 vol.% TiC.

2.3. Characterization of samples

The weight loss associated with the dehydrogenation is quantified by thermogravimetric analysis (TGA) in a Setaram TG 92 on pellets in helium atmosphere (8 mm diameter and 4 mm thick). Densification of these pellets is studied by dilatometry (Setaram TMA 92) under argon atmosphere. The temperature is measured using a thermocouple C (Tungsten 5% Rhenium/Tungsten 26% Rhenium). To avoid contamination of the probe, fine alumina platelets (99% purity) are positioned before each test on each side of the sample. The thermal profiles TGA and TMA are the same than those chosen for the sintering process and presented in Section 3.1.

The 12 mm diameter pellets, for microstructural analysis, are sintered in a horizontal tubular furnace under argon atmosphere at various temperatures between 800 and 1375 °C. A high purity argon grade is used (ALPHAGAZ 2 of AIR LIQUIDE purity >99.9995%) to limit contamination of the powders. For the same reason, a "getter" (zirconium chips) was placed between the gas flow and the sample. The sintering cycle was adapted with 60 min holding time at 350 °C to allow the de-binding of the formulated pellets before the dehydrogenation process starts.

Table 1
Laser granulometry of powders.

Reference	Powder	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
TiH_2 5 μm	TiH_2-003B	1.9	4.0	8.3
TiH_2 20 μm	TiH_2-0420	12.3	21.1	35.1
TiC	TiC	1.0	2.6	5.6
Atomized Ti	Ti	34.6	69.1	117

Table 2
Chemical composition of powders (mass %).

Reference	d_{50} (μm)	Ti	H	C	N	O	Fe
TiH_2 5 μm	5	>95.0	<3.86	–	0.01	~1	0.03
TiH_2 20 μm	20	>95.0	>4.0	–	<0.01	~0.2	<0.04
TiC	2.6	Balance		19.7	0.85	0.69	0.13
Atomized Ti	70	Balance		<0.10	<0.01	0.16	0.016

The relative density of the composite is measured by the Archimedes method in ethanol. The microstructure of the samples was observed after cutting and polishing by FEG-SEM on a JEOL 6500 electron backscatter device. The EBSD analysis is performed at 20 kV and provides the grain size of titanium carbide and titanium. The grain boundary is defined by a misorientation threshold of 15°. A 5 kg load is chosen for the Vickers hardness of the samples. This measure provides an average value of composite material hardness and provides comparative information on the mechanical properties of the samples. Chemical analysis of hydrogen and oxygen is obtained with a Leco analyzer by fusion on bulk samples and gas desorption.

3. Results and discussions

3.1. Dehydrogenation study – thermo-gravimetric analysis

According to literature results, the titanium hydrogenation/dehydrogenation reaction is reversible under temperature and pressure conditions at about 680–700 °C, in a vacuum or an inert gas atmosphere flow for one to two hours [8,10]. The quality of the final microstructure depends on the complete achievement of this process. However, the presence of an outer oxide layer on the powder granules cannot be avoided. This oxide layer makes the hydrogen desorption more difficult and modify the reaction temperature by forming a diffusion barrier [11,12]. In the present work, this stage is studied by TGA (Fig. 1) with a heating rate of 5 and 10 °C/min. Dehydrogenation begins at 350–400 °C for both hydride powders, mixed or not with 10 vol.% reinforcement particles, and reaches 90% between 790 and 850 °C. The derivative of the mass loss reaches the main peak value towards 650 °C. Subsidiary peaks (2 or 3) with variable intensity are observed during the dehydrogenation stage probably due to the oxide presence as reported in Refs. [11,12]. The profile of mass loss is detailed in the work of Jiménez et al. [13], Matijasevic-Lux et al. [14] and Liu et al. [15]. They report that the temperatures correspond to a series of dehydrogenation reactions with phase transformations until the final αTi phase. Whatever the size of the TiH_2 particles, the presence of TiC up to 10 vol.% leads to the same profile of mass loss evolution. However the size of the particles influences the rate of dehydrogenation through the variation of specific area (increasing the surface exchange). The dehydrogenation rate is much higher for the lower particle size. The presence of TiC also affects the shrinkage rate but more specifically in the sintering stage, analyzed in Section 3.2.

Table 4 shows the maximum values of dehydrogenation rate and the corresponding temperatures. The maximum speed of dehydrogenation is recorded at 645 °C for a heating rate of 5 °C/min and 665 °C for 10 °C/min. The finer the titanium hydride powder, the greater are the maximum speeds. The theoretical hydrogen mass content is 4.01 g per 100 g of stoichiometric titanium hydride. After heating at 10 °C/min 20 μm particles samples, only 92% of the theoretical hydrogen content is desorbed for both pure TiH_2 and mixed TiH_2 with 10 vol.% TiC. This result is close to that reported by Matijasevic-Lux et al. [14]. During the heating at 5 °C/min of the 10 vol.% TiC with 5 μm and 20 μm particles, at least 96% of the hydrogen is eliminated. Indeed at 5 °C/min the heating stage duration is twice longer than for 10 °C/min. The mismatch observed (remaining hydrogen content after dehydrogenation) on the hydrogen mass balance may be due to: