Features of structure formation in sintered Ti$_2$AlNb-based alloy produced by cold compaction and pressureless sintering

K S Senkevich, O Z Pozhoga and M M Serov
Moscow Aviation Institute (National Research University), 125993, Volokolamskoe shosse 4, Moscow, Russia
E-mail: senkevichks@yandex.ru

Abstract. The possibility of obtaining a high-density Ti$_2$AlNb-based alloy by cold compaction and pressureless sintering of rapidly solidified fibers of the alloy is studied in the initial state of fibers and after hydrogenation and milling. The possibilities of obtaining high-density sintered materials with lower oxygen content are analyzed.

1. Introduction
Powder metallurgy (PM) is actively used in the production of orthorhombic titanium aluminides based on Ti$_2$AlNb which are promising high-temperature aviation materials. Conventional PM methods are used thereto – cold compaction and pressureless sintering, hot pressing (including HIP) and electrospark sintering, and novel methods of additive manufacturing [1–4]. Each method has its own advantages and disadvantages. The simplest and most economical method is conventional powder metallurgy which is pressureless sintering of cold-compacted mixtures of elemental alloy powders. However, this method is characterized by the highest residual density in sintered materials (in comparison with other PM methods) and requires the use of long-term high-temperature treatments to carry out homogenizing diffusion processes during sintering of multicomponent powder mixtures of refractory elements (Ti, Nb, W, Mo, etc.). The use of cold compacted and pressureless sintered atomized spherical alloy powders is difficult because of their low compressibility at room temperature [5] and they are sometimes subjected to cold compaction with the use of plasticizing additives [5, 6]. Such powders are used in the production of PM-alloys by hot pressing and electrospark sintering. In work [7] we have shown the possibility of obtaining rapidly solidified fibers from a commercial orthorhombic titanium alloy by pendant drop melt extraction (PDME) method and high plasticity of the alloy upon compaction [8]. This should make it possible to fabricate a green body by cold compaction for subsequent high-temperature pressureless sintering.

The aim of this work is to study the features of cold compaction and pressureless sintering of rapidly solidified fibers in the initial and milled hydrogenated state to obtain high-density sintered materials.

2. Materials and procedures
The VTI-4 alloy (based on Ti$_2$AlNb compound) with the following composition: Ti-12Al-41.2Nb-0.89Mo-0.83V-1.27Zr-0.13Si, wt. %, obtained by vacuum-arc melting served as an investigated material. To obtain continuous alloy fibers of the VTI-4 alloy, the method of PDME was carried out by electron-beam melting equipment. Rapidly solidified fiber with a great hydrogen absorption [9]
ability was hydrogenated according to the Sieverts method with hydrogen concentrations of 0.65 and 1.2 % \(^1\). Dispersed powders were produced by ball milling of the fiber hydrogenated with 1.2 % H in a planetary ball mill for 5 minutes in argon with the use of tungsten carbide balls. Fibers and powders were compacted at room temperature at pressures of 500 and 700 MPa into pellets with a diameter of 6.5 mm. Sintering was carried out in a vacuum furnace at temperatures of 1200-1400 °C during an hour. Microstructure of the sintered samples was examined using the Olympus optical microscope and scanning electron microscope (SEM) (Vega 3LMH, Tescan, Czechia). The X-ray diffraction (XRD) analysis was performed using a DRON-7 diffractometer (Russia).

3. Results and discussion
The high plasticity of initial fiber made it possible to compact it at 500 MPa into a cylindrical porous pellet with large elongated pores. An increase in pressure up to 700 MPa did not change the porous structure of the compact. Sintering of the compacted fiber at temperatures of 1200-1400 °C showed the impossibility of obtaining a high-density sintered material (figure 1, a). The structure still has large elongated pores formed during cold compaction of the fibers, but there are no small pores in the area of tight contact of the compacted fibers. This shows that at these sintering temperatures active diffusion processes occur which contribute to the formation of high-quality diffusion joint between fibers, but they are not enough for diffusion overgrowing of large pores. In the contact area separate interfaces can be observed which are formed under strong etching of the fiber during repeated microstructure etching, which had to be performed due to the poor wettability of the fiber surface with the etchant and the acid flow into the pores of the material. X-ray spectral microanalysis in the sintering area of the fibers showed the presence of the main alloy elements (Ti, Al, Nb) and a small amount of V (figure 1, a). The high sintering temperature resulted in a sharp growth of grains. Large grains with a size of more than 100 µm formed in the rapidly solidified fibers of the alloy with initial grain size of 3-25 µm and grew within the boundaries of the fibers. XRD analysis showed that after high-temperature sintering in the β-region at 1400 °C and slow cooling to room temperature the β-phase partially transformed into the O-phase which is represented by the oval and elongated rounded particles in the initial β-grain (figure 1, b); the β-phase also became ordered at such high temperatures. Thus, XRD analysis showed that the sintered material has a two-phase β(B2) + O composition (figure 1, c).

To mill the fiber, it was hydrogenated since it has a high strength in the initial state and is not subject to ball milling [10]. XRD analysis showed that hydrogenation of the rapidly crystallized alloy leads to the formation of a two-phase β + O structure (at 0.65 % H) or a highly hydrogenated β-phase (at 1.2 % H) designated as β-hydride [11]. At low hydrogen content (less than 0.8 % H) the fiber is only partially milled to large and small fragments [10], therefore, the fiber with 0.65 % H was compacted without preliminary milling. We have partially succeeded in obtaining a denser structure of the compact with small pores in the compacted sample due to deformation of hydrogenated brittle fiber fragments under high pressure. The pores size has decreased significantly, but they are still quite large. Sintering at 1200-1400 °C made it possible to obtain a porous sintered material with many pores (figure 2). There are no pores in the sintering area at the former boundary of the contacting fibers; the main chemical elements of the alloy (Ti, Al, Nb) and a small amount of V, Ni and Si are registered. Sintered material has phase composition and microstructure similar to those of sintered material from unhydrogenated fibers.

Milling of the fiber hydrogenated with 1.2 % H allowed obtaining a fine-dispersed alloy powder with a size of 0.5-50 µm which was also compacted at 500-700 MPa, and a strong green body was prepared. The structure of the powder compact sintered at 1400 °C has a solider central part and a porous periphery, but the porosity visually observed is significantly less than in the sintered sample of compacted fiber (figure 3, a). Peripheral area is more porous possibly due to the inhomogeneity of plastic deformation of the “rigid” hydrogenated fine-dispersed powder of the alloy. However, the use

\(^1\) From here on, the content of hydrogen is given in wt %.
of dispersed powders resulted in small pores size in the compacted green body and stimulated more active diffusion processes during sintering. The diametral shrinkage of the compact sintered at 1400 °C was about 10%.

![Porous structure](image1)

**Figure 1.** Porous structure (a), microstructure (b) and XRD pattern (c) of the material from fiber sintered at 1400 °C.

![Porous structure and chemical composition](image2)

**Figure 2.** Porous structure and chemical composition of the material from fiber hydrogenated with 0.65 % H and sintered at 1400 °C.

Metallographic analysis showed (figure 3, b) separate inclusions of a darker color in the alloy matrix, and X-ray spectral microanalysis revealed that they contain mainly titanium (68 %), niobium (19.1 %) and a large amount of oxygen (9 %). The alloy base has composition close to the nominal one (44.9 % Ti, 43.9 % Nb, 7.3 % Al) and also high oxygen content (3 %). The presence of oxygen in the sintered
sample is associated with the contamination of the powder with oxygen during milling of the fiber in a planetary mill. This effect is well-known, and depending on the milling conditions (method, medium, time and rate), the oxygen content can vary from several tenths to several percent [12–14]. Titanium actively interacts with oxygen and forms separate areas enriched with titanium [13]. High oxygen content is also observed in the alloy matrix, but it is difficult to precisely determine oxygen content according to the X-ray spectral microanalysis data. It can be assumed that partial contamination of the sintered sample also occurs during metallographic analysis since elemental mapping showed a predominant amount of oxygen and especially carbon impurities in the pores of the sintered sample on the periphery (figure 4). However no oxygen traces visible in SEM in the sintered materials made of the milled initial fiber and containing 0.65 % H exhibit the main role of milling in contamination of the alloy with impurities. XRD analysis showed that the sintered material has the β(B2)-phase and the O-phase (figure 3, c).

The results of the study showed that hydrogenation and milling allows production of a fine-dispersed powder which is well-compacted and actively sintered and contributes to significant shrinkage rather than in the material from sintered fibers. This is also affected by hydride decomposition upon heating, which promotes the activation of diffusion processes in titanium powder [15] including rapidly solidified one [16]. The change in the type of raw material from fibers to powders also contributes to a decrease in the size of the initial pores in the green body and, as a result, makes it possible to produce sufficiently dense sintered material from orthorhombic titanium aluminate. A higher density can be obtained due to greater degree of hydrogenation of orthorhombic titanium aluminate which can absorb more than 2.0 % of hydrogen [9]. This will allow achieving a greater degree of milling of the

![Figure 3](image-url)
hydrogenated fiber and providing more active dehydrogenation and shrinkage during sintering. It is also necessary to improve the protection of the powdered alloy against interaction with oxygen in order to obtain a sintered material with lower impurities content.

Figure 4. Chemical elements distribution in peripheral area of the material sintered from powder hydrogenated with 1.2 % H.

4. Conclusions
The features of sintering and the regularities of the formation of microstructure and porosity in cold compacted and pressureless sintered rapidly solidified fibers in the initial and hydrogenated state have been studied.

1. It has been stated that sintering at temperatures of 1200-1400 °C promotes the formation of high-quality diffusion joints between the fibers, however the high porosity formed during compaction and large pores are retained in the sintered material.

2. Hydrogenation and milling of the fiber make it possible to obtain fine-dispersed powders of the intermetallic alloy with good compactability and high activity during sintering, which allows significantly increasing the density of the sintered material. However, milling of the fiber results in severe contamination of the powders with oxygen and the formation of oxides.

3. It is assumed that in order to further increase the density of sintered orthorhombic titanium aluminide, the fiber needs to be hydrogenated with a concentration of about 2.0 wt. % H, which will allow the production of finer and more actively sintered powders by milling.

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