Fracture analysis of Ag nanobrazing of NiTi to Ti alloy

(Análise da factura da brasagem de NiTi a liga de NiTi utilizando nanoparticulas de prata)

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Abstract

Dissimilar joining of shape memory alloys to Ti alloys has long been attempted by several research groups due to the foreseen potential industrial applications. However, the very dissimilar thermo-physical properties of both materials place several difficulties. Brazing can be a solution since the base materials are subjected to a less sharp thermal cycle. In the present study brazed overlap joints of 1 mm thick plates of equiatomic NiTi and Ti6Al4V were produced using nano silver based filler materials. Surfaces were analyzed to assess the type of fracture and the capability of achieving bonding and involved mechanisms are discussed.

Key words: *NiTi, Ti6Al4V, laser, silver nanopaste, silver nanoparticles, fracture, nanobrazing.*

Resumo: *A ligação dissimilar entre ligas de memória de forma e ligas de Ti tem sido tentada por vários investigadores devido ao potencial de aplicação industrial que estes materiais apresentam. No entanto as diferente propriedades termo-físicas dos dois matérias criam sérias dificuldades. A brasagem pode ser uma solução para ligar estes materiais uma vez que estes são submetidos a um ciclo térmico menos drástico. No presente estudo analisou-se a possibilidade de ligar chapas com 1 mm de espessura em NiTi equiatómico e Ti6Al4V utilizando nano partículas de prata, em formas diferentes, como materiais de adição. Analisam-se as superfícies obtidas para determinar o tipo de fractura e discutem-se os mecanismos envolvidos com vista a determinar a possibilidade de se conseguir uma ligação eficaz com esta técnica.*

Palavras-chave: *NiTi, Ti6Al4V, laser, nano pasta de prata, nanoparticulas de prata, fractura, nanobrasagem.*

1. Introduction

NiTi shows significant properties like biocompatibility, good strength and ductility and extensive research is being performed to fully exploit their potential in innovative applications. The possibility to bond these materials in dissimilar joining as to Ti based alloys can open new industrial applications, as in biomedical components or for the aerospace industry [1,2].

The very dissimilar thermal and physical properties of both alloys advise against fusion welding processes though high energy beams have been tested in this application with limited success [3,4]. Laser welding has been performed over a range of parameters in pulsed and continuous mode with a Nd/YAG laser in overlap welds of 1 mm thick samples of equiatomic NiTi and Ti6Al4V with good results [5]. This is particularly relevant in NiTi since the superelastic behavior of the alloy was not affected [6,7].

However the narrow window of parameters to prevent solidification cracking may limit the use of this process in mass production.

The difficulty of bonding NiTi to Ti alloys could be overcome by brazing. In this process the filler material is added under liquid state, while base materials remain in solid state. So dilution is almost inexistent. When joining dissimilar metals, welding problems such as solidification cracking, oxidation of titanium and degradation of mechanical properties are absent.

The success of the bonding depends on the characteristics of the interfacial products which is influenced by the reactions between the brazing alloy and the base material.

Pure silver and silver based alloys have been reported to braze titanium to steel with good results [8,9] and to ceramic-glass [10]. Silver nanoparticle paste has been successfully used in bonding micrometric copper wires of 50 micron diameter [11,12] and research work has been done to understand the

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Table 1. Experimental

			Nd-YAG Laser	
	Room temperature 7 days	Compression P=200 N t=60 min	P=1.3 kW F=10 Hz t=3 ms D=3.5 mm v=48 mm/min	P=1.6 kW t=3 ms D= 0.6 mm v=48 mm/min
Silver nanopaste	T1	T2	T4	--
Silver membrane		T3	T5	T6

interfacial bonding mechanisms of these nanoparticle pastes to bulk materials [13,14]. No information exists on the use of Ag nanopaste to bond parts in the 1 mm range, thus the relevance of analyzing its applicability.

The main goal of the present study was to assess the potential to use silver nanopaste for brazing 1 mm thick NiTi to Ti6Al4V plates using different brazing strategies and paste shapes. Analysis of the fracture surfaces and the interfacial microstructure and the characterization of the fracture surfaces was performed

2. Experimental Procedure

Base materials in this study were equiatomic NiTi and Ti6Al4V alloys. These were cut into strips of 10 mm width, etched in a solution of 7.5% HF + 20% HNO_3 + H_2O and further cleaned with acetone and ethanol to fully remove surface oxides.

Coupons were positioned with an overlap of 3 mm, creating a contact zone of 10x3 mm, in which a nano silver based filler material was applied.

Two types of filler material were used:

i) Ag paste

ii) Ag membrane

With the Ag paste, samples were prepared by applying five successive layers on each side using a brush. Each layer was allowed to dry before depositing the following one. Details on manufacturing of the nanopaste can be found elsewhere [11].

The membrane of silver nanoparticles (under patent registration) was cut to measure and placed between the two surfaces.

Several strategies, summarized on table 1, were tested for sample clamping and irradiation aiming to bond the contact surfaces of the two materials.

Bonding of the first set of samples was experimented by applying pressure and allow sufficient time for the curing of the Ag nanopaste. The experimental approach was the following:

1 - Samples were clamped with bonder clips at room temperature and left in open air during a time period of seven days (test T1).

2 - Samples were bonded at 250 C for 1 hour under a compression force of 200 N imposed in a tensile testing machine from Instrom. The sample with the filler Ag paste did not bond though the one with the Ag membrane showed bonding. However, it was seen to separate later under low mechanical stresses (tests T2 and T3).

The second set of experiments aimed at analyzing the heating effect on bonding nanosilver fillers to base materials. Starting point was to use parameters giving good results in overlap welding of 1 mm NiTi, since NiTi and Ti have similar thermal conductivity; these procedures were expected to lead to melting of the Ag filler.

Samples were irradiated with a Nd:YAG laser beam focused on the NiTi surface. The parameters used were 1.3 kW power, a frequency of 10 Hz, a peak duration of 3 ms, and a speed of 48 mm/min. The spot of 0.6 mm diameter was positioned in the center of the overlap zone. This procedure has led to 0.5 mm penetration welds. The energy density in this case was of 13.8 kJ/mm^2 . Both the nano Ag paste and nano Ag membrane were tested (tests T4 and T5).

A further test conducted with a laser power of 1.6 kW led to full penetration butt welds in 1 mm tick coupons NiTi/Ti alloy (test T6).

3. Results and discussion

The very first observation was that though the silver paste is deformable it does not promote sufficient strength to thick joints when these were compressed for a certain amount of time, nor a reaction could be triggered at room temperature, since the plates easily separated while manipulating the specimens. An external heat source was thus considered and laser radiation was selected due to its high precision with minimal collateral damage.

Silver based brazing alloys both in nanopaste and membrane

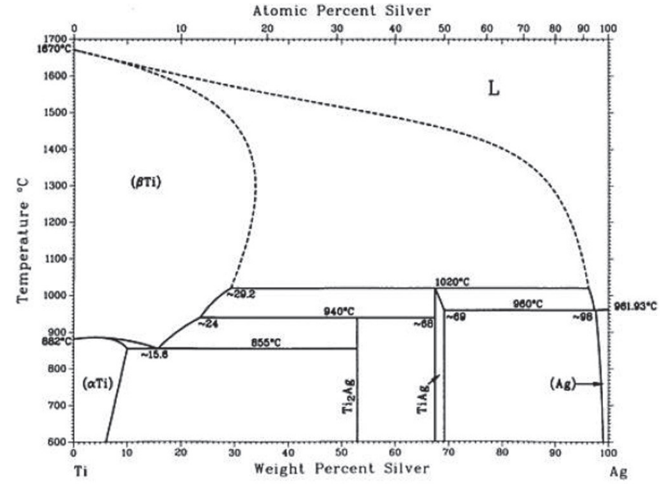


Fig. 1. Ti-Ag binary phase diagram [16]

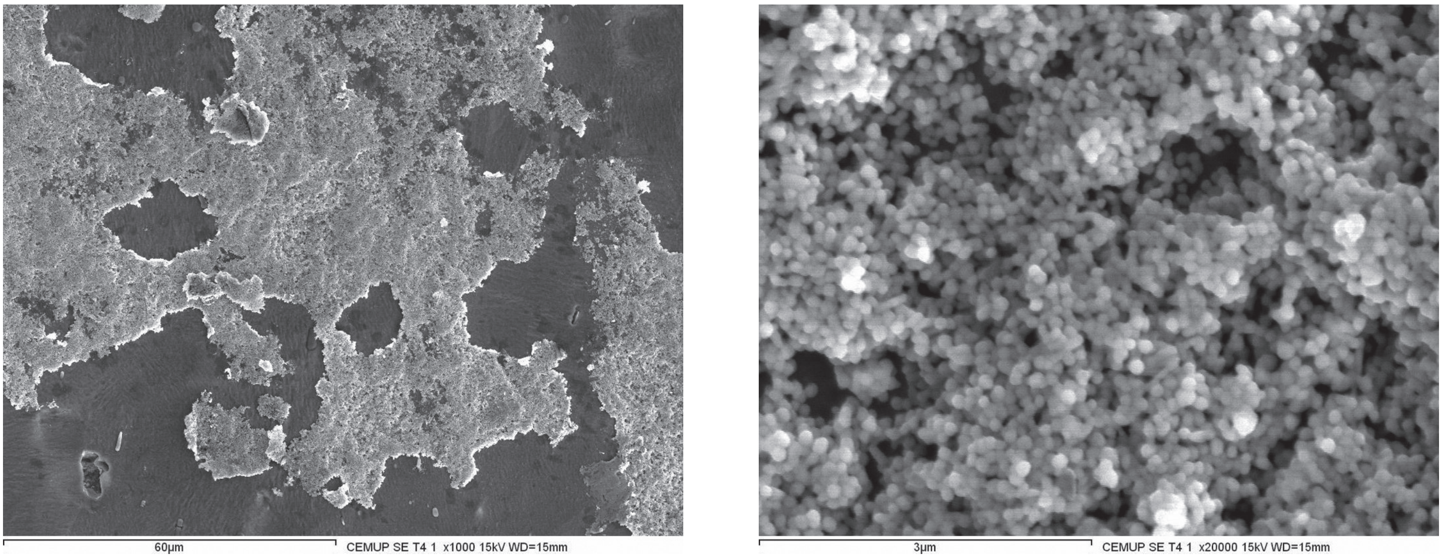


Fig. 2. SEM image of NiTi surface with adherent Ag nanoparticle paste
a) lower magnification; b) higher magnification

shape were tested for laser brazing NiTi to Ti6Al4V in lap joints configurations. This brazing alloy had already been used in other applications successfully [11,12]. Ag has a high melting point (960 ºC), however, it was seen that the bulk Ag has a higher melting temperature than individual nanoparticles in a paste [15], so the heat necessary to melt the brazing alloy is lower. Thus potential applications could be foreseen in microfabrication (e.g. microchips, MEMS, solar cells. medical devices).

Additionally, silver has a good solubility with Ni forming a solid solution in the full range of composition. The same is not observed with Ti, where Ag is less soluble in Ti, forming intermetallic phases as shown in Fig. 1.

The results show that achieving a desirable bonding stress is difficult, thus microstructure analysis of the fracture surfaces was performed to find clues to allow for further procedure development.

The fracture surfaces were analyzed under SEM to assess the type of fracture and the bonding mechanisms involved. When using the silver nanopaste, no fusion of this filler was homogeneously obtained as shown in Figs 2 and 3. In most cases, this was a consequence of a non homogeneous preparation of the surfaces prior to bonding, since the filler was manually disposed on the surfaces. The paste adheres to either the NiTi or the Ti alloy coupons. In areas where the paste is thinner, spots of melted silver were seen adherent to one coupon but completely detached from the other. So, almost all joints showed adhesive failures or mixed adhesive/cohesive ones in points where adhesion was effective. Fig. 2 shows a zone of adhesion of the nanopaste to NiTi. A bright region around the adherent silver is observed and under higher magnification (Fig. 2b) a dimple structure is displayed which suggests a ductile fracture of the sintered Ag nanoparticles.

The fracture surface of the NiTi coupon showed a martensitic structure with randomly distributed particles. These were analyzed by EDS and were seen to be TiC carbides often associated with manufacturing of shape memory alloys as depicted in Fig 3.

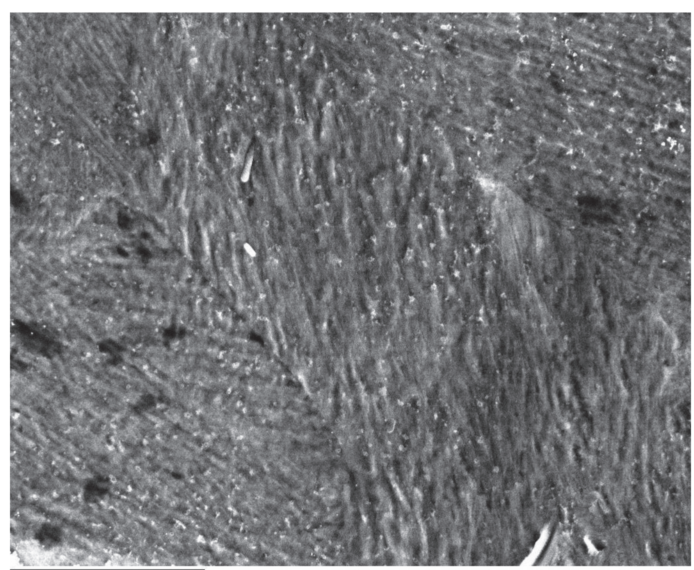


Fig. 3. Microstructure of NiTi with a martensitic phase

Looking into the Ti alloy side, a wider area covered with Ag nanopaste is seen with a network of randomly dispersed cracks within the melted spots (Fig. 4). These cracks can result from simple solidification cracking of silver with evaporation of constituent water of the Ag nanoparticle paste. This also points to the fact that the paste is more adherent to the Ti alloy than to NiTi eventually due to the existence of the carbide particles.

Even in regions where the nanopaste is very thin, there is no migration of Ni into Ti alloy as shown by the EDS spectrum

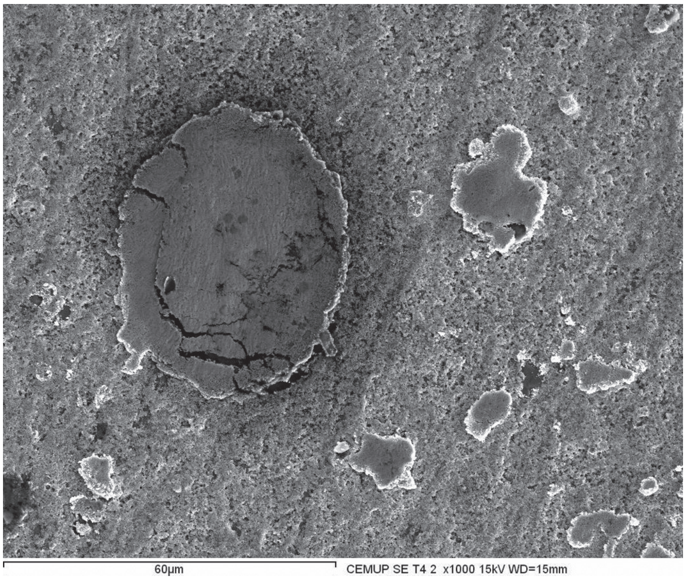
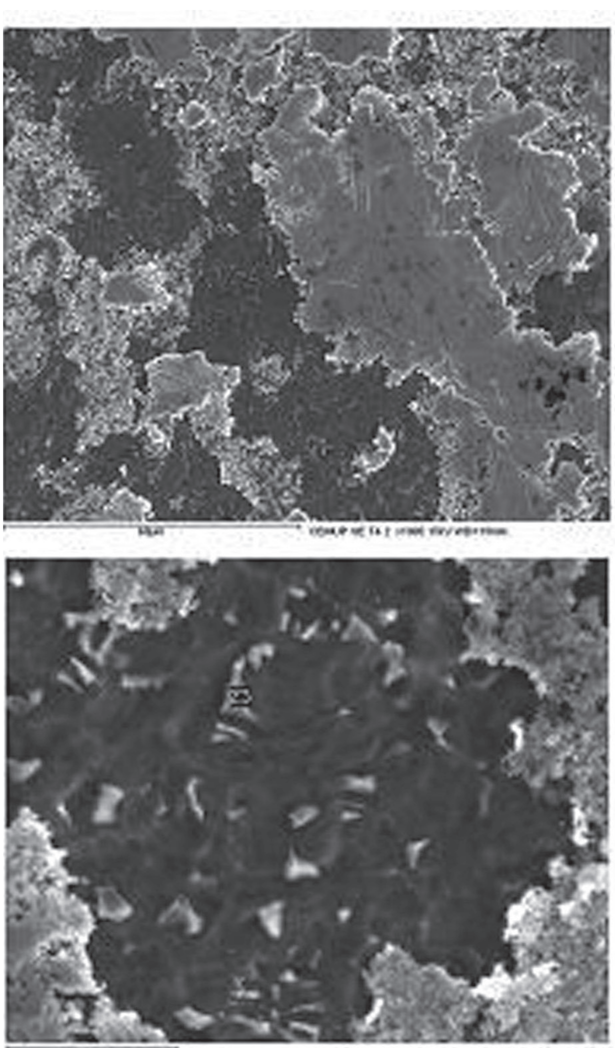


Fig 4 . Melted silver paste adherent to NiTi coupon

measured on the Ti matrix and the precipitates (Figs. 5 and 6), that is, the heat generated in insufficient to trigger diffusion of Ni and silver acts as a barrier to atomic mobility.

No traces of Ni were detected on the Ag paste analysed on the Ti alloy surface, that is, conditions for diffusion were not met under the processing conditions tested.

Using the Ag membrane, it is observed partial melting of the nanoparticles of the membrane along the laser beam traveling direction (Fig. 7). The melted quantity is higher than in the previous trials with the nanopaste and lack of adhesion is observed responsible for the poor joint quality. Additionally, cracks inside the membrane were also clearly seen in Fig 8 where the membrane is seen to crack and is not adherent to none of the substrates.



Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic %
C K	1.68	0.8024	3.20	0.46	11.38
Na K	0.44	0.8416	0.80	0.15	1.48
Al K	2.75	0.9090	4.62	0.14	7.32
Si K	0.19	0.9751	0.29	0.09	0.45
Ti K	48.22	0.9806	75.19	0.56	67.02
V K	7.58	0.9638	12.02	0.34	10.07
Fe K	1.19	0.9023	2.01	0.24	1.54
Ag L	1.13	0.9336	1.85	0.24	0.73
Totals			100.00		

Fig 5. Precipitate in Ti6Al4V and chemical composition by EDS

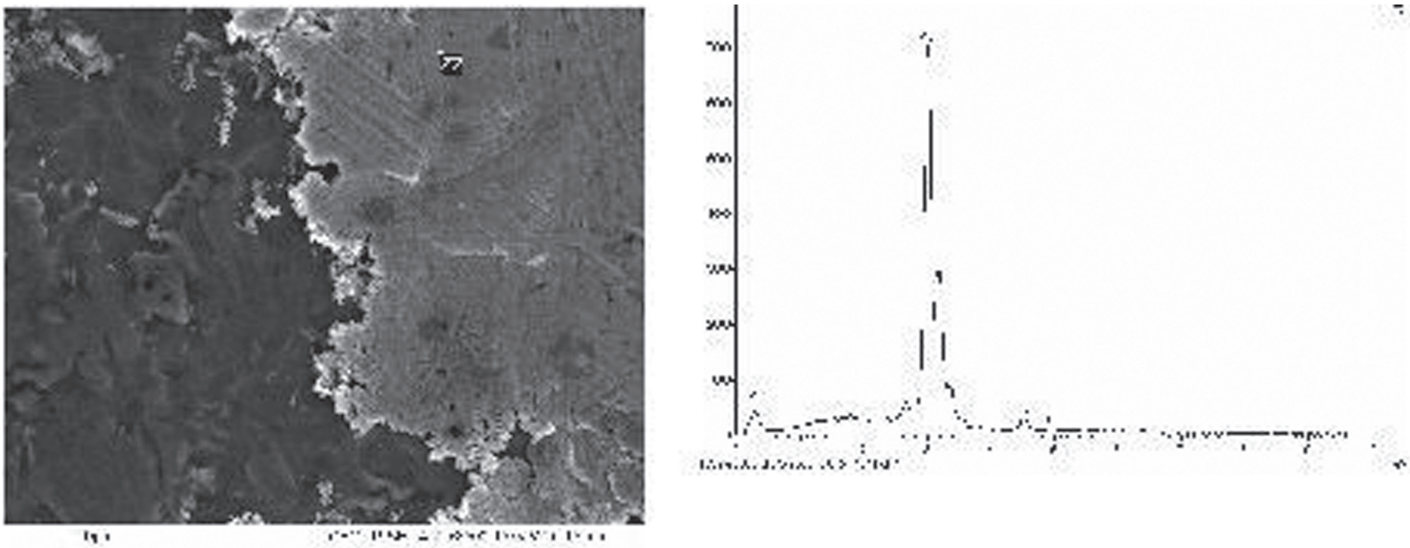


Fig. 6. EDS analysis of Ag paste adherent to the TiAlV coupon

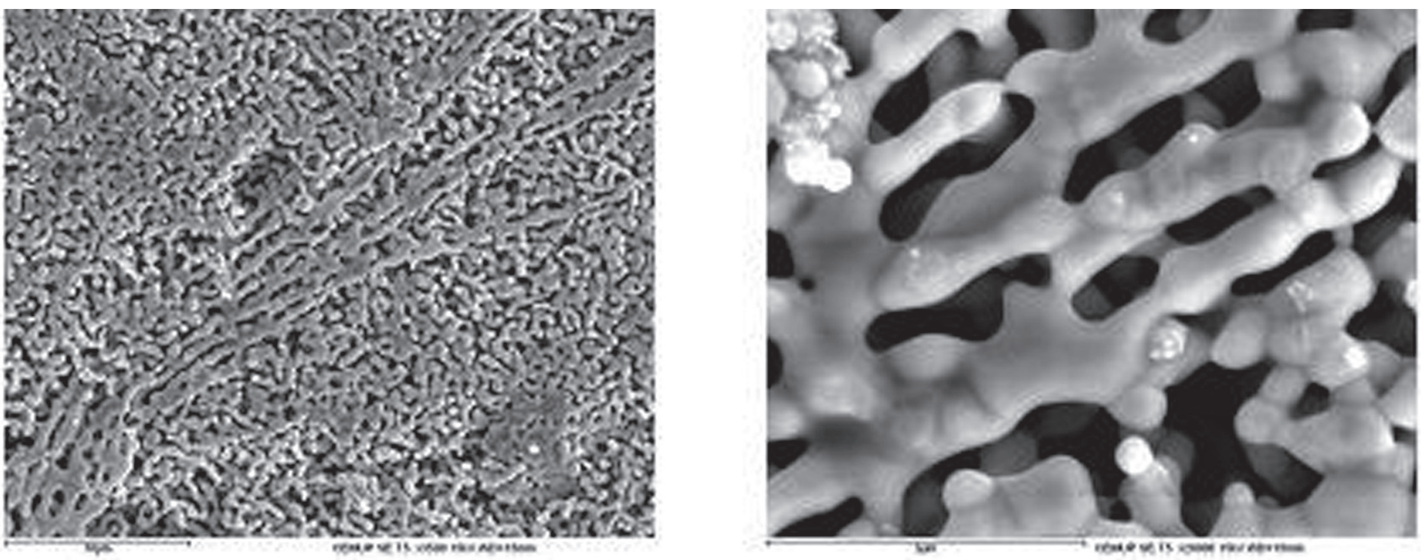


Fig. 7. Melted Ag membrane

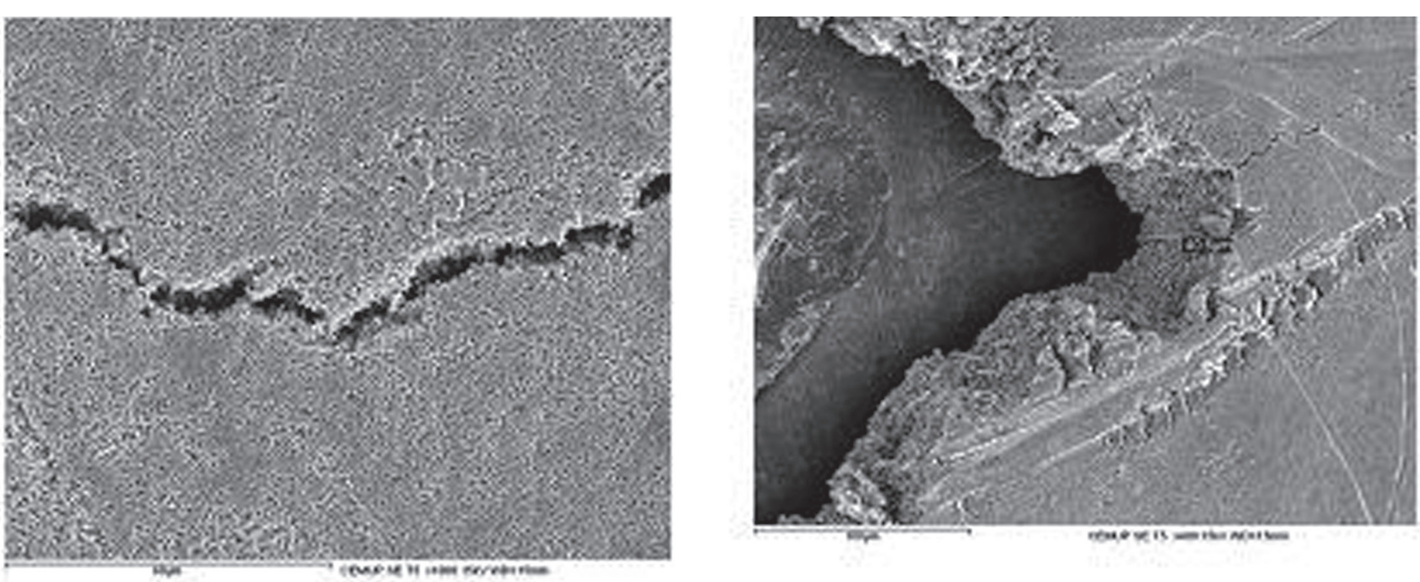


Fig. 8. Aspect of the Ag membrane fracture

4. Conclusions:

Silver nanoparticles were tested for laser brazing of 1 mm thick NiTi to Ti6Al4V

Several strategies for clamping and positioning material plates in lap joint configurations were tested. The overall mechanical strength of the produced joints was low.

No reaction between the silver nanoparticle paste or the membrane with the substrates was triggered in the absence of an external heat source, thus, laser irradiation with different power densities was tested.

From the present work and comparing to published research, it can be concluded that the use of Ag nanopaste as a brazing alloy is limited to small scale parts with potential applications in microfabrication. The microstructural analysis of the fracture surfaces revealed insipient melting of the filler, with poor adherence to the substrates. No traces of Ag were seen on the surface substrates suggesting that no surface diffusion occurred to promote joining.

The typical failure surfaces were mostly adhesive, though when using the Ag membrane cohesive fracture mode was also identified under SEM. The fracture types were very similar in all the tests performed.

5. Acknowledgements

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