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Efecto de la adición de nanopartículas de tungsteno sobre la microestructura de una aleación base Co unida por el proceso brazing.

Effect of Tungsten Nanoparticles on the Microstructure of Co-based Alloy joined by Brazing Process.

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Resumen

Muestras fracturadas de aleación de cobalto fueron unidas por el proceso brazing con y sin la impregnación superficial de nanopartículas de tungsteno, con el fin de observar el efecto de estas nanopartículas sobre la microestructura de la unión. El material de aporte seleccionado para este trabajo fue la pasta BCo-1, la cual fue caracterizada por Microscopia Electrónica de Barrido (MEB) y Espectroscopia de Fluorescencia de Rayos-X. Las muestras fracturadas se generaron a partir de ensayos de flexión de probetas de 10 mm. x 10 mm. x 60 mm. Dichas fracturas fueron inspeccionadas por MEB. La impregnación de las nanopartículas de tungsteno se llevó a cabo colocando las muestras fracturadas de cobalto dentro de una mezcla de 0.5 gr. de las nanopartículas con 100 ml. de etanol, la cual fue colocada en el equipo de ultrasonido durante 15 minutos. El proceso brazing se realizó en un horno tubular de alta temperatura con atmosfera de argón a 1200 °C por 60 minutos. Las muestras soldadas fueron observadas en el Microscopio Óptico y MEB. La interacción de las nanopartículas de tungsteno con el material de aporte en la zona de fusión modifico el tamaño y la morfología de las fases formadas, observándose fases con una microestructura más fina y uniformemente distribuida.

Abstract

Tungsten nanoparticles (NP's) were impregnated in fractured samples of a Co-based alloy in order to evaluate their effect over the microstructure of the joint during a brazing process. The brazing filler metal selected for this work was BCo-1 and it was characterized by scanning electron microscopy (SEM) and Spectrometry X-Ray Fluorescence. Cracks were generated in Co-based alloy rectangular samples of 10 mm x 10mm x 60 mm by bending them with a mechanical testing machine; these fractures were inspected by SEM. For the impregnation of the cracks with NP's, a mixture of 0.5 g of tungsten NP's in 100 ml of ethanol was sonicated for 15 min. The brazing process was conducted in a sealed tube furnace under an Ar gas flow at 1200 °C for 60 min. Brazed samples were analyzed by Optical Microscopy and MEB. The interaction of tungsten nanoparticles with the metallic filler in the melting zone modified the size and the morphology of the formed phases into a finer and uniformly distributed microstructure.

Keywords: Brazing, nanoparticles, Co-based alloy.

1. Introduction

Superalloys are unique high temperature materials used in gas turbine engines, which display excellent resistance to mechanical and chemical degradation at temperatures close to their melting points. The superalloys are employed in the very hottest sections of the turbines, under the heaviest loads, with the utmost importance placed on assuring the integrity of the components fabricated from them [1]. One example of these high temperature materials are Co-based alloys (Stellites) that have been used to resist wear, particularity in hostile environments and also as structural material at high temperature [2].

One of the procedures for gas turbine reparation is brazing, which ensure high resistance joints, similar to metal base or even more resistant joints. Brazing produces coalescence of materials by heating them to the brazing temperature in the presence of a filler metal having a liquidus above 450 °C and below the solidus of the base metal [3-5]. However, brazed joints often contain hard and brittle intermetallic phases, which decrease the mechanical and corrosion properties of the bonding areas [6, 7-9].

An alternative to prevent the formation of intermetallics is the use of transient liquid phase (TLP) bonding (also named as diffusion brazing) [6, 7, 10-12], which consists of a complete isothermal solidification of the TLP that exists temporarily during the brazing process. In the TLP bonding, the brazing metal filler should contain melting point depressants (MPD) elements such as boron, silicon and phosphorous [6, 10, 13, 14]. MPD elements should exhibit high solubility in the base metal, which will reduce the growth of intermetallics as a function of brazed time. Currently, for development of the TLP bonding process, some alternatives have been used such as the use of nanoparticles (NP's) as effective agents for retarding or avoiding the growth of intermetallic compounds [15-17].

In previous work, nanotechnology has been used to modify joints microstructure in brazing of a 304 stainless steel. The literature mentioned that microstructure in the joining zone is positively influenced in such a way that incorporation of the silicon or tungsten NP's leads to a finer eutectic microstructure with a significantly lower microhardeness as compared to that samples without nanoparticles [18, 19]. In It has been reported that the microcracks, together with the impregnated particles and the liquid phase form a capillary system in which, due to the wetting of the particles and microcrack surfaces by the liquid phase, after solidification and cooling to room temperature, the microstructure is characterized by a fine and uniform phase distribution, desirable for optimum mechanical behavior in service [19].

In this context, this research work is aimed at modifying the brittle eutectic phase in the joining area of Co-based alloy using BCo-1 as filler metal, through a systematic study of incorporating tungsten NP's into microcracks, by brazing process.

2. Experimental procedure

2.1 Characterization of the tungsten NP's and brazing filler metal.

The brazing filler metal selected for this work was BCo-1 in according to the nomenclature of American Welding Society (AWS) and it was characterized by scanning electron microscopy (MEB) in a Philips XL30 microscope and Spectrometry X-Ray Fluorescence brand Bruker model S4 Pionner.

2.2 Generation of cracks in Co-based alloy and their impregnation with tungsten NP's.

In order to study the brazing process and the effects of tungsten NP's, cracks were generated in Co-based alloy (25.53 Cr, 0.19 Ni, 1.87 C, 0.22 Sb, 0.54 Fe, 0.41 Mn, 0.11 Si, Co balance, wt%) rectangular samples of 10 mm x 10m x 60 mm by bending them with a mechanical testing machine; these fractures were inspected by SEM. For the impregnation of the cracks with NPs, a mixture of 0.5 g of tungsten NP's in 100 ml of ethanol was sonicated for 15 min. Subsequently, the cracks were placed in the dispersed tungsten NP's and sonicated for another 15 min. This sonicating time promotes the diffusion of tungsten inside the microcracks. Additionally, in order to evaluate the effect of tungsten NP's in the brazing process of the Co-based alloy, a sample without and with tungsten NP´s was characterized by SEM, without paste filler metal.

2.3 *Brazing of cracked Co-based alloy.*

The brazing process was conducted in a sealed tube furnace under an Ar (99.999 %) gas flow of 200 ml/min at the brazing temperature of 1200 °C for 60 min; the heating and cooling rates were fixed at 10 °C/min. After testing, brazed samples were ground using 80, 120, 320, 500, 800, 1200 and 2400 grit SiC papers, and then were finally polished using a 1 μm diamond paste. In order to reveal phases in the microstructure, samples were chemically attack with a solution of 10 ml de H_3PO_4, 50 ml H_2SO_4 y 40 ml HNO_3 with 3.0 Volts and 0.4 Amperes for 3 s. After the attack, samples were analyzed by Optical Microscope brand Olympus and, the nature chemical of phases were analyzed by EDX in a SEM. Additionally, in order to determine the reactivity of the tungsten NP's on the cracked Co-based alloy, one impregnated cracks sample was subjected to the same conditions describe above. The resulting sample was characterized by SEM.

3. Results and discussions

3.1 Characterization of BCo-1 filler metal.

The chemical composition of the BCo-1 filler metal is presented in Table 1. As can be seen, in the Table 1, a considerable content of W is the paste. This can change the morphology of the intermetallics in the brazing of 304 stainless steels [19, 20].

Table 1. Chemical composition in % of the BCo-1 paste filler metal analyzed by Spectrometry X-Ray Fluorescence.

Al	Si	Na	W	Ni	Cr	Fe	P	S	Ca	Co
0.038	4.290	0.120	4.730	18.320	19.020	0.193	0.262	0.042	0.148	balance

Fig. 1 shows the SEM analysis of the BCo-1 paste filler metal. The SEM micrograph shows round shaped particles with wide size dispersion. It can be observed that the particles size runs from around of 20 to several tens of micrometers.

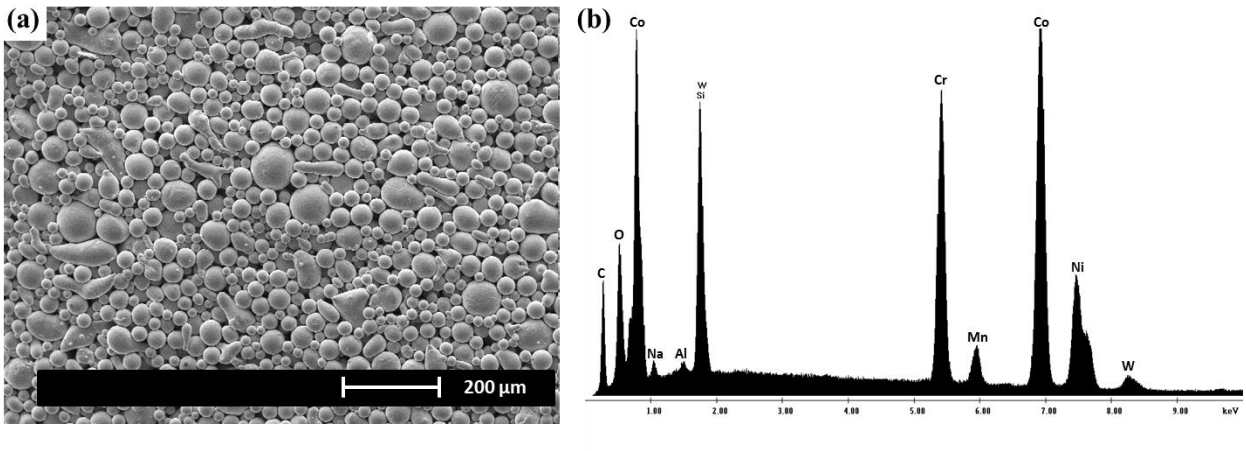

Figure 1. (a) SEM image of the BCo-1 filler and **(b)** EDX spectrum.

3.2 Impregnation of tungsten NP's on Co-base alloy.

As a preliminary step to the brazing process, the behavior of tungsten NP´s on the Co-based alloy was evaluated by SEM. Fig. 2 shows SEM micrographs on the fracture surface of the Co-based alloy before and after the tungsten NP´s impregnation process. In Fig. 2(a) microcracks between 50 and 400 µm in size can be observed on the fracture surface, as well as micropores. Fig. 2(b) shows the result of the interaction of tungsten NP's with the Co-based alloy at 1200 °C for 60 min. The insets shown in Fig. 2(b) display SEM image, it can be appreciated growth of round-shaped tungsten particles in the Co-based alloy fracture surface due to the sinterization processes by transient liquid phase on the surface of nanoparticles. These results agree with a previous work that mention similar behavior of tungsten NP's on 304 stainless steel fractured samples [8].

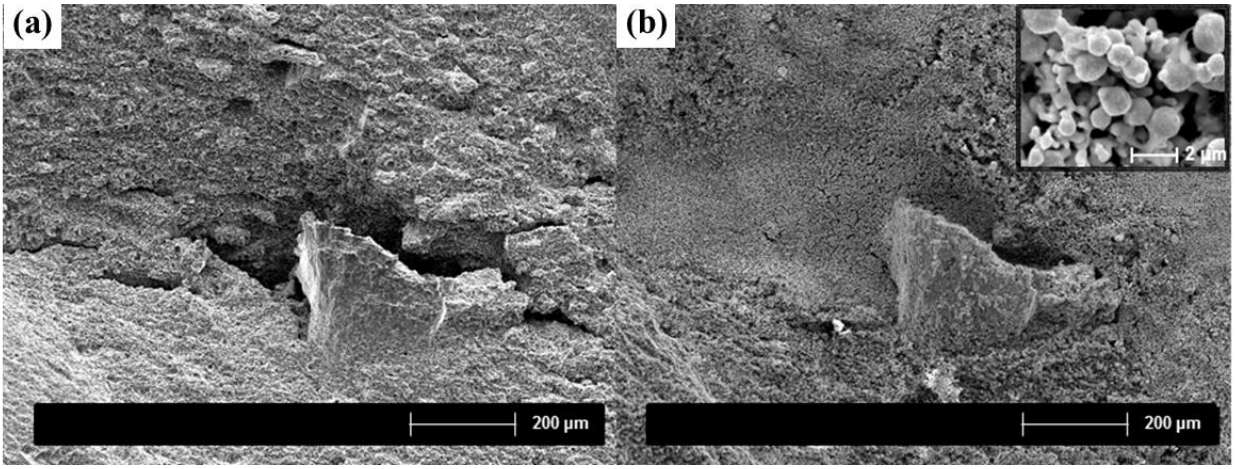

Figure 2. SEM micrographs of the fracture surface of the Co-based alloy: **(a)** without tungsten NP's; **(b)** with NP's after annealing process at 1200 °C for 60 min, the inset shows a zoom of annealed NP's.

3.3 Brazing of Co-based alloy without and with tungsten NP´s.

Fig. 3 shows images from optical microscope of the bonding region conducted without and with tungsten NP's. Fig. 3(a) shows that MZ (Melting Zone) includes large acicular morphologies structures which composition corresponds to Cr-rich phases. On the contrary, as observed in Fig. 3(b), the tungsten NP's used in the brazing process promotes a noticeable change in the size, morphology and distribution of the structures of the MZ. As can be seen, in the Fig. 3(b) that brazed sample with tungsten NP's shows the presence of an ISZ (Isothermal Zone) which is not found in the sample without tungsten NP's. This zone is important because it becomes mechanical properties similar to the MB (Metal Base). The growth of ISZ can be influenced by the previously formation of transient liquid phase [7, 21]. Meanwhile, the MZ shows greater solidified zones areas (light areas). Finally, the microstructure of the base metal was not affected during the brazing process.

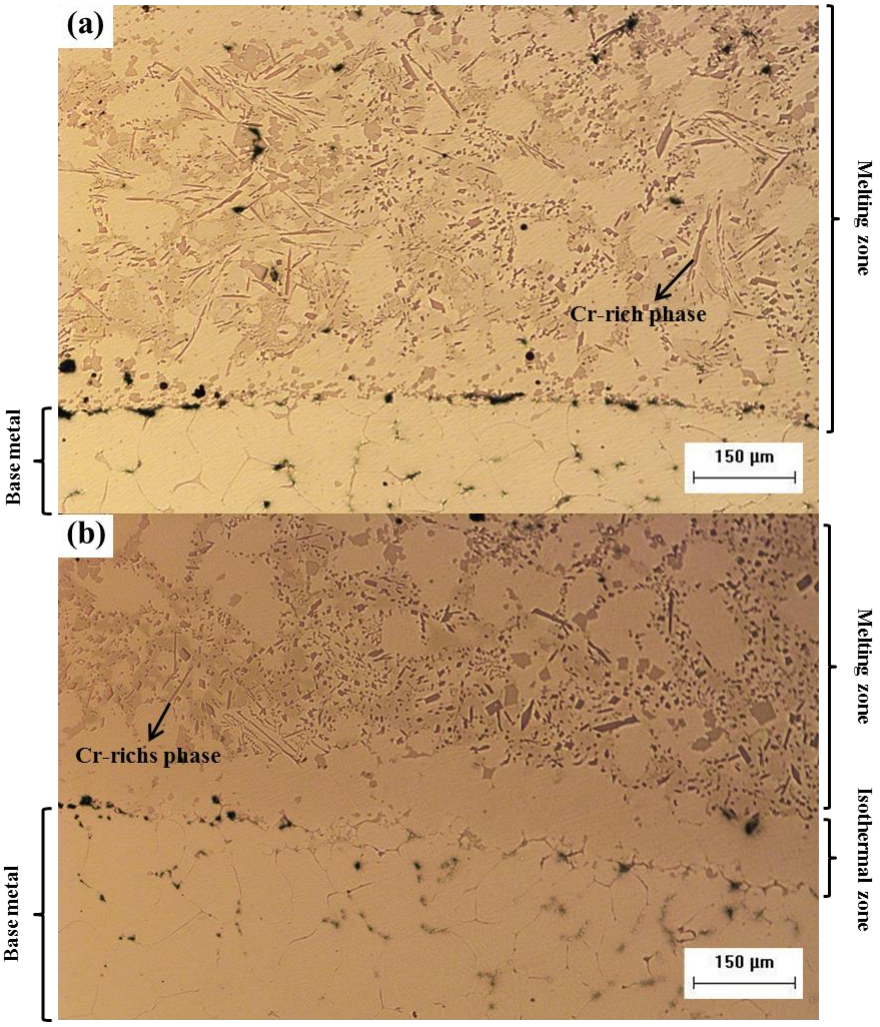

Figure 3. Optical microscope images of the weld bead on the Co-based alloy joined by brazing at 1200 °C for 60 min: **(a)** without tungsten NP's, **(b)** with tungsten NP's.

At high amplifications in the MZ, Fig. 4(a) and (b) shows images from Optical microscope and EDX spectra by SEM of the bonding region conducted with and without tungsten NP's impregnation. Fig. 4(a) confirms that the composition of the large morphology structures is mainly Cr. Comparatively; these Cr-rich structures are smaller in the brazed sample with tungsten NP's (Fig. 4 (b)). So far there is no detail explanation about the mechanism by which the microstructure becomes finer with the presence of tungsten nanoparticles, but it is generally accepted that during the dissolution step between the melting interlayer and the base metal, the tungsten nanoparticles act as a diffusion barrier for Cr. Moreover, some reports in the literature confirm that tungsten somehow modifies the morphology and size of phases [20, 22, 23].

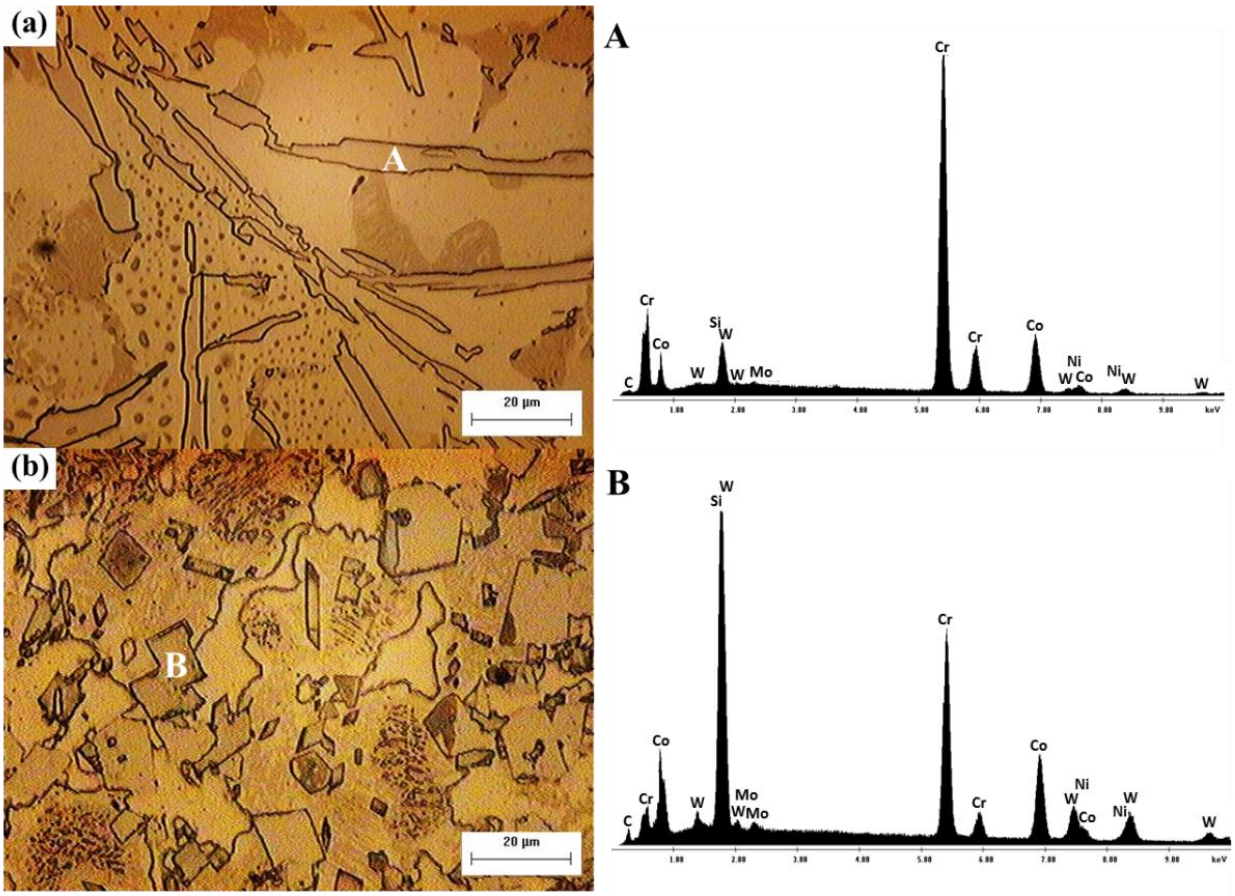

Figure 4. Optical microscope images and EDX spectra of the weld bead on the Co-based alloy joined by brazing at 1200 °C for 60 min: **(a)** without tungsten NP's and **(b)** with tungsten NP's.

4. Conclusions

The microstructure in the joining zone is positively influenced in such a way that incorporation of the tungsten NPs leads to a finer microstructure with more homogenous distribution as well as the growth of the Isothermal Zone. The tungsten can diminish the diffusion of Cr and avoid a larger Cr-rich phases. The interactions between the tungsten NP´s and the Metal Base promotes the growth of Isothermal Zone due to formation of transient liquid phase.

5. References

[1] The super alloys. Fundamental and Applications. Roger C. Reed. Cambridge University Press, 2006.

[2] J. L. De Mol Van Otterloo, J. TH. M. De Hosson, Microstructural Features and Mechanical Properties of a Cobalt-based Laser Coating, Acta Materialia, 45 (3) (1997) 1225-36.

[3] D.L. Olson, T. A. Siewert, S. Liu, G.R. Edwards, “ASM Handbook, Welding, Brazing and Soldering”, Vol. 6 (ASM International, Metals Park, Ohio, 1993).

[4] M. Schwartz, “Brazing: For the Engineering Technologist” (Chapman & Hall, New York, 1995) p. 1.

[5] G. Humpston, D.M. Jacobson, “Principles of Soldering and Brazing” (ASM International, Metals Park, Ohio, 1993) p. 1.

[6] V. Jalilvand, H. Omidvar, H. R. Shakeri, M. R. Rahimipour, Microstructural Evolution during Transient Liquid Phase of Inconel 7389LC using AMS 4777 Filler Alloy. Mater. Charact. 75 (2013) 20-28.

[7] G. O. Cook III, Carl D. Sorensen, Overview of Transient Liquid Phase and Partial Transient Liquid Phase Bonding. J. Mater. Sci. 46 (2011) 5305-23.

[8] J.T. Stover, Review of the State of the Art of High-Temperature Brazing for Combustion Turbine Components. ERPI, Palo Alto, CA: (2003). 1005029.

[9] M.A. Arafin, M. Medraj, D.P. Turner, P. Bocher, Transient Liquid Phase Bonding of Inconel 718 and Inconel 625 with BNi-2: Modeling and Experimental Investigations. Mater. Sci. Eng. A 447 (2007) 125-33.

[10] M. Mosallaee, A. Ekrami, K. Ohsasa, K. Matsuura, Microstructural Evolution in the Transient-Liquid-Phase Bonding Area of IN.738LC/BNi-3/IN-738LC. Metall. Mater. Trans. A 39 (2008) 2389-402.

[11] O.A. Idowu, O.A. Ojo, M.C. Chaturvedi, Microstructural Study of Transient Liquid Phase Bonded Cast INCONEL 738LC Superalloy. Metall. Mater. Trans. A 37 (2005) 2787-96.

[12] M. Pouranvari, A. Ekrami, A.H. Kokabi, Effect of Bonding Temperature on Microstructure Development during TLP Bonding of Nickel Base Superalloy. J. Alloy. Compd. 469 (2009) 270-75.

[13] N.P. Wikstrom, A.T. Egbewande, O.A. Ojo, High Temperature Diffusion Induced Liquid Phase Joining of a Heat Resistant Alloy. J. Alloy. Compd. 460 (2008) 379-85.

[14] N.R. Philips, C.G. Levi, A.G. Evans, Mechanisms of Microstructure Evolution in an Austenitic Stainless Steel Bond Generated using a Quaternary Braze Alloy. Metall. Mater. Trans. A 39 (2008) 142-49.

[15] S.Y. Chang, C.C. Jain, T.H. Chuang, L.P. Feng, L.C. Tsao, Effect of Addition of TiO_2 Nanoparticles on the Microstructure, Microhardeness and Interfacial Reactions of Sn3.5AgXCu Solder. Mater. Des. 32 (2011) 4720-27.

[16] R. Eluri, B.K. Paul, Silver Nanoparticle-Assisted Diffusion Brazing of 3003 Al Alloy for Microchannel Applications. Mater. Des. 36 (2012) 13-23.
[17] R. Eluri, B. Paul, Hermetic Joining of 316L Stainless Steel using a Patterned Nickel Nanoparticle Interlayer. J. Manuf. Process. 14 (2012) 471-77.
[18] H. M. Hdz-García, A. I. Martinez, R. Muñoz-Arroyo , J. L. Acevedo-Dávila, F. García-Vázquez, F. A. Reyes-Valdés, Effects of Silicon Nanoparticles of the Transient Liquid Phase Bonding of 304 Stainless Steel. Journal of Materials Processing Technology, 30(3) (2014) 259-62.
[19] H. M. Hdz-García, M. I. Pech-Canul, R. Muñoz-Arroyo, A. I. Mtz-Enriquez, J. L. Acevedo-Dávila, M. J. Castro-Román, F. A. Reyes-Valdés, 304 Stainless Steel Brazing Incorporating Tungsten Nanoparticles. Journal of Materials Processing Technology, 215 (2015) 1-5.
[20] McGuire, D., Huang, X., Nagy, D., Chen, W. Effect of Tungsten Addition on the 319 Nucleation of Borides in Wide Gap Brazed Joint. In: Proceedings of ASME Turbo Expo 320 Power for Land, Sea and Air GT, (2009), June 8-12, Orlando, Florida, USA, 1-9
[21] A. Ghoneim, O.A. Ojo. Microstructure and mechanical response of transient liquid phase joint in Haynes 282 superalloy. Materi. Charac. 62 (2011), 1–7.
[22] Park, Chan-Jin, Ahn, Myung-Kyu, Kwon, Hyuk-Sang, Influences of Mo substitution by W on the precipitation kinetics of secondary phases and the associated localized corrosion and embrittlement in 29% Cr ferritic stainless steels. Materi.Sci. Eng. A 418 (2006) 211–217.
[23] Kim, Sang-Beom, Paik, Kyung-Wook, Kim, Young-Gil, Effect of Mo substitution by W on high temperature embrittlement characteristics in duplex stainless steels. Mater. Sci. Eng. A 247 (1998) 67–74.