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Co-based alloy brazing incorporating tungsten nanoparticles

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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 structure and morphology of the tungsten NP's were characterized by high resolution transmission electron microscopy (TEM). The brazing filler metal selected for this work was Nicrobraz 210 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. This sonicating time promotes the diffusion of tungsten inside the microcracks. The 210-S filler metal was used in the cracked samples with and without tungsten NP's impregnation. 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 microscope and SEM. 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, Tungsten.**

I. 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 (Satellites) that have been used to resist wear, particularity in hostile environments and also as structural material at high temperature [2].However, under certain conditions, Co-based alloys components are damaged because their mechanical properties are reduced or zones susceptible to corrosive attacks appear.

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 jointsoften contain hard and brittleintermetallic 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 oftransient liquid phase (TLP) bonding (also named as diffusionbrazing) [6], [7],[10]-[12], which consists of a complete isothermalsolidification of the TLP that exists temporarily during thebrazing process. In the TLP bonding, the brazing metal fillershould contain melting point depressants (MPD) elements suchas boron, silicon and phosphorous [6],[10], [13], [14]. MPD elementsshould exhibit high solubility in the base metal, which willreduce the growth of intermetallics. Currently, for developmentof the TLP bonding process, some alternatives have been usedsuch as the use of nanoparticles (NP's) as effective agents for retardingor avoiding the growth of intermetallic compounds[15]-[17].

In previous work, nanotechnology has been used to modify joints microstructure in brazing ofa 304 stainless steel. The literature mentioned that microstructure in the joining zone is positively influenced in such a way that incorporation of the siliconor 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, through a systematic study of incorporating tungsten NP's into micro cracks, by brazing process.

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II. EXPERIMENTAL PROCEDURE

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

The structure and morphology of the NP's were characterized by high resolution transmission electron microscopy (HR-TEM and EDX) in a FEI Titan microscope. The brazing filler metal selected for this work was Nicrobraz 210-S(Wall Colmonoy) and it was characterized by scanning electron microscopy (SEM) in a Philips XL30 microscope and Spectrometry X-Ray Fluorescence brand Bruker model S4 Pionner.

B. 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.Likewise, the fractures were placed in a beaker containing ethanol inside a ultrasonic tank for 15 min to remove impurities of the microcracks and microporous and trapped airAdditionally, in order to determine the reactivity of the tungsten NP's on the cracked Co-based alloy, one impregnated cracks sample was subjected at 1200°C for 60 min. using heating/cooling rates of 10 °C/min. in a sealed tube furnace under an Ar (99.999 %) gas flow of 200 ml/min. Finally, the samplewas characterized by SEM, without paste filler metal.

C. Brazing of crackedCo-based alloy without and with tungsten NP's.

Both fracture surfaces without and with tungsten nanoparticles were spread with the paste filler metal and closed approach 1 mm of gap. At this point, in the brazing was not used a soldering flux because samples were immediately cleaned as was described in Section 2.2.The brazing process was conductedin a sealed tube furnace under an Ar(99.999 %) gas flow of 200ml/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 attackwith a solution of 10 ml de H3PO4, 50 ml H2SO4 y 40 ml HNO3 with 3.0 Volts and 0.4 Amperes for 3 s. After the attacked, samples were analyzed by Optical Microscope brand Olympus and,the nature chemical of phases were analyzed by EDX in a SEM.. The resulting sample was characterized by Optical Microscope, SEM and EDX.

III. RESULTS AND DISCUSSIONS

A. Characterization of tungsten NPs and filler metal

Fig 1 (a) is a TEM micrograph showing that the size of the tungsten NP's used before impregnating on the Co-based alloy fracture surfaces is less than 400 nm. Unlike, Fig. 1 (b) is a TEM image of dispersed tungsten NP´s that were impregnated on the fracture surfaces with sizes of 100 nm, approximately. Likewise, EDX spectrum, revealing the W, Cr, Co peaks of the elements constituting the NP's.

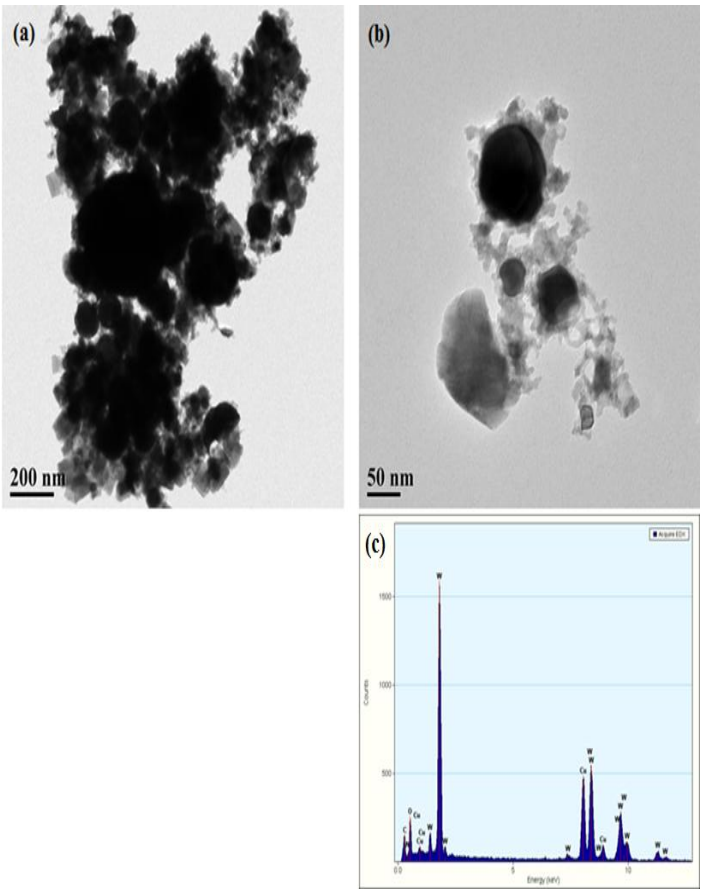

Fig. 1.(a) Tungsten NP's of 100-400 nm;(b)Dispersed tungsten NP'sand (c) EDX spectrum of the dispersed tungsten NP's.

The chemical composition of the 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]. Fig. 2 shows the SEM analysis of the 210-S paste filler metal. The SEM micrograph

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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.

Table I. Chemical composition in % of the 210-S 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

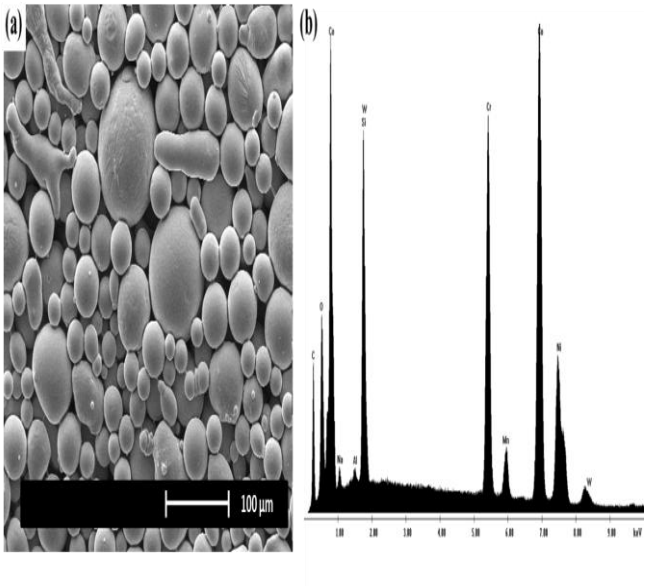

Fig. 2.(a)SEM image of the 210-S filler and(b) EDX spectrum.

B. Effect of tungsten NP's on the brazing process.

As a preliminary step to the brazing process, the behavior of tungsten NP´s on the Co-based alloy was evaluated by SEM. Fig. 3shows SEM micrographs on the fracture surface of the Co-based alloy before and after the tungsten NP´s impregnation process. In Fig. 3 (a) microcracks between 50 and 400 µm in size can be observed on the fracture surface, as well as micropores. Fig. 3 (b) shows the same fracture surface impregnated with dispersed tungsten NP´s. As can be seen,in the Fig. 3(b), the micro cracks and micropores were almost entirely covered by the clusters of tungsten NP´s. The main objective of this step is to introduce by ultrasound the smallest within the micropores and micro cracks where the paste filler metal cannot flow and, later by brazing can be joined. Fig. 3 (c) 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. 3 (c) 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].

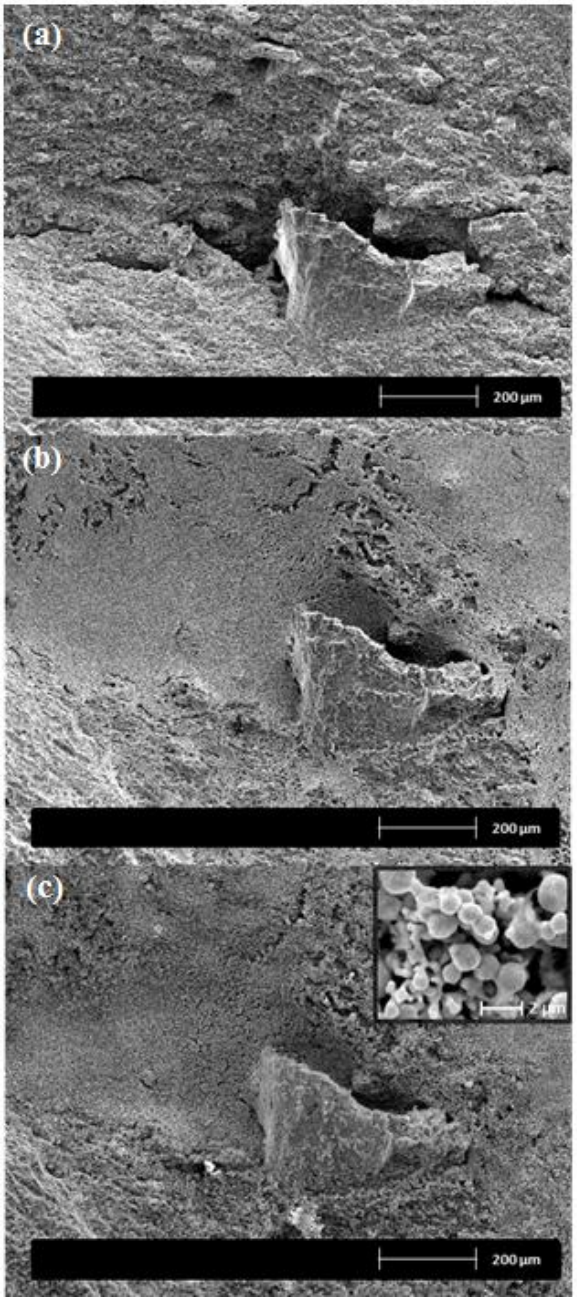

Fig. 3.SEM micrographs of the fracture surface of the Co-based alloy:(a)without tungsten NP's;(b) with tungsten NP's after impregnation process and (c) with NP's after annealing process at 1200 °C for 60 min, the inset shows a zoom of annealed NP's.

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

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Fig. 4 shows images from optical microscope of the bonding region conducted without and with tungsten NP's. Fig. 4 (a) shows that MZ (Melting Zone) includes largeacicular morphologies structures. By contrast, as observed in Fig. 4 (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. 4 (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].On the other hand, the MZ shows greater solidified zones areas (light areas). Finally, themicrostructure of the base metal was not affected during the brazing process.

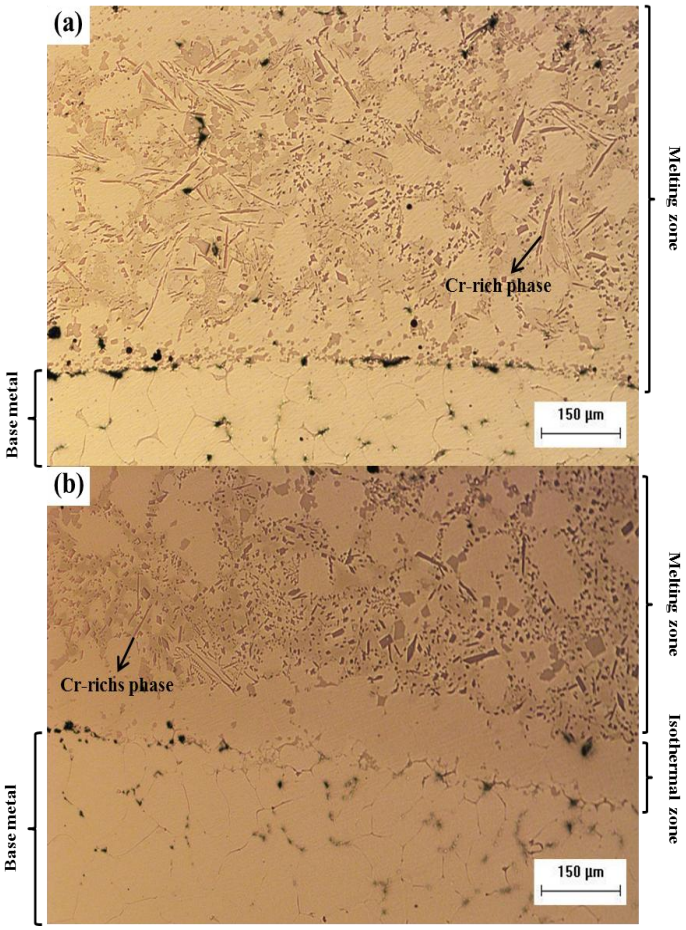

Fig. 4.Optical microscope images of the weld bead on the Co-based alloy joined bybrazing at 1200 °C for 60 min:(a)without tungsten NP's, (b) with tungsten NP's.

At high amplifications in the MZ, Fig. 5 (a) and (b) shows SEM images and chemical analysis by mapping of samples without and with tungsten nanoparticles brazing at 1200°C for 60 min. Fig. 5(a) shows phase of the large morphology structures corresponds to Cr-rich phases. Comparatively; these Cr-rich structures are smaller and dispersed in the brazed sample with tungsten NP's (Fig. 5 (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 MB, the tungsten nanoparticles act as adiffusion barrier for Cr. Moreover, some reports in the literature confirm that tungsten somehow modifies the morphology and size of phases [20], [22], [23].

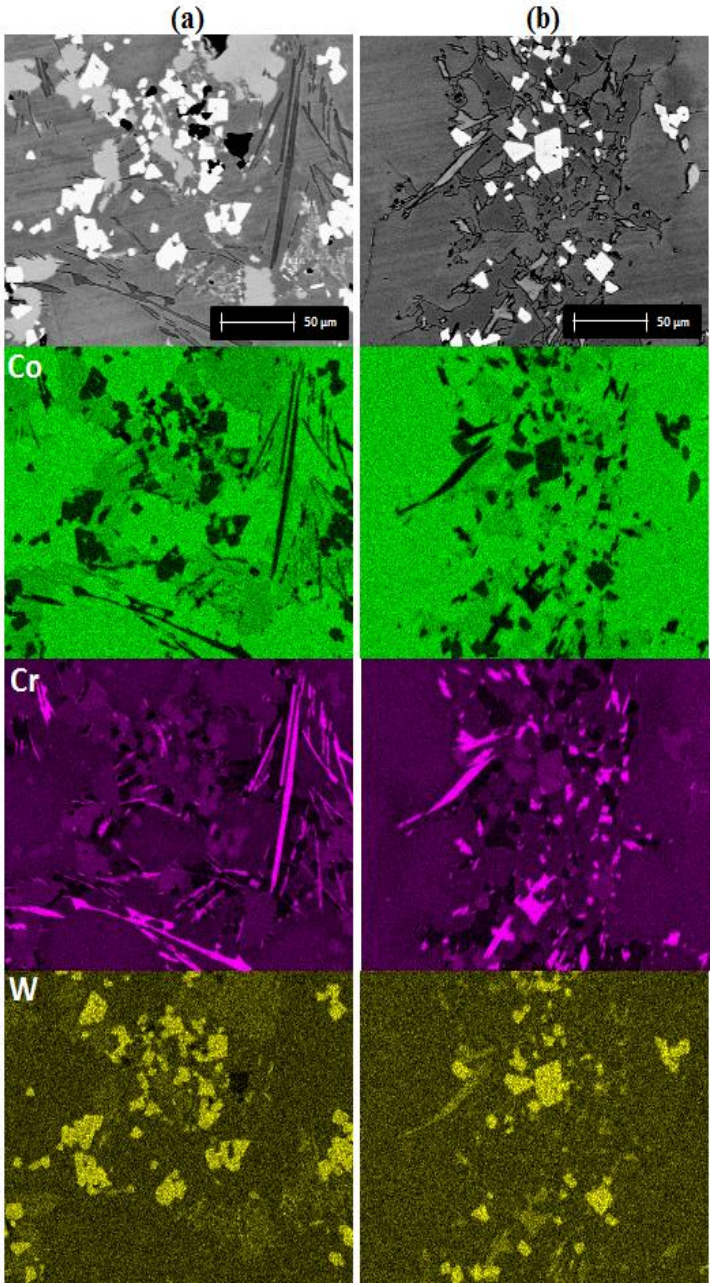

Fig. 5.SEM imagesof the weld bead on the Co-based alloy joined by brazing at 1200°C for 60 min: (a)without tungsten NP's and (b) with tungsten NP's.

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Additionally, Fig. 6 (a) and (b) shows an SEM images of phases in the samples without and with tungsten NP´s, respectively. As can be seen, in the Fig. 6 (a), the chemical composition of σ has a high content of Cr which that is immersed in a matrix rich in cobalt (γ). Report in the literature [24] suggests that the σ phase is one of the mainreasons for the deterioration of mechanical properties as well as corrosion resistance, and weldability.It is difficult to preventthe precipitation of the σ phase when the Cr content isabove a certain level. Therefore, the samples with tungsten NP´s avoid the effect of σ growth. Fig. 6 (b) shows the chemical composition by EDX of two different carbides: MC and $M_{23}C_6$. The light areas are rich in chromium and the gray areas are cobalt. However, both have an approximate content of tungsten. It is thought that the tungsten isassociated with the partition of cobalt and chromium during the diffusion between Isothermal Zone and Metal Base.

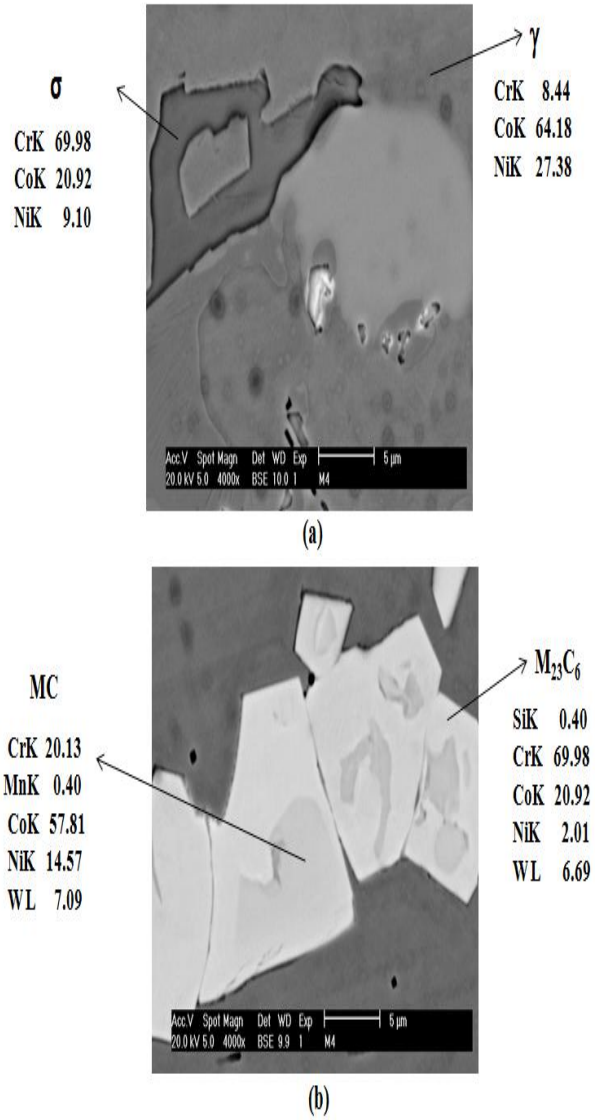

Fig. 6. SEM imagesof phases on the Co-based alloy joined by brazing at 1200°C for 60 min: (a) without tungsten NP's and (b) with tungsten NP's.

IV. CONCLUSIONS

The microstructure in the joining zone is positively influenced in such a way that incorporation of the tungsten NP's leads to a finer microstructure with more homogenous distribution and segmented 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. Additionally, the tungsten can modify the partition of cobalt; chromium and carbon in order to obtain the $M_{23}C_6$ and MC carbides.Nevertheless, this work require an evaluation of the elastic properties as well as the effect of such phases under corrosive environments in order to be applicate as an alternative to repair turbine components.

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