Structural characterization of the Ta5Si3 and Cr5Si3 phases

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ABSTARCT

In recent studies, much research is focused on the silicides alloys based in refractory transitions metal, becoming these materials as potential candidate for structural applications in high-temperatures for the fact of them possess excellent balance of properties, of is extreme importance for aeronautical and aerospace industries. This work presents results of microstructural characterization of the Ta5Si3 and Cr5Si3 important phases. These silicides were obtained by arc melting under argon atmosphere. Analyzes generated by X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) were used to obtain information about chemical and crystallographic characteristics of the samples generated before and after the heat-treatment.

KEY WORDS: *Silicides, intermetallics, Hf-Ti-Si system, X-ray diffraction, microstructure.*

INTRODUCION

Actually, only nickel-based super-alloys of last generation can be used under loading in temperatures near of 1250ºC. Recent studies show that this limit cannot be increased (Gigolotti, 2003), whilst exist a very large demand of new materials for structural applications at temperatures as high as 1250ºC, these materials are required in various fields such as aerospace and heat engines (Ikarashi et al, 1995). The materials of potential greater for this type of application in higher temperatures must present microstructure contend intermetallics phases in equilibrium with a metal or refractory alloys (Ward-Close; Minor; Doorbar, 1996).

Therefore, silicides form an important class of materials, particularly for high temperature applications, due to their interesting physical properties. For example, Me_5Si_3-type (Me=transition metal) materials exhibit high melting point (2453, 2403 and 2757 K, respectively for Mo_5Si_3, Ti_5Si_3 and Nb_5Si_3) (Schneibel et al, 2004). It has been found that $MoSi_2$ exhibit high temperature oxidation resistance. Become these composites in the class of materials that have the potential to replace nickel-based super alloys in the hottest sections of turbines engines. Composites formed by metal matrix and silicides have been developed to enhance oxidation and creep resistances (Ramberg et al, 1994). For the fact to possess hexagonal structure (Mn_5Si_3-Type), the thermal expansion of Me_5Si_3-type silicides have been measured in order to search for material with reduced thermal expansion coefficients anisotropy.

In this work we present our results of microstructural characterization of the Ta_5Si_3 and Cr_5Si_3 phases, with the objective of analyze of the morphology of the alloys generated before and after the heat-treatment, homogeneity of the material and the composition and distribution of the phases generated after the production and heat-treatments.

EXPERIMENTAL PROCEDURE

Four different alloys containing the phases of the interesting are used for this study; the composition was defined based on the single-phase interesting region of the phase diagram (Massalski, 1990). The alloys were prepared by arc melting, from high-purity materials, Cr (min. 99.996%), Ta (min. 99.998%) and Si (min. 99.998%) powder mixtures under argon atmosphere in a water-cooled copper crucible with nonconsumable tungsten electrode and titanium getter. Each alloy was melted three times in an effort to produce homogeneous ingots. Table 1 shows the nominal compositions of the alloys.

After the stage of production, the alloys, with melting point of 1900°C and 1300°C of the Ta_5Si_3 and Cr_5Si_3, were heat-treated at 1200°C for 24 hours, under argon atmosphere, for formation of the microstructure of equilibrium and alleviate tensions generated during the production.

Table 1 – Chemical composition of the alloys produced.

System Ta_5Si_3		System Cr_5Si_3	
Identification Alloy	Composition (%at)	Identification Alloy	Composition (%at)
1	$Ta_{62,5}Si_{37,5}$	1	$Cr_{62,5}Si_{37,5}$
2	$Ta_{62,5}Si_{38}$	2	$Cr_{62}Si_{38}$

The alloys in the as-cast and heat-treated conditions were characterized through powder X-ray diffraction (XRD) at room temperature (RT) and Scanning Electron Microscope/Back-Scattered Electron images (SEM/BSE). The SEM/BSE images were acquired in the LEO ZEISS 1450 VP equipment.

For the XRD experiments the samples were mechanically ground and the powder sieved to below 80 mesh. The experiments were carried out in a Seifert ISODEBYEF EX 1001 diffractometer, using CuK_α radiation, angular interval (2θ) from 20° to 90°; angular step of 0.05° and 3s counting time. The XRD patterns were indexed using simulated diffraction patterns obtained from the PCW software (Krans; Nolze, 1996) and crystallographic data from the compilation of Villars and Calvert (1991).

RESULTS & DISCUSSION

The nominal compositions of the alloys are showing in the table 1. The mass losses due to the melting process were lower than 5%. With this, in the case of the Ta-Si systems, it was verified in the alloy with composition $Ta_{62,5}Si_{37,5}$,

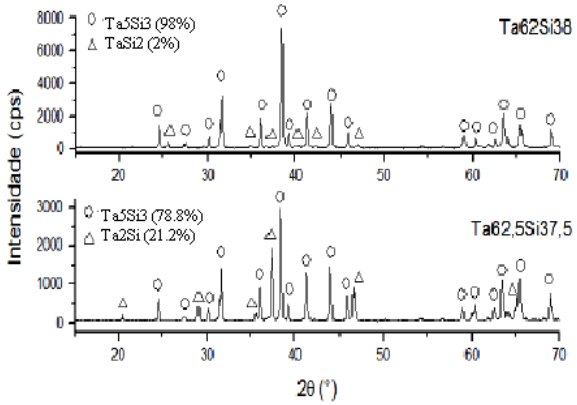

Figure 1 – X-ray diffractions of the samples of the Ta-Si system, in the state as-cast.

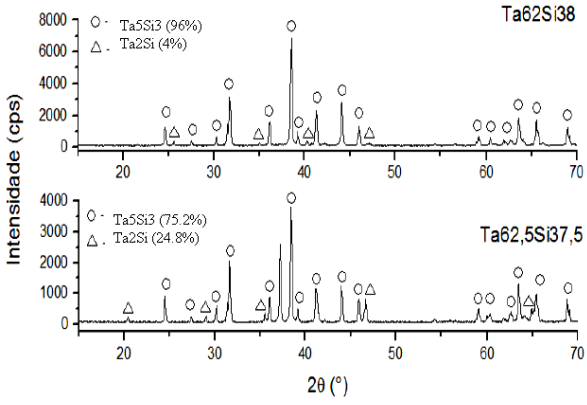

Figure 2 – X-ray diffractions of the samples of the Ta-Si system, after heat-treatment.

in the as-casting state that this alloy is formed by the phases Ta_5Si_3 and Ta_2Si, due to the loss of silicon during the casting process.. After the heat-treatment had an increase of the phase Ta_2Si with respective reduction of the phaseTa_5Si_3, proceeding from the non-equilibrium state during the cooling process after casting. In the alloy with composition $Ta_{62}Si_{38}$ it was observed that the alloy in the as-cast state possess large volumetric fraction of the interest phase Ta_5Si_3 and a small portion of the $TaSi_2$ phase. It was inquired that after the heat-treatment had a small reduction of the phase Ta_5Si_3 with increase of the $TaSi_2$ phase.

It was verified in the alloy of the Cr-Si system in the as-cast step with $Cr_{62,5}Si_{37,5}$ (% at.) composition that this alloy is formed only by the phase Cr_5Si_3. After the heat-treatment we could observer that the alloys remain with the same composition. The same occurs in the alloy with $Cr_{62}Si_{38}$ composition (% at.), is possible to observe that the alloy in the casting state possess only the phase of Cr_5Si_3 and was verified that after the heat-treatment only existed the Cr_5Si_3 phase, evidencing then that this alloy remained with the interest phase. This occurs because of the melting point of the Cr and Si, different from Ta, it does not have a disparity in the melting points, thus during the p casting process, occurs a similar loss of the two elements.

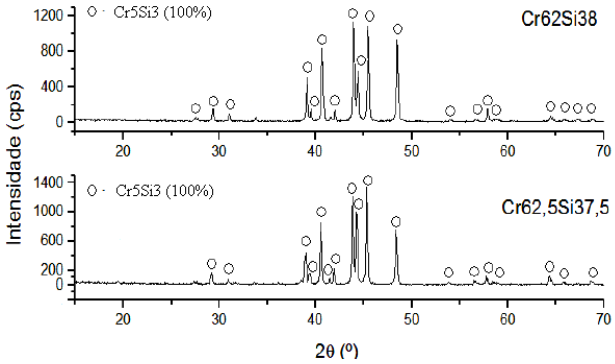

Figure 3 – X-ray diffractions of the samples of the Ta-Si system, in the state as-cast.

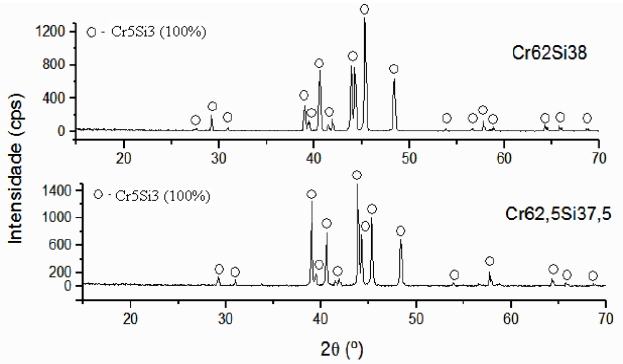

Figure 4 – X-ray diffractions of the samples of the Ta-Si system, after heat-treatment.

The figures 5 to 8 show the SEM/BSE micrographs of the as-casting samples, where a large volume fraction of the Ta_5Si_3 and Cr_5Si_3 can be observed. The presence of the phase Ta_2Si in the microstructure indicates that after heat-treatment these alloys are located in the two-phase field, we can observe that the samples of the Cr are fragile too generated during the nom-equilibrium cooling, due to the microcracking in the samples.

Ta-Si System – alloys As-Cast

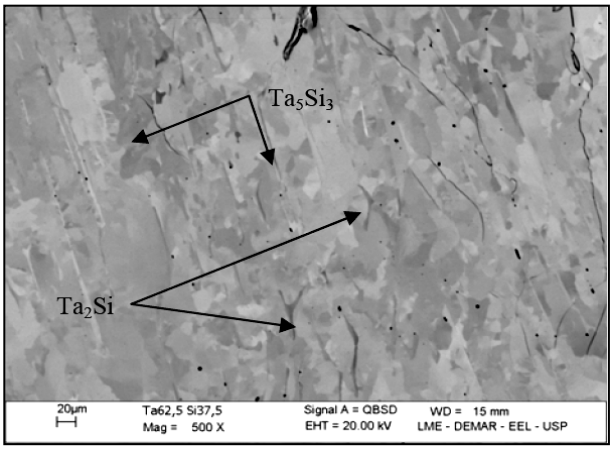

Figure 5 – SEM micrograph of sample $Ta_{62,5}Si_{37,5}$ AC.

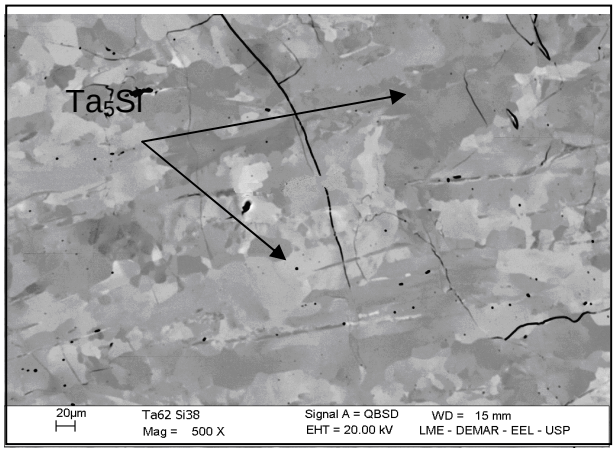

Figure 6 – SEM micrograph of sample $Ta_{62}Si_{38}$ AC.

Cr-Si System – alloys As-Cast

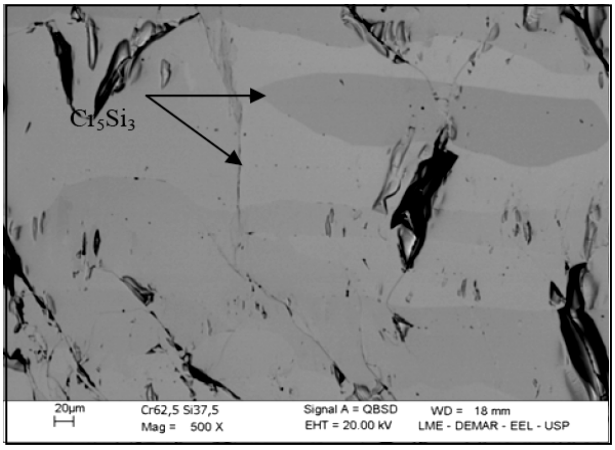

Figure 7 – SEM micrograph of sample $Cr_{62,5}Si_{37,5}$ AC.

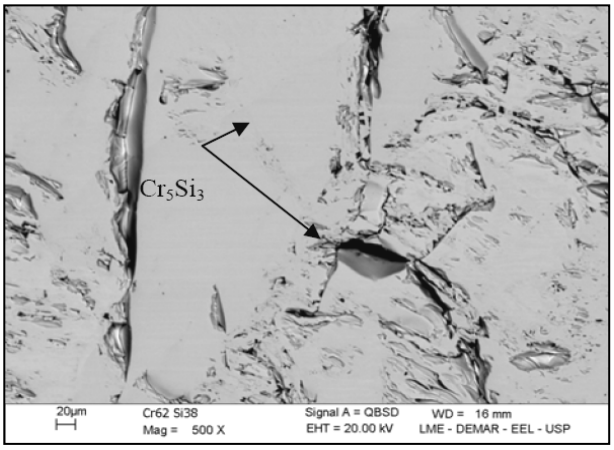

Figure 8 – SEM micrograph of sample $Cr_{62}Si_{38}$ AC.

Figures 9 to 12 **–** Shows a SEM/BSE micrograph of the alloys in the state heat-treated. A large volume fraction of the interest phases can be observed and more homogeneity

Ta-Si System – alloys heat-treated

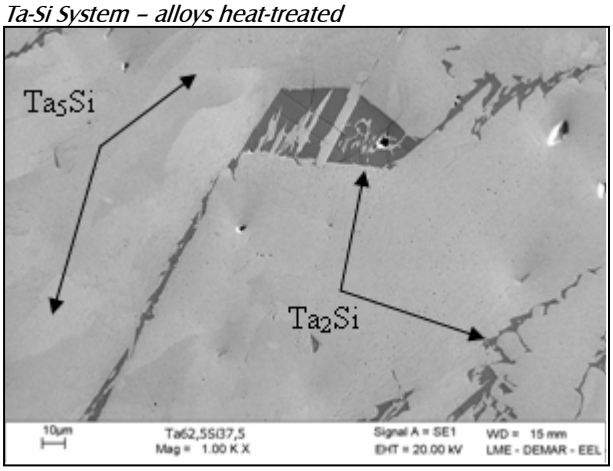

Figure 9 – SEM micrograph of sample $Ta_{62,5}Si_{37,5}$ HT.

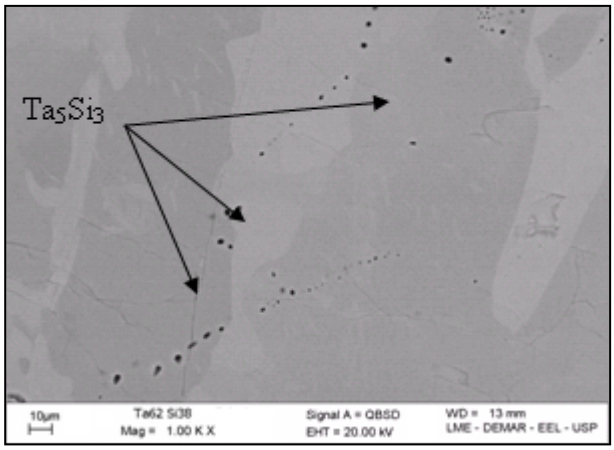

Figure 10 – SEM micrograph of sample $Ta_{62}Si_{38}$ HT.

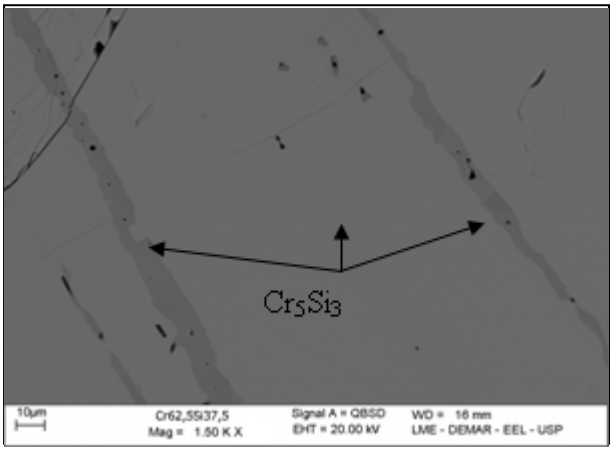

Figure 11 – SEM micrograph of sample $Cr_{62,5}Si_{37,5}$ HT.

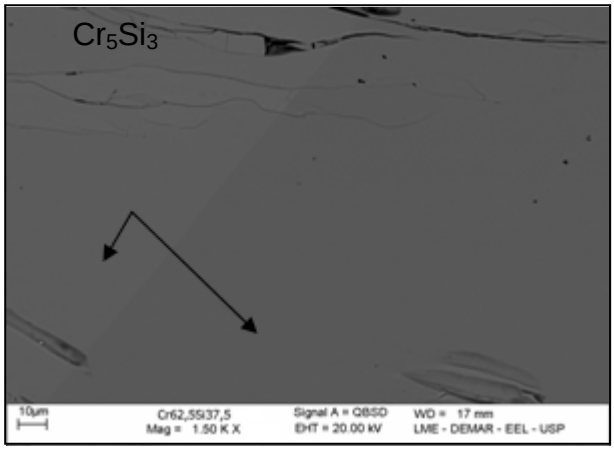

Figure 12 – SEM micrograph of sample $Cr_{62}Si_{38}$HT.

The referring reflections to both the Ta_5Si_3 phases are well evidences in the X-rays diffractograms this alloy, which is shown in the figure 1. The significant intensity of the reflections associates to the phase Ta_2Si suggests an important amount of this phase in the sample, indicating that during the melting of the alloy a preferential evaporation of Si occurred, dislocating the global composition for bigger texts Ta. In view of that the separation of the fields Ta_2Si and approximately 4 at% Si in binary Ta-Si [5], any important variation in the text of Si provokes significant variations in the volumetric fractions of the phases in the balance condition. However, is observed in the figure 2, that the reflections of the phase Ta_2Si do not intervene of important form with those of the phase Ta_5Si_3.

The figures 7 and 8, shows micrographs of this alloy in as-cast state. The solidification of this alloy if initiates with the primary precipitation of the phase Ta_5Si_3, occurring an increase of the concentration Ta to the measured that the solid fraction increases. After a heat-treatment we not were being observed important modifications of the microstructure (figures 11 and 12). This indicates that this alloy if finds in the αTa_5Si_3+ Ta_2Si 1900°C two-phase field In the case of the Cr-Si system, to both the Cr_5Si_3 phases are well evidences in the X-rays diffractograms this alloy, which is shown in the figure 2. Verify that in the alloys in the as-cast and heat-treated state, only Cr_5Si_3 phase appears. With this we can speaks that, due the miscibility band, the production of this phase becomes easier, considering the loss of mass during the arc-melting, and the melting point of the used elements.

CONCLUSIONS

The adopted conditions for production of the congruent phases of the systems Ta-Si and Cr-Si was studied. In both alloys with high melting point verified that homogenization in all the alloys was reached considering heat-treatment below of the melting point. Moreover with basis in the micrographs, also we verify that the adopted temperature and the time was enough for alleviate of the generated internal tensions during the melting process.

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REFERENCES

GIGOLOTTI, J. C. J., Estudo Experimental do Sistema Cromo–Boro, Dissertação de Mestrado Dissertação em Engenharia de Materiais, Departamento de Engenharia de Materiais, Faculdade de Engenharia Química de Lorena, Lorena, 2003.

IKARASHI, Y., ISHIKAKI, K., NAGAI, T., HASHIZUKA, Y. & KONDO, Y., Reduction of Thermal expansion Anisotropy for Intermetallic Silicides of 16H Crystal Structure. Intermetallics, vol.4, p.141-145, 1995.

KRANS, W., NOLZE, G., POWDERCELL — a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. J Appl Crystallogr 1996;29:301–3.

MASSALSKI, T.B., editor. Binary Alloy Phase Diagrams, 2nd edition, vol. 3. Materials Park, OH: ASM International; 1990.

RAMBERG, C. E., High Temperature Oxidation Behavior of Structural Silicides. In: BRIANT, C. L. et al. (Eds.) High Temperature Silicides and Refractory Alloys. Pittsburgh: MRS, p. 243-253 (Materials Research Society Symposium Proceedings, 322), 1994.

SCHNEIBEL, J. H.; RAWN, C. J.; PAYZANT, E. A.; FUU, C. L. Controlling the thermal expansion anisotropy of Mo5Si3 and Ti5Si3 silicides. Intermetallics, vol. 12, p. 845-850, 2004.

WARD-CLOSE, C. M.; MINOR, R.; DOORBAR, P. J. Intermetallic-matrix composites - a review. Intermetallics, vol. 4, p. 217-219, 1996.

VILLARS P, CALVERT LD. Pearson's handbook of crystallographic data for intermetallic phases, vol. 4. Materials Park, OH: ASM International; 1991.