

## EFFECT OF COOLING RATE DURING SOLIDIFICATION ON THE HARD PHASES OF $M_{23}C_6$ -TYPE OF CAST CoCrMo ALLOY

Received – Prispjelo: 2015-08-26

Accepted – Prihvaćeno: 2016-01-20

Preliminary Note – Prethodno priopćenje

Microstructural morphology of CoCrMo alloy by control of the cooling rate during the solidification was investigated. Samples were obtained using both an induction furnace for slow cooling rate and electric arc furnace for fast cooling rate. Microstructural characterizations were performed with metallographic techniques. It was found that the difference between the formation temperature of hard secondary phases of  $M_{23}C_6$ -type carbides determine the reduction of carbide size by increasing the cooling rate.

*Key words:* CoCrMo alloy, cast, solidification, cooling rate, microstructure

### INTRODUCTION

The CoCrMo alloys are widely used in medical application as implant materials such as prosthetic hips and knees bearings. Cast implants of CoCrMo alloy have a long history of successful use since Vitallium alloy was developed at the beginning of the last century due to their wear resistance, strength, impact resistance and low friction in the human body [1].

Many efforts to improve the mechanical and tribological properties of cast CoCrMo alloys have been made. There are CoCrMo alloys available in several different conditions defined primarily by their starting composition (e.g. low or high carbon content) [2], the conditions of manufacture (e.g. casting or forging) [3], subsequent thermal treatments (solution heat treatment, hot isostatic pressing or sintering) [4,5] and engineering surfaces by physical vapor deposition and chemical vapor deposition [6]. Henriques et al. [7] performed studies on mechanical properties of CoCrMo alloy compacts produced by hot pressing powders in a graphite die at different temperatures. However, there are few studies assessing the effect of cooling rate during the solidification on the microstructure. Zhuang et al. [8] has studied the dendritic and equiaxial grain structures and the mechanical property of fatigue improvement by cooling rate. Studies performed by Ramirez et al. [9] have shown the effect of different carbon content and cooling rate on microstructure of secondary phase. Lia et al. [10] examined the microstructural and mechanical properties of the hard phases of  $M_{23}C_6$ -type in CoCrMo alloys in both cast and wrought conditions. They found

the origin of the nanostructured hard phase mixture to be related to slow cooling during casting.

The aim of the present work was to provide more information about the effect on microstructure of CoCrMo alloy by control of the cooling rate during the solidification process.

### MATERIAL AND METHODS

Samples of CoCrMo alloy were prepared using both induction and electric arc furnaces. Type R thermocouples were used to obtain the temperature curves. The cooling curves and their derivatives were analyzed in order to obtain the temperature of start and end of solidification process. The chemical composition analyses of the CoCrMo alloys according to ASTM F-75 07 [11] are given in Table 1.

### RESULTS AND DISCUSSION

The temperature and cooling rate curves are shown in Figure 1. A typical cooling curve obtained from the experimental technique is shown in Figure 1a). In this case, two reactions are observed, the first peak is associated to onset of solidification process at 1 383 °C corresponding to the primary phase Co- $\alpha$  matrix exothermic reaction (A), and the second is associated to the end of solidification at 1 258 °C, having 6,7 °C/s average cooling rate (B). These results are agreed with Ramirez et al. [9] research showing the first thermal signal at 1 390 °C, and the second peak around 1 200 °C.

In Figure 1b) is shown a higher cooling rate curve having 23,2 °C/s. The liquid temperature and the end of solidification decreased to 1 264 °C (C) and 1 190 °C (D), respectively as solidification velocity increased. After the solidification is completed, the transformation

M. Alvarez-Vera, A. Hernández-Rodríguez, COMIMSA- Corporación Mexicana de Investigación en Materiales SA de CV, M. A. L. Hernández-Rodríguez, A. Juárez Hernández, J. R. Benavides-Treviño, J. H. García-Duarte, Universidad Autónoma de Nuevo León, México.

Table 1 **Chemical composition of the alloys studied / wt. %**

Alloy	Co	Cr	Mo	Ni	Fe	C	Si	Mn	B
ASTM F-75 07	Bal.	27-30	5-7	<0,5	<0,75	<0,35	<1	<1	<0,01
Slow cooling	Bal.	28,3	5,9	0,19	0,13	0,21	0,32	0,41	0,003
Fast cooling	Bal.	29,2	6,1	0,18	0,17	0,23	0,28	0,43	0,002

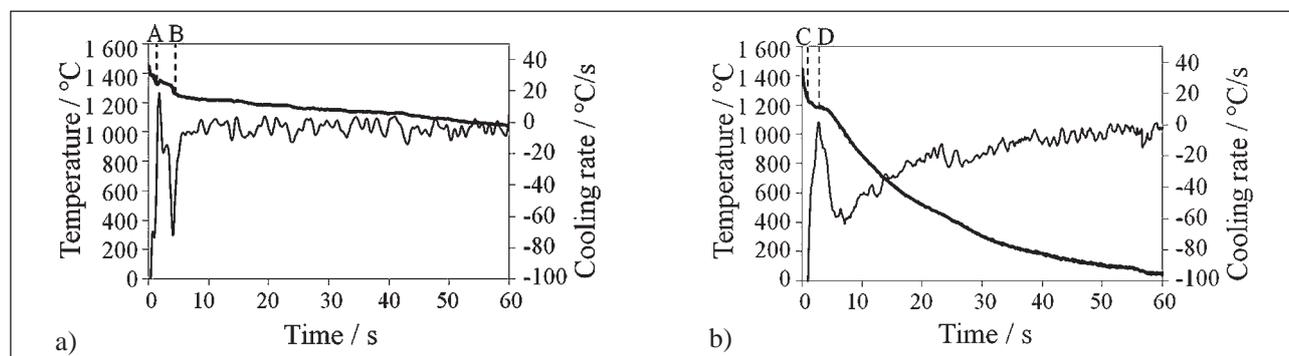
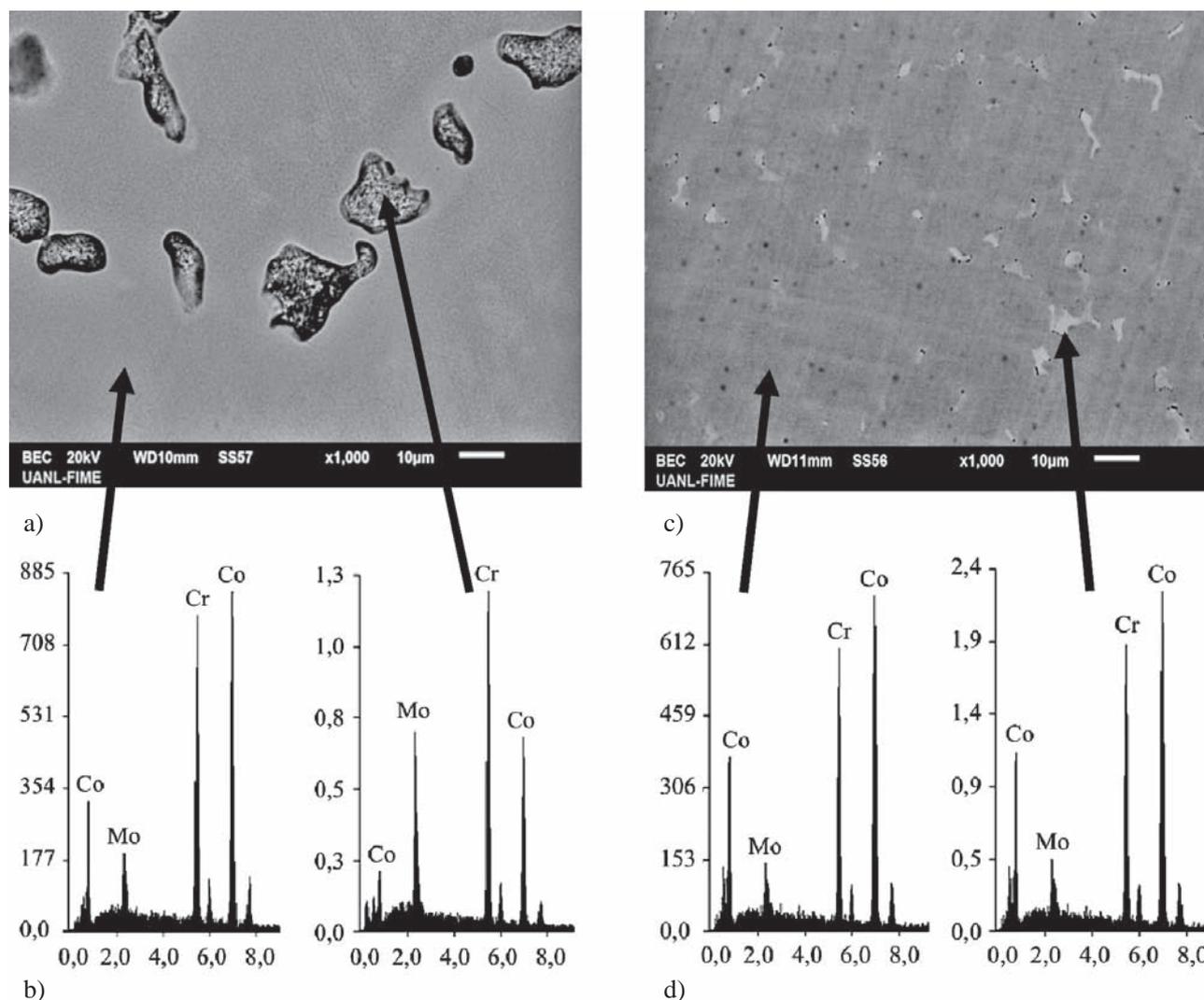

**Figure 1** Cooling curves and their derivatives obtained by thermal analysis of CoCrMo alloy. a) Slow cooling and b) fast cooling

Table 2 **Main features by controlling cooling rates of the CoCrMo test samples**

Alloy	Hardness / HV	Error*	Nominal secondary particle size / $\mu\text{m}$	Error*	Fraction area of secondary phase / %	Error*
Slow cooling	355,8	7,2	10,1	1,2	7,6	0,8
Fast cooling	347,6	5,3	4,4	0,9	9,7	0,9

\*Error: Standard error of the mean.


**Figure 2** SEM micrographs for both conditions a) slow and c) fast cooling rates, EDS analysis in the Co- $\alpha$  matrix and secondary phases b) slow and d) fast cooling rates

of the sigma phase to ( $M_{23}C_6$ ) blocky carbides between 1 150 and 1 050 °C, has been reported [9]. This effect was not detected in both at 1 050 °C, slow and fast cooling rate. Micrographs for both cooling rate conditions were obtained using a scanning electron microscope (SEM) (Jeol model JSM-6490). The microstructures for both conditions are shown in Figure 2. It can be observed the effect of fast cooling which results in a finer microstructure leaving smaller secondary precipitates.

All the samples were identified, the secondary phases ( $M_{23}C_6$  blocky carbide and sigma phase) embedded in the cobalt-base alpha matrix (fcc). The EDS analysis, Figure 2b), shows cobalt-base alpha matrix and the intermetallic compound sigma phase (CoCr).

The microstructure of fast cooling samples, consisted of a dendritic cobalt-base alpha matrix (fcc) and interdendritic precipitates of ( $M_{23}C_6$ ) “blocky type” carbide resulted in a chromium-rich as shown in Figure 2d). Gianchi et al. [3] have reported that the “blocky type” and lamellar carbide formation consisted of inter-layer plates of ( $M_{23}C_6$ ) and cobalt-rich alpha matrix (fcc). This is in agreement with the results in this work. The fraction area of blocky carbides and eutectoid constituent were affected by cooling rates. The effect of the main features of the test samples are shown in Table 2.

## CONCLUSIONS

Microstructural precipitation of secondary phases and grain size of CoCrMo alloys were modified by the control of the cooling rate during the solidification process. The precipitation of secondary phases of fast cooling rate showed a reduction of nominal particle and grain size. An slight difference between microhardness of slow and fast cooling rate from 347,6 to 355,8 HV was observed.

## Acknowledgments

Authors would like to thanks to CONACYT Mexico, for its founding support.

## REFERENCES

- [1] J. Cawley, J. Metcalf, A. Jones, T. Band, D. Skupien. A tribological study of cobalt chromium molybdenum alloys used in metal-on-metal resurfacing hip arthroplasty, *Wear* 255 (2003), 999-1006.
- [2] J. Tipper, P. Firkins, E. Ingham, J. Fisher. Quantitative analysis of the wear and wear debris from low and high carbon content cobalt chrome alloys used in metal on metal total hip replacements, *J Mater Sci Mater med* 10 (1999), 353-362.
- [3] J. Giacchi, C. Morando, O. Fornaro, P. Microstructural characterization of as cast biocompatible Co-Cr-Mo alloys, *Mater Charact* 62 (2011), 53-61.
- [4] H. Mancha, E. Carranza, J. Escalante, G. Mendoza, M. Méndez.  $M_{23}C_6$  carbide dissolution mechanisms during heat treatment of ASTM F-75 implant alloys, *Metall Mater Trans* 32 (2001), 979-984.
- [5] A. Clemow, B. Daniell. Solution treatment behavior of Co-Cr-Mo alloy, *J Biomed Mater Res* 13 (1979), 265-279.
- [6] G. Dearnaley, J. Arps. Biomedical applications of diamond-like carbon (DLC) coatings: A review, *Surf Coat Tech* 200 (2005), 2518-2524.
- [7] B. Henriques, A. Bagueri, M. Gasik, J. C. M. Souza, O. Carvalho, F. S. Silva, R. M. Silva, R. M. Nascimento. Mechanical properties of hot pressed CoCrMo alloy compacts for biomedical applications, *Mater Des* 83 (2015) 829-834.
- [8] L. Zhuang, E. Langer. Effects of cooling rate control during the solidification process on the microstructure and mechanical properties of cast Co-Cr-Mo alloy used for surgical implants, *J Mater Sci* 24 (1989), 381-388.
- [9] L. Ramirez, M. Castro, M Herrera, C. Garcia, E. Almanza. Cooling rate and carbon content effect on the fraction of secondary phases precipitate in as-cast microstructure of ASTM F75 alloy, *J Mater Process* 209 (2009) 1681-1687.
- [10] Y. Liao, R. Poursal, P. Stemmer, M. A. Wimmer, J. J. Jacobs, A. Fisher, L. D. Marks. New insights into hard phases of CoCrMo metal-on-metal hip replacements, *J Mech Behav Biomed Mater* 12 (2012) 39-49.
- [11] A.S.T.M. F75-07, Standard Specification for Cobalt-28 Chromium-6 Molybdenum Alloy Castings and Casting Alloy for Surgical Implants, (UNS R30075), 2007.

**Note:** The responsible for English language is the lecturer from COMIMSA Saltillo, México