Effect of Zr Additions on Mechanical Properties of an ASTM F-75 Alloy

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The ASTM F-75 alloy is widely used for orthopedic implants. In order to improve the mechanical properties, in particular ductility, the components fabricated by the investment casting process are generally heat treated to partially dissolve carbide precipitates. In the present work, the effect of Zr additions on the mechanical properties of a solution-treated ASTM F-75 alloy was studied. The Zr contents were 0.1, 0.05, 0.017, and 0%. Among the alloys chemically modified, that with 0.017% of Zr provided an appropriate microstructure for thermal processing. After the solution treatment, the latter alloy showed markedly increased tensile properties when compared with the Zr-free alloy. This was associated to the role of Zr as a grain refiner, as revealed by the microstructural analysis. Thus, the addition of Zr constitutes an effective way to enhance the mechanical properties of solution-treated alloys.

Keywords ASTM F-75, carbide, Zr, mechanical properties, solution treatment

1. Introduction

Alloy ASTM F-75 (Co-Cr-Mo-C) is widely used in orthopedic implants.[1,2] The components manufactured by investment casting exhibit a microstructure consisting of a cored base Co-rich face-centered cubic matrix with interdendritic and grain boundary carbides. The carbide precipitation represents the major strengthening mechanism in as-cast conditions; it is also mostly responsible for the low ductility observed, which is frequently insufficient to satisfy the aforementioned standard. In order to increase the ductility, grain size and carbide distribution are controlled during the solidification by using initial low temperatures in both metal and mold.[2–4] However, such thermal conditions also induce the formation of porosity, which is notably detrimental to the mechanical properties.[2] Thermal processing constitutes the alternative most commonly used to improve ductility. It has been shown that a heat treatment, to partially dissolve the carbides, at temperatures around 1493 K (1220 °C), improves not only the ductility, but also other mechanical properties.[5,6] Cohen and Rose[5] stated that further improvement can be achieved by an adequate aging of solution-treated alloys. Additionally, these authors reported increased mechanical properties as a result of thermal processing, which included pre-heating and solution treatment. The favorable effect of a pre-heating stage previous to the solution treatment on the tensile properties has been recently confirmed.[7]

Another alternative, which has been scarcely investigated, involves modification of the chemical composition. Cohen and Rose[5] mentioned in little detail about the helpful effect of minor additions up to 0.1% of elements such as Al, B, Cb, Ta, Ti, and Zr. These additions minimize casting defects such as shrinkage porosity, alloy segregation, coarse grain size, and inclusion content. Further research is necessary to increase the knowledge and to exploit this alternative rationally. In this work, Zr was added, at various levels up to 0.1%, to a liquid ASTM F-75 alloy searching for the best Zr contents aiming to improve the mechanical properties after solution treatment.

2. Experimental Procedure

A Co-Cr-Mo-C alloy complying with the ASTM F-75 standard[8] was employed. Heats were conducted in an induction furnace; the alloy was heated under vacuum, melted, and cast under argon atmosphere at 1873 K (1600 °C) into a ceramic mold at 1223 K (950 °C). A bar of 99.9% Zr was submerged into the liquid bath for its dissolution. The chemical analysis of the resulting alloys is given in Table 1, in which the requirements of the standard are also included. The mold consisted of a set of cylindrical cavities, 11 cm in length and 1.5 cm in diameter, designed in such a way as to allow all cavities to have the same filling conditions in order to minimize microstructural variations among the solidified bars.

The thermal processing of the selected alloys was carried out according to Cohen and Rose:[5] solution treatment for 4 h at 1493 K (1220 °C) followed by quenching in water and subsequent aging at 1088 K (815 °C) for 30 min. It must be emphasized that the temperature of 1493 K is inferior to the carbide melting temperature (1498 K) as determined in previous work.[9] The heat treatments were conducted in a resistance furnace, and the bars were covered with several layers of graphite paint in order to prevent oxidation.

Tension tests were conducted on as-cast, solution-treated, and aged specimens; at least two repetitions were performed per specimen. The tested specimens were machined from the bars according to the ASTM E-8 standard.[10] The tests were carried out in a 15 ton Instron machine, using a deformation rate of 3 mm min^{-1}.

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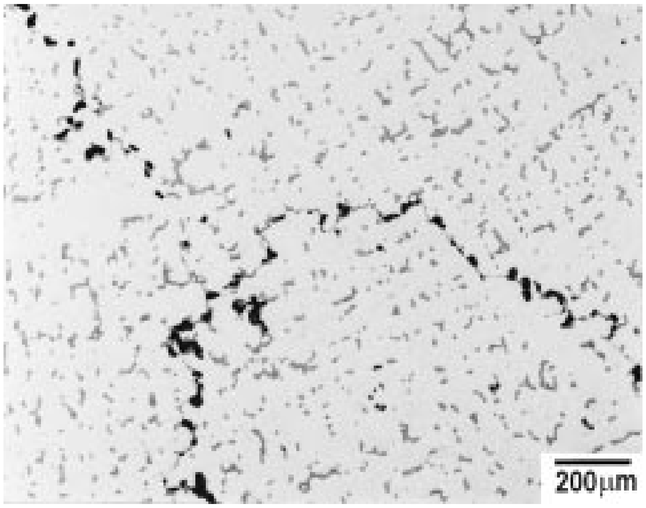

Fig. 1 As-cast microstructure

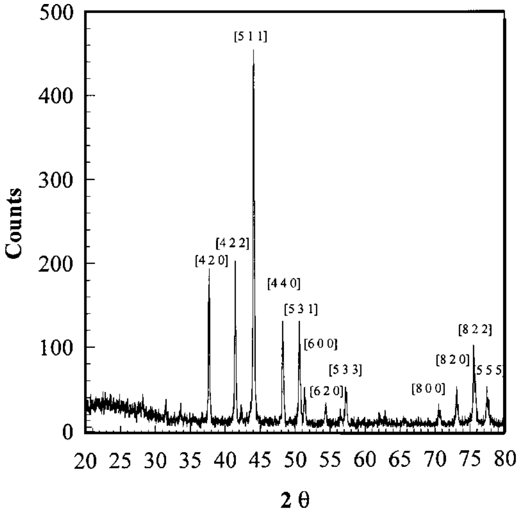

Fig. 2 X-ray diffraction pattern of electrolytically extracted carbides

Table 1 Chemical composition of the cast alloys

	Element (wt.%)								
Heat	Cr	Mo	C	Zr	Si	Mn	Ni	Fe	Co
1	27.94	5.89	0.24	…	0.77	0.35	0.56	0.33	Balance
2	27.95	6.15	0.23	0.017	0.82	0.37	0.58	0.32	Balance
3	28.15	6.55	0.22	0.05	0.91	0.37	0.60	0.35	Balance
4	27.87	6.11	0.23	0.1	0.85	0.38	0.57	0.31	Balance
ASTM F-75	27-30	5-7	0.35 max	…	1 max	1 max	1 max	0.75 max	Balance

Optical microscopy coupled with image analysis was used for the microstructural characterization; the specimens were conventionally prepared by grinding and polishing. Each quantitative determination of the carbide content was made at 200× on 20 fields, which accounted for a total analyzed area of about 3 mm^2. Specimens from the as-cast and solution-treated conditions were subjected to electrolytic carbide extraction, as described by Weeton and Signorelli;[11] the particles thus obtained were analyzed by x-ray diffraction. Complementary chemical information from the carbides was obtained by energy-dispersive spectroscopy (EDS).

3. Results and Discussion

Figure 1 shows the as-cast microstructure of the Zr-free alloy, in which interdendritic and grain boundary carbides were observed. X-ray diffraction of the electrolytically extracted carbides revealed the presence of $M_{23}C_6$ carbides, as shown in Figure 2. The EDS microanalysis showed Co, Cr, Mo, and Si as carbide constituents. The presence of porosity was not observed in the cast bars as a result of the thermal conditions used.[9] Microscopic analysis of the alloys containing 0.1 and 0.05% Zr showed the presence of angular blocky precipitates constituted by Zr and C, as identified by EDS. This morphology, typical of MC carbides, which forms before solidification, is undesirable due to the well-known fact that angular carbide particles act as preferential sites for crack initiation in detriment of the ductility.[12] Furthermore, this carbide type cannot be modified by solution treatment due to its great stability. In contrast, the alloy with 0.017% Zr showed a very similar microstructure to the Zr-free alloy. The x-ray diffraction revealed the presence of $M_{23}C_6$ carbides, and EDS indicated the presence of Zr in such carbides. On the basis of the results observed, only the alloys with 0 and 0.017% Zr content were subjected to a subsequent thermal processing.

The solution treatment led to an appreciable reduction of the initial carbide content, from 9.3 to 3.2%, and from 8.9 to 2.9% for the alloys with 0 and 0.017% Zr, respectively. Most of the residual carbides were interdendritic, and only a few small film boundary carbides were visible.

The aging treatment of solution-treated alloys induced subsequent microstructural changes, which were visible under the optical microscope. Both alloys exhibited a fine and aligned precipitation, which is associated with slip lines and twin boundaries formed from thermal stresses developed during water quenching of specimens subjected to solution treatment.[11] Such precipitation was more accentuated in the alloy with Zr addition due to the strong affinity of this element to C.

The alloys subjected to solution treatment exhibited different mechanical behaviors, as observed in the stress-strain curves presented in Fig. 3, in which curves corresponding to the alloy without Zr in as-cast conditions were also included. The different mechanical behaviors are evidenced in Fig. 4(a) and (b),

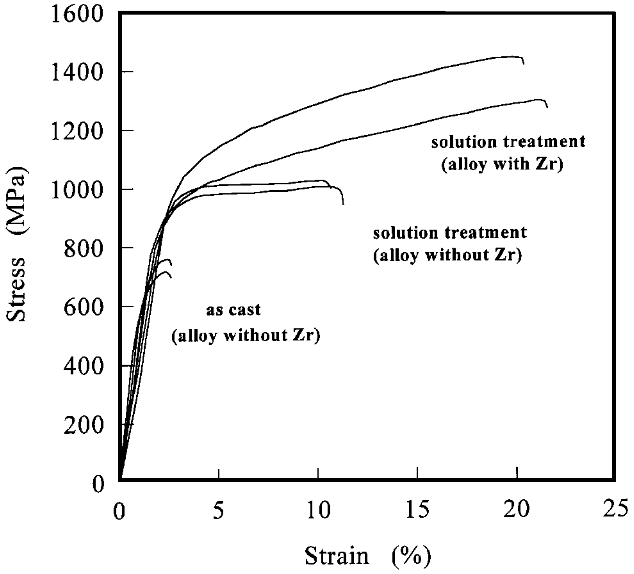

Fig. 3 Stress-strain curves

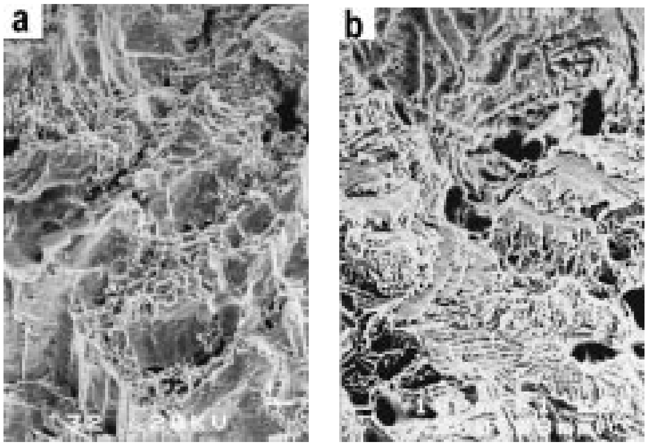

Fig. 4 Fracture surfaces for the alloys (**a**) without Zr and (**b**) with Zr

which show the fracture surface of tension-tested specimens. Both alloys showed a ductile failure mode, in which deformation bands zones and dimples were observed. However, the alloy with Zr exhibited a more pronounced ductile behavior.

The values of the tensile properties, namely, ultimate tensile strength (UTS), yield strength (YS), and elongation to fracture (%) were evaluated for both alloys in the as-cast condition as well as after the solution treatment and aging stages. The results are presented in Fig. 5, which also includes the standard ASTM F-75 values.

For both alloys, the as-cast microstructure provided superior UTS and YS values than the standard specification; the higher values corresponded to the alloy with Zr addition. The higher properties in the latter were associated with grain size differences, which were 650 μm compared to 950 μm for the Zr-free alloy. By considering that both alloys were cast and solidified under essentially the same conditions, only minor microstructural differences would be expected as a result of the solidification process. Hence, the smaller grain observed in the alloy with Zr resulted from the grain refining effect of this element. On the other hand, the elongation levels were not appropriated with respect to the ASTM F-75 standard, which, in view of the absence of porosity in the specimens under study, was associated with carbide precipitation.

After the solution treatment, the values of tensile properties were enhanced. It is noteworthy to underline the exceptional increase in ductility for both alloys, especially for the alloy with Zr. The resulting increased elongation in solution-treated conditions arises from the modification of the as-cast carbide features. In view of the similitude of the observed carbide features in both alloys, the contribution of carbide precipitation to the resulting properties can be assumed to be the same. Therefore, the higher elongation observed in the alloy with Zr resulted from the combined effect of carbides modification and finer grain size.

In aging conditions, the UTS and YS were enhanced; however, the elongation was remarkably affected. This behavior is attributed to the interrupted dislocation motion in the matrix by the precipitates located along slip lines and twin boundaries. The adverse effect on the elongation in the alloy with Zr is related to the appreciable precipitation observed in this alloy. Thus, despite the gain in UTS and YS, this treatment, under the conditions used, is not recommended for these alloys.

The obtained properties in the alloy with Zr are comparable with those obtained by Cohen and Rose,[5] and also superior to those reported by Montero *et al.*,[7] in alloys subjected to preheating and subsequent solution treatment. The latter authors explained the favorable effect of the pre-heating treatment on mechanical properties of solution-treated alloys by the restrained grain growth during solution treatment. This is associated with the pinning of grain boundaries by precipitates appearing from the pre-heating treatment. This indicates that the mechanical properties in this alloy are greatly sensitive to the grain size, and that a finer grain size may lead to increased mechanical properties. This fact was confirmed by the results observed in the present work, in which the superior mechanical properties were associated with a finer grain size. Thus, the addition of Zr appears to be an appropriate way to enhance the mechanical properties in solution-treated alloys. This alternative represents an advantage since a pre-heating operation is not required.

The cast conditions used in this work for the Zr-free alloy, *i.e.*, high temperatures for mold and metal, induced a coarse grain size; however, the porosity formation was inhibited. The results showed that, despite the coarse grain size, the elimination of porosity led to satisfactory mechanical properties. This suggests that, regardless of the thermal processing, the minimization of porosity is essential to improving the mechanical properties as much as possible.

4. Conclusions

An ASTM F-75 alloy was modified with Zr additions in order to improve the response of mechanical properties to thermal processing. For Zr additions up to 0.1%, that of 0.017% originated a suitable microstructure for thermal processing, which included solution treatment and aging. Comparison of

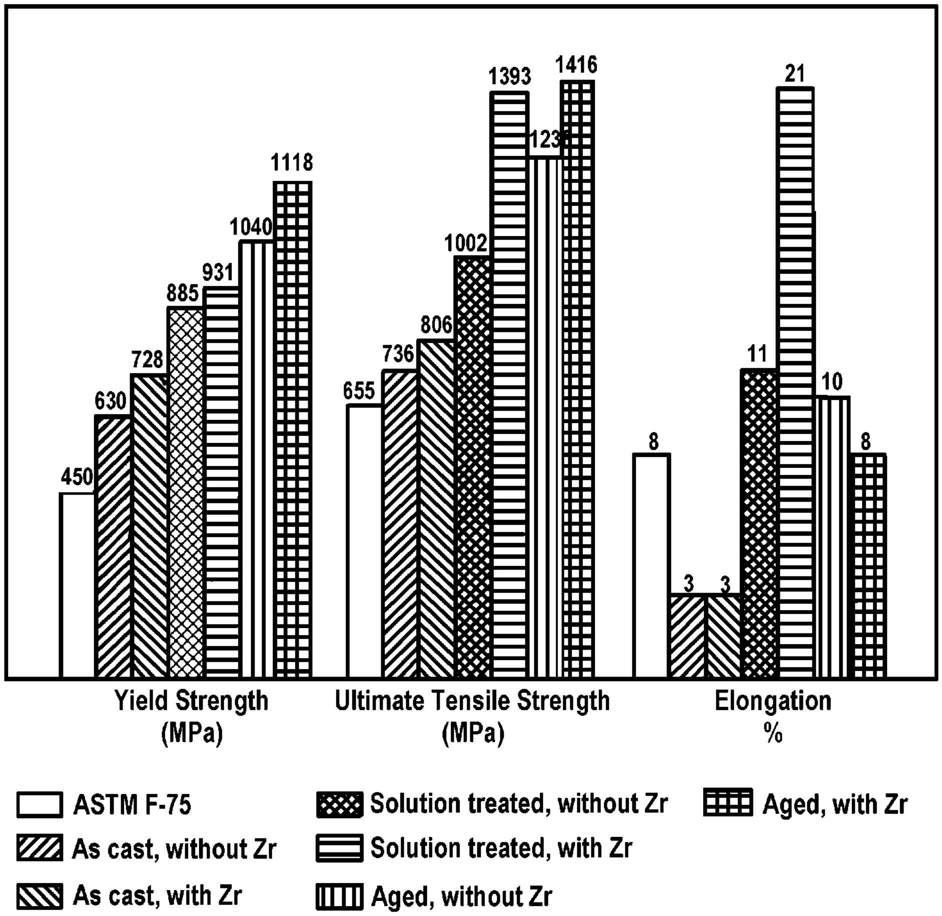

Fig. 5 Variation of tensile properties with thermal processing

the resulting mechanical properties to those achieved by the Zr-free alloy allows for the following conclusions to be drawn.

- The as-cast microstructure provided for both alloys higher UTS and YS values than those specified by the ASTM F-75 standard. In contrast, the ductility levels were largely inferior than the minimum required.
- Solution treatment increased the tensile properties in both alloys. The substantial enhancement of ductility, especially in the alloy with Zr addition, is noteworthy.
- In solution-treated conditions, both alloys surpassed the requirements imposed by the ASTM F-75 standard.
- The aging treatment had a favorable effect on the UTS and YS; however, the resulting ductility was notably affected. This deleterious effect was more pronounced in the alloy with Zr.
- The addition of Zr to ASTM F-75 alloys arises as an effective means of enhancing the mechanical properties of solution-treated components.

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References

1. *Metals Handbook,* 9th ed., 1988, vol. 15, p. 813.
2. K. Asgar and F.A. Peyton: *J. Design. Res.,* 1961, vol. 40, pp. 73-86.
3. K. Asgar and F.A. Peyton: *J. Design. Res.,* 1961, vol. 40, pp. 63-72.
4. M. Riddihough: *J.,* 1959, Nov., 1959, pp. 421-28.
5. J. Cohen and R.M. Rose: *J. Biomed. Mater. Res.,* 1978, vol. 12, 1978, pp. 935-937.
6. H.S. Dobbs and J.L.M. Robertson: *J. Mater. Sci.,* 1983, vol. 18, pp. 391-401.
7. Montero-Ocampo C., M. Talavera, and H. Lopez: *Metall. Mater. Trans. A,* 1999, vol. 30A, pp. 611-620.
8. *Annual Book of ASTM Standards,* ASTM, Philadelphia, PA. 1989, vol. 13.01.
9. De le Garza Z.: Master's Thesis, CINVESTAV, Saltillo, Mexico, 1999.
10. *Annual Book of ASTM Standards,* ASTM, Philadelphia, PA., 1992, vol. 3.01.
11. J.W. Weeton and R.A. Signorelli: *Trans. ASM,* 1955, vol. 47, pp. 815-52.
12. C.T. Sims, N.S. Stoloff, and W.C. Hagel: *Cobalt.Base Alloys, Superalloys II,* J.ohn Willey & Sons, New York, NY, 1987, pp. 135-62.