Thermomechanical and annealing processing effect on a rapid solidified Co – 20 wt. % Cr alloy

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Abstract. The microstructure influence on the mechanical properties in a rapid solidified Co – 20 wt. % Cr alloy processed by hot – rolling (HR), and hot – rolling plus annealing (HR + A) is presented. The characterization consisted of a scanning electron microscopy inspection and its correlation with hardness, tensile test measurements and the corresponding fractography. The results showed that the as – cast (AC) condition is conformed by columnar dendrites aligned on a preferential direction. Additionally, numerous striations associated with the massive athermal transformation were observed. From the hot – rolled condition, athermal ε – martensite plates inside block austenitic grains were identified. On the other hand, the specimen subjected to hot – rolling plus annealing treatment showed an important internal stresses relief, reflected in the ductility improvement from 4.3 ± 2.18 % in the AC condition, and 13.73 ± 3.74 % in the HR condition to 27.8 ± 4.35 % for the HR + A condition.

1. Introduction
Co – based alloys are widely use in biomedical applications due to their excellent corrosion resistance, biocompatibility and high performance in terms of their mechanical properties [1,2]. They have been successfully applied as dental and orthopedic implants, hip and knee joints, and as cardiovascular devices (stents) [3].

Generally, in Co – Cr alloys, the predominant phase at room temperature corresponds to the FCC, also known as γ phase [4]. However, thermodynamically, the γ phase is stable only at high temperatures, so the phase with greater stability is that which has an HCP structure, known as ε phase [5]. Since the martensitic transformation γ - Co ↔ ε - Co, is severely limited under normal solidification conditions. Recent research has shown that rapid solidification with cooling regimes higher than 300 K/s promotes the formation of a large number of crystalline defects. As a result, the nucleation sites that give rise to the formation of martensite embryos facilitating that the phase transformation occurs are present in a higher amount compared with normal solidification conditions [6]. This defect promotion is reflected in the drastic increase of the athermal ε – martensite volume fraction with more than 90 % exhibited in the AC condition. Another notable effect is the solute trapping which experimentally results in the extension of the solid solution of Cr in Co and the elimination of segregated regions in the alloy matrix [7,8,9]. Furthermore, a decrease in the amount of precipitates and a microstructural refinement were also achieved since the AC condition.
ASTM F – 75 is the most study Co – based alloy, its standard specification establishes a minimum ductility of 8 %, yield strength (YS) of 450 MPa, and an ultimate tensile strength (UTS) of 650 MPa [12]. However, many variations in the composition, thermomechanical processing and heat treatments have been proposed to modulate the microstructure and improve their mechanical behavior. Yamanaka et. al reported the fabrication of a Ni – free Co–29Cr–6Mo alloy via conventional hot forging with ultrafine – grained microstructure, as a consequence of 83.4 % in reduction. The reported mechanical properties are 1450 MPa in UTS, and a uniform elongation of 5.5 % [13]. A hot – rolled Co–28Cr–9W–1Si – C alloy combined with a microalloying and composed by refined grains and a high density of lattice defects were obtained as result of dynamic recrystallization [14]. The sample with carbon doping of 0.06 wt. % showed a maximum elongation of 46 %, and a UTS of 1282 MPa [14]. The present work exhibits the microstructural influence on the mechanical behavior of a hot – rolled and hot – rolled plus annealing of a rapidly solidified Co – Cr alloy.

2. Experimental Procedure
A Co – 20 wt. % Cr alloy was fabricated in a vacuum induction furnace under argon (Ar) atmosphere. The raw metals correspond to high purity cobalt (99.99%) and chromium (99.99%). The foundry processing consisted of three vacuum and argon purges, each one of twenty minutes before melting, with the purpose to remove any residual oxygen. The liquid alloy was casted at a temperature of 1873 K (1600º C) in a rectangular shaped Cu – mold coupled with a cooling system where water was recirculating all the time during melting to keep the temperature always around 298 K (25º C) [6].

A solution heat treatment at 1323.15 K (1050° C) was applied to the AC alloy in a resistance furnace for 3.6 ks, and then it was processed by unidirectional hot – rolling. Multiple passes were performed until a final thickness of 0.8 mm was achieved (rolling reduction: 80.29 pct; equivalent strain: 1.875 and strain rate: 7.51 s^{-1}). To prevent fractures during the process, the sample was re – heating at 1323 K (1050º C) for 300 s after each pass. The hot – rolling was performed at a rolling speed of 0.0665 m s^{-1} using two rolling mills with a roll diameter of 127 mm. The resulting plate was finally air – cooled after the last rolling pass. An annealing heat treatment at a temperature of 923.15K (650 °C) for 1.8 ks was applied to the hot – rolled alloy. The metallographic preparation consists of a mechanical grinding and mirror polishing with 1 μm alumina slurry followed by electrolytic etching at 10 V using a 60 vol. % HNO3 + 40 vol. % H2O solution. All conditions were examined by scanning electron microscopy (SEM; JEOL, 7600f). The mechanical properties at room temperature were evaluated using a uniaxial tensile test with an INSTRON 1125 universal testing machine and hardness Vickers testing (n = 3). Standard deviations and standard errors of the mean were calculated for the ultimate tensile strength, the yield strength, and the elongation to failure.

3. Results and Discussion
In Figure 1a, columnar dendrites are observed and a morphology of transgranular marks delimited by stacking faults called “striations” is present [6]. This characteristic morphology corresponds to athermal e – CoHCP martensite (ε_{ater}), it is noteworthy that there is no presence of interdendritic segregation in the AC condition. The ε_{ater} presents a preferential arrangement arising from the stacking faults. A minimum of precipitates corresponding to (Co3Cr) and (CoCr) are also present as white dots.

In the Figure 1c, deformation bands oriented parallel to the rolling direction are distinguished, grains of different sizes with a block shape are the product of the phenomenon of recrystallization and heterogeneous grain growth, main characteristics of dynamic recrystallization [15]. After hot – rolling, the growth of ε_{ater} plates is delimited by grain size, and in some cases the orientation prevails between grains [16].
Deformation bands aligned along the rolling direction are showed in Fig. 1e, and well-defined grains of various sizes can be observed. Cavities located at grain boundaries are associated with clusters of defects such as vacancies and reorganized dislocations during recovery at high temperature [15]. The larger grains preserve the block shape and have cavities over the entire matrix. Recrystallized grains were found with semicircular in shape. The minimum of precipitates was preserved as a benefit of rapid solidification.

![Figure 1. Co – 20 wt. Cr alloy: a) SEM micrograph, and b) fractography of the AC condition; c) SEM micrograph, and d) fractography of the HR condition; e) SEM micrograph, and f) fractography of the HR + A condition.](image)

With the support of the microstructural features and the phenomenological characterization of the HR+ A Co – 20 wt. % Cr alloy, dynamic recrystallization during hot rolling was determined [17]. This recrystallization processing has as main characteristics: 1) being an intermittent deformation process at a homologous temperature higher than 0.5 [15], 2) producing grains of various sizes because recovery occurs at the same time as recrystallization. On the other hand, dynamic recovery is the dominant mechanism during annealing. At this stage, the dislocations are reorganized, however, the dislocation structure is not eliminated, but reaches a metastable state [15]. Microstructural features (see Fig. 1c – e) are in accordance with the exhibited mechanical behavior, under this criterion, the micrographs show a higher density of dislocations in the HR sample compared to the HR + A sample.
Figure 2. True stress vs true strain curves of the Co – 20 wt. % Cr alloy in the AC, HR, and HR + A conditions.

Figure 3. Work hardening exponents of the AC, HR, and HR + A conditions.

Table 1. Mechanical properties of the Co – 20 wt. Cr alloy in the AC, HR, and HR + A conditions.

| Condition | ε(%)       | UTS(MPa)            | E(GPa)       | n      | HV 0.1         |
|-----------|------------|---------------------|--------------|--------|----------------|
| AC        | 4.31 ± 2.18| 278.97 ± 23.65      | 17.30 ± 5.11 | 0.44   | 333.33 ± 13.32 |
| HR        | 13.73 ± 3.74| 1006.48 ±119.57    | 82.38 ±15.77 | 0.39   | 435.00 ±6.56   |
| HR+A      | 27.80 ±4.35| 1166.26 ± 36.65    | 180.02 ± 8.68| 0.23   | 462.67 ± 19.14 |

As show in the true stress – true strain curves in Figure 2, the mechanical properties of AC condition are the lowest due to the dendrite alignment and high internal stresses as a consequence of rapid solidification. However, a drastic increase in elongation and UTS is noticeable after HR and HR + A conditions. The most promising results correspond to the HR + A condition where ductility increased 6.5 times, and also the UTS increases 4.2 times with respect to the AC condition. The results of the tensile tests are organized in the Table 1, where the hardening coefficient and vickers hardness are also reported.

The hardening coefficient indicates the resistance capacity of the material; therefore, it is a function of the microstructure. The AC condition shows a high amount of internal stresses produced by multiple factors as a high number of flat defects, stacking faults and intersections, which act like as physical barriers for the movement of dislocations. After hot rolling, a microstructure of partially deformed recrystallized grains with εατερ plates was found. This change increased the capacity of movement and interaction of dislocations during plastic deformation when a charge is applied to the material. The HR + A sample present a balance between the formation of dislocations and the dynamic recovery during the deformation. Also, it is important to remark that the annealed microstructure presents a higher percentage of recrystallization than the HR sample, therefore, it will support a higher proportion of dislocations generated during deformation. In this sense, the annealing grains show less internal stresses.

Figure 1b shows the fractography of AC condition, it presents crystallographic facets of εατερ plates and cleavage marks. On this surface few precipitates are detected, in addition to a dendrite – dendrite interface. HR fractography exhibited in Figure 1d, has a ductile behavior based on the pronounced plastic deformation at the edges of the grains. Similar to these conditions, intergranular fracture with formation and coalescence of voids were observed on the surface of the HR + A sample, see Figure 1f. The fracture mechanism in these two last conditions are the same, however, the fracture surface on the annealed condition shows smaller voids and
homogeneous plastic deformation caused by the recrystallized and grain refinement, while the HR sample accumulate the load at the grain boundaries. In this sense, annealing relief residual stresses from martensite plates, increasing ductility.

4. Conclusions
- After thermomechanical and annealing processing, the benefits of rapid solidification were preserved.
- The morphological evolution of the hexagonal athermal phase after HR and HR + A treatments, represent a significant improvement in mechanical properties compared to AC condition.
- The annealing heat treatment activates the recovery and dynamic recrystallization. The resulting martensite plates are thicker, which means a remarkable elimination of internal stress in comparison with the AC and HR conditions.
- The mechanical resistance is increased due to the plastic deformation during hot rolling, inducing a significant grain refinement. Ductility, between cast and annealed condition, increased from 4.3 ± 2.18 to 27.8 ± 4.35%, and a UTS from 278.97 ± 23.65 to 1166.26 ±36.65 MPa.
- The fractography analysis of the AC conditions belongs to a fragile material, while the fracture related to the HR and HR + A specimens presents the formation and coalescence of voids, typical of a ductile material.

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