

Paragraph Ran in the Queries

Paper Title: Effect of Nb and Ti additions on microstructure, hardness and wear properties of AlCoCrFeNi high-entropy alloy

Content :

Hardness and wear

Hardness mapping was carried out using the Vickers method (HV) with an automatic EMCO TEST Dura Scan microindenter. Indentations were spaced at 300 μm intervals, applying a load of 0.05 kgf for a dwell time of 15 s. The measurement mesh covered half of the ingot's cross-section area. Nanoindentation analyses were performed at room temperature using an Anton Paar NHT² nanoindenter equipped with a Berkovich-type diamond indenter, following the Oliver and Pharr method. A load of 100 mN was applied with a loading and unloading rate of 200 mN/min and a dwell time of 10 s. The reported values of the indented elastic modulus (EIT) correspond to the average of 10 measurements taken at random regions of the ingot cross section. To determine the hardness of each phase, at least five measurements were carried out on each of them.

To evaluate the tribological properties of the alloys, dry linear reciprocating sliding wear tests were carried out at room temperature. Samples, 3 mm thick, were polished following the same metallographic preparation procedure mentioned above. The wear tests were performed on a UMT CETR tribometer, applying a load of 10 N, amplitude of 5 mm, and speed of 5 mm.s⁻¹. The 4 mm diameter ZrO₂ sphere served as the counterbody due to their high hardness, thermal resistance and chemical inertness. Dry sliding was performed for 600 cycles at a frequency of 0.2 Hz, corresponding to a duration of 1200 s. The reported values of the coefficient of friction (COF) correspond to the average of 3 rails. Prior to each wear test, the sphere was inspected using a Veeco optical profilometer, model Wyko NT1100, to ensure the contact region was perfectly intact and free from third-body contamination. Surfaces of both the samples and the counterbody were cleaned with ethyl alcohol before starting the tests. The wear volume and wear rate were determined by analyzing cross-section profile of the wear rails and were calculated by Archard's equation. The profile and morphology of the worn surfaces and counterbody were examined by optical profilometry and SEM-EDS, respectively, allowing detailed study of the wear mechanisms.

Hardness and wear behaviour

The hardness profile of the ingot's cross-section and the average hardness and elastic modulus values are seen in [Fig. 7](#) and [Table III](#), respectively. The three HEA have high

average hardness, 790 HV, 597 HV and 731 HV for the alloys AlCoCrFeNiNb_{0.6}, AlCoCrFeNiTi_{0.5} and AlCoCrFeNiTi_{1.2}, respectively. [Table III](#) compares the hardness values obtained by microindentation and nanoindentation. The AlCoCrFeNiNb_{0.6} and AlCoCrFeNiTi_{1.2} alloys show very similar values between the two methods. However, the AlCoCrFeNiTi_{0.5} HEA presents a greater variation in the average compared to the microindentation map, where more measurements were performed in random regions.

The influence of each individual phase on hardness is detailed in [Table IV](#). The Nb-containing HEA presented the highest average hardness, which is associated with the high hardness of Laves phase and the B2/Laves fine eutectic microstructure with high mechanical strength (see [Fig. 7a](#) and [Table IV](#)). The small spacing between lamellae increases the area fraction of phase boundaries, which hinders the dislocations movement and enhances hardness [\[32\]](#). It is important to highlight that accurately estimating the hardness of the A2 phase was not possible. The A2 phase is fine and predominantly located at the grain boundaries, making it difficult to resolve by the optical microscopes coupled to the durometers used in this study.

Despite the high hardness of the interdendritic region, particularly of the Laves phase which can reach values close to 1100 HV, the AlCoCrFeNiTi_{1.2} alloy presents a microstructure with 3 distinct phases, contributing to the high measurement deviation. The highest values in the hardness profile of alloys containing Ti are associated with Cr-rich phases and Laves phase, which predominate in the Interdendritic regions. It is observed that the standard deviation ([Table III](#)) increases with the number of phases that constitute the microstructure, since each phase has distinct mechanical properties due to the different chemical compositions.

When comparing the hardness values of the HEAs containing Ti, it is observed that the hardness of the B2 phase increases with Ti concentration. This trend suggests that solid solution hardening is the primarily mechanism enhancing the mechanical resistance of this phase. The increased Ti concentration, due to its large atomic radius, results in substantial lattice distortions [\[33\]](#).

As well established in the literature, the high distortion of the lattice is one of the four characteristic effects of HEA. This distortion plays a direct role in yielding mechanical properties superior to those found in conventional alloys [\[5\]](#), [\[6\]](#), [\[7\]](#), [\[34\]](#). This high distortion is primarily associated with the differences between the atomic radius of the constituent elements. Moreover, from a statistical point of view, each chemical component has the same probability of occupying a lattice site, thereby contributing to the increase in configurational entropy [\[5\]](#). Considering the randomness between the constituent elements in the lattice, this can result in high distortions [\[5\]](#), [\[34\]](#).

The literature highlights [4], [5], [6], [11] that the incorporation of aluminum (Al) with its relatively large atomic radius of 0.143 nm into the AlCoCrFeNi HEA system provides stabilization of the BCC phases and induce large lattice distortions, thereby increasing mechanical strength [11], [35]. Furthermore, the addition of Nb and Ti in this system contributes significantly to the increase in mechanical strength through solid solution mechanism, due their large atomic radius, 0.146 nm and 0.147 nm, respectively. In addition, Nb and Ti promote the formation of intermetallic secondary phases, such as the Laves phase, which act as an additional mechanism to increase mechanical resistance [33], [36].

Fig. 8 presents typical curves obtained by nanoindentation. The estimate indented elastic modulus was obtained using the Oliver and Pharr method, with the average values shown in Table III. It is observed that the HEAs AlCoCrFeNiNb_{0.6} and AlCoCrFeNiTi_{1.2} present elastic modulus values comparable to those of conventional metallic alloys and nickel superalloys [7], [37], Conversely, the AlCoCrFeNiTi_{0.5} HEA has a lower elastic modulus (close to Ti alloys) [7], indicating the potential for mechanical forming despite high hardness.