Abstract

Due to the development of technology in the aerospace industry, the demand for the high performance materials at elevated temperatures has increased dramatically these days. Refractory high-entropy alloys have been designed by Air Force Research Laboratory (AFRL) in 2010 as a candidate for new materials that can operate at higher temperatures, where Ni-base superalloys have incipient melting.

HfNbTaTiZr refractory high-entropy alloy with simple BCC structure was first reported by AFRL, with high strength and large ductility from room temperature to 1200℃. As a result of its poor oxidation resistance, Al was added to improve oxidation resistance in previous research. According to the conclusions of this research, $Al_{0.5}HfNbTaTiZr$ has the balanced performance of oxidation resistance and mechanical properties. In this study, we have adjusted this composition based on the previous conclusions and added Si for the sake of improving oxidation resistance further.

According to the outcomes of experiments, after Si was added into Al-Hf-Nb-Ta-Ti-Zr refractory high-entropy alloys, oxidation resistance,

hardness and strength was advanced significantly. However, due to the formation of Si compound, as Si was added more amount into alloys, the room ductility reduced considerably. In general, a suitable amount of Si addition had the balanced performance of oxidation resistance, strength and room temperature ductility.

In conclusion, the oxidation improvement is still insufficient compared with the majority of superalloys. The inferiority is mainly due to the large proportion of active elements which cause looser aluminum oxide. Further improvement for oxidation resistance in refractory high-entropy alloys is still required in the future.

摘 要

以五元主要元素以上設計的新合金-高熵合金,已漸受國內外矚目。基此理念，美國空軍實驗室在 2010 年開發以耐火金屬元素所組成之耐火高熵合金，並證實耐火高熵合金 W-Nb-Mo-Ta 及 W-Nb-V-Mo-Ta 於高溫下之強度優於鎳基超合金，至 1600 °C 仍有 400 MPa 的強度，但兩合金在室溫下為脆性斷裂。接著,他們以較輕的 Ti、Zr 替換 W、Mo,製備出 Hf-Nb-Ta-Ti-Zr 合金,此合金在室溫下壓縮延性大於 50 % 以上，但其高溫軟化較快。

雖然 Hf-Nb-Ta-Ti-Zr 密度較輕且具極佳的室溫延性，但卻有耐火元素先天抗氧化性不佳的缺點，而限制其高溫的應用性。先前實驗室研究在耐火高熵合金中添加鋁來增加抗氧化能力，在 $Al_xHfNbTaTiZr$ 耐火高熵合金系統中，$Al_{0.5}HfNbTaTiZr$ 不論在機械性質或抗氧化性質都有不錯的表現[1]。因此本研究以此合金為基礎，設計不同耐火高熵合金系統以及添加變量的 Si 作為實驗合金,探討 Si 的添加對此耐火高熵合金微結構、機械性質及抗氧化性之影響。

研究結果發現不同耐火高熵合金系統以及不同 Si 添加量的合金

共晶體結構皆為簡單 BCC 固溶相，而隨著 Si 含量的增加，矽化物的峰值開始出現。微結構為典型的樹枝狀結構，但隨著 Si 的添加樹枝間相有更多的共晶矽化物形成。合金經過 1400 ℃ 均質化 12 小時後，未添加 Si 的合金可以完全消除偏析的樹枝狀結構，但添加 Si 的合金均質化無法消除共晶矽化物，整體來說均質化後合金由於部分強鍵結元素固溶回基地相而使硬度有所提升。在高溫抗氧化方面，在 1100 ℃ 以及 1300 ℃ 氧化試驗結果都顯示隨著 Si 含量的增加，抗氧化能力有明顯的提升，但 1300 ℃ 高溫下無法形成較緻密氧化層，氧化速率甚快。均質化處理對合金抗氧化能力並沒有明顯提升作用，其氧化機制與鑄造態相似。在壓縮試驗方面，隨著 Si 的添加合金在室溫下的強度有所提升，但延性相對減少。而 700~1100 ℃ 整體強度亦有所提升，且抗軟化能力增加。整體而言，添加適量的 Si 進入合金中在密度、室溫及高溫強度、延性及抗高溫氧化的能力有最佳的綜合表現。