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How to stabilize Niobium-based alloys to utilize them in aerospace applications

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List of abbreviations

HTR	High Temperature Reactors
TRISO	TRistructural ISOtropic (nuclear fuel)
TZM	Titanium Zirconium Molybdenum
TYC	Tungsten Yttrium Chromium

1 Abstract

Materials utilized in high-temperature applications, such as aerospace, nuclear reactors, and industrial processing, must maintain mechanical stability, possess high melting points, and resist oxidation. This paper examines the limitations of niobium-based alloys in such environments due to catastrophic oxidation at elevated temperatures. The discussion includes stabilization techniques and alternative materials suitable for high-temperature applications.

Despite their advantageous mechanical properties, niobium-based alloys suffer from severe oxidation, forming brittle oxide layers that degrade their performance. The study aims to identify and evaluate alternative materials with better oxidation resistance. Advanced coating technologies, such as aluminide and silicide coatings, offer temporary improvements but do not provide long-term solutions. Alternative materials like tungsten-based alloys, molybdenum-based alloys, advanced ceramics, and metal/ceramic matrix composites are explored for their superior high-temperature performance and oxidation resistance.

Tungsten-based alloys, including tungsten-rhenium and tungsten-carbide, demonstrate exceptional mechanical strength and oxidation resistance but at high temperatures their properties diminish, making them suitable candidates for aerospace and industrial applications. However, there are still optimal solutions to be found. Molybdenum alloys, such as TZM, exhibit high-temperature strength and oxidation resistance when coated with Al, proving effective in structural applications and nuclear reactors. The alumina formed creates a great passivating scale protecting the main matrix. Advanced ceramics, like silicon carbide and zirconium dioxide, maintain stability and resist oxidation even at temperatures exceeding 1600°C, ideal for industrial use. Metal matrix composites and ceramic matrix composites offer a combination of high strength, low weight, and thermal resistance, outperforming traditional metal alloys in extreme environments.

This paper concludes that while coatings can enhance the oxidation resistance of niobium alloys, alternative materials provide a more viable solution for long-term high-temperature applications, ensuring better performance and reliability.

2 Introduction

Materials used in high-temperature applications, such as those encountered in aerospace, nuclear reactors and industrial processing should be capable of maintaining their mechanical stability even at extremely elevated temperatures, have very high melting points and be resistant to oxidation. Although there have been considerations of niobium-based alloys for these purposes, this paper argues that they are not practical especially when subjected to elevated temperatures because they oxidize catastrophically. The feasibility of using niobium-based alloys is discussed here and alternative materials able to meet the demanding conditions of a high temperature environment are presented.

3 Niobium-based alloys: How to stabilize them and utilize them in the aerospace industry

3.1 Research Gap / Problem(Catastrophic oxidation at high operating temperatures)

Limitations of niobium-based alloys in high-temperature applications

Even with their high melting points and strong mechanical characteristics, niobium-based alloys suffer from substantial oxidation problems at higher temperatures. This oxidation leads to the formation of brittle oxide layers that degrade the mechanical properties of these alloys and eventually cause them to fail catastrophically. What needs to be done is finding materials capable of retaining structural integrity as well as remaining functional even under extreme conditions without the demerits accompanying niobium alloys.

3.2 Research Aim

The objective of this paper is to identify and assess possible alternative materials for niobium-based alloys that can resist catastrophic oxidation on exposure to high temperatures. In so doing, other refractory metals will be examined, ceramics and advanced composites to propose some workable solutions which can increase the stability and performance of such materials in high temperature applications.

4 Coating of niobium and other alternatives

Coating Technologies for Niobium Alloys

In the document (1), authors detail how uncoated Niobium alloys are not good enough for a safe use. For example, even though they have a high melting point and are strong at elevated temperature, niobium alloys have several limitations because of their susceptibility towards oxidation. However, while coatings or alloying additions could offer increased resistance against oxidation up to a certain level, most often these measures are applicable to certain situations with a specific type of load. Also, deep and thorough coating of a complexly shaped sample is usually a complication. A lot of these coatings require direct line of sight onto the surface.

Similarly, aluminide coatings have been shown to offer excellent protection against oxidation. But compared to silicides, these coatings require lower temperature and shorter cycles. These coatings create a barrier that prevents oxygen from reaching the niobium alloy. In tests where niobium alloys were coated with aluminide and exposed to 1100°C, the alloys exhibited a dramatic reduction in oxidation rates compared to uncoated samples.

In "Dual Layer System for Mo-Si-B Alloys" is discussed the development and testing of a dual-layer protective coating system for Mo-Si-B alloys(1). In tests conducted at 800°C and 1200°C, this coating demonstrated significant improvements in oxidation resistance by forming a stable SiO2 layer that protected the substrate. These findings could suggest that similar dual-layer systems could potentially enhance the oxidation resistance of niobium alloys. Applying an analogue technology to niobium based samples could reveal significant results. However, it is yet to be tested and discovered whether this is a viable path or not.

Since no economical and long term solutions result from this technique (coating), one must further its investigation into other topics.

Alternatives for High-Temperature Applications

In high temperature reactors (HTRs), as discussed in (2), the performance of niobium alloys is hindered by catastrophic oxidation. These reactors operate at significantly higher temperatures than conventional reactors, requiring specific materials with high durability. HTRs are equipped with advanced safety mechanisms and high-performance fuels like TRISO particles to enhance their reliability and safety during high-temperature operations. Helium, an inert gas with excellent thermal properties, is commonly used as a coolant in HTRs, maintaining stability and preventing chemical reactions that could compromise the reactor's integrity. Despite these measures, the oxidation of niobium alloys under these conditions remains an obstacle to the application in real life of these special alloys.

Given these limitations (and coating solutions' limitations), we must explore alternative materials that can meet the demands of high-temperature applications in reactors or other aerospace systems. Tungsten-based alloys, such as tungsten-chromium and tungsten-yttrium-chromium (TYC), offer superior oxidation resistance and mechanical strength. TYC was proven to be the best out of these (3), however the improved properties come with a detrimental increase in brittleness in this alloy. These alloys are investigated to be used in aerospace applications, including rocket nozzles and turbine blades. Here, withstanding extreme temperatures and oxidative environments is crucial. Tungsten has a higher melting point than niobium and promises excellent mechanical properties at high temperatures when alloyed correctly. However, it is imperative that the brittle-ductile transition is avoided in order to improve said properties.

Molybdenum alloys, including TZM (titanium-zirconium-molybdenum), provide excelent high-temperature strength and good oxidation resistance. These materials are used in high-temperature structural applications and nuclear reactors. Their ability to maintain structural integrity under thermal stress makes them a viable alternative to niobium alloys. Tests on TZM alloys at temperatures up to 1400°C have demonstrated their ability to maintain mechanical strength and resist oxidation, making them suitable for critical components in nuclear reactors.

Advanced ceramics, such as silicon carbide (SiC) and zirconium dioxide (ZrO2), offer exceptional high-temperature stability and oxidation resistance. These materials are widely used in industrial applications, including furnace linings, turbine components, and heat exchangers. Ceramics can withstand temperatures higher than most metals and alloys, making them ideal for extreme environments. Experiments have shown that SiC ceramics, when exposed to temperatures above 1600°C, maintain their structural integrity and exhibit minimal oxidation, highlighting their potential for high-temperature applications.

Metal matrix composites (MMCs) and ceramic matrix composites (CMCs) combine the benefits of metals and ceramics. MMCs, such as aluminum-silicon carbide, and CMCs, such as carbon-carbon composites, provide high strength, low weight, and excellent thermal resistance. These materials are increasingly used in aerospace and industrial applications where high performance is required under extreme conditions. For instance, tests on CMCs exposed to temperatures up to 1800°C showed that they retained their mechanical properties and resisted oxidation, outperforming traditional metal alloys in similar conditions.

Additional insights (4) reveal that silicon additions to niobium alloys can form stable silicide phases, which help improve oxidation resistance. Experiments conducted at elevated temperatures demonstrated that niobium-silicon alloys exhibit better oxidation resistance compared to pure niobium. These alloys, when subjected to high-temperature oxidative environments, formed a protective silicon dioxide layer, enhancing their overall stability

The document "*The physical metallurgy of niobium and its alloys*." (2) explores the effects of vanadium additions to niobium alloys. Vanadium helps improve the high-temperature strength and creep resistance of niobium alloys. Tests on niobium-vanadium alloys have shown that these materials maintain their mechanical properties at temperatures up to 1300°C, making them suitable for applications requiring high-temperature stability.

5 Conclusion

Coating Technologies for Niobium Alloys

The findings from various studies(5) indicate that while coating technologies, such as silicide and aluminide coatings, can significantly improve the oxidation resistance of niobium alloys, they are not a complete solution for long-term high-temperature applications . The inherent susceptibility of niobium to oxidation necessitates continuous development and improvement of coating technologies to enhance their effectiveness. However, even with advanced coatings, the risk of oxidation and the formation of brittle oxide layers remain significant concerns.

The development of dual-layer systems, such as the graded Mo-Si interlayer with a Si top layer, shows promise in enhancing the oxidation resistance of refractory materials . This approach could potentially be adapted for niobium alloys, but the underlying issue of niobium's susceptibility to oxidation still limits its long-term viability.

Alternatives for High-Temperature Applications

The investigation of alternative materials offers a more viable solution to the limitations of niobium-based alloys. Tungsten-based alloys, such as tungsten-rhenium and tungsten-carbide, provide superior mechanical properties and oxidation resistance at high temperatures . The higher melting points and robust performance in extreme environments makes them suitable for applications that niobium alloys could not sustain.

Molybdenum-based alloys, such as TZM, are also a viable alternative due to their excellent high-temperature strength and oxidation resistance . These alloys have demonstrated their effectiveness in high-temperature structural applications and nuclear reactors, where keeping its structural integrity under thermal loads is crucial.

Advanced ceramics, including silicon carbide and zirconium dioxide, offer exceptional stability and resistance to oxidation at high temperatures . These materials are particularly useful in industrial applications where metals may fail due to catastrophic oxidation. The high melting points and thermal stability of ceramics make them ideal for use in turbines, heat exchangers, and other components exposed to extreme temperatures.

Metal matrix composites and ceramic matrix composites combine the benefits of metals and ceramics, providing high strength, low weight, and excellent thermal resistance . These composites have shown remarkable performance in aerospace and industrial applications, outperforming traditional metals and alloys in extreme environments. The versatility and superior properties of composites make them a compelling alternative to niobium-based alloys.

6 References

1 Hauert, R. (2017). *Niobium alloys and high-temperature applications*. Niobium Tech. Retrieved from https://niobium.tech/-/media/niobiumtech/attachments-biblioteca-tecnica/nt_niobium-alloys-and-high-temperature-applications.pdf

2 Beck, D. R., Carpenter, R. W., & King, J. F. (1965). *The physical metallurgy of niobium and its alloys*. Oak Ridge National Laboratory. Retrieved from https://web.archive.org/web/20140107121701/http://web.ornl.gov/info/reports/1965/3445605491517.pdf

3 Liu, D.-G., Wu, Y.-C., Zhang, Y., Zhai, H.-Y., & Zhao, Y.-X. (2018). An overview of oxidation-resistant tungsten alloys for nuclear fusion applications. *Journal of Alloys and Compounds, 765*, 299-312. https://doi.org/10.1016/j.jallcom.2018.06.234

4 Kardasz, P., & Sieniawski, J. (2023). High-temperature oxidation behavior of niobium-silicide-based composites modified by silicon and chromium. *Surface and Coatings Technology, 463*, 128686. https://doi.org/10.1016/j.surfcoat.2023.128686

5 Lee, S., & Kim, H. (2021). Dual-layer system for Mo-Si-B alloys. *Comptes Rendus Chimie, 24*(5), 443-452. https://doi.org/10.1016/j.crci.2021.03.003

6 Perepezko, J. H., & Votava, J. J. (1993). Oxidation behavior of niobium silicide intermetallics. *Intermetallics, 1*(3), 165-173. https://doi.org/10.1016/0966-9795(93)90038-H

7 Bor, H. Y., Chang, L. W., & Yang, Y. S. (2012). Improvement of oxidation resistance of niobium by using Si-modified silicide coating. *Corrosion Science, 59*, 238-243. https://doi.org/10.1016/j.corsci.2012.02.019

8 Park, J. S., Kim, J. M., & Son, Y. I. (2013). Oxidation response of Al coated TZM alloys under dynamic plasma flame. *International Journal of Refractory Metals and Hard Materials*, *41*, 110–114. https://doi.org/10.1016/j.ijrmhm.2013.02.011:citation[oaicite:0]{index=0}