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Investigating the Replacement of Nickel-based Superalloys with Niobium-Based Superalloys in the New Generation of Turbine Blades in the Aerospace Industry

Armin Ashrafi*

Department of Materials Science and Metallurgy, Sharif University, Tehran, Iran.

*Correspondence: armin.ashraf.78@gmail.com (Armin Ashrafi, Master of Material Science, Department of Materials Science and Metallurgy, Sharif University, Tehran, Iran).

ABSTRACT

To improve the thermal properties of superalloys or replacing them with new materials is necessary to increase engine efficiency. When considerable progress in superalloys is unlikely, researchers started to turn their attention to alternative materials. Metallic silicide alloys are cheaper choices for increasing engine efficiency. The melting point for molybdenum and niobium silicide is much higher than the melting point of the current alloys. This shows these alloys have the potential to increase temperature in gas turbine engines. These alloys have poor oxidation resistance. Improving oxidation resistance of each alloy system is a significant step toward a new material for turbine blades. To improve oxidation resistance in these alloys, many experiments have been done in which alloy elements such as Ti, Cr, Al, Zr, Ta, and Sn have been used. According to these experiments, it can be concluded that Zr is practically ineffective and it cannot improve oxidation resistance in alloys. In some temperatures, Ta is even harmful for oxidation resistance. Sn has the best function to increase oxidation resistance by forming a rich layer of Sn, oxygen penetration into depth is prevented. Despite these alloy elements, they are not enough resistant to oxidation to function in higher temperatures. To be replaced by nickel-based superalloys in gas turbine blades in the aerospace industry they need to have higher oxidation resistance.

Keywords: Oxidation, Nb-Si alloy, Turbine blades, Engine turbine, Superalloys, and Direct metal deposition.

INTRODUCTION:

Engine turbine is one of researchers' favourite parts in aerospace industry. Aircrafts engines turbine receives fuel and combustion air from combustion chamber directly. This gas is under high pressure and it contains corrosive substances and it also has high temperature. In current engines of civilian aircrafts, the temperature can reach up to 1500°C that can be a hostile environment for most substances. Suitable substances should have good strength in high temperatures. These parts are made of substances that are resistant to creep deformation in loads lower than the yield point of that substance. Because in high temperatures deformation such as creep increases. These substances must resist oxidation. Oxidation is a significant problem in high temperatures because atoms have the required energy to overcome activation energy for oxidation reactions. Nickel-based superalloys have been used for such functions since the 1940s. Nickel-based superalloys have good resistance at high temperatures. By removing grain boundaries, single crystal alloys increase resistance against creep considerably. Superalloys are also oxidation-resistant. They contain a high concentration of aluminum and chromium that help the formation of stable oxide layers (Douglas, 2020). There is great pressure on the aerospace industry to reduce emissions as ecological targets across the globe become more stringent. Lowering fuel consumption also benefits airlines by reducing fuel costs and/or increasing the number of passengers that can be transported (Moniruzzaman *et al*., 2022).

Efficiency improvements can be made in the turbine section of the engine, hence why it is an area of significant research. Above mentioned points show that considerable improvement in thermal properties of superalloys or replacement them with a new material is needed to improve the engine efficiency. When considerable progress in superalloys is unlikely, researchers have turned their attention to alternative materials. Metals in the platinum group have high melting points that are higher than the current temperature of the engine. These materials are flexible in standard temperatures and most of their compounds are resistant to corrosion in high temperatures because they have a low thermodynamic potential to form oxide. However, these alloys are condensed. The density of pure platinum is 21.45gr/cm3 but the density of superalloys is 8gr/cm3. This leads to an increase in concentration, weight, and a decrease in engine efficiency. The high cost of alloys of this kind is a bigger problem. In the markets, palladium and platinum are sold at 40/000 and 27/000 pounds for each kilogram, respectively. One kilogram of nickel costs 11 pounds. The turbine blade is an important part, each blade in an engine costs up to 8000 pounds. Such an increase in the cost of materials causes a considerable increase in the cost of an engine. It looks unlikely that airlines would accept such increased costs without considering efficiency improvements.

Theoretical foundations

Gas turbine engines

For the past 70 years gas-turbine engines have been the primary power source for most aerospace vehicles. When compared to piston engines, gas-turbine engines do not lose propulsive efficiency when approaching the speed of sound, have reduced maintenance requirements and greater efficiency over the majority of flight plans (Douglas, 2020). This efficiency is achieved by greater thrust to weight ratio. Piston engines only remain economically viable where power requirements and altitude of flight are low (Soares, 2011). Gas-turbine engines are commercially available in several different configurations, each suited to a specific need. Turbojets were the first gas-turbine engine to be produced. These are efficient above Mach 1 but below this speed the efficiency of these engines decreased significantly (Farokhi, 2021). Turbofan is a kind of jet engine in which a large amount of compressed air exists through the exhaust nozzle without passing the combustion chamber. Such an engine is suitable for average velocity. Engineers devised the turbofan engine to overcome this inefficiency at Subsonic speeds. Turbofans are the most common engine found in civilian aircraft. Among different kinds of drone engines, turbofan has more efficiency than jet engines. This engine is suitable for average velocity. Thus, the engine of most jet airliners is turbofan.

Nickel-based superalloys

Superalloys are corrosion-resistant. They are high-temperature alloys by the base elements of nickel, iron, or cobalt that function in temperatures above 500 °C. Superalloys have properties including strength, creep, strength and fatigue, corrosion resistance, and high strength at high temperatures for long periods. Superalloys are high-temperature corrosion and oxidetion resistance that chemically can be based on iron, cobalt, or nickel-iron and can be used based on their functional temperature. These days, nickel-based alloys are used in industrial sections as single-phase, precipitation-hardened by acidic precipitations and composites. Nickel-based superalloys have been the material of choice since the 1940s. **Fig. 2** shows that this material has excellent retention of strength at high temperatures (Douglas, 2020).

The advent of single crystal alloys significantly improved the creep resistance by eliminating grain boundaries, thereby removing one of the mechanisms that contribute to elongation. Superalloys are also resistant to oxidation, with significant amounts of aluminium and chromium helping to form stable oxide layers (Gasson, 2008). The aviation industry is notorious for emitting green-house gases and not decarburization. Environmental effects of air travel happen when aircraft engines produce heat, noise, particulates, and gas which can cause climate changes and decrease direct beam solar radiation gradually. Aircraft produce particulates and gases such as carbon dioxide, water vapour, hydro-carbon, carbon monoxide, nitrogen oxide, sulphur oxide, lead and carbon leading to reactions between these particulates and the atmosphere. There is great pressure on the aerospace industry to reduce emissions as ecological targets. Across the globe become more stringent. Lowering fuel consumption also benefits airlines by reducing fuel costs and/or increasing the number of passengers that can be transported. Efficiency improvements can be made in the turbine section of the engine, hence why it is an area of significant research. The idealised Brayton cycle, **Fig. 2**, shows the entropy vs temperature profile as the airstream passes through the engine. Energy is extracted from the airstream as it passes through the turbine and exits the nozzle (Shirey, 2019).

DISCUSSION:

Multicomponent alloys containing silicon and the niobium

It is obvious that two-component systems are not suitable for turbine blades. Commercial steels often contain seven or several different elements for optimizing steel for a special function. It is also true about aluminium alloys and nickel-based superalloys. Element redundancy allows metallurgists to regulate the microstructure and mechanical properties of alloy systems according to their needs. Elements such as Ti and Al are very useful for Nb-Si-based alloys (Douglas, 2020). The current nickel-based superalloys are manufactured using single-crystal investment casting but it has been proved that using such a method is difficult for Nb-Si-based alloys. In the next chapter, the reasons and alternative methods for producing Nb-Si-based alloys will be discussed.

The effect of the additive elements

Titanium

Titanium was one of the first elements considered for introduction into the Nb-Si alloys. With increased titanium addition the solidus temperature of the eutectic continually decreases, eventually reaching a minimum of 1330°C at maximum Ti content. The production of the Nb5Si3 silicide is slowly inhibited as Ti content increases above 25 at. %, replaced by the formation of Ti_5Si_3. This phase is a hexagonal closed-packed phase which has been shown to be detrimental to material properties (Douglas, 2020). To inhibit the formation of Ti_5Si_3 and keep the eutectic temperature >1700°C it is suggested to add no more than 25 at. % of titanium in a niobium silicide alloy. With added Ti content there is a significant increase in the fracture toughness, with values over 15 MPa $m^{0.5}$ achieved for alloy Nb-33Ti-16 Si, and dramatically improves the oxidation resistance of the solid solution phase. (Douglas, 2020).

Chromium

Cr is often added to alloys to improve corrosion resistance as it forms a stable oxide. Cr primarily partitions to the Nb_{ss} phase if the alloy atomic concentration of Cr is <6 at. %. Small concentrations, typically less than 2 at. %, can be observed in the silicide phase (Douglas, 2020).

Aluminium

As with Cr, Al mainly partitions to the Nb_{ss}, though Al is stable in the Nb_5Si_3 phase to a lesser extent. Al appears to supress the Nb_3Si phase and it supresses the phase more strongly than Cr does. The primary purpose of Al additions is to improve the oxidation resistance, the formation of an alumina scale seen as the optimal oxide scale at high temperature. (Douglas, 2020). With sufficient concentration aluminise phases can form, such as Nb_3Al. These do not tend to be beneficial to material properties as they possess poor ductility and result in poor creep resistance, though can increase high temperature strength (Douglas, 2020) Al has a relatively low melting temperature of ~660°C. It is generally recommended to keep Al addition ≤ 5 at % to keep the eutectic temperature at a sufficient temperature for the intended application. Al additions of 9-10 at % were shown to also have an adverse effect on the fracture toughness of Nb-Cr-Ti-Al alloys.

Molybdenum

In the literature, molybdenum tends to be included at low atomic percentage, >5 at. %. Small additions have been shown to increase the yield strength at high temperatures (1773 K) compared to binary niobium silicide. This is due to the solid solution strengthening of the Nb_{ss} phase. Mo addition also tends to favor the production of the βNb_5Si_3 over the alpha equivalent. This can lead to more brittle alloys with a lower fracture toughness (Douglas, 2020).

Producing niobium-silicide alloys (Nb-Si alloys)

Casting

Today, investment casting or lost-wax casting as an old process is of high importance to produce complicated parts with high-dimensional precision. High quality of surface, high-dimensional precision, unlimited capability in complex components, and casting all kinds of alloys without any parting line or flash are some of its advantages. Some of the disadvantages of this method are the high cost of making patterns and mold, the high cost of work, and the limitation in the size of objects (3gr - 5gr). However some aircraft components with a weight of 450 kg are manufactured using this method. Investment casting also called lost-wax casting or precision casting is an industrial process based on lost-wax casting which is used to manufacture metallic components of any type of alloy. It is usually used to produce complex components that have thin drafts. At the first stage, an expansible model made of wax or plastic should be provided, then this model is covered by a suitable refractory layer, it is dried and it is extracted from the mould. During refractory heating process materials are bonded, wax model is melted and it is extracted from the mould. Plastic model (usually polystyrene) is burnt without any residues. Then, the melted material is poured into the mould. The model is built by pouring or injecting wax into a metal mould. In some cases a simple model is produced in one step or by a gating system. In other cases, complex models are manufactured by assembling several separated components which have been made separately.

After forming wax model, in ceramic shell process the model is immersed in a slurry of soft refractory particulates via immersion methods to have a smooth surface, after that it is coated by more coarse refracttories and it is dried. These steps are repeated until a mould with a suitable thickness is prepared. Basic and secondary immersion coatings usually have binders such as ethyl silicate and refractories are mainly zircon, silimanite, and aluminium. Coating process is done via scattering or immersing a fluidized bed, a combination of both can also be used, one-piece moulding can be replaced (Douglas, 2020) In this method, the model is covered by a primary coating, then it is placed into the mould box. Secondary coatings are poured around to obtain a uniform mould. Ceramic shell casting is mostly used in manufacturing large components of metals with high melting point such as steel and nickel. One-piece casting is usually used for light alloys and for producing small and medium components. This kind of casting gives nickel-based superalloys by high creep resistance and maintaining strength at high temperatures in contrast to manufactured alloys (Douglas, 2020). This is due to decrease in grain boundaries created because of larger grains. However, grains of casting nickel-based alloys are still small. Considerable studies have been done on how to decrease grain boundaries (Douglas, 2020). Researchers have found out that directional solidifications in melted metal can lead to microstructures with parallel and large grains that grow. This can be done using a Bridgman furnace (**Fig. 1**).

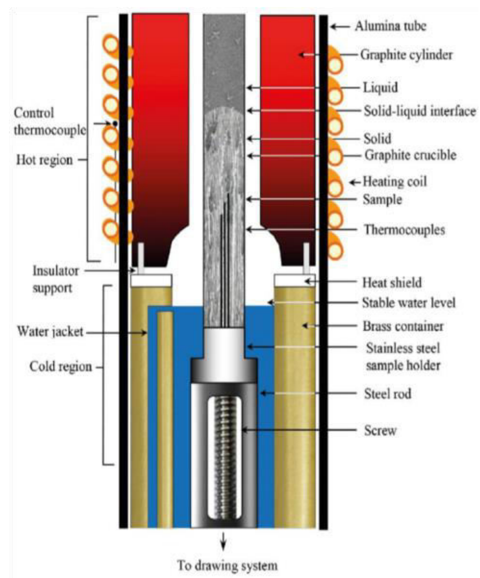

Fig. 1: Bridgman furnace scheme (Douglas, 2020).

Directional solidification is a suitable method to cast nickel-based alloys at high temperatures. Single-crystal nickel-based alloys have a high potential to have microstructure defects such as large dendrite defects, large lateral dendrites, and porosity-morphology of these defects can be understood by investigating the G/V ratio (in which G is the temperature gradient against the solidification rate and V is the solidification rate). This ratio needs to be within a suitable limit to create a single crystal with a correct microstructure having lateral dendrites. It is known that an increase in the cooling rate in the solidification rate can accelerate the improvement of material mechanical properties, and due to refined impurities in directional solidification, the age of single-crystal cleavage increases (Douglas, 2020). In directional solidification while single-crystal grows and when melted metal is poured in a cleavage between solid metal and the mould, some fake grains are created.

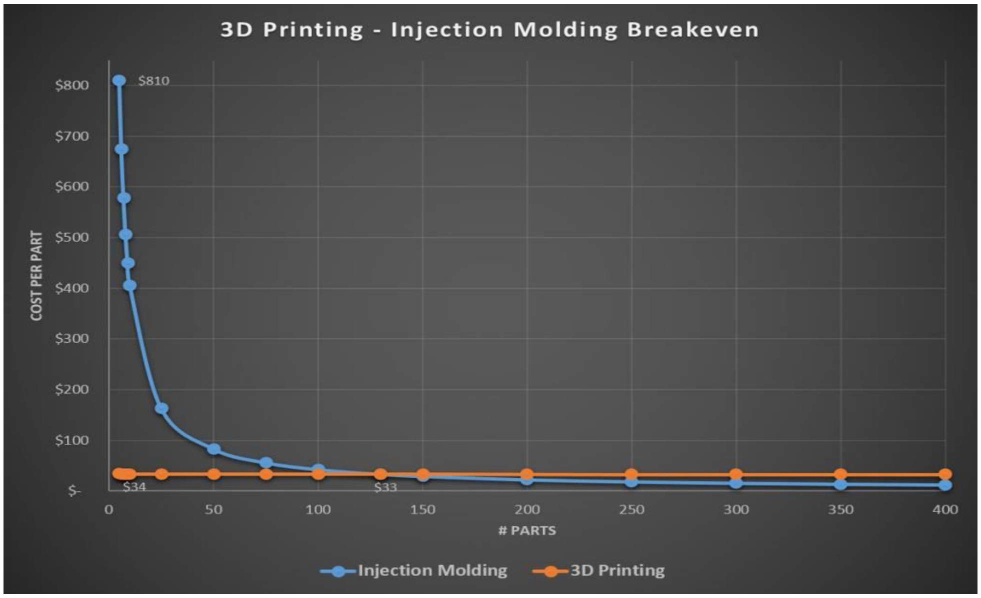

Fig. 2: Cost analysis of 3D printing vs injection moulding.

Casting shows an exponential decrease in cost per unit as the size of the production run increases. LAM shows a constant line, with cost per unit mostly independent of the size of the production run. When produced in large quantities, casting has a lower cost per unit. However, when small production runs are considered, LAM has a lower cost per unit. This make LAM suitable for products than only require a small number to be manufactured per year and for prototyping. Unfortunately, the high temperature of the liquid alloy results in catastrophic interaction with most standard ceramics used in investment casting, such as alumina or silica .

This interaction destroys the mould, so materials such as this cannot be used. Some success has been found using yttria as a mould mate-rial. However, in Nb-Si alloys containing Hf, research has shown that hafnium can replace the Y atoms in the mould, resulting in reduced Hf content and Y impurities in the solidified alloy. So far, there has not been a mould material that can successfully create a cast Nb-Si alloy without some interaction with the mould material. There is no suggestion in the literature that a useful mould material is on the horizon.

Direct Metal Deposition (DMD)

Direct Metal Deposition (DMD) is one of the metallic 3D printing technologies that is complicated in terms of process and technical knowledge. Besides the capability to manufacture components, it can be used to repair and rebuild metal components. This helps to repair expensive implements such as turbine blades and impellers using DMD printers to be reused. Similar to other metal 3D printing methods (such as SLM), the DMD printer uses an energy resource such as laser, electron beam, or plasma arc to melt materials. The difference is that the material (including metal powder or metal wire) is melted by laser while injected into the nozzle channel, fusion happens in a point near the nozzle (Douglas, 2020). Injection and melting by laser are done using nozzles which are on a multi-axis arm (usually 4 or 5 axis). Such nozzles usually have a complicated structure in which some channels are considered to carry the powder by carrier gas and inject it in several directions, laser ray or electron is located in the centre of the route. The process of metal melting happens in laser-powder interface (Douglas, 2020). Manufacturing complicate metal components with high precision is the main function of DMD printer. Each kind of metal that can be casted has the capability to be used in DMD process. Some of these metals include titanium and its alloys, nickel-chrome superalloys, tantalum, niobium, tungsten, aluminum, and stainless steel. In the DMD process, the size of the metal powder grain is usually 50-150 microns. When the wire is used in the process, the diameter is 1-3 mm. The capability to rebuild damaged metal components using a metal printer is one of the exclusive functions of DMD technology. DMD printers can rebuild destructed parts caused by corrosion or fracture. This requires cleaning the destructed part from any pollutants (Douglas,2020).

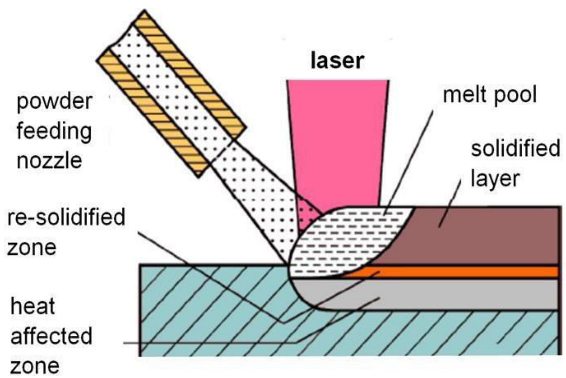

Fig. 3: Schematic of direct metal deposition.

Comparison of casting and DMD

Creating metallic parts using laser additive manufacture of any kind is still in its infancy. It is unlikely that it will replace casting in large production items, casting tends to become more cost efficient as the number of items in a production run increases. LAM does possess other benefits that can warrant its use over traditional casting. It can reduce the total time to go from design to product. When casting a new product, new master moulds need to be created and tools modified. In additive manufacture, once a CAD design is drawn then production can begin (Douglas, 2020). LAM can produce complex geometries with relative ease. This is because casting relies on the flow of molten melt into a predefined mould. Porosity, introduced from trapped atmospheric gas to void formation, is a problem familiar to castings; LAM has thus far not been able to eliminate this problem and can often have worse porosity than a cast component. Again, further treatment can reduce this problem at the expense of more production time (Douglas, 2020).

Oxidation of Niobium Silicides

Oxidation resistance is the ability of metallic materials to resist the chemical degradation caused by the action of air or other gaseous medium at high temperatures. The oxidation resistance of a metal or alloy in an oxidizing atmosphere is determined by the properties of the oxide layer-scale- that forms on the surface of the metal and inhibits the diffusion of gas into the metal, thus reducing the development of gaseous corrosion. The quantitative characteristics of oxidation resistance are the increase in the weight of the sample being studied (because of oxygen uptake by the metal), or the weight loss after removal of the scale from the surface of the sample, relative to a unit surface and the duration of the experiment. The condition of the surface of the sample or part is simultaneously taken into account; it may differ qualitatively even though its quantitative characteristics may be the same. Along with heat resistance, oxidation resistance is a basic criterion of the suitability of a given material for high-temperature service. In the past ten years, oxidation of niobium-silicide alloys has been the subject of numerous studies. Oxidation properties at temperatures above 700 ºc remain poor for these alloys. There have also been significant improvements made in the oxidation performance, primarily by using different elemental additions. Silicon increases oxidetion resistance to niobium alloys. There is still a long way to go before these alloys meet the required criteria, but the improvements suggest it will be possible to achieve an oxidation-resistant niobium silicide alloy. Because these alloys have the potential to be added to new alloys. Nickel-based superalloys can be used, which can lead to increased oxidation resistance. To rise in temperature needs creativity in adding alloy elements because new systems need improvements to replace with nickel-based superalloys. (Douglas, 2020)

Findings

In the future, aircraft engines need to be adapted to the environment and its functional goals. Such goals can be achieved by increasing thermal efficiency. Materials with more capabilities than nickel-based superalloys. Niobium-silicide alloys have the potential to achieve these goals. These alloys can have 12 additional elements. Nb_{ss} solid solution with bcc and

Nb_5Si_3 with tetragonal or hexagonal structure are two important phases in the microstructure of these alloys. Other intermetallic phases such as Nb_3Si can also be stable in this microstructure. Non-alloy Nb_5Si_3 has a better creep and oxidation resistance to non-alloy tetragonal Nb_3Si. Toughness strength and oxidation resistance in Nb_{ss} phase depends on the dissolved elements in solid solution. For instance, based on their concentration, elements of Al, Cr, HF, or Ti can have a positive or negative effect on the toughness strength of Nb_{ss}. Alloying can improve the properties of Nb_{ss} and affects the stability of different shapes of silicides. For instance, at low temperatures, it makes the tetragonal shape of α-Nb_5Si_3 stable, or at high temperatures, it makes tetragonal β-Nb_5Si_3 stable. The type and stability of silicate compounds in Ni-Si alloys depend on solidification conditions in alloying. For instance, binary alloys of amorphous Nb Si binary alloys and a eutectic near point we are created via rapid cooling of melt, and Nb_3Si alloy is created during the annealing function. Ni-Si alloys are subjected to more than 100 hours of heat treatment at temperatures higher than 1773 k. Based on the references it was concluded that the DMD method can be an appropriate method to manufacture oxidation-resistant Nb-Si alloys. Whether made materials using additive elements in DMD have an uneven elemental distribution or not, is one of the important cases in macro segregation. Fortunately, there is no sign of macro segregation in made alloys using this method. Two similar alloys, one made by DMD and one produced by a casting method are compared; DMD sample has better quality than the cast sample. In DMD, the total time of the process from design to production decreases. Creating metallic parts using laser additive manufacture of any kind is still in its infancy. It is unlikely that it will replace casting in large production items, casting tends to become more cost-efficient as the number of items in a production run increases. Thus, the production cost is the main challenge in replacing casting with the DMD method. The current study aimed to investigate the replacement of new alloys of Nb-Si which are oxidetion-resistant at high temperatures to be replaced with nickel-based superalloys. Alloys with poor oxidation resistance at high temperatures were the main challenge ahead. Considering elements properties, additive elements to manufacture these alloys include aluminium, titanium, chrome, and molybdenum. By using these elements and niobium and silicide, a reference alloy named Chemistry A is made. In contrast to the simple binary alloy of Ni-Si alloy, Chemistry A oxidation resistance considerably improves at 800 and 1200 ºc. However, it is not still suitable for replacing nickel-based superalloys in gas engine blades. Accordingly, it needs to add other elements to this alloy. Addition of Zr at 800 ºc in low concentration was the main idea in literature to improve oxidation resistance of these alloys which have a few advantages. This additive element cannot prevent fracture in silicide phases at 800 ºc, so it cannot prevent exfoliation. It was also proved that Zr has no impact on 1200 ºc. TCAZ is made by adding Ta. Ta functions weakly at 800 ºc. It is accompanied by weak linear velocity and deep fracture in IOZ layer and external oxide layer. The mechanism for this is not yet understood. It may be related to increase in the amount of Nb_{ss} phase. At 1200 ºc TCAZ and especially TCAZ1 containing Ta showed a better function than Chemistry A. This is due to improvement in Ta resistance to oxygen penetration via Nb_{ss} phase. Overall, despite Zr not performing as well as was hoped, improvement to the oxidation resistance of Nb-Si alloys was gained. Thus, it can be said that Zr addition to replace nickel-based superalloys has no use. Although Ta functions well at1200 ºc, another element is needed to improve oxidation resistance at 800. For this reason, alloys containing Sn were tested. Sn addition helps oxidation resistance at 800 and 1250 ºc. Formation of a Sn-rich layer between oxide layer and substrate, this layer functions as an obstacle to oxygen penetration that leads to a decrease in oxygen penetration into inner layers. Thus, Si-based alloys have the best oxidation resistance. As it was mentioned 2Sn alloy could reach an acceptable oxidation resistance with undamaged, even, and no cracking morphology. Generally, despite Zr not performing as well as was hoped, improvement to the oxidation resistance of Nb-Si alloys was gained.

CONCLUSION:

In short, this study has shown that DMD can Produce Nb-Si alloys that are at least as oxidation resistant as a cast counterpart. This can be done without fear of uneven elemental distribution. Generally, poor oxidation resistance of these alloys at high temperatures is the most important obstacle to replace nickel-based superalloys with niobium-based alloys in gas engine turbine blades. At high temperatures, the formation of Nb_2O_5 causes faster oxidation that prevents the formation of a continuous silicide layer. Niobium-based alloys have the potential to be replaced with nickel-based superalloys in gas turbine engine blades. The used alloy must contain alloy elements including Si, Ti, Cr, Mo, Al, and Sn. Despite these alloy elements, they do not have enough oxidation resistance to function at high temperatures. To replace with nickel-based superalloys in gas turbine engine blades in aerospace industry, they need to have an oxidation resistance higher than the obtained limit. One thing this study did not achieve was to analyse the effect of these additions on the material properties such as fracture toughness, tensile strength, and creep. Fracture toughness is of primary concern as this is often the property that is weakened at the expense of improved oxidation resistance. Future works can be done on material properties and improvement of Ni-Si alloy properties particularly for fracture toughness. Experimenting with higher temperatures is another concern. Turbine blades made of nickel-based superalloys can resist 1350 ºc. Niobium-based alloys have the potential to function above 1900 ºc. This is in favour of airlines because efficiency improvements can be made in the engine and the number of passengers that can be transported increases. Experiments on Ni-based alloys at 1250 ºc showed oxidation resistance is unacceptable at this temperature. Some improvements were achieved but current nickel-based superalloys can resist this temperature. Some experiments must be done on niobium-based alloys near 1900 ºc to increase their oxidation resistance to replace Ni-based superalloys in gas-turbine blades in the aerospace industry.

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CONFLICTS OF INTEREST:

The author has declared no conflict of interest.

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