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**USING MAGNETRON SPUTTERED, NANOSTRUCTURED COBALT-BASED ALLOYS WITH CHROMIUM COMPONENTS IN A GAMMA AND GAMMA PRIME PHASE AS A FORM OF CORROSION CONTROL ON AIRCRAFT TURBINE ENGINES**

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***Abstract****—Corrosion is a costly, natural, destructive process with numerous causes. The cost of corrosion is not limited to monetary value—it can also be costly in terms of safety. Due to high temperature environments, the rate of corrosion increases in aircraft turbine engines, which poses a safety hazard. Hot corrosion is the primary type of corrosion impacting aircraft engines while corrosion due to external environmental factors impacts aircraft turbines. An effective solution to corrosion in both aircraft turbine engines is the application of a nanomaterial coating to create a barrier between the corrosive agent and the substrate. Nanomaterials’ higher grain boundary density reduces the volume of open space between the substrate and corrosive agents, while their higher surface energy allows them to resist a phase change at higher temperatures. An example of real-world usage of this technology by a current company is studying nanolayered materials for corrosion control. Cobalt’s resistive characteristic to corrosion at high temperatures makes it one of the only suitable materials to combat corrosion in aircraft turbine engines. While nanostructured cobalt-based alloys with tungsten and chromium components in a gamma and gamma prime phase have benefits in the application of corrosion resistance in aircraft turbine engines, there are possible drawbacks of using cobalt in terms of physical properties such as weight and ethical dilemmas. The possibilities for further research in the application of this technology will be explored. Through analysis of these cobalt-based alloys in a gamma and gamma prime phase along with the properties characteristic to nanostructured materials, their suitability for corrosion prevention in aircraft turbines and engines will be delineated.*

*Key Words—Nanomaterials, corrosion control, cobalt, high heat output machinery, aircraft safety*

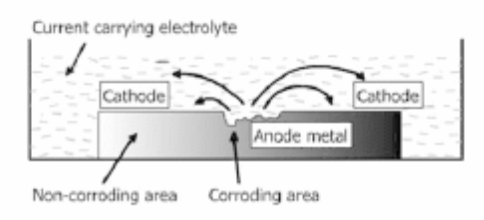
**CORROSION AND AIRCRAFT TURBINE ENGINES**

Corrosion is a natural chemical process that occurs when metals are exposed to reactive environments, which causes surface wastage [1]. According to Zaki Ahmad, author of *Principles of Corrosion Engineering and Corrosion Control*, “Corrosion is an aspect of the decay of materials by chemical or biological agents” [1]. Corrosion prevention on aircraft turbines is an important research topic due to the extreme environmental conditions they are exposed to which subjugate them to high corrosion rates.

**THE BASICS: CORROSION**

**Basic Corrosion Science**

Corrosion can only occur when there’s formation of a corrosion cell—as shown in figure 1—which is made up of four parts: the anode, cathode, electrolyte, and metallic path [1].



**Figure 1 [1]**

**Illustration of a Corrosion Cell**

The anode is the negative terminal for the corrosion cell, where electrons are released. An anode is the area in the cell where metal is lost due to oxidation reactions [1]. The counterpart to the anode is the cathode, the positive terminal of the corrosion cell. The reactions that take place at the cathode are reduction reactions, where the cathode consumes the electrons released by the anode [1].

Corrosion requires an electrolyte—an electrically conductive solution—to occur, because the electrolyte carries charge from anode to cathode, thus allowing for the oxidation and reduction reactions that cause corrosion [1].

The last piece required for a corrosion cell is the metallic path, which is simply an external metallic conductor which allows conventional current to flow [1]. Once all four parts are present, a corrosion cell can form, and the oxidation and reduction reactions begin corroding the metal.

The formation of corrosion cells generally falls under the category of localized corrosion, meaning the corrosion affects a small piece of the metallic structure instead of the whole structure [2]. The most common localized corrosion to result from localized chemical damage is pitting corrosion. Pitting corrosion causes holes or cavities in the metallic structure of the substrate through an abnormal anodic site using the surrounding metal as the cathodic site [2]. Compared to generalized corrosion, pitting corrosion can be more dangerous due to its relative difficulty in being spotted before it can cause larger problems, such as stress corrosion cracking, where the combination of corrosion and stress can split and crack metallic objects [2].

**Corrosion and Air Safety**

Aircrafts are an integral part of modern society, with both commercial and recreational ties. People are impacted by aircrafts every day. According to the Federal Aviation Administration (FAA), aircrafts were responsible for the transportation of 39.9 billion pounds of freight in 2016 [3], which is a large fraction of goods transported in the United States. In addition to the commercial sector’s dependence on aircrafts for transportation, the public also greatly relies on aircrafts daily. A study by the FAA found that an average 2,587,000 passengers fly in and out of United States airports alone every day [3]. People use aircrafts for reliable travel, and it’s important to maintain the safety of passengers by maintaining the integrity of the aircraft’s structure and mechanical parts.

**CORROSION SCIENCE IN AIRCRAFT TURBINE ENGINES**

**Corrosion Types Impacting Aircraft Turbine Engines**

Aircraft turbine engines are in conditions when flying that allow for the formation of corrosion cells. Without proper protection, the moisture in the atmosphere can act as the electrolyte in the corrosion cell. While this moisture is mostly water, it will also contain other environmental pollutants such as particulate matter, which can physically damage parts inside the engine and act as the electrically conductive solution through which electrons can flow and cause corrosion [4].

Besides oxidation corrosion, aircraft engines are susceptible to a specialized form of corrosion called hot corrosion, which has been referred to as “accelerated corrosion” [5]. Hot corrosion results from the presence of salt contaminants such as sodium sulfate (Na2SO4) and vanadium oxide (V2O5) [5]. When gas turbine engines combust fuel, which can contain between 0.3-1.0% sulfur, the sulfur is released into the engine to react with salt contaminants from the outside air [6]. Sulfur commonly reacts with sodium chloride from saltwater to create sodium sulfate [6]. The formed salt contaminants form molten deposits on the inside of the engine’s parts and damage protective surface oxides by accelerating oxidation in that localized area [6].

The specific type of hot corrosion impacting aircraft turbine engines is Type 1, which is characterized to take place in environments over the temperature of 850 degrees Celsius [5]. The most commonly used protective oxide layers have a high concentration of chromium, which allows for strengthening of the protective coating [4]. When hot corrosion begins to oxidize inside an aircraft engine, chemical reactions begin to deplete the chromium inside the protective layer [5]. This begins the four stages of hot corrosion, beginning at initial onset and continuing until mechanical failure. The first stage begins with the localized breakdown of the oxidized layer, but chromium depletion doesn’t begin until the second stage [5]. Once chromium depletion begins, the corrosion moves into the third stage of breakdown where the mechanical integrity of the metal is compromised [5]. The final stage of hot corrosion can be recognized by drastic color changes in the metal (ex. The metal turning green) or peeling [5]. At this final stage, failure of the part is likely due to a great loss of structural material [5].

**When the Aircraft is at Highest Risk for Corrosion**

In addition to the external corrosive conditions, conditions inside aircraft engines make corrosion prevention a bigger challenge than in other environments. Because of the combustion of fuel, aircraft engines’ internal temperatures can reach up to 1,400 degrees Celsius [7]. The first law of thermodynamics states that energy cannot be created or destroyed, so the change in an object's internal energy is equal to the heat added to the system minus the work done by the system [8]. In an isolated system, this equals zero. As heat is added to the system, the gas particles push outward and do work in the process. According to the second law of thermodynamics, the universe is always moving towards a more disordered state [8]. These two laws draw the conclusion that while energy is conserved, a thermal engine will never be at 100% thermal efficiency because no engine is a perfectly isolated system, so energy will change into a non-usable form and the work done by the system will not be equal to the heat energy added.

According to Gay Lussac’s Law, as the temperature of a gas increases, so does the pressure [8]. This can be seen in the Brayton cycle, which states that the thermal efficiency is dependent on the ratio of the internal pressure to the external pressure raised to a negative number based on the gases [8]. Thus, thermal efficiency can be increased by increasing the temperature of an engine [4]. This is why it is more beneficial in both a cost effective and environmentally friendly manner to run an aircraft turbine engine at a hotter temperature since it will do more work. Because the engine has to run at a higher temperature to remain efficient, the internal environment is nearly always hot when the engine is running. The rate of corrosion is temperature dependent, meaning when environmental temperature increases, as does the rate of corrosion [4]. Due to the aircraft engine’s high internal temperature, the rate of corrosion inside the engine and on the turbines increases, making the metallic parts more susceptible to corrosion.

Another factor affecting the rate of corrosion in aircraft turbine engines is pressure. Higher pressures increase the rate of corrosion. Changes in pressure change the rates of corrosion, meaning that an aircraft turbine engine is most vulnerable to corrosion during take-off and landing, when the pressure inside the engines is changing rapidly [4]. This also means that the amount of corrosion doesn’t entirely depend on the time an aircraft is in the air, but it depends more on how many times the plane takes off and lands, meaning smaller planes making more trips are more likely to be majorly affected by corrosion [4]. While increasing the temperature and pressure of the engine may make it more efficient, it also makes it more susceptible to corrosion which is why anti corrosion methods are necessary.

**SPECIFIC CORROSION IN AIRCRAFT TURBINES AND ENGINES**

**How an Aircraft Engine Works**

According to Scientific American, a typical turbojet engine is divided into three main sections: the compressor, combustion chamber, and turbine [9]. The compressor is made up of many fans with blades that direct the flow of air through the compressor. The compressor then squeezes the air resulting in a high pressure to increase the energy potential of the air and is forced into the combustion chamber. Here the air is sprayed with fuel and ignited by an electric spark which causes a rapid expansion of the compressed gas through the turbine, which is made up of a series of blades like the compressor. The hot air rapidly passing through the turbine spins the turbine blades subjecting them to high temperatures and pressure. The spinning turbine is connected to shafts that drive the compressor which will then draw in more air to repeat the process. The expelled air leaves the turbine rapidly with a large momentum. Due to the conservation of momentum, the aircraft will gain a forward thrust in the opposite direction of the gas at the same momentum as the gas leaving the turbine [9].

**The Importance of Harsh Conditions in Aircraft Turbine Engines**

Parts on an aircraft have a life expectancy measured in the number of take-offs and landings it performs [10]. This conclusion can be drawn from the increase in the corrosion rate caused by the thermal energy released during take-offs and landings, and the quick increase in pressure during landing [10]. Increasing the aircraft’s resistance to corrosion will result in more cost-effective maintenance caused by fewer replacements being required and an overall increased air travel safety by reducing the chance of unexpected failures in the turbine engines.

**The Importance of Material Selection**

Because of a unique set of factors affecting corrosion in aircraft turbine engines, a specific type of material must be used as a form of corrosion prevention. A reason that certain other methods of corrosion prevention aren’t used in aircraft engines is simply because they couldn’t withstand the harsh environment. For effective corrosion prevention in an aircraft turbine engine, the material used as a corrosion inhibitor must have a high melting point so it can stay bonded to the substrate regardless of environmental temperature.

This high temperature also causes a problem because of the inevitable rise in the rate of corrosion. A rise in the temperature, and consequently the rate of corrosion, means that the material being used as protection against corrosion must have a higher corrosion resistance [4]. As the rate of corrosion increases, the protection against corrosion must be strong enough to withstand the rate increase, so some materials that work as great corrosion inhibitors at room temperature can start to fail as temperature increases [4].

**Aircraft Mechanical Failure Caused by Corrosion**

While it is rare for aircrafts to have mechanical failure during a flight due to corrosion, there are instances where this has happened. On June 24th, 2013, an Airbus A330-243’s take-off was aborted when the right engine caught fire on the way down the runway [11]. Upon investigation of the incident, it was discovered that corrosion had caused the dislocation of a turbine blade, which then detached and caused a high-power engine surge. This surge irreparably damaged the engine, causing it to catch fire [11]. While this incident had no casualties, corrosion inside the aircraft turbine engine put the passengers’ safety unnecessarily in danger.

**THE IMPORTANCE OF CORROSION CONTROL**

**Basic Corrosion Control**

Corrosion can be prevented through various techniques, one of the most effective being coatings. The coating is chosen specifically to protect the substrate from corrosive agents, which means it must have good resistance against corrosion [1]. In choosing possible materials, the degree of adhesion to the substrate must be considered so that the coating will remain on the substrate throughout the necessary conditions the object will be subjected to [1]. The three most important factors in coatings are the resistance, discontinuity, and diffusion rate of ions. Higher resistance to the flow of electrons makes it harder for a corrosion cell to form, therefore making the coating more effective against corrosion [1]. An ideal coating has minimum discontinuity, meaning the coating is not porous, which would allow for greater oxidation and risk of corrosion [1]. Along with this, a strong coating will also have a low diffusion rate for ions [1]. These elements when utilized are part of what makes protective coatings effective, and one of the preferred approaches to corrosion prevention.

Protective coatings are designed and chosen for applications based on their ability to form an oxide layer with the low porosity and diffusion rate, but also a high resistance to electron flow [1]. Coatings are chosen based on the environment they will be in and what they’re most likely to react to. The film reacts with the corrosive agents to form a non-porous oxide layer, which will prevent the corrosive agents from reaching the substrate [12]. This is different from corrosion oxidation because this is selective oxidation, meaning that the coating oxidizes in place of the substrate. Based on specific properties of the chosen coating, the formed oxide layer will prevent further oxidation to the substrate, thus preventing corrosion [12]. The chromium in specific cobalt-based alloys will oxidize before any other elemental compound in the alloy and is used as a sacrificial component by oxidizing to create the film to combat corrosion [4].

**Magnetron Sputtering**

An effective technique for depositing thin films and coatings is sputtering—a specific type of physical vapor deposition (PVD). Sputtering uses plasma in a vacuum to bombard the target plate with ions, which remove target atoms from the plate [13]. The target atoms then collect on the substrate as a thin film. This technique is effective because it allows for a thin, uniform coating of film, which can be monitored in real time to control thickness [13].

A more effective, specific type of sputtering is magnetron sputtering, where a magnetic field is used parallel to the target surface [13]. This magnetic field increases the chances of collisions between the ions and the target atoms, which directly increases ionization efficiency. The addition of this magnetic field fixes problems with traditional sputtering such as low deposition rate and high substrate heating [13]. However, the deposition rate is limited by the heating curve with respect to current. As the current increases, so does the sample temperature [14].

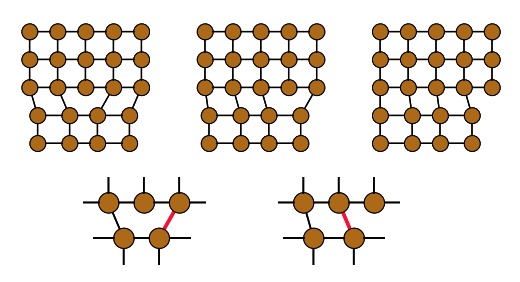
**The Cost of Corrosion**

Corrosion control is important not only in terms of safety, but also in monetary terms. Despite the preventative measures that exist, corrosion costs the economy money, both through direct fixes to infrastructure and damaged materials as well as losses in efficiency [1]. In 1998, corrosion directly cost the United States ca. $276 billion, $29.7 billion being directly related to corrosion in transportation [15]. In the aerospace industry specifically, 10% of aircraft maintenance in the United States is directly related to corrosion [16]. Due to these large expenses, effective corrosion control can limit the amount of money spent on repairing corrosion damage.

**NANOMATERIALS FOR CORROSION CONTROL**

A nanomaterial is any material that has an average particle or grain size between one and 100 nanometers. A nanometer is one billionth of a meter or 1.0x10-9th of a meter.

When crystals are first formed during industrial processes, miniscule errors in the crystalline formation will form discontinuities in the bonds between the layers of the crystal called dislocations, as shown in figure 2 [17]. A material’s strength and resistance to deformation is linked to its ability to resist the movement of dislocations [17].



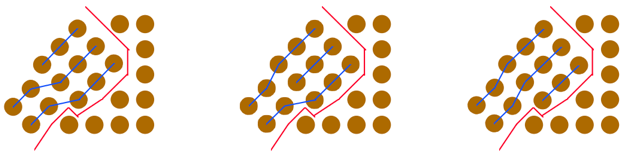
**FIGURE 2 [17]**

**An illustration of a dislocation**

A crystal’s slip plane is the plane of direction where dislocations can move easily and is therefore the weakest direction of a material [17]. The more a material’s grains are compacted, the more predominant the slip plane is parallel to its direction, but the less space is available for dislocations to move [4]. Forces do this by applying stress, which causes the atoms to move further apart while remaining tied together, similar to a spring. This stretches the loose bond between them and can cause yielding, which is when the stress exceeds the elastic limit [17]. When a bond yields, it will break, causing the shifted atom to re-form at a shifted position to another atom of the crystal. This causes permanent deformation which effects the structural integrity of the material. Any direction parallel to the discontinuity’s plane will have a maximum effect at shifting the dislocation compared to a perpendicular force [17].

When dealing with nanoparticles, the random orientation of each dislocation will cause the net orientation of every slip plane to be averaged out to result in a uniform strength in all of 3-dimensional space [4]. Because of this, compacting grains will not be affected by their slip planes and will instead only minimize the space for dislocations to move [4]. Any increase in temperature will result in an overall increase in kinetic energy available for a shift in a discontinuities position. This is known as thermal creep deformation [4]. This means that a material is much more susceptible to permanent deformation at higher temperatures, highlighting the need for stronger materials to counteract the effect [17].

When liquid metals solidify, the atoms crystallize into grains, which are the small units that make up the metallic structure. When acted on by a force, dislocations are stopped by the position of another grain in the direction of the force [18]. The area of this boundary between grains is called the grain boundary. Dislocations are not transferred between grains so once a dislocation has reached a grain boundary, it is no longer able to continue in that direction [18].



**FIGURE 3 [18]**

**An illustration of grain boundaries preventing the movement of a dislocation**

The total shift in dislocations adds up to an observable deformation [18]. Because of this, the strength of a material is based on the material’s ability to resist movement, and the higher the grain boundary density—the ratio of grain boundaries to dislocations—the more a material is able to resist dislocations [18]. Nanoparticles’ reduced size causes a greater ratio of surface area to volume, which in turn leads to a greater grain boundary density. Any increase in the grain boundary density caused by a reduction in a particles size will therefore have an overall increase in the material’s strength. This method is known as Hall-Petch Strengthening [18].

**Nanomaterials for Corrosion Control**

Nanostructures have a strong ability to oxidize selectively in order to create the protective, oxidized coating on the substrate [19]. Their ability to selectively oxidize is a direct result of the higher grain boundary density within their structures [15]. As the grain boundary density increases, as do the number of fast diffusion paths, which will promote selective oxidation and the formation of the protective oxide [20]. Another aspect of nanomaterials that make them ideal corrosion inhibitors in a harsh environment such as an aircraft engine is their high surface energy [15]. Higher surface energy means the materials can resist a phase change for higher temperatures [15], which is effective in aircraft engines with a high environmental temperature.

**Real-Life Example of Nanomaterials for Corrosion Control**

A company currently researching and manufacturing advanced nanolaminated materials is MODUMETAL [20]. MODUMETAL was the gold winner for the Edison Awards 2017 in the metal manufacturing category because of their unique metal additive process [22]. MODUMETAL produces their research and products through, as the CEO as, “growing metal like trees” [20]. Their specially-manufactured nanolaminated metals are produced through modulating an electric field to create a metal layered structure [20]. MODUMETAL creates a variety of materials that are designed as coatings to protect against corrosion, such as ModuGalv® [23] and NanoGalv® [24]—both of which have been through successful trials in different industries. In addition to this, MODUMETAL is researching and developing nanolaminated metal coatings specifically for corrosion in high temperature environments [20].

**COBALT-BASED ALLOYS FOR CORROSION CONTROL**

**Benefits of Cobalt-Based Alloys for Controlling Corrosion**

Currently, chromium-based coatings are a common form of corrosion control [25]. However, chromium has been found to cause health risks to employees working in an environment with a large amount of chromium present. Outside of this, the main problem with chromium-based coatings is they have relatively low plating efficiency [25]. According to current research, cobalt-based alloys with chromium included appear to be the best alternative to chromium coatings as a form of corrosion control [25]. This research shows that these cobalt-based alloys have proper characteristics that not only make them ideal for corrosion prevention in general, but also for corrosion prevention in a harsher environment such as an aircraft turbine engine [25].

In materials science engineering, an alloy is mixture of two or more metals, while a superalloy is an alloy that has the following characteristics: excellent mechanical strength, resistance to thermal creep deformation, good surface stability, and resistance to corrosion and oxidation [4]. A face centered cubic structure has atoms arranged in all eight corners of a cube shape with another atom at the center of each face and is also called austenic [4]. The gamma phase of a superalloy such as a cobalt superalloy is a face centered cubic structured cobalt-based salt solution that contains large portions of solid-solution elements such as tungsten, nickel, chromium, and molybdenum [4]. A precipitate is an insoluble solid formed in a reaction. The gamma prime phase of is the solid-state solution that precipitates onto the gamma phase causing an increase in strength [4]. Figure 4 shows an image of a superalloy, illustrating the different appearances of the gamma and gamma prime phases.



**FIGURE 4 [26]**

**Image of gamma and gamma prime phase**

Solubility is the ability of a solute to be dissolved in a solvent and is temperature dependent. The same effect is present when a precipitate forms on a solid salt solution such as the gamma phase [4]. As the temperature decreases, there is a larger percent of the precipitate, such as tungsten, that will form. Metallurgists often use this principle in precipitation heat treatment. This is when the temperature is increased to the desired gamma prime precipitate percentage and is rapidly cooled in a process called quenching [4]. If the metal is annealed—which is cooled slowly—the precipitates will aggregate into clumps causing an uneven distribution making the metal more brittle [4]. In industry, the metal is instead cooled rapidly so that the precipitate will form as fast as possible with the smallest amount of aggregation with one another [4]. An example of this gamma and gamma prime phase is a cobalt based superalloy as a solid salt solution serving as the gamma phase with a tungsten component to form the gamma prime precipitate.

**Benefits of Cobalt-Based Alloys in Aircraft Turbines and Engines**

In research conducted on alloys, researchers found that compared to nickel-based alloys, cobalt-based alloys are more resistant to hot corrosion [6]. The best performance was Co-25Cr-10Ni-7.5W, a cobalt-based alloy with components of chromium, nickel, and tungsten [6].  Furthermore, due to an aircraft turbine engine’s average temperature of 1,400 degrees Celsius, cobalt’s high specific heat and melting point of 1,495 degree Celsius allow for it to resist a phase change. With the addition of tungsten to create a cobalt based alloy, tungsten’s melting point of 3,400 degrees Celsius greatly increases the alloy’s resistance to heat.

**Nanostructured Cobalt-Based Alloys**

Nano materials resist phase changes more than their macro counterpart. When energy is added to particles, their average kinetic energy increases causing them to move and with enough energy, break the intermolecular forces holding them together. Once the particles reach a certain temperature, the changing of their phase will require a magnitude of energy based on its enthalpy of fusion and vaporization constants [4]. By increasing these constants, a solid material will resist melting at higher temperatures. Nanoparticles will increase these constants compared to their macro sized companions and thus will be able to withstand higher temperatures before a phase state change [27].

**Drawbacks to Cobalt-Based Alloys**

While cobalt-based alloys scientifically are an effective solution to corrosion prevention, there are other drawbacks to using cobalt as a thin film to prevent corrosion. In 2017, the price of cobalt nearly doubled, primarily due to the rise in popularity of electric cars [28]. A main component of an electric car’s battery is cobalt, and with the market for electric cars growing, the demand for cobalt is also growing, therefore making the prices increase. In addition to this price increase, the price of tungsten has also increased in recent years due to supply constraints from China—the leading producer of tungsten in the world [28]. This is a problem because tungsten is an ideal element for the gamma prime phase in cooperation with a cobalt-based gamma phase.

**Further Drawbacks to Nanostructured Cobalt-Based Alloys**

There are additional drawbacks to using nanostructures in general, as well as cobalt-based alloy nanostructures to prevent corrosion. Nanoparticles can be toxic even if the original version of the particle is not [29]. The only way to determine its toxicity is to collect experimental data during in vitro cellular toxicology experiments, which is the study of the effects of toxic chemical substances on bacterial or mammal cells or by the traditional measurement of a lethal dose to 50% of organisms in a population [29]. Since there is no experimental data on these cobalt-based alloys relative to toxicology, its effects are currently unknown. However, a similar nanomaterial called tungsten carbide-cobalt is shown to be toxic in its powdered form which is released during the grinding of large pieces of metal through any inhalation or absorption by the skin [30]. The finished product itself is in no way toxic but safety measures are strongly recommended during this process due to its toxicity [30].

Most of the earth’s cobalt is concentrated in its core and is inaccessible. Most cobalt is found in the form of ore as a byproduct of nickel and copper mining [31]. Cobalt’s highest known concentration that is accessible is found in the Democratic Republic of the Congo [31]. The mining of Cobalt raises ethical issues concerning the usage of child labor in its extraction. For example, Chinese based companies such as Congo Dong Bang Mining (CDM) and Congo Loyal Will Mining are both companies mining in the Democratic Republic of the Congo and have been reported as using child labor at an age as young as ten [31]. This is illegal under the International Labor Organization which was ratified by both the Democratic Republic of the Congo and China [31].

**THE FUTURE OF CORROSION CONTROL**

Research on super alloys being used to prevent corrosion has been primarily on nickel-based alloys. According to Dr. Brian Gleeson, a professor of materials science engineering at the University of Pittsburgh, due to an infinite number of possible alloys, it can be very difficult to think to use or change something in a current alloy [4]. However, one article shows how cobalt and tungsten has been researched and implemented in corrosion prevention at a 2.2% and 32% composition of a nickel-based alloy respectively [32]. In the last ten years, research has been done with cobalt being used as the base of the metal and chromium as a component [33]. This has shown promise which will lead to the funding of continued research.

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