Superalloys – characterization, usage and recycling

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Article abstract
Superalloys are a group of alloys developed for use during long-term heat exposure above 650 °C. Properties and applications of superalloys are described in the present work. The work includes statistics about superalloys demand, market value and the current price. Division of superalloys according to basic element is mentioned. Nickel-based superalloys are further divided into two groups according to their use. Afterwards, the paper is focused mainly on nickel-based superalloys. Examples of nickel-based superalloys are listed in the work. Recycling possibilities of nickel-based superalloys are stated and analysed. General scheme of processing nickel-based superalloy scrap with regard to the content of rhenium is proposed and shortly discussed. The best-known companies dealing with superalloy scrap recycling are mentioned further.

Keywords
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Nickel
Recycling

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1 Introduction
The title “superalloy” started to be used shortly after World War II to define a group of alloys developed for use in aircraft turbine engines and turbosuperchargers that required high performance at elevated temperatures. The range of applications in which superalloys are used has also expanded to include rocket engines, aircraft and land-based gas turbines, and plant equipment for petroleum and chemical industry. Superalloys can maintain high strength and excellent surface stability even during long-term heat exposure above 650 °C, which is the limit temperature for the use of refractory steels. Superalloys are based on Group VIIIB elements and generally consist of various combinations of nickel, cobalt, iron and chromium as well as smaller amounts of aluminium, titanium, tantalum, niobium, molybdenum, and tungsten. Superalloys could be generally characterized as heat-resistant alloys with high strength at elevated temperatures (up to 1200 °C). They have good resistance to corrosion and oxidation, high toughness and ductility. They possess excellent cryogenic temperature properties [1][2][3][4][5].

2 Applications
The high demand for superalloys is attributed to their wide use in various industries. The main use of superalloys is in the aviation industry (rocket engines, combustion engine exhaust valves, blades, disks, combustion chambers of turbines and jet engines...), industrial gas turbines (electrical and mechanical), automotive industry, petrochemical industry, medicine and industrial production (maritime industry – production of submarines, processing of chemical substances...). Superalloys are also used in the production of nuclear reactors and heat exchangers, high temperature fasteners, tools and dyes exposed to high temperature [3][4][6][7][8][9].

3 Statistics
The global superalloys market value was estimated at $6.2 billion (€6.35 billion) at 2019 and it is expected to reach $9.2 billion (€9.43 billion) by 2027. Superalloy demand has increased from essentially zero in the early 1950’s to 54431084.4 kg in 2008. The demand for superalloys is expected to increase in industrial gas turbine applications, for the manufacturing of next-generation aircraft, for the marine industry and for the chemical industry in the coming years. The demand for superalloys is increasing by approximately 10 – 15 % per annum. It is difficult to know the exact cost of the different materials. Superalloys have various compositions and therefore price of each superalloy is different. In general, price of nickel-based superalloys is from $16.58/kg (€17/kg) to $24.88/kg (€25.5/kg). For example, Inconel 600, which is registered trademark of Special Metals, is an austenitic nickel-
4 Classification

Named after the base (or most abundant) element, superalloys are divided into three major classes: nickel-, iron-, and cobalt-based alloys. As it is shown in Fig. 1, nickel-based superalloys are the most used group of superalloys. They possess high-temperature mechanical properties and oxidation resistance. Cobalt-based superalloys in comparison to nickel-based superalloys have greater stability and they exhibit higher sulphidation resistance. Even though cobalt-based superalloys are the fastest growing group of the superalloys during the forecast period, nickel-base superalloys are still the most widely used for the hottest parts, they are the most complex and, for many metallurgists, the most interesting of all superalloys. This is the reason why the article is focused mainly on nickel superalloys.

Nickel superalloys are divided into two large groups according to their use, namely:

- anti-corrosion nickel superalloys,
- refractory nickel superalloys (heat resistant and high strength at high temperature)

Anti-corrosion nickel superalloys are used when other materials:

- do not meet their mechanical properties,
- have an extremely high price,
- do not have sufficiently high resistance to corrosion.

Refractory superalloys often replace refractory steels. They are used at temperatures above 750 °C.

5 Chemical composition

The majority of nickel-based superalloys comprise 10 – 20 % Cr, 5 – 10 % Co, up to 8 % Ti and Al, and small amounts of C, Zr and B. Fe is added to substitute some of Ni as it has lower cost. Effect of alloying elements on nickel superalloys is listed in Tab. 1. Names of selected superalloys, their chemical composition and principal uses are provided in Tab. 2.

<table>
<thead>
<tr>
<th>Effect</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC matrix stabilization</td>
<td>Co</td>
</tr>
<tr>
<td>Substitution strengthening</td>
<td>Co, Cr, Mo, Fe, W, Ta</td>
</tr>
<tr>
<td>Types of carbides:</td>
<td></td>
</tr>
</tbody>
</table>
### Tab. 2 Selected superalloys, their composition and principal uses [1]

<table>
<thead>
<tr>
<th>Name of superalloy</th>
<th>Chemical composition (wt. %)</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Astroloy (powder)</td>
<td>Ni 55, Cr 15, Co 17, Mo 5, Al 4, Ti 4, Zr 4</td>
<td>High pressure turbine discs and blade retainers.</td>
</tr>
<tr>
<td>CMSX2-10 (single crystal alloys)</td>
<td>Ni 67, Cr 8, Co 5, Mo 1, Al 6, Ti 1, W 8, Ta 6</td>
<td>Turbine blades.</td>
</tr>
<tr>
<td>FT750DC</td>
<td>Ni 67, Cr 20, Al 2, Ti 2, W 4, B trace</td>
<td>Creep resistant, power plant applications.</td>
</tr>
<tr>
<td>Inconel 718</td>
<td>Ni 53, Cr 19, Co 1, Mo 3, Ti 1, Nb 4</td>
<td>Jet engine, gas turbine operations.</td>
</tr>
<tr>
<td>Hastelloy G–50</td>
<td>Ni 50, Cr 20, Co 3, Cu 1, Mo 9, Mn 1, Si 1, W 1</td>
<td>Oil production applications, resists corrosion from sour gas environments.</td>
</tr>
<tr>
<td>Hastelloy S</td>
<td>Ni 62, Cr 16, Co 2, Mo 15, Mn 1, W trace</td>
<td>Seal rings in gas turbine engines, has low thermal expansion coefficient.</td>
</tr>
<tr>
<td>Hastelloy X</td>
<td>Ni 47, Cr 22, Co 2, Mo 9, Mn 1, Si 1, W 1</td>
<td>Furnace applications (rolls, trays), jet engine tailpipes, afterburner components, turbine blades, nozzle vanes, cabin heaters, gas turbine combustion cans, and ducting.</td>
</tr>
<tr>
<td>Inconel MA758 (oxide dispersion strengthened)</td>
<td>77 Ni, Cr 20, Y₂O₃ 1</td>
<td>A range of high performance thermal processing applications.</td>
</tr>
<tr>
<td>Mar-M200</td>
<td>60 Ni, Cr 9, Co 10, Al 5, Ti 2, W 12, Nb 1</td>
<td>Single crystal turbine airfoils.</td>
</tr>
<tr>
<td>Nimonic 80</td>
<td>76 Ni, Cr 20, Al 1, Ti 2</td>
<td>Turbine blades.</td>
</tr>
<tr>
<td>Rene 41</td>
<td>55 Ni, Cr 19, Co 11, Mo 10, Al 2, Ti 3</td>
<td>Jet engines.</td>
</tr>
<tr>
<td>TMS 63</td>
<td>71 Ni, Cr 7, Mo 7, Al 6, Ta 8</td>
<td>Single crystal turbine blades.</td>
</tr>
<tr>
<td>Udimet 500</td>
<td>54 Ni, Cr 18, Co 19, Mo 4, Al 3, Ti 3</td>
<td>Turbine blades.</td>
</tr>
<tr>
<td>Waspaloy</td>
<td>58 Ni, Cr 20, Co 14, Mo 4, Al 1, Ti 3</td>
<td>Numerous rotating and nonrotating turbine engine components.</td>
</tr>
</tbody>
</table>

Astroloy is a trademark of General Electric Company. CMSX–2 is a registered trademark of Cannon-Muskegon Corporation. Hastelloy, and Waspaloy are registered trademarks of Haynes International, Inc. Inconel, Nimonic, and Udimet are registered trademarks of Special Metals Corporation. MAR–M200 is a trademark of Martin Marietta Corporation. Rene is a registered trademark of Teledyne Allvac Company [1].

### 6 Microstructure

Nickel-based superalloys consist of three major phases: γ (gamma) phase, γ' (gamma prime) phase and carbides. The continuous matrix of nickel superalloys in the cast state is the γ (gamma) phase, i.e. solid solution of nickel...
with other additives. This matrix is strengthened by the \( \gamma' \) (gamma prime) phase (most often it is an intermetallic compound \( \text{Ni}_3(\text{Al}, \text{Ti}) \)), carbides of various types (mainly \( \text{M}_2\text{C}_6 \) and \( \text{MC} \), where \( \text{M} \) means metal) or other strengthening phases, such as borides. The \( \gamma \) (gamma) phase and the \( \gamma' \) (gamma prime) phase form two-phase equilibrium microstructure. They are both face-centred-cubic, have nearly identical lattice dimensions and similar orientation. Therefore, two phases are almost coherent. The lattice sites in the \( \gamma \) (gamma) phase are completely equivalent and the atoms constituting the solid solution are distributed randomly. Microstructure of Ni-based superalloy is displayed in Fig. 2 [2][3][8][9][17][18][19].

![Microstructure of Ni-based superalloy](image)

**Fig. 2** Microstructure of Ni-based superalloy. On the left side, there is a SEM micrograph showing the \( \gamma/\gamma' \)-microstructure of a single crystal Ni-based superalloy. On the right side, there are unit cell crystal structures of the ordered L12 \( \gamma' \)-phase (top) and the FCC \( \gamma \)-phase (bottom) [19].

7 Mechanical and physical properties

The specific weight of nickel-based superalloys ranges from 7700 to 9100 kg/m³. The mechanical and physical properties of nickel-based superalloys are summarized in Tab. 3 [4][20].

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus of elasticity</td>
<td>Melting point</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>Specific heat capacity</td>
</tr>
<tr>
<td>Yield strength</td>
<td>Coefficient of thermal expansion</td>
</tr>
<tr>
<td>Ductility</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>Vickers hardness</td>
<td>Max. operating temperature</td>
</tr>
<tr>
<td>Fracture toughness</td>
<td>Electrical resistance</td>
</tr>
</tbody>
</table>

8 Recycling of superalloys

The importance of recycling superalloys is undeniable. Many of the alloying additives, such as Hf, Nb, Co, Ta, belong to the current List of critical raw materials (CRM) for the European Union (EU). Due to their high economic importance and supply risk, these elements also have a high price, which is one of the reasons to recycle superalloys. Alloying elements of nickel-based superalloys that belong to the 2020 list of critical raw materials for the EU are marked in Fig. 3 [21].
Superalloys are characterized by a complex of chemical and physical properties. Therefore, their recycling is difficult. Numerous processes have been proposed to recover valuable metals in the superalloy scrap. In general, recycling processes can be divided into:

- pyrometallurgical,
- hydrometallurgical,
- combined pyro- and hydrometallurgical [20][22].

Modern nickel superalloys contain 3 to 6 % of rare elements such as rhenium and ruthenium. The current price of rhenium is $1590.80/kg (€1629.64/kg) and of ruthenium is $620.00/oz (Troy Ounce) (635.42€/oz). Despite the relatively low weight content, these two metals make up the highest share of the price. Before recycling itself, firstly, it is advisable to determine the chemical composition of the superalloy, e.g. using an XRF spectrometer. Subsequently, the scrap (waste from superalloys) should be sorted on the basis of chemical composition, especially with regard to the content of rhenium. Scrap without rhenium content (older superalloys) is more suitable to be processed by pyrometallurgical methods, but superalloys with a rhenium content of 3 – 6 wt. % (advanced superalloys) are worth recycling by hydrometallurgical methods. Flowchart for recycling of nickel-based superalloys is presented in Fig. 4 [20][22][23][24][25].
Currently, the most widely used approach is remelting of metal components with mixing of primary raw materials. Pyrometallurgical process includes e.g. remelting of scrap in an electric arc furnace followed by vacuum refining of the resulting ingot. Using this procedure, ingots with a non-oxidized metal content of 93% were obtained. To minimize evaporation loss, limestone and fluorite were used [20].

Main advantages of pyrometallurgical processes are:
- simpler operation,
- obtaining a product with good mechanical properties [20].

Main disadvantages of pyrometallurgical procedures are:
- loss of elements to a slag / by vaporization,
- high energy consumption [20].

Hydrometallurgical processes are currently being studied on a laboratory scale. Their goal is to obtain compounds and/or pure metals. For example, two-stage leaching of nickel and rhenium from nickel superalloy PWA 1484 with HCl solutions was studied. By smelting with Al-granulate, a melt was obtained. The melt was cooled by air and, after solidification, the alloy was crushed. Nickel forms intermetallic phases with aluminium, which are easily crushed. The first stage of leaching took place in an electrochemical cell, which was divided into a cathode and an anode compartments by an anion exchange membrane. Metals, such as Ni, Co, Cr and Al entered the solution, while Re remained in the solid residue. The second stage of leaching took place in a glass leaching reactor, while the electrically generated chlorine from the first leaching was used as an oxidizer. Re was leached from the solid residue [20][22].

Main advantages of hydrometallurgical procedures are:
- selectivity,
- product of high purity,
- lower energy consumption [20].

Main disadvantages of hydrometallurgical procedures are:
- requirement of leaching agents,
- corrosive environment – more resistant devices,
- difficult phase separation [20].

The difficulty of converting all metal components from superalloy scrap into a value-added final product by hydrometallurgical route has prompted several researches to investigate combined pyro-hydrometallurgical processes. Their goal is to enable leaching of metal components, or to increase the surface area [20].

For example, a process was patented, the first step of which was high-temperature decomposition in a salt melt containing 60 – 95 wt. % NaOH, 5 – 40 wt. % Na₂SO₄ and additional oxidizing agent (NaNO₃ or K₂S₂O₈). The
process is carried out in a rotary furnace, oxygen-enriched air is blown into the melt. The second step is cooling, crushing and grinding of the melt. The material is subsequently leached using water as the lixiviant. The 6 and 7th group elements dissolve. The resulting slurry is further filtered to separate insoluble metals such as Fe, Ni, Co, Cr and Mn from the leachate. Magnetic separation is applied to the insoluble residue and the filtrate proceeds to ion exchange. A solution containing Re and Ta is obtained [26][27].

Main advantages of combined pyro-hydrometallurgical processes are:

- Easy to granulate or to grind intermediate product,
- leaching efficiency,
- high purity product [20].

Main disadvantages of combined pyro-hydrometallurgical processes are:

- high energy consumption,
- loss of elements,
- high pH and temperature requirement [20].

9 Companies recycling super alloy scrap

Examples of superalloy scrap recycling companies include:

- **Greystone Alloys, Houston, USA**
  
  This company recycles scrap from the following metals and alloys: Inconel 625, Inconel 718, Hastelloy C, spray powders, tantalum, Haynes, molybdenum, Monel, tool steel, zirconium [28].

- **Monico Alloys, Rancho Dominiqes (near Los Angeles), USA**
  
  In addition to high-purity metals, it recycles and sells recycled superalloy scrap, e.g. from Hastelloy, Haynes, Inconel, Monel, Rene, Waspaloy [29].

- **Umicore (worldwide representation in refineries in Belgium, the USA, the Philippines and China)**
  
  It provides environmentally responsible and commercially attractive methods of recycling scrap and residues containing cobalt, nickel-rhenium and tantalum. In addition to other types of metal waste, superalloy scrap from the aviation industry is recycled here [30].

- **United Alloys and Metals; Los Angeles, California and Columbus, Ohio**
  
  It is one of the leading global processors of titanium scrap and superalloy scrap, e.g. from Inconels, Hastelloys, Udimets, Renes and Waspalloy. As a division of the Cronimet family, UAM is part of one of the largest metal recycling companies in the world [31].

10 Conclusion

According to the main element, superalloys are divided into superalloys based on nickel, cobalt and iron. Nickel superalloys are the most widely used of the groups mentioned. In addition to nickel, these alloys contain various alloying elements, in particular chromium, cobalt, aluminium, titanium, tungsten, niobium and molybdenum. The evolution of Ni-based superalloys composition is closely related to the development of individual applications. Modern superalloys are characterized by 3 – 6 % content of ruthenium and rhenium. Superalloy waste therefore represents a complex source of various elements. In practice, pyrometallurgical methods of recycling superalloy scrap are currently applied. Hydrometallurgical and combined pyro-hydrometallurgical methods are still being studied on a laboratory scale. In the future, hydro- and pyro-hydrometallurgical methods could have potential in terms of obtaining individual elements or their compounds, but they need expansion to achieve cost-effectiveness on an industrial scale, and the efficiency of metal dissolution must reach a technologically and economically acceptable level.

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References


