Nitrogen hardening of creep-resistant G-NiCr28W alloy

Z. Pirowski*, J. Wodnicki, A. Gwiżdź

Foundry Research Institute, 30-418 Kraków, ul. Zakopiańska 73, Poland
*Corresponding author. E-mail address: pirowski@ iod.krakow.pl

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Abstract

In the group of creep-resistant materials, most important are heat-resistant nickel-based alloys. The G-NiCr28W alloy subject to detailed examinations was observed to have two different austenite-like phases. In the interdendritic spaces of alloy matrix, the presence of another phase, also characterised by paramagnetic properties, was detected. Inside this interdendritic phase, local areas of a lamellar structure, composed of both of the above mentioned phases, were present. Nitrogen treatment was observed to raise the microhardness of both these phases.

The presence of nitrogen made the regions of a lamellar structure disappear completely. Their place was occupied by precipitates dispersed in the matrix, and occasionally forming large clusters.

It has been observed that cold work can harden the G-NiCr28W alloy to a very small degree only, in spite of the fact that hardness is increasing systematically with the increasing degree of cold work. The said alloy, when enriched with nitrogen added as an alloying element, is characterised by hardness higher than the hardness of its nitrogen-free counterpart. The value of hardness is increasing even more under the effect of low-degree cold work, although increasing further the degree of cold work seems to have no effect on hardness increase.

The problem faced in nickel-based materials is the possibility of making defect-free castings from alloys with high nitrogen content. Alloys investigated in the present study were remelted, cast and subject to solidification under high nitrogen pressure in the furnace chamber. However, melting carried out under these conditions could not prevent the occurrence of non-metallic inclusions which, while being unable to pass to a riser, formed local clusters or even thin films, resulting in numerous microcracks or discontinuities encompassing large regions of the casting. This problem seems to be of major concern and is the first one to require prompt solution in the currently executed large research project.

Keywords: creep-resistant alloys, superalloys, nickel alloys, structure transformation, hardening, melting technology

1. Introduction

Hardening is the phenomenon that occurs during cold plastic deformation of metals. Its essence consists in permanent increase of the deformation resistance. Due to this effect the metal raises its strength on the cost of decreasing ductility.

In the process of metal hardening, a very important part, is played by dislocations, and along with dislocations by other lattice defects operating through interacting stress fields. For example, the atoms of nitrogen are attracted to edge dislocations, forming Cottrel atmosphere, i.e. clusters of atoms of various admixtures arresting the movement of dislocations.

The precipitation of fine particles can be sometimes (quantity, size, distribution, etc.) beneficial for alloy hardening. A mechanism of this effect was proposed by Orowan [16], and its was based on an assumption that hardness increase is due to the
arrested movement of dislocations. The dislocations should be free to move between the precipitated particles, and hence the stress necessary to move the dislocations in the presence of the precipitated particles should be higher than the stress in perfect lattice. Activated by stress, the dislocations are “flowing” around the particle, forming loops similar to Frank-Read source. When these loops are sufficiently well curved, they form rings around the particles and regenerated dislocations, which can now move further increasing the degree of alloy plastic deformation. Yet, the field of stress created by the forming loops makes next dislocations more “movement resistant”, and hence the formation of next loops and, consequently, of the next batch of the regenerated dislocations, becomes very difficult. According to this mechanism, the presence of dispersion precipitates should favour alloy hardening.

The factors described above, arresting the free movement of dislocations, and hence reducing the degree of plastic deformation, are of an internal (endogenous) character and as such result in alloy hardening. Very beneficial in this group of materials are e.g. alloys containing nitrogen as an interstitial element or metal nitrides. Nitrides precipitate due to physico-chemical reactions taking place between the alloying additions such as chromium, molybdenum, tungsten, vanadium, titanium, etc. and nitrogen present in the furnace working space, i.e. above the mirror of the melt, or injected directly into the melt, or contained in special ferroalloys [8].

Nickel and its alloys are used when high corrosion resistance and good mechanical properties at standard and elevated temperatures are required. The said alloys can be divided into the following groups [1, 4, 5, 9]:

- Ni-Cu and Ni-Cu-Si alloys – the most popular in this group is Monel metal, used for cast valves and seats, turbine blades and marine applications,
- Ni-Cu-Zn alloys – called “new silver” owing to a silvery colour, they are widely used in plastic forming,
- Ni-Cu-Sn and Ni-Cu-Sn-Pb alloys – are characterised by good sliding and mechanical properties at high temperatures,
- Ni-Cr and Ni-Cr-Fe alloys - are characterised by high resistivity and heat resistance (e.g. Nichrom, Chromel, Evanohm), offer satisfactory mechanical properties at high temperatures and high resistance to oxidation and corrosion (e.g. Nimonic, Inconel, AH Inconel),
- Ni-Mo-Fe and Ni-Mo-Cr-Fe alloys – are resistant to corrosion when operating under extra hard conditions in different concentrations of the corrosive medium, and at high temperatures under constant loads,
- Ni-Be and Ni-Ti alloys - are characterised by high resistance to cavitation corrosion,
- Ni-Al alloys – e.g. Alumel of maximum 1000°C temperature of continuous operation and Duranickel resistant to cold and hot corrosion, both used for cast fittings and parts of pumps,
- Ni-Fe alloys - e.g. Permalloy characterised by high magnetic permeability.

Yet, the available technical literature makes no reference to nickel alloys which would contain nitrogen as an important alloying element.

2. Research material

Within the programme of investigations covered by a Commissioned Research Project (PBZ/KBN/114/T08/2004), studies of heat-resistant nickel alloys have been undertaken. The said alloys are widely used, especially for the structural parts of airplanes, rockets, gas turbines and other devices operating at high temperatures and in the medium of chemically aggressive agents. They occupy a leading position in the group of creep- and heat-resistant materials, mainly due to a very beneficial combination of these two parameters, additionally supported by satisfactory thermal fatigue behaviour and crack resistance at high temperatures, as well as other equally beneficial physico-chemical properties.

Chemical composition of alloys from this family is very complex and often enriched with numerous alloying additions, although in standard cases they contain 10-20 % Cr and aluminium, titanium, carbon, cobalt, tungsten, molybdenum, niobium, boron and zirconium. These alloys are usually melted and poured in vacuum furnaces because of aluminium, titanium and zirconium they contain, and the resulting necessity to keep the content of gas and admixtures as low as possible, often at a level of several thousand or ten thousand parts of percent (Bi, Te, Ti), bearing in mind the strong and adverse effect they have on alloy mechanical properties.

The structure of these alloys is determined by [4, 7, 9]:
1. alloy matrix crystallising in an aluminium systems – it is the solid solution of substitutional alloying elements in nickel, strengthening this solution due to lattice deformations,
2. alloy hardening, mainly due to the presence of a precipitated phase coherently combined with matrix; it is characterised by very beneficial properties, mainly strength increasing with an increase of temperature and satisfactory ductility, which improves alloy creep resistance without increasing its brittleness, contrary to the hardening effect obtained with phases of high hardness values, e.g. carbides, where phase effect on alloy properties largely depends on the size and shape of precipitates,
3. type and morphology of carbides, largely depending on alloy composition and the type of applied heat treatment.

The creep- and heat-resistant nickel alloys usually contain 0,05-0,20% carbon, which forms the primary MC type carbides in combination with tungsten, molybdenum, titanium, chromium and niobium. During heat treatment or under service conditions, some transformations take place in the alloy, due to which complex carbides of a M23C6 type are formed. The said carbides improve alloy creep resistance, while their effect on alloy ductility depends on morphology.
Typical heat treatment applied to creep- and heat-resistant nickel-based alloys consists in precipitation hardening \([9, 11]\), i.e. solution heat treatment by heating in the temperature range of \(1040 - 1230\, ^\circ\text{C}\), followed by cooling in air and ageing at a temperature of \(700 - 1000\, ^\circ\text{C}\), usually for 8 - 16 hours, followed by cooling in air.

Solution heat treatment dissolves some of the carbides and intermetallic phases present in alloy matrix. On the other hand, ageing results in precipitation of the above described coherent phase and of carbides uniformly dispersed in alloy matrix. Heating is carried out under neutral atmosphere, sometimes in vacuum. The aim of the precipitation hardening is to produce a structure in which the size, shape and distribution of phases hardening the alloy will be such as to ensure optimum mechanical properties and maximum structural stability at service temperatures.

The creep- and heat-resistant nickel alloys are operating at temperatures of up to \(1100\, ^\circ\text{C}\). The operating temperature of cast alloys is by 100 - 150\, ^\circ\text{C} higher than that of alloys for plastic forming.

Besides aviation, which is the main field of application of the examined alloys, they are also used in power industry and chemical industry, mainly for parts of machines and equipment operating under the most challenging conditions (turbines, steam superheaters, handling pipelines, moving belts in tunnel kilns, etc.).

Considering the fact that progress in the field of aircraft drive systems and systems operating in the equipment used by chemical and power industries depends largely on the development of creep- and heat-resistant nickel-based alloys, for several years now the leading industrial countries have been allocating large amounts of money for studies of this type. The outcome has been notable progress in this field. The increase in creep resistance and service temperatures has been obtained in this group of alloys through \([9, 13]\):

- vacuum refining to remove the low melting point precipitates from grain boundaries, reduce porosity and the content of non-metallic inclusions in alloy,
- directional solidification to produce in alloy the grains of orientation parallel to stress direction,
- monocrystallisation, which eliminates grain boundaries,
- directional solidification of eutectic alloys, during which one of the eutectic phases (carbides, nitrides) precipitates in the form of fibres parallel to stress direction,
- hardening of alloy matrix with dispersed particles of various compounds (mainly oxides), obtained through sintering of nickel or nickel alloys with fine particles of stable oxides,
- hardening of alloy matrix with tungsten or molybdenum wire.

Tests were carried out on creep-resistant G-NiCr28W alloy. This alloy is used by SPECODLEW, a company co-owned by the Foundry Research Institute, to cast, among others, pans used in the fabrication of glass fibres. A photograph of such pan is shown in Figure 1.

In side walls of this pan, holes of a less than 1 mm diameter were made by laser technique. Through these holes, applying a centrifugal force, the glass slurry is squeezed out to form fibres of the required diameter. The main problem observed in these pans during operation at high service temperatures is the strong tendency to crack formation in areas between the holes.

### 3. Tests and Research

Within the scope of the present studies, an attempt has been made to improve further the mechanical properties of G-NiCr28W alloy by introducing to its composition nitrogen as an alloying element. Table 1 gives the starting chemical composition of alloy and the composition after remelting and nitrogen treatment. Alloys were subjected to metallographic examinations carried out in a Complex of Research Laboratories operating at the Foundry Research Institute in Krakow. The examples of microstructures are shown in Figures 2 and 3; the results of phase microhardness measurements are compiled in Table 2 \([15]\).

<table>
<thead>
<tr>
<th>Chemical composition of the examined heat-resistant nickel alloys</th>
<th>Chemical composition: %\text{mass}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy designation</td>
<td>C</td>
</tr>
<tr>
<td>5N</td>
<td>0.33</td>
</tr>
<tr>
<td>5P</td>
<td>0.44</td>
</tr>
<tr>
<td>5N – remelted under high nitrogen pressure</td>
<td></td>
</tr>
<tr>
<td>5P – melted under atmospheric pressure</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.

Microhardness of the examined nickel alloy matrix

<table>
<thead>
<tr>
<th>Alloy designation</th>
<th>Examined phase</th>
<th>Microhardness HV 0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5N</td>
<td>austenite tinted in blue</td>
<td>378</td>
</tr>
<tr>
<td>5N</td>
<td>colourless austenite</td>
<td>454</td>
</tr>
<tr>
<td>5P</td>
<td>austenite tinted in blue</td>
<td>198</td>
</tr>
<tr>
<td>5P</td>
<td>colourless austenite</td>
<td>225</td>
</tr>
</tbody>
</table>
For both examined nickel alloys, the X-ray phase analysis was carried out. The ready specimens were examined by the Laboratory of the Chair of Metals Science and Powder Metallurgy, Faculty of Metals Engineering and Industrial Computer Science, AGH University of Science and Technology in Cracow. The examinations were made on an X-ray diffractometer applying filtered radiation of a copper anode tube (λKα = 0.154 nm). The diffraction lines from the diffractometer were recorded in the range of double Bragg angle (2θ) from 15° to 100°. During these examinations, a phase analysis was performed to determine the presence of nitrogen-containing phases in the examined alloys. The obtained results are illustrated in Figure 4. The austenite lattice parameters were also measured and the results are shown in Figure 5 [13].

The examined nickel alloys were evaluated for their hardenability under the effect of applied external forces. The effect of cold work on hardness increase in the examined material was also tested. Hardness was measured by the Vickers method in indentations formed by varied pressure of a φ10 mm ball. The technique used in these measurements was discussed in [3]. The obtained test results are compiled in Table 3 [14].

### Table 3.

<table>
<thead>
<tr>
<th>Ball pressure</th>
<th>Indentation diameter (μm)</th>
<th>Hardness HV 30 (N-R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 kN</td>
<td>5 kN</td>
<td>15 kN</td>
</tr>
<tr>
<td>5P</td>
<td>211</td>
<td>1,97</td>
</tr>
<tr>
<td>5N</td>
<td>250</td>
<td>1,80</td>
</tr>
</tbody>
</table>
4. Discussion of results and conclusions

The results of laboratory investigations of the creep-resistant G-NiCr28W nickel alloy revealed the presence of a double austenite phase (Fig. 2). In the interdendritic spaces of the phase tinted in blue, a colourless paramagnetic phase was also detected. In the interior of the interdendritic phase, local areas of a lamellar structure, composed of both phases, occurred. Different features of these phases were confirmed by the results of microhardness measurements, which gave the values of 198 HV0.2 and 225 HV0.2 for the microhardness of alloy matrix and interdendritic phase, respectively. This is most probably due to microsegregation of the substitutional alloying elements, the presence of which affects matrix hardenability [9].

Nitrogen addition introduced to this alloy considerably raised the microhardness of both these phases, introducing even greater discrepancies to the obtained values: matrix – 378 HV0.2 and interdendritic phase – 454 HV0.2. The hardening effect observed in individual phases proves the high nitrogen solubility in these phases and the formation of interstitial solutions with iron and nickel. The solubility depends on the type and amount of the substitutional alloying elements present in austenite cells, changing the dimensions of tetra- and octaedric voids in which nitrogen is located. Because of definitely larger dimensions of the octaedric voids present in fcc lattice, as compared to bcc lattice [10], the said element mainly dissolves in austenite.

An addition of nitrogen to the examined alloy has made the regions of a lamellar structure disappear completely. On the other hand, the dispersion precipitates scattered over the matrix and occasionally forming larger clusters have appeared (Fig. 3). In an image of alloy microstructure, along the grain boundaries, one can see the chains of nitrides (carbonitrides) present. This is confirmed by an X-ray phase analysis (Fig. 4.). In nitrogen-containing alloy (5N), some peaks originating from the (Ni,Fe)2N, type precipitates are visible. They were not so clearly visible in nitrogen-free alloys.

Measurements of austenite lattice parameters (Fig. 5.) did not show any significant differences between alloys with and without nitrogen. This proves that nitrogen, having slightly smaller atomic diameter, "pushes" carbon out from the interstitial spaces of a crystallographic lattice. The differences in the atomic radii of nitrogen and carbon (rN = 0.53Å, rC = 0.77Å) are quite insignificant for the austenite lattice parameters, which are consistent with what the technical literature states [10]. Removed from austenite, carbon can dissolve in nitrides and form complex carbonitrides with nickel, iron and various substitutional alloying elements.

Nitrogen effect on hardenability increase in the examined nickel alloy under the effect of applied external forces is shown in Figure 6.

Hence it follows that the G-NiCr28W alloy is hardened under the effect of pressure to a very small degree only, in spite of the fact that its hardness is systematically growing with the growing degree of cold work. Nitrogen introduced to this alloy as an alloying element raises hardness to a level much higher than the level obtained in the same alloy without nitrogen. Hardness is growing even more after the application of low degree cold work, although further increase in the degree of cold work has no longer the beneficial effect on hardness improvement.

The results of laboratory tests have proved that, introduced to the examined nickel alloy, nitrogen affects in a significant way its microstructure and hence also its properties increasing, among others, both hardness and hardenability under the effect of applied external forces.

The problem put forward for discussion during the investigation of nickel alloys was the possibility of making defect-free castings from alloys with increased nitrogen content. Within the programme of the present studies, alloys were fabricated by remelting and casting under high N2 pressure maintained in the furnace chamber during melting and solidification [1, 2, 6, 9]. Unfortunately, melting under these conditions could not prevent the presence of non-metallic inclusions which, while being unable to flow into a riser, formed local clusters, or even thin films, resulting in numerous microcracks and discontinuities wide-spread on large areas of the alloy casting, thus making the preparation of defect-free laboratory specimens impossible (Fig. 7). Therefore, the obtained tensile strength of 525 MPa with elongation of 9,9 % cannot be a fully trustworthy result.
This problem will be considered one of the top issues to be solved in a large-scale research project, currently prepared for execution with partners from the United States and Bulgaria. The preliminary scanning examinations carried out recently have proved that the discontinuities which appear in metal cast into ceramic moulds after remelting under high nitrogen pressure in furnace with inert lining are due to the presence of numerous non-metallic impurities originating from the furnace lining and foundry mould. A scanning analysis of these inclusions is shown as an example in Figure 8 [12].

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References