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AN EFFECT OF CHROMIUM ON MECHANICAL PROPERTIES OF THE Ni_3Al-BASED ALLOYS AND SINTERS IN COMPRESSION TESTS

WPŁYW CHROMU NA WŁASNOŚCI MECHANICZNE STOPÓW ODLEWANYCH ORAZ SPIEKÓW NA BAZIE Ni_3Al W PRÓBIE ŚCISKANIA

Mechanical properties of the Ni75Al(25-x)Crx cast alloys and sinters were investigated using compression tests conducted within a wide range of compositions and temperature. The alloys and sinters exhibiting the best mechanical properties from a point of view of their intended use as constructional materials suitable for high-temperature applications were selected.
Keywords: mechanical properties, compression test, intermetallics, Ni_3Al, plasticity

Zbadano własności mechaniczne stopów odlewanych oraz spieków Ni75Al(25-x)Crx z zastosowaniem metody ściskania. Próby przeprowadzono w szerokim zakresie składów oraz temperatury. Wytypowano stopy i spieki o najkorzystniejszych własnościach mechanicznych z punktu widzenia zastosowania tych materiałów jako materiał konstrukcyjny do pracy w wysokich temperaturach.

1. Introduction

The Ni_3Al intermetallic compound is a candidate material for high-temperature applications due to its high mechanical strength, high corrosion resistance, also at high temperature, and relatively low density and price. However, a serious drawback of this compound is its high brittleness: the Ni_3Al monocrystal is plastic, whereas in a polycrystalline form it is brittle [1].

One of the main methods for increasing plasticity of the Ni_3Al compound is an introduction of alloy additives. For instance, Aoki and Izumi have found that micro-addition of boron significantly influences plasticity of these materials [2], and Świątnicki and Grabski have proved that introduction of boron results in a reduced mobility of grain boundaries [3]. Investigations performed by Jóźwik and Bojar [4] indicate that the heat treatment has significant effect on microstructure and properties of Ni_3Al with additions of B, Zr and Cr. Besides, brittleness can be reduced if powder metallurgy techniques are used. In this work both these methods have been applied. Chromium and chromium-containing alloys were selected for an alloy additive due to their high corrosion resistance, and it was also expected that they should increase material plasticity and provide possibilities of industrial applications [5, 6, 7]. A sintering method known from powder metallurgy has also been applied as an alternative for conventional metallurgy. Application of this method enabled elimination of the brittleness problem encountered at the stage of mechanical processing thus giving the possibility of direct fabrication of final product. Also in this case chromium was added to the alloy in order to improve its plasticity.

Presented studies are part of wide program of investigations of different intermetallic phases, including application of calorimetric methods for determination of formation enthalpies of different aluminides [8]. This work was not intended to go into details of the phenomena taking place after the introduction of specific additives to the cast alloys or those occurring in the sinters. The focus has been put on a comparison of properties of the obtained cast alloys and sinters, and on the choice of the most valuable material from the point of view of industrial applications.

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2. Experimental

The Ni_3Al-based alloys were melted in Balzers' V5G-02 type induction vacuum furnace, in alundum crucible at the vacuum of an order of 10^{-2} Torr. As a charge components aluminium (99.95 %), electrolytic nickel N1U(99.9) and chromium (99.5 %) were used. Liquid metal was cast into moulds made of a quartz bentonite mass, which were dried at the temperature of 453 ÷ 473K. The casting temperature was about 1870K. After knocking out of castings and cut-off of the gating systems rods were obtained 3÷5 mm in diameter and 50 ÷ 60 mm long. The alloys were vacuum-sealed in quartz ampoules, and the material under investigation was separated from quartz by means of an alundum tube. Next, the alloys were subjected to homogenising annealing conducted at the temperature of 1273K for 96 hours and then they were held at 1150K for the same period of time. After annealing, the alloys were rapidly quenched in an iced water.

The sinters were prepared using the simultaneous pressing and sintering method. The main equipment used was the Fritsch KG DSP 25AT pressing furnace, which enables pressure sintering of a powder material placed in a graphite die heated by a current flowing between pressing punches. The tests were made using dies for pressing cylindrical samples 12 mm in diameter. The starting material was a mixture of pure metal powders: nickel carbonyl, Al-1-0.15-grade atomised aluminium, and chromium 99.9 with a particle size below 100 μm. Tests were also made with the sinters containing products of mechanical synthesis of alloys. The synthesis was conducted in a ball mill 200 mm in diameter, in the atmosphere of argon, using balls from tungsten carbide 10 ÷ 24 mm in diameter. The ratio of ball mass to powder mass was 30:1, and experimentally selected rotational speed was about 100 rev/min. The milling time was 160 hours.

The preliminarily cold-pressed powder mixtures were subjected to pressure sintering conducted under the pressure of 15 MPa at the heating rate of about 200 deg/min. The upper temperature limit was set at 1270K, and holding time at this temperature was 5 minutes. The main reason for such selection was that over that temperature no significant changes in a sample density are observed and rapid burning of graphite punches takes place.

One of the most important physical and chemical properties influencing quality of the sinters obtained is compressibility of powder materials. The basis for sample density measurements made during simultaneous pressing and sintering were the changes in sample height and final density of the product obtained, which were monitored during the process. From this point of view, the applied method of simultaneous pressing and sintering proved to be very effective. It was clearly seen when the obtained results were compared with those from the tests performed with the same starting material (Ni75Al25) subjected first to pressing at a room temperature at considerably higher pressure of 300 MPa and next sintered at the temperature of 1270K. The material density of 4.6 g/cm^3 was then obtained, whereas it was reaching 7.1 g/cm^3 when simultaneous pressing and sintering method was used. The detailed results of studies on the possibility of compressing the discussed powdered materials have been described in the literature [9] confirming that very high densities can actually be obtained, close to those calculated theoretically assuming, as a reference state, the density of solid components.

In order to make clear comparison of the properties of the alloys and sinters possible, an attention was paid to ensuring similarity of the samples subjected to tests. This work was a part of major investigation, and because of the character of other measurements the shape of the samples had to be cylindrical. Moreover, because of the expected brittleness of many materials, since e.g. the products of mechanical synthesis were studied, compression tests were selected as a method for the examination of mechanical properties despite its limitations. It should be emphasised that the studies under this work were of comparative character, and the variable parameters were chromium content and temperature.

Compression tests at a room temperature were carried out using *INSTRON 1195* testing machine. The normal samples (h_0/d_0 = 1.5) were compressed between two polished flat plates at the beam displacement rate v_b = 0.1 mm/min. As a result of tests, yield strength $\sigma_{0.2}$, maximum true stress σ_{max} and uniform percentage contraction (compression) A_r have been determined. The compression curves have also been measured for all the samples taken from the material after casting, which did not exhibit the existence of a destructive force, and the samples were undergoing flattening until the upper force limit of the machine was reached. Therefore, the true stress-strain curves were drawn. Relative contraction (shortening) of the samples compressed up to σ_{max} has been denoted by A_r. The *INSTRON 4505* testing machine was also used to carry out tests at a room temperature and at elevated temperature. Its compression plates were made from tungsten carbide, and before the tests conducted under argon atmosphere the samples were heated up to the specific temperature and held at that temperature for 15 minutes. The compression tests were performed with the rate of 0.1 mm/min. The results of these tests have been analysed similarly as those obtained from the tests described earlier, carried out at an ambient temperature.

3. Results and discussion

The results obtained have been shown in Figs 1÷4. Room-temperature tests were made in two different research centres within the entire contents range of a pseudo-two-component system Ni75Al25-Ni75Cr25 (Fig. 1).

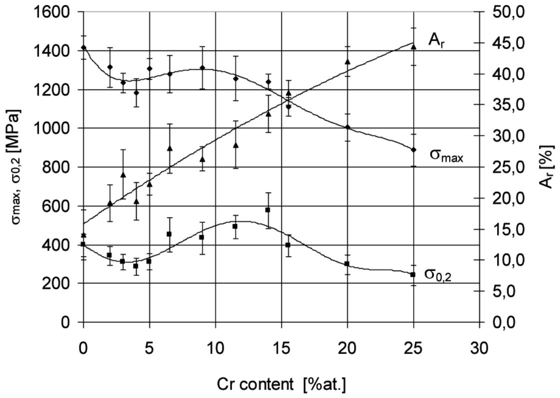

Fig. 1. Mechanical properties of the $Ni_{75}Al_{(25-x)}Cr_x$ alloys at room temperature

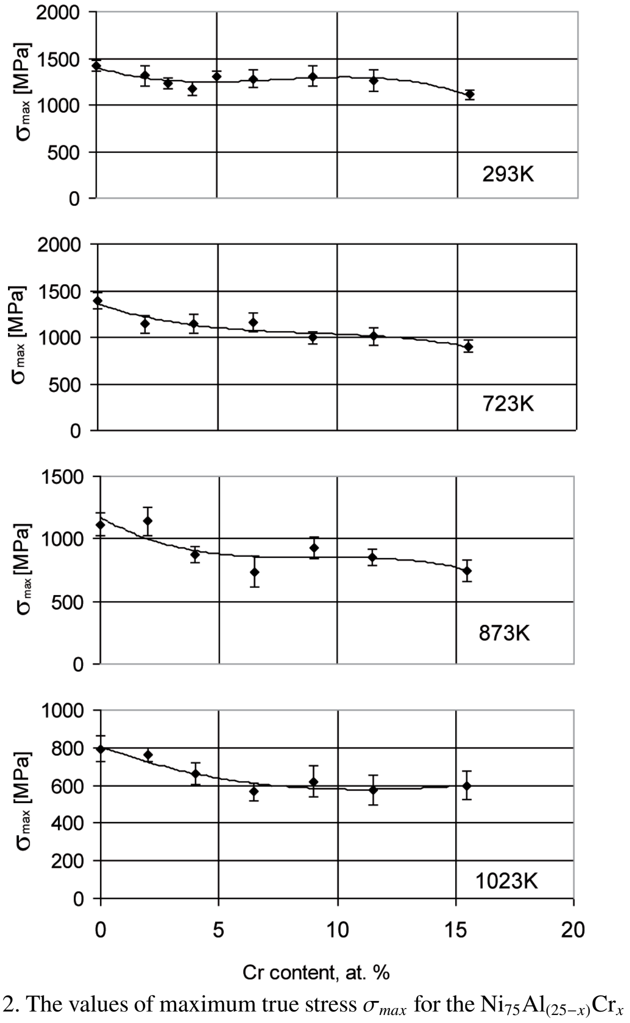

Fig. 2. The values of maximum true stress σ_{max} for the $Ni_{75}Al_{(25-x)}Cr_x$ alloys

With the increase of chromium content, a close-to-linear increase of a uniform contraction A_r (which is a measure of plasticity) was observed, reaching 46% at Cr content of 25 at.%. It was found that the values of σ_{max} were clearly decreasing for the alloys containing over 14 at.% Cr. The yield stress $\sigma_{0.2}$ exhibited clear maximum close to the middle of the pseudo-two-component system, reaching the value of about 500 MPa.

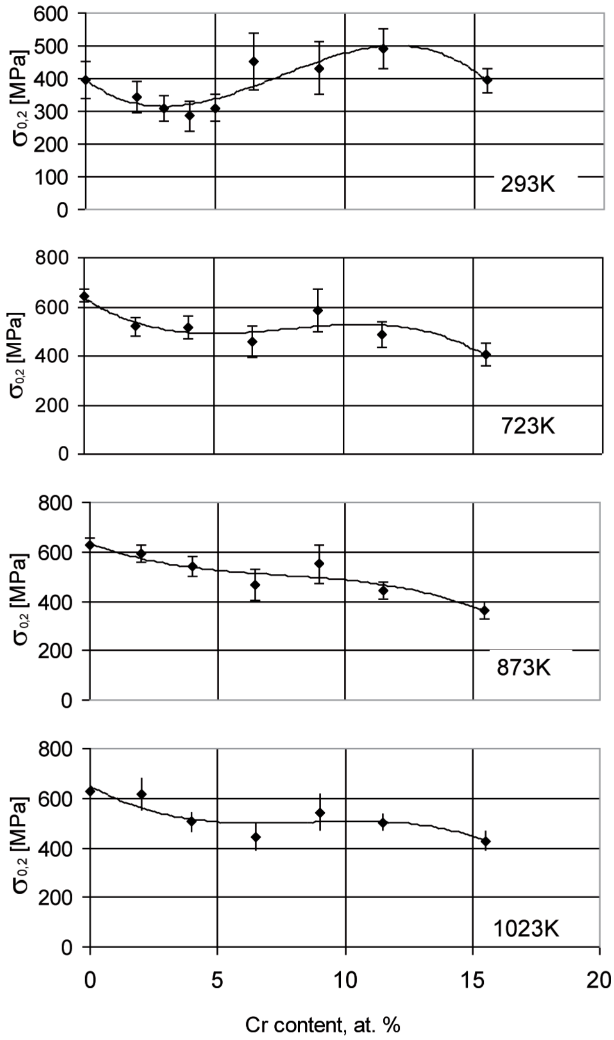

Fig. 3. The values of yield strength $\sigma_{0.2}$ for the $Ni_{75}Al_{(25-x)}Cr_x$ alloys

In accordance with the scope of this work, the next tests were focused on the alloys with lower Cr content, i.e. up to 15.5 at.%. Mechanical properties of these alloys were investigated not only as a function of chromium content but also in dependence on the temperature. Besides the room temperature, compression tests were also made at 723, 873 and 1023K. The dependences of σ_{max} and $\sigma_{0.2}$ on Cr content are shown in Figs 2 and 3, respectively. It is seen in Fig.3 that $\sigma_{0.2}$ of an additive-free Ni_3Al increases with temperature reaching a maximum at 873K, and with further temperature increase this parameter takes decreasing values. An introduction of small amount of chromium, particularly at lower temperature, leads to the decrease in yield stress (the minimum is reached at about 4-6 at.% Cr), but with further increase in Cr content the values of $\sigma_{0.2}$ are again increasing. Detailed analysis of the yield stress values determined for these alloys at particular temperature shows that the changes in these values are relatively small, which is undoubtedly beneficial from a point of view of potential applications of these alloys. In case of the Ni75Al13.5Cr11.5 alloy the changes in $\sigma_{0.2}$ values are particularly slight: from 442 to 503 MPa over the temperature range of 298÷1023K. From this point of view the alloy containing 9 at.% Cr is also very interesting: its $\sigma_{0.2}$ value at a room temperature is 440 MPa, whereas at elevated temperature of 723, 873, 1023K it takes the values close to each other, i.e. 580, 550 and 540MPa, respectively. As far as σ_{max} is concerned, gradual decrease of the values of this parameter with temperature was observed.

Plasticity of the alloys A_r (Fig.4) changes in a very interesting way. As it was already mentioned before, contraction A_r at a room temperature was increasing almost linearly with the chromium content. This behaviour can be attributed firstly to plastifying role played by the boundaries of fine antiphase domains formed as a result of rapid quenching, which in turn are accompanied by the remains of non-ordered γ phase [10]. However, the alloys with lower chromium content exhibit a decrease in plasticity at elevated temperature, which results from the disappearance of the above-mentioned reasons during annealing – ductility of these alloys only slightly changes compared to chromium-free Ni_3Al. At elevated temperature, however, beginning from a certain chromium content decreasing with temperature, clear ductility increase was observed. These chromium contents correspond to the $\gamma'/\gamma + \gamma'$ interphase boundary described elsewhere [11], which might suggest that clear ductility increase at elevated temperature results from the appearance of a non-ordered γ phase apart from the ordered γ' phase. However, it is undoubtedly necessary to confirm this hypothesis during further, more detailed investigation.

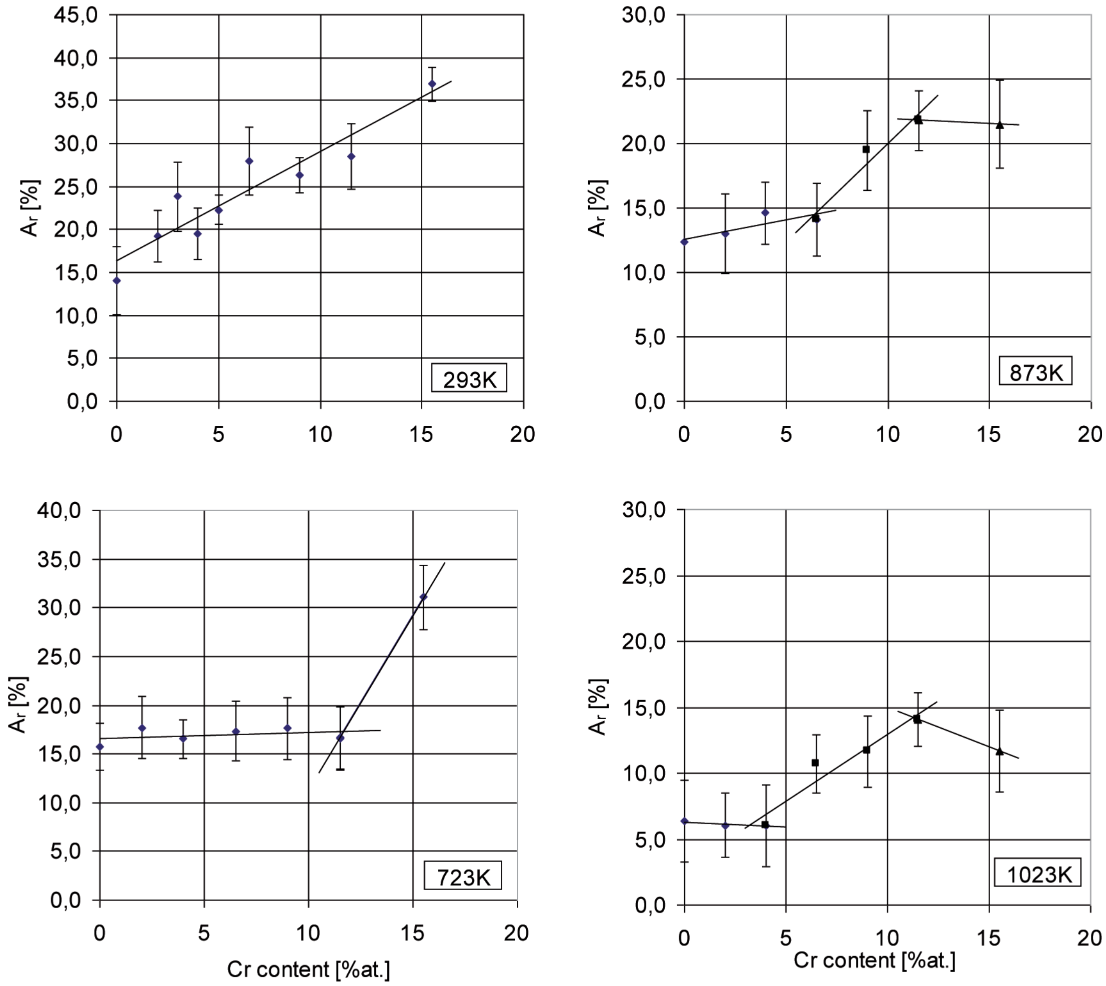

Fig. 4. The values of uniform contraction A_r for the $Ni_{75}Al_{(25-x)}Cr_x$ alloys

Besides the compression tests, three-point bending tests were also made for a limited number of samples. The samples from the most interesting Cr content range of 6.5÷11.5% were examined at the temperature of 293 and 573K. The results obtained for all three alloys were very similar and, therefore, their average value was given. It was found that an average value of yield strength at bending $R_{g0.2}$ is practically the same at both temperature (840 and 835 MPa, respectively), whereas higher values of R_g have been obtained at the temperature of 573K (1140 and 1440 MPa, respectively). Comparison of the yield strength values from the bending test and compression test confirmed general agreement between the results obtained by both these methods. The difference in absolute values of the yield strength results from different methods of applying a load to the samples, which make the results obtained at uniaxial stresses (compression) by about 25% lower.

Under this work mainly the alloys with chemical composition $Ni_{75}Al_{(25-x)}Cr_x$ were investigated, but compression tests were also made for other materials having a chance to find industrial applications [3]. These were two alloys, the first one (denoted as P1) had the following composition: Al 7.98, Cr 7.74, B 0.008, Zr 1.70. Mo 1.43, Ni 81.15 wt %, and the second one (P2): Al 8.69, Cr 8.08, B 0.02, Zr 0.20, Ni 83.01 wt %. The results obtained from the tests are given in Figure 5. They are similar to those obtained for the $Ni_{75}Al_{(25-x)}Cr_x$ alloys, especially in case of the P2 alloy containing smaller amount of alloy additives other than chromium. This similarity refers particularly to the alloys containing 9 and 11.5 at. % Cr. The values of σ_{max} exhibit similar variability, and for the three-component alloy they are by about 100 MPa lower than for the P2 alloy. On an average, the values of $\sigma_{0.2}$ do not differ from each other, but their changes at temperature increase are more evident for the alloy P2 than for the alloys Ni75Al16Cr9 and Ni75Al13.5Cr11.5. The values of uniform contraction A_r are also very similar, with characteristic minimum observed at the temperature 723K both in the case of alloys P1 and P2, and three-component alloys discussed earlier. This similarity evidences that the choice of chromium as an alloy additive was appropriate from a point of view of potential technological application of the Ni_3Al-based alloys.

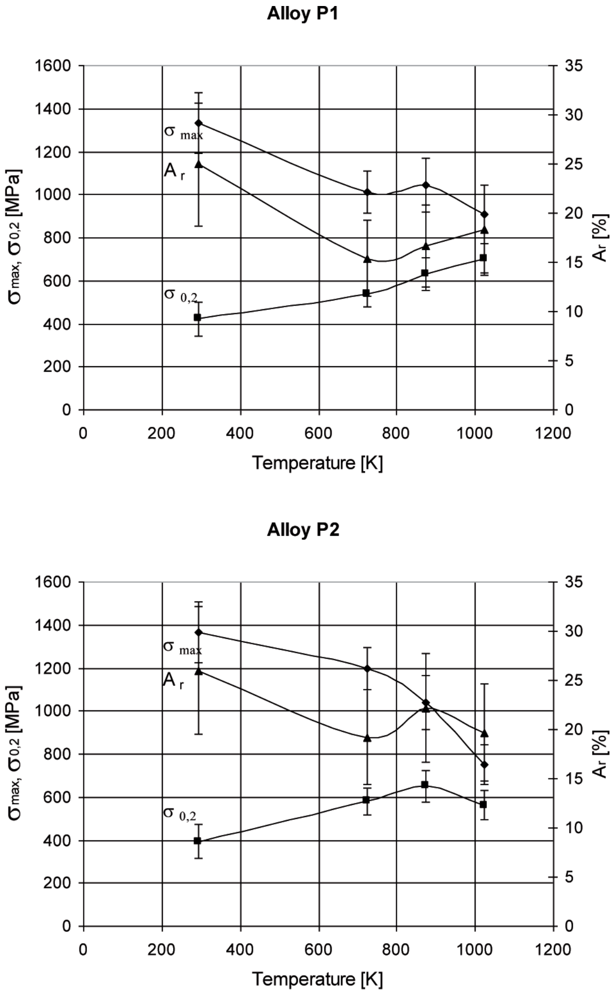

Fig. 5. Mechanical properties of the alloys P1 and P2

The next stage of this work were compression tests performed for the sinters obtained. Similarly as in the case of cast alloys, dependence of mechanical properties of the sinters on the chromium content were examined at several temperature. The tests were carried out using the same methods as those for previously discussed alloys, and the results obtained are presented in Figures 6÷9. The analysis presented below is focused on the comparison of properties of the obtained alloys and sinters.

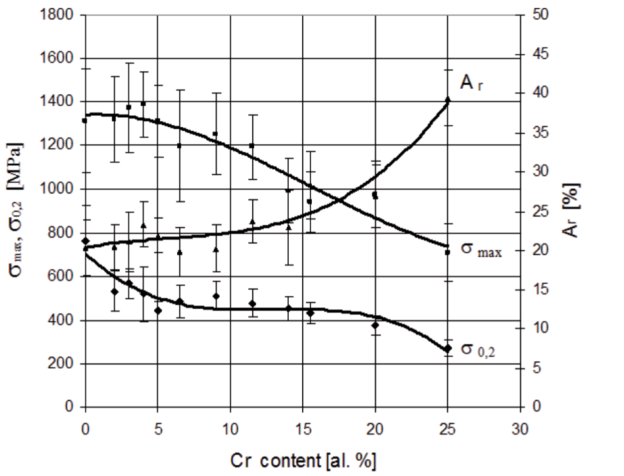

Fig. 6. Mechanical properties of the $Ni_{75}Al_{(25-x)}Cr_x$ sinters at a room temperature

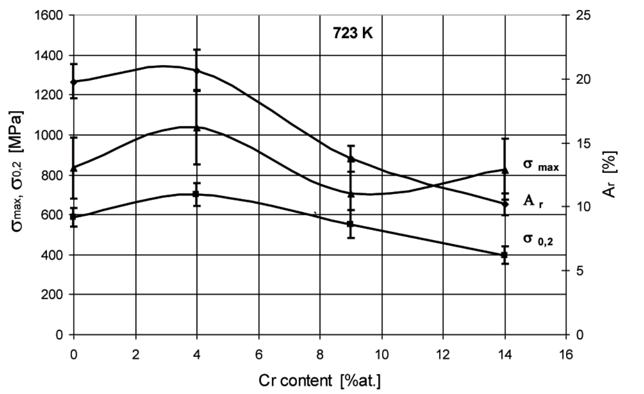

Fig. 7. Mechanical properties of the $Ni_{75}Al_{(25-x)}Cr_x$ sinters at the temperature of 723K

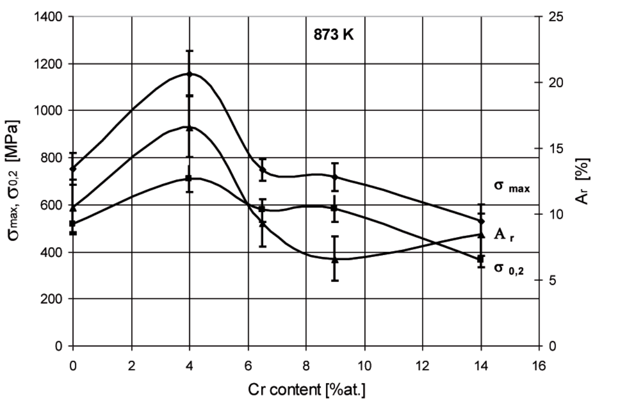

Fig. 8. Mechanical properties of the $Ni_{75}Al_{(25-x)}Cr_x$ sinters at the temperature of 873K

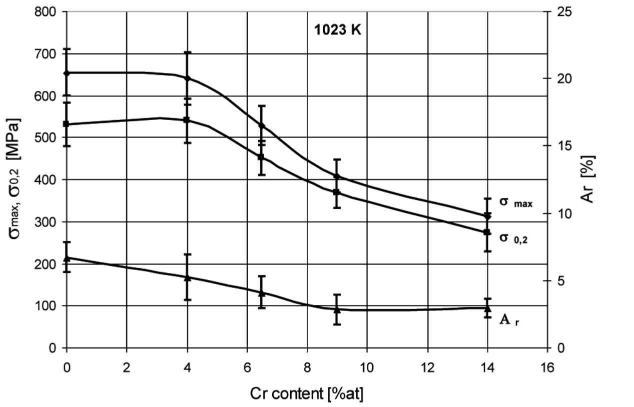

Fig. 9. Mechanical properties of the $Ni_{75}Al_{(25-x)}Cr_x$ sinters at the temperature of 1023K

In case of sinters, the tests carried out at a room temperature revealed the existence of a maximum of the value of σ_{max} for the material containing 4 at. % Cr. In case of the alloys, however, the parameter σ_{max} at this Cr content assumed the minimum value. At low chromium contents, the maximum true stress value was similar for the sinters and alloys (about 1400 MPa). With the increase in Cr content the decrease in σ_{max} was observed, but in the case of Ni75Cr25 sinters the limit values were lower (about 700 MPa) than for the Ni75Cr25 alloys (about 900 MPa). The yield strength $\sigma_{0.2}$ assumed similar values but in case of the alloys a maximum was observed at the Cr content of about 12%, whereas in case of sinters the highest values of $\sigma_{0.2}$ were obtained for the sinter without chromium (about 760 MPa). The ductility (A_r) of the Ni75Cr25 alloys and sinters with zero chromium content was 15% and 20%, respectively, and it was increasing in both cases with the increase in Cr content (up to 45% and 39% for the alloys and sinters, respectively).

The temperature increase to 723K resulted in the decrease of maximum true stress. In case of the alloys "smoothening" of the curve σ_{max} – Cr content (compared to the curve determined at a room temperature) was observed, i.e. characteristic minimum of this curve at Cr content of 4 at.% disappeared. In case of the sinters, however, existence of a maximum of σ_{max} has been maintained. An increase in yield strength up to about 650 MPa (0% Cr, alloy) and to about 700 MPa (4% Cr, sinter) was also observed in case of both material types. Ductility of the alloys and sinters significantly decreased – the respective curves describing this material property were more irregular than at a room temperature. It was found that up to the chromium content of 11.5% the value of A_r was steady (about 18%), and next its rapid increase up to 31% at the Cr content of 15.5% was observed in case of alloys. For the sintered materials maximum of the A_r parameter, reaching 17%, appeared at the Cr content of about 3%, and its minimum of 12% was found at the Cr content of 9%.

This behaviour remained unchanged at further temperature increase up to 873K. The value of A_r (17%) for the sinter containing 4% Cr was still higher compared to similar values for other sinters, and it remained unchanged compared to the value determined at 723K. In case of the alloys, the scope of compositions ensuring small changes in the A_r values with the Cr content increase has narrowed to 6.5%, and then A_r was evidently increasing so that at the alloys containing 11.5% Cr it was 22%.

The maximum true strain σ_{max} was still decreasing at temperature increase, but for the Ni75Al21Cr4 sinter exhibiting particularly high properties its value was still high (about 1150 MPa) and, similarly as A_r, it was considerably higher than the corresponding values determined for the remaining sinters. In case of alloys, the highest value of σ_{max} was similar – it was about 1100 MPa (Ni75Al25 and Ni75Al23Cr2). The yield strength $\sigma_{0.2}$ was (again) the highest for the Ni75Al21Cr4 sinter (700 MPa), and in case of alloys it was consistently decreasing at chromium content increase (from 630 MPa for Ni75Al25 to 360 MPa for Ni75Al9.5Cr15.5).

At the temperature of 1023K very clear decrease in plasticity was observed in case of sinters, A_r for the aforementioned Ni75Al21Cr4 sinter dropped to 4%, but the strength properties remained high: σ_{max}= 640 MPa and $\sigma_{0.2}$= 530 MPa. In case of the alloys, strength properties for Ni75Al16Cr9 were similar: σ_{max}=610 MPa, $\sigma_{0.2}$=540 MPa, but the ductility was much higher: A_r=12%. For the Ni75Al25 alloy we have obtained σ_{max}=800 MPa, $\sigma_{0.2}$=630 MPa, but its ductility was low: A_r=6%. The alloy containing 11.5% Cr is also worth noting: its strength properties were slightly lower, i.e. σ_{max}=590 MPa, $\sigma_{0.2}$=500 MPa, but it had the highest ductility at this temperature: A_r=14%.

This work also included examination of sinters containing the products of mechanical alloying. On one hand, the pressure-sintered products of mechanical alloying are extremely brittle: A_r=0 (see Fig. 10; sinters 3 and 4), but on the other hand they are valuable additive to the sintered mixture of pure metals. Fig. 10 shows results of compression tests carried out at room temperature for the sinters containing, besides a mixture of pure metals Ni75Al25 (80 wt %), the chromium-containing products of mechanical alloying (Ni75Al15Cr10, 20 wt % – sinter No 1) or chromium-free products (Ni75Al25, also 20 wt % – sinter No 2). These results, and those obtained at elevated temperature, are presented in Figs 11 and 12. These results are generally consistent with to those obtained for the Ni75Al21Cr4 sinters, and the proposed operating temperature range of these materials (up to about 873K) remains applicable also in this case.

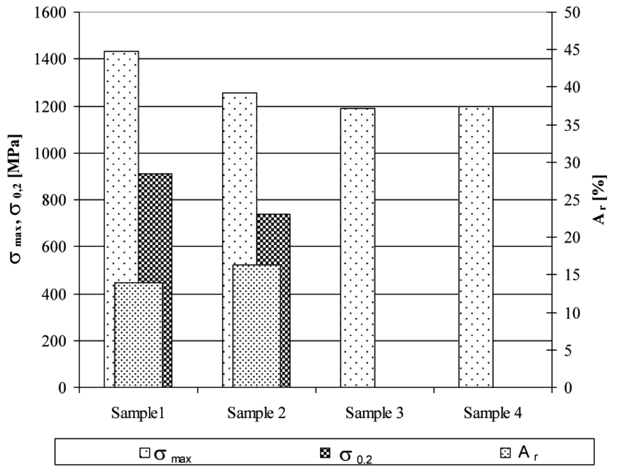

Fig. 10. Mechanical properties of the sinters at a room temperature. The sinter made from:

1. 80% – a mixture of Ni, Al powders (3:1 at. %) + 20% – mechanical alloying product at the same composition of powders
2. 80% – a mixture of Ni, Al powders (3:1 at. %) + 20% – mechanical alloying product with the initial composition of Ni75Al15Cr10.
3. product of mechanical alloying from the Ni, Al. powders (3:1 at.).
4. product of mechanical alloying from the powders Ni:Al:Cr = 75:15:10 (at. %).

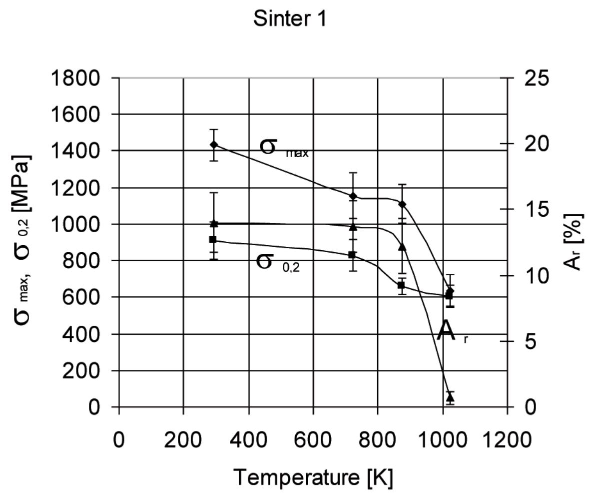

Fig. 11. Mechanical properties of a sinter obtained from: (80%) a mixture of Ni and Al powders (3:1 at.%) + (20%) mechanical synthesis product with the same powders composition

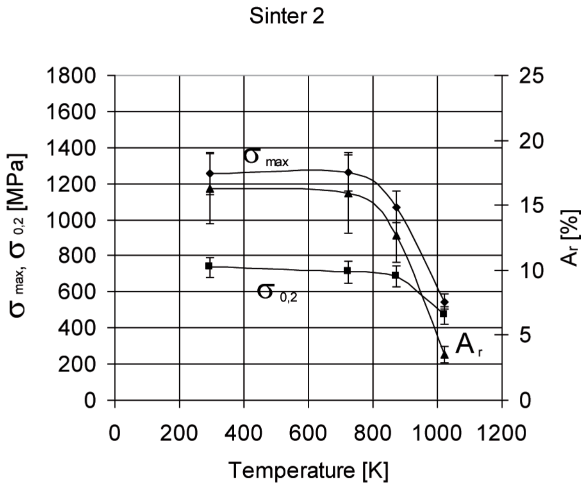

Fig. 12. Mechanical properties of a sinter obtained from: (80%) a mixture of Ni and Al powders (3:1 at.%) + (20%) mechanical synthesis product with the composition Ni75Al15Cr10

4. Summary and conclusions

Under this work alloys and sinters exhibiting the best mechanical properties from a point of view of their potential high-temperature application as constructional materials have been selected. Analysis of the results of tests showed that particular attention, from among the sinters examined, should be paid to the material containing 4% Cr. Its maximum true stress at a room temperature is high (σ_{max} = 1390 MPa), yield strength reaches about 500 MPa, and its ductility is relatively high – uniform contraction A_r is about 23%. With the temperature increase σ_{max} gradually decreases, but at the temperature of 873K it is still high (1150 MPa), and at 1023K it is 640 MPa. The yield strength increases with temperature, similarly as in the case of cast alloys. At a room temperature $\sigma_{0.2}$ is about 500 MPa, and at elevated temperature (723K, 873K) it keeps a constant value of 650 MPa, and next decreases with temperature to 540 MPa at 1023K. The ductility A_r assuming the value of 23% at a room temperature decreases with temperature, but at 873K it is still as high as 13%. Further temperature increase up to 1023K results in ductility decrease to A_r=5 %.

The Ni75Al16Cr9 and Ni75Al13.5Cr11.5 cast alloys also deserve attention - their strength properties are a little bit lower: σ_{max}= 920, 850 MPa, $\sigma_{0.2}$=560, 440MPa, respectively, at the temperature of 873K, and σ_{max}=620, 580 MPa, $\sigma_{0.2}$=555, 500 MPa, respectively, at 1023K, but they maintain plastic properties to higher temperature level: A_r= 12, 14% at the temperature of 1023K. Another worth noting material are the sinters containing mechanical alloying products (20 mass %), exhibiting the properties similar to those of the sinters containing 4% chromium.

The results obtained from this work are promising and suggest the necessity to undertake further research of the discussed alloys and sinters with an account of their industrial application for operation up to the temperature of about 873K. Both in the case of alloys and sinters this research should be focused on (a) identification of the phenomena influencing mechanical properties of the studied materials, determined in this work, and (b) carrying out examination of their mechanical properties by other methods, first of all by the tensile test and impact test.

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