Phase Constituents and Compressive Yield Stress of Ni-Co Base Alloys


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Phase constituents and compressive yield stress of Ni-Co base alloys have been investigated. The results showed that two-phases of γ and γ' were the main constituents in all the alloys. Ni3Ti-type (η) phase was observed in the alloys with lower Co and Ti content (alloy20); while a new intermetallic (Ni3Co3)(Ti,Al) phase with a hexagonal structure was detected in the higher Co and Ti containing alloy(alloy50). At temperatures lower than 1023 K, the compressive yield stress increased with increasing Co content up to 28.6 mass% and Ti content up to 7.4 mass%, but decreased with more Co and Ti addition. At temperatures higher than 1273 K, all the alloys showed similar yield stress.

Keywords: nickel-cobalt alloys, phase constituents; yield stress

1. Introduction

Recently, Ni-Co base alloys, termed as TMW alloys, have been developed for turbine disk applications.1,2) In this alloy system, it contains about 20 to 31 mass% Co, 5.0 to 7.4 mass% Ti, 12 to 16 mass% Cr, 1.5 to 2.5 mass% Al, 2 to 3 mass% Mo, 1 to 1.3 mass% W, Ni balance. The contents of Co and Ti are actually higher than those in commercially used disk alloys, such as 15 mass% Co and 5 mass% Ti in U720LI (developed by Special Metals Corporation),3) 18.5 mass% Co and 3.6 mass% Ti in RR1000 (developed by Rolls-Royce Corporation).4) It is known that Ni3Ti (η) phase with a hexagonal close packed (hcp) structure forms easily in Ni-base superalloy with high Ti content.5) Although TMW alloys contain higher amount of Ti than U720LI and RR1000, some of TMW alloys are only composed of γ and γ' two phases. Also, TMW alloys exhibit improved phase stability, superior tensile strength up to 1023 K and higher creep resistance up to 998 K than those of the U720LI.6) On the other hand, Ni3Ti (η) phase forms in some of TMW alloy with high Ti content.7) The η phase is generally considered to have a deleterious effect on alloy’s ductility.7)

It has been suggested that the formation of η phase can be restrained by more Co addition.8) Up to now, the maximum Co and Ti contents in TMW alloys are 31 mass% and 7.4 mass%, respectively. It is still unknown whether the η phase exists or any other compounds would form in higher Co and Ti containing alloys. Thus, this paper investigates the phase constituents and compressive yield stress of new Ni-Co base alloys with higher Co and Ti.

2. Experimental

Table 1 lists the nominal chemical composition of the alloys investigated in present study. The base alloys, U720LI and Co-16.9 mass%Ti, were first cast. The alloys were prepared by mixing the above two base alloys in proportion as listed in Table 1. The heat treatment was carried out in a similar manner to U720LI, which is 1373 K/7200 s water quenching (WQ) followed by 923 K/86400 s and 1033 K/57600 s air cooling (AC). For microstructural observations, the samples were etched in a solution of kalling reagent (100 mlHCl, 100 ml methanol and 50 g CuCl2). The micro-structures were then observed by using a scanning electron microscope (SEM). The phase constituents were determined by X-ray diffraction (XRD) under 40 kV and 300 mA and differential thermal analysis (DTA). The thin foils for transmission electron microscope (TEM) observations were prepared by a twin-jet electron polisher in a chemical solution of 23% perchloric acid and 77% acetic acid at about 233 K and then examined using a Philips CM200 operated at 200 kV.

Compressive specimens with 3 mm in diameter and 6 mm in height were cut by an electric discharge machining (EDM) from the heat-treated samples. Compressive tests were performed at a nominal strain rate of 2.5 × 10−4 s−1 on a SHIMADZU AG50KNI testing machine in a vacuum from room temperature to 1423 K.

3. Results and Discussion

A typical DTA thermogram up to 1673 K obtained at a heating rate of 0.17 K/s is shown in Fig. 1. Only one exothermic peak at 1609 K in alloy0 (U720LI) and 1453 K in alloy100 (Co-16.9 mass%Ti) was observed, which corresponds to the alloy’s melting temperature. While in alloy20 with 20 mass%Co-16.9 mass%Ti addition, alloy50 with 50 mass%Co-16.9 mass%Ti addition and alloy70 with 70 mass%Co-16.9 mass%Ti addition, two exothermic peaks appeared at the heating curves, one at higher temperature was the melting temperature and another at lower temperature was believed to be associated with the melting of other phases, which will be identified in the following microstructural analysis. In addition, the DTA results also showed that the melting temperature of the alloys decreased with increasing Co and Ti content, indicating that the Co-16.9 mass%Ti addition can reduce the melting temperature.

Figure 2 shows the XRD pattern of the alloys. A similar curve was observed in alloy0, alloy70 and alloy100, those diffraction peaks can be identified as γ and γ’ phases. However, extra peaks as indicated by arrows in alloy20 were detected, and those peaks can be indexed as the (201) and...
In alloy 50, extra diffraction peaks marked by arrows were also observed and could not be indexed as \(\gamma'\) Ni \(_3\) Ti or other known phases. In order to identify the new phase, TEM analysis was performed.

The microstructures of the tested alloys are shown in Fig. 3. Alloy 0 (U720LI) mainly consisted of \(\gamma\) and \(\gamma'\) phases. The dark particle-like phase was \(\gamma'\) and the matrix was \(\gamma\) phase. The average particle size of \(\gamma'\) phase was about 0.8 \(\mu\)m and the volume fraction of \(\gamma'\) phase was measured to be about 45% (Fig. 3(a)). For the alloy 20 with 20 mass\% Co-16.9 mass\% Ti addition, three phases (\(\gamma\), \(\gamma'\) and plate phase) were observed (Fig. 3(b)). The volume fraction was measured to be about 49% for \(\gamma'\) and 6% for the plate phase, respectively. Energy dispersive spectrometer (EDS) analysis showed that there was more Ti content in plate phase than in \(\gamma'\). The analysis of selected area electron diffraction (SAED) pattern confirmed that the plate phase is a \(\chi\)-\(\gamma'\) intermetallic compound with a hexagonal structure (\(a = 0.51 \) nm and \(c = 1.25 \) nm). The plate phase had a higher Ti and lower Al content compared to that of \(\gamma'\) phase. The total volume fraction of \(\gamma'\) was estimated to be about 40% and the plate phase was about 20%. The microstructure of the alloy 70 with 70 mass\% Co-16.9 mass\% Ti addition only exhibited two phases, which were identified to be \(\gamma\) and \(\gamma'\) phase, based on the XRD pattern. The blocky phase was \(\gamma\) and the matrix phase was \(\gamma'\). The volume fraction of \(\gamma'\) was estimated to be about 5%.

Based on microstructural observations, two exothermic peaks in Fig. 1 were determined to be \(\gamma\) and \(\chi\) in alloy 20, \(\gamma\) and \(\gamma'\) in alloy 50, \(\gamma\) and \(\gamma'\) in alloy 70, respectively. In alloy 20 and alloy 50, no exothermic peak from \(\gamma'\) was detected. This was probably related to the \(\gamma'\) size and content. It is known that U720LI consists of three types of \(\gamma'\), that is, primary \(\gamma'\) with size of 1–10 \(\mu\)m, secondary \(\gamma'\) and tertiary \(\gamma'\) with size smaller than 1 \(\mu\)m. In order to know the effect of \(\gamma'\) size on exothermic peak, two samples with and without primary \(\gamma'\) were obtained by selecting suitable heat treatment. The DTA results showed that exothermic peaks from phases other than \(\gamma\) and \(\gamma'\).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>U720LI/Co-Ti</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Ti</th>
<th>Al</th>
<th>C</th>
<th>B</th>
<th>Zr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 0</td>
<td>100 : 0</td>
<td>16.0</td>
<td>15.0</td>
<td>3.0</td>
<td>1.3</td>
<td>5.0</td>
<td>2.5</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>57.2</td>
</tr>
<tr>
<td>Alloy 20</td>
<td>80 : 20</td>
<td>12.8</td>
<td>28.6</td>
<td>2.4</td>
<td>1.0</td>
<td>7.4</td>
<td>2.0</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>45.7</td>
</tr>
<tr>
<td>Alloy 50</td>
<td>50 : 50</td>
<td>8.0</td>
<td>49.1</td>
<td>1.5</td>
<td>0.6</td>
<td>10.9</td>
<td>1.3</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>28.6</td>
</tr>
<tr>
<td>Alloy 70</td>
<td>30 : 70</td>
<td>4.8</td>
<td>62.6</td>
<td>0.9</td>
<td>0.4</td>
<td>13.3</td>
<td>0.8</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>17.2</td>
</tr>
<tr>
<td>Alloy 100</td>
<td>0 : 100</td>
<td>83.1</td>
<td></td>
<td></td>
<td></td>
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</table>
peak from γ′ appeared only in the sample with primary γ′, indicating that exothermic peak from γ′ was sensitive to the γ′ size. As shown in Fig. 3, the size of γ′ in alloy20 and alloy50 was about 1 μm, which was similar to that in alloy0 (U720Li) without γ′ peak during heating, while the size of γ′ in alloy70 was much larger (>10 μm). Moreover, the content of γ′ in alloy20, alloy50 and alloy70 was 40%, 49% and 70%, respectively.

Figure 4 gives the compressive yield stress of the alloys as a function of temperature. In alloy0, the yield stress decreased with increasing temperature. In alloy20, the yield stresses were higher than those of alloy0, in particular, the yield stress of the alloy20 dropped very slowly at temperatures below 1023 K. In alloy50, alloy70 and alloy100, anomalous yield behavior was observed, that is, yield stresses increased with increasing temperature, reached the maximum strength at temperature about 1023 K, and then decreased with increasing temperature. This anomalous yield behavior could be related to the high content of AB₃ type intermetallics (60% (40% γ′ + 20% (Ni,Co,Cr)₃(Ti,Al)) in alloy50, 70% in alloy70, and 95% in alloy100), which usually display anomalous yield behavior.² It is noted that, at temperatures lower than 1023 K, when the Co-16.9 mass%Ti addition was lower than 20 mass%, the compressive yield stress increased with increasing Co-16.9 mass%Ti addition. The strength increase was ascribed to the solid-solution strengthening of γ and γ′ and precipitate strengthening (higher fraction of γ′).³ When the Co-16.9 mass%Ti addition was more than 20 mass%, the strengths decreased with increasing the Co-16.9 mass%Ti addition. The strength drop was related to the decrease of solid solution strengthening and precipitation strengthening. The amount of refractory elements Cr, Mo, W decreased greatly with increasing the Co-16.9 mass% addition, as listed in Table 1. In addition, the (Ni,Co,Cr)₃(Ti,Al)
Phase also contained high amount of Cr, thus the effect of solid-solution decreased with the increasing of Co-16.9 mass%Ti addition. The volume fractions of precipitate phase were 40% in alloy50, 30% in alloy70 and 5% in alloy100, so the effect of precipitate strengthening also decreased with increasing Co-16.9 mass%Ti addition. At temperature higher than 1273 K, all the alloys showed similar strengths.

According to the binary and Ni-Co-Ti ternary phase diagram,13) as well as the microstructural observations, a partial phase diagram of Ni-Al-Co-Ti is plotted in Fig. 5. Since a fcc/L1₂ structure was found in all the tested alloys, the fcc/L1₂ structure existed continuously from Ni-Al side to Co-Ti side. On the other hand, two three-phase regions existed in the quaternary phase diagram, that is, γ, γ' and η existed in the alloys with about 20 mass% Co-16.9 mass%Ti addition, and γ, γ' and (Ni,Co,Cr)₃(Ti,Al) existed in the alloy with about 50 mass% Co-16.9 mass%Ti addition. Since a fcc/L1₂ structure is thought to be a key role for keeping the excellent high-temperature properties for applications, we believe that this partial quaternary phase diagram is helpful for developing new alloys with a fcc/L1₂ structure.

4. Conclusions

The phase constituents and compressive yield stress of Ni-Co base alloys have been examined and the following conclusions were drawn:

(1) γ and γ' phases with a fcc/L1₂ structure existed continuously from Ni-side to Co-side.

(2) η phase formed in alloys with about 28.6 mass% Co and 7.4 mass%Ti content (alloy20), and the (Ni,Co,Cr)₃(Ti,Al) phase with a hexagonal structure formed in alloys with about 49.1 mass% Co and 10.9 mass%Ti (alloy50).

(3) The compressive yield stress increased with the increasing of Co-16.9 mass%Ti addition up to 20 mass%, but decreased with more Co-16.9 mass%Ti additions at temperatures up to 1023 K.

REFERENCES