

# A review on the progress towards PT-base superalloys for ultra high temperature applications

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Pt-Al-X alloys have shown good mechanical properties and adequate oxidation resistance. Starting from a promising Pt-Al-Cr alloy, the influence of Ni additions was investigated. After ageing finely dispersed precipitates are observed. Nb, Ta, Ti and Re increase strength when added as partial substitute for Al. Minor additions of B increase creep resistance and rupture time remarkably, owing to strengthening of the grain boundaries. The evolution of the alloy development programme as well as selected properties of the multi-component Pt-base alloys are presented.

## Introduction

Exceptional chemical stability paired with high thermal stability make Pt alloys interesting for many high-temperature applications. While pure Pt has low mechanical strength at high temperatures, alloying with Ir or Rh increases stress rupture strength remarkably<sup>1</sup>. However, above 1100°C, Pt-Ir alloys show relatively high mass loss whereas Pt-Rh alloys are stable but are more and more difficult to form at Rh contents higher than 20 wt.%.

A promising approach for a strong Pt-base alloy is to mimic the microstructure of Ni-base superalloys. Appropriate alloying and heat treatment of a so called Pt-base superalloy should lead to a fine distribution of a  $\gamma'$  phase with  $L1_2$  structure coherently embedded in the Pt rich face centred cubic (fcc)  $\gamma$  matrix<sup>4</sup>.

Hill and co-workers<sup>2,3</sup> conducted an extensive assessment of systems with Pt as major constituent based on these criteria: high phase stability, high melting point, oxidation and hot corrosion resistance, high thermal conductivity, low thermal expansion, and (if possible) low density. Alloys based on Pt-Al turned out to have the highest potential, not only because of possible precipitation strengthening through  $Pt_3Al$  but also due to high oxidation resistance.

However, in the Pt-Al system, the cubic  $L1_2$   $Pt_3Al$  phase that exists at high temperatures transforms to a tetragonal structure at lower temperatures. Since such good properties exist with the  $\gamma+\gamma'$  structure in Ni-base superalloys, alloying with additional elements was envisaged to stabilize the high temperature  $L1_2$  structure of  $Pt_3Al$ .

## Alloy development programme

The starting point for the development programme for precipitation hardened Pt alloys at the University Bayreuth and the University of Applied Sciences Jena were the ternary Pt-Al-X, alloys which had already been investigated by the South African group at MINTEK<sup>5</sup>.

## Screening of ternary Pt-Al based alloys

The creep behaviour of several ternary Pt-Al-Z (Z = Cr, Ru and Ir) alloys at 1300°C was investigated. Cr was added to stabilize the  $L1_2$  modification of the  $\gamma'$  phase. The ternary elements were selected either to further stabilize the  $L1_2$  form of  $Pt_3Al$  or as solid solution strengthening elements for the Pt matrix.

The results<sup>5</sup> were very promising, especially for the  $PtAl_{10}Cr_4$  alloy which has relatively high stress-rupture strength as well as good ductility. The creep strengths at 1300°C were higher than Ni- and Co-based superalloys whose precipitates dissolve in this high temperature regime. The creep strength of the  $PtAl_{10}Z_4$  system is comparable to mechanical alloyed ferritic ODS alloys like PM2000. The ternary alloy  $PtAl_{10}Cr_4$  was selected for further optimizations.

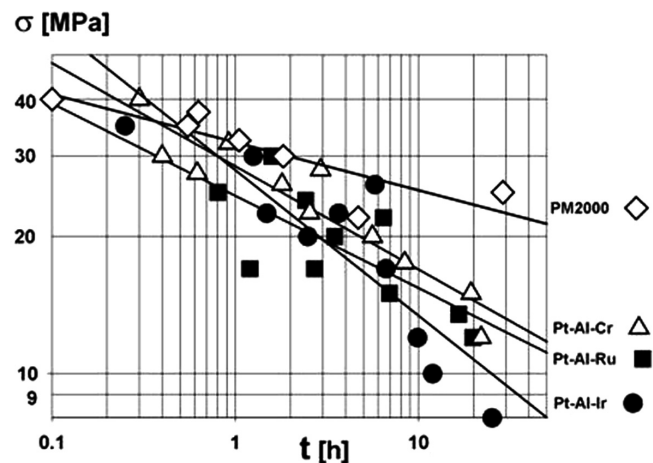
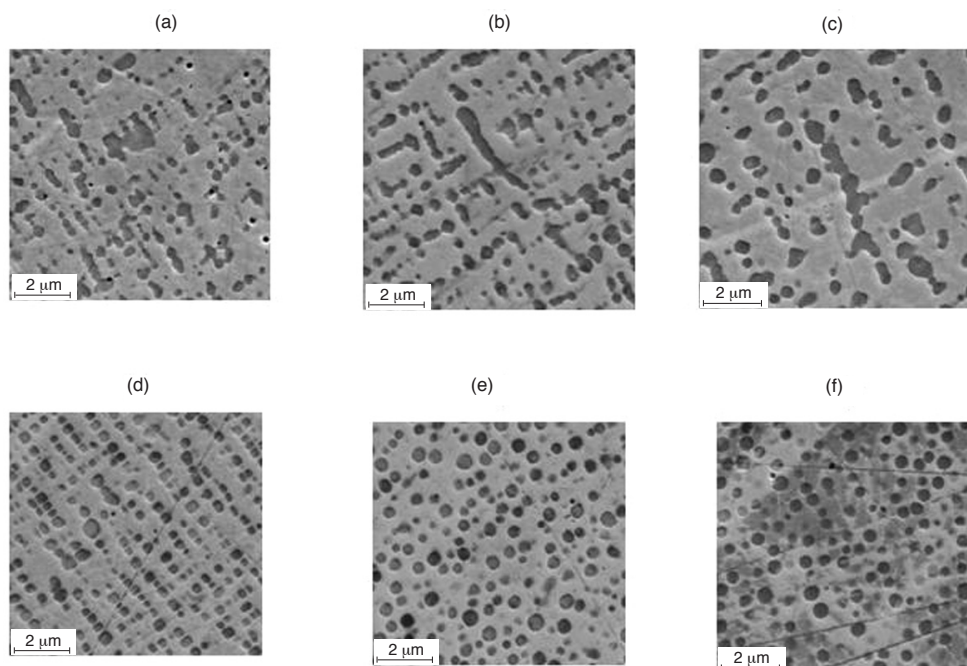


Figure 1. Stress-rupture curves of PM2000 and  $PtAl_{10}Z_4$  alloys at 1300°C<sup>5</sup>



**Figure 2. SE images of Pt-Al-Cr-Ni alloys after solution heat treatment at 1450°C for 24 h and ageing at 1000°C for 120 h. (a) PtAl<sub>11</sub>Cr<sub>3</sub>, (b) PtAl<sub>11</sub>Cr<sub>3</sub>Ni<sub>2</sub>, (c) PtAl<sub>11</sub>Cr<sub>3</sub>Ni<sub>4</sub>, (d) PtAl<sub>11</sub>Cr<sub>3</sub>Ni<sub>6</sub>, (e) PtAl<sub>10</sub>Cr<sub>3</sub>Ni<sub>8</sub>, (f) PtAl<sub>10</sub>Cr<sub>3</sub>Ni<sub>10</sub>**

### Quaternary Pt-Al-Cr-Ni alloys

Because nickel has a good solid-solution strengthening effect on the (Pt) matrix, it was added to a Pt-Al-Cr alloy in varying amounts<sup>6</sup>. Nominal compositions of the alloys preserve a Pt: Al: Cr ratio of about 86: 11: 3, reflecting preceding results on the alloy PtAl<sub>10</sub>Cr<sub>4</sub><sup>5</sup>. PtAl<sub>11</sub>Cr<sub>3</sub>Ni<sub>0-10</sub> alloys with up to 10 at.% Ni were melted.

Alloying the Pt-Al system with both Cr and Ni stabilized consistently the L<sub>12</sub> high temperature modification of Pt<sub>3</sub>Al at room temperature. PtAl<sub>11</sub>Cr<sub>3</sub>Ni<sub>0-10</sub> alloys were all single-phase after solution heat treatment at 1450°C. Ageing at 1000°C produces microstructures similar to Ni-base superalloys (Figure 2). Precipitates in alloys with less than 6 at.% Ni appear to lose coherency after ageing. The alloy PtAl<sub>11</sub>Cr<sub>3</sub>Ni<sub>6</sub> after ageing not only has the highest  $\gamma'$  volume fraction of about 23% but also well-aligned cuboidal precipitates with 0.2–0.5  $\mu\text{m}$  edge lengths and a misfit of -0.1% like Ni-base superalloys. Spherical particles are observed in alloys with more than 6 at.% Ni. These changes of  $\gamma'$  morphologies are attributed to a decreasing absolute value of the misfit with increasing Ni concentration. Ageing at 1100°C lead to coarse  $\gamma'$  particles and reduced  $\gamma'$  volume fractions. However, volume fractions decline less with temperature in alloys containing Ni than without Ni.

### Variation of the Al content for high $\gamma'$ volume fraction

PtAl<sub>12-15</sub>Cr<sub>3</sub>Ni<sub>4-8</sub> alloys with Al contents from 12–15 at.% were chosen near the solubility limit of about 15 at.% in order to achieve high  $\gamma'$  volume fractions. Alloys with up to 13 at.% Al could successfully homogenized in single phase  $\gamma$ -region at 1500°C. Still higher Al contents led to eutectic two-phase interdendritics even after heat treating at 1530°C.

Ageing alloys with up to 13 at.% Al for 120 h at 1000°C led to homogeneous distributions of Pt<sub>3</sub>Al particles. Alloy

PtAl<sub>14</sub>Cr<sub>3</sub>Ni<sub>6</sub> showed cubical Pt<sub>3</sub>Al particles with 520  $\mu\text{m}$  average edge lengths (Figure 3b), hence a microstructure very close to that of Ni-based superalloys. Absolute lattice misfit between  $\gamma$  and  $\gamma'$  turned out to decrease with increasing Ni content. Slightly negative misfit values measured at room temperature together with cubical or spherical particles, respectively, signify coherency between  $\gamma$  and  $\gamma'$  in alloys with more than 5 at.% Ni (Figure 3b and c). Coherency seems to be missing in an alloy with Ni content of less than 5 at.% and high negative misfit of about -0.5 % (Figure 3a). By raising the concentration of the major  $\gamma'$ -forming element Al up to 13 at.% the  $\gamma'$  volume fraction could be increased to 30 %<sup>7</sup>.

### Variation of the CR $\gamma'$ volume fraction

It turned out that the Al content in Pt-Al-Cr-Ni alloys is limited to about 12.5 at.%. In another test series the Cr content of PtAl<sub>12.5</sub>Cr<sub>0-6</sub>Ni<sub>6</sub> alloys was varied between 0 and 6 at.%. The Ni content was fixed at nominal 6 at.% in order to ensure coherency between  $\gamma$  and  $\gamma'$ .

Dendritic as-cast structures of PtAl<sub>12.5</sub>Cr<sub>3</sub>Ni<sub>6</sub>, PtAl<sub>12</sub>Ni<sub>6</sub> and PtAl<sub>12</sub>Cr<sub>6</sub>Ni<sub>6</sub> could be homogenized by heat treatment at 1500–1510°C. Formation of Pt<sub>3</sub>Al precipitates was almost completely suppressed in PtAl<sub>12.5</sub>Cr<sub>3</sub>Ni<sub>6</sub> after homogenization for 12 h at 1500°C and subsequent water quenching (Figure 4a). Whereas air cooling leads to homogeneous distributions of Pt<sub>3</sub>Al particles with 200  $\mu\text{m}$  average edge lengths and a volume fraction of about 30% (Figure 4b). The same alloy shows a bimodal particle distribution with a coarse particle fraction after furnace cooling from 1500°C (Figure 4c). The entire  $\gamma'$  volume fraction was 34%. Increasing the Cr content to 6 at.% leads to average edge lengths of 500  $\mu\text{m}$  and a volume fraction of 50% in PtAl<sub>12</sub>Cr<sub>6</sub>Ni<sub>6</sub> after homogenization for 6 h at 1500°C + 6 h at 1510°C in Ar, followed by air cooling. For the investigated Pt-base superalloys, controlled air cooling after solution heat treatment is sufficient to provoke an aspired microstructure similar to Ni-base superalloys.

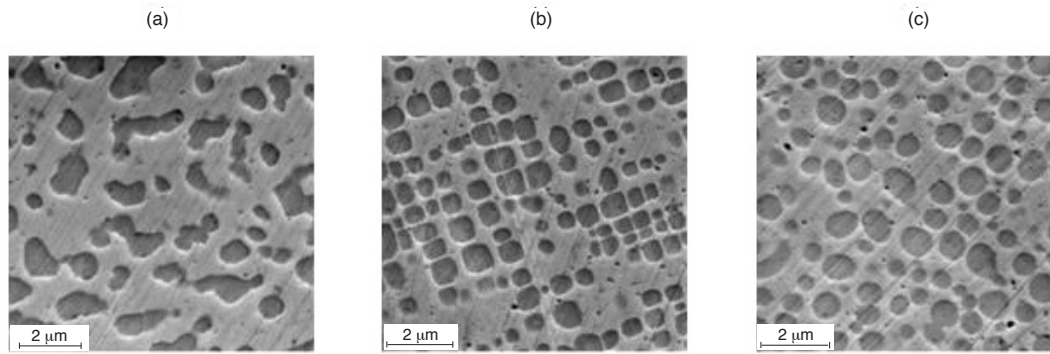


Figure 3. Secondary electron SEM micrographs of the investigated alloys, annealed for 12 h at 1500°C and 120 h at 1000°C in Ar. The dark areas are precipitates, the brighter areas the matrix phase. (a) PtAl<sub>4</sub>Cr<sub>3</sub>Ni<sub>4</sub>, (b) PtAl<sub>4</sub>Cr<sub>3</sub>Ni<sub>6</sub>, (c) PtAl<sub>4</sub>Cr<sub>3</sub>Ni<sub>8</sub>

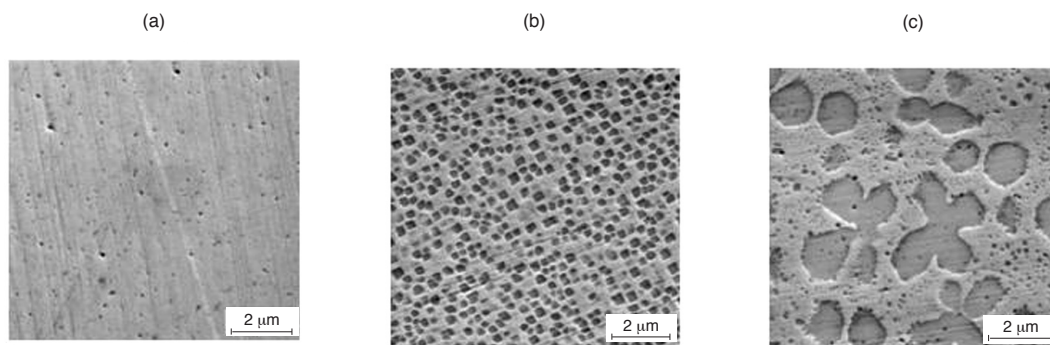


Figure 4. Secondary electron SEM micrographs of PtAl<sub>12.5</sub>Cr<sub>3</sub>Ni<sub>6</sub> after homogenization for 12 h at 1500°C and different cooling regimes. (a) water quenched, (b) air cooled, (c) furnace cooled

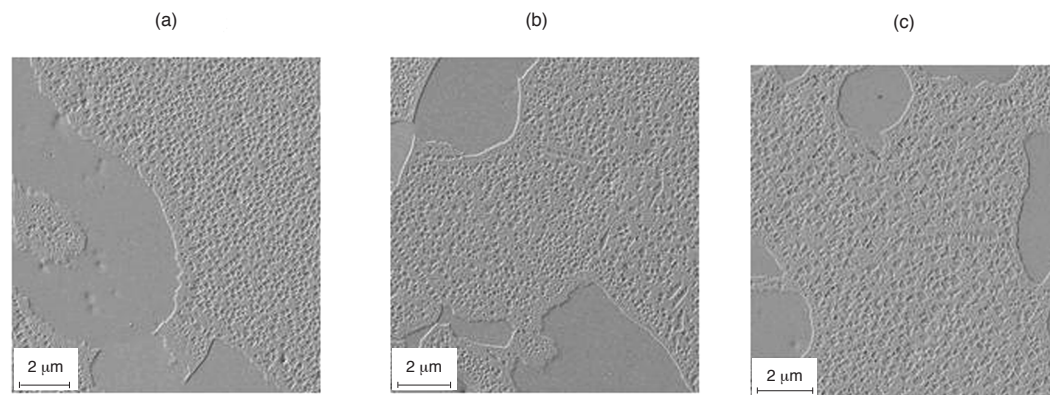


Figure 5. SEM secondary electron micrographs of the  $\gamma$ - $\gamma'$  microstructures of after heat treatment for 6 h at 1500°C and 6 h at 1510°C with air cooling. (a) PtAl<sub>7</sub>Cr<sub>6</sub>Nb<sub>5</sub>, (b) PtAl<sub>7</sub>Cr<sub>6</sub>Ta<sub>5</sub>, (c) PtAl<sub>7</sub>Cr<sub>6</sub>Ti<sub>5</sub>

### Substitution of Ni

In a trial and error approach the high melting elements Nb, Ta and Ti were chosen to substitute Ni. By XRD analysis, the fcc  $\gamma$  matrix and the L<sub>12</sub>-ordered  $\gamma'$  phases are identified in PtAl<sub>7</sub>Cr<sub>6</sub>Nb<sub>5</sub>, PtAl<sub>7</sub>Cr<sub>6</sub>Ta<sub>5</sub> and PtAl<sub>7</sub>Cr<sub>6</sub>Ti<sub>5</sub>. The lattice misfits are at about  $-3 \cdot 10^{-3}$  in all alloys. After homogenization the alloys show bimodal size distributions of  $\gamma'$  particles (Figure 5a-c). Beside coarse and irregularly shaped particles with a volume fraction in between 10 and 20%, small cuboids of up to 300  $\mu\text{m}$  in size are observed. After subsequent ageing for 264 h at 1200°C with water

quenching, measurement of the chemical compositions revealed Nb and Ta to be almost evenly distributed to  $\gamma$  matrix and  $\gamma'$  phase, whereas Ti is enriched in the  $\gamma'$  phase. The  $\gamma'$  volume fractions after ageing amounted to 34% in PtAl<sub>7</sub>Cr<sub>6</sub>Nb<sub>5</sub>, 33% in PtAl<sub>7</sub>Cr<sub>6</sub>Ta<sub>5</sub> and 35% in PtAl<sub>7</sub>Cr<sub>6</sub>Ti<sub>5</sub>.

Compression strengths of polycrystalline PtAl<sub>7</sub>Cr<sub>6</sub>Nb<sub>5</sub>, PtAl<sub>7</sub>Cr<sub>6</sub>Ta<sub>5</sub> and PtAl<sub>7</sub>Cr<sub>6</sub>Ti<sub>5</sub> are higher than that of PtAl<sub>12</sub>Cr<sub>5</sub><sup>5</sup> (Figure 6). At 800°C PtAl<sub>7</sub>Cr<sub>6</sub>Ta<sub>5</sub> is strongest, whereas at higher temperatures PtAl<sub>7</sub>Cr<sub>6</sub>Nb<sub>5</sub> shows the highest strength. Above 1200°C PtAl<sub>7</sub>Cr<sub>6</sub>Nb<sub>5</sub> and PtAl<sub>7</sub>Cr<sub>6</sub>Ta<sub>5</sub> outperform the single-crystal Ni-base superalloy CMSX-4.

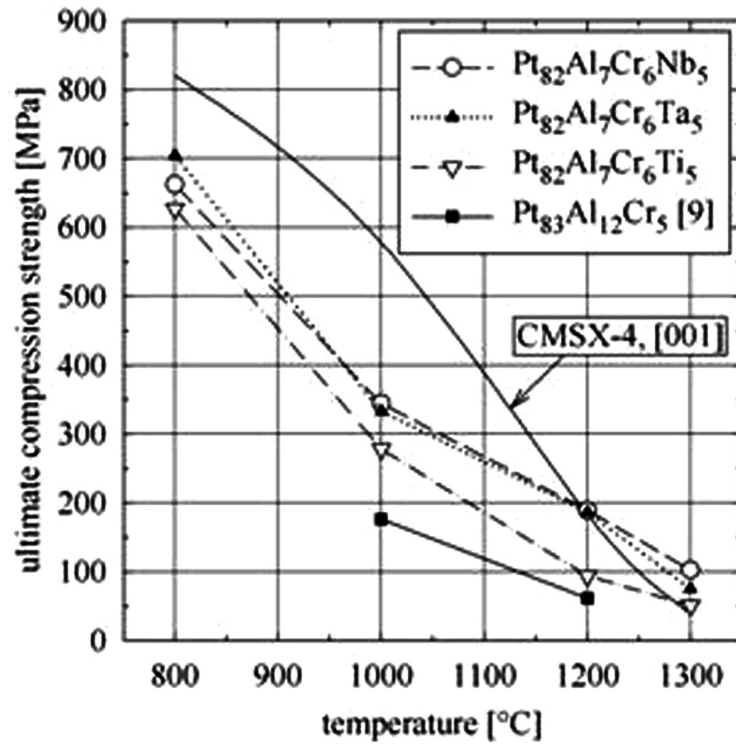


Figure 6. High-temperature compression strength of the polycrystalline Pt-Al-Cr-X alloys<sup>5</sup> and single-crystal Ni-base superalloy CMSX-4

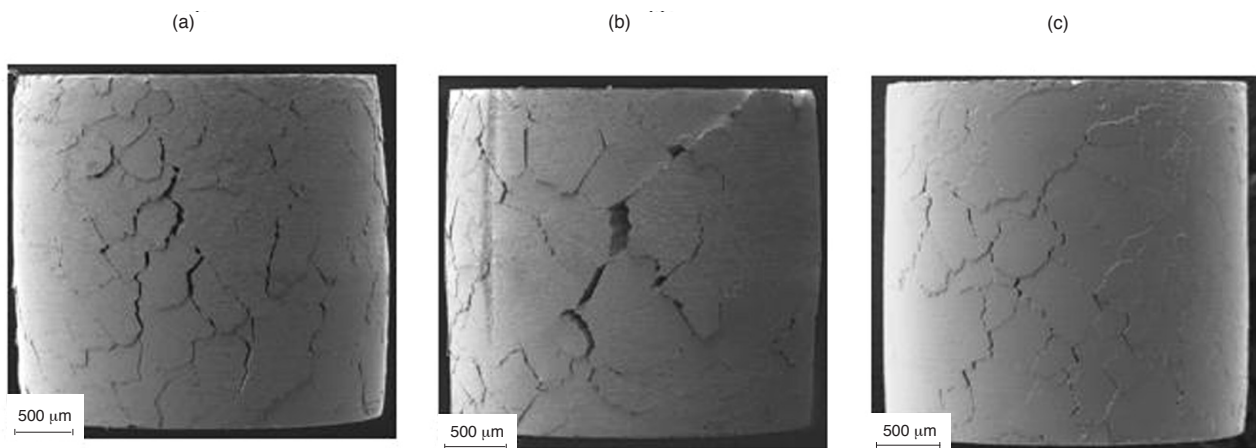


Figure 7. SEM micrographs of the PtAl<sub>7</sub>Cr<sub>6</sub>Ta<sub>5</sub> compression samples deformed at (a) 800°C, (b) 1000°C, (c) 1300°C

The deformed samples indicate rupture on the outside surface, which was also observed in case of the Nb- and the Ti-containing Pt-base alloys (Figure 7a-c).

#### Micro alloying

Small B atoms often segregate to grain boundaries and can therefore influence grain boundary adhesion. Re is very beneficial for the creep strength of Ni-base superalloys. Therefore B and Re were added to the PtAl<sub>12</sub>Cr<sub>6</sub>Ni<sub>5</sub> alloy base in various amounts. Compression creep tests at 1200°C revealed that minor B additions increase both creep strength and ductility considerably (Figure 8a). Additions of 0.3 at.% B together with 2 at.% Re further increase creep strength (Figure 8b).

#### Conclusions

Starting from a promising alloy in the system Pt-Al-Cr, the influence of additions of further elements on mechanical strength and microstructure was investigated. The evolution of the alloy development programme together with selected properties was presented. Nb, Ta and Ti increase strength when added as partial substitute for Al, however, with higher susceptibility to internal oxidation. After ageing, precipitates finely dispersed in the matrix are observed. Minor additions of B increase creep resistance and rupture time remarkably, owing to strengthening of the grain boundaries. Re was found to slow down precipitate growth and to increase creep strength further.

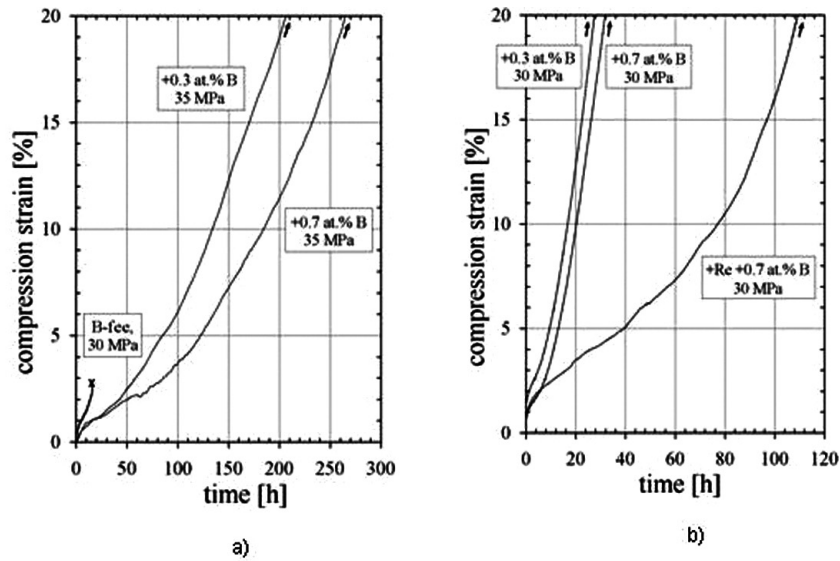


Figure 8. Compression creep curves of pure and micro alloyed PtAl<sub>12</sub>Cr<sub>6</sub>Ni<sub>5</sub>. a) Pure alloy compared to alloys micro alloyed with 0.3 and 0.7 at. % B at 1200°C. b) Alloys micro alloyed with 0.3, 0.7 at. % B and with both 2 at. % Re and 0.7 at. % B at 1300°C

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