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(54) **ALUMINIUM OXIDE FORMING NICKEL  
BASED ALLOY**

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(57) **ABSTRACT**

Nickel based alloy intended for use at high temperatures  
wherein it comprises in percent by weight (wt-%)

C 0.05-0.2  
Si max 1.5  
Mn max 0.5  
Cr 15-20  
Al 4-6  
Fe 15-25  
Co max 10  
N 0.03-0.15  
O max 0.5

one or more elements selected from the group consisting of  
Ta, Zr, Hf, Ti and Nb 0.25-2.2

one or more elements selected from the group consisting of  
REM max 0.5

balance Ni and normally occurring impurities.

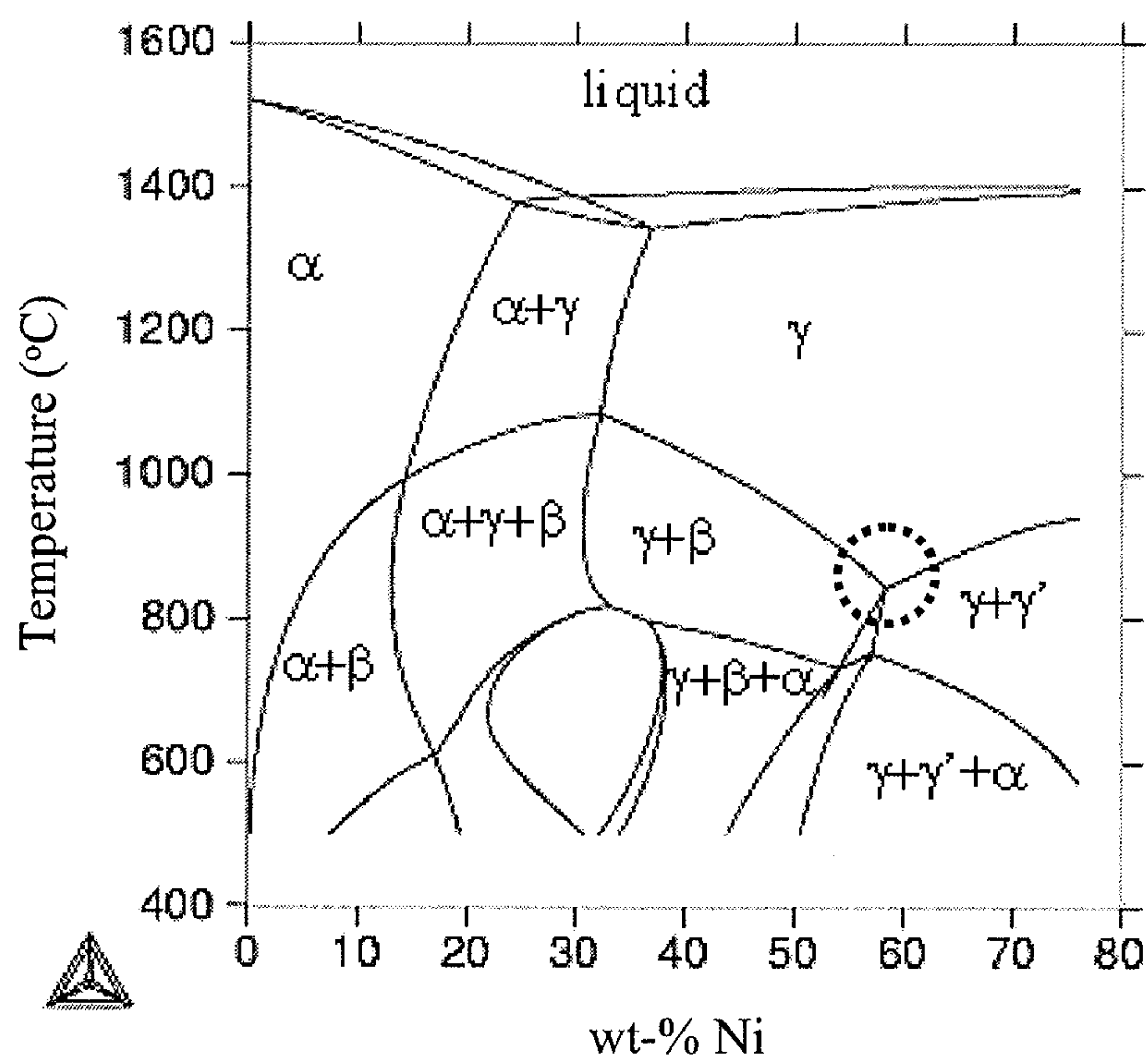


Fig 1a.

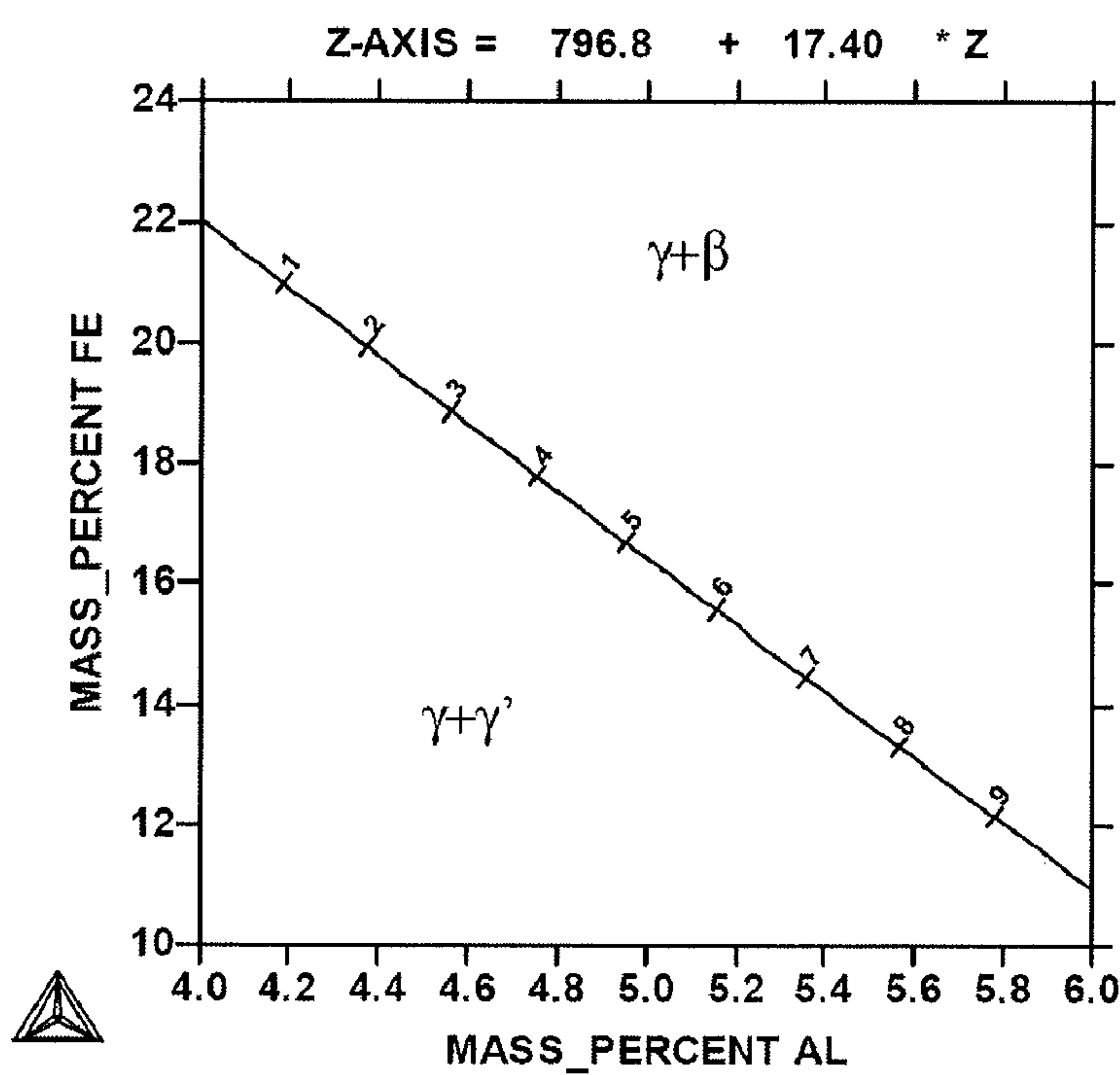


Fig 1b.

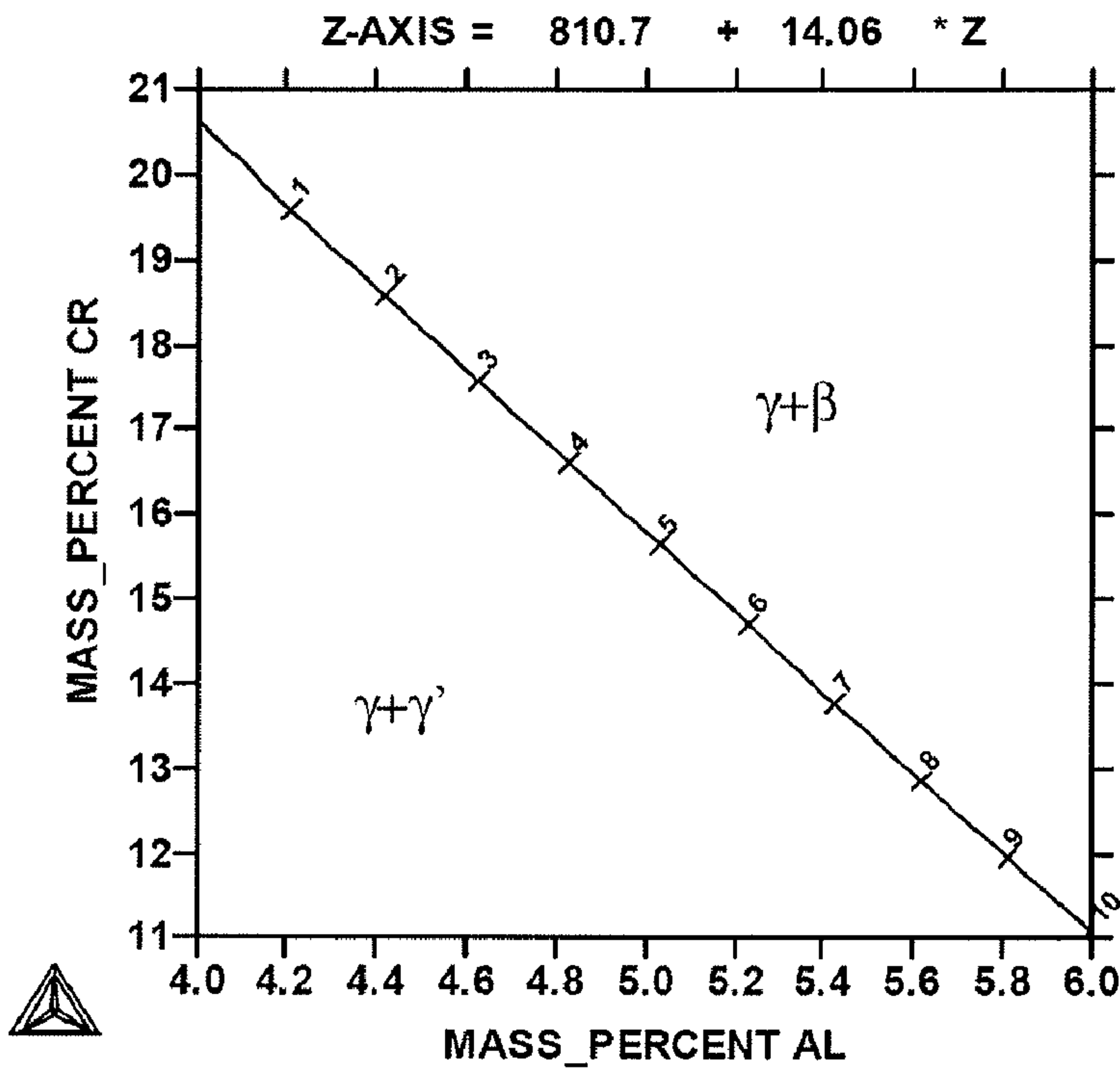


Fig 1c.

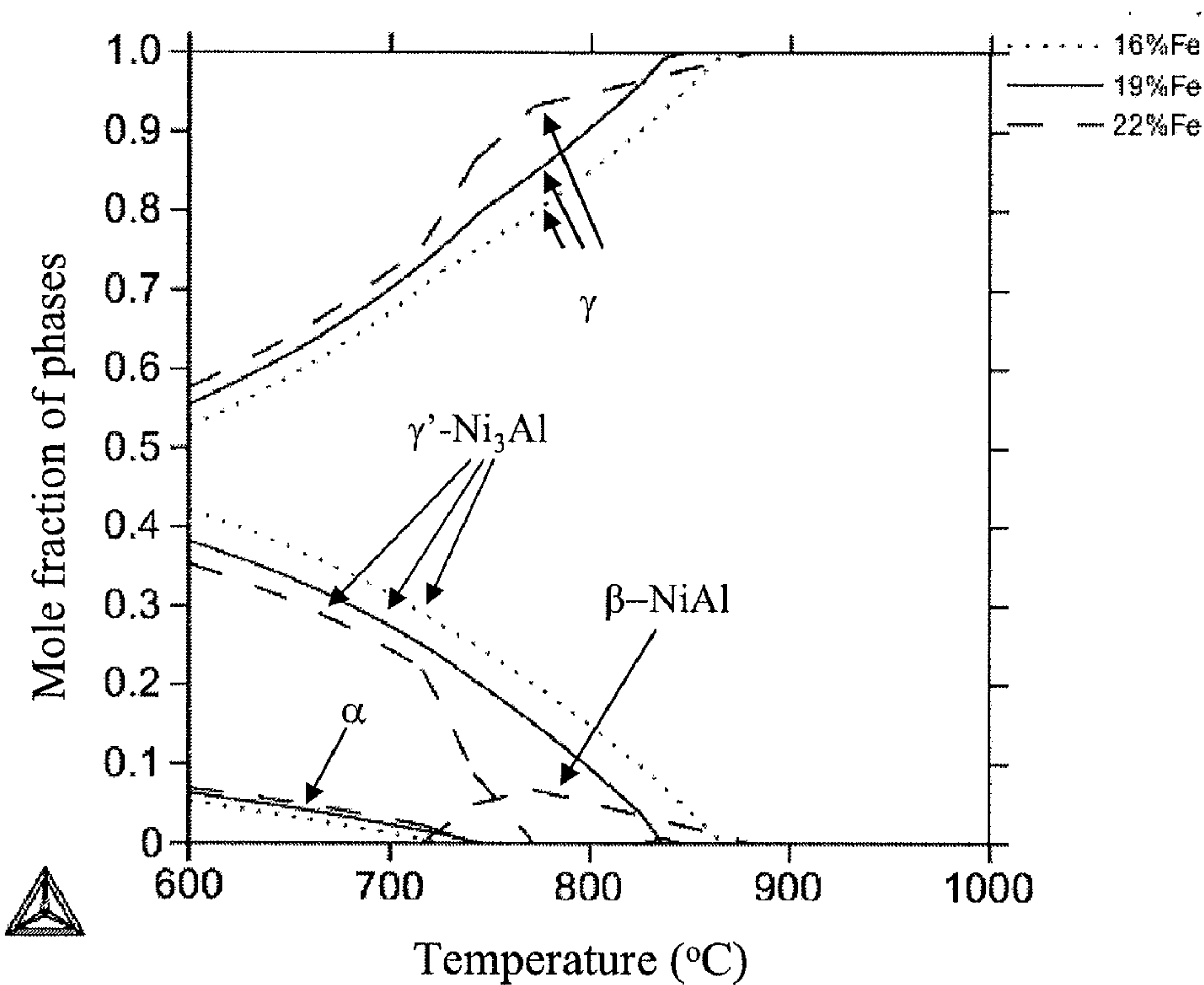


Fig 2.

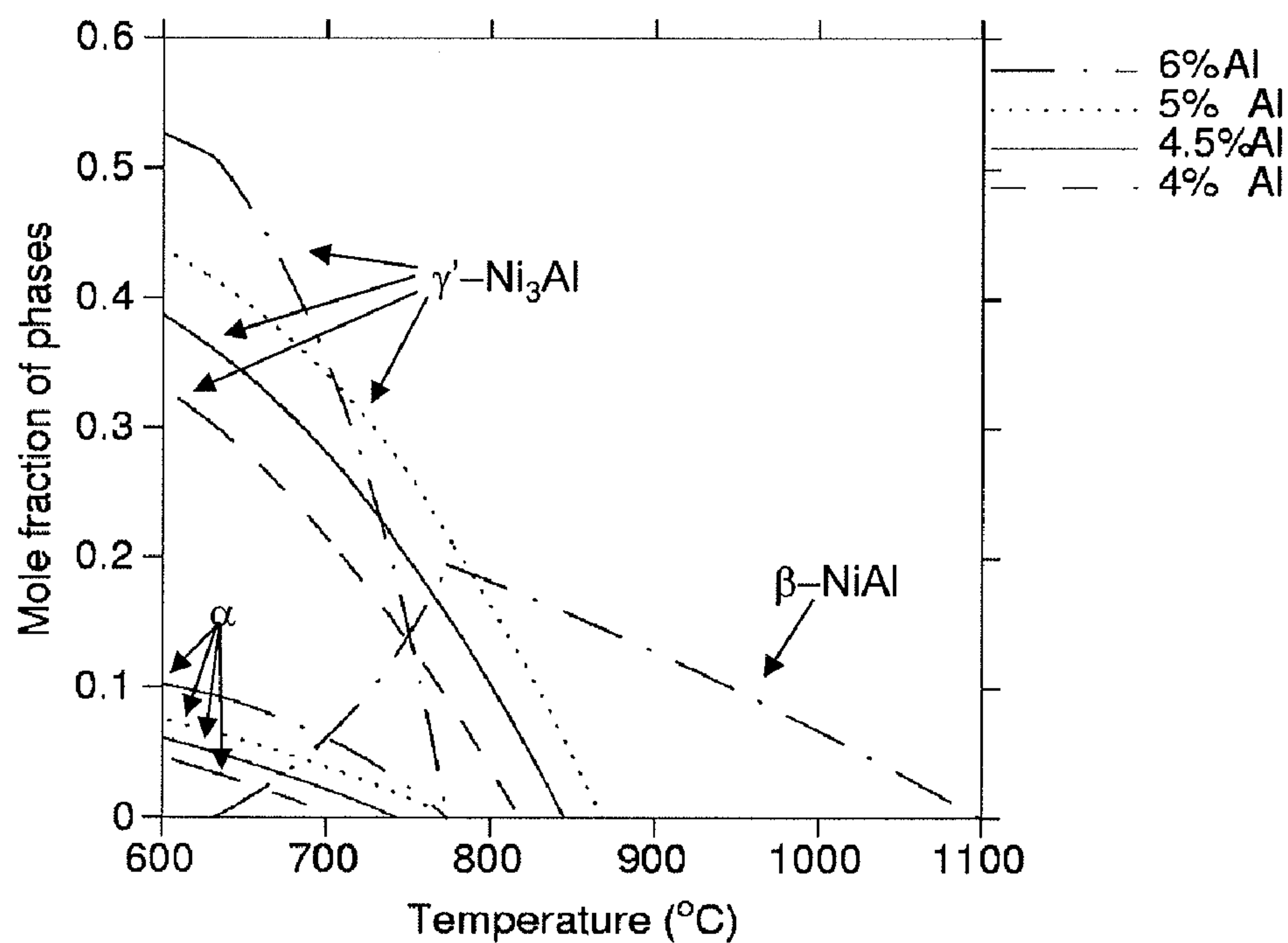


Fig 3.

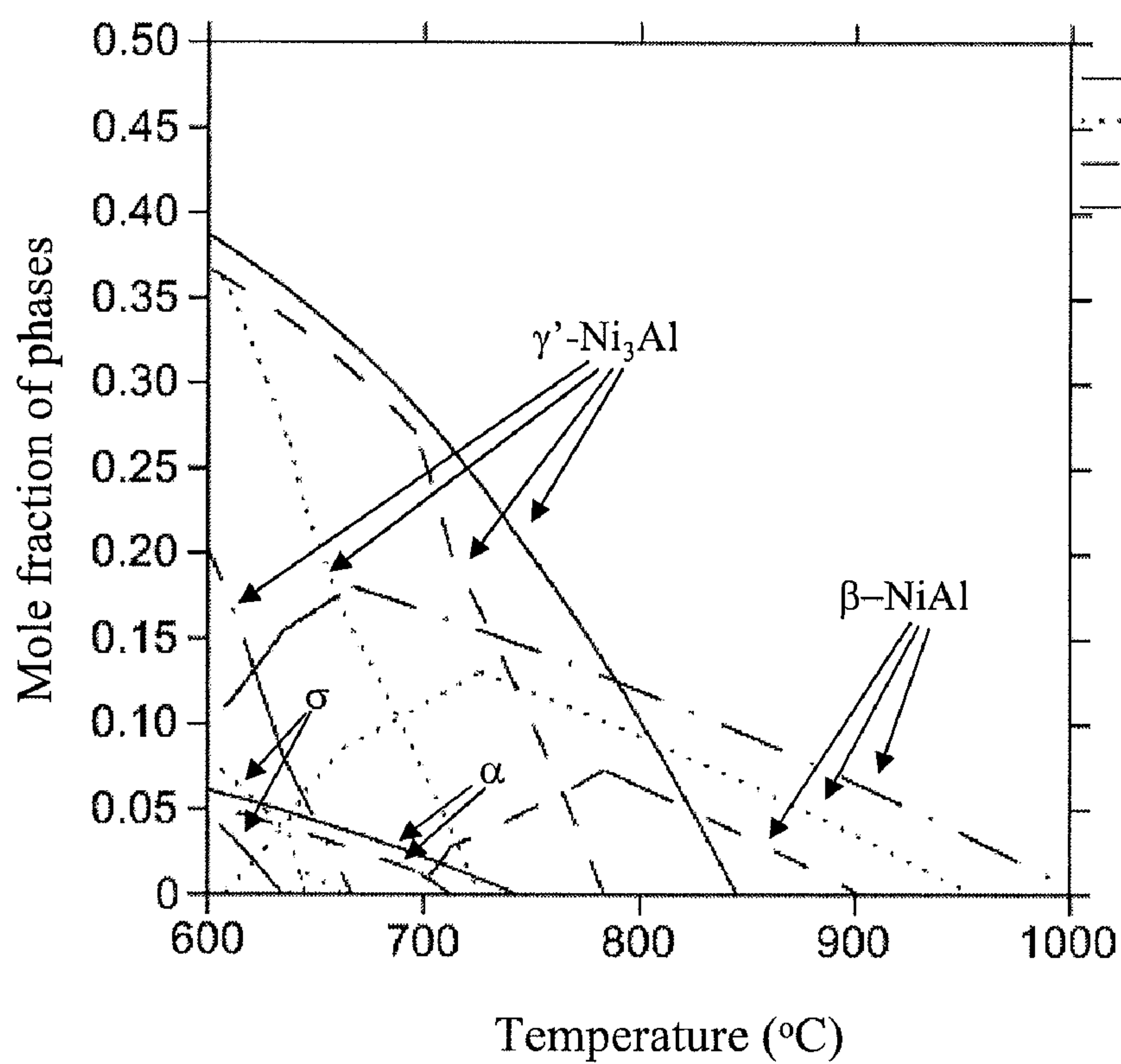


Fig 4.

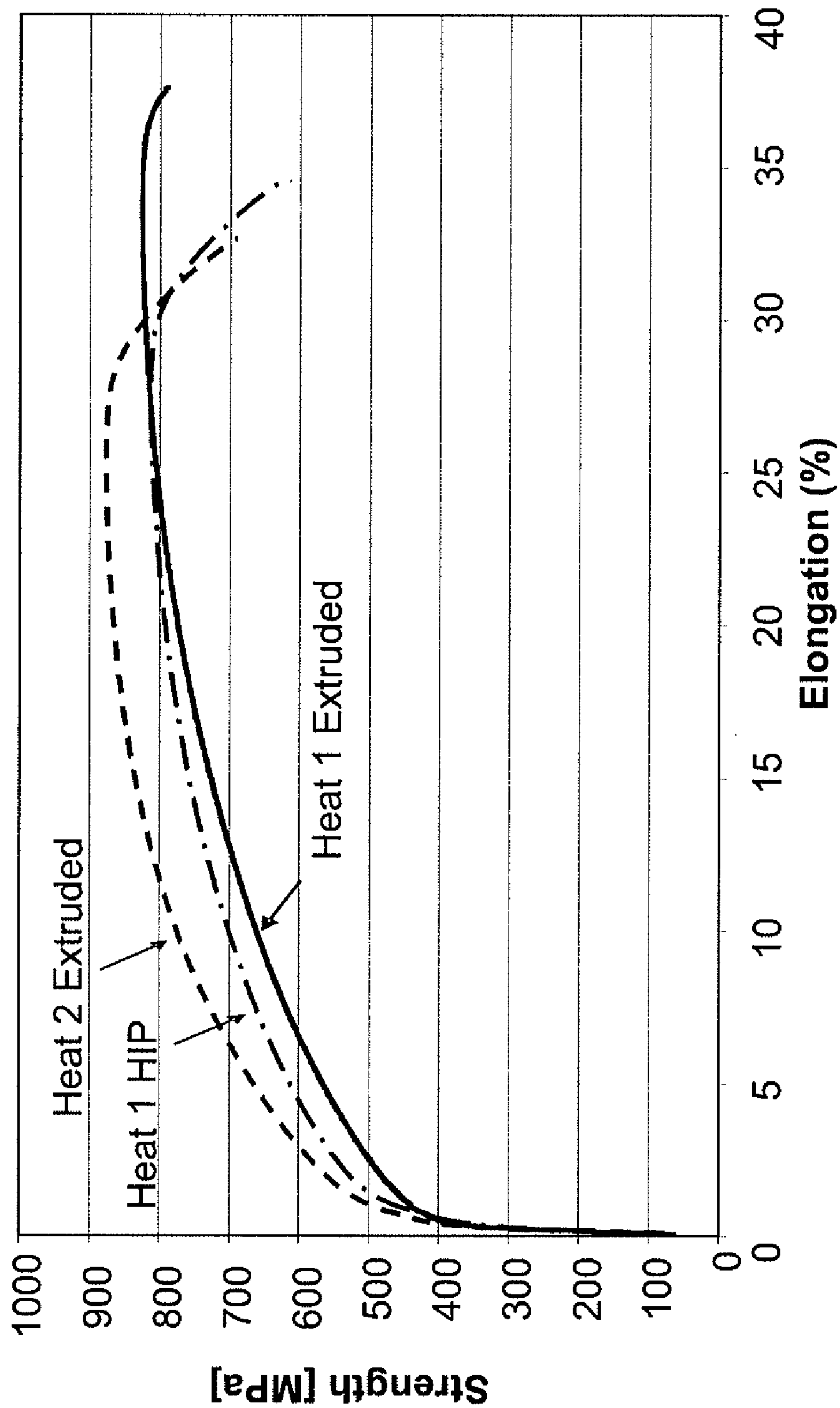


Fig 5.



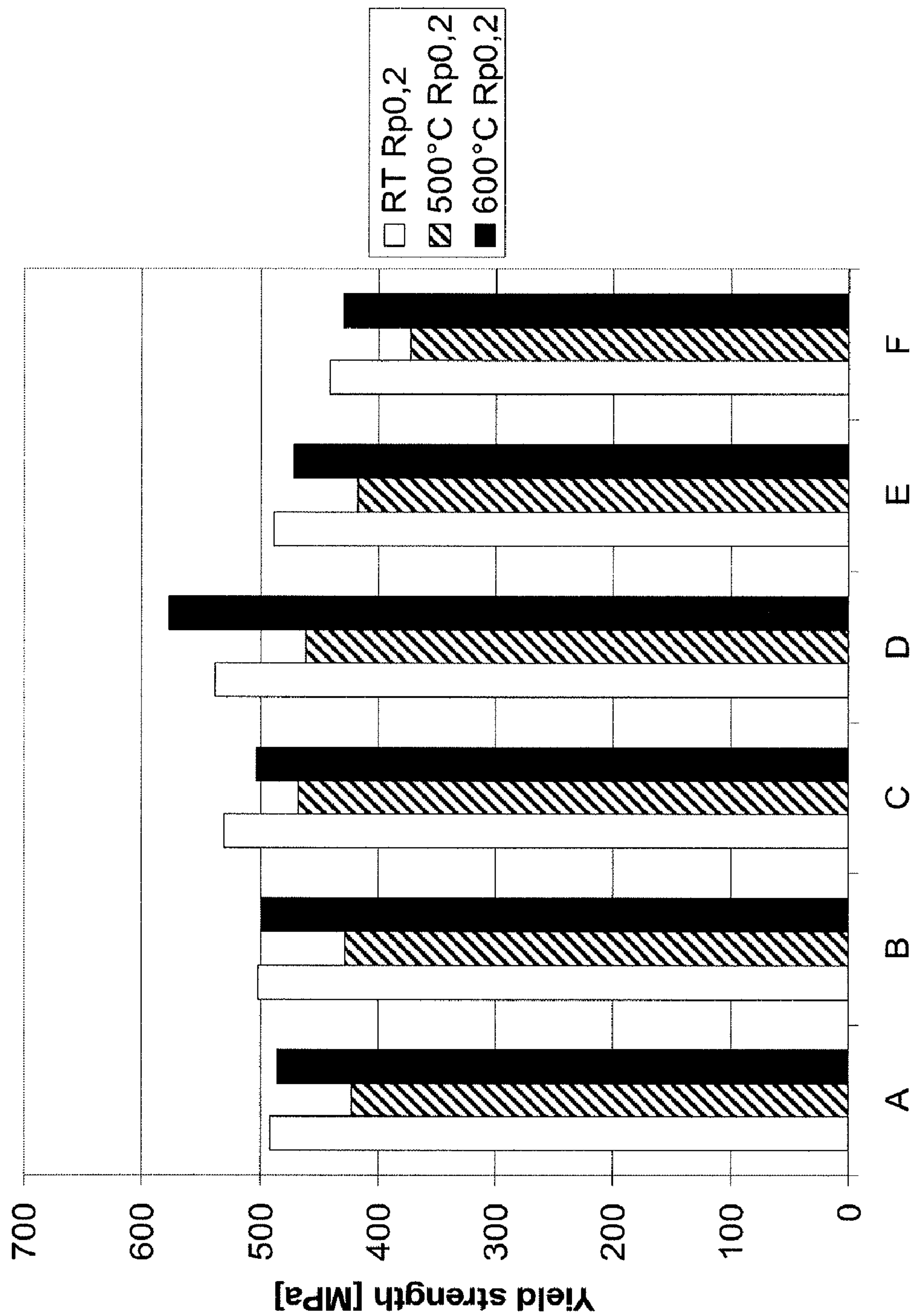


Fig 6.

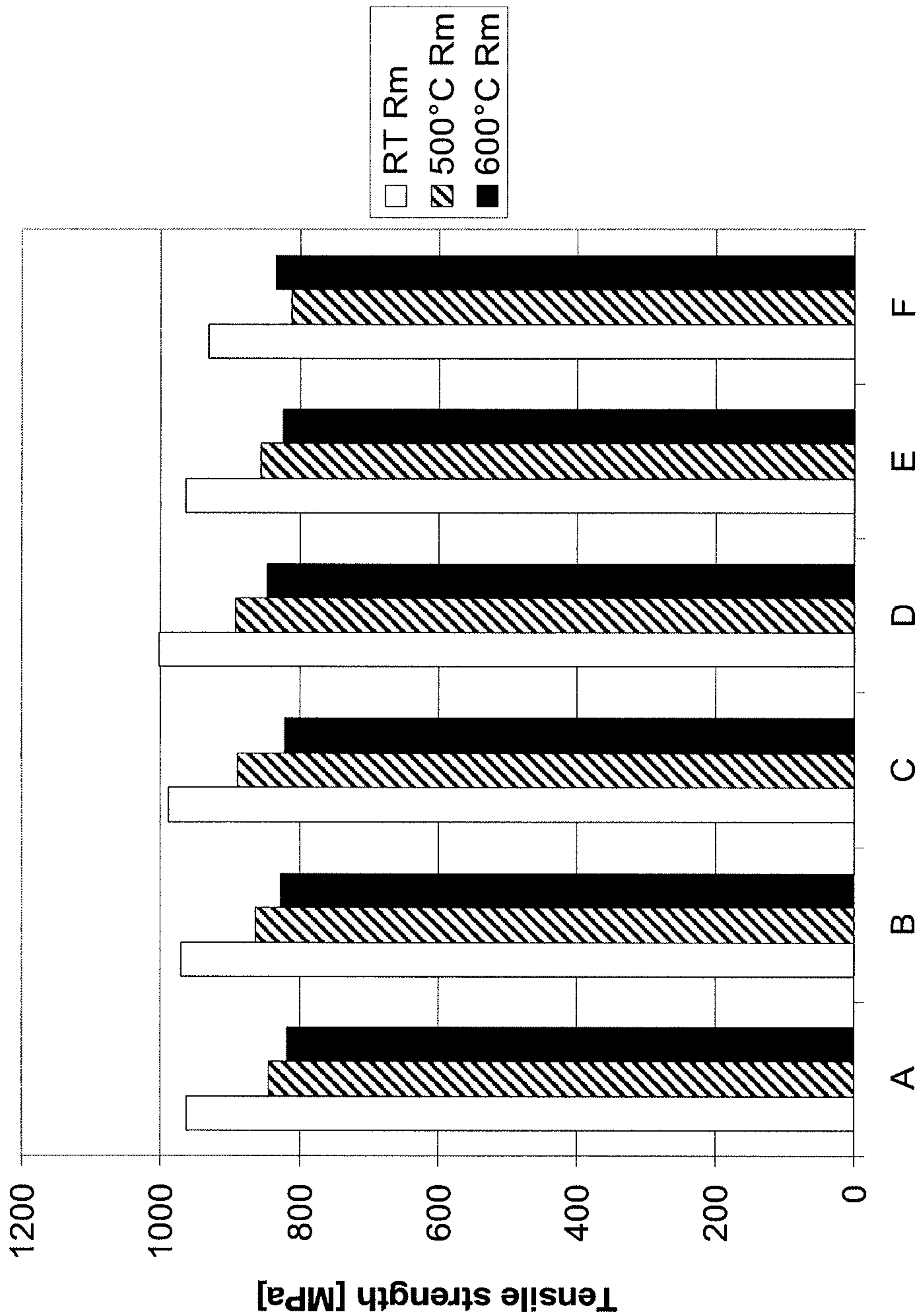


Fig 7.

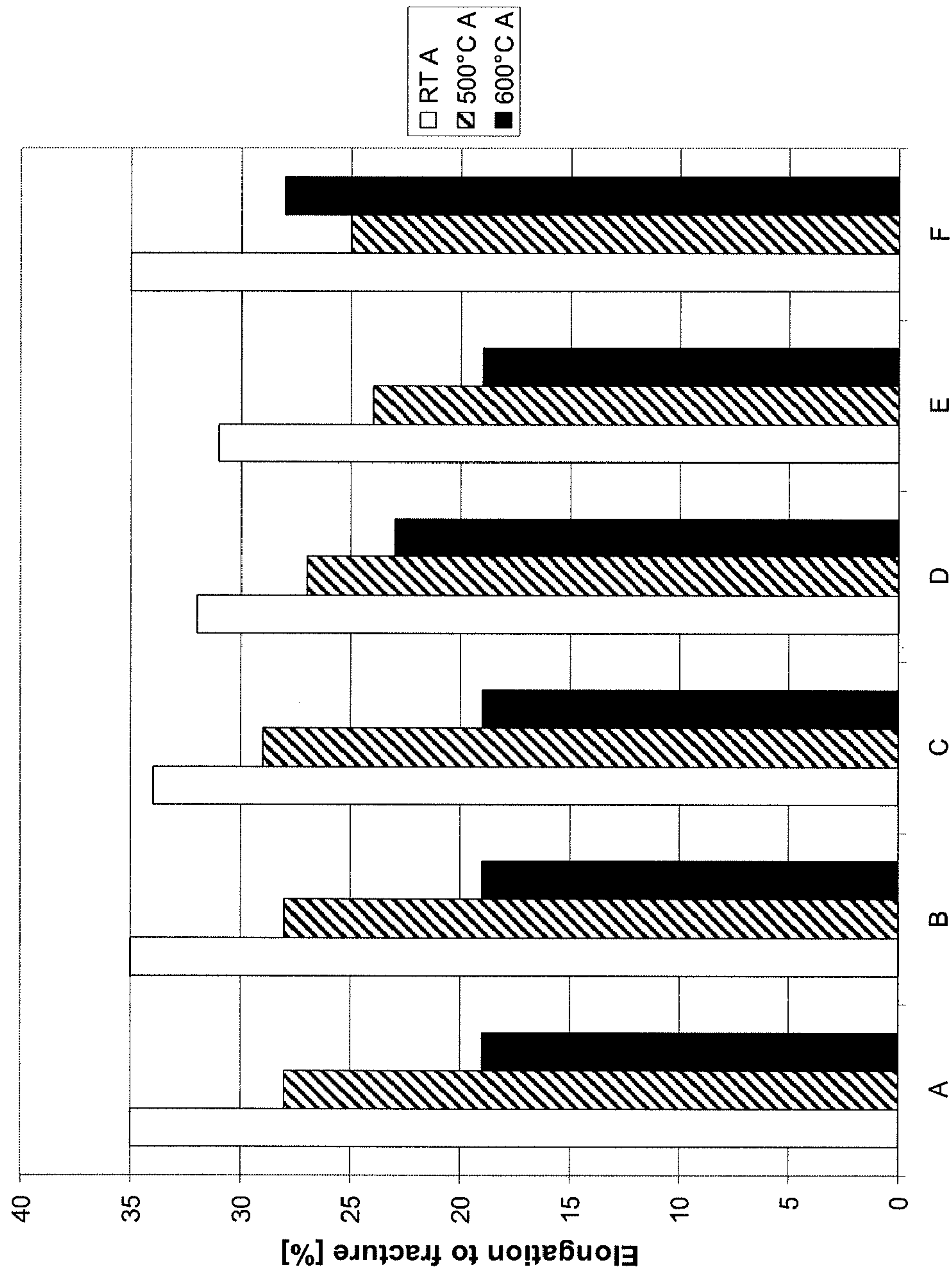


Fig 8.



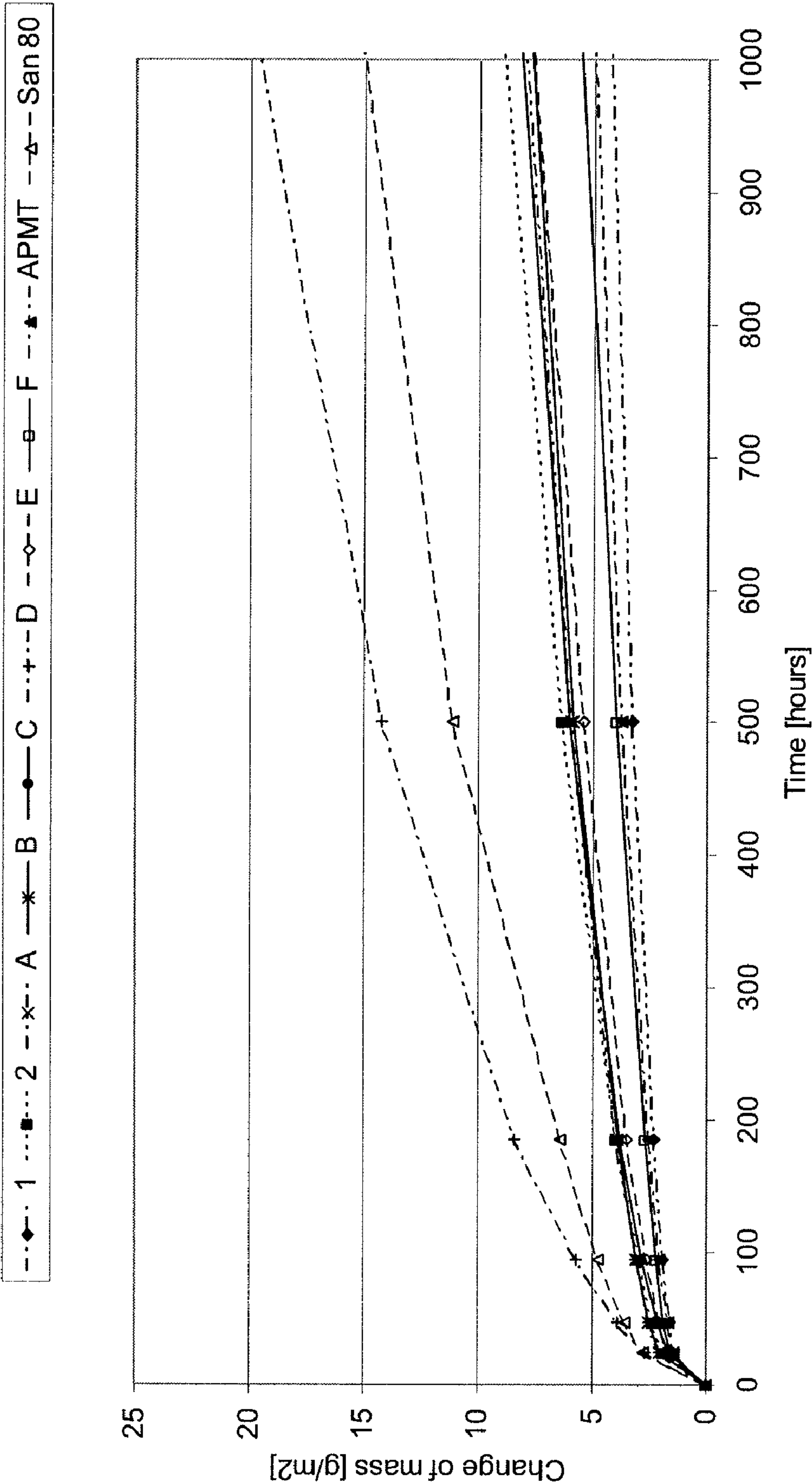


Fig 9.

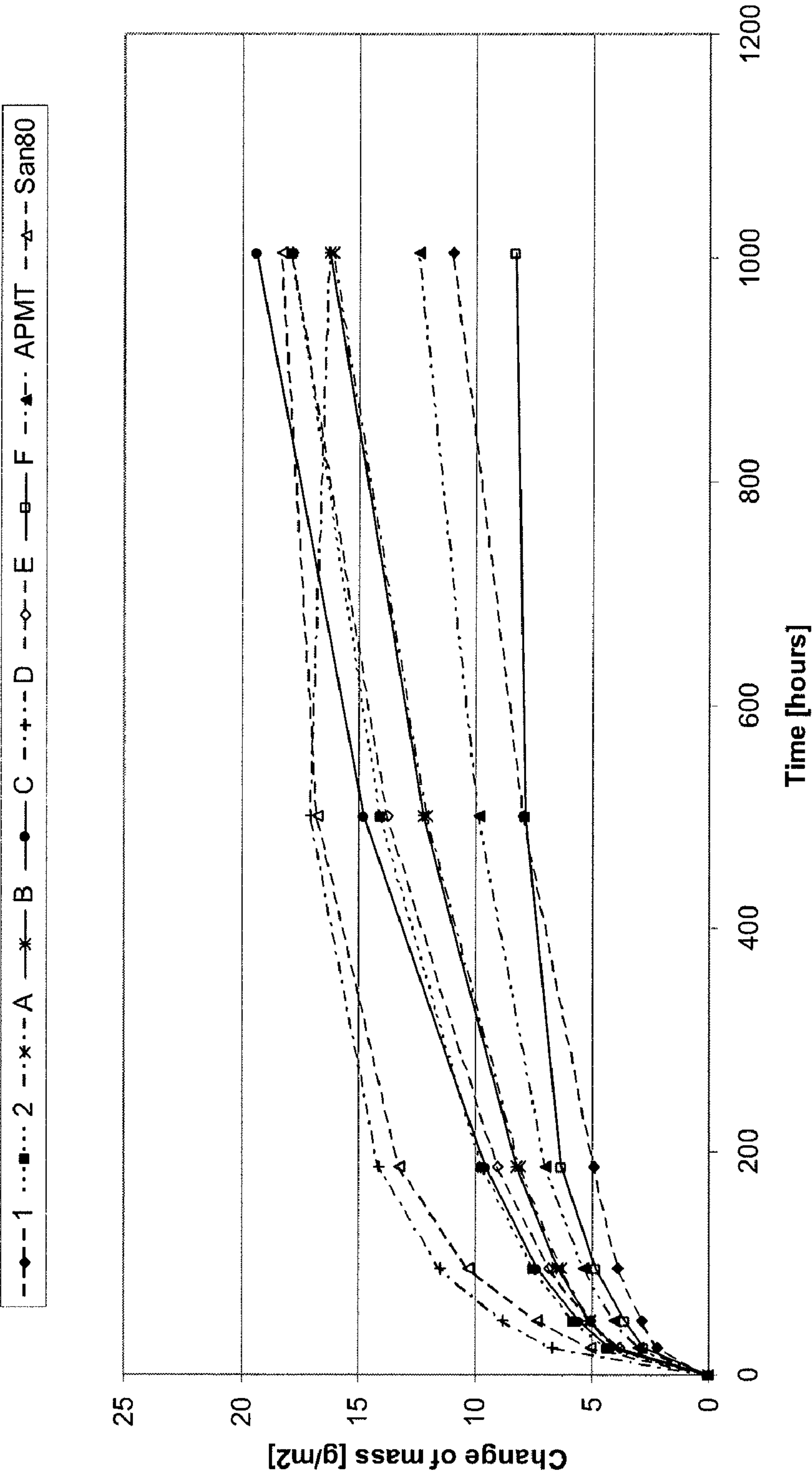
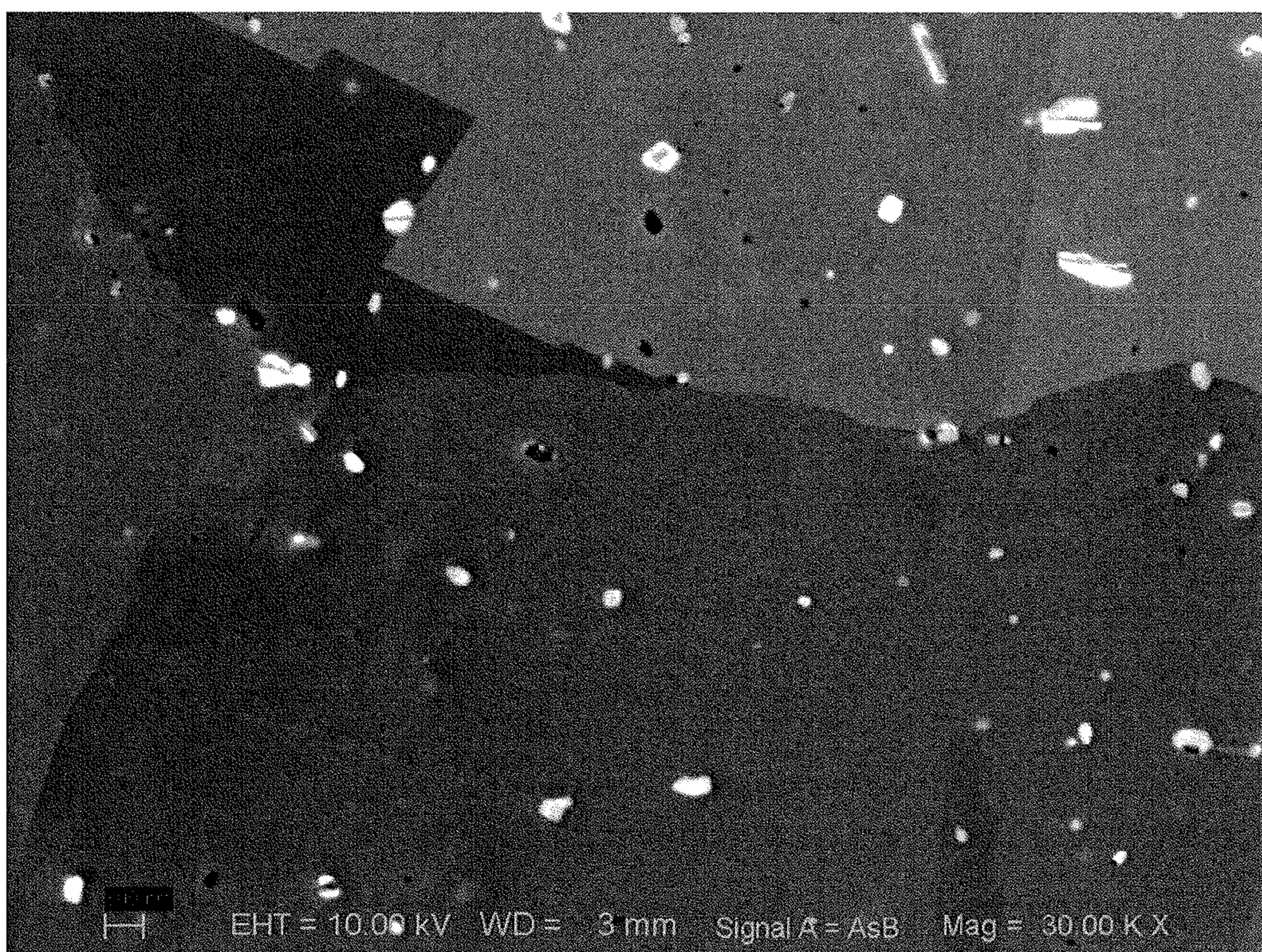


Fig 10.





*Fig 11.*



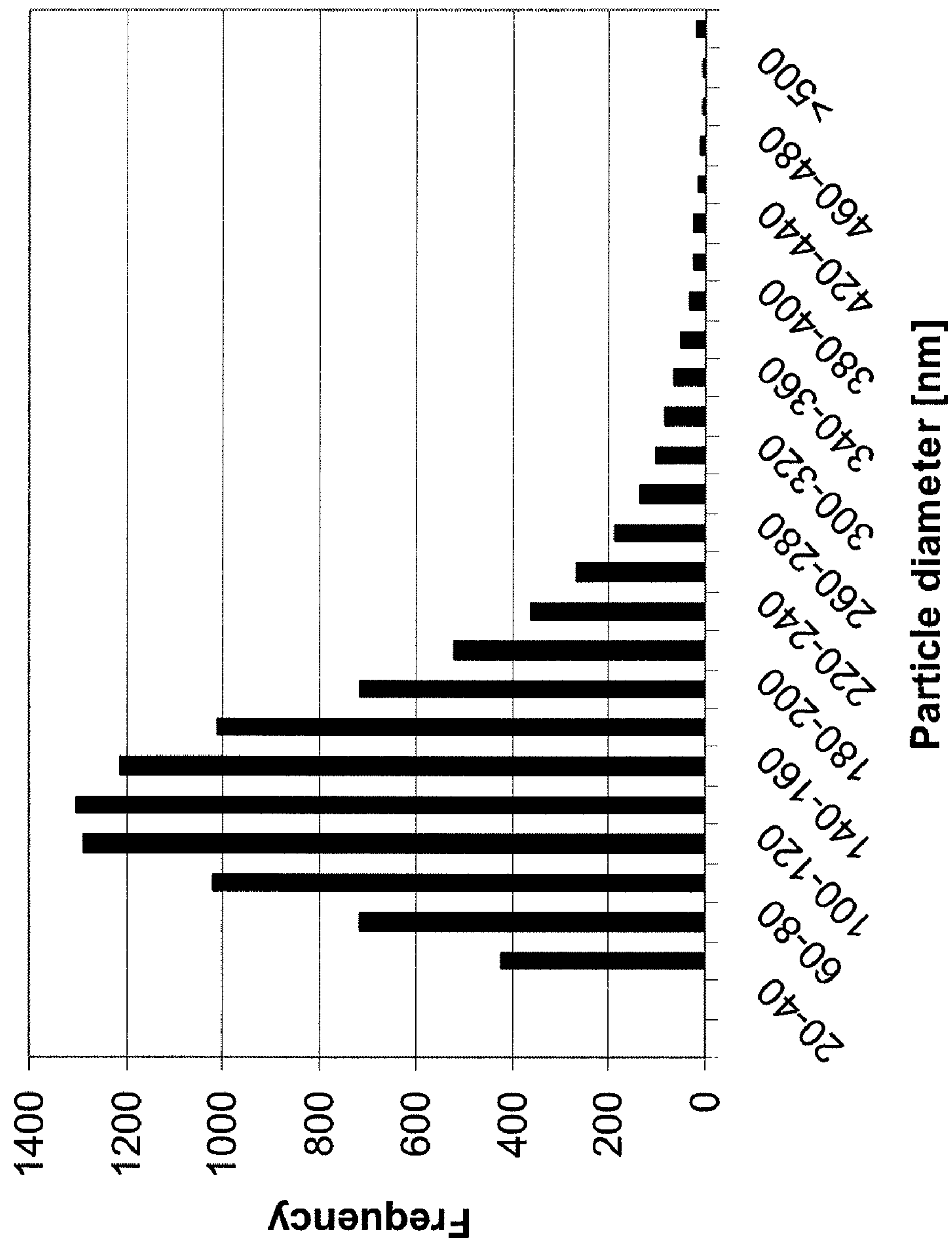


Fig 12a.

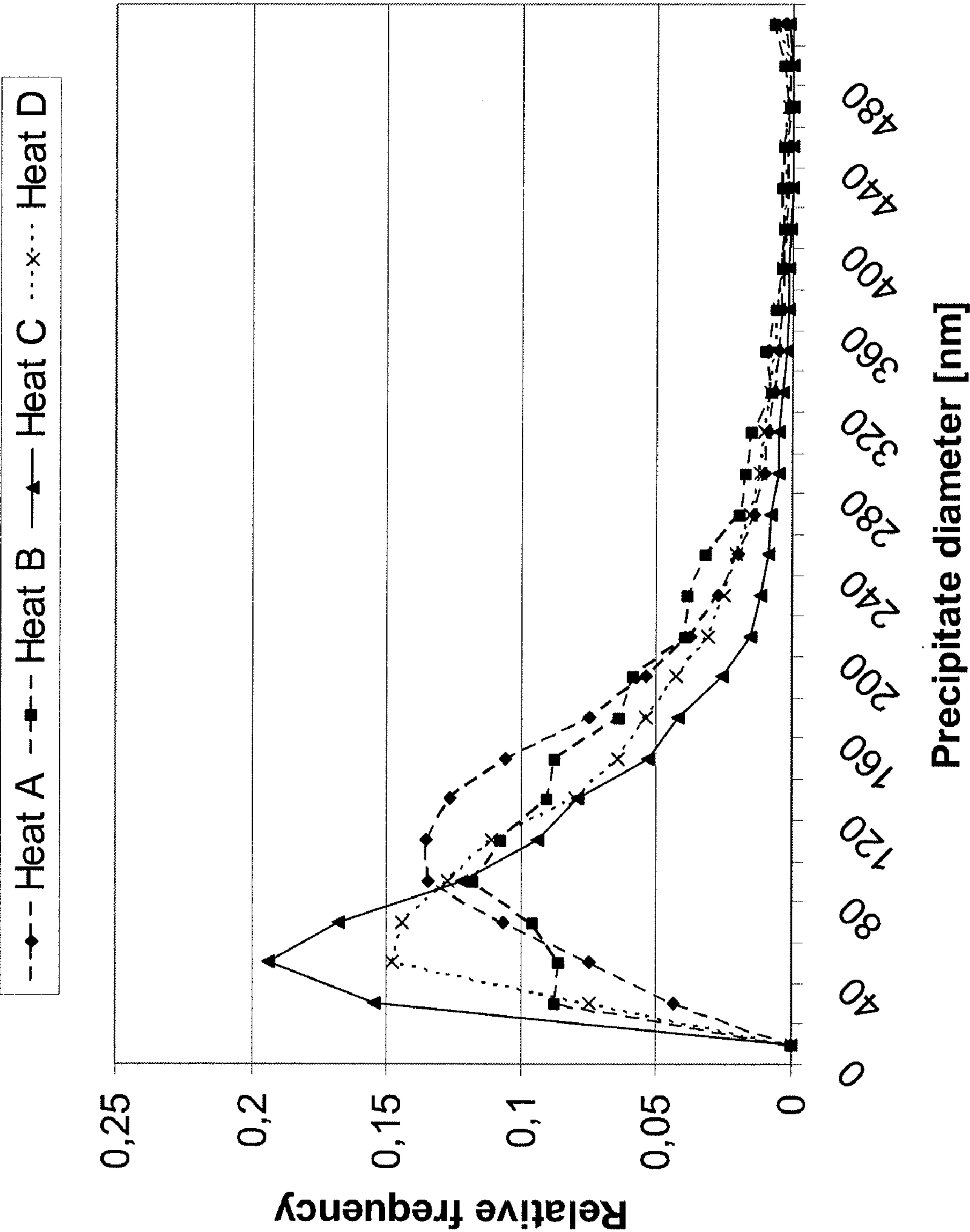


Fig 12b.



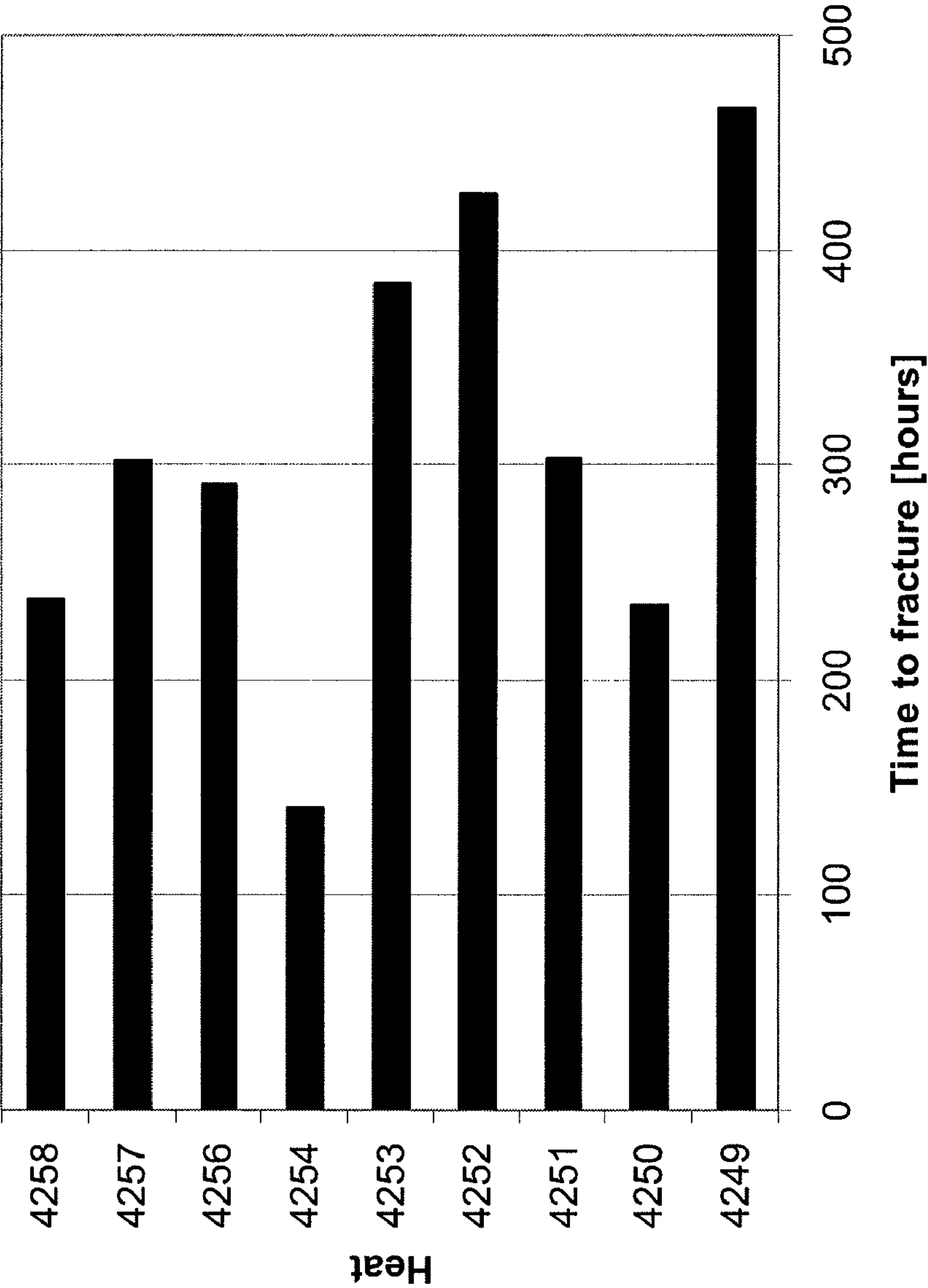


Fig 13.

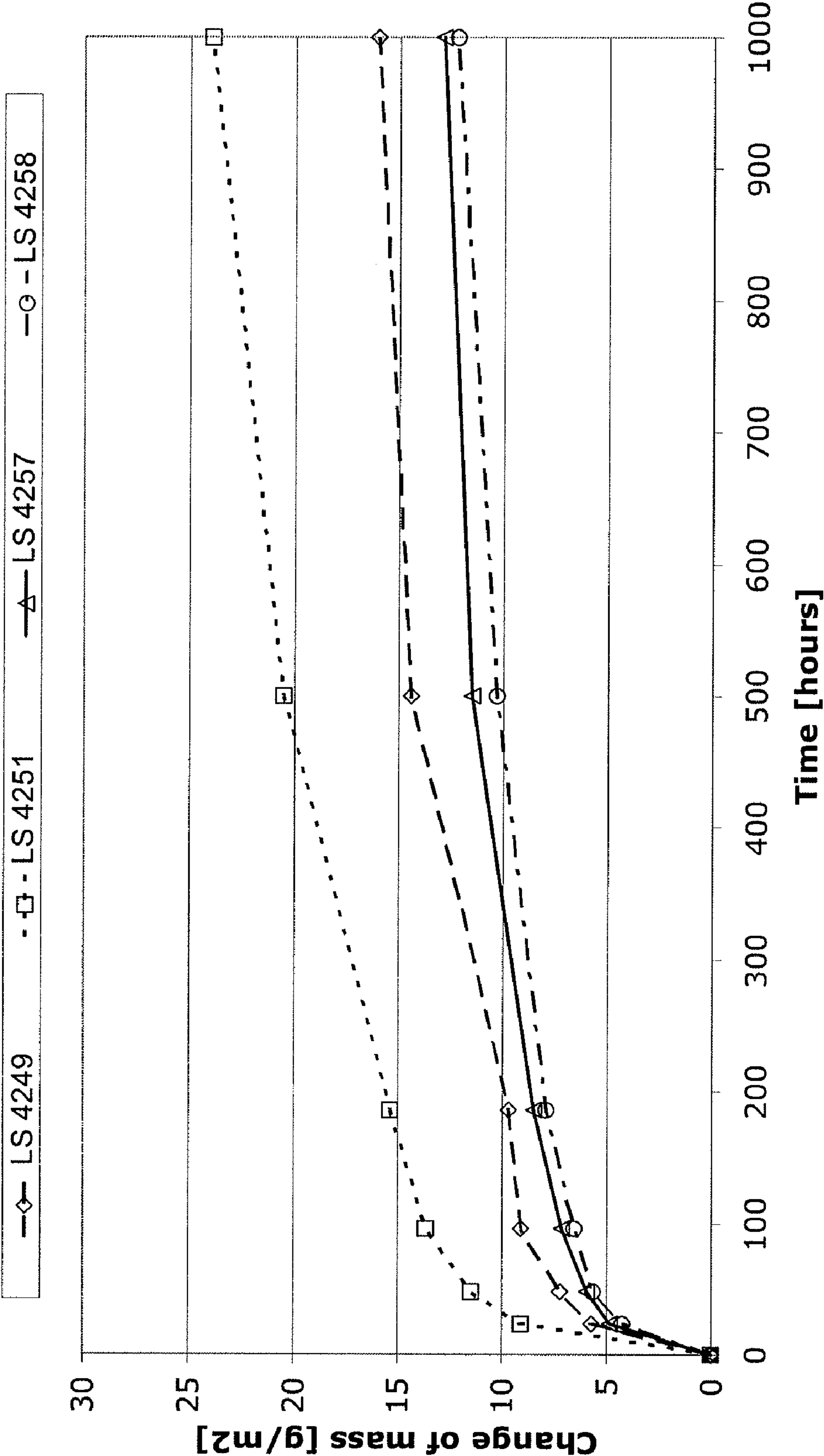


Fig 14.

## ALUMINIUM OXIDE FORMING NICKEL BASED ALLOY

**[0001]** The present invention relates to a nickel based alloy intended for use at high temperatures, such as above 900° C. Specifically, the present invention relates to a dispersion strengthened nickel based alloy alloyed with aluminium which enables formation of a stable aluminium oxide on the surface whereby the alloy has a good oxidation resistance. Moreover, the present invention relates to a powder of the nickel based alloy and to the use of the nickel based alloy.

### BACKGROUND ART

**[0002]** Nickel based alloys alloyed with aluminium are used in a variety of high temperature applications, such as in heat treatment furnaces, since they form a stable and protective aluminium oxide on the surface. The aluminium oxide often has a very good adhesion and does not tend to spall or fall off the surface. Moreover, the aluminium oxide has a low growth rate even at high temperatures. This type of alloys therefore often has a very good oxidation resistance.

**[0003]** Aluminium oxide forming nickel based alloys are known to be difficult to manufacture, especially to hot-work. A strongly contributing factor to this is the intermetallic phase  $\gamma'$  ( $\text{Ni}_3\text{Al}$ ) which is formed at temperatures below approximately 900° C. during slow cooling/heating, such as during heat treatments or during hot working. This intermetallic phase makes the alloy hard and brittle and consequently difficult to work. The precipitation of  $\gamma'$  also reduces the activity of aluminium in the alloy and thereby makes formation of the protective aluminium oxide on the surface more difficult.

**[0004]** One example of an aluminium oxide forming nickel based alloy is disclosed in U.S. Pat. No. 4,882,125. The alloy comprises 27-35% Cr, 2.5-5% Al and 2.5-6% Fe. It is disclosed that high contents of aluminium reduces the toughness of the material and that the Al content should be at least 2.75% in order to generate a good oxidation protection, but preferably not exceed 4% in order not to deteriorate the ductility. The patent further teaches that high contents of Fe deteriorate the oxidation properties, for which reason the iron content should not exceed 6%.

**[0005]** Another example of an aluminium oxide forming nickel based alloy is disclosed in U.S. Pat. No. 4,460,542. The alloy comprises 14-18% Cr, 4-6% Al and 1.5-8% Fe. This patent teaches that additions of 4-6% of Al render superior oxidation properties compared to nickel based alloys which form chromium oxide on the surface. Also in this patent it is disclosed that Fe has a negative effect on the oxidation properties, for which reason the iron content should be maximally 8%.

**[0006]** WO 2004/067788 A1 discloses yet another example of an aluminium oxide forming nickel based alloy. In this case, the alloy comprises 15-40% Cr, 1.5-7% Al and 0.5-13% Fe. Best results are said to be accomplished when the alloy comprises max 26.5% Cr, max 11% Fe and 3-6% Al.

**[0007]** WO 00/34541 A1 discloses a nickel based alloy comprising 19-23% Cr, 3-4.4% Al and 18-22% Fe. The alloy is intended for use at high temperatures. WO 00/34541 A1 discloses that the combination of 19-23% Cr and 3-4% Al is critical for formation of the protective  $\text{Al}_2\text{O}_3$ — $\text{Cr}_2\text{O}_3$  scale. The nickel based alloy is strengthened by precipitation of 1 to 5 mole percent of granular  $\text{Cr}_7\text{C}_3$  which is said to be accomplished by a 24 hour heat treatment. The alloy is produced by

melting is such as vacuum melting, casting and working into standard engineering shapes, such as rod, bar etc. This alloy shows good oxidation resistance up to 1000° C.

**[0008]** It is also previously known with iron based ferritic aluminium oxide forming alloys. However, this type of alloys often has low mechanical strength at high temperatures. Therefore, small particles are often added to increase the creep strength of the material. This is described for example in Metals Handbook, 10<sup>th</sup> edition, volume 2, page 943. Another problem with this type of alloys is that their ductility at room temperature often is very low which makes welding more difficult. In order to accomplish a reliable weld in a ferritic material a preheating of the material to be welded to at least 200° C. is often required. In many cases, a stress-relieving anneal at 750-850° C. is also required after welding.

### SUMMARY OF THE INVENTION

**[0009]** The object of the present invention is to accomplish an alloy with excellent oxidation resistance at high temperatures, specifically from about 900° C. to at least about 1250° C., and which still has a good hot workability and good creep strength.

**[0010]** The above identified object is achieved by a dispersion strengthened nickel based alloy comprising in percent by weight (wt-%)

C	0.05-0.2
Si	max 1.5
Mn	max 0.5
Cr	15-20
Al	4-6
Fe	15-25
Co	max 10
N	0.03-0.15
O	max 0.5
one or more elements selected from the group consisting of Ta, Zr, Hf, Ti and Nb	0.25-2.2
one or more elements selected from the group consisting of the rare earth metals (REM)	max 0.5,
balance Ni and normally occurring impurities.	

The nickel based alloy in accordance with the present invention is austenitic and has a very good oxidation resistance, especially at high temperatures, such as above 900° C. The oxidation resistance is high even at temperatures of about 1100° C. Since the present alloy forms a stable aluminium oxide on the surface, it can be used even at temperatures above those where chromium oxide forming materials suffer from extensive oxidation, i.e. above approximately 1150° C.

**[0011]** It has been found that by adding relatively high contents of Fe to an aluminium oxide forming nickel based alloy it is possible to reduce the stability of the intermetallic phase  $\gamma'$ , which in turn makes the alloy easier to manufacture and work. A reduced stability of  $\gamma'$  renders a slower formation of such precipitations for a given cooling rate, which facilitates hot working of the alloy. This also leads to a reduced risk of reduced activity of Al, which in turn ensures that a stable and oxidation resistant aluminium oxide can be formed on the surface of the alloy.

**[0012]** The nickel based alloy according to the invention is more ductile at room temperature than known ferritic aluminium oxide forming alloys. Therefore, preheating or keeping the alloy warm before welding is unnecessary and subsequent stress-relieving annealing can be avoided. The nickel



based alloy according to the invention consequently enables a facilitated welding procedure compared to ferritic aluminium oxide forming alloys.

**[0013]** The nickel based alloy according to the invention is dispersion strengthened. This is achieved by the addition of one or more elements selected from the group consisting of Ta, Zr, Hf, Ti and Nb. These elements form dispersion strengthening particles with C and/or N and optionally added O. The dispersion contributes to the mechanical strength and gives the alloy excellent creep strength even at high temperatures without impairing the hot-workability of the alloy.

**[0014]** The nickel based alloy is produced by means of powder metallurgy. The powder metallurgical manufacturing process results in a rapidly solidified material wherein brittle phases do not have time to form and no great composition variations are developed by segregation. A mixture of rapidly solidified powder will therefore render a metal body with essentially homogenous composition and an essentially even distribution of very small dispersion particles.

**[0015]** A powder produced of the nickel based alloy will comprise dispersion strengthened particles as described above, which will render a product produced is of the powder excellent mechanical properties, especially at high temperatures. Furthermore, a powder of the nickel based alloy enables, in addition to manufacturing of traditional forms such as tube, rod, wire, plate and strip, also manufacturing of solid components with complex geometry. Moreover, compound materials wherein the nickel based alloy is incorporated can easily be manufactured if desired, for example in order to produce a final product with a first load-bearing component and with a second corrosion resistant component.

**[0016]** The nickel based alloy according to the invention is especially suitable for use at high temperatures, such as above 900° C. and up to at least 1250° C., and especially in applications wherein the mechanical load on the material can become high. Furthermore, the alloy according to the invention is suitable for use in environments with high requirements for good oxidation resistance. Examples of suitable applications are as construction materials for heat treatment furnaces, in rollers for roller hearth furnaces, as muffle tubes for annealing in protective atmosphere, as construction material for heating elements, combustion chamber material in gas turbines, as gas-to-gas heat exchangers for example in the glass manufacturing industry or in gas turbines, as transportation belts woven from wire intended for heat treatment furnaces, in radiation tubes for heating in heat treatment furnaces or as protective tubes for thermocouples.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0017]** FIG. 1a shows the result of a simulation of the effect of the Ni content on the phase stability at different temperatures.

**[0018]** FIG. 1b shows the influence of varying contents of Al and Fe on the minimum stability of  $\gamma'$ .

**[0019]** FIG. 1c shows the influence of varying contents of Al and Cr on the minimum stability of  $\gamma'$ .

**[0020]** FIG. 2 shows the result of a simulation of the effect of the Fe content on the stability of nickel aluminides.

**[0021]** FIG. 3 shows the result of a simulation of the effect of the Al content on the stability of nickel aluminides.

**[0022]** FIG. 4 shows the result of a simulation of the effect of Co on the stability of nickel aluminides.

**[0023]** FIG. 5 shows result from tensile testing of examples of the alloy according to the invention.

**[0024]** FIG. 6 shows the yield strength of six different heats according to the invention at room temperature, 500° C. and 600° C.

**[0025]** FIG. 7 shows the tensile strength of six different heats according to the invention at room temperature, 500° C. and 600° C.

**[0026]** FIG. 8 shows the elongation to fracture of six different heats according to the invention at room temperature, 500° C. and 600° C.

**[0027]** FIG. 9 shows the result from oxidation testing in air at 1000° C. of eight different heats according to the invention and two comparative materials.

**[0028]** FIG. 10 shows the result from oxidation testing in air at 1100° C. of eight different heats according to the invention and two comparative materials.

**[0029]** FIG. 11 shows a photograph of the microstructure of Heat A taken in SEM.

**[0030]** FIG. 12a shows the size distribution of carbonitrides precipitates in Heat A.

**[0031]** FIG. 12b shows the size distribution of precipitates in Heats A-D.

**[0032]** FIG. 13 shows the result from creep testing of compositions which are not dispersion strengthened.

**[0033]** FIG. 14 shows the result from oxidation testing in air at 1100° C. of four compositions which are not dispersion strengthened.

#### DETAILED DESCRIPTION

**[0034]** As mentioned above, nickel based alloys alloyed with aluminium are generally considered difficult to hot-work. An important factor is that there is only a limited temperature window between melting of the alloy and precipitation of unwanted intermetallic phases, such as nickel aluminides. The alloying elements Al and Cr are both beneficial for the oxidation resistance but makes a nickel based alloy difficult to work since they increase the stability of nickel aluminides and therefore reduces the temperature window for hot-working of the alloy. The hot workability of the alloy is a very important factor for enabling that products thereof can be readily and economically produced. It has been found that the alloy in accordance with the present invention has an increased temperature window for hot-working as a result of its composition which gives the alloy a good hot-workability.

**[0035]** The present invention is based on the discovery that relatively high addition of Fe to a nickel based alloy with 4-6% Al and high content of Cr reduces the stability of the intermetallic phase  $\gamma'$ . Precipitations of the phase  $\gamma'$  improves the creep strength at low temperatures but makes the production more difficult since the alloy becomes hard and brittle at too high contents of  $\gamma'$ . Moreover,  $\gamma'$  reduces the activity of Al in the alloy which makes the formation of the protective aluminium oxide on the surface more difficult. For an alloy intended for use at high temperatures, such as above 900° C., it is consequently important to reduce the content of  $\gamma'$ , which is achieved by the composition of the alloy in accordance with the present invention.

**[0036]** Moreover, precipitations of  $\gamma'$  in previously known aluminium oxide forming nickel based alloys are not stable above approximately 1000° C. whereby its influence on the creep strength ceases during use of such alloys above this temperature. The alloy according to the present invention comprises a minimum content of  $\gamma'$  and is furthermore primarily intended for use at high temperatures where there consequently is a risk of dissolution of  $\gamma'$ . In order to keep the creep



strength the alloy is therefore dispersion strengthened. This is accomplished above all by the selected contents of carbon and nitrogen and possibly oxygen in combination with the selected contents of Ta, Zr, Hf, Ti and Nb. It is possible to produce the alloy by conventional melting production process, but in that case the dispersion strengthening will be insufficient if even achieved. The alloy is therefore produced by way of powder metallurgy. Solid components can thereafter be manufactured from the produced powder by compaction in accordance with previously known techniques such as hot isostatic pressing (HIP) or cold isostatic pressing (CIP). If needed the manufactured solid component can thereafter be further worked, for example by rolling, extrusion or drawing in order to achieve the desired product form. It is also possible to produce complex geometries directly from the powder by means of sintering.

[0037] The composition of the present alloy and the fact that it is dispersion strengthened has resulted in a nickel based alloy which has an excellent oxidation resistance even at temperatures as high as at least 1100° C., is relatively easy to hot-work and has good creep strength.

[0038] According to a preferred embodiment of the dispersion strengthened nickel based alloy according to the invention, the dispersed particles have an average diameter of less than 1 µm, preferably less than 500 nm. Best results are achieved when the dispersed particles have an average diameter of 50-200 nm.

[0039] According to yet a preferred embodiment of the dispersion strengthened nickel based alloy according to the invention, more than 85% of the dispersed particles should be equal to or less than 300 nm in diameter.

[0040] The effect of the various elements on the properties of the alloy will now be discussed below, wherein all given contents are in percent by weight.

#### Carbon

[0041] Carbon in free form will take interstitial locations in the crystal structure and thereby lock the mobility of dislocations at temperatures up to approximately 400-500° C. Carbon also forms carbides with other elements in the alloy such as Ta, Ti, Hf, Zr and Nb. In a microstructure with finely dispersed carbides, these carbides provide obstacles for the dislocation movement and have effect even at higher temperatures. Carbon is an essential element to improve the alloy's creep strength since the dislocation mobility is the mechanism that generates creep elongation. Too high contents of C will however lead to the alloy becoming difficult to cold work due to deteriorated ductility at lower temperatures, such as below 300° C. The alloy therefore comprises 0.05-0.2% C.

#### Silicon

[0042] Silicon can be present in the alloy in contents up to 1.5%. Silicon in too high contents can in nickel based alloys lead to increased risk for precipitations of nickel silicides, which have an embrittling effect on this type of alloy. Results from creep testing of similar alloys have shown that the creep life time, i.e. the time to creep fracture, is reduced with Si contents close to 1.5%. The reason for this is however not known. Because of this, the Si content should preferably be

maximally 1%. According to a preferred embodiment, the alloy only comprises impurity contents of Si, i.e. up to 0.3%.

#### Manganese

[0043] Manganese is present in the alloy as an impurity. It is likely that up to 0.5% can be allowed without negatively influencing the properties of the alloy whereby the alloy comprises maximally 0.5% Mn. According to a preferred embodiment, the alloy only comprises impurity contents of Mn, i.e. up to 0.2%.

#### Chromium

[0044] Chromium is an element which for a long period of time has been the leading element when it comes to creating a dense and protective oxide scale. Less than 15% Cr in an austenitic structure tends to render an oxide which is not entirely covering the surface and which is not dense and consequently render an insufficient oxidation resistance to the alloy. There is also a risk that the material closest to the oxide is depleted of Cr such that possible damages to the oxide can not heal since there is not sufficient Cr to form new oxide.

[0045] A nickel based alloy comprising 4% Al should however not comprise more than about 20% Cr as higher contents increases the risk of formation of  $\gamma'$  and  $\beta$  phases. (This will for example be shown below with reference to FIG. 1c, calculated for an alloy comprising approximately 19% Fe.)

[0046] Therefore, in order to minimise the presence of the  $\gamma'$  and  $\beta$  phases, the alloy comprises max 20% Cr. There may also be a risk of formation of other unwanted phases, such as  $\sigma$ -phase and chromium rich ferrite, at too high Cr contents. Moreover, Cr may also at high contents stabilise nickel aluminides.

[0047] Therefore, the alloy comprises 15-20% Cr, preferably 17-20% Cr. Best results are achieved when the alloy comprises 17-19% Cr.

#### Aluminium

[0048] Aluminium is an element that generates a much denser and more protective oxide scale compared to Cr. Aluminium can however not replace Cr since the formation of the aluminium oxide is slower than the chromium oxide at lower temperatures. The alloy comprises at least 4% Al, preferably more than 4% Al, which ensures a sufficient oxidation resistance at high temperatures and that the oxide covers the surface entirely. The relatively high content of Al provides excellent oxidation resistance even at temperatures of about 1100° C. At Al contents above 6% there is a risk of formation of such an amount of intermetallic phases in a nickel based matrix that the ductility of the material is considerably deteriorated (this will also be discussed below with reference to FIG. 3). The alloy should therefore comprise 4-6% Al, preferably >4-5.5%, more preferably >4-5.2% Al.

#### Iron

[0049] It has been shown in accordance with the present invention that relatively high contents of Fe in an aluminium oxide forming nickel based alloy can have positive effects. Additions of Fe generate a metallic structure which is energetically unfavourable for the formation of embrittling  $\gamma'$ , which in turn leads to the risk of the alloy becoming hard and brittle reducing considerably. Consequently, the workability is improved. Therefore, the alloy comprises at least 15% Fe.



High contents of iron may however lead to formation of unwanted phases. Therefore, the alloy shall not comprise more than 25% Fe.

**[0050]** Moreover, at Fe contents over approximately 21-22% the risk of formation of a  $\beta$ -phase (NiAl), which in some cases can be embrittling, increases. (This will for example be shown below with reference to FIGS. 1b and 2.)

**[0051]** Preferably, the alloy should therefore comprise 16-21.5% Fe. According to a preferred embodiment, the alloy comprises 17-21% Fe.

#### Nickel

**[0052]** The alloy according to the invention is a nickel based alloy. Nickel is an element which stabilises an austenitic structure in alloys and thereby counteracts formation of some brittle intermetallic phases, such as  $\sigma$ -phase. The austenitic structure of the alloy is beneficial for example when it comes to welding. The austenitic structure also contributes to the good creep strength of the alloy at high temperatures. This could be a result of that the diffusion rate is lower in an austenitic structure than for example in a ferritic.

**[0053]** According to one embodiment, the alloy comprises 52-62% Ni, preferably 52-60% Ni.

#### Cobalt

**[0054]** In some commercial alloys, a part of the Ni is substituted with Co in order to increase the mechanical strength of the alloy which may also be done in the alloy according to the invention. A part of the Ni of the alloy can be replaced with an equal amount of Co. This increases the stability of the BCC-aluminide NiAl, which then grows at the expense of  $\gamma'$ , which can be advantageous in certain temperature ranges. This Co addition must however be balanced against the oxidation properties since the presence of NiAl will reduce the activity of Al and thereby deteriorate the ability to form aluminium oxide. The addition of Co will also affect the melting point of the alloy. For example, an addition of 10% Co will render an alloy with precipitations of NiAl which are stable up to 950° C. but lower the melting point with approximately 20° C. According to one embodiment of the present invention, nickel is therefore partly substituted with Co. The Co content shall, however, not exceed 10%.

#### Nitrogen

**[0055]** In the same way as C, free N takes interstitial locations in the crystal structure and thereby locks the dislocation mobility at temperatures up to approximately 400-500° C. Nitrogen also forms nitrides and/or carbonitrides with other elements in the alloy such as Ta, Ti, Hf, Zr and Nb. In a microstructure where these particles are finely dispersed they confer obstacles for the dislocation mobility, especially at higher temperatures. Therefore, N is added in order to improve the creep strength of the alloy. However, when adding N to aluminium alloyed alloys the risk is high for formation of secondary aluminium nitrides and the present nickel based alloy therefore has a very limited N content. The alloy comprises 0.03-0.15% N, preferably 0.05-0.15% N, more preferably 0.05-0.10% N.

#### Oxygen

**[0056]** Oxygen may be present in the present alloy either in the form of an impurity, or as an active addition up to 0.5%. Oxygen may contribute to increasing the creep strength of the

alloy by forming small oxide dispersions together with Zr, Hf, Ta and Ti, which, when they are finely distributed in the alloy, improves its creep strength. These oxide dispersions have higher dissolution temperature than corresponding carbides and nitrides, whereby oxygen is a preferred addition for use at high temperatures. Oxygen may also form dispersions with Al, the elements in group 3 of the periodic table, Sc, Y and La as well as the fourteen lanthanides, and in the same manner as with the above identified elements thereby contribute to higher creep strength of the alloy. According to a preferred embodiment, the alloy comprises 200-2000 ppm O, preferably 400-1000 ppm O.

#### Tantalum, Hafnium, Zirconium, Titanium and Niobium

**[0057]** The elements in the group consisting of Ta, Hf and Zr forms very small and stable particles with carbon and nitrogen. It is these particles which, if they are finely dispersed in the structure, help to lock dislocation movement and thereby increase the creep strength, i.e. provides the dispersion strengthening. It is also possible to accomplish this effect with addition of Ti. Additions of Ti can, however, sometimes lead to problems, especially during powder metallurgical production of the alloy, since it forms carbides and nitrides already in the melt before atomisation, which in turn may clog the orifice during the atomisation.

**[0058]** Niobium also forms stable dispersions with C and or N and can therefore suitably be added to the alloy according to the invention.

**[0059]** The alloy comprises one or more elements selected from the group consisting of Ta, Zr, Hf, Ti and Nb in an amount of 0.25-2.2%, preferably 0.3-1.5%, more preferably 0.6-1.5%.

**[0060]** The alloy preferably comprises such an amount of the elements Ta, Zr, Hf, Ti and Nb that essentially all C and N is bound to these elements. This ensures that for example the risk of formation of chromium carbides during high temperature use of the alloy is significantly reduced.

**[0061]** According to a preferred embodiment, the alloy comprises 0.1-0.5% Hf. According to another embodiment, the alloy comprises 0.05-0.35% Zr. According to yet another embodiment, the alloy comprises 0.05-0.5% Ta. According to yet another embodiment, the alloy comprises 0.05-0.4% Ti. According to yet another embodiment, the alloy comprises 0.1-0.8% Nb.

#### Rare Earth Metals (REM)

**[0062]** Rare earth metals (REM) relates in this context to the elements of group three of the periodic table, Sc, Y, and La as well as the fourteen lanthanides. REM affects the oxidation properties by doping of the formed oxide. Excess alloying of these elements often gives an oxide which tends to spall of the surface and a too low addition of these elements tends to give an oxide with weaker adhesion to the metal surface. The alloy may comprise one or more elements from the group consisting of REM in a content of up to 0.5% in total, preferably 0.05-0.25%. According to a preferred embodiment, yttrium is added to the alloy in an amount of 0.05-0.25%.

**[0063]** The nickel based alloy according to the invention may also comprise normally occurring impurities as a result of the raw material used or the selected manufacturing process. Examples of impurities are Ca, S and P.

**[0064]** The dispersion strengthened nickel based alloy has a very good oxidation resistance inter alia as a result of the Al



and Cr contents. It also has very good mechanical properties, such as yield and tensile strength as well as ductility. It has very good workability, especially hot workability, which makes it easy to manufacture products by for example hot extrusion or hot rolling.

**[0065]** The above identified nickel based alloy is foremost intended for use at high temperatures. Examples of applications wherein the alloy is especially suitable are construction materials for heat treatment furnaces, rollers for roller hearth furnaces, muffle tubes for annealing in protective atmosphere, construction material for heating elements, combustion chamber material in gas turbines, gas-to-gas heat exchangers for example in the glass manufacturing industry or in gas turbines, tubular reactors in high temperature processes, transportation belts of woven wires intended for heat treatment furnaces, radiation tubes for heating of heat treatment furnaces or protective tubes for thermocouples.

#### Simulation

**[0066]** The stability of phases at different alloy compositions and temperature has been studied by thermodynamic simulations using the software Thermo-Calc. A thermodynamic database for nickel based alloys called “NiFe-Super version 4” was used for the simulations. It is commonly known that this type of calculations in most cases correspond well to the reality.

**[0067]** The influence of iron on the stability of the nickel aluminides  $\beta$  (NiAl) and  $\gamma'$  (Ni<sub>3</sub>Al), and the stability of a (chromium rich ferrite) was studied. The calculations were made for the chromium content 18 wt-% and the aluminium content 4.5 wt-%. The result for a simulation wherein temperature and nickel content have been varied is shown in FIG. 1. Along the x-axis iron is replaced with nickel in the alloy.

**[0068]** These simulations have shown that there is an area for an alloy with 4.5 wt-% Al and 18 wt-% Cr where the stability of  $\gamma'$  has a minimum. This minimum is at 58 wt-% Ni and with an iron content of approximately 19 wt-%, and is marked in the figure by the dotted circle. Lower contents of Fe increases the stability of  $\gamma'$  whereas higher contents render formation of the nickel aluminide  $\beta$  (NiAl).

**[0069]** Compositions around this minimum give a wide temperature interval between melting of the alloy and precipitation of nickel aluminides and therefore facilitate the hot-workability as explained above.

**[0070]** The influence of variations in Al and Cr content on the minimum identified above has also been studied. By varying the Al content between 4 and 6% and at the same time adjusting the Fe content such that the minimum in  $\gamma'$ -stability is achieved, FIG. 1b can be calculated. FIG. 1b shows how the minimum is moved when the contents of Fe and Al are varied. The minimum is moved along the line in the figure at the same time as the temperature is changed. It is clear from the figure that increased Al content reduces the amount of Fe necessary to achieve the minimum. Moreover, the temperature rises for the minimum from 814° C. at tic-mark 1 to 953° C. at tic-mark 9.

**[0071]** FIG. 1c shows the same type of calculation as in FIG. 1b but wherein the Cr and Al contents have been varied and the Fe content is kept at approximately 19%. It is clear from the figure that increased Al content reduces the amount of Cr necessary to achieve the minimum. Moreover, the temperature rises from 815° C. at tic-mark 1 to 951° C. at tic-mark 10.

**[0072]** In FIG. 2, the influence of different iron contents on the stability of nickel aluminides, ferrite and austenite is shown. The composition was in this case 18 wt-% Cr, 4.5 wt-% Al, balance Ni with three different iron contents 16 wt-%, 19 wt-% and 22 wt-%, respectively. The lowest dissolution temperature for nickel aluminides was obtained for the Fe content of 19%. At the highest Fe content,  $\beta$  is stable whereas the lowest Fe content increases the stability of  $\gamma'$  which results in a higher dissolution temperature.

**[0073]** In FIG. 3, the influence of different Al contents on the stability of nickel aluminides and ferrite is shown. The composition was in this case 18 wt-% Cr, 19 wt-% Fe, balance Ni with four different Al contents 4 wt-%, 4.5 wt-%, 5 wt-% and 6 wt-% respectively. Increasing Al contents increases the dissolution temperature for nickel aluminides. At the Al content of 6% the intermetallic 3-phase is stable up to temperatures around 1100° C. Increasing Al contents increase the stability of ferrite at lower temperature ranges, below approximately 800° C.

#### Simulation of the Effect of Cobalt Addition

**[0074]** In order to investigate which effect cobalt would have on the alloy simulations were made using the software Thermo-Calc. A thermodynamic database for nickel based alloys called “NiFe-Super version 4” was used for the simulations. The calculations were made with the starting composition 18% Cr, 19% Fe, 4.5% Al, balance Ni. Nickel was substituted with 5, 10, and 15% Co in the starting composition and the balance fraction of precipitations was calculated as a function of temperature. The influence of Co on the stability of the nickel aluminides  $\beta$  (NiAl) and  $\gamma'$  (Ni<sub>3</sub>Al), a (chromium rich ferrite) as well as  $\sigma$ -phase was studied. The result is shown in FIG. 4.

**[0075]** The calculations show that additions of Co increase the dissolution temperature for nickel aluminides. Additions of Co also increase the stability of the nickel aluminide  $\beta$  relative to  $\gamma'$ . At the two highest contents of Co there is also a risk for precipitations of  $\sigma$ -phase at temperatures below approximately 650° C., Up to 10 wt-% Co can be used in the alloy for uses at temperatures above 950° C.

#### Tensile Testing

**[0076]** A number of compositions of the alloy according to the invention were produced by means of powder metallurgy and compacted by hot isostatic pressing followed by hot extrusion and subsequent water quenching. The compositions of the different heats are given in Table 1.

TABLE 1

Heat	1	2	A	B	C	D	E	F
C	0.05	0.14	0.072	0.083	0.11	0.17	0.12	0.12
Si	0.05	0.10	0.09	0.05	0.04	0.04	0.08	0.09



TABLE 1-continued

Heat	1	2	A	B	C	D	E	F
Mn	0.06	0.10	0.10	0.10	0.06	0.06	0.10	0.09
Fe	19.0	18.8	18.8	18.8	19.1	19.1	19.8	21.0
Cr	18.2	17.7	17.7	17.8	17.8	18.0	18.0	18.1
Ni	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Al	4.50	4.54	4.80	4.59	4.64	4.66	4.59	4.65
Co	0.02	0.02	0.03	0.04	0.18	0.35	2.56	6.93
Nb	<0.01	0.01	<0.01	<0.01	0.24	0.57	<0.01	<0.01
Ti	<0.01	<0.01	<0.01	<0.01	0.14	0.33	<0.01	0.02
Zr	<0.01	0.33	0.39	0.41	0.18	0.40	0.40	0.41
Ta	<0.001	0.353	0.42	0.46	0.22	0.48	0.46	0.44
Hf	0.395	0.455	0.56	0.48	0.36	0.41	0.45	0.50
Y	0.273	0.285	0.26	0.21	0.26	0.21	0.19	0.13
N	0.071	0.072	0.068	0.071	0.068	0.067	0.077	0.077
O	0.025	0.034	0.0394	0.0345	0.0349	0.0238	0.0368	0.0290
Ta + Zr + Hf + Ti + Nb	0.395	1.148	1.37	1.35	1.14	2.19	1.31	1.37

**[0077]** Tensile testing of the compositions was performed according to standard SS-EN 10002-1 at room temperature. Three samples of each composition were tested and the results from the tensile testing in the form of the average of the three samples are shown in Table 2. Moreover, Heat 1 was also tested directly after HIP (i.e. prior to extrusion).

TABLE 2

Sample	Yield strength Rp <sub>0.2</sub> [N/mm <sup>2</sup> ]	Yield strength Rp <sub>1.0</sub> [N/mm <sup>2</sup> ]	Tensile strength R <sub>m</sub> [N/mm <sup>2</sup> ]	Elongation to fracture A [%]
1 (after HIP)	400	not analysed	826	37
1 (extruded)	389	not analysed	814	34
2	430	not analysed	877	32
A	492	548	963	35
B	501	557	971	35
C	530	587	989	34
D	538	602	1002	32
E	488	553	964	31
F	441	510	932	35

**[0078]** The results show that the alloy according to the invention has a good elongation to fracture at room temperature which reduces the risk for crack formation during cold working. Furthermore, the alloy has a yield strength which is higher than many austenitic steels and nickel based alloys, which generally have a yield strength of approximately 200-300 MPa. The results can for example be compared with an austenitic chromium-nickel steel with a nominal composition of 0.07 wt-% C, 1.6 wt-% Si, 1.5 wt-% Mn, 25 wt-% Cr, 35 wt-% Ni, 0.16 wt-% N, 0.05 wt-% Ce and balance Fe (corresponding to UNS S35315), which has a yield strength Rp<sub>0.2</sub> of about 260 MPa, a tensile strength R<sub>m</sub> of about 600 MPa and an elongation to fracture of about 35%. The results could also be compared to a dispersion strengthened aluminium oxide forming ferritic steel known under the trade name KANTHAL APMT® which has a nominal composition comprising 21 wt-% Cr, 5 wt-% Al, 3 wt-% Mo, max 0.7% Si, max 0.4 wt-% Mn, max 0.08 wt-% C, and which has a yield strength Rp<sub>0.2</sub> of about 550 MPa, a tensile strength R<sub>m</sub> of about 750 MPa and an elongation to fracture of about 25%.

**[0079]** Moreover, tensile testing at 500° C. and 600° C. respectively of Heats A-F given in Table 1 was made in

accordance with standard SS-EN 10002-5. Three samples of each composition were tested and the results from the tensile testing in the form of the average of the three samples are shown in Table 3.

**[0080]** The results from the tensile testing at 500° C. and 600° C. indicates that the alloy according to the invention has good high temperature mechanical properties and has good elongation to fracture at these temperatures. This, together with successful results from hot extrusion and hot rolling, indicates that the alloy has good hot-workability.

**[0081]** The results from the tensile testing of Heats 1 and 2 are shown in FIG. 5 and the results from the tensile testing of Heats A-F are shown in FIGS. 6 to 8.

TABLE 3

Sam- ple	Yield strength Rp <sub>0.2</sub> at 500° C. [N/mm <sup>2</sup> ]	Tensile strength R <sub>m</sub> at 500° C. [N/mm <sup>2</sup> ]	Elon- gation to fracture A at 500° C. [%]	Yield strength Rp <sub>0.2</sub> at 600° C. [N/mm <sup>2</sup> ]	Tensile strength R <sub>m</sub> at 600° C. [N/mm <sup>2</sup> ]	Elon- gation to fracture A at 600° C. [%]
A	423	845	28	486	817	19
B	428	864	28	499	827	19
C	467	889	29	503	820	19
D	461	892	27	577	848	23
E	417	857	24	472	824	19
F	373	812	25	430	834	28

#### Impact Testing

**[0082]** Impact testing was performed on material produced from the metal powders from the heats given in Table 1. Samples were produced by hot isostatic pressing (HIP) and subsequent hot extrusion with water quenching. Testing according to SS-EN 10045-1 was performed at room temperature and was performed on three samples each of the compositions. The results are shown in Table 4.

TABLE 4

Heat	Sample	Impact strength [J]	Average value [J]
1	1	133	119
	2	106	
	3	117	



TABLE 4-continued

Heat	Sample	Impact strength [J]	Average value [J]
2	1	50	45
	2	42	
	3	44	
A	1	84	92
	2	91	
	3	102	
B	1	82	81
	2	92	
	3	68	
C	1	48	47
	2	46	
	3	48	
D	1	64	64
	2	64	
	3	64	
E	1	50	49
	2	50	
	3	46	
F	1	68	65
	2	64	
	3	62	

**[0083]** The impact strength for all heats is well above the 27 Joule which is generally used as a limit value between ductile and brittle material.

#### Oxidation Test at 1000° C.

**[0084]** Samples in the form of coupons were produced from the heats given in Table 1. The coupons were grid with 220  $\mu$ m paper. Furthermore, one sample of a nickel based alloy known under the trade name SANDVIK SANICRO® 80 (corresponding to UNS N06003) and one sample of the dispersion strengthened aluminium oxide forming ferritic steel known under the trade name KANTHAL APMT (which has a nominal composition comprising 21 wt-% Cr, 5 wt-% Al, 3 wt-% Mo, max 0.7% Si, max 0.4 wt-% Mn, max 0.08 wt-% C), were produced for comparison.

**[0085]** Oxidation test was performed at 1000° C. in air. The samples were removed from the furnace and cooled to room temperature after 24, 48, 95, 186, 500 and 1005 hours respectively and weighed. After weighing, the samples were inserted into the furnace for continued heating and oxidation. The results from the oxidation test are shown in FIG. 9.

**[0086]** The results show that the alloy according to the invention has a very good oxidation resistance at 1000° C. All heats except D have considerably better oxidation resistance than SANDVIK SANICRO 80. Furthermore, the alloys according to the invention have an oxidation resistance at this temperature which is comparable to that of KANTHAL APMT, which is an alloy that is considered to have an excellent oxidation resistance.

**[0087]** The alloys according to the present invention quickly form a protective oxide which after formation has a very slow growth rate. No negative effects of the high iron content, which have previously been reported in U.S. Pat. No. 4,882,125 and U.S. Pat. No. 4,460,542 could be observed. It can be noted that most chromium oxide forming austenitic alloys commonly used at high temperatures have an oxide growth rate which is more than 4-8 times as high at this temperature.

#### Oxidation test at 1100° C.

**[0088]** Samples were produced from the same compositions and in the same manner as in the case of the oxidation

test at 1000° C. An oxidation test was performed at 1100° C. in air. Samples were removed after 24, 48, 95, 186, 500 and 1005 hours respectively and weighed. The results from the oxidation test are shown in FIG. 10.

**[0089]** The results show that the alloy according to the invention has very good oxidation resistance at 1100° C. The reference alloys used in this work, SANDVIK SANICRO 80 and KANTHAL APMT, are known to have excellent oxidation resistance for chromia formers and for ferritic alumina formers, respectively. The oxidation test of the alloys according to the present invention shows, in general, better oxidation resistance than that of SANDVIK SANICRO 80 and some even better than that of KANTHAL APMT. All tested alloys show a substantially better oxidation resistance than that of the alloy presented in WO 00/34541. Tentative oxidation studies at 1200° C. indicate that the alloy according to the present invention shows an even higher degree of oxidation resistance compared to the chromia forming alloys SANDVIK SANICRO 80 and the previously mentioned UNS S35315. This shows that the aluminium addition in the developed alloy increases the oxidation resistance, especially at temperatures above 1100° C.

#### Microstructure

**[0090]** An example of the microstructure in a material, with the composition according to Heat A, produced from metal powder which was compacted by HIP, hot extruded and water quenched is shown in FIG. 11. The photograph was taken in a scanning electron microscope (SEM) with a 30 000 $\times$  magnification. The light precipitates seen in the microstructure are carbonitrides containing mainly Hf, Ta and Zr.

**[0091]** An image analysis of close to 10000 carbonitride precipitates of the material in FIG. 11 was performed using SEM. The average diameter of the precipitates was about 130 nm. The frequency of carbonitride precipitates in different size ranges from the image analysis is shown in FIG. 12a.

**[0092]** Furthermore, the size of the dispersion strengthening precipitates in Heats B to D was investigated. FIG. 12b shows the relative frequency of the particle diameter of Heats A to D. It is clear that the dispersions in all heats generally have a diameter of less than 300 nm.

#### Creep Testing of Heats 1 and 2

**[0093]** The creep strength for Heat 1 and Heat 2 given in Table 1 was performed. Test samples were produced from metal powder which was compacted by HIP. During the creep testing threaded samples with a length of 35 mm and a 5 mm diameter at the waist were used. The testing was performed at the temperature 1200° C. and 4 MPa load. The test was performed for double samples. Heat 1, which comprises only a small content of dispersion strengthened particles due to the low content of C (0.05%) and only 0.395% Hf (no additions of Nb, Ti, Zr and Ta), showed a time to fracture of 358 and 387 hours respectively, for the samples. However, Heat 2 which has a relatively high content of dispersion strengthened particles due to the relatively high content of C (0.14%) and 1.148% in total of Zr, Ta and Hf, showed a time to fracture of 3064 and 4576 hours respectively. The beneficial effect of the dispersion strengthening is thus clear from these results.

#### Creep Testing of Heats A-F

**[0094]** Test samples for creep testing were produced from metal powder which was compacted by HIP and thereafter



hot extruded from 77 mm diameter to 25 mm diameter followed by water quenching. During the creep testing threaded samples with a length of 35 mm and a 5 mm diameter at the waist were used. The testing was performed at the temperature 1200° C. with 5 MPa load and at the temperature 1000° C. with 15 MPa load. The time to rupture for the different materials is shown in the Table 5.

TABLE 5

Heat	Time to rupture t <sub>r</sub> (h)	Time to rupture t <sub>r</sub> (h)
	1200° C./5 MPa	1000° C./15 MPa
A	571	337
B	689	1629
C	780	496
D	4041*	4007*
E	223	286*
F	327	263

\*Ongoing test

**[0095]** The results show how material according to the invention has a creep strength superior to commercially available wrought nickel base alloys. It also shows how material according to the invention has sufficient creep strength and oxidation resistance for practical usage at temperatures exceeding 1200° C. in contrast to a vast majority of commercially available nickel base alloys.

**[0096]** The high creep strength of Heat D is believed to be a result of the high content of carbon as well as the high contents of Ti, Nb, Ta, Hf and Zr.

Creep Testing of Heats which are not Dispersion Strengthened

**[0097]** A number of experimental heats of approximately 1 kg size were produced by induction melting and casting under a protective argon atmosphere for sake of comparison. The heats were not dispersion strengthened since they were not powder metallurgically produced. The compositions are given in Table 6.

**[0098]** The produced materials were then turned to rods with a diameter of 15 mm and thereafter hot rolled at 1200° C. Test samples for creep testing were produced from work pieces which had been hot rolled to 10 mm square cross section. During the creep testing threaded samples with a length of 35 mm and a diameter of 5 mm at the waist were used.

**[0099]** The creep testing was performed at the temperature of 1200° C. and 4 MPa load. The result is shown in FIG. 13.

**[0100]** A comparison of the times to fracture in FIG. 13 with those of the tests of Heat 2 above shows the beneficial effect on the creep strength when the material has been produced by powder metallurgy. Heat 2 was tested under the same load and temperature as the comparative melts given in Table 6, and showed times to fracture above 3000 hours, whereas the comparative melts all fractured well under 500 hours.

**[0101]** Heat 4249, which has a high content of C (0.13%) and a relatively high content of Ta+Zr+Hf (0.96%), still has a creep strength below 500 hours to fracture whereas Heat 2 comprising approximately the same amount of C (0.14%) and a slightly higher content of the dispersion strengthening elements (1.148%) showed more than 6 times the time to fracture.

Oxidation Test at 1100° C. of Heats which are not Dispersion Strengthened

**[0102]** Samples in the form of coupons were produced from heats 4249, 4251, 4257, and 4258 and grid with 220 μm paper. The samples were oxidation tested at 1100° C. in air. The samples were removed after 24, 48, 96, 186, 500, and 1000 hours respectively and weighed. Results from the oxidation test are shown in FIG. 14.

**[0103]** The results show that the alloy has a very good oxidation resistance at 1100° C. Since the oxidation properties of the material should be independent of the dispersion strengthening, the results indicate that powder metallurgically produced dispersion strengthened alloys with the same compositions, that is, the alloy according to the invention, should exhibit equally good oxidation resistance at this temperature.

1. Dispersion strengthened nickel based alloy comprising in percent by weight (wt-%)

C	0.05-0.2
Si	max 1.5
Mn	max 0.5
Cr	15-20
Al	4-6
Fe	15-25
Co	max 10

TABLE 6

Heat	4249	4250	4251	4252	4253	4254	4256	4257	4258
C	0.13	0.13	0.05	0.09	0.12	0.06	0.13	0.09	0.05
Si	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Cr	18.8	18.7	18.3	17.3	18.0	18.0	17.9	17.9	17.8
Ni	55.5	52.0	52.2	58.3	58.2	58.1	57.8	58.3	58.9
Al	5.2	4.2	4.1	4.3	4.3	4.2	4.2	4.3	4.1
Nb	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Ti	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Ta	0.35	0.14	0.13	0.32	0.14	0.14	0.14	0.35	0.32
Zr	0.37	0.49	0.47	0.51	0.50	0.47	0.16	0.13	0.03
N	0.048	0.057	0.06	0.012	0.061	0.058	0.054	0.014	0.054
Y	0.01	0.01	0.006	0.005	0.009	0.011	0.006	0.019	0.012
Fe	19.3	26.0	25.2	18.1	18.6	18.6	18.5	18.5	18.7
Hf	0.24	0.17	0.16	0.35	0.15	0.15	0.24	0.20	0.16
Ta + Zr + Hf + Nb + Ti	0.96	0.80	0.76	1.18	0.79	0.76	0.54	0.68	0.51

n.a. = not added



-continued

N	0.03-0.15
O	max 0.5
one or more elements selected from the group consisting of Ta, Zr, Hf, Ti and Nb	0.25-2.2
one or more elements selected from the group consisting of REM	max 0.5
balance Ni and normally occurring impurities.	

2. Nickel based alloy according to claim 1, wherein the alloy comprises 16-21.5 wt-% Fe.
3. Nickel based alloy according to claim 1, wherein the alloy comprises 17-20 wt-% Cr, preferably 17-19 wt-% Cr.
4. Nickel based alloy according to claim 1, wherein the alloy comprises max 1 wt-% Si, preferably max 0.3 wt-% Si.
5. Nickel based alloy according to claim 1, wherein the alloy comprises one or more elements selected from the group consisting of REM in a total content of 0.05-0.25 wt-%, preferably 0.05-0.25 wt-% Y.
6. Nickel based alloy according to claim 1, wherein the alloy comprises one or more elements selected from the group consisting of Ta, Zr, Hf Ti and Nb in a total content of 0.3-1.5%, preferably 0.6-1.5%.
7. Nickel based alloy according to claim 1, wherein the alloy comprises 0.1-0.5 wt-% Hf.
8. Nickel based alloy according to claim 1, wherein the alloy comprises 0.05-0.35 wt-% Zr.
9. Nickel based alloy according to claim 1, wherein the alloy comprises 0.05-0.5 wt-% Ta.
10. Nickel based alloy according to claim 1, wherein the alloy comprises 0.05-0.4 wt-% Ti.
11. Nickel based alloy according to claim 1, wherein the alloy comprises 0.1-0.8 wt-% Nb.
12. Nickel based alloy according to claim 1, wherein the alloy comprises >4-5.5 wt-% Al, preferably >4-5.2 wt-% Al.
13. Nickel based alloy according to claim 1, wherein the alloy comprises 200-2000 ppm O, preferably 400-1000 ppm O.
14. Nickel based alloy according to claim 1, wherein the alloy comprises 52-62 wt-% Ni, preferably 52-60 wt-% Ni.

15. Nickel based alloy according to claim 1, wherein the alloy is essentially free from carbides of the form  $M_7C_3$ , wherein M is a metal.
16. Powder of a dispersion strengthened nickel based alloy comprising in percent by weight (wt-%)''

C	0.05-0.2
Si	max 1.5
Mn	max 0.5
Cr	15-20
Al	4-6
Fe	15-25
Co	max 10
N	0.03-0.15
O	max 0.5
one or more elements selected from the group consisting of Ta, Zr, Hf, Ti and Nb	0.25-2.2
one or more elements selected from the group consisting of REM	max 0.5
balance Ni and normally occurring impurities.	

17. Solid component comprising an aluminium oxide forming nickel based alloy wherein the nickel based alloy is compacted, such as by hot isostatic pressing or cold isostatic pressing, of a powder according to claim 16.
18. Use of the nickel based alloy according to claim 1, in products in the form of tube, rod, strip, plate or wire.
19. Use of the nickel based alloy according to claim 1, as construction material for heat treatment furnaces, in rollers for roller hearth furnaces, as muffle tubes for annealing in protective atmosphere, as construction material for heating elements, combustion chamber material in gas turbines, as gas-to-gas heat exchangers for example in the glass manufacturing industry or in gas turbines, as tubular reactors in high temperature processes, as transportation belts woven of wire intended for heat treatment furnaces, in radiation tubes for heating of heat treatment furnaces or as protection tubes for thermocouples.

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