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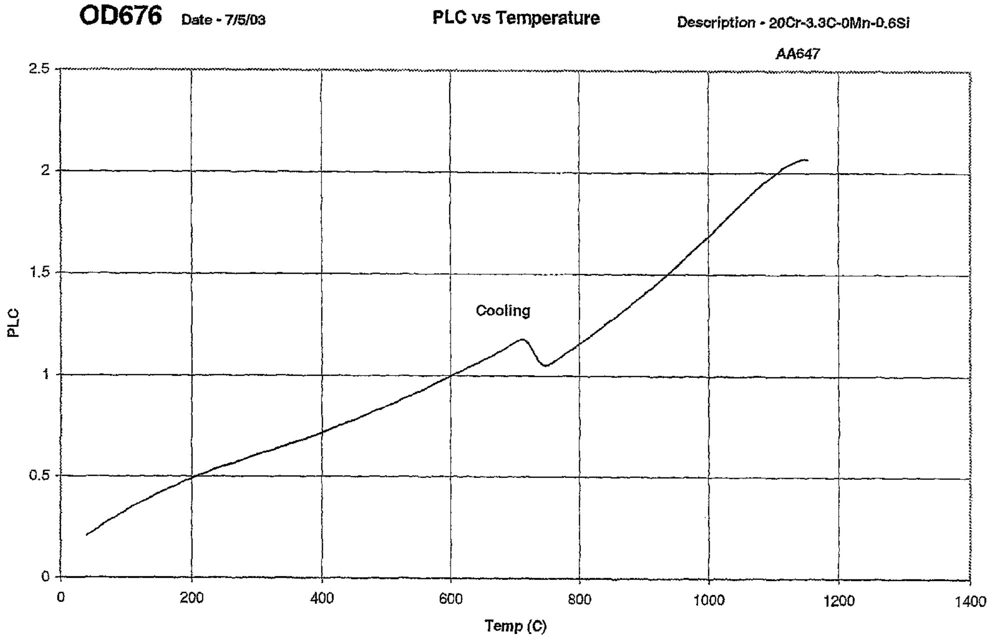
(54) Title: WEAR RESISTANT CAST IRON



(57) Abstract: A casting of a white cast iron alloy is disclosed. The casting comprises the following alloy composition, in weight%: chromium: 12 - 25%; carbon: 1.5 - 6%; manganese: 2 - 7%; silicon: up to 1.5%; molybdenum: up to 2; nickel: up to 4%; microalloying elements selected from the group consisting of titanium, zirconium, niobium, boron, vanadium, and tungsten: up to 2% of each of one or more of the elements; and iron: balance. The microstructure of the casting comprises 15 - 60 vol% eutectic carbides and primary carbides dispersed in a ferrous matrix that comprises martensite and is at least substantially free of pearlite.

WO 2004/104253 A1

WEAR RESISTANT CAST IRON

The present invention relates to white cast iron alloys for high erosion and high abrasion applications and to a method of producing castings of white cast iron alloys.

The components of most mining and processing equipment that are subject to wear (eg slurry pumps, cyclones and crushers) are produced from wear resistant white cast iron alloys.

Castings of these white cast iron alloys have high wear resistance and provide good service life for process equipment that is subject to erosion and abrasion wear.

Australian Standard 2027 describes inter alia the following two families of wear resistant white cast iron alloys:

(a) high chromium white cast iron alloy, eg 27%Cr; and

(b) chromium - molybdenum white cast iron alloy, eg 20Cr-2Mo and 15Cr-3Mo.

The microstructures of all these white cast iron alloys consist of two phases, namely:

(a) M_7C_3 carbides (where M = Fe, Cr, Mn, Mo), which have a hardness of 1200 - 1500 HV; and

(b) ferrous matrix that consists of one or more of the following structures(i) a saturated solution of austenite which is metastable at room temperature, (ii) solute-depleted austenite containing secondary carbide precipitates and is destabilised at room temperature (iii) destabilised, retained austenite partially transformed to martensite and (iv) destabilised, retained austenite wholly transformed to martensite.

The wear resistance of these white cast iron alloys is due to (a) the presence of the extremely hard M_7C_3 carbides and (b) the presence of a hard martensitic structure in the ferrous matrix.

It is essential to avoid the formation of pearlite in the ferrous matrix in these alloys during cooling after heat treatment in order to ensure adequate wear resistance in service.

It is a common practice to subject white cast iron alloys to an intermediate annealing process to deliberately form pearlite in order to soften the alloy for machining purposes. However, the machined white cast iron alloys are then subjected to a final heat treatment process to harden the alloys prior to service.

The ferrous matrix of AS2027, Grade 27%Cr (high chromium) white cast iron alloys can be readily hardened by forming martensite in the ferrous matrix during air cooling after heat treatment. One of the functions of the chromium in the alloys is to suppress the formation of pearlite during cooling from elevated temperatures.

However, white cast iron alloys containing lower chromium contents, eg 20Cr-2Mo and 15Cr-3Mo, require the addition of molybdenum and/or nickel to suppress the formation of pearlite on cooling after heat treatment, particularly in heavy section castings, ie castings greater than 10cm thick. However, molybdenum and nickel are each expensive alloying elements and add substantially to the material cost of white cast iron alloys.

An object of the present invention is to provide a white cast iron alloy that is a lower cost alternative to the currently available white cast iron alloys described above.

The present invention is based on the realisation that it is possible to produce a white cast iron alloy that can produce castings that have at least comparable wear resistance to castings of currently available white cast iron alloys at considerably lower cost by substituting manganese for at least some of the molybdenum, nickel, and chromium in the currently available white cast iron alloys.

According to the present invention there is provided a casting of a white cast iron alloy that comprises the following alloy composition, in weight%:

chromium: 12 - 25%;
carbon: 1.5 - 6%;
manganese: 2 - 7%;
silicon: up to 1.5%;
molybdenum: up to 2;
nickel: up to 4%;
microalloying elements selected from the group consisting of titanium, zirconium, niobium, boron, vanadium, and tungsten: up to 2% of each of one or more of the elements; and
iron: balance.

According to the present invention there is also provided a casting of a white cast iron alloy that comprises:

(a) the following alloy composition, in wt%:

chromium: 12 - 25%;
carbon: 1.5 - 6%;
manganese: 2 - 7%;
silicon: up to 1.5%;
molybdenum: up to 2;
nickel: up to 4;
microalloying elements selected from the group consisting of titanium, zirconium, niobium, boron, vanadium, and tungsten: up to 2% of each of one or more of the elements; and
iron: balance; and

(b) a microstucture that comprises 15 - 60 volume% eutectic carbides and primary carbides dispersed in a ferrous matrix that comprises martensite and is at least substantially free of pearlite.

The term "at least substantially free of pearlite" indicates that the objective of the present invention is that there be no pearlite in the matrix but at the same time recognises that in any given situation in practice there may be a small amount of pearlite.

With the above in mind, the term "substantially free of pearlite" is understood herein to mean that the casting contains no more than 2 volume% pearlite.

Preferably the white cast iron alloy comprises 15 - 23 weight% chromium.

As indicated above, chromium suppresses pearlite formation and, therefore, as the chromium concentration within the stated range of 12 - 25 weight% in the white cast iron decreases it is necessary to increase the concentrations of manganese (or other additives) to counteract the higher susceptibility to pearlite formation at lower concentrations of chromium. One advantage of using lower concentrations of chromium is that lower chromium concentrations increase the instability of austenite. This results in an increase in the amount of the desirable hard martensite phase in the white cast iron.

Preferably the white cast iron alloy comprises 2.5 - 6 weight% manganese.

The applicant has found that as the concentration of manganese increases, the temperature at which the retained austenite starts to transform to martensite (Ms temperature) on cooling from the precipitation hardening temperature decreases. At manganese concentrations above 6 weight% manganese, the martensite start temperature may be below room temperature and thus the matrix may be predominantly retained austenite. Accordingly, for applications requiring high hardness, it is preferred that the manganese concentration be no more than 6 weight%.

More preferably the white cast iron alloy comprises 2.5 - 5.5 weight% manganese.

It is preferred particularly that the white cast iron alloy comprises 3.5 - 5.5 weight% manganese.

Preferably the white cast iron comprises up to 1.5 weight% silicon.

Preferably the white cast iron comprises no nickel and molybdenum.

However, it is within the scope of the present invention for the white cast iron to include molybdenum and nickel up to the stated maximums of 2 and 4 weight%, respectively.

Preferably the ferrous matrix comprises martensite and retained austenite.

Preferably the eutectic carbides, and primary carbides comprise M_7C_3 carbides, where "M" is a metal and "C" is carbon.

According to the present invention there is also provided a method of producing the above-described casting of the white cast iron alloy which comprises the steps of:

(a) forming a molten melt of the above-described white cast iron alloy;

(b) pouring the molten melt into a mould to form the casting;

(c) allowing the casting to air cool to room temperature.

The method produces a casting having a microstucture that comprises 15 - 60 volume% eutectic carbides and primary carbides dispersed in a ferrous matrix that comprises martensite and retained austenite and is at least substantially free of pearlite.

Preferably the method further comprises heat treating the room temperature casting by:

(a) heating the casting to an elevated temperature where austenite decomposes to form secondary carbide precipitates in a solute-depleted austenite; and thereafter

(b) air cooling the casting to room temperature and transforming the solute-depleted austenite to martensite.

Preferably the austenite-destabilising temperature is in the range of 950 - 1000°C.

Preferably step (a) includes holding the casting at the austenite-destabilising temperature for at least 4 hours to ensure substantial secondary carbide precipitation has occurred.

The present invention is described further by reference to the following experimental work which was carried out for the purpose of comparing the performance of castings of white cast iron alloys in accordance with the present invention against the performance of castings of currently available white cast iron alloys.

EXPERIMENTAL PROGRAM

A number of white cast iron alloys containing systematic variations in chromium, molybdenum and manganese levels from a base alloy composition (Fe-20Cr-3.3C - 0.6Si (weight%)) were manufactured in an electric arc melting furnace under an inert atmosphere. The alloys were then processed as described below and the resultant samples were evaluated using the following test procedures:

Test Procedure	Purpose
Dilatometry	Phase changes that occur during cooling of white cast iron alloys are often accompanied by changes in the contraction of the alloys as a function of temperature.

Metallography	The presence of pearlite and other phases are readily detected by microstructural examination.
Hardness testing	Different phases in white cast iron alloys exhibit a range of hardness values.
Ferrite content	The magnetic response of white cast iron alloys is an indication of the presence of various phases.

SUMMARY OF TEST RESULTS

A first series of pin samples of the base alloy (Fe-20Cr-3.3C - 0.6Si (weight%)) and the variations of the base alloy were heated in a dilatometer to 1150°C, held for one hour to ensure equilibrium, and furnace cooled to obtain contraction cooling curves.

The above test procedure closely simulates the cooling rate of castings in a sand mould after solidification. Accordingly, the samples have properties and microstructures that are representative of properties and microstructures of as-cast castings.

The pin samples were subjected to hardness testing, ferrite content and metallographic examination.

A summary of the metallographic, hardness, and ferrite test results for each alloy is set out in Table 1 below.

Table 1 - Summary of Test Results

Alloy (Wt%)	Test No	Hardness (HV 50)	Ferrite (%)	Microstructure

Base alloy + 2Mn +2Mo	OD674	766	32	No Pearlite
Base alloy (no Mn/Mo)	OD676	380	49	Pearlite
Base alloy + 1Mn	OD677	420	47	Pearlite
Base alloy + 2Mn	OD673	533	40	Pearlite
Base alloy + 3Mn	OD681	719	33	Trace of pearlite
Base alloy + 4Mn	OD675	700	24	No Pearlite

The test results for four of the above alloys (OD676, OD674, OD675, and OD681) are discussed further below, particularly in the context of the dilatometry results.

Base alloy (OD676) - no Mo/Mn

The contraction characteristics of the base alloy (ie alloy with no molybdenum and no manganese) during furnace cooling from 1150°C is illustrated in the dilatometer curve of Figure 1.

The total percent linear contraction (PLC) is about 2.1% on cooling through the temperature range. There is a sharp discontinuity in the cooling curve at a temperature of about 700°C indicating the formation of undesirable pearlite at that temperature.

Final Hardness = 380 HV50 due to the presence of the soft ferrite phase in the pearlite.

Ferrite Content = 49% due to complete transformation of the high temperature austenite phase to body-centred-cubic ferrite which is ferromagnetic and absence of any retained face-centred-cubic austenite which is paramagnetic.

Metallographic examination demonstrated the presence of pearlite throughout the microstructure.

Base alloy + 2Mn + 2Mo (OD674)

The contraction characteristics of the conventional white cast iron 20Cr-2Mo-2Mn alloy during furnace cooling from 1150°C is illustrated in the dilatometer curve of Figure 2.

The percent linear contraction (PLC) is about 2.1% on cooling through the temperature range. The observed contraction is continuous down to a temperature of about 300°C where the discontinuity in the linear contraction curve indicates the onset of martensite formation (Ms temperature).

Final Hardness = 766 HV50 due to the presence of martensite.

Ferrite Content = 32% due to the presence of martensite and some retained austenite.

Metallographic examination demonstrated the presence of martensite and the absence of undesirable pearlite in the microstructure.

Base alloy + 4Mn (OD675)

The contraction characteristics of the base alloy containing no molybdenum and 4% manganese in accordance with the present invention during furnace cooling from 1150°C is illustrated in the dilatometer curve of Figure 3.

The total percent linear contraction (PLC) is about 2.3% on cooling through the temperature range. There is a discontinuity in the linear cooling curve at a temperature of about 200°C indicating the onset of formation of martensite (Ms temperature) at that temperature.

Final Hardness = 700 HV50 due to the presence of partial transformation of the austenite phase to secondary carbides and partial decomposition of the solute-depleted austenite to martensite on cooling to room temperature.

Ferrite Content = 24% due to the presence of martensite and some retained austenite in the microstructure.

Metallographic examination demonstrated the absence of pearlite in the microstructure.

Base alloy + 3Mn (OD681)

The contraction characteristics of the base alloy containing no molybdenum and 3% manganese in accordance with the present invention during furnace cooling from 1150°C is illustrated in the dilatometer curve of Figure 4.

The total percent linear contraction (PLC) is about 2.0% on cooling through the temperature range. There is a discontinuity in the linear cooling curve at a temperature of about 230°C indicating the onset of decomposition of the retained austenite to martensite (Ms temperature) as that temperature.

Final Hardness = 719 HV50 due to the presence of martensite.

Ferrite Content = 33% due to the presence of martensite and some retained austenite in the microstructure.

Metallographic examination demonstrated the presence of a trace amount of undesirable pearlite in a ferrous matrix that is otherwise solute-depleted austenite that is partially transformed to martensite.

In summary, the above results for simulated as-cast samples indicate that the Base alloy + 4Mn (OD675) and the Base alloy + 4Mn (OD681) in accordance with the present invention had comparable performance to the conventional white cast iron 20Cr-2Mo-2Mn alloy (OD674) and considerably better performance than the Base alloy (OD676), ie with no Mn and no Mo.

As indicated above, the above-described experimental program involving the formation of rapidly chilled pin samples and heating the samples to 1150°C and thereafter cooling the samples in the dilatometer simulates the cooling of white cast iron alloys in a sand mould after solidification.

In practice, such castings are finally hardened by heat treatment, typically by holding at 950-970°C for a period of time and air cooling to room temperature.

In order to investigate the impact of heat treatment on the above-tested range of white cast iron alloys, pin samples of each alloy prepared as described above were heat treated at 960°C for 4 hours and thereafter allowed to cool to room temperature.

A summary of the metallographic, hardness, and ferrite test results for four of the alloys (OD674, OD676, OD681, and OD675) is set out in Table 2 below.

Table 2 - Summary of Test Results

Alloy (Wt%)	Test No	Hardness (HV 50)	Ferrite (%)	Microstructure
Base alloy + 2Mn + 2Mo	OD674	857	32	No Pearlite

Base alloy	OD676	371	52	Pearlite
Base alloy + 3Mn	OD681	779	35	Trace amount of pearlite
Base alloy + 4Mn	OD675	807	33	No Pearlite

It is evident from Table 2 that the heat treated Base alloy + 4Mn (OD675) and Base alloy + 4Mn (OD681) in accordance with the present invention had comparable performance to the conventional heat treated white cast iron 20Cr-2Mo alloy (OD674) and considerably better performance than the Base alloy (OD676), ie with no Mn and no Mo.

In a further series of test work a number of white cast iron alloys containing systematic variations in chromium, molybdenum and manganese levels from a base alloy composition (Fe-20Cr-3.3C - 0.6Si (wt%)) were manufactured in an electric arc melting furnace under an inert atmosphere. The alloys were then processed as described below and the resultant samples were evaluated by hardness testing, ferrite content testing, dilatometry testing, and metallographic examination

The samples were processed as follows.

(a) simulated casting in sand mould - heating to 1150°C in a dilatometer furnace under an inert atmosphere at a rate of 3°C per minute, holding at temperature for 2 hours to achieve equilibrium, and furnace cooling to ambient temperature; and

(b) heat treatment of the simulated castings - heating to 960°C in a dilatometer furnace under an inert atmosphere at a rate of 3°C per minute, holding at temperature for 4 hours, and air cooling to ambient temperature to simulate the microstructure after heat treatment.

A summary of the metallographic, hardness, and ferrite test results for each alloy is set out in Tables 3 and 4 below.

Table 3 - Summary of Test Results Simulated Castings

Alloy (Wt%)	Test No	Hardness (HV 50)	Ferrite (%)	Microstructure
Base alloy + 5Mn	OD744	666	17	No Pearlite
Base alloy + 6Mn	OD745	574	8.4	No Pearlite
Base alloy + 7Mn	OD759	645	9.6	No Pearlite
Base alloy + 8Mn	OD749	536	2.5	No Pearlite

Table 4 - Summary of Test Results -Heat Treated Samples

Alloy (Wt%)	Test No	Hardness (HV 50)	Ferrite (%)	Microstructure
Base alloy + 5Mn	OD744	727	27	No Pearlite
Base alloy + 6Mn	OD745	629	10	No Pearlite
Base alloy + 7Mn	OD759	622	13.6	No Pearlite
Base alloy + 8Mn	OD749	557	3.8	No Pearlite

The microstructural and dilatometry evaluations of the above samples indicated that the amount of martensite in the matrix of each sample decreased with increasing manganese concentration to the point that at high manganese concentrations (13%) there was no martensite and the matrix comprised retained austenite.

The test data in Table 4 demonstrates that manganese levels above 7 weight% stabilises the softer austenite phase and suppresses the transformation to the harder martensite phase. Consequently, manganese contents greater than 7 weight% adversely affect the final hardness of these wear resistant alloys.

Many modifications may be made to the present invention as described above without departing from the spirit and scope of the present invention.

CLAIMS:

1. A casting of a white cast iron alloy that comprises the following alloy composition, in weight%:

chromium: 12 - 25%;
carbon: 1.5 - 6%;
manganese: 2 - 7%;
silicon: up to 1.5%;
molybdenum: up to 2;
nickel: up to 4%;
microalloying elements selected from the group consisting of titanium, zirconium, niobium, boron, vanadium, and tungsten: up to 2% of each of one or more of the elements; and
iron: balance.

2. A casting of a white cast iron alloy that comprises:

(a) the following alloy composition, in wt%:

chromium: 12 - 25%;
carbon: 1.5 - 6%;
manganese: 2 - 7%;
silicon: up to 1.5%;
molybdenum: up to 2;
nickel: up to 4;
microalloying elements selected from the group consisting of titanium, zirconium, niobium, boron, vanadium, and tungsten: up to 2% of each of one or more of the elements; and
iron: balance; and

(b) a microstucture that comprises 15 - 60 vol% eutectic carbides and primary carbides dispersed in a ferrous matrix that comprises martensite and is at least substantially free of pearlite.

3. The casting defined in claim 1 or claim 2 wherein the alloy composition comprises 15 - 23 wt% chromium.

4. The casting defined in any one of the preceding claims wherein the alloy composition comprises 2.5 - 7 wt% manganese.

5. The casting defined in claim 4 wherein the alloy composition comprises 3.0 - 5.5 wt% manganese.

6. The casting defined in claim 4 wherein the alloy composition comprises 3.5 - 5.5 wt% manganese.

7. The casting defined in any one of the preceding claims wherein the alloy composition comprises up to 1.5 wt% silicon.

8. The casting defined in any one of the preceding claims wherein the alloy composition comprises no nickel and molybdenum.

9. The casting defined in any one of claims 1 to 7 wherein the alloy composition include molybdenum and nickel up to the stated maximums of 2 and 4 wt%, respectively.

10. The casting defined in any one of the preceding claims wherein the ferrous matrix comprises martensite and retained austenite.

11. The casting defined in any one of the preceding claims wherein the eutectic carbides comprise M_7C_3 carbides, where "M" is a metal and "C" is carbon.

12. A method of producing the casting of the white

cast iron alloy defined in any one of the preceding claims which comprises the steps of:

(a) forming a molten melt of the white cast iron alloy;

(b) pouring the molten melt into a mould to form the casting;

(c) allowing the casting to air cool to room temperature.

13. The method defined in claim 12 further comprises heat treating the room temperature casting by:

(a) heating the casting to an austenising temperature and precipitating secondary carbides from the ferrous matrix; and thereafter

(b) air cooling the casting to room temperature and transforming the solute-depleted austenite to martensite.

14. The method defined in claim 13 wherein the heat temperature is in the range of 950 - 1000°C.

15. The method defined in claim 13 or claim 14 wherein step (a) includes holding the casting at the heat temperature for at least 4 hours.

FIGURE 1

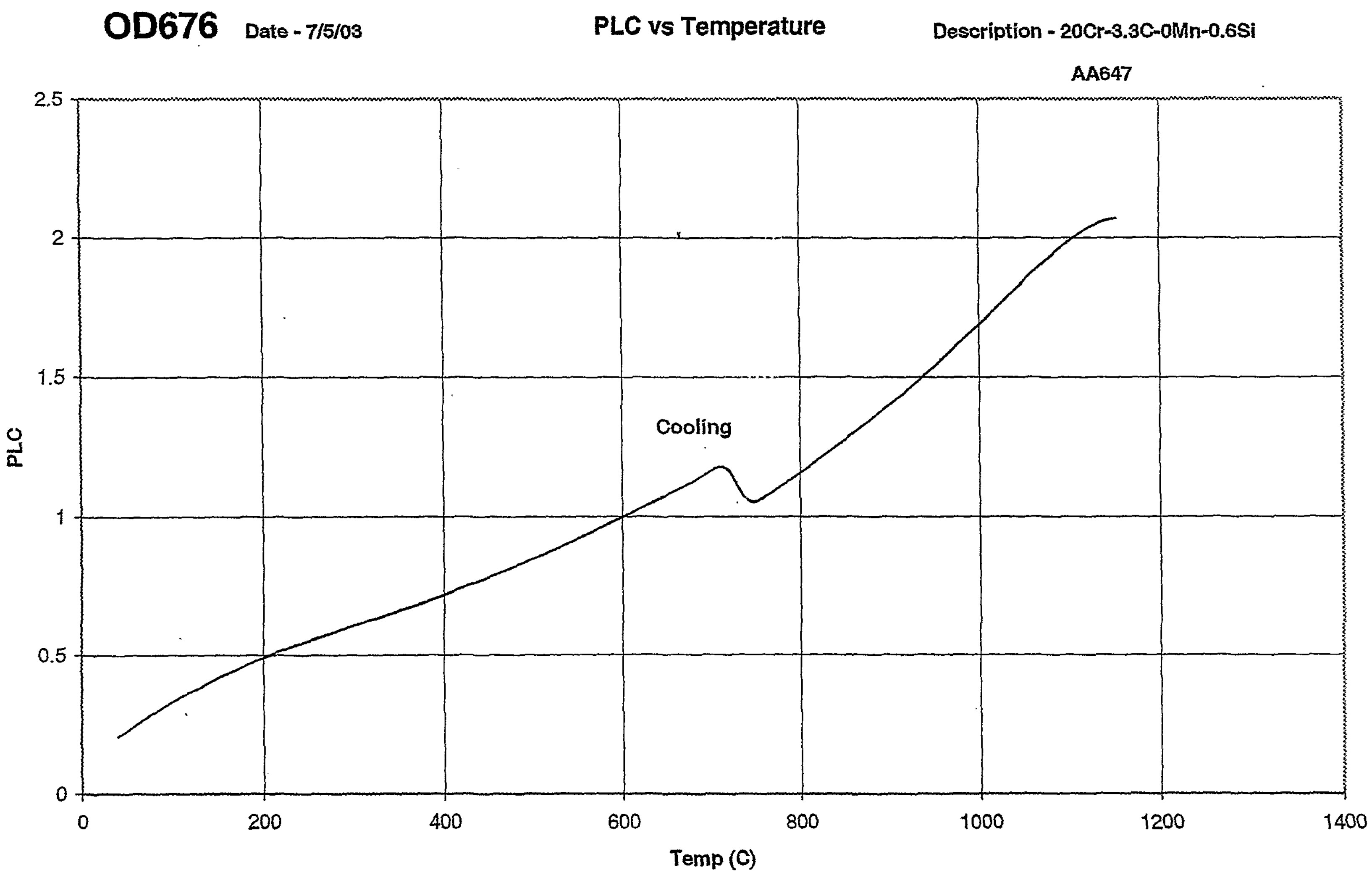

OD676
Date - 7/5/03
PLC vs Temperature
Description - 20Cr-3.3C-0Mn-0.6Si
AA647
PLC
2.5
2
1.5
1
0.5
0
Cooling
0
200
400
600
800
1000
1200
1400
Temp (C)

FIGURE 2

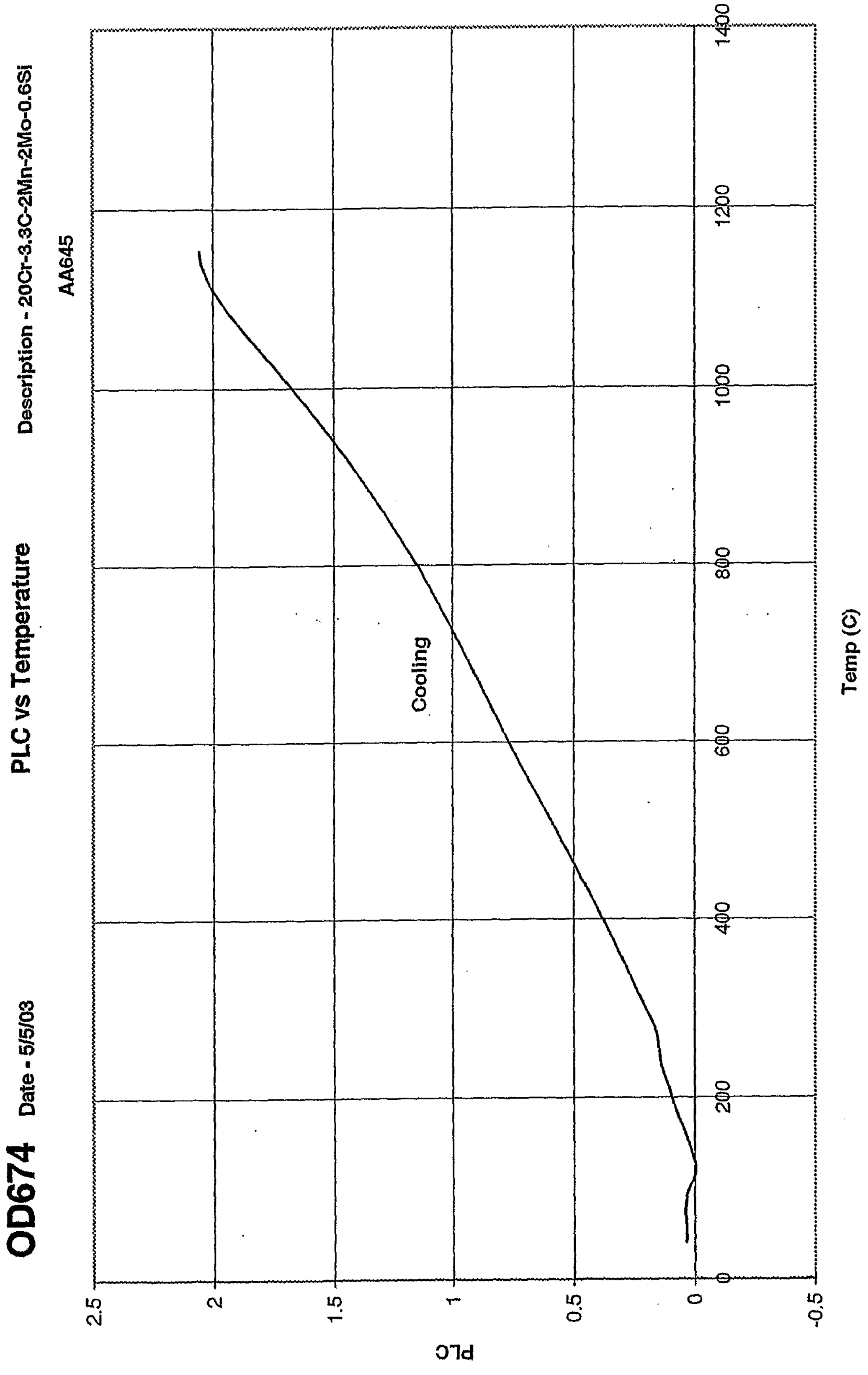

OD674
Date - 5/5/03
PLC vs Temperature
Description - 20Cr-3.3C-2Mn-2Mo-0.6Si
AA645
Cooling
PLC
2.5
2
1.5
1
0.5
0
-0.5
Temp (C)
0
200
400
600
800
1000
1200
1400

FIGURE 3

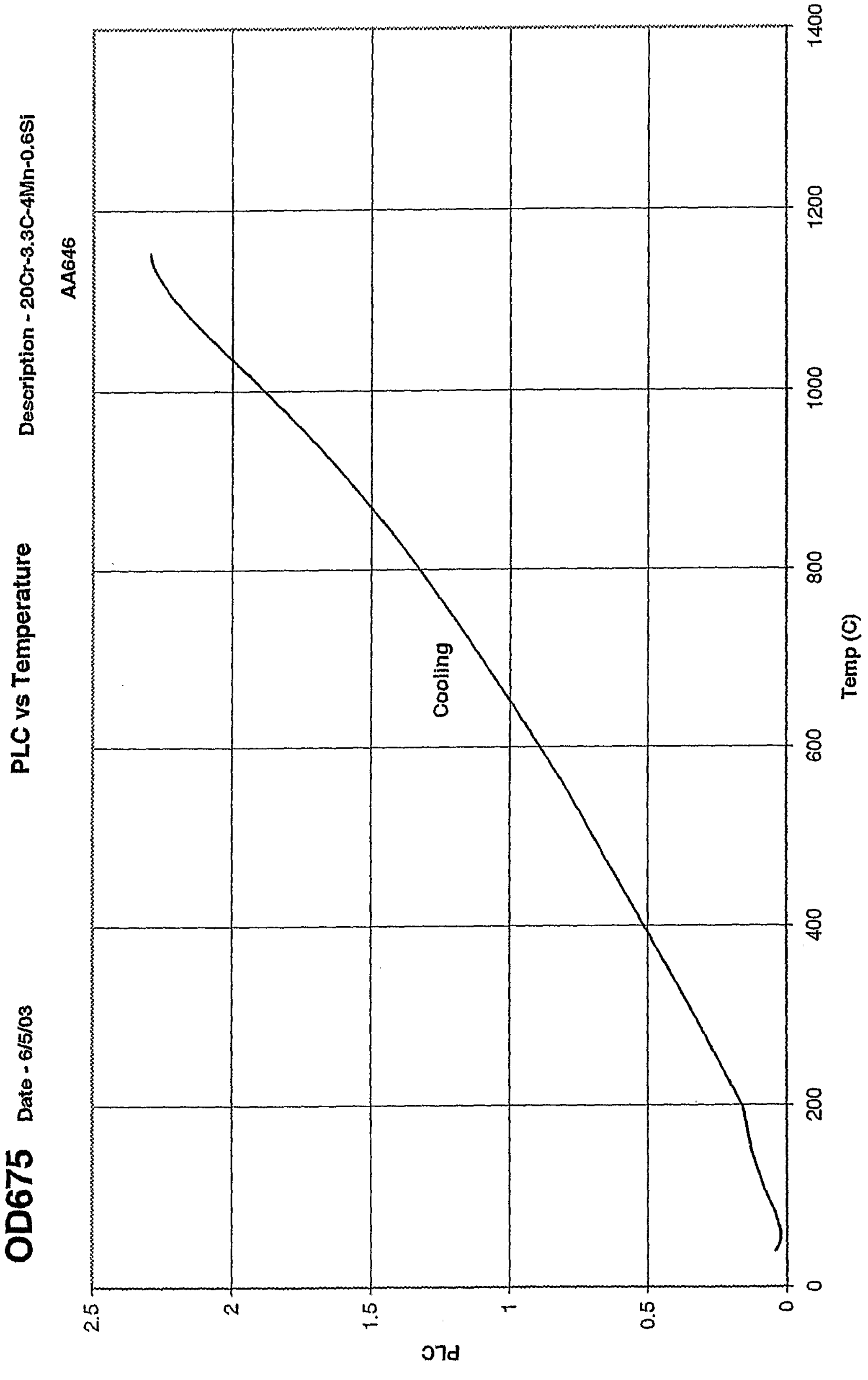
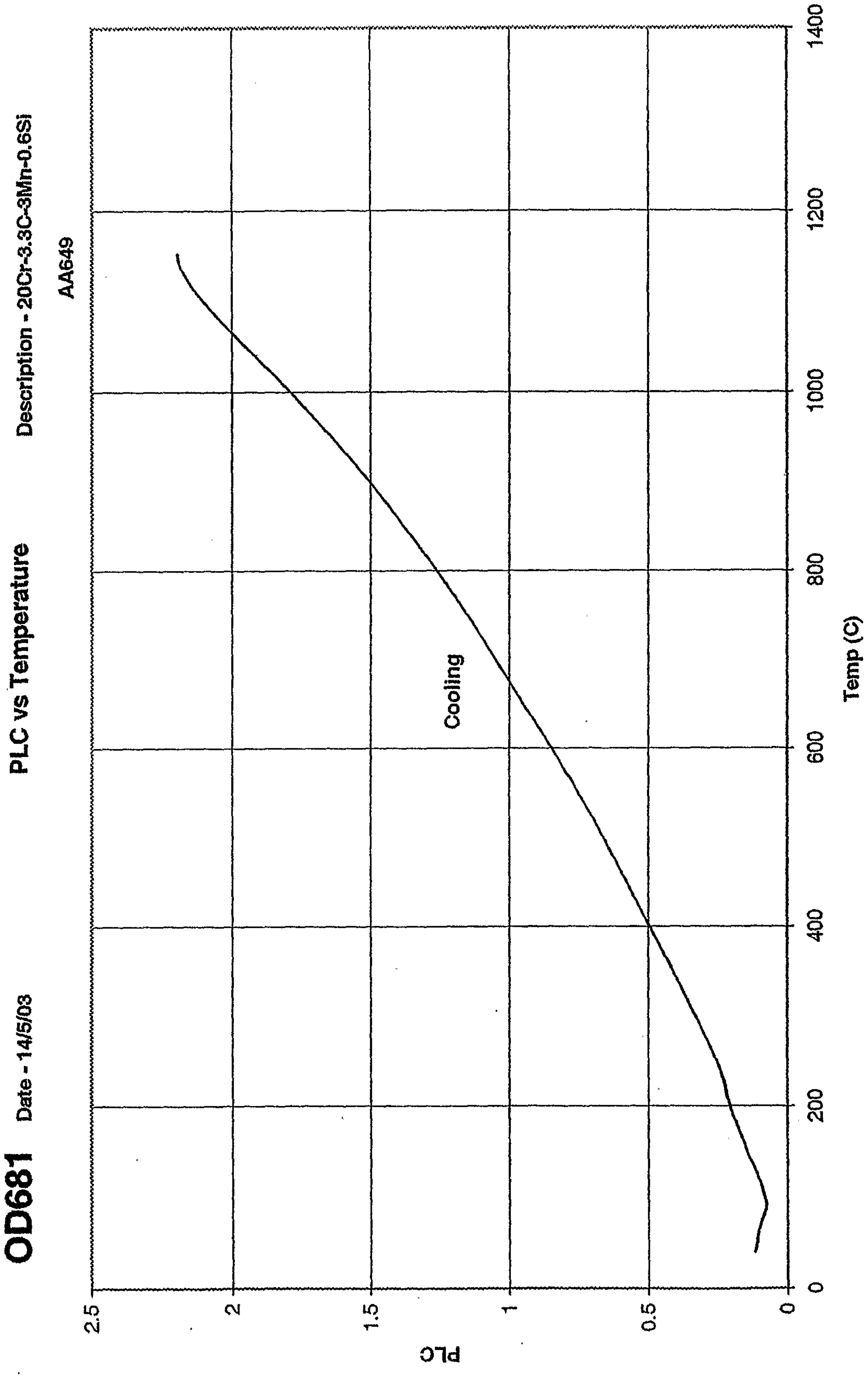

OD675
Date - 6/5/03
PLC vs Temperature
Description - 20Cr-3.3C-4Mn-0.6Si
AA646
Cooling
PLC
2.5
2
1.5
1
0.5
0
Temp (C)
0
200
400
600
800
1000
1200
1400

FIGURE 4


OD681
Date - 14/5/03
PLC vs Temperature
Description - 20Cr-3.3C-3Mn-0.6Si
AA649
Cooling
PLC
2.5
2
1.5
1
0.5
0
Temp (C)
0
200
400
600
800
1000
1200
1400

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2004/000678

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. ^{7}: C22C 37/06, 37/08, 37/10, 38/38, 38/58, C21D 5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
REFER TO ELECTRONIC DATA BASES CONSULTED

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI, CAPLUS, IPC: C22C 37/06, 37/08, 37/10, 38/38, 38/58, C21D 5/04 and CAST+, CHROMIUM, CARBON , MANGANESE, TIANIUM, ZIRCONIUM, NIOBIUM, BORON, VANADIUM, TUNGSTEN, SILICON, MOLYBDENUM, NICKEL, WOLFRAM, IRON, MARTENSITE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 984185 A (VSESOJUZNY NAUCHNO-ISSLEDOVATELSKY I PROEKTNO-TEKHNOLOGICHESKY INSTITUT UGOLNOGO MASHINOSTROENIA) 24 February 1976 page 2, line 17 to page 3, line 11, page 7, lines 4 to 27	1, 4-15
X	Patent Abstracts of Japan, JP 63-121635 A (HITACHI LTD) 25 May 1988 whole abstract	1-7, 9-11
X	Derwent Abstract Accession No. 53116X/28, Class M27, JP 51-061422 A (MITSUBISHI HEAVY INDUSTRIES KK) 28 May 1976 & JP 51-061422 whole abstract and document	1, 3-7, 9-15
X	DD 94263 A (Sallaba et al.) 5 December 1972 column 3, lines 3 to 16, column 4, lines9 to 20	1, 4-7, 9, 10, 12-15

☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

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"&" document member of the same patent family

Date of the actual completion of the international search
14 July 2004

Date of mailing of the international search report
23 JUL 2004

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstracts Accession No. 58021 E/28, Class M27 (M24), JP 57-089453 A (NIPPON NENRYO KK) 3 June 1982 whole abstract	1, 3-5, 7-10, 12, 13
X	Derwent Abstract Accession No. 93-165447/20, Class M27, SU 1735425 A (AZOVMASH PRODN ASSOC) 23 May 1992 whole abstract	1, 3-7, 9-12
X	Derwent Abstract Accession No. 93-318925/40, Class M27, SU 1765236 A (DON POLY) 30 September 1992 whole abstract	1, 3, 4, 7, 9

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member
CA	984185	NONE
JP	63121635	NONE
JP	51061422	NONE
DD	94246	NONE
JP	57089453	NONE
SU	1735425	NONE
SU	1765236	NONE

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX