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(54) **CREEP RESISTANT CU-BASED CUCRNBZR ALLOY WITH HIGH THERMAL CONDUCTIVITY**

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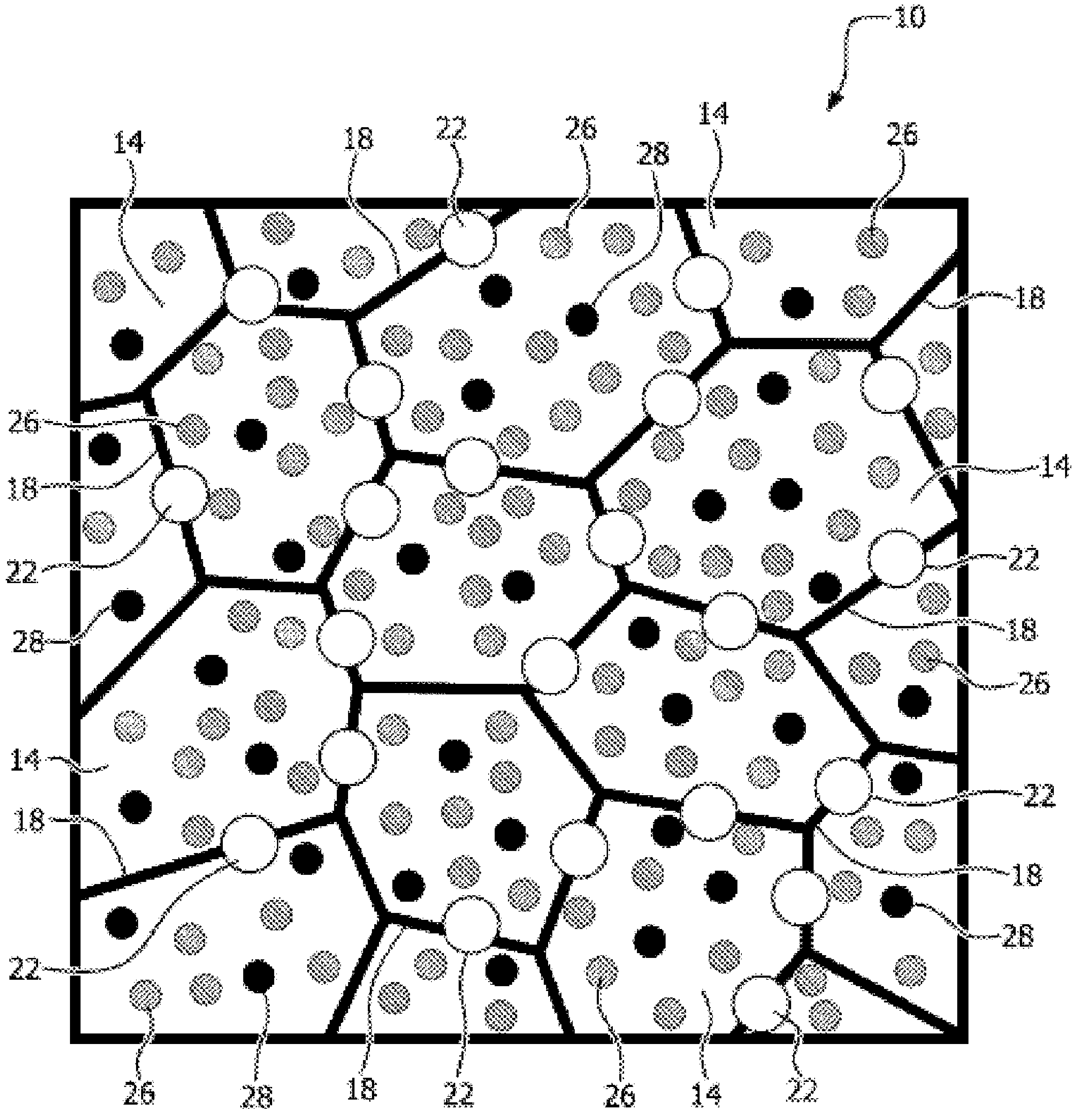
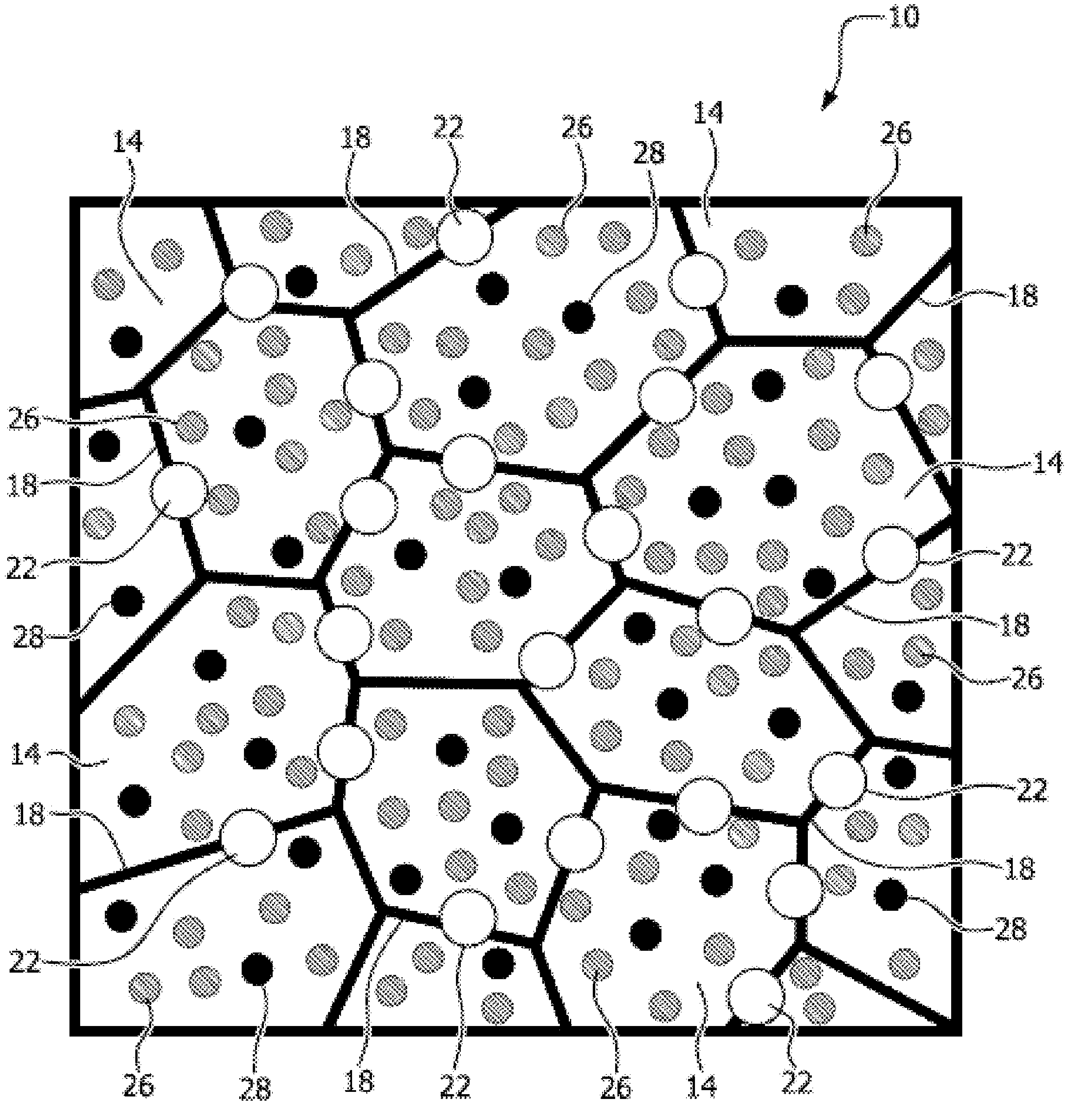
(57) **ABSTRACT**

A Cu-based alloy according to the present invention comprises 1.0-2.0 wt % Cr, 0.5-1.5 wt % Nb, 0.1-0.5 wt % Zr, and balance Cu. The alloy has a matrix and grain boundaries, and has Cr_2Nb precipitates within the grain boundaries and at least one selected from the group consisting of CuZr and Cr precipitates in the grain matrix. The CuZr precipitates can be at least one selected from the group consisting of Cu_5Zr and $Cu_{51}Zr_{14}$ precipitates. A method of making a CuCrNbZr alloy is also disclosed.




10
14
18
22
26
28
14
26
18
26
18
14
22
22
28
18
26
14
18
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22
18
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18
22
26
14
22

FIG. 1

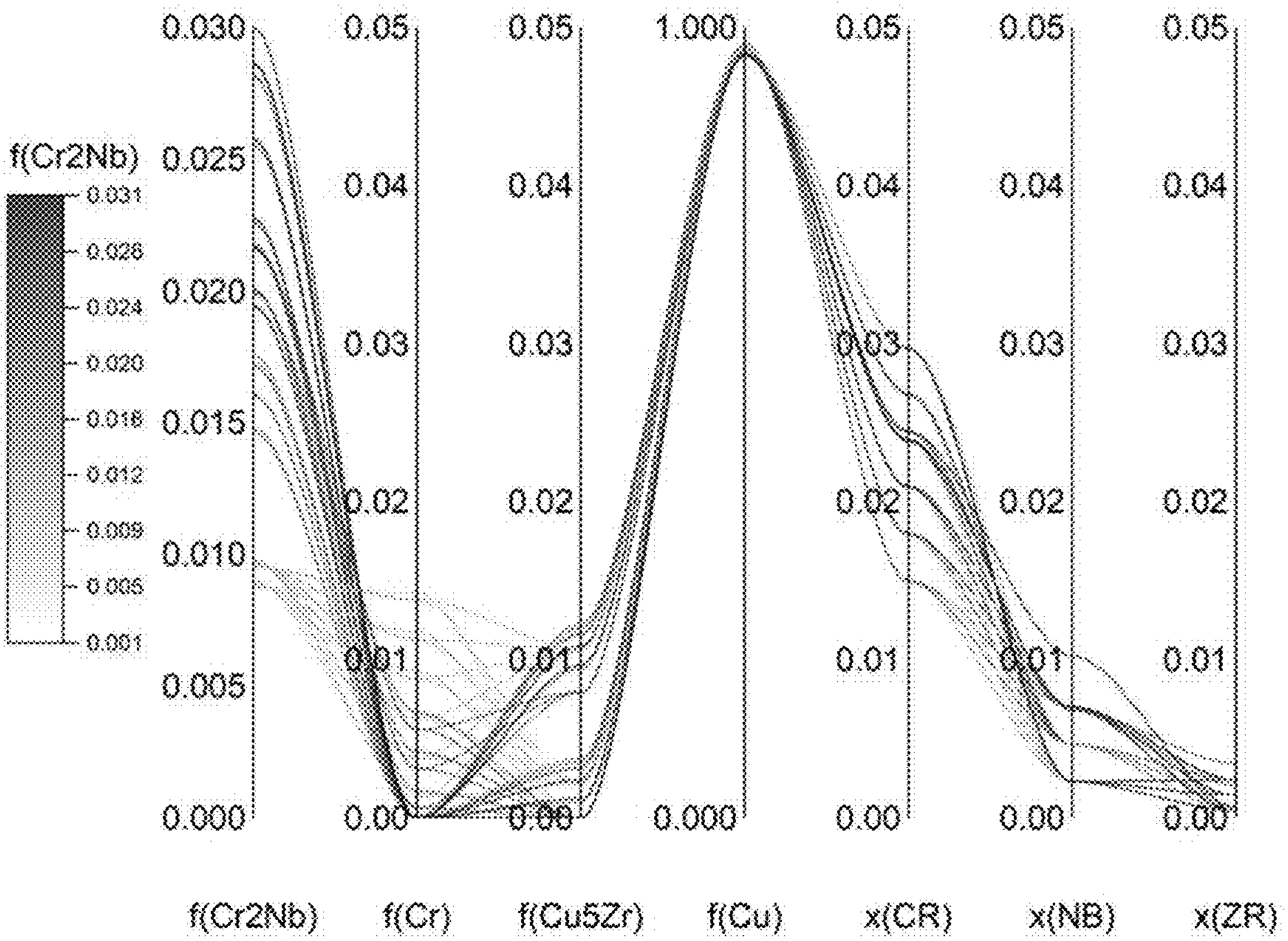
f(Cr2Nb)
0.031
0.026
0.024
0.020
0.018
0.012
0.009
0.005
0.001
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0.05
0.04
0.03
0.02
0.01
0.00
1.000
0.000
f(Cr2Nb)
f(Cr)
f(Cu5Zr)
f(Cu)
x(CR)
x(NB)
x(ZR)

FIG. 2

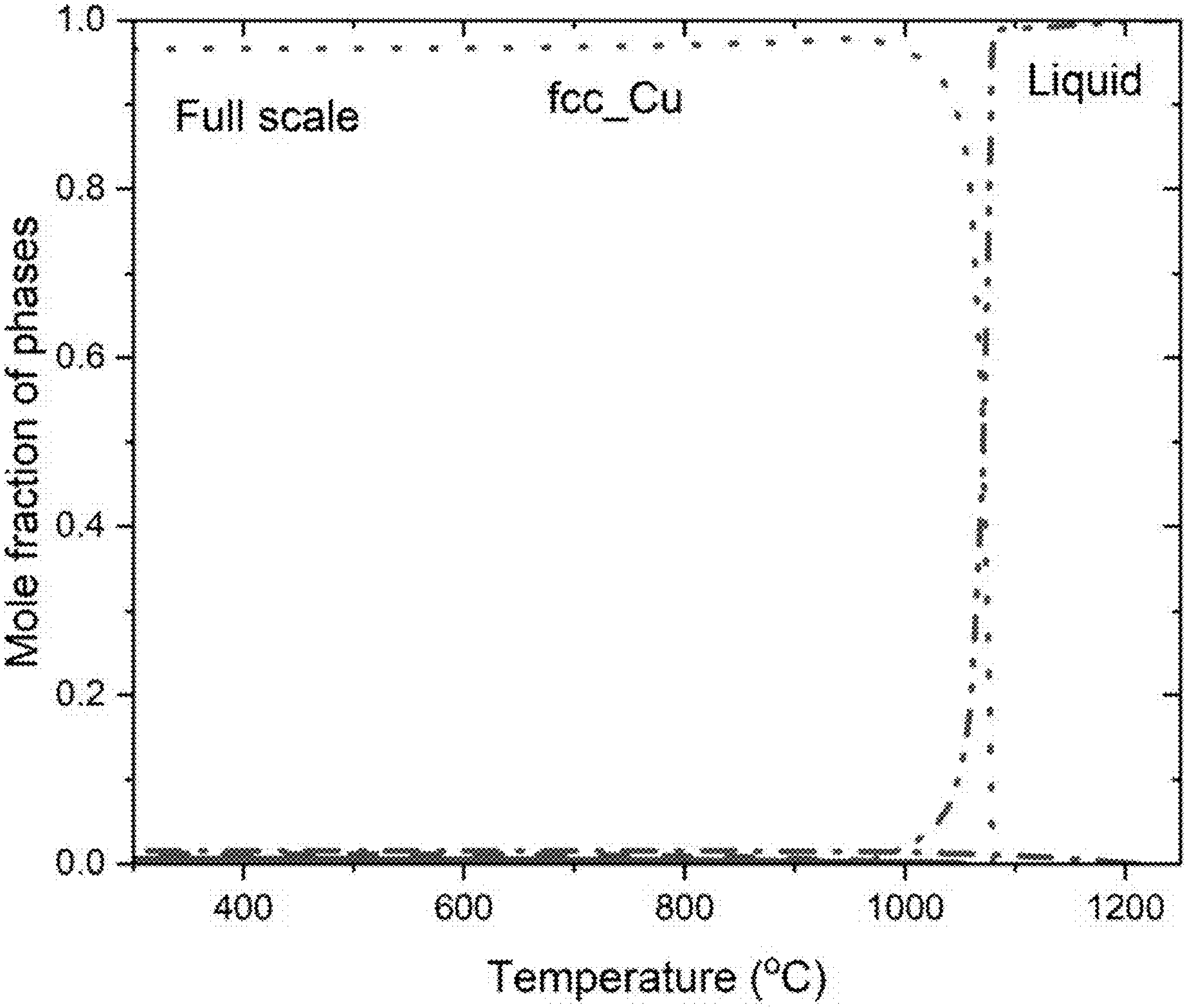
Full scale
fcc_Cu
Liquid
Mole fraction of phases
0.0
0.2
0.4
0.6
0.8
1.0
400
600
800
1000
1200
Temperature (°C)

FIG. 3

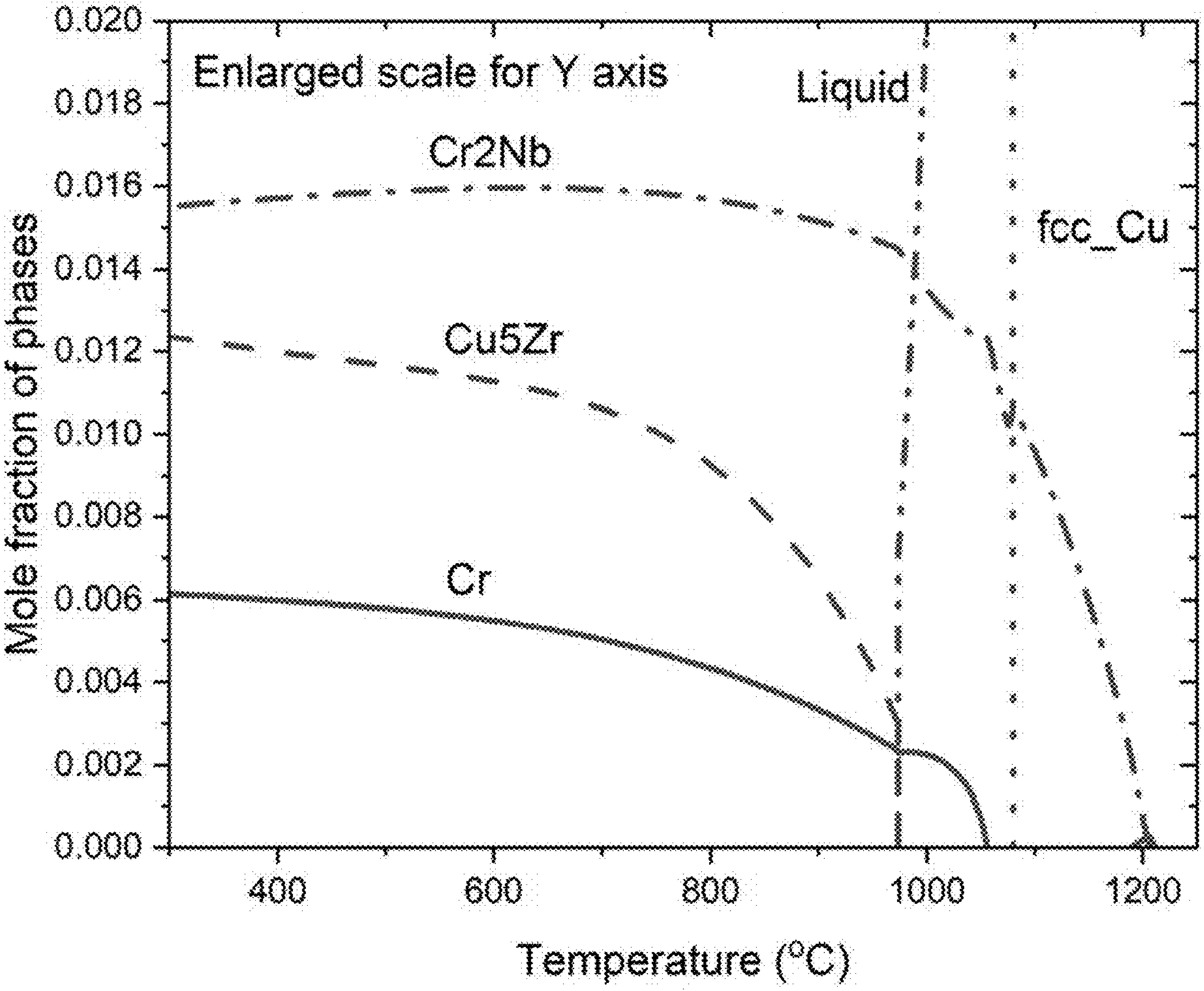
Enlarged scale for Y axis
Liquid
Cr2Nb
fcc_Cu
Cu5Zr
Cr
Mole fraction of phases
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
400
600
800
1000
1200
Temperature (°C)

FIG. 4

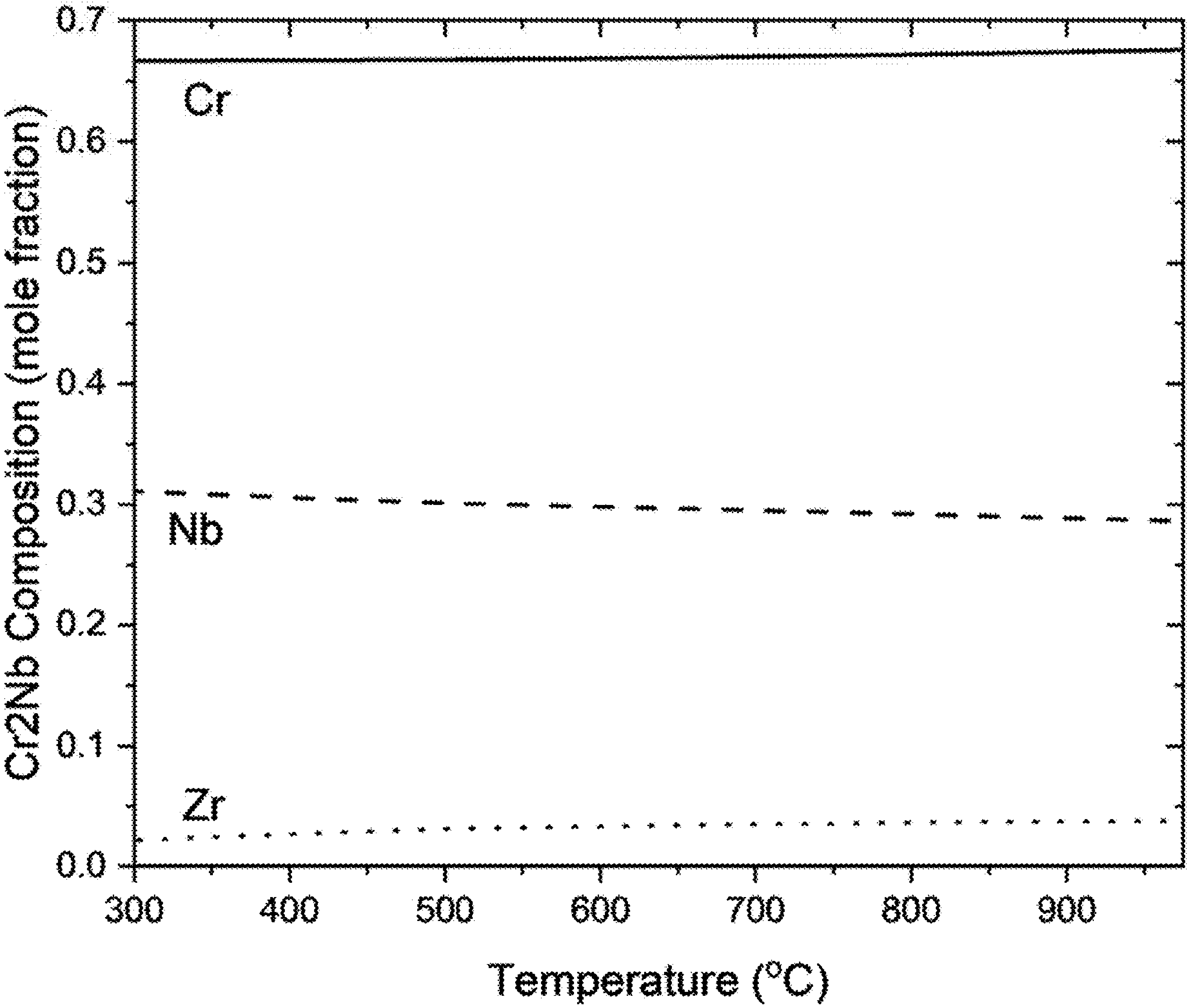
Cr
Nb
Zr
Cr2Nb Composition (mole fraction)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
300
400
500
600
700
800
900
Temperature (°C)

FIG. 5

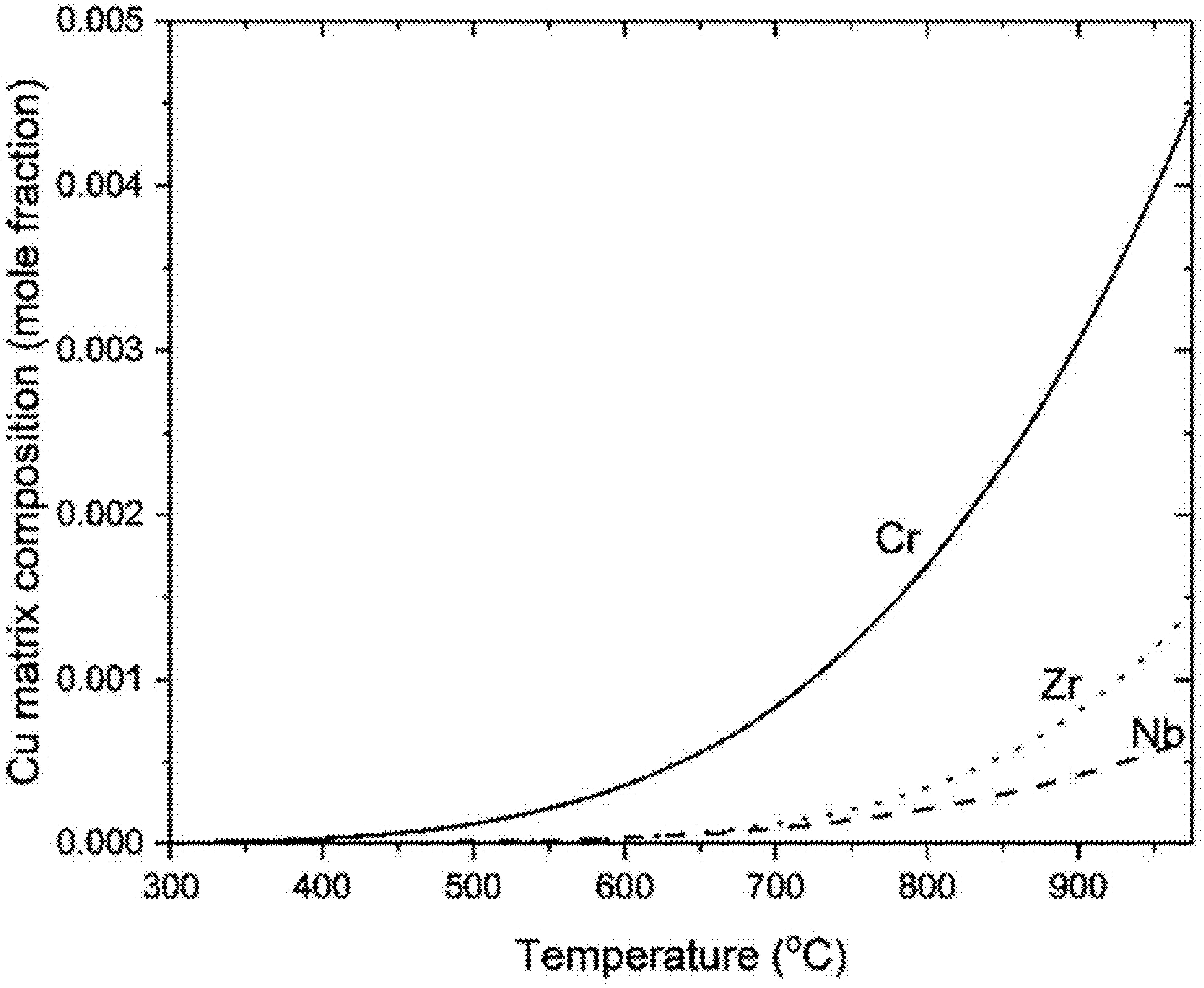
Cu matrix composition (mole fraction)
0.005
0.004
0.003
0.002
0.001
0.000
300
400
500
600
700
800
900
Temperature (°C)
Cr
Zr
Nb

FIG. 6

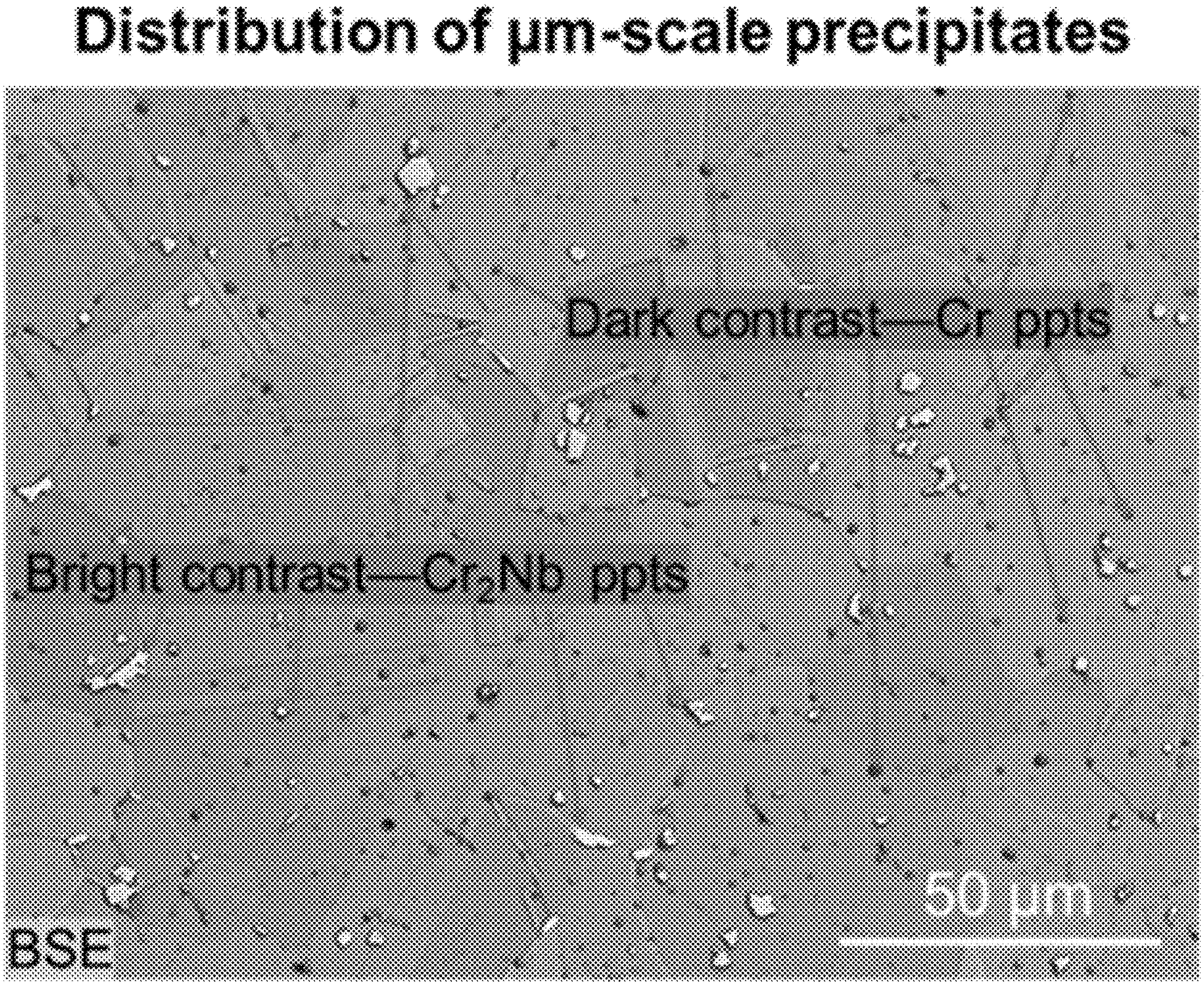
Distribution of µm-scale precipitates
Dark contrast—Cr ppts
Bright contrast—Cr_2Nb ppts
50 µm
BSE

FIG. 7

Distribution of nm-scale precipitates

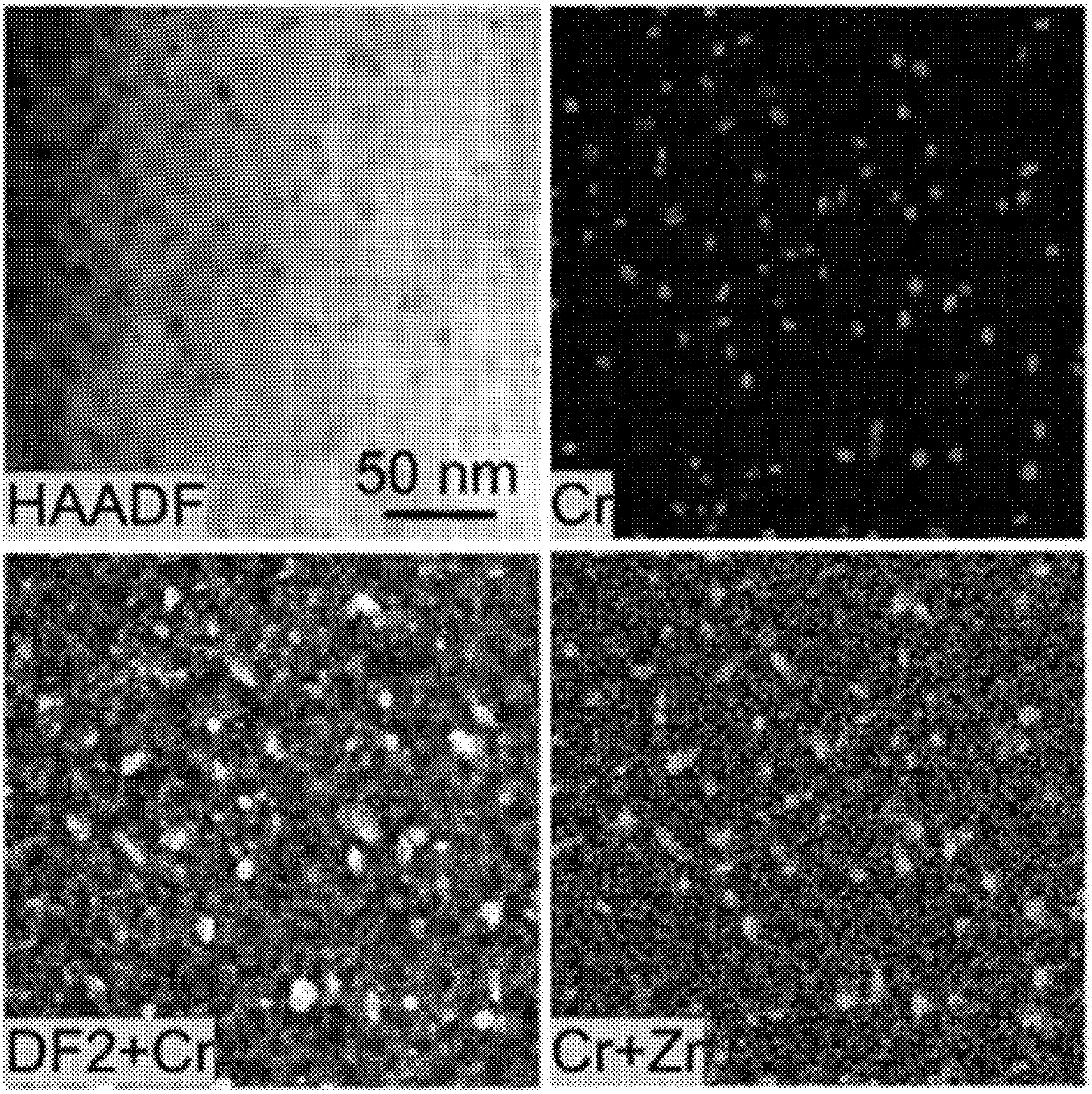

FIG. 8

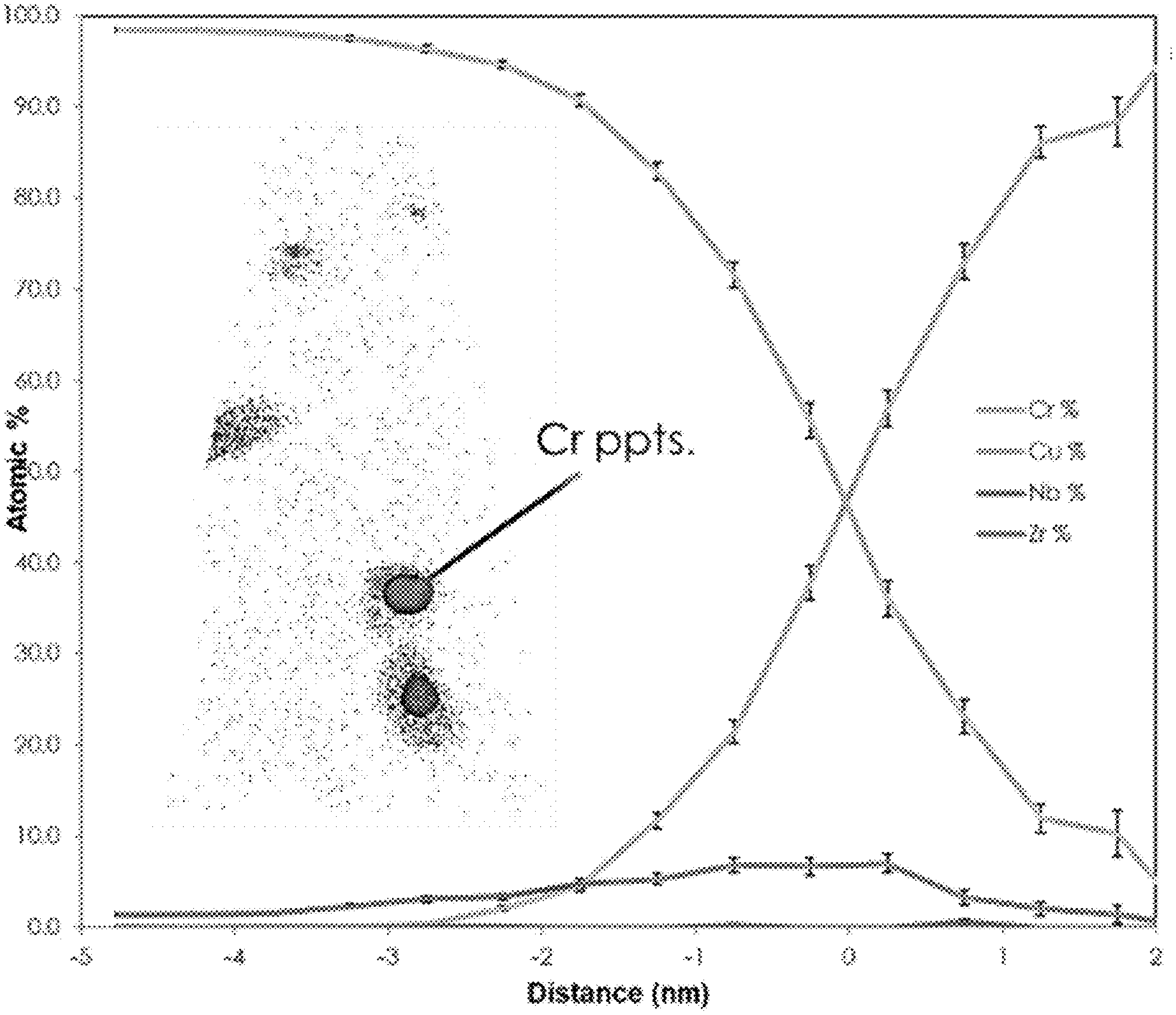
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Atomic %
-5
-4
-3
-2
-1
0
1
2
Distance (nm)
Cr ppts.
Cr %
Cu %
Nb %
Zr %

FIG. 9

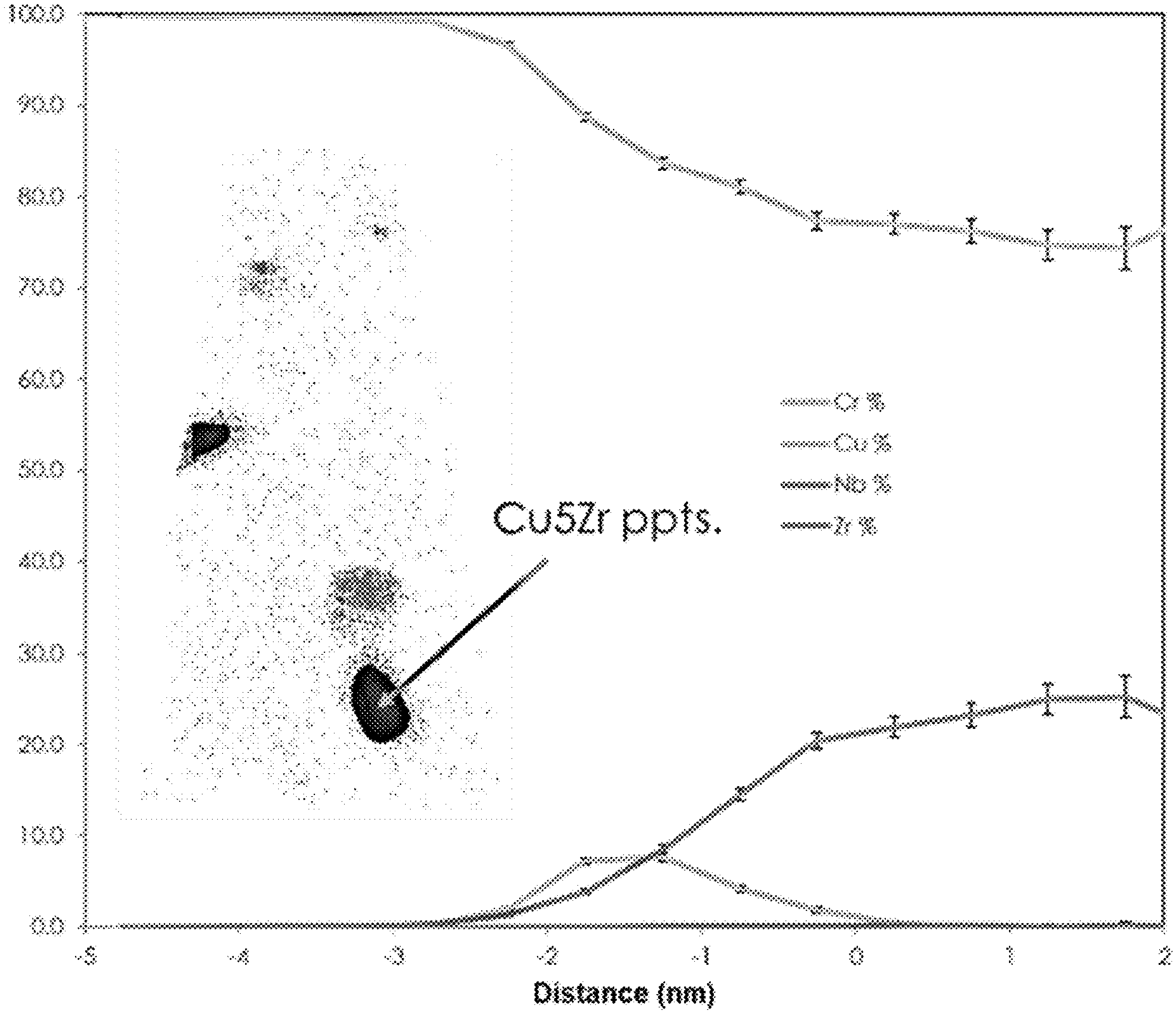
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-5
-4
-3
-2
-1
0
1
2
Distance (nm)
Cr %
Cu %
Nb %
Zr %
Cu5Zr ppts.

FIG. 10

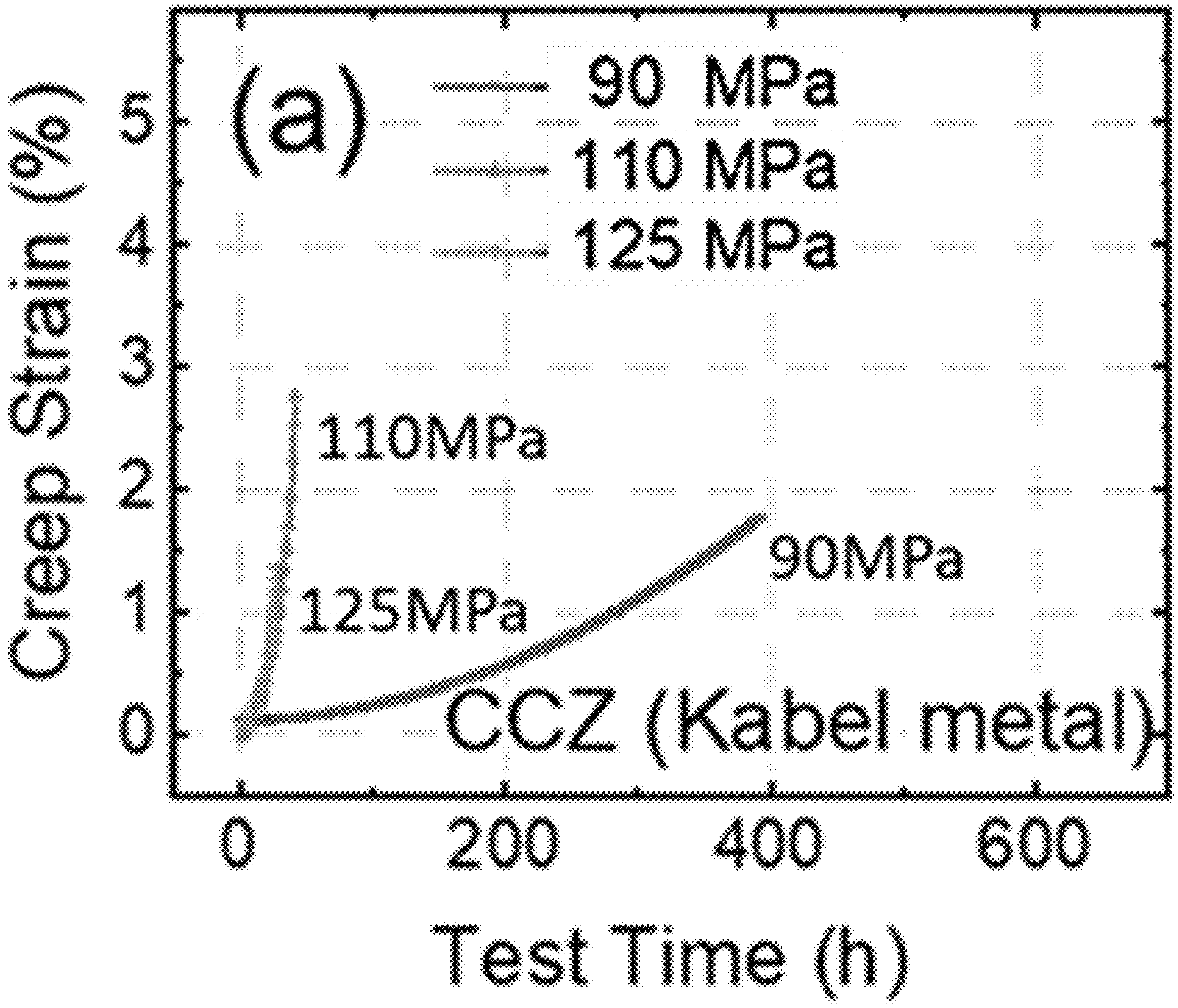
(a)
90 MPa
110 MPa
125 MPa
110MPa
125MPa
90MPa
CCZ (Kabel metal)
Creep Strain (%)
0
1
2
3
4
5
0
200
400
600
Test Time (h)

FIG. 11

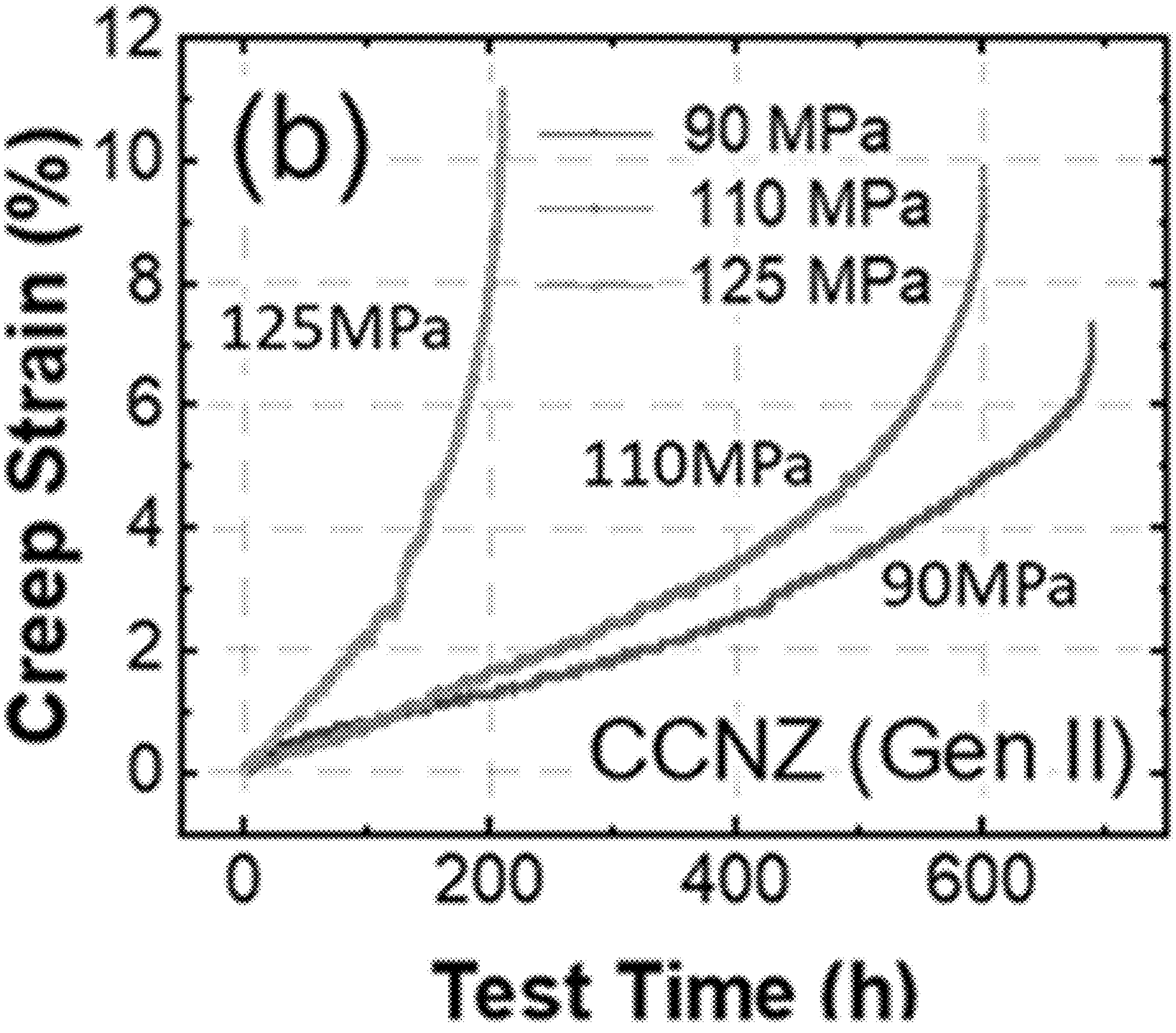
(b)
90 MPa
110 MPa
125 MPa
125MPa
110MPa
90MPa
CCNZ (Gen II)
Creep Strain (%)
0
2
4
6
8
10
12
0
200
400
600
Test Time (h)

FIG. 12

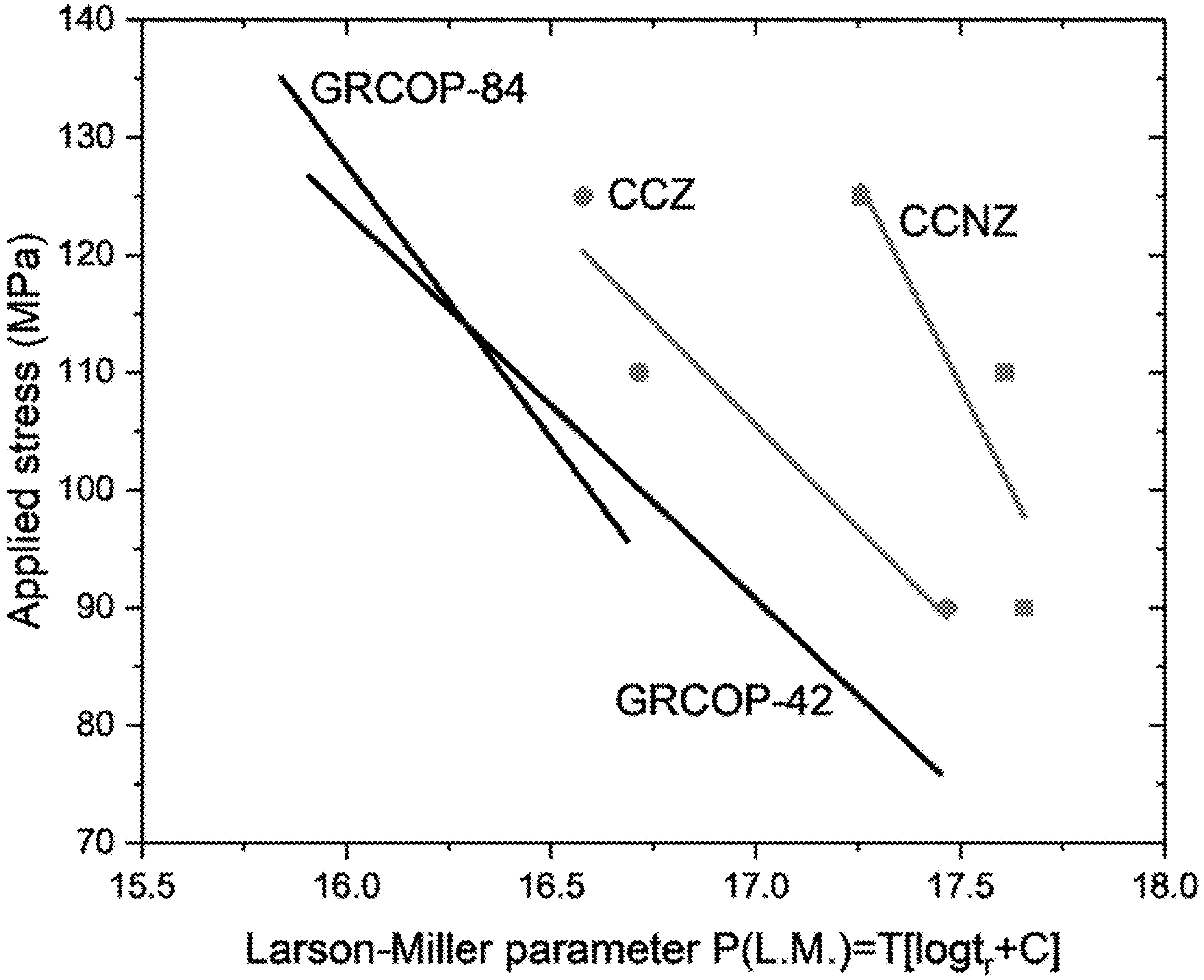
140
130
120
110
100
90
80
70
Applied stress (MPa)
15.5
16.0
16.5
17.0
17.5
18.0
Larson-Miller parameter P(L.M.)=T[logt$_r$+C]
GRCOP-84
CCZ
CCNZ
GRCOP-42

FIG. 13

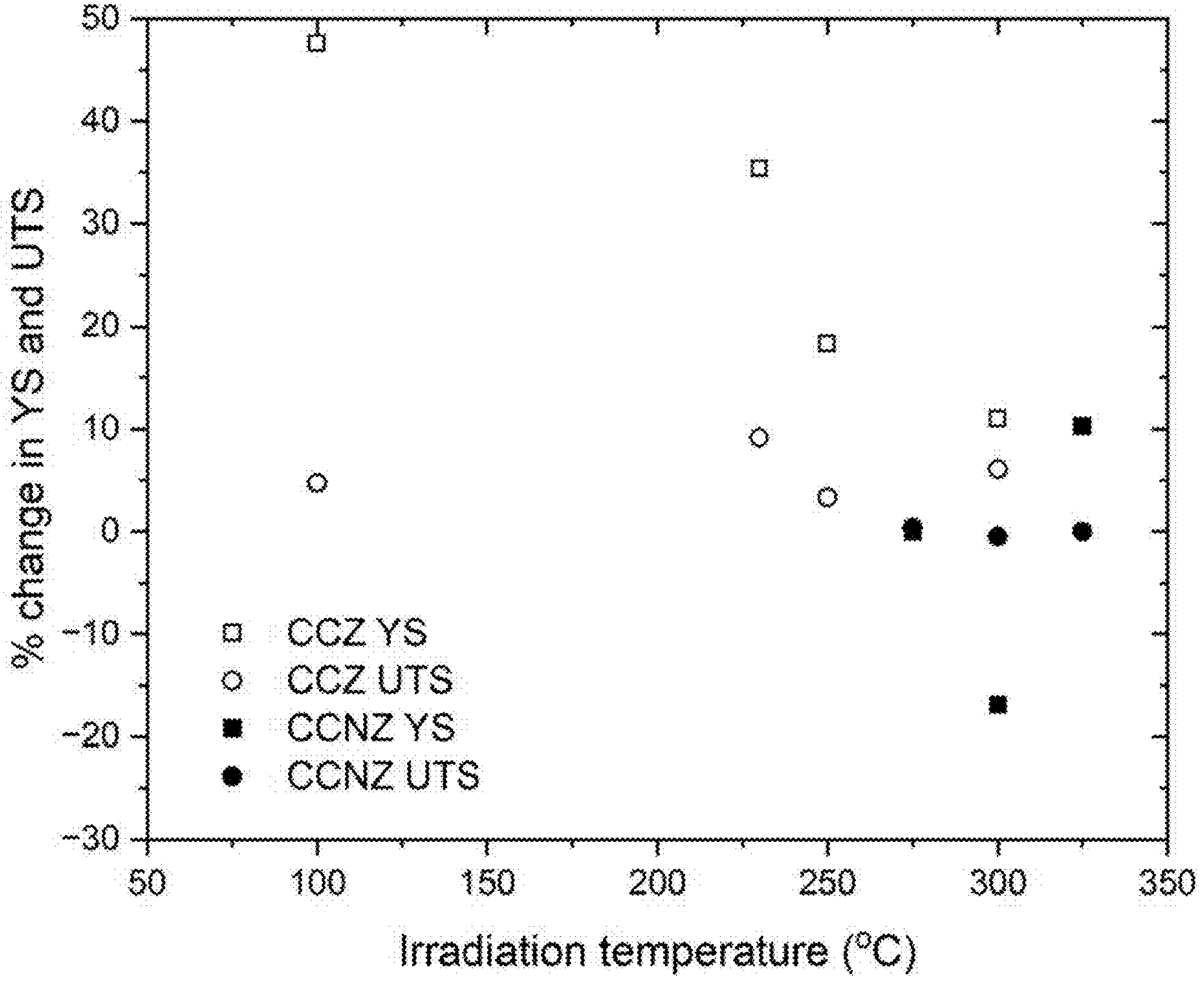
50
40
30
20
10
0
−10
−20
−30
% change in YS and UTS
50
100
150
200
250
300
350
Irradiation temperature (^{o}C)
□ CCZ YS
○ CCZ UTS
■ CCNZ YS
● CCNZ UTS

FIG. 14

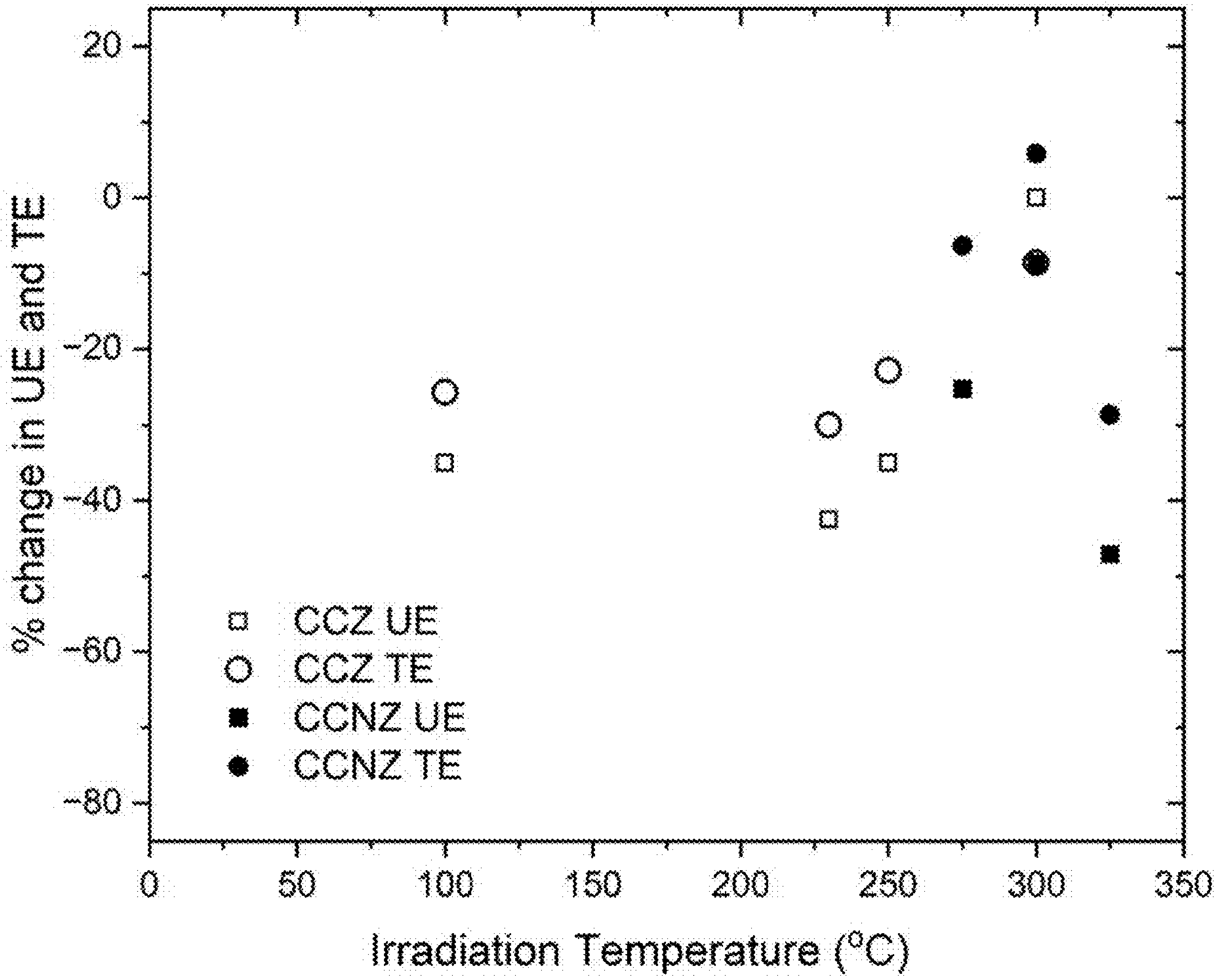
% change in UE and TE
20
0
-20
-40
-60
-80
0
50
100
150
200
250
300
350
Irradiation Temperature (°C)
□ CCZ UE
○ CCZ TE
■ CCNZ UE
● CCNZ TE

FIG. 15

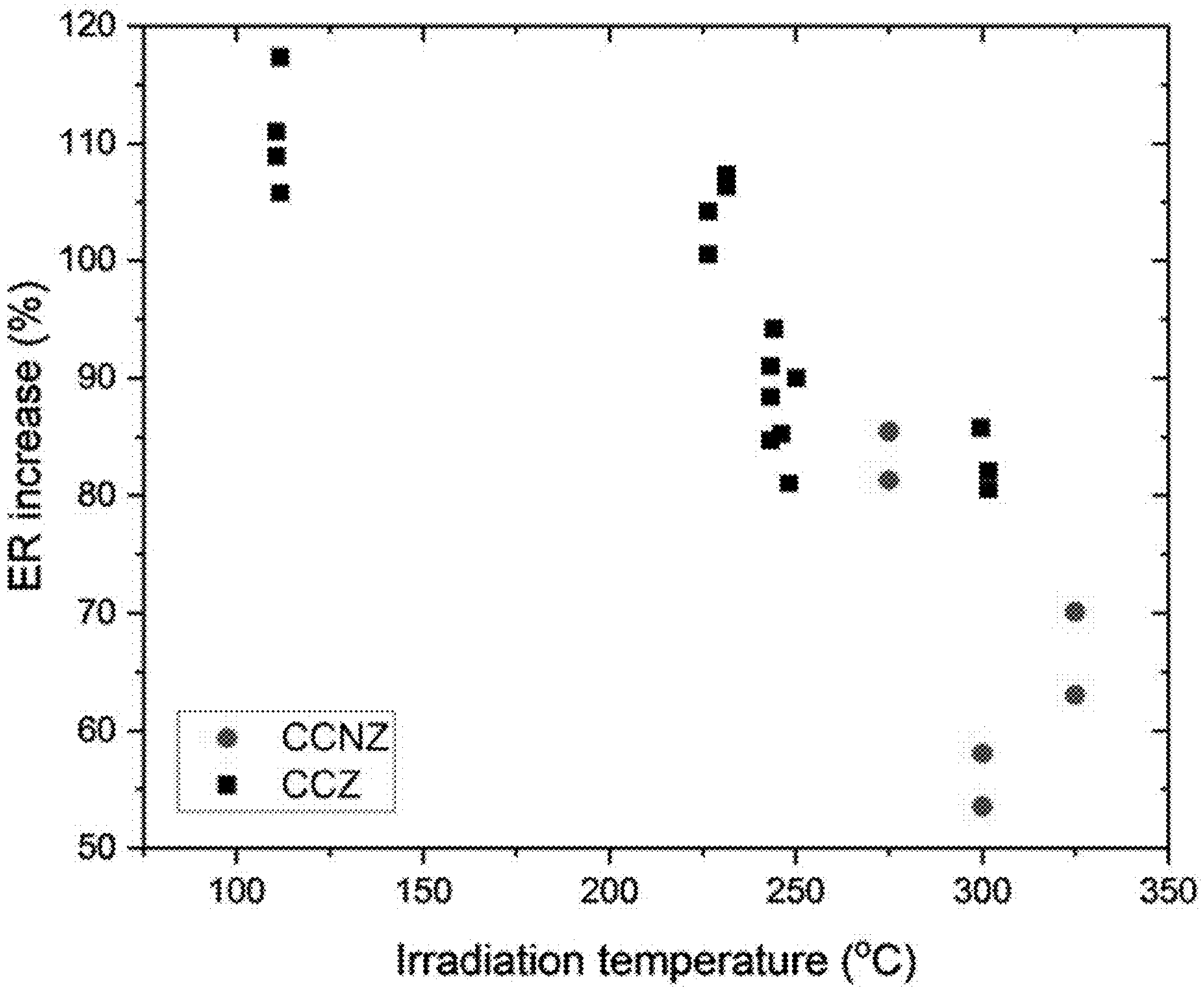
ER increase (%)
120
110
100
90
80
70
60
50
Irradiation temperature (°C)
100
150
200
250
300
350
● CCNZ
■ CCZ

FIG. 16

CREEP RESISTANT CU-BASED CUCRNBZR ALLOY WITH HIGH THERMAL CONDUCTIVITY

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. 63/398,302 filed on Aug. 16, 2022, entitled "CREEP RESISTANT Cu-BASED CuCrNbZr ALLOY WITH HIGH THERMAL CONDUCTIVITY", the entire disclosure of which incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

[0002] This invention was made with government support under Contract Nos. DE-AC05-00OR22725 and DE-SC0018332 awarded by the U.S. Department of Energy. The government has certain rights in this invention.

FIELD OF THE INVENTION

[0003] The present invention relates to copper-based alloys, and more particularly to copper based alloys with high thermal conductivity and creep resistance.

BACKGROUND OF THE INVENTION

[0004] Development of technologies such as turbines, rockets, electronics, and fusion reactor components requires efficient removal of excessive heat flux from their surfaces. One method of mitigating excessive heat flux is to use a high thermal conductivity material to rapidly transfer heat by active or passive cooling. Copper is a standard for heat transfer media due to its high thermal conductivity and good formability. However, pure copper is soft and cannot provide enough high temperature strength. High creep-strength high conductivity copper alloys are needed, and particularly to such alloys which are with excellent creep resistance at temperatures above 300-400° C.

[0005] Creep resistant Cu alloys are described in U.S. Pat. No. 3,841,921, "Process for Treating Copper Alloys to Improve Creep Resistance", which describes improving the creep resistance and stress relaxation resistance of copper base alloys having a low stacking fault energy by cold working from about 10 to 90 percent; heating from about 25 to 360° C. and cooling to room temperature. The disclosed Cu alloys have elements of Ge, Ga, Sn, In, Si, Zn, Ni, Fe, Co, Mn, and Zr. High conductivity copper-based alloys applicable to elevated temperatures are disclosed in U.S. Pat. No. 4,421,570 "Method for Manufacturing Copper Alloys", and U.S. Pat. No. 7,553,385 "Cold Gas Dynamic Spraying of High Strength Copper."

[0006] Precipitation hardenable copper alloys are disclosed in U.S. Pat. No. 4,434,016 "Precipitation Hardenable Copper Alloy and Process"; U.S. Pat. No. 3,824,135 "Copper Base Alloys"; U.S. Pat. No. 4,551,187 "Copper Alloy"; U.S. Pat. No. 5,334,346 "Copper Alloys for Electrical and Electronic Parts"; U.S. Pat. No. 2,225,339, "Precipitation Hardened Copper Alloy", and US2011/0005739, "Copper Alloy for Heat Exchanger Tube".

SUMMARY OF THE INVENTION

[0007] A Cu-based alloy comprises:

[0008] 1.0-2.0 wt % Cr;
[0009] 0.5-1.5 wt % Nb;
[0010] 0.1-0.5 wt % Zr

balance Cu. The alloy has a matrix and grain boundaries, and comprises Cr_2Nb precipitates within the grain boundaries, and comprises at least one selected from the group consisting of CuZr and Cr precipitates in the grain matrix. The CuZr precipitates can comprise at least one selected from the group consisting of Cu_5Zr and $Cu_{51}Zr_{14}$. The crystal structure of the matrix is face centered cubic.

[0011] The mole fraction, based on the total number of moles in the alloy, of the matrix Cr precipitates can be from 0.005 to 0.02. The mole fraction, based on the total number of moles in the alloy, of the matrix CuZr precipitates can be from 0.005 to 0.02.

[0012] The mole fraction of Cr_2Nb precipitates, based on the total mole composition of the alloy at 500° C., can be from 0.01 to 0.04. The mole fraction of Cr_2Nb precipitates, based on the total mole composition of the alloy at 500° C., can be from 0.02 to 0.03. The combined mole fraction of Cr and CuZr precipitates, based on the total mole composition of the alloy at 500° C., can be from 0.01 to 0.04. The combined mole fraction of Cr and CuZr precipitates, based on the total mole composition of the alloy at 500° C., can be from 0.01 to 0.02.

[0013] The alloy can be first solution annealed at from 950 to 980° C., and then aged at from 460 to 490° C. Other methods of preparation are possible.

[0014] The alloy can consist essentially of Cr, Nb, Zr and Cu. The alloy can consist of Cr, Nb, Zr and Cu. The can in some instances comprises some level of impurities. The amounts of the impurities should be limited, for example, the impurities can be limited to:

[0015] $O<0.025$ wt %;
[0016] $N<0.01$ wt %;
[0017] $C<0.01$ wt %;
[0018] $Sn<0.12$ wt %; and,
[0019] $Fe<0.1$ wt %.

[0020] The Cr_2Nb grain boundary precipitates can be from 2 to 20 μm in diameter. The Cr matrix precipitates can be from 1 to 10 nm in diameter. The CuZr matrix precipitates can be from 10 to 50 nm in diameter.

[0021] The mole fraction, based on the total number of moles in the alloy, for the Cr_2Nb precipitates can be from 0.01 to 0.04. The mole fraction for the Cr precipitates can be from 0.01 to 0.02. The mole fraction of the CuZr precipitates can be from 0.01 to 0.03.

[0022] The mole ratio of Cr to Nb can be from 2.5 to 4.0. The mole ratio of Zr to Nb can be from 0.2 to 1.

[0023] The creep performance of the alloy as measured by the Larsen-Miller (L-M) parameters can be, for an operational stress level of from 90 to 125 Mpa, an L-M parameter of from 17 to 18. The alloy can have an electrical resistivity of from 2.0043×10^{-8} to 2.157×10^{-8} $\Omega\cdot m$. The alloy can have a thermal conductivity as measured against pure copper according to International Annealed Copper Standard (IACS) at 20° C. of from 70 to 90% IACs. The alloy can have a thermal conductivity of from 4.06×10^{7} to 5.22×10^{7} S/m.

[0024] The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in yield strength of from −20 to 10%. The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in ultimate tensile strength of from −20 to 10%. The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in uniform elongation of from −50 and 10%. The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in total elongation of from −50 and 10%. The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is an increase in electrical resistivity of from 50 and 90%.

[0025] A method of making a Cu-based alloy includes the steps of providing starting materials comprising from 1.0 to 2.0 wt % Cr, from 0.5 to 1.5 wt % Nb, from 0.1 to 0.5 wt % Zr, and balance Cu, and melt-casting the starting materials into as-cast ingots. The as-cast ingots as cold rolled to a cold rolled plate with a thickness reduction of from 60 to 80% of the thickness of the plate before cold rolling. The cold-rolled plate is solution annealed at from 950 to 980° C. for from 15 to 30 minutes to form a solution annealed alloy with grain boundaries and Cr_2Nb precipitates having a diameter of from 2 to 20 μm, wherein the Cr_2Nb precipitates are within the grain boundaries. A water quench is performed on the solution annealed alloy at a temperature of 20 to 25° C. to form a quenched alloy. The quenched alloy is aged at a temperature of from 460 to 490° C. for from 150 to 210 minutes to form a CuCrNbZr alloy comprising at least one selected from the group consisting of matrix Cr and matrix CuZr precipitates. The Cr matrix precipitates can be from 1 to 10 nm in diameter, and the CuZr matrix precipitates can be from 10 to 50 nm in diameter. The alloy can comprise both Cr and CuZr matrix precipitates.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] There are shown in the drawings embodiments that are presently preferred it being understood that the invention is not limited to the arrangements and instrumentalities shown, wherein:

[0027] FIG. **1** is a schematic diagram of the microstructure in an alloy according to the invention

[0028] FIG. **2** is a correlation plot of phase fractions for Cr_2Nb, Cr and Cu_5Zr, and bulk compositions of Cr, Nb and Zr.

[0029] FIG. **3** is a plot of mole fraction of phases for a CuCrNbZr alloy versus temperature (° C.).

[0030] FIG. **4** is a plot of mole fraction of phase for a CuCrNbZr alloy versus temperature (° C.) with an enlarged scale for the Y axis.

[0031] FIG. **5** is a plot of Cr_2Nb composition (mole fraction) versus temperature (° C.).

[0032] FIG. **6** is a plot of Cu matrix composition (mole fraction) versus temperature (° C.).

[0033] FIG. **7** is an image showing the distribution of μm-scale precipitates at the grain boundary.

[0034] FIG. **8** is an image showing the distribution on nm-scale precipitates in HAADF, Cr composition, DF2+Cr, and Cr+Zr composition modes, respectively.

[0035] FIG. **9** is a plot of atomic % versus distance (nm) across the Cr precipitate/Cu matrix interface.

[0036] FIG. **10** is a plot of atomic % versus distance (nm) for across the Cu_5Zr precipitate/Cu matrix interface.

[0037] FIG. **11** is a plot of creep strain (%) versus test time (hr) for a CuCrZr (CCZ) alloy.

[0038] FIG. **12** is a plot of creep strain (%) versus test time (hr) for a CuCrNbZr (CCNZ) alloy.

[0039] FIG. **13** is a plot of applied stress (MPa) versus Larson-Miller Parameter (L.M.)=T[log t_r+C].

[0040] FIG. **14** is a plot of neutron irradiation-induced % change in room-temperature yield strength (YS) and ultimate tensile strength (UTS) versus irradiation temperature (° C.).

[0041] FIG. **15** is a plot of neutron irradiation-induced % change in room-temperature tensile uniform elongation (UE) and total elongation (TE) versus irradiation temperature (° C.).

[0042] FIG. **16** is a plot of neutron irradiation-induced increase (%) electrical resistivity (ER) versus irradiation temperature (° C.).

DETAILED DESCRIPTION OF THE INVENTION

[0043] A Cu-based alloy according to the present invention comprises 1.0-2.0 wt % Cr, 0.5-1.5 wt % Nb, 0.1-0.5 wt % Zr, and balance Cu. The alloy has a matrix and grain boundaries, and has Cr_2Nb precipitates within the grain boundaries and at least one selected from the group consisting of CuZr and Cr precipitates in the grain matrix. The CuZr precipitates can be at least one selected from the group consisting of Cu_5Zr and $Cu_{51}Zr_{14}$ precipitates. The alloy can have a crystal structure of the matrix that is face centered cubic.

[0044] The mole fraction of Cr_2Nb based on the total mole composition of the alloy at 500° C. can be from 0.01 to 0.04. The mole fraction of Cr_2Nb based on the total mole composition of the alloy at 500° C. can be 0.01, 0.011, 0.012, 0.013, 0.014, 0.015, 0.016, 0.017, 0.018, 0.019, 0.02, 0.021, 0.022, 0.023, 0.024, 0.025, 0.026, 0.027, 0.028, 0.029, 0.03, 0.031, 0.032, 0.033, 0.034, 0.035, 0.036, 0.037, 0.038, 0.039, or 0.04, and can be within a range of any high value and low value selected from these values.

[0045] The mole fraction, based on the total number of moles in the alloy, of the matrix Cr precipitates can be from 0.005 to 0.02. The mole fraction, based on the total number of moles in the alloy, of the matrix Cr precipitates can be 0.005, 0.006, 0.007, 0.008, 0.009, 0.01, 0.011, 0.012, 0.013, 0.014, 0.015, 0.016, 0.017, 0.018, 0.019, or 0.02, and can be within a range of any high value and low value selected from these values.

[0046] The mole fraction, based on the total number of moles in the alloy, of the matrix CuZr precipitates can be from 0.005 to 0.02. The mole fraction, based on the total number of moles in the alloy, of the matrix Cr precipitates can be 0.005, 0.006, 0.007, 0.008, 0.009, 0.01, 0.011, 0.012, 0.013, 0.014, 0.015, 0.016, 0.017, 0.018, 0.019, or 0.02, and can be within a range of any high value and low value selected from these values.

[0047] The combined mole fraction of Cr and CuZr precipitates based on the total mole composition of the alloy at 500° C. can be from 0.01 to 0.04. The combined mole fraction of Cr and CuZr precipitates based on the total mole composition of the alloy at 500° C. can be 0.01, 0.011, 0.012, 0.013, 0.014, 0.015, 0.016, 0.017, 0.018, 0.019, 0.02, 0.021, 0.022, 0.023, 0.024, 0.025, 0.026, 0.027, 0.028, 0.029, 0.03, 0.031, 0.032, 0.033, 0.034, 0.035, 0.036, 0.037, 0.038, 0.039, or 0.04, and can be within a range of any high value and low value selected from these values.

[0048] The mole ratio of Cr to Nb can be from 2.5 to 4.0. The mole ration of Cr to Nb can be 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, or 4.0, and can be within a range of any high value and low value selected from these values.

[0049] The mole ratio of Zr to Nb can be from 0.2 to 1. The mole ratio of Zr to Nb can be 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, or 1.0, and can be within a range of any high value and low value selected from these values.

[0050] The alloy can consist essentially of Cr, Nb, Zr and Cu. The alloy can consist of Cr, Nb, Zr and Cu. Limited impurities can be tolerated. Examples of such impurities, and preferred limitations to the amounts of these impurities, include: O<0.025 wt %; N<0.01 wt %; C<0.01 wt %; Sn<0.12 wt %; and, Fe<0.1 wt %.

[0051] The Cr_2Nb grain boundary precipitates can be from 2 to 20 μm in diameter. The Cr_2Nb grain boundary precipitates can have a diameter of 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 μm, and can have a diameter withing a range of any high value and low value selected from these values.

[0052] The Cr matrix precipitates can be from 1 to 10 nm in diameter. The Cr matrix precipitates can have a diameter of 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 nm, and can have a diameter within a range of any high value and low value selected from these values.

[0053] The CuZr matrix precipitates can be from 10 to 50 nm in diameter. The CuZr matrix precipitates can have a diameter of 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49 or 50 nm, and can have a diameter within a range of any high value and low value selected from these values.

[0054] The alloy of the invention exhibits very good creep performance. The creep performance as measured by the Larsen-Miller (L-M) parameters can be, for an operational stress level of from 90 to 125 Mpa and operation temperature from 450 C to 550 C, an L-M parameter of from 17 to 18.

[0055] The alloy of the invention exhibits very good electrical conductivity and electrical resistivity characteristics. The alloy can have an electrical resistivity of from 2.0043×10^{-8} to 2.157×10^{-8} Ω·m.

[0056] The alloy can have a thermal conductivity as measured against pure copper according to International Annealed Copper Standard (IACS) at 20° C. of from 70 to 90% IACs. The thermal conductivity of the alloy as measured against pure copper according to International Annealed Copper Standard (IACS) at 20° C. can be 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, or 90% IACs, and can be within a range of any high value and low value selected from these values. The alloy can have a thermal conductivity of from 4.06×10^{7} to 5.22×10^{7} S/m.

[0057] The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in yield strength of from −20 to 10%. The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation, there is a change in yield strength of −20, −19, −18, −17, −16, −15, −14, −13, −12, −11, −10, −9, −8, −7, −6, −5, −4, −3, −2, −1, 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10%, and can be within a range of any high value and low value selected from these values.

[0058] The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in ultimate tensile strength of from −20 to 10%. The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in ultimate tensile strength of −20, −19, −18, −17, −16, −15, −14, −13, −12, −11, −10, −9, −8, −7, −6, −5, −4, −3, −2, −1, 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10%, and can be within a range of any high value and low value selected from these values.

[0059] The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in uniform elongation of from −50 and 10%. The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in uniform elongation of −50, −49, −48, −47, −46, −45, −44, −43, −42, −41, −40, −39, −38, −37, −36, −35, −34, −33, −32, −31, −30, −29, −28, −27, −26, −25, −24, −23, −22, −21, −20, −19, −18, −17, −16, −15, −14, −13, −12, −11, −10, −9, −8, −7, −6, −5, −4, −3, −2, −1, 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10%, and can be within a range of any high value and low value selected from these values.

[0060] The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in total elongation of from −50 and 10%. The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in total elongation of −50, −49, −48, −47, −46, −45, −44, −43, −42, −41, −40, −39, −38, −37, −36, −35, −34, −33, −32, −31, −30, −29, −28, −27, −26, −25, −24, −23, −22, −21, −20, −19, −18, −17, −16, −15, −14, −13, −12, −11, −10, −9, −8, −7, −6, −5, −4, −3, −2, −1, 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10%, and can be within a range of any high value and low value selected from these values.

[0061] The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is an increase in electrical resistivity of from 50 and 90%. The alloy can have a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is an increase in electrical resistivity of 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, or 90%, and can be within a range of any high value and low value selected from these values.

[0062] The method of making the CuCrNbZr alloy of the invention can vary. The Cu-based alloy can be first solution annealed and then aged. The alloy can be solution annealed at from 950 to 980° C., and then aged at from 460 to 490° C. The method can include the step of providing starting materials comprising from 1.0 to 2.0 wt % Cr, from 0.5 to 1.5 wt % Nb, from 0.1 to 0.5 wt % Zr, and balance Cu. The starting materials are melt-cast into ingots. The as-cast ingots are cold rolled into a cold rolled plate with a thickness reduction of from 60 to 80% of the thickness of the plate before cold rolling. The cold rolled plate is then solution annealed at from 950 to 980° C. for from 15 to 30 minutes to form a solution annealed alloy with grain boundaries and Cr_2Nb precipitates having a diameter of from 2 to 20 μm, wherein the Cr_2Nb precipitates are within the grain boundary regions. A water quench is performed on the solution annealed alloy at a temperature of 20 to 25° C. to form a quenched alloy. The quenched alloy is aged at a temperature of from 460 to 490° C. for from 150 to 210 minutes to form a CuCrNbZr alloy comprising at least one selected from the group consisting of matrix Cr and matrix CuZr precipitates. The Cr matrix precipitates can be from 1 to 10 nm in diameter, and the CuZr matrix precipitates can be from 10 to 50 nm in diameter. Variations of this method and other methods of making this CuCrNbZr alloy are possible.

[0063] The alloy design concept is schematically shown in FIG. **1**. The alloy exhibits an improved creep property without degrading the electric conductivity of Cu alloy. There is schematically shown in FIG. **1** an alloy **10** with a matrix **14** and grain boundary regions **18**. Cr_2Nb precipitates **22** are intersected by the grain boundary regions **18**. Matrix precipitates including Cr precipitates **26** and CuZr precipitates **28** can be present alone or in tandem. The presence of the Cr_2Nb precipitates at and within the grain boundary regions **18** resists sliding at the grain boundaries, and improves the creep resistance of the alloy. The presence of the Cr matrix precipitates **26** and the CuZr matrix precipitates **28** can resist the movement of dislocation and mitigate dislocation creep.

[0064] The detailed compositions (wt %) of the CuCrNbZr alloys were designed with the aid of computational thermodynamics. Screening the phase equilibrium in the Cu—Cr—Nb—Zr is performed with the assistance of high-throughput calculation (HTC) using Pandat software. Based on the results, the following criteria were utilized for the alloy design—a mole fraction of Cr_2Nb in between 0.01 and 0.04, and a combined mole fraction of other precipitates ($Cr+Cu_5Zr$) in one embodiment is between 0.01 and 0.05, at the target maximum operation temperature 500 C. The representative calculated phase fractions and their associated bulk compositions presented in these alloys are shown as a parallel plot in FIG. **2**. The mole fraction of Cr_2Nb in one embodiment is from 0.02 to 0.03. The combined mole fraction of other precipitates ($Cr+Cu_5Zr$) in one embodiment is from 0.01 to 0.04.

[0065] The calculation results on the equilibrium mole fraction of phase vs. temperature in a representative alloy are shown in FIGS. **3** and **4**. Three types of precipitates are present in this CuCrNbZr alloy: Laves Cr_2Nb, Cr and CuZr precipitates. FIG. **4** has an enlarged scale to show the mole fractions of the precipitates. The formation of these precipitates not only improves creep strength but also retains high thermal conductivity by depleting the solute atoms in Cu matrix. FIGS. **3** and **4** show that when solution annealed at 970° C., a ~1.7% Cr_2Nb Laves phase and 0.2% Cr phase is formed, and when annealed at 475° C., the amount of Cr_2Nb Laves remains about the same, but the mole fraction of Cr and Cu_5Zr precipitates will significantly increase from 0.2% to 0.7% for Cr and from 0 to 1% for Cu_5Zr. The composition of Cr and Cu_5Zr remains as constant values of 100% Cr and Cu-16.7 mol % Zr, respectively, as a function of temperatures. FIGS. **5** and **6** show the phase compositions of Laves Cr2Nb precipitate and the Fcc Cu matrix. The composition of Cr_2Nb is also relative constant and a significant amount of Zr was dissolved in this phase, as shown in FIG. **5**. The composition of the fcc_Cu matrix phase shown in FIG. **6** suggests that the content of Cr, Nb and Zr are all significantly reduced with decreasing temperature. These solutes deplete them from the matrix by forming Cr, Cr_2Nb and CuZr precipitates as shown in FIG. **4**. The formation of precipitate increases the strength of the alloy through particle strengthening mechanism, and also enhances the electric conductivity through purifying the matrix.

[0066] A Cu-1.65 Cr-0.48 Nb-0.24 Zr, at % or (Cu-1.35 Cr-0.7 Nb-0.35 Zr, wt %) ingot within the designed chemistry range was synthesized through a conventional ingot making method, in this example melted in an argon protected arc-melting furnace followed by drop-casting into the shape of $1.25\times1.25\times7.5$ cm^3 bar, with an approximate mass of 100 g. The as-cast bar was then subjected to multiple-pass cold rolling at room temperature for a total 70% reduction in thickness. The as-rolled materials were then solution annealed at 970° C. for 20 min, followed by water quench, and then aged at 475° C. for 3 h followed by air cooling.

[0067] Metallographic samples for microscopy were prepared by conventional mechanical grinding up to #4000 grit SiC paper and final polishing using a Buehler's VibroMet polisher with a 50% colloidal silica and 50% distilled water suspension. Scanning Electron Microscope (SEM)-X-ray energy dispersive spectroscopy (EDS) was performed in a Zeiss EVO SEM at 20 kV using an Oxford software to analyze the chemical composition of coarse precipitates in the matrix and at the grain boundaries. The transmission electron microscopy (TEM) samples were prepared via focused ion beam (FIB) lift-out techniques with Ga +ions at 30 kV and a finishing energy of 5 kV using a Zeiss Crossbeam Auriga FIB-SEM system. Conventional TEM examination was performed in a JEOL 2100F TEM/STEM instrument operated at 200 kV to characterize the precipitate microstructures. TEM-EDS mapping was performed in a FEI Titan 80-300 probe aberration corrected microscope which is equipped with a X-FEG field emission electron source and four Bruker SuperX energy dispersive spectrum detectors. Such configuration, also known as the ChemiSTEM method, facilitates the collection of characteristic X-ray signals at high counts per second and, furthermore, enables qualitative mapping of the elemental distribution. The microstructure of resulted CCNZ alloy is shown in FIGS. **7** and **8**. FIG. **7** shows the micron scale Cr_2Nb and Cr ppts, which are primarily formed during homogenization at 970 C with a small fraction of Cr_2Nb directly solidified from liquid. FIG. **8** shows the matrix Cr and the Cu_5Zr ppts which are imaged under the HADDF, Cr Composition, DF2+Cr and (Cr+Zr) composition modes, respectively.

[0068] A FEI Nova 200 dual-beam focused-ion beam (FIB) instrument was used to perform site-specific lift-outs of regions of interest (ROIs) followed by annular milling to fabricate the needle-shaped APT specimens. A wedge lift-out geometry was used to mount multiple samples on a Si microtip coupon to enable the fabrication of multiple APT needles from one wedge lift-out. A final 2 kV polishing step minimized Ga implantation damage and sharpened the APT needle within the specific ROI. The APT data were acquired using a local electrode atom probe (CAMECA Instruments LEAP 4000× HR) equipped with an energy compensated reflection lens and a 36% detection efficiency. The APT experiments were conducted at a specimen base temperature of 30 K by applying 60-85 pJ, 355 nm wavelength, 10 ps laser pulses at a repetition rate of 100 kHz, and a detection rate of 0.5-1.0%. The laser energy was chosen to keep an Fe++/Fe+ m/q peak ratio of approximately 10. Data reconstruction and analyses were performed using CAMECA IVAS 3.8 software.

[0069] FIGS. **9** and **10** show composition profiles measured from APT for the Cr/matrix and Cu_5Zr/matrix interfaces. The APT results show the composition profiles across the Cr/matrix interface (FIG. **9**) and the Cu_5Zr/matrix interface (FIG. **10**), showing the solute levels in matrix in both cases are very low, which is consistent with the calculation result. The CuCrNbZr alloys have excellent thermal conductivity despite increased alloying addition in the bulk alloys, because most of the alloying atoms were precipitated out from the matrix and did not increase the electron scattering in the matrix.

[0070] The CuCrNbZr alloy at 500° C. has outstanding extended creep rupture time under 90-125 MPa, compared to the CuCrZr alloy (kabelmetal GmbH, Windeck DE). The creep test results for a CCZ alloy (FIG. **11**) are compared with the creep test results of the CuCrNbZr alloy of the invention (FIG. **12**). The commercial CCZ alloys have no grain boundary precipitates, but only matrix Cr precipitates and uniform grain size, and show the shortest creep life. The CuCrNbZr alloy, with uniformly distributed Cr_2Nb grain boundary precipitates and matrix Cr and Cu_5Zr precipitates and uniform grain size, and show prolonged creep life in all testing conditions. Specifically, the creep rupture life at high stress level at 110 and 125 MPa has been almost increased by one order of magnitude.

[0071] The Larson-Miller parameter is a means of predicting the lifetime of material vs. time and temperature using a correlative approach based on the Arrhenius rate equation. Creep stress rupture data for high-temperature creep-resistant alloys are often plotted as log stress to rupture versus a combination of log time to rupture and temperature. One of the most common time-temperature parameters used to present this kind of data is the Larson-Miller (L.M.) parameter, which in generalized form is usually expressed as LMP=T(C+log t), where C is a material specific constant, often approximated as 20, t is the stress-rupture time in hours, and T is the temperature in kelvins. According to the L.M. parameter, at a given stress level the log time to stress rupture plus a constant of the order of 20 multiplied by the temperature in kelvins or degrees Rankine remains constant for a given material. The LMP values for CCNZ, CCZ and GRCOP-42 alloys (Cu—Cr—Nb based alloys) are plotted in FIG. **13**. It shows that CuCrNbZr alloy performs better than both CCZ alloy and GRCOP alloys.

[0072] Four-wire electrical resistivity measurement was performed on two SS3 tensile specimens (overall length of 16 mm and nominal gage dimensions of 7.62×1.52×0.76 mm^3, with the gauge length parallel to the rolling direction) of as received CCNZ_HZ alloys near room temperature with a Keithley Model 182 Sensitive Digital Voltmeter. Current was applied to the outer electrodes in 10 mA increments from 10 to 100 mA with a Model 237 High Voltage Source Measure Unit. Individual specimen thickness and width in the tensile gage region were measured using a Mitutoyo digital micrometer to an accuracy of +1 micrometers, and the room temperature was recorded at the beginning and end of the measurement period with a thermometer. Controlled electrical resistivity measurements were performed on similar tensile specimens machined from a pure, annealed copper plate (1.72×10-8 ohm·m resistivity, 102% International Annealed Copper Standard, IACS at 20° C.) to confirm the absolute value of the measurement equipment. The resistivity values at environment temperature were determined from the average of at least 3 electrical measurements for each alloy, then corrected to a standard reference temperature of 20° C. using the Cu matrix electrical resistivity temperature coefficient of 6.7×10-11 ohm·m/K.

$$\frac{V}{I} = R = \rho\frac{L}{S}$$

$$\rho = \frac{RS}{IL} = \frac{VS}{IL}$$

Sample 1:

$$\begin{aligned}\rho &= \frac{0.0115482\ \text{mV} \times 0.707\ \text{mm} \times 1.487\ \text{mm}}{100\,\text{mA} \times 5.61\ \text{mm}}\\ &= 2.164 \times 10^{-8}\,\Omega \cdot m(22^\circ\text{ C.})\\ &= 2.157 \times 10^{-8}\,\Omega \cdot m(20^\circ\text{ C.}) = 81.3\%\ IACS\end{aligned}$$

Sample 2:

$$\begin{aligned}\rho &= \frac{0.0110696\ \text{mV} \times 0.69\ \text{mm} \times 1.477\ \text{mm}}{100\ \text{mA} \times 5.61\ \text{mm}}\\ &= 2.011 \times 10^{-8}\,\Omega \cdot m(22^\circ\text{ C.})\\ &= 2.0043 \times 10^{-8}\,\Omega \cdot m(20^\circ\text{ C.}) = 87.53\%\ IACS\end{aligned}$$

[0073] A total of 6 CCNZ samples were irradiated at the Oak Ridge National Laboratory (ORNL) High Flux Isotope Reactor (HIFR) at temperatures of 275, 300 and 325° C. for a dose of 5 dpa. The room-temperature mechanical property (tensile test) and electrical resistivity were measured on samples before and after neutron irradiation. The changes in tensile strength, elongation and electrical resistivity are plotted in FIGS. **14**, **15** and **16**, respectively. FIG. **14** shows the change in room-temperature yield strength (YS) and ultimate tensile strength (UTS) of CCNZ before and after irradiation at 275, 300 and 325° C. for 5 dpa, respectively, compared to those of CCZ alloys. FIG. **15** shows the change in room-temperature tensile uniform elongation (UE) and total elongation (TE) of CCNZ before and after irradiation at 275, 300 and 325° C., respectively, compared to those of CCZ alloys. FIG. **16** shows the change in room-temperature electrical resistivity of CCNZ before and after irradiation at 275, 300 and 325° C., respectively, compared to those of CCZ alloys.

[0074] The invention as shown in the drawings and described in detail herein disclose arrangements of elements of particular construction and configuration for illustrating preferred embodiments of structure and method of operation of the present invention. It is to be understood however, that elements of different construction and configuration and other arrangements thereof, other than those illustrated and described may be employed in accordance with the spirit of the invention, and such changes, alternations and modifications as would occur to those skilled in the art are considered to be within the scope of this invention as broadly defined in the appended claims. In addition, it is to be understood that the phraseology and terminology employed herein are for the purpose of description and should not be regarded as limiting.

We claim:

1. A Cu-based alloy, comprising:

1.0-2.0 wt % Cr

0.5-1.5 wt % Nb

0.1-0.5 wt % Zr

balance Cu, the alloy having a matrix and grain boundaries, and comprising Cr_2Nb precipitates within the grain boundaries and at least one selected from the group consisting of CuZr and Cr precipitates in the grain matrix.

2. The alloy of claim **1**, wherein the mole fraction, based on the total number of moles in the alloy, of the matrix Cr precipitates is from 0.005 to 0.02.

3. The alloy of claim **1**, wherein the mole fraction, based on the total number of moles in the alloy, of the matrix CuZr precipitates is from 0.005 to 0.02.

4. The alloy of claim **1**, wherein the CuZr precipitates comprise at least one selected from the group consisting of Cu_5Zr and $Cu_{51}Zr_{14}$.

5. The alloy of claim **1**, wherein the mole fraction of Cr_2Nb based on the total mole composition of the alloy at 500° C. is from 0.01 to 0.04.

6. The alloy of claim **1**, wherein the mole fraction of Cr_2Nb based on the total mole composition of the alloy at 500° C. is from 0.02 to 0.03.

7. The alloy of claim **1**, wherein the combined mole fraction of Cr and CuZr precipitates based on the total mole composition of the alloy at 500° C. is from 0.01 to 0.04.

8. The alloy of claim **1**, wherein the combined mole fraction of Cr and CuZr precipitates based on the total mole composition of the alloy at 500° C. is from 0.01 to 0.02.

9. The Cu-based alloy of claim **1**, wherein the alloy is first solution annealed at from 950 to 980° C., and then aged at from 460 to 490° C.

10. The alloy of claim **1**, wherein the alloy consists essentially of Cr, Nb, Zr and Cu.

11. The alloy of claim **1**, wherein the alloy consists of Cr, Nb, Zr and Cu.

12. The alloy of claim **1**, wherein the alloy comprises impurities, and the impurities are limited to:

$O<0.025$ wt %;

$N<0.01$ wt %;

$C<0.01$ wt %;

$Sn<0.12$ wt %; and,

$Fe<0.1$ wt %.

13. The alloy of claim **1**, wherein the Cr_2Nb grain boundary precipitates are from 2 to 20 μm in diameter, the Cr matrix precipitates are from 1 to 10 nm in diameter, and the CuZr matrix precipitates are from 10 to 50 nm in diameter.

14. The alloy of claim **1**, wherein the mole fraction, based on the total number of moles in the alloy, for the Cr_2Nb precipitates is from 0.01 to 0.04, the mole fraction for the Cr precipitates is from 0.01 to 0.02, and the mole fraction of the CuZr precipitates is from 0.01 to 0.03.

15. The alloy of claim **1**, wherein a mole ratio of Cr to Nb is from 2.5 to 4.0.

16. The alloy of claim **1**, wherein a mole ratio of Zr to Nb is from 0.2 to 1.

17. The alloy of claim **1**, wherein the creep performance as measured by the Larsen-Miller (L-M) parameters is, for an operational stress level of from 90 to 125 Mpa, an L-M parameter of from 17 to 18.

18. The alloy of claim **1**, wherein the alloy has an electrical resistivity of from 2.0043×10^{-8} to 2.157×10^{-8} $\Omega\cdot m$.

19. The alloy of claim **1**, wherein the alloy has a thermal conductivity as measured against pure copper according to International Annealed Copper Standard (IACS) at 20° C. of from 70 to 90% IACs.

20. The alloy of claim **1**, wherein the alloy has a thermal conductivity of from 4.06×10^{7} to 5.22×10^{7} S/m.

21. The alloy of claim **1**, wherein the alloy has a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in yield strength of from −20 to 10%.

22. The alloy of claim **1**, wherein the alloy has a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in ultimate tensile strength of from −20 to 10%.

23. The alloy of claim **1**, wherein the alloy has a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in uniform elongation of from −50 and 10%.

24. The alloy of claim **1** wherein the alloy has a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is a change in total elongation of from −50 and 10%.

25. The alloy of claim **1**, wherein the alloy has a neutron irradiation resistance such that, when subjected to neutron irradiation at temperature range of from 275 to 325° C. with an irradiation dose of 5 dpa, and compared to the alloy without irradiation there is an increase in electrical resistivity of from 50 and 90%.

26. The alloy of claim **1**, wherein the crystal structure of the matrix is face centered cubic.

27. A method of making a Cu-based alloy, comprising the steps of:

providing starting materials comprising from 1.0 to 2.0 wt % Cr, from 0.5 to 1.5 wt % Nb, from 0.1 to 0.5 wt % Zr, and balance Cu;

melt-casting the starting materials into ingots;
cold rolling the as-cast ingots to a cold rolled plate with a thickness reduction of from 60 to 80% of the thickness of the plate before cold rolling;
solution annealing the cold-rolled plate at from 950 to 980° C. for from 15 to 30 minutes to form a solution annealed alloy with grain boundaries and Cr_2Nb precipitates having a diameter of from 2 to 20 μm, wherein the Cr_2Nb precipitates are within the grain boundaries;
performing a water quench on the solution annealed alloy at a temperature of 20 to 25° C. to form a quenched alloy;
aging the quenched alloy at a temperature of from 460 to 490° C. for from 150 to 210 minutes to form a CuCrNbZr alloy comprising at least one selected from the group consisting of matrix Cr and matrix CuZr precipitates, the Cr matrix precipitates being from 1 to 10 nm in diameter, and the CuZr matrix precipitates being from 10 to 50 nm in diameter.

28. The method of claim **27**, wherein the alloy comprises both Cr and CuZr matrix precipitates.

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