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(54) **ENHANCED THERMAL STABILITY ON
MULTI-METAL FILLED CERMET BASED
SPECTRALLY SELECTIVE SOLAR
ABSORBERS**

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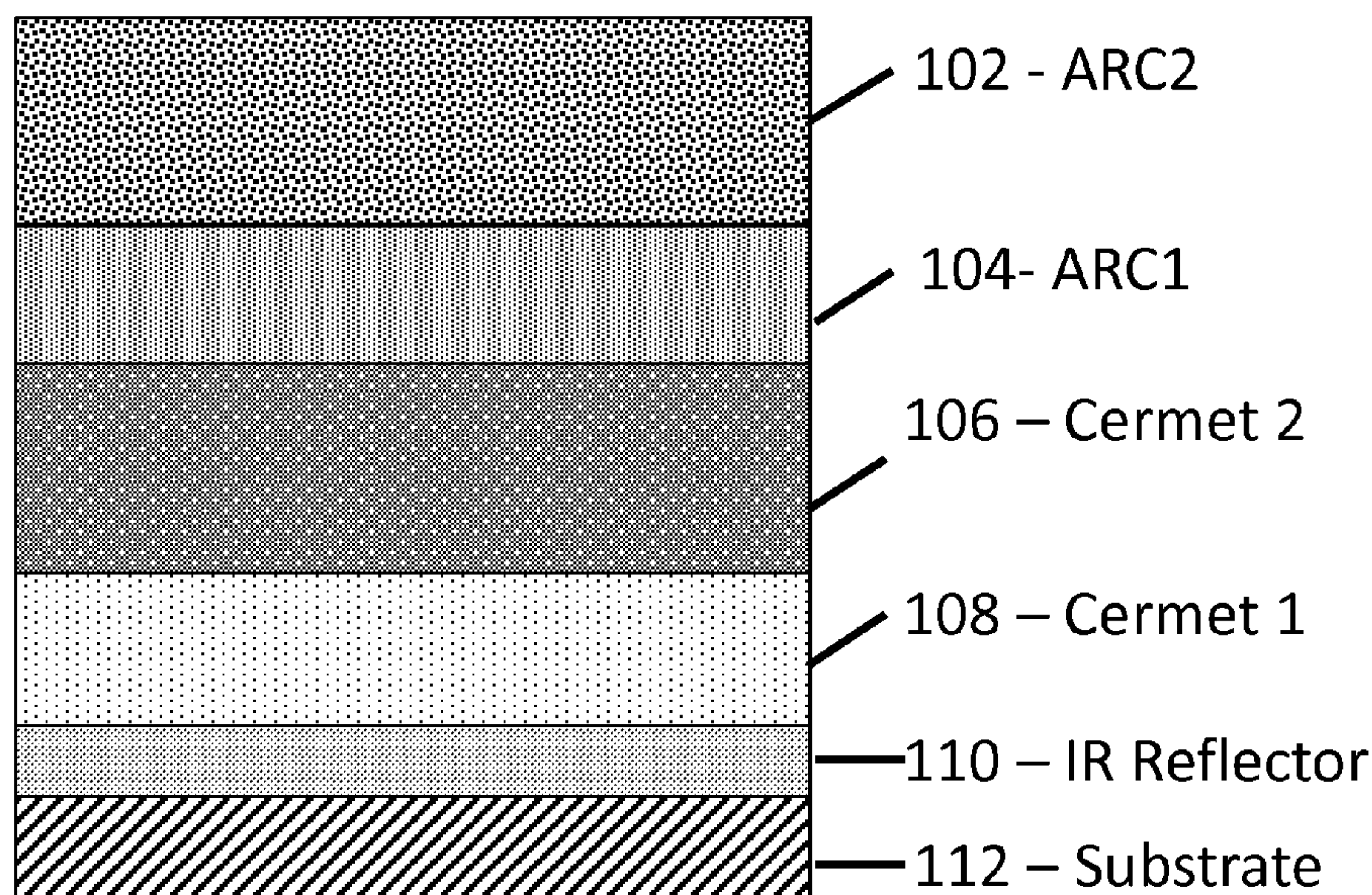
(57) **ABSTRACT**

A spectrally selective solar absorber is described and comprises a substrate, double cermet layers comprising multi-metal nanoparticles embedded in a dielectrics matrix, and double antireflection layers deposited on cermet layers. The tungsten or titanium or tantalum infrared reflector layer suppressing the diffusion of substrate elements and multi-metal nanoparticles in the cermet are disclosed.

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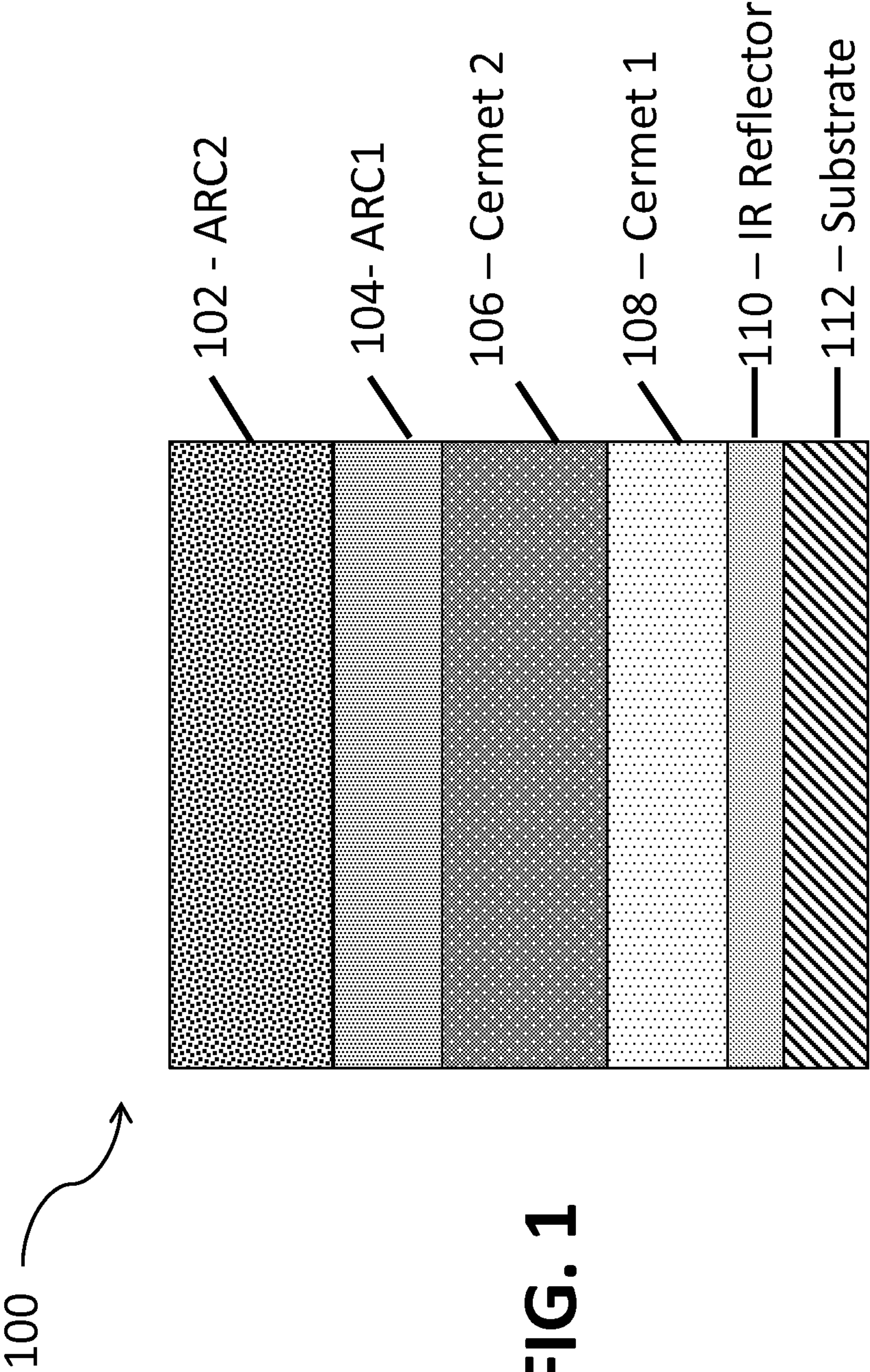


FIG. 1

FIG. 2

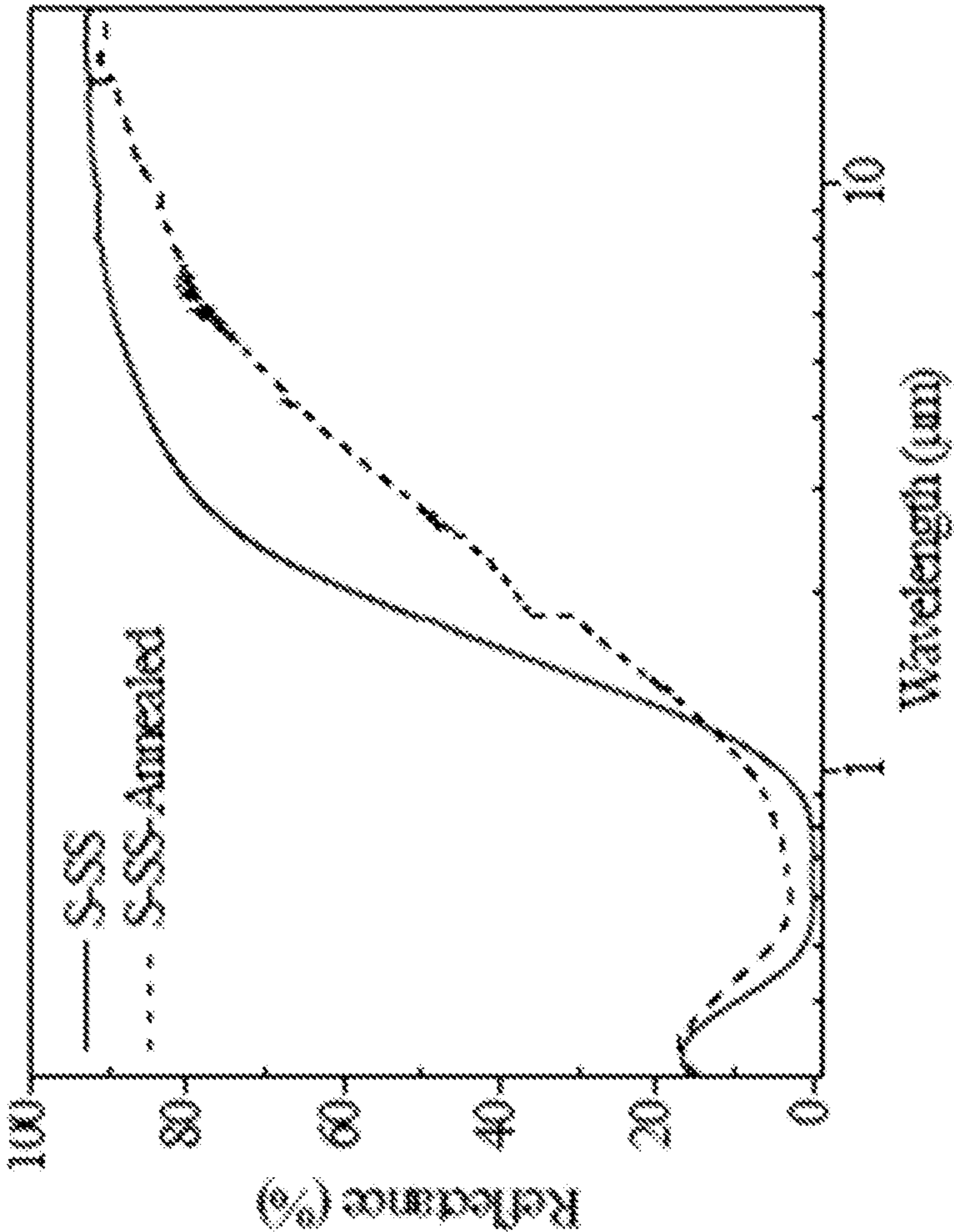


FIG. 3A

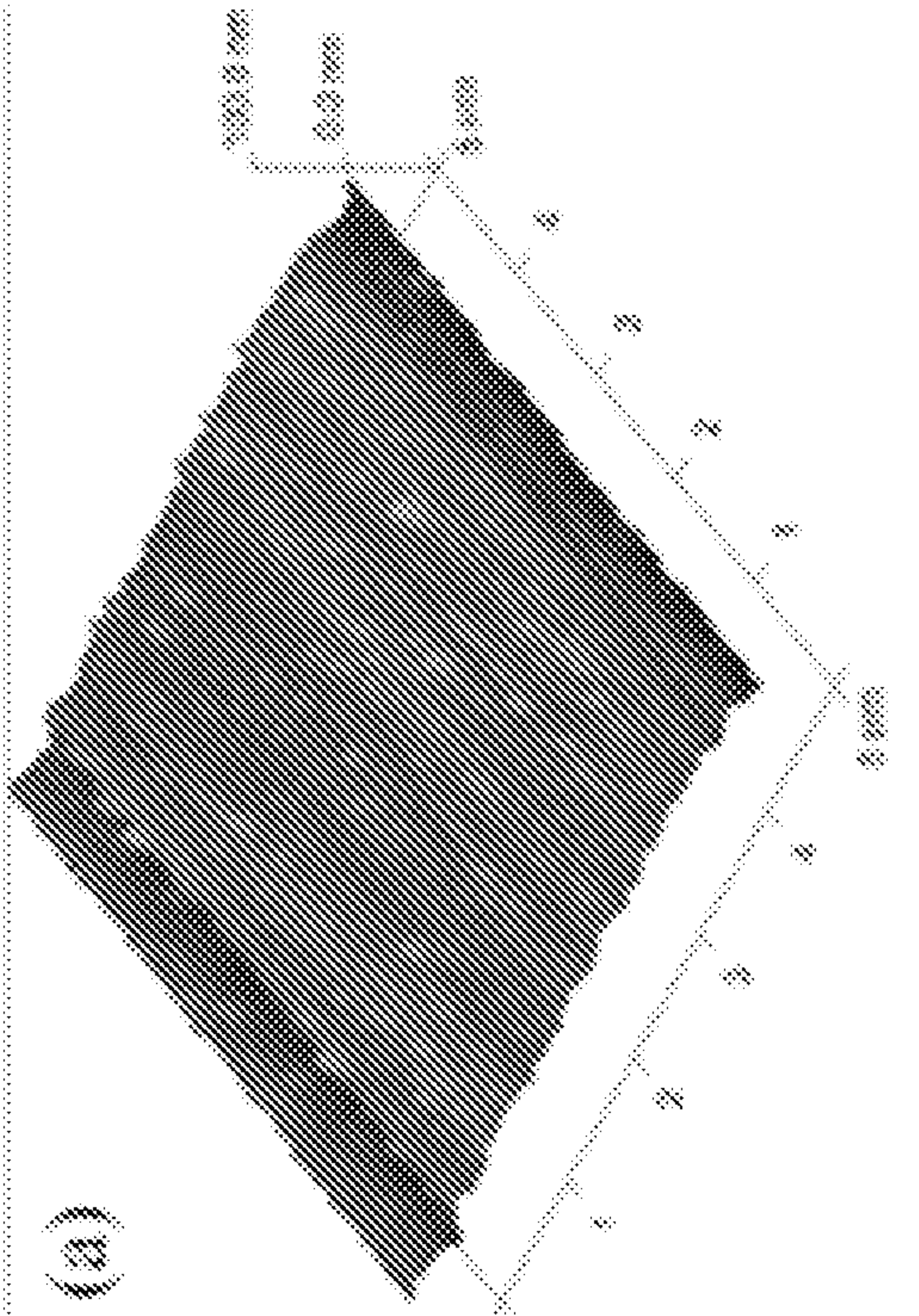


FIG. 3B

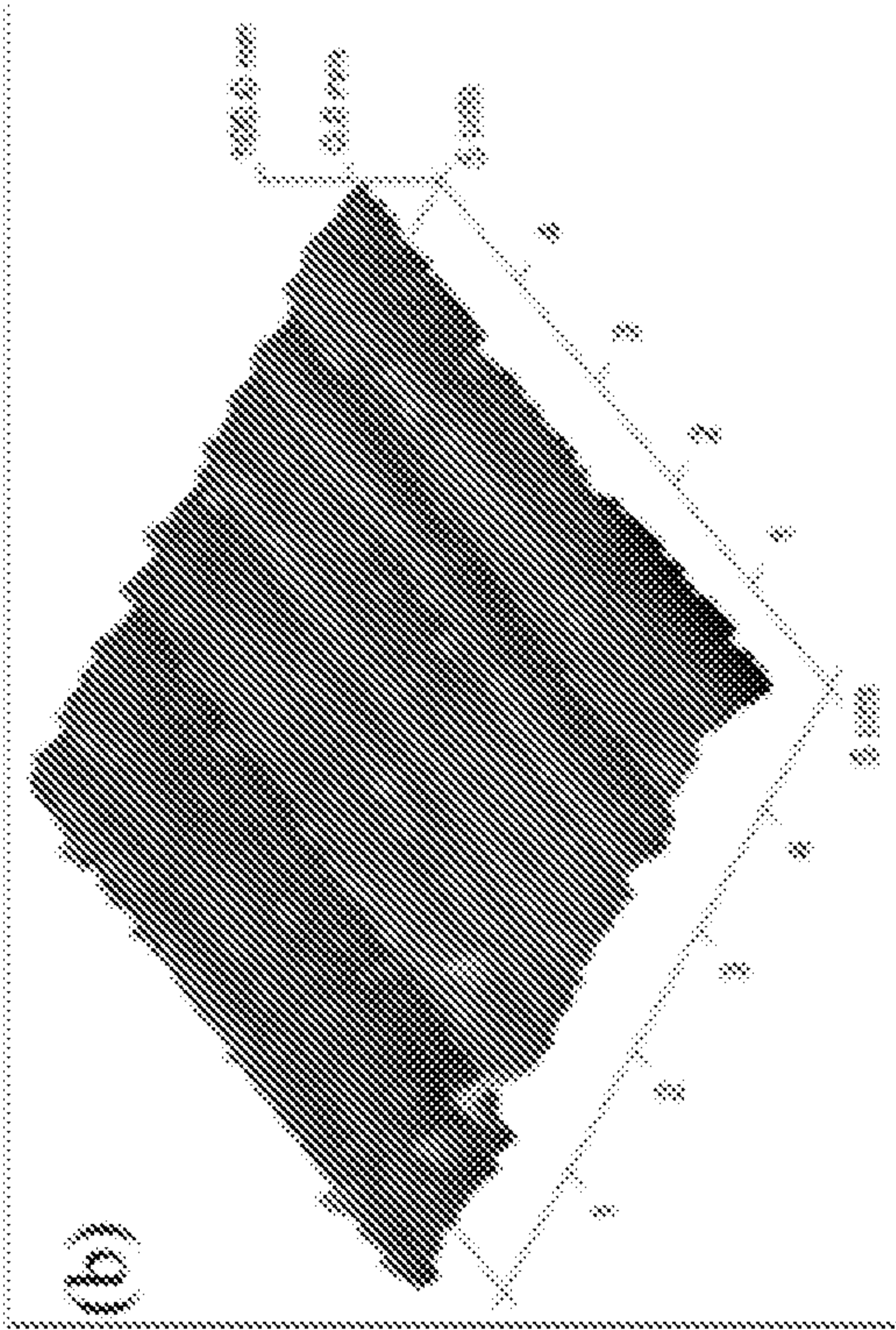


FIG. 4A

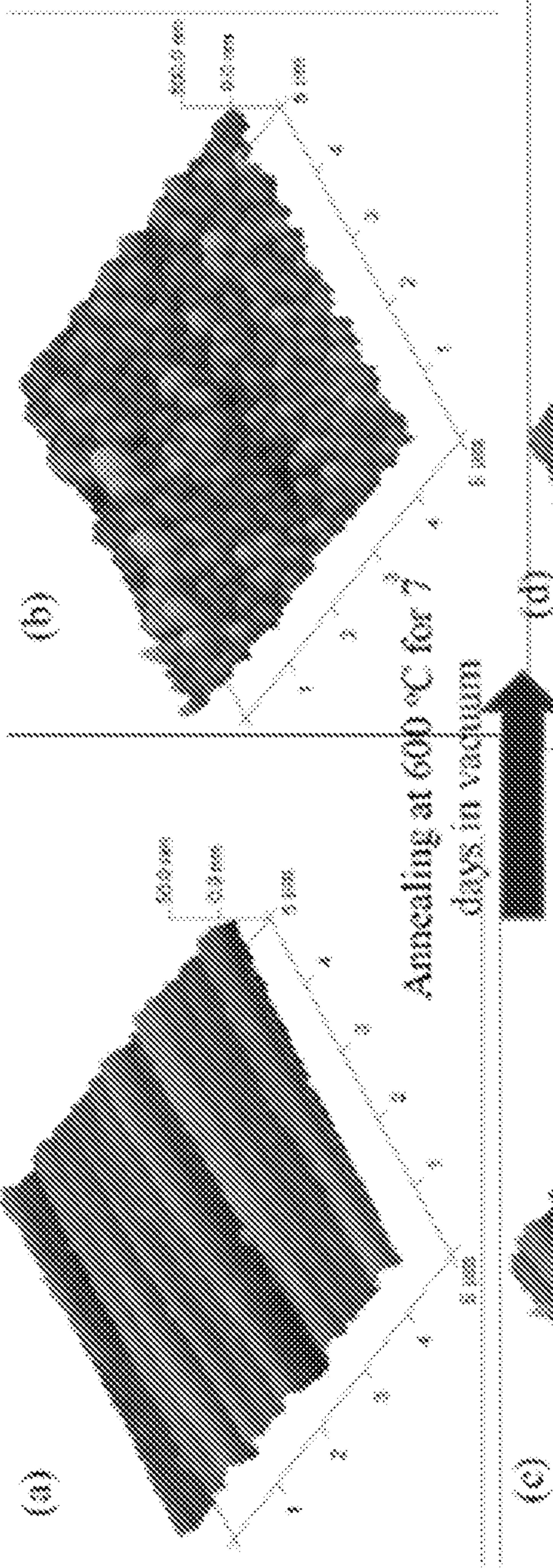


FIG. 4B

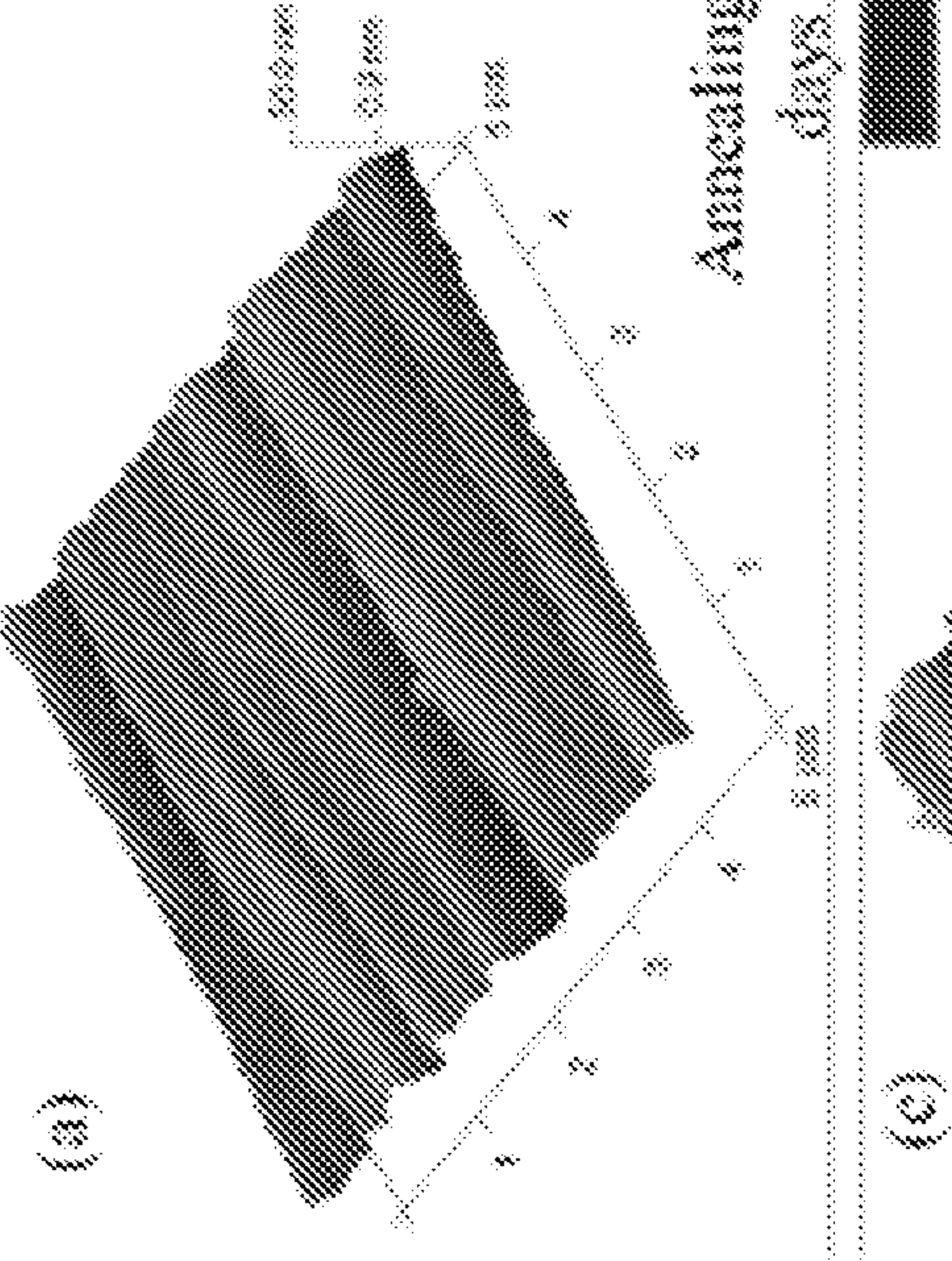


FIG. 4C

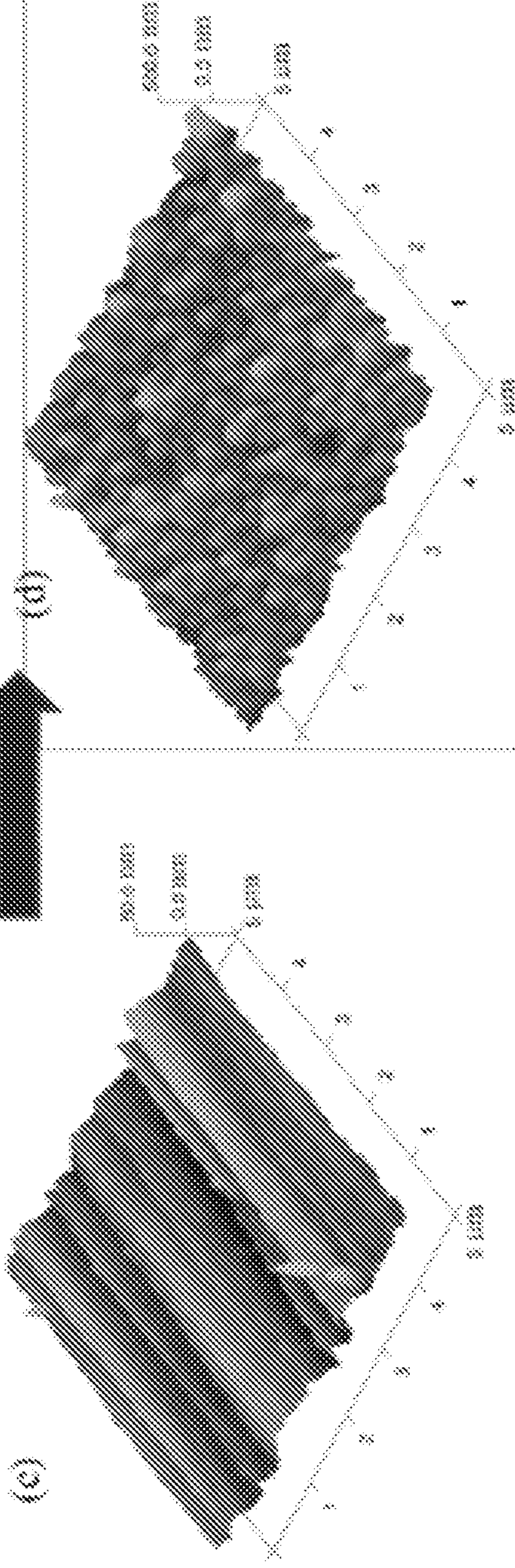
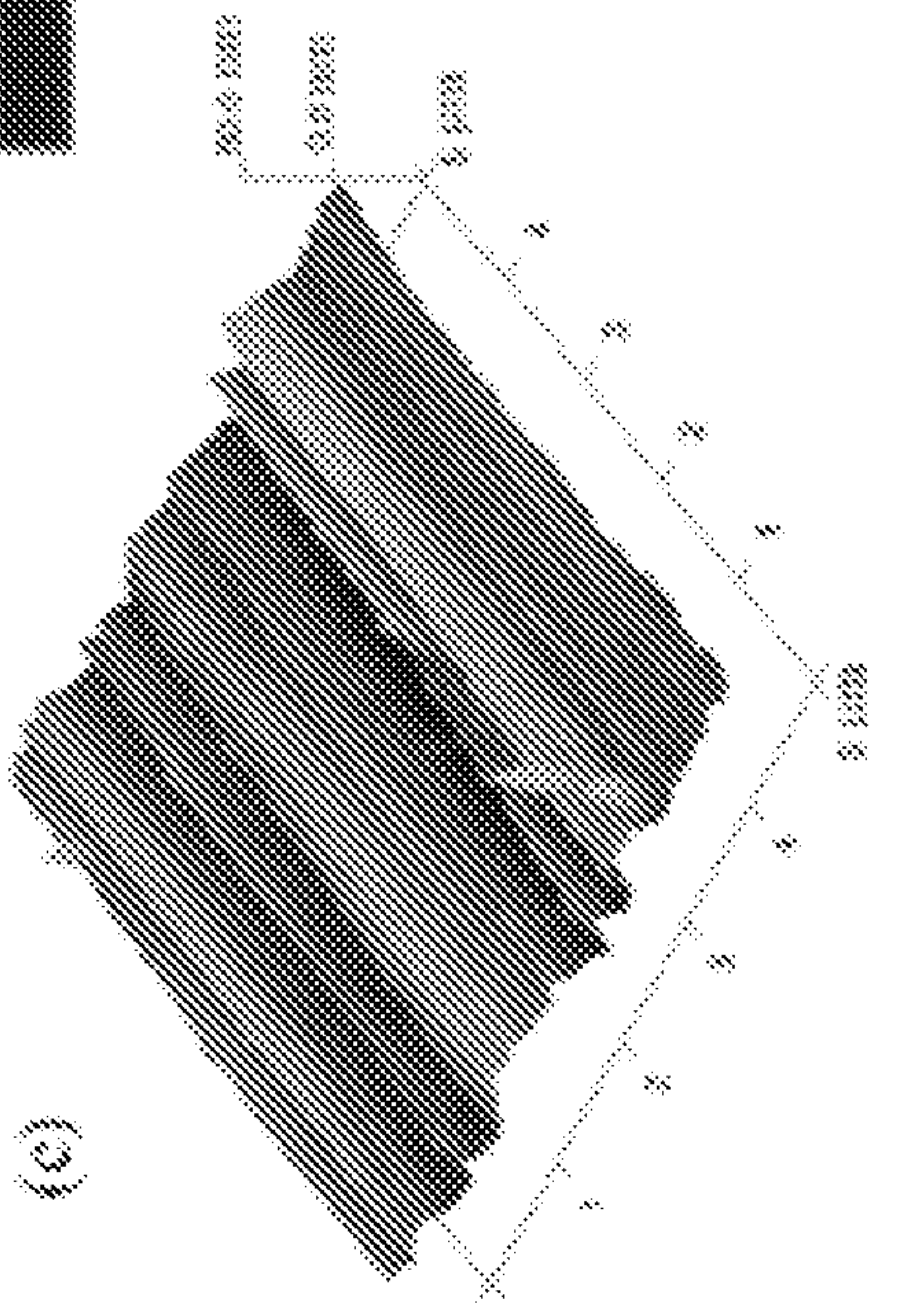


FIG. 4D



Annealing at 600 °C for 7 days in vacuum

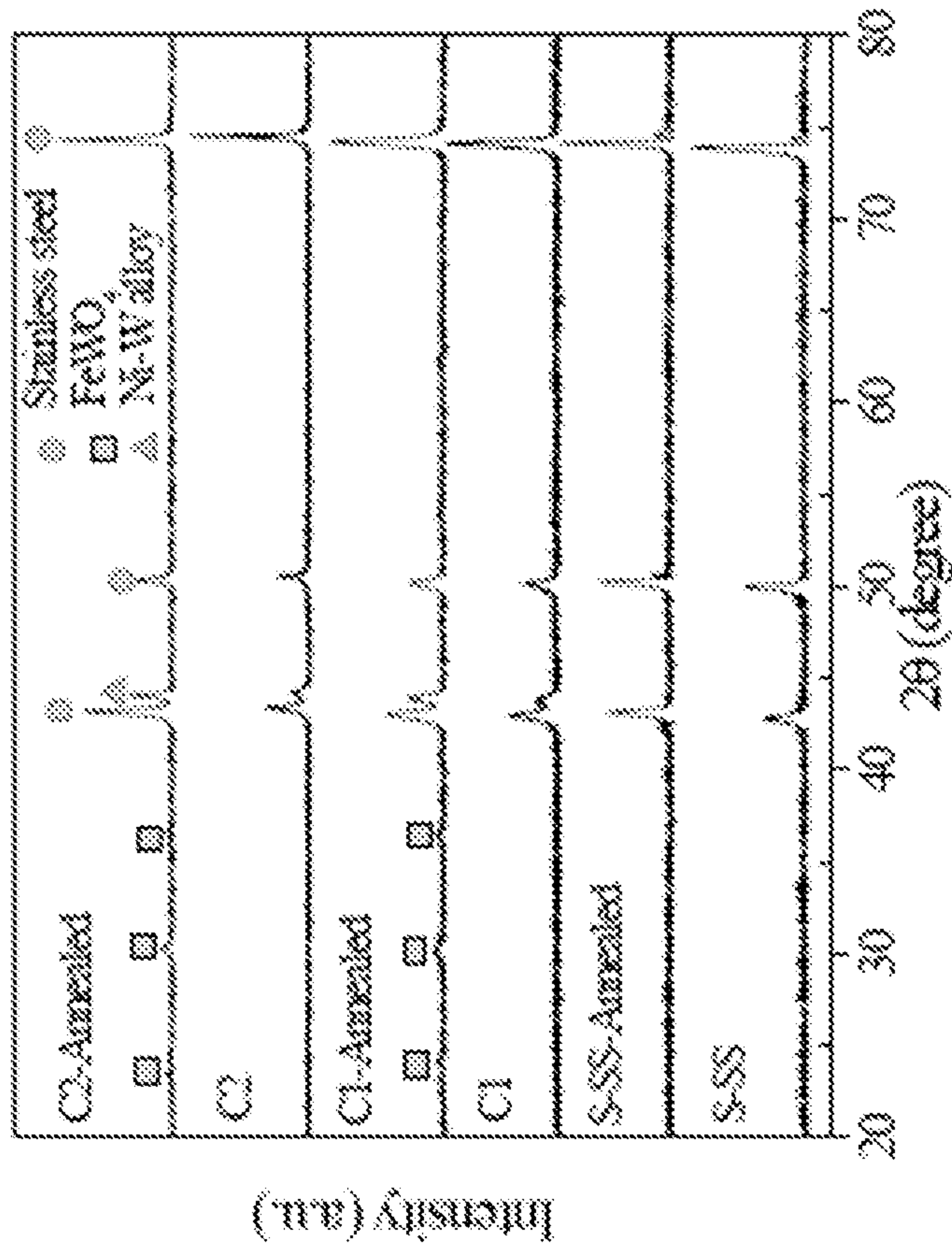


FIG. 5

FIG. 6

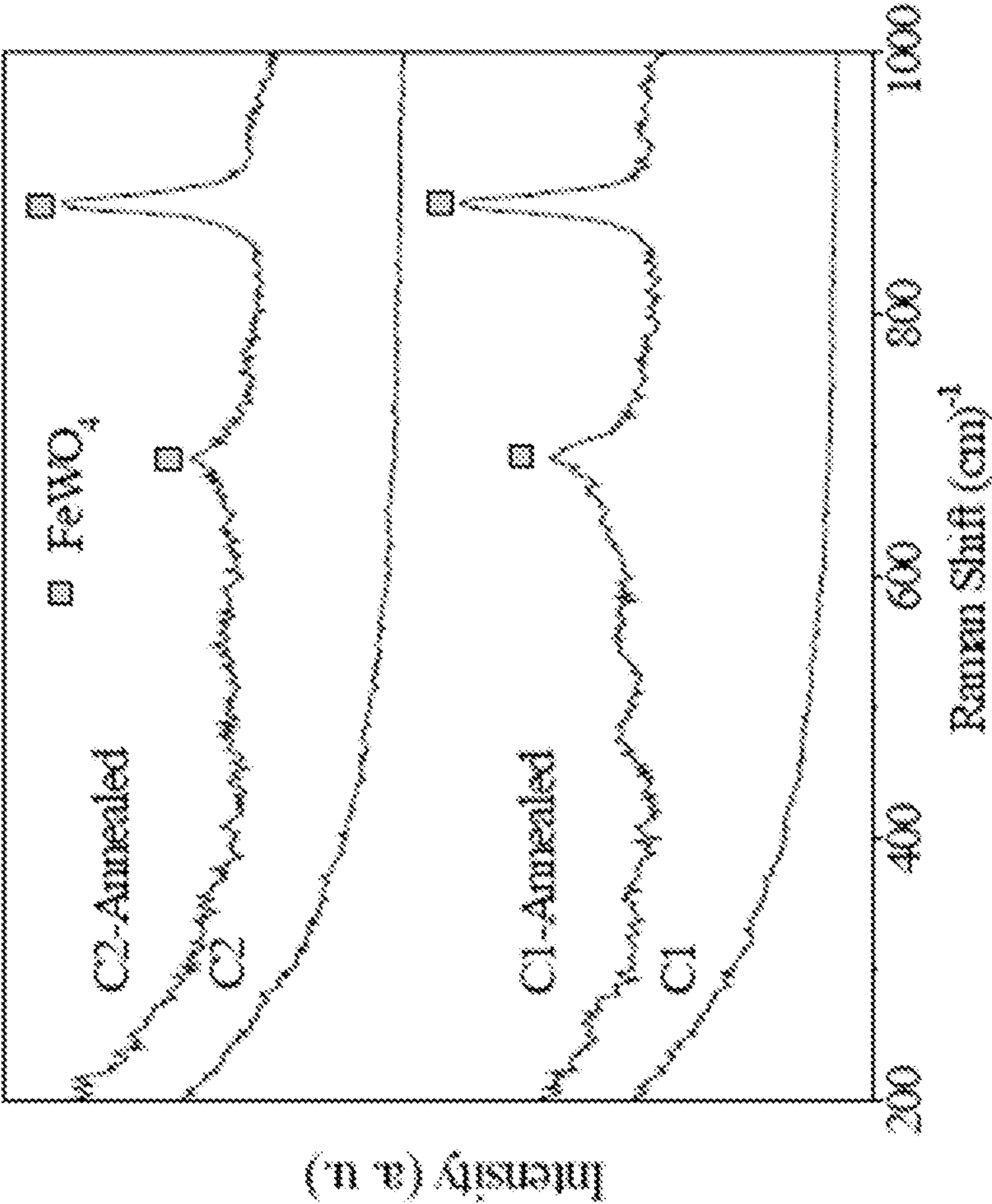


FIG. 7

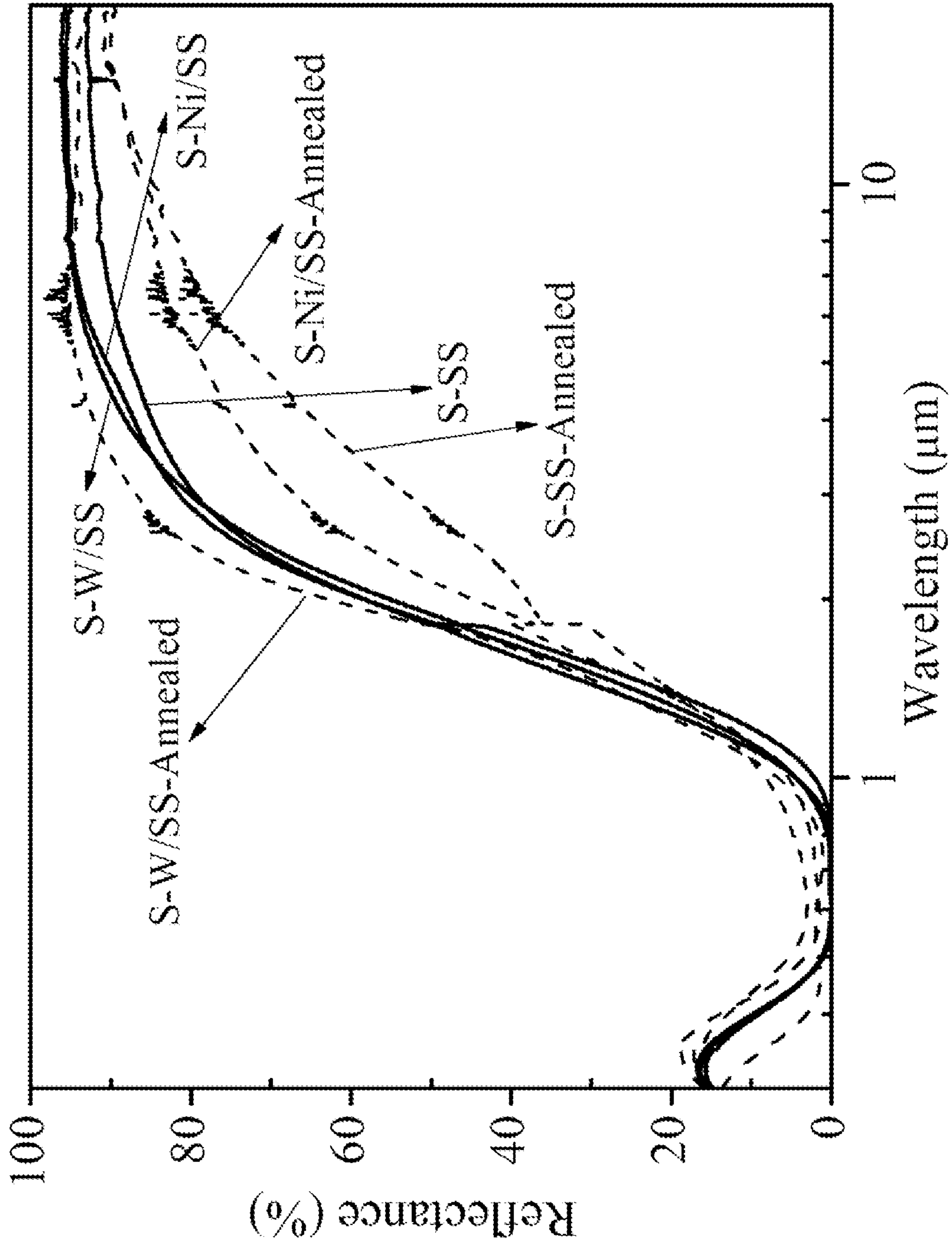


FIG. 8

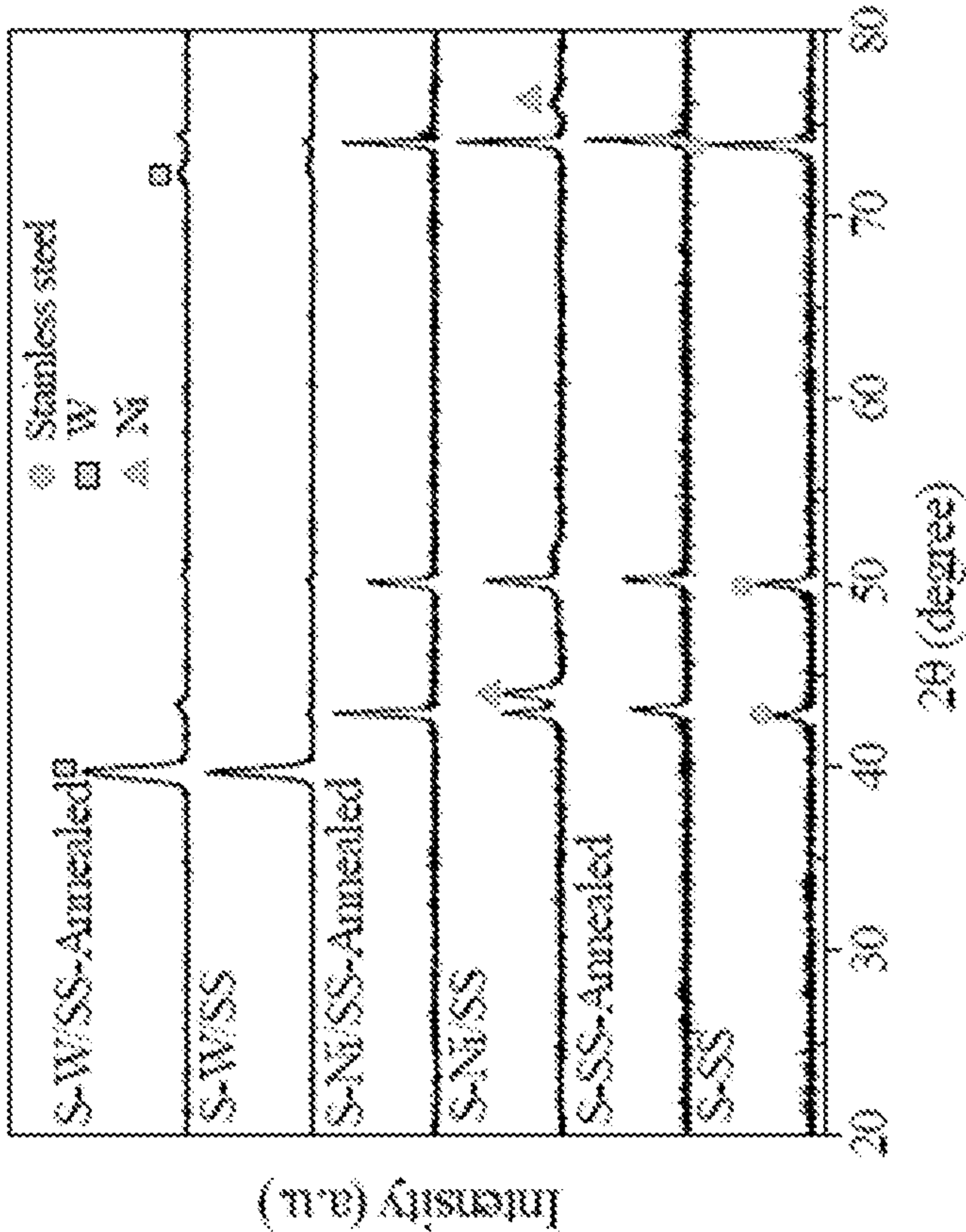


FIG. 9

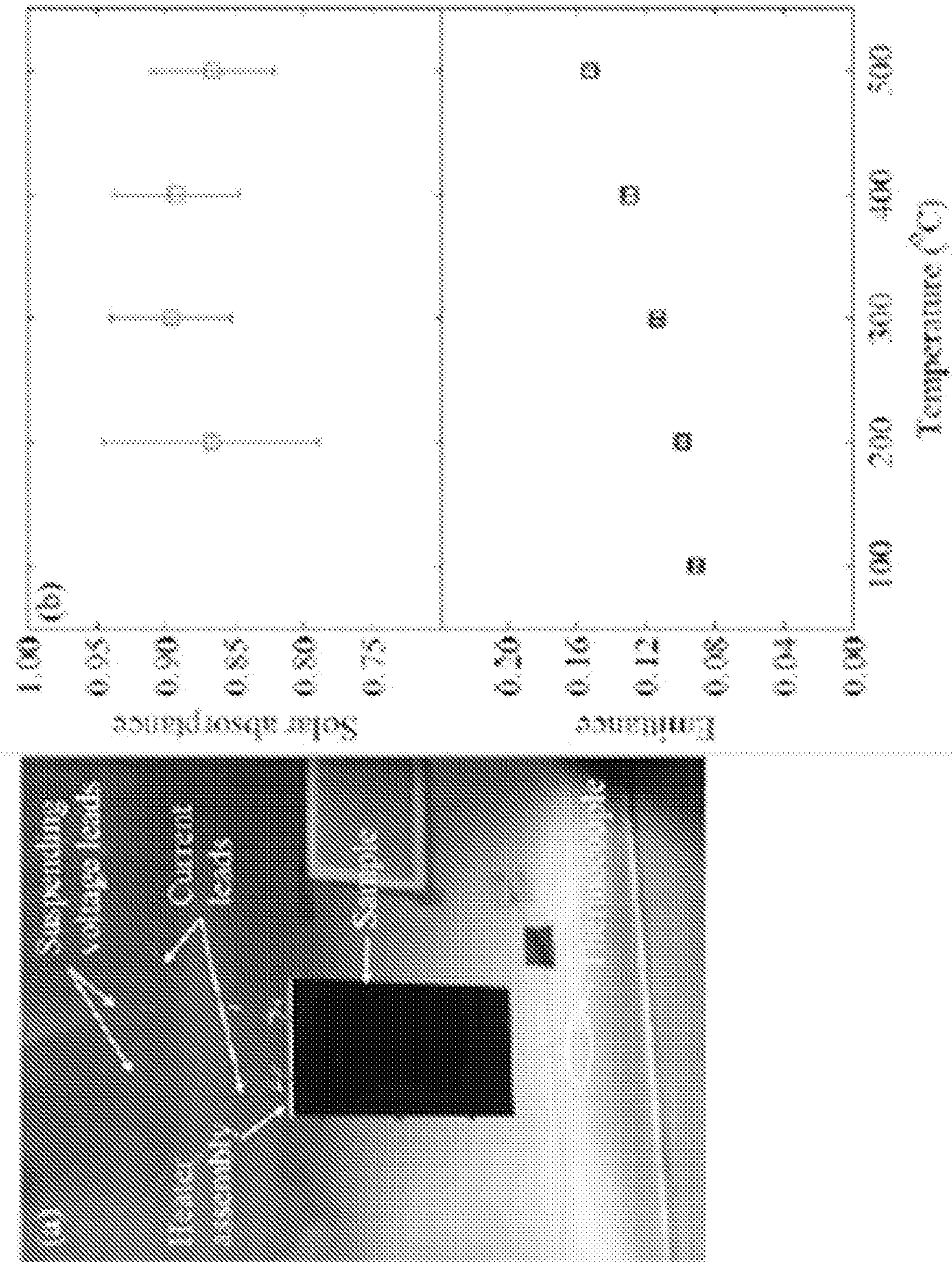
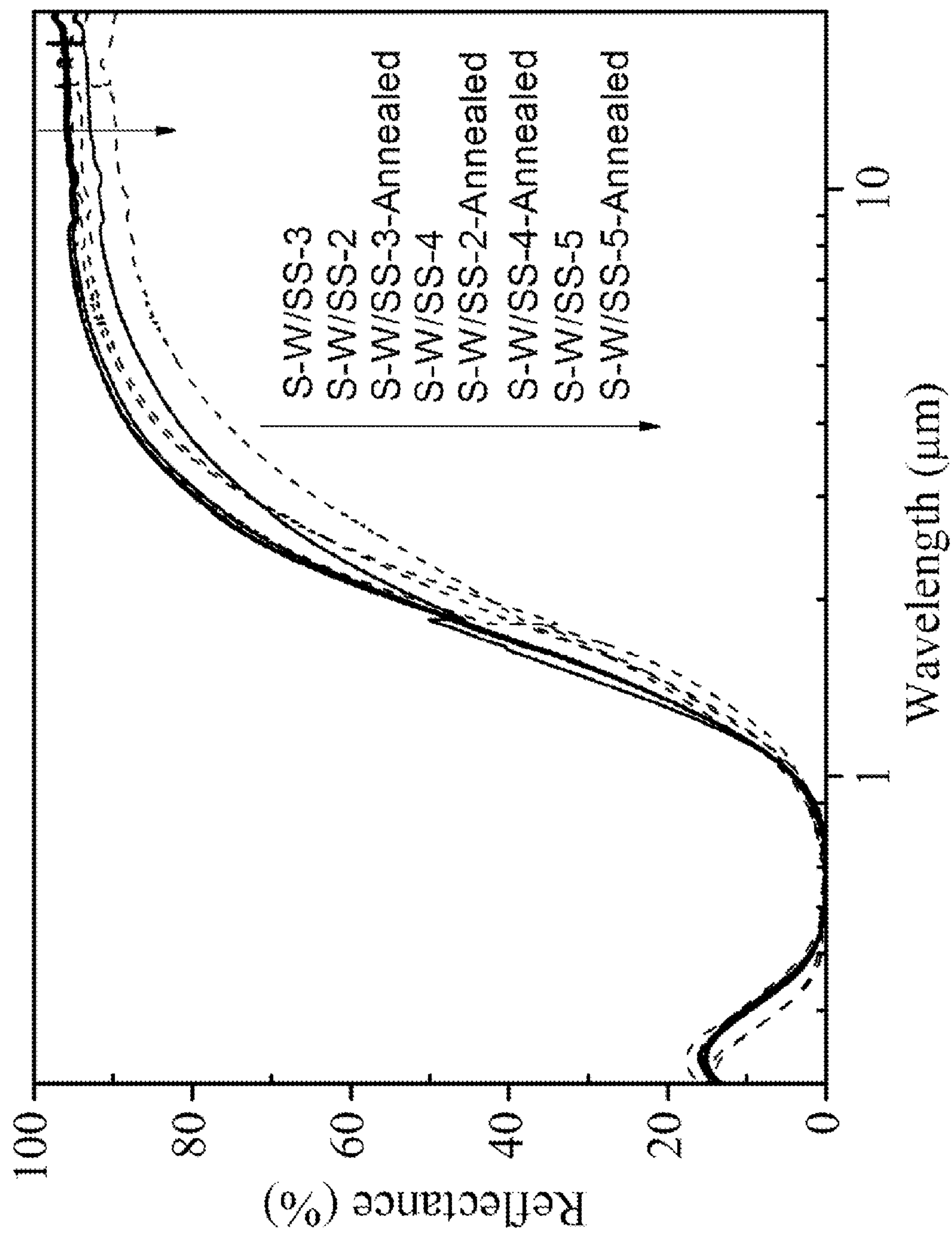


FIG. 10



ENHANCED THERMAL STABILITY ON MULTI-METAL FILLED CERMET BASED SPECTRALLY SELECTIVE SOLAR ABSORBERS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a 35 U.S.C. §371 national stage application of PCT/US2015/052952 filed Sep. 25, 2015, and entitled “Enhanced Thermal Stability on Multi-Metal Filled Cermet Based Spectrally Selective Solar Absorbers,” which This patent application claims priority to and incorporates in its entirety U.S. Provisional Patent Application 62/072,124 filed Oct. 29, 2014, and entitled “Enhanced Thermal Stability on Multi-Metal Filled Cermet Based Spectrally Selective Solar Absorbers,” filed Oct. 29, 2014 each of which are hereby incorporated herein by reference in their entirety for all purposes.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This work was partially supported by “Concentrated Solar Thermoelectric Power (CSP)”, DOE SunShot CSP grant, under award number DE-EE0005806 and “Solid State Solar-Thermal Energy Conversion Center (S³TEC),” an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Science under award number DE-SC0001299/DE-FG02-09ER46577 (GC and ZFR).

BACKGROUND

Background of the Technology

[0003] Solar thermal technologies such as solar hot water and concentrated solar power trough systems employ spectrally-selective solar absorbers. These solar absorbers are designed to efficiently absorb the sunlight while suppressing re-emission of infrared radiation at elevated temperatures.

BRIEF SUMMARY OF THE DISCLOSURE

[0004] In an embodiment, a method of fabricating solar absorbers comprising: disposing a first layer in contact with a substrate; disposing a second layer in contact with the first layer; disposing a third layer in contact with the second layer; disposing a fourth layer in contact with the third layer; and disposing a fifth layer in contact with the fourth layer, wherein disposing the fifth layer forms a solar absorber comprising an absorbance within a first predetermined range and an emittance within a second predetermined range.

[0005] In an embodiment, a solar absorber comprising: a reflector layer disposed in contact with a substrate; a first cermet layer disposed in contact with the reflector layer; a second cermet layer disposed in contact with the first cermet layer; and at least two anti-reflective coating (ARC) layers, wherein at least one ARC layer is disposed in contact with the second cermet layer.

[0006] In an embodiment, a solar absorber comprising: a reflector layer disposed in contact with a substrate; a first cermet layer disposed in contact with the reflector layer, wherein the reflector layer comprises at least one of at least tungsten (W) or nickel (Ni).

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] For a detailed description of the exemplary embodiments disclosed herein, reference will now be made to the accompanying drawings in which:

[0008] FIG. 1 is a schematic of a spectrally selective solar absorber configuration according to certain embodiments of the present disclosure.

[0009] FIG. 2 illustrates the bidirectional reflectance spectra of solar absorbers before and after annealing that were fabricated according to certain embodiments of the present disclosure.

[0010] FIGS. 3A and 3B illustrate the surface roughness of a solar absorber upon annealing where the solar absorber was fabricated according to certain embodiments of the present disclosure.

[0011] FIGS. 4A-4D are AFM images illustrating the morphology change of a single cermet layer before and after annealing according to certain embodiments of the present disclosure.

[0012] FIG. 5 illustrates XRD patterns for pristine and annealed cermet coatings where the coatings were fabricated according to certain embodiments of the present disclosure.

[0013] FIG. 6 is a chart of Raman spectra of cermet coatings before and after annealing where the coatings were fabricated according to certain embodiments of the present disclosure.

[0014] FIG. 7 illustrates the spectral bidirectional reflectance response of solar absorbers that were fabricated according to certain embodiments of the present disclosure.

[0015] FIG. 8 illustrates XRD patterns of solar absorbers fabricated according to certain embodiments of the present disclosure.

[0016] FIG. 9 illustrates the experimental set up and results for steady state calorimetric measurements of samples fabricated according to certain embodiments of the present disclosure.

[0017] FIG. 10 illustrates the spectral properties of a plurality of solar absorbers that were fabricated according to embodiments of the present disclosure.

DISCUSSION OF DISCLOSED EXEMPLARY EMBODIMENTS

[0018] The paper by F. Cao, D. Kraemer, G. Chen, and Z. Ren, entitled *Enhanced Thermal Stability of W—Ni—Al₂O₃ Cermet-based Spectrally Selective Solar Absorbers with W Infrared Reflector*, is incorporated by this reference in its entirety.

[0019] Efforts for the development of thermally stable selective solar absorbers may focus on spectral selectivity and thermal stability for high temperature applications. Selective solar absorbers, which may be referred to as “solar absorbers” herein, were fabricated according to certain embodiments of the present disclosure and may be based on two cermet layers and were fabricated using a magnetron sputtering technique on mechanically polished stainless steel substrates. Cermets are composite materials comprising metallic and ceramic materials that may therefore comprise desirable properties of both ceramics and metals. For example, cermets may be resistant (to loss of properties and deformation) to high temperatures like a ceramic, and may be able to undergo plastic deformation like metallic materials. Cermets may be used in both electronic and mechanical applications including in solar applications and for

cutting and machining tools that may also experience high temperature. Reflector layers provide solar reflectance by reflecting wavelengths in various wavelength ranges, including the visible, infrared, and ultraviolet ranges, in order to reduce the heat transferred to the surface of an apparatus employing the reflector layer. In some embodiments herein, infrared reflector layers may be employed in solar absorbers. Wavelength ranges may comprise infrared wavelengths above 700 nm (10^{-9} m) to about 1 mm, visible wavelengths may range from about 400 nm to about 700 nm, ultraviolet light wavelengths may range from less than 400 nm (e.g., shorter wavelengths than visible light) to about 10 nm, x-rays may range from less than about 10 nm (e.g., shorter than ultraviolet light) to about 10 pm (picometers, 10^{-12} m), and gamma rays may be less than about 10 pm, that is, shorter than x-ray wavelengths.

[0020] In various contexts and applications, the emittance (emissivity) of a surface may be considered because a low emittance may indicate that the solar absorber wastes less energy through emitting thermal radiation than materials with a high emittance. The same principle may apply, for example, in insulation applications where it may be desirable for a window to retain heat using a coating or a film. In an embodiment, an operating temperature where selective solar absorbers may be desired is from about 500 to about 600° C. Nickel and tungsten were employed in certain embodiments for the infrared reflector layer in selective thermal absorbers discussed herein, the results of those experiments are discussed herein, including one in which a stable solar absorptance of about 0.90 and total hemispherical emittance of 0.15 at 500° C. was obtained using tungsten as the infrared reflector layer. While the infrared reflector layer may be referred to in some embodiments as “a layer,” the infrared reflector layer may be a plurality of individual (separate) layers which may be of the same or differing layer types and/or varying thicknesses, or combinations or the same type of material and different types of material with the same or varying thicknesses depending upon the embodiment.

[0021] In one embodiment, a spectrally selective solar absorber comprises a substrate (stainless steel, tantalum, titanium, copper, aluminum, nickel, silicon, quartz, and combinations thereof), an infrared reflector layer or bonding layer (tungsten, tantalum, titanium, nickel, silver, gold, aluminum, and combinations thereof), a first and a second cermet layer which may comprise multi-metal nanoparticles in dielectric matrix and two anti-reflection coatings. The term “selective” may be used to describe the manner in which the solar absorber is fabricated so that the solar absorber provides an absorbance within a first predetermined wavelength range and an emittance within a second predetermined wavelength range. Herein, a “cermet layer,” is a combination of two or more metals and a ceramic, and in some embodiments, a combination of at least two layers cermet1 (“C1”) and cermet 2 (“C2”) may be employed in a solar absorber, where each of C1 and C1 comprises a combination of any two or more metals, including but not limited to Nickel (Ni), Cobalt (Co), Iron (Fe), Tungsten (W), Tantalum (Ta), Titanium (Ti), Molybdenum (Mo), Chromium (Cr), Vanadium (V), Niobium (Nb), Zirconium (Zr), and at least one of Al_2O_3 , SiO_2 , ZrO_2 , Ta_2O_5 , AlN, or other dielectric materials as appropriate for the end application’s desired absorbance and emittance ranges.

[0022] The introduction of multi-metal nanoparticles in cermet, as discussed in certain embodiments of the present disclosure, as compared to the use of solely single-metal nanoparticles provides additional tuning parameters (e.g., the metal/ceramic concentrations and different component selections) with which to tailor the optical properties of the cermet absorption layers. The anti-reflection coatings (“ARC”), also referred to as “ARC layers” discussed herein may comprise Al_2O_3 , MgO, TiO_2 , V_2O_5 , Ta_2O_5 , ZrO_2 , SiO_2 , and other oxide layers that may be appropriate for various desired ranges of emittance and reflectance in solar absorbers. In some embodiments, the stable infrared reflector layer suppresses the diffusion of the substrate elements into the cermet layer and results in enhanced thermal stability of the solar absorber at elevated temperature. The metal infrared reflector layer also improves to some extent the spectral selectivity of the solar absorber due to its low infrared emittance.

[0023] Introduction

[0024] Sunlight may be converted into a useful terrestrial heat source by employing sunlight absorbing surfaces in the form of solar absorbers. Solar absorbers may be employed in solar thermal systems such as solar hot water systems and concentrated solar power (CSP) trough systems, as well as in emerging technologies such as solar thermoelectric, solar thermo-photovoltaic, and solar thermionic generators. The solar thermal receiver efficiency may depend on the optical properties of the solar absorber. To maximize the efficiency of a solar absorber, it may be desirable for a solar absorber to comprise a near-blackbody absorptance (α) in the solar spectrum range while retaining a low emittance (ϵ) in the infrared (IR) range, and be thermally stable at their operational temperatures. The solar absorbers discussed herein may be employed in processes, methods, and products to convert received wavelengths into energy sources.

[0025] Discussed herein is a spectrally-selective solar absorber (“solar absorber”) and methods of fabricating the solar absorber comprising a layer disposed between a substrate and an absorber coating that demonstrates a long-term stability at high temperatures ($T > 400^\circ \text{C.}$) as well as a stable solar absorptance of about 0.90 and a hemispherical emittance of 0.15. As used herein, a “spectrally selective” solar absorber may be defined by the range of wavelengths it is designed to reflect and/or absorb.

[0026] As for mid-temperature (about $100^\circ \text{C.} < T < \text{about } 400^\circ \text{C.}$) and high-temperature ($T > \text{about } 400^\circ \text{C.}$) applications, cermet-based coatings may be employed and comprise ceramic metallic composites which may be good candidates for inclusion in the solar absorber due to their high solar absorptance, low emittance, and good thermal stability. These desirable properties may be attributed to the high temperature stable ceramic host. Cermet-based spectrally selective solar absorbers may present and be employed as single, double, and triple cermet layers. The thin cermet layer is typically in contact with a metallic surface for high solar absorptance that is transparent to IR radiation. The absorption of solar radiation in the cermet layer may be due to interband transitions in the metal and small particle plasmonic resonances.

[0027] A “graded metal volume fraction” is the term used herein to describe a combination of two or more cermet layers comprising different metal volume fractions (weight of metallic/(weight of metallic+ceramic combined)). The graded metal volume fraction between and within the cermet

layers gives it a gradual increase in the refractive index from surface to the substrate, which reduces reflection compared with single cermet layer absorbers that often use black metals such as black chrome, black nickel, or black tungsten as their metal fillers. Solar absorbers fabricated according to embodiments of the present disclosure that comprise cermet multilayers (C1 and C2 in this example) with different metal volume fractions introduces a stepwise change in the refractive index that may result in a low reflection of visible light due to interference effects.

[0028] In some embodiments, additional anti-reflection coatings may be applied to the solar absorbers to further reduce reflection losses. Consequently, cermet-based solar absorbers have a tunable parameter space (range) based upon their constituents, coating thicknesses, particle concentration, size, shape, and orientation to optimize their spectral selectivity. Various combinations of host materials such as Al_2O_3 , AlN , and SiO_2 with metallic filler atoms such as Ni, Co, Ti, Mo, W, Pt, Stainless steel (SS), Cu, Ag, Au have been investigated in terms of their respective effectiveness for the optical performance and thermal stability of the cermet surfaces. These combinations of host materials have ceramic host materials in common that possess high temperature stability, and are therefore complimentary. The metal filler atoms may be chosen for their high melting point and their resistance to both nitriding and oxidation, in order to enhance and ensure thermal stability.

[0029] In an embodiment, in the case of solar absorbers with mid-temperature applications, the cermet layers may be deposited on metal substrates such as polished aluminum or copper due to their low IR emittance and high thermal conductivity. In an embodiment, a diffusion barrier between the substrate and the cermet layer was introduced with a spontaneously formed Fe_2O_3 layer by annealing the stainless steel substrate at 500°C . in air. However, the surface roughness of the substrate changes when forming an Fe_2O_3 layer, which eventually affects the surface roughness of solar absorber and then increases the emittance. Also, the Fe_2O_3 layer on the back side of the stainless steel may introduce another thermal resistance layer in a solar absorber, which will decrease the heat transport efficiency from the absorber to the thermal system. Surface smoothness may be a desirable property in solar absorbers, so the impact of annealing was evaluated and is discussed herein.

[0030] The embodiments herein discuss depositing, for example, a nickel (Ni) or tungsten (W) layer that may be referred to as an inter-reflector (IR) layer onto a mechanically polished substrate that may comprise stainless steel. Depending upon the embodiment and the substrate material employed, the substrate may not be polished. This IR layer may act not only to bond the substrate to other layers but also as a diffusion barrier and as a low IR emittance coating to improve spectral selectivity. The performance of the metal IR reflector layer with a double-layer cermet structure and two antireflection coatings (ARCs) is discussed herein. In contrast to cermet structures that may be filled with particles of one metal type, the cermet layers based on an Al_2O_3 ceramic host material may be filled with high temperature stable Ni—W alloy prepared by co-sputtering. Therefore, the cermet layers may each comprise not only the metal volume fraction in each cermet layer but also the volume fraction of the individual constituent which may be adjusted

to tailor the optical properties of a solar absorber depending upon the end application, subsequent processing, or customer specifications.

[0031] In one example experiment, a plurality of individual layers of the solar absorbers were deposited using a magnetron sputtering technique. The spectral bidirectional reflectance responses of the fabricated solar absorbers were measured at room temperature before and after annealing at 600°C . for 7 days. The solar absorptance and total hemispherical emittance were measured at elevated temperatures of up to 500°C .

[0032] In an embodiment, the spectrally-selective solar absorbers may be deposited in contact with a substrate, for example, a mechanically polished stainless steel substrate. The deposition may be performed using a commercial magnetron sputtering equipment (AJA international, Inc.). For the thickness measurement of the C1 and C2 layers, the materials may be simultaneously deposited on Si wafer substrates partly covered by a mask. Prior to the deposition process, the chamber may be evacuated to lower than 4×10^{-7} Torr. The deposition targets are high purity nickel (99.999%, 2" Dia.), tungsten (99.95%, 3" Dia.), Al_2O_3 (99.98%, 2" Dia.), and SiO_2 (99.995%, 3" Dia.). DC power is supplied to the metal targets (Ni, W) to deposit the metal layer and for the metal particle. The dielectric layer is deposited by RF magnetron sputtering. Co-sputtering may be employed to deposit more or one dielectric layers, such as the C1 and C2 layers. The metal fill fractions of the cermet layers may be controlled by independent input power control to the corresponding targets. The complete deposition process may be performed in an argon plasma environment at a pressure of 3 mTorr. The detailed preparation parameters are summarized in Table 1 herein.

[0033] Regarding the thermal stability, the solar absorbers fabricated according to embodiments of the present disclosure are characterized in terms of their phase, morphology, and optical properties both before and after annealing the samples at 600°C . for 7 days at a vacuum pressure of about 5×10^{-3} Torr using a tubular furnace. The X-ray diffraction (XRD) patterns were obtained using a PANalytical multi-purpose diffractometer with an X'Celerator detector and $\text{Cu K}\alpha$ radiation ($\lambda=1.54056\text{ \AA}$) operating at 45 kV and 40 mA. Raman scattering spectra measurements were carried out on a T64000 Raman system (Horiba Jobin Yvon) at room temperature. The excitation source is the 514 nm laser line of an air cooled Ar-ion laser.

[0034] The thickness of the cermet films were measured with an Alpha-step 200 Profilometer (Tencor). The growth rates of metal and dielectric layers comprising the cermet layers (films) were measured by a quartz crystal monitor equipped in the sputtering system. The morphology and roughness of the films were measured with a Veeco Dimensions 3000 Atomic Force Microscope (AFM). The spectral bidirectional reflectance was measured at room temperature with a Spectrophotometer by Varian (Cary 500i, angle of incidence 8° , absolute spectral reflectance accessory) covering the wavelength range of 0.3-1.8 μm , and with an FT-IR Spectrometer by Thermo Scientific (Nicolet 6700, angle of incidence 12°) covering the wavelength range of 1.8-20 μm . The latter (relative measurement) requires a reference with known spectral reflectance which is chosen to be a specular gold mirror (Thorlabs).

[0035] FIG. 1 is a schematic of a spectrally selective solar absorber configuration according to certain embodiments of

the present disclosure. It is to be appreciated that, while different patterns are used to distinguish the layers, these indications are not necessarily indicative of differences in the layers that are visible to the naked eye, and it is also to be understood that the relative thickness of layers may vary between embodiments. The spectrally selective solar absorbers fabricated according to certain embodiments of the present disclosure for mid- and high-temperature applications are based on a double cermet layer configuration with two ARC layers and a metal layer with high IR reflectance as diffusion barrier. The two ARC layers ARC1 and ARC2 may also be Al_2O_3 and SiO_2 thin films, respectively.

[0036] In alternate embodiments, the ARC1 layer may comprise MgO , TiO_2 , V_2O_3 , ZrO , or combinations thereof. In order to investigate the effect of the ARC layers, the solar absorber multilayer structures were fabricated according to certain embodiments of the present disclosure with tungsten, optically thick nickel, or very thin nickel layer as and IR reflector or bonding layer. The detailed parameters are summarized in Table 1. In the embodiment in Table 1, the substrate may comprise a metal layer, for example, nickel having a DC power density of 12.3 W/cm^2 or tungsten having a DC power density of 2.2 W/cm^2 for tungsten. The C1 layer may comprise $\text{W}+\text{Ni}+\text{Al}_2\text{O}_3$ with a DC power density of 0.33 W/cm^2 for tungsten and 0.99 W/cm^2 for nickel, and a RF power density of 9.9 W/cm^2 for Al_2O_3 . The cermet2 layer may comprise $\text{W}+\text{Ni}+\text{Al}_2\text{O}_3$ with a DC power density of 0.26 W/cm^2 for tungsten, and 0.74 W/cm^2 for nickel, and a RF power density of 9.9 W/cm^2 for Al_2O_3 . The ARC1 layer may comprise Al_2O_3 with a RF power density of 9.9 W/cm^2 and the ARC2 layer may comprise SiO_2 with a RF power density of 4.4 W/cm^2 .

bility of optimized coatings was evaluated on stainless steel with a 10 nm thin nickel bonding layer which may act as a diffusion barrier (the S-SS sample). Details about multilayer stack composition and preparation parameters are summarized in Table 1 above.

[0038] FIG. 2 illustrates the bidirectional reflectance spectra of the pristine (where “pristine” is the term used to describe a condition before annealing) and annealed solar absorbers fabricated according to certain embodiments of the present disclosure. The reflectance of the pristine sample is close to zero in the visible range, which is expected for a double-cermet-absorption-layer combined with a double-ARC-layer due to the intrinsic absorption of the double-cermet layer and the reflectance reducing interference effects. The sharp transition wavelength range from low reflectance to high reflectance appears to be from about 1 to about $3 \mu\text{m}$, which can result in promising spectral selectivity even at high temperatures. However, the degraded optical properties of the solar absorber upon annealing at 600°C . for 7 days show a detrimental effect on spectral selectivity. The spectral reflectance below about $1.1 \mu\text{m}$ increases while it decreases above about $1.1 \mu\text{m}$ which results in a broadening of the transition wavelength range and ultimately decreases the solar absorptance and increases the IR emittance.

[0039] FIGS. 3A and 3B illustrate the surface roughness of the absorber subsequent to annealing. No significant surface roughness change upon sample annealing is observed, indicating that the annealing process does not significantly (e.g., to where it would be noticeable or negatively impact functionality) degrade the surface roughness. FIG. 3A is an atomic force microscopy (“AFM”) image of an S-SS solar absorber with a 10 nm thick nickel layer before annealing

TABLE 1

Sample	Substrate material	Bonding layer/IR layer thickness/type	C1 thickness (nm)	C2 thickness (nm)	ARC1 (nm)	ARC2 (nm)
C1	SS	10 nm Ni	180	N/A	N/A	N/A
C2	SS	10 nm Ni	N/A	28	25	55
S-SS	SS	10 nm Ni	11	28	25	55
S-Ni/SS	SS	300 nm Ni	11	28	25	55
S-W/SS	SS	300 nm W	11	28	25	55
S-W/SS-2	SS	200 nm W	11	28	25	55
S-W/SS-3	SS	100 nm W	11	28	25	55
S-W/SS-4	SS	50 nm W	11	28	25	55
S-W/SS-5	SS	10 nm W	11	28	25	55

[0037] The multilayer stack that makes up the spectrally selective solar absorbers fabricated according to certain embodiments of the present disclosure may comprise one bonding or IR reflector layer, double cermet absorption layers and double ARC layers which further reduce reflection in the visible range. In some embodiments, multiple IR-reflector layers of the same or differing compositions and/or concentrations (metal fractions) may be used in different arrangements in a solar absorber. The use of mechanically polished stainless steel as the substrate may provide high temperature stability and may be cost-effective, which can promote large scale deployment as a potential solar absorber candidate in high temperature solar receivers. It has been shown that elemental diffusion of iron and carbon from a stainless steel into the cermet layer can be detrimental for the optical properties, and a diffusion barrier may be employed to combat this diffusion. Thus, the thermal sta-

and FIG. 3B is an AFM image of the S-SS solar absorber the 10 nm thick nickel layer after annealing at about 600°C . for 7 days. The sample retains the groove structure created by the mechanical polishing process applied to the stainless steel substrate. The root mean square roughness (R_q) of the sample before and after annealing is calculated to be 6-8 nm using a NanoScope Analysis software.

[0040] FIGS. 4A-4D are AFM images illustrating the morphology change of a single cermet layer before and after annealing. FIGS. 4A-4D are AFM images of the morphology changes of a single cermet layer deposited on a mechanically polished stainless steel substrate coated with a 10 nm Ni layer without any ARC layer after annealing at 600°C . for 7 days. FIG. 4A illustrates the morphology of a cermet1 layer with a high metal volume fraction in Al_2O_3 before annealing and FIG. 4B illustrates the morphology of the same sample after annealing. In an embodiment, a “high

metal volume fraction” refers to a metal volume fraction above about 62% and a “low metal volume fraction” refers to a metal volume fraction below about 56%. FIG. 4C illustrates the morphology of a cermet2 layer with a low metal volume fraction in Al_2O_3 before annealing and FIG. 4D illustrates the morphology of the same sample after annealing.

[0041] In another embodiment, two cermet samples (C1 and C2) were fabricated without being disposed in contact with anti-reflective coating (“ARC”) layers, and were evaluated in terms of their phases and morphology before (“pristine”) and after annealing. The multilayer stacks deposited onto the stainless steel substrates consist of a 10 nm nickel bonding layer and a single cermet layer with the only difference between the two samples being the metal particle concentration in the cermet layers and their respective thicknesses (C1 and C2 as detailed in Table 1). Both samples C1 (FIG. 4B) and C2 (FIG. 4D) show significant changes in their film morphology upon annealing. Similar to the previous sample (S-SS), the C1 and C2 samples start out with a groove surface structure; however, the annealing process leads to a rapid growth of the Ni—W alloy within the cermet layer from diameters of about 80 nm to about 300 nm or, in some embodiments, about 400 nm. And the roughness increases from about 6-8 nm to about 47-50 nm. The difference in the metal volume fraction and layer thickness between sample C1 and C2 does not affect the particle growth and roughness change. However, the unchanged roughness of the previous sample (S-SS) with double ARC and much thinner double-cermet layer may indicate that the ARC layers suppress the particle growth within the cermet or the particle growth is much less pronounced in significantly thinner cermet layers.

[0042] FIG. 5 illustrates XRD patterns for pristine and annealed cermet coatings. FIG. 5 illustrates the phase analysis before and after annealing for cermet coatings with 10 nm nickel layers disposed on stainless steel for both cermet1 and cermet2 as noted, this phase analysis was conducted using X-ray diffraction and shows the sharp peaks for the stainless steel substrate and the Ni—W alloy in the single-cermet layers. No diffraction peaks are observed for the dielectric Al_2O_3 even after annealing at 600° C. for 7 days due to its stable amorphous nature. However, X-ray diffraction spectra show an additional monoclinic FeWO_4 phase after sample annealing. Iron atoms diffuse at high temperatures from the stainless steel substrate into the cermet layer and may react with tungsten and residual oxygen to form the observed FeWO_4 phase.

[0043] FIG. 6 is a chart of Raman spectra of pristine and annealed cermet coatings. In particular, FIG. 6 illustrates Raman measurements showing two distinct peaks located at 882 cm^{-1} and 691 cm^{-1} for the annealed samples which can be traced back to A_g modes of FeWO_4 . Also, the solar absorber with thin nickel layer (S-SS) after annealing displays a very low reflectance in mid-IR range compared to that before annealing as shown in FIG. 2, which may indicate a destruction of IR reflector and a formation of nonmetallic phase between substrate and coatings. Thus, the degradation of the optical properties for the solar absorber sample (S-SS) may be the formation of FeWO_4 phase in the cermet layers at high temperature.

[0044] FIG. 7 illustrates the spectral bidirectional reflectance response of solar absorbers fabricated according to certain embodiments of the present disclosure. The solar

absorber samples (indicated by S—Ni/SS and S—W/SS in Table 1) were fabricated with 300 nm thick metal layers as the diffusion barrier between the stainless steel substrate and the double cermet layer. Nickel and tungsten were employed as indicated as the diffusion barrier metals due to their high melting point and low IR emittance which improves the spectral selectivity of the solar absorber compared to the previous sample S-SS with a very thin nickel layer. Both thick metal layers in the samples S—Ni/SS and S—W/SS significantly increased the spectral reflectance in the mid-IR range without altering the spectral response below 2.5 μm .

[0045] FIG. 8 illustrates XRD patterns of solar absorbers fabricated according to certain embodiments of the present disclosure. FIG. 8 illustrates that the sample with the thick nickel layer (S—Ni/SS) shows two nickel peaks which disappear after sample annealing, indicating that the nickel reacts with iron atoms from the SS substrate. The sample with a thick tungsten layer (S—W/SS) did not appear to be affected by the sample annealing, thus demonstrating a stable tungsten layer which prevents the iron diffusion.

[0046] FIG. 9 illustrates the experimental set up and results for steady state calorimetric measurements of samples fabricated according to certain embodiments of the present disclosure. FIG. 9 illustrates both the solar absorptance and total hemispherical emittance of a fabricated solar absorber (S—W/SS) was directly measured at elevated temperatures (up to 500° C.) using simple steady state calorimetric methods. Samples were attached to a heater assembly and suspended in a vacuum chamber. The electrical heater power input employed was directly related to the radiation heat loss from the sample surface. Thus, the total hemispherical emittance can be calculated with the electrical heater power inputs and the measured sample and surrounding temperatures. The solar absorptance was measured at elevated temperatures using a solar simulator. The sample/heater assembly is suspended in the vacuum chamber facing a viewport allowing the solar simulator beam to irradiate the sample surface. The solar absorptance can be obtained by varying the incident radiation power onto the sample and measuring the corresponding electric heater power adjustments to maintain the sample surface at a constant temperature. The near normal solar absorptance and total bidirectional emittance are calculated from the spectral reflectance data, indicating that the developed spectrally selective solar absorber with tungsten infrared reflector layer can be a good candidate for high temperature solar thermal applications (See Table 2 below).

TABLE 2

Sample	Before Annealing		After Annealing	
	Absorptance	Emittance	Absorptance	Emittance
S-SS	91.7%	8.63%	90.66%	15.99%
S-Ni/SS	93.20%	5.46%	91.38%	14.10%
S-W/SS	92.2%	5.65%	90.77%	5.7%

[0047] The near-normal solar absorptance (divergence half angle of about 15°) is close to independent of temperature with a value of about 0.9 which is in good agreement with the calculated solar absorptance from the spectral data. It has been theoretically shown that cermet-based solar absorbers exhibit a solar absorptance with only weak angle dependence. Thus, only little deviation from here demon-

strated solar absorptance should be expected even for concentrated solar power applications with a large range of incident angles. However, future research efforts could experimentally investigate the angle dependence of the solar absorptance to quantify the effect. The total hemispherical emittance shows the typical temperature dependence of a spectrally selective solar absorber with approximately 0.09 at 100° C. and 0.15 at 500° C.

[0048] FIG. 10 illustrates the spectral properties of a plurality of solar absorbers fabricated according to embodiments of the present disclosure. The tungsten metal layer thickness may be optimized to keep the production cost minimal without losing the low emittance and long term thermal stability of the solar absorber. A plurality of solar absorbers with tungsten layer thicknesses of 10, 50, 100, and 200 nm were fabricated as indicated in Table 1 and their spectral properties were compared before and after the annealing at 600° C. for 7 days. The curves in FIG. 10 of wavelength v. % reflectance are in the following order, and the corresponding compositions/configurations are listed in order below in Table 3, which comprises the same values for each composition/configuration as Table 1.

TABLE 3

Ordered Results from FIG. 10						
Sample	Substrate material	Bonding layer/IR layer thickness/type	C1 thickness (nm)	C2 thickness (nm)	ARC1 (nm)	ARC2 (nm)
S-W/SS-3	SS	100 nm W	11	28	25	55
S-W/SS-2	SS	200 nm W	11	28	25	55
S-W/SS-3 (annealed)	SS	100 nm W	11	28	25	55
S-W/SS-4	SS	50 nm W	11	28	25	55
S-W/SS-2 (annealed)	SS	200 nm W	11	28	25	55
S-W/SS-4 (annealed)	SS	50 nm W	11	28	25	55
S-W/SS-5	SS	10 nm W	11	28	25	55
S-W/SS-5 (annealed)	SS	10 nm W	11	28	25	55

[0049] For the pristine (as-made, prior to annealing if annealing is performed) samples, the tungsten layer thickness only affects the spectral reflectance at wavelength larger about 2 μ m. The annealing process, however, alters the spectral response in the complete wavelength range with the largest effect at wavelengths longer than about 1.2 μ m. The spectral reflectance increases and the thermal stability improves with increasing tungsten layer thickness. A tungsten layer thickness of 100 nm (as in examples S—W/SS-3) is sufficient to provide good (commercially scalable and usable) thermal stability and to act as a low emittance coating on stainless steel at high temperatures.

CONCLUSIONS

[0050] Iron atoms diffusing from the stainless steel substrate into the cermet layer may not have a desirable effect on the optical properties of a selective solar absorber. The spectrally selective solar absorbers fabricated according to certain embodiments of the present disclosure may be based on double cermet layers (W—Ni—Al₂O₃ cermet) with double antireflection layers on a mechanically polished stainless substrate fabricated according to embodiments of the present disclosure. In some embodiments, a 100 nm thick tungsten layer may be employed to suppress the degradation of the optical properties at high temperatures and to lower the emittance relative to the stainless steel

substrate, which improves the spectral selectivity of the solar absorber, for example, in applications where Ni may not be as effective an Fe-diffusion barrier and IR reflector. Using the materials, apparatus, systems and methods discussed herein, a solar absorber was fabricated with a solar absorptance of about 0.9 and total hemispherical emittance of about 0.15 at an operating temperature of 500° C. In alternate embodiments, this layer may comprise Tantalum (Ta), Titanium (Ti), Molybdenum (Mo), Chromium (Cr), Vanadium (V), Niobium (Nb), Zirconium (Zr), or combinations thereof.

[0051] Exemplary embodiments are specifically disclosed and variations, combinations, and/or modifications of the embodiments and/or features of the embodiments made by a person having ordinary skill in the art are within the scope of the disclosure. Alternative embodiments that result from combining, integrating, and/or omitting features of the embodiments are also within the scope of the disclosure. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g.,

from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). For example, whenever a numerical range with a lower limit, R_l , and an upper limit, R_u , is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed: $R=R_l+k*(R_u-R_l)$, wherein k is a variable ranging from 1 percent to 100 percent with a 1 percent increment, i.e., k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent, . . . , 50 percent, 51 percent, 52 percent, . . . , 95 percent, 96 percent, 97 percent, 98 percent, 99 percent, or 100 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed. Use of broader terms such as “comprises,” “includes,” and “having” should be understood to provide support for narrower terms such as “consisting of,” “consisting essentially of,” and “comprised substantially of.” Accordingly, the scope of protection is not limited by the description set out above but is defined by the claims that follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as further disclosure, and each claim is an exemplary embodiment of the present invention.

[0052] While exemplary embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the

scope or teachings herein. The embodiments described herein are exemplary only and are not limiting. Many variations and modifications of the compositions, systems, apparatus, and processes described herein are possible and are within the scope of the invention as claimed. Accordingly, the scope of protection is not limited to the embodiments described herein, but is only limited by the claims that follow, the scope of which shall include all equivalents of the subject matter of the claims. Unless expressly stated otherwise, the steps in a method claim may be performed in any order. The recitation of identifiers such as (a), (b), (c) or (1), (2), (3) before steps in a method claim are not intended to and do not specify a particular order to the steps, but rather are used to simplify subsequent reference to such steps.

1. A method of fabricating a solar absorber, comprising:
disposing a first layer in contact with a substrate;
disposing a second layer in contact with the first layer;
disposing a third layer in contact with the second layer;
disposing a fourth layer in contact with the third layer; and
disposing a fifth layer in contact with the fourth layer,
wherein disposing the fifth layer forms a solar absorber
comprising an absorbance within a first predetermined
range and an emittance within a second predetermined
range.
2. The method of claim 1, wherein the substrate comprises
at least one of stainless steel, tantalum (Ta), titanium (Ti),
copper (Cu), aluminum (Al), silicon (Si), quartz, and com-
binations thereof.
3. The method of claim 1, wherein the first layer com-
prises at least one of tungsten (W), tantalum (Ta), titanium
(Ti), and combinations thereof, and wherein a thickness of
the first layer is from about 10 nm to about 300 nm.
4. The method of claim 1, wherein the first layer com-
prises Tungsten (W), Tantalum (Ta), Titanium (Ti), Molyb-
denum (Mo), Chromium (Cr), Vanadium (V), Niobium
(Nb), Zirconium (Zr), or combinations thereof and wherein
the thickness of the first layer is from about 100 nm to about
200 nm.
5. The method of claim 1, wherein the second layer and
the third layer each comprise at least one of Nickel (Ni),
Cobalt (Co), Iron (Fe), Tungsten (W), Tantalum (Ta), Tita-
nium (Ti), Molybdenum (Mo), Chromium (Cr), Vanadium
(V), Niobium (Nb), Zirconium (Zr), and Al_2O_3 .
6. The method of claim 1, wherein the third layer has a
lower metal volume fraction than the second layer.
7. The method of claim 1, wherein the fourth layer
comprises at least one of Al_2O_3 , MgO , TiO_2 , V_2O_3 , ZrO , or
combinations thereof.
8. The method of claim 1, wherein the fifth layer com-
prises SiO_2 .
9. The method of claim 1, wherein disposing the second
layer on the first layer bonds the second layer to the
substrate.
10. A solar absorber comprising:
a reflector layer disposed in contact with a substrate;
a first cermet layer disposed in contact with the reflector
layer;
a second cermet layer disposed in contact with the first
cermet layer;

and at least two anti-reflective coating (ARC) layers,
wherein at least one ARC layer is disposed in contact
with the second cermet layer.

11. The solar absorber of claim 10, wherein the substrate
comprises at least one of stainless steel, tantalum, titanium,
copper, aluminum, silicon, quartz, and combinations
thereof.

12. The solar absorber of claim 10, wherein the reflector
layer comprises at least one of tungsten (W), tantalum (Ta),
titanium (Ti), and combinations thereof, and wherein a
thickness of the reflector layer is from about 10 nm to about
300 nm.

13. The solar absorber of claim 10, wherein the first
cermet layer and the second cermet layer each comprise at
least one of Nickel (Ni), Cobalt (Co), Iron (Fe), Tungsten
(W), Tantalum (Ta), Titanium (Ti), Molybdenum (Mo),
Chromium (Cr), Vanadium (V), Niobium (Nb), Zirconium
(Zr), and Al_2O_3 , and wherein the second cermet layer has a
lower metal volume fraction than the first cermet layer.

14. The solar absorber of claim 10, wherein the first layer
of the at least two ARC layers comprises at least one of
 Al_2O_3 , MgO , TiO_2 , V_2O_3 , ZrO , or combinations thereof.

15. The solar absorber of claim 10, wherein the second
layer of the at least two ARC layers comprises SiO_2 .

16. The solar absorber of claim 10, wherein the reflector
layer is a bonding layer between the substrate and the first
cermet layer.

17. The solar absorber of claim 10, wherein the reflector
layer comprises a plurality of separately deposited reflector
layers.

18. A solar absorber comprising:

- a reflector layer disposed in contact with a substrate;
- a first cermet layer disposed in contact with the reflector
layer, wherein the reflector layer comprises at least one
of tungsten (W) or nickel (Ni).

19. The solar absorber of claim 17, further comprising a
second cermet layer disposed in contact with the first cermet
layer and at least two anti-reflection (ARC) layers, wherein
at least one ARC layer is disposed in contact with the second
cermet layer.

20. The solar absorber of claim 17, wherein the substrate
comprises at least one of stainless steel, tantalum, titanium,
copper, aluminum, silicon, quartz, and combinations
thereof.

21. The solar absorber of claim 17, wherein a thickness of
the first cermet layer is from about 10 nm to about 300 nm.

22. The solar absorber of claim 17, wherein the first
cermet layer and the second cermet layer each comprise at
least one of Nickel (Ni), Cobalt (Co), Iron (Fe), Tungsten
(W), Tantalum (Ta), Titanium (Ti), Molybdenum (Mo),
Chromium (Cr), Vanadium (V), Niobium (Nb), Zirconium
(Zr), and Al_2O_3 , wherein the second cermet layer comprises
a lower metal volume fraction than the second layer.

23. The solar absorber of claim 17, wherein the first layer
of the at least two ARC layers comprises at least one of
 Al_2O_3 , MgO , TiO_2 , V_2O_3 , ZrO , or combinations thereof.

24. The solar absorber of claim 17, wherein the second
layer of the at least two ARC layers comprises SiO_2 .

25. The solar absorber of claim 17, wherein the reflector
layer bonds the substrate and the first cermet layer.

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