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(54) **METHOD FOR PRODUCING HIGH-PLASTICITY TI-RE ALLOYS, TI-RE ALLOYS PRODUCED USING THIS METHOD, AND THEIR APPLICATION**

(57) The invention relates to a method for producing titanium and rhenium alloys with high mechanical and thermal resistance and high plasticity, as well as titanium and rhenium alloys produced using the present method, and their application.

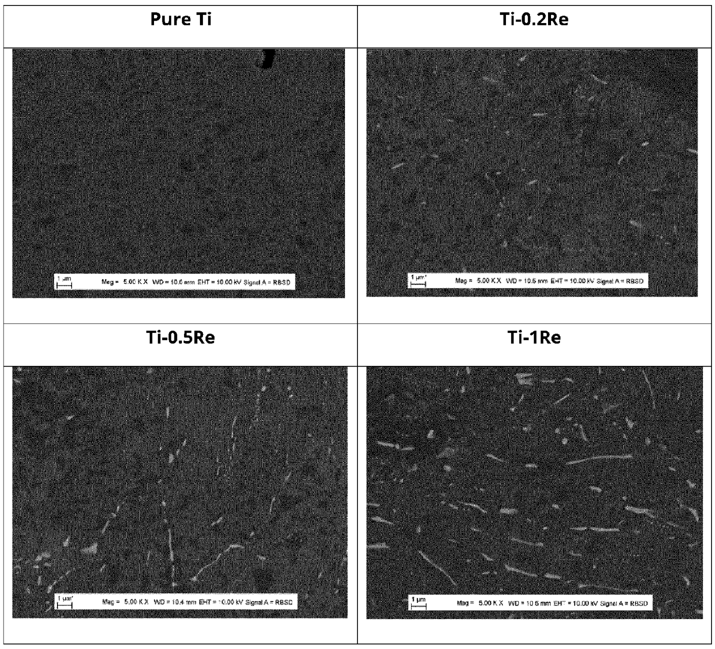

Fig. 2

EP 4 206 341 A1

Description

Technical Field

[0001] The present invention generally relates to the field of Ti metallurgy, and especially the production of alloying materials, intended for application at elevated temperatures. More particularly, the invention relates to a method for producing titanium and rhenium alloys with high mechanical and thermal resistance and high plasticity, as well as titanium and rhenium alloys produced using the present method, and their application.

Prior Art

[0002] Titanium (Ti) belongs to the group of transition metals, and it can exist as two allotropes (phases) - the low-temperature, hexagonal α-Ti, and the high-temperature, regular, spatially centred β-Ti. Mixing of titanium with other metals allows for the creation of solutions of alloying additives in said phases, and/or the creation of ordered systems of various configurations. Each of the allotropes of titanium is characterised by a different atomic structure (a different arrangement of atoms and geometry of unit cells), which translates into different physical and chemical properties of each of these allotropes. The α-Ti alloys are characterised by low density, limited plasticity, high resistance to corrosion, and good biocompatibility, while β-Ti alloys - by high absolute strength and good plasticity, also having increased density. The α-Ti phase exhibits much better resistance to high temperatures than the β-Ti phase, which is manifested by the much lower diffusivity of Ti and alloying elements in α-Ti. As a result, due to the influence of a constant load and the impact of high temperatures, elements made of α-Ti exhibit much lower structural stability, but much higher strength. Due to this, all commercial high-temperature material solutions based on titanium have the form of α-Ti alloys enriched with a number of additives occurring in the form of an α-Ti solution and small precipitates of other, usually ordered phases. The properties of the material are also influenced by the used admixtures. For example, simple metals and light elements, such as Al, Sn, O, and N, are neutral or serve the function of stabilisers of the α-Ti phase, while most transition metals, e.g. V, Mo, Cr, Fe, and Ni increase the stability of the β-Ti phase. Therefore, in order to improve the physical and chemical properties of titanium-based materials, research on the creation of alloys with admixtures of transition metals is underway. Rhenium (Re) seems to be a good candidate for an admixture; however, no wide-scale research on this element has been performed as of yet, and the collected data have not been comprehensively described, exhibiting considerable discrepancies. As a transition metal with a complex valence band, rhenium is a strong stabiliser of the β phase, and it can form other configurations having an ordered structure (intermetallic phases). The initial diagrams of thermodynamic stability assumed the presence of a complex Ti_5Re_{24} phase, while the latest research also indicates the presence of a stable TiRe phase (the ordered structure of β-Ti).

[0003] The mechanical properties of metals strongly depend on their electron and atomic structure, which is why, as already mentioned, phases with a different structure and chemical composition exhibit, e.g. different plastic properties. The basic mechanism of plastic deformation, also responsible for hardening, is the slip of dislocations - linear defects of the atomic structure, whose motion results in permanent deformation of material. Linear defects interact with the components of the alloy, which is the most important mechanism of hardening metallic materials. This hardening is more noticeable at low temperatures, while it usually weakens along with an increase at the temperature due to the activation of new motion possibilities for a linear defect. The most effective methods for hardening metals at elevated temperatures involve the creation of submicrometric precipitates of other, more stable phases, which strongly inhibit the motion of dislocations. Another method for hardening high-temperature materials is the clustering of alloying elements, which attract and immobilise linear defects by creating locally ordered clusters. Yet another effective hardening mechanism is the segregation of alloying elements on linear defects. This mechanism also involves local accumulation of admixtures which stabilise a linear defect, preventing its motion. The hardening mechanisms listed herein are currently used in Ti alloys which have very complex chemical compositions, e.g. TIMETAL 834 and TIMETAL 1100. Specific alloying additives stabilise the α-Ti phase, form small precipitates, or inhibit diffusion. Identification of the possible forms of occurrence of Re in α-Ti and their effectiveness in the context of interaction with dislocations is of fundamental significance for the application of Re, not only at high-temperature alloys, but also in typical systems, where rhenium could serve the function of an admixture, improving the final properties of the product.

[0004] The currently used titanium alloys include single-phase materials with a hexagonal (α alloys), a regular spatially centred structure (β alloys), two-phase $\alpha + \beta$, martensitic systems, as well as precipitation-hardened compositions. The primary difference between the listed types of titanium alloys is the type and concentration of alloying elements. The α alloys contain stabilising elements, or neutral towards the hexagonal phase (e.g. Al, Sn, and Zr), while the β alloys require the presence of transition metals (e.g. Nb, V, Mo, Ta, and Cr) in an amount of at least about a dozen percent by weight. Martensitic systems are derived from β alloys with the share of admixtures reduced to several percent by weight. Precipitation-hardened alloys contain the smallest amount of alloying elements, whose concentration exceeds the solubility limit in the phase undergoing hardening. The elements of precipitation-hardened alloys can include both simple metals (Al, Sn), metalloids (Si) or transition metals (e.g. Fe, Cr, Mo, and Nb) added in an amount between 0.1 and approximately 4-5% by weight to hexagonal Ti. A preferable feature of precipitation-hardened systems is the high titanium hardening capability relative to the share of admixtures, which at the same time requires the use of precise thermal treatments in order to achieve a proper size and distribution of the precipitates. However, the biggest drawback of precipitation-hardened alloys is their low ductility, hindering or even preventing plastic forming processes, and reducing the cracking resistance.

[0005] The latest achievements in the field of precipitation-hardened Ti alloys include attempts at combining various heat treatments and alloying elements resulting in a further increase in the strength of the material, without improving its plasticity - the breaking strain reaches a maximum of 15-20%, as presented, e.g. in the publication Direct imaging of short-range order and its impact on deformation in Ti-6Al (R. Zgang et al., Science Advances, 5(12), 2019), or Creep of a cast intermetallic TiAl-based alloy (J. Lapin, Kovove Materialy, 43, 2005).

[0006] The article: *Titanium alloyed with rhenium by selective laser melting* (E. Chlebus, B. Kuinicka, R. Dziedzic, T. Kurzynowski; Materials Science and Engineering: A, 620. 2015) relates to creating Ti-Re alloys using the selective laser melting method (sintering of pure Ti and Re powders). It describes the preparation and tests of Ti-Re samples with Re shares of 0.5%, 1.0%, and 1.5%. Peaks corresponding to hcp (hexagonal) α-Ti were present on the diffractograms of all samples. Very faint peaks corresponding to hcp Re occurred additionally in the diffraction images of Ti-Re samples. There were no recorded peaks originating from other phases, i.e. α", β, and ω. The authors of the publication also observed an improvement in the properties of a Ti-Re alloy compared to pure Ti - an addition of small amounts of Re dissolved in martensite increases its hardness (by a maximum of 85%), yield point (by a maximum of 125%), and tensile strength (by a maximum of 96%).

[0007] The publication: *Solid solution mechanism and thermodynamic properties of Ti-Re alloy system. Experiment and theory* (Y. Wu, W. Hu, S. Yang, S. Lou, Intermetallics, 15(8), 2007) in turn relates to the tests of thermodynamic properties of a Ti-Re alloy (Ti100-xRex [x = 4.26, 13.87, 27.78, 47.48, and 73.88 at.%]), prepared using the arc melting method. The results produced using the XRD method indicated that the lattice constant of β-Ti decreased along with an increase in the share of Re.

[0008] On the other hand, the publication: *Phase stability and thermodynamic modelling of the Re-Ti system supplemented by first-principles calculations* (Zacherl, Chelsey L., Shang, Shun-Li, Saengdeejing, Arkapol, Liu, Zi-Kui, Calphad, 38, 2012) relates to the modelling of phase stability and thermodynamics of the Re-Ti system by means of the CALPHAD technique, based on the density functional theory (the DFT method). It was predicted by calculation that the hcp phase would have positive enthalpy of mixing, and the bcc phase would have negative enthalpy of mixing, which indicates a strong tendency to dissolve Re in bcc-Ti.

[0009] The Japanese application JP1989252746A discloses a titanium-based alloy containing between 0.01% and 5% by weight of rhenium, which is characterised by high corrosion resistance in an acidic environment. The alloy can also contain Ni, Mo, W, V, Nb, Zr, Ta, Ru, and Pd.

[0010] On the other hand, the European patent application EP0504218A1 relates to an alloying material treatment method, namely an aluminium alloy treatment method, whose steps include annealing of the alloy at a given temperature, cold rolling as well as fast heating and cooling, which are performed after cold rolling in order to recrystallise the structure.

[0011] The European Patent EP2563942B1 in turn discloses an alloy of titanium and other metals, and a method for its production, the method comprising an annealing step intended to create a single-phase microstructure of the β phase, preferably at a temperature of up to approximately 950°C, and a step of cooling the alloy from the β phase to the α phase.

[0012] Another patent document FR2213986B1 discloses an alloy of titanium with Al, Zr, Sn, Mo, W, Si, and Cr, additionally containing 0.05 - 0.1% by weight of rhenium. According to this document, the addition of rhenium to such an alloy results in increasing the resistance and thermal stability of the alloy, as well as increasing its fatigue limit and resistance to creep.

[0013] Therefore, the latest achievements in the field of Ti alloys (and methods for creating other hardened alloys) include attempts at combining various heat treatments and alloying elements, usually by sintering pure powders, which results in increased strength of the material, but with no significant improvement in its plasticity - in the case of Ti alloys, the breaking strain reaches a maximum of 15-20%.

[0014] It should be pointed out that the melting point of rhenium is 3185°C, and the boiling point of titanium is approximately 3287°C.

Summary of the Invention

[0015] The method for creating a titanium and rhenium alloy according to the invention comprises the following steps:

(i) preparing a mixture of titanium and rhenium, the mixture containing between 0.2 and 1.0% by weight of rhenium, titanium and possible impurities, preferably in an amount of up to 0.5% Fe and 0.4% O;
(ii) recasting the mixture at least once at a temperature at least equal to the melting point of Re;

(iii) casting the alloy;
(iv) performing homogenisation annealing at a temperature at least equal to the $\alpha \rightarrow \beta$ transition temperature of the alloy;
(v) cooling the alloy in water from the β phase to the α phase;
(vi) performing alloy forming processes;
(vii) optionally, performing recrystallisation annealing at the temperature of stability of the α-Ti phase, below the $\alpha \rightarrow \beta$ transition temperature;
(viii) cooling the resulting material.

[0016] Impurities can serve the function of regular, i.e. desirable alloying elements in specific alloys.
[0017] Preferably, in step (ii), the recasting temperature is higher than the melting point of Re and lower than the boiling point of Ti.
[0018] Most preferably, recasting of the mixture in step (ii) is performed using the arc melting method.
[0019] Preferably, recasting of the mixture in step (ii) is performed five times.
[0020] Homogenisation annealing in step (iv) can be performed at a temperature of at least 882°C, preferably at least 900°C.
[0021] Preferably, homogenisation annealing in step (iv) is performed for a time of at least 30 minutes.
[0022] Most preferably, cooling in step (v) is performed in water, preferably at room temperature.
[0023] In step (vi), the forming processes can be performed by cold rolling of the cooled alloy, followed by recrystallisation annealing in accordance with step (vii) and cooling in accordance with step (viii), with a furnace or in the air.
[0024] Preferably, cold rolling in step (vi) is performed until reaching a reduction of at least 50% of the thickness of the material, preferably 80% of the thickness of the material.
[0025] Preferably, recrystallisation annealing in step (vii) is performed at the temperature between 800°C and 880°C, preferably 820°C.
[0026] Most preferably, recrystallisation annealing in step (vii) is performed for a time of at least 15 minutes.
[0027] Cooling in step (viii) can be performed with a furnace, preferably at a rate of at least 1°C/min, or in the air, preferably at room temperature.
[0028] Alternatively, in step (vi), the forming processes can be performed by hot forging above the α -> β transition temperature, followed by the performance of cooling in the air, preferably at room temperature, in accordance with step (viii).
[0029] The titanium and rhenium alloy according to the invention is produced using the method for creating a titanium and rhenium alloy according to the invention.
[0030] The titanium and rhenium alloy according to the invention is applicable to the production of bearing elements of light constructions, and/or sheathing in the form of sheet metal and/or elements of mechanical systems and/or elements intended for working at elevated temperatures.

Preferable Effects of the Invention

[0031] The biggest drawback of known precipitation-hardened Ti alloys is their low ductility, hindering or even preventing plastic forming processes, and reducing the cracking resistance. The maximum value of the breaking strain of Ti alloys known from the literature is 15-20%, which is a relatively low value, and it does not allow for full exploitation of the potential of titanium alloys. Because of the method according to the present invention, it is possible to produce a material with both high strength as well as extremely high plasticity and ductility. This enables smooth forming processes of such materials, with a reduction in the cross-section reaching 80%. Such high plasticity is desired in materials based on Ti, and at the same time virtually unheard-of in known commercial alloys. Moreover, the hardening efficiency of Re expressed as the shares of alloying elements by weight (in relation to the weight of the materials used to produce the alloy) is several times higher than in the case of typical additives (e.g. Al and Sn).

Brief Description of Drawings

[0032]

Figs. 1a, 1b present the binding energy E_B of the alloying element - vacancy (Fig. 1a) and alloying element - alloying element (Fig. 1b) pairs in the α-Ti phase, respectively, as a function of their distance expressed as the next closest position, the positive/negative values meaning the attraction/repulsion of the defects.
Fig. 2 presents the structure of pure Ti as well as the Ti-0.2Re, Ti-0.5Re, and Ti-1Re alloys (observations performed under a scanning electron microscope);
Fig. 3 presents the structure of the Ti-0.5Re alloy (observations performed under a transmission electron microscope);

Fig. 4 presents the stress-strain curves of the Ti-0.2Re, Ti-0.5Re, and Ti-1Re alloys (concentration by weight), and pure Ti (the reference system);

Figs. 5-7 present the stress-strain curves of the Ti-3(6)Al(Sn,In) alloys, the symbols P and W indicating the type of heat treatment: cooling in a furnace and cooling in water, respectively, and the numerical values within a range of 750-930 describe the annealing temperature;

Fig. 8 presents a graph depicting changes in the lattice parameters of the α-Ti structure as a function of the Re content;

Fig. 9 presents the results of measuring the electrical resistance of the Ti-0.5Re alloy as a function of temperature;

Fig. 10 presents the results of measuring the electrical resistance of the Ti-0.5Re alloy as a function of temperature.

Detailed Description of the Preferred Embodiment

[0033] The developed research methodology included work of a theoretical (modelling of the structure of Ti-Re alloys and other selected reference systems) and experimental nature (production and treatment, observations of the structure, measurements of mechanical properties).

The Theoretical Part

[0034] Theoretical studies preceding the experimental tests were performed using the VASP package (*Vienna Ab Initio Simulation Package*), and they were based on the DFT (*Density Functional Theory*). The capabilities of the DFT approach were used generally to determine the stability of Re in α-Ti, the preferred allotrope, which determines the hardening capability, the mobility, and interactions with other potential elements present in known Ti alloys. These results allowed for conscious control of the properties of the tested systems by modifying the chemical composition and the form of heat treatment. The applied parameters and numerical algorithms enabled achieving high precision of the whole procedure, which has been assessed based on a comparison of the calculated parameters of the crystal structure of α-Ti (a = 2.92 A, c = 4.63 A, c/a = 1.586) with experimental data (a = 2.95 A, c = 4.68 A, c/a = 1.587).

[0035] The energy of formation E_T is one of the basic thermodynamic values describing the stability of the tested systems. Calculations of the energy of formation for point defects in the lattice of α-Ti (for Al, Si, Re, and Mo) proved that the lower its value, the higher the thermodynamic stability of the system, which, considering the calculated values of the energy of formation, means that Al and Si have a greater tendency to create the α-Ti phase, while Mo and Re are characterised by lower solubility in hexagonal Ti. The values of $E_{T(iso)}$ also (indirectly) indicate the strongest hardening effect in the case of Re. The energies of formation of point defects - Re, Mo, Al, and Si in α-Ti - are presented in Table 1 below, $E_{T(bulk)}$ standing for the structural stability of α-Ti solutions with respect to two independent and most stable phases of the elements forming an alloy, and $E_{T(iso)}$ standing for absolute structural stability, taking into account overall structural stability.

Table 1. The energies of formation of point defects: Re, Mo, Al, and Si in α-Ti.

	Re	**Mo**	**Al**	**Si**
$E_{T(bulk)}$ [eV]	0.235	0.565	-0.917	-1.560
$E_{T(iso)}$ [eV]	-10.911	-9.998	-4.569	-6.824

[0036] Identifying the binding energy E_B of the alloying elements (Fig. 1) was particularly important for determining the form of occurrence of Re in α-Ti (which directly influences the properties of the alloy). The produced results indicate very strong binding of Re, which proves a tendency to create clusters or precipitates. Moreover, the attraction of Re-Re pairs occurs in each of the analysed positions. Mixing Re with other alloying elements also results in mutual attraction, which suggests high efficiency in the ordering of alloying elements. This behaviour is particularly preferable at high-temperature alloys, where stable precipitates/clusters of atoms constitute the most efficient hardening mechanism. The very strong ability to create clusters of admixtures also leads to local deformation of the α-Ti structure. The lattice deformation observed in the case of Re suggests the possibility of diffusional generation of an ordered configuration of the β-Ti phase (the TiRe structure), which in addition is highly resistant to dislocation slip. The calculated values presented in Fig. 1 indicate the strongest binding of vacancies by Re, which is one of the factors determining the diffusivity and structural stability of the system at elevated temperatures. However, determination of these features required identifying the migration energy of the elements.

[0037] The migration energy E_M of the alloying elements is determined by an energy barrier accompanying the process of changing the position of an alloying element by a vacancy (the mutual exchange of positions of the admixture and the vacancy) or interstitial mechanism. The analysed systems have the nature of substitutional solutions, which is why only the vacancy mechanism is active. In the case of a hexagonal structure, diffusion of an atom can proceed in two directions, i.e. along the base of a unit cell ($E_{M(a)}$), and perpendicularly thereto ($E_{m(c)}$). The results of the calculated migration energies for the tested alloying elements are presented in Table 2.

Table 2. The migration energies of selected alloying elements determined for diffusion along the base of a unit cell ($E_{M(a)}$) of α-Ti, and perpendicularly thereto ($E_{M(c)}$).

	Re	Mo	Al	Si
$E_{M(a)}$	0.647	0.327	0.754	1.075
$E_{M(c)}$	0.763	0.332	0.920	1.405

[0038] Based on the produced results, it was concluded that: (i) Si exhibits the highest value of migration energy (for this reason, Si is the primary additive at high-temperature Ti alloys); (ii) the migration energy of Re is relatively high compared to Mo; (iii) Al and Re are characterised by similar values of migration energy, which along with the high energy of binding the vacancies by Re proves its strong capability of clustering and/or generating precipitates. It is a desired structural effect, since it results in the highest material hardening capabilities. High Re atom binding values also mean high stability of clusters/precipitates at elevated temperatures. This feature is required in the case of high-temperature materials.

The Experimental Part

[0039] Experimental work included the creation of a series of model Ti-Re systems with variable Re concentrations ranging from 0.2 to 1.0% by weight, using the arc melting technology. The research methodology also included processing the material to the form in which commercial Ti alloys are offered. To this end, a remelted, thermally homogenised and cooled material underwent cold forming processes and single-stage heat treatment, aimed at obtaining a final, recrystallised and equiaxial microstructure. The work sequence, the range of the used draft (thickness reduction during rolling) and of the annealing temperatures fully corresponded to the real, large-scale Ti production processes. The resulting material underwent tests aimed at: (i) measuring the mechanical properties of the produced materials; (ii) analysing the microstructure in a normalised state; (iii) determining the phase composition and its homogeneity. Therefore, the technological work also included preparation of samples for the individual tests, including cutting, chemical and ultrasonic cleaning, grinding, polishing, mounting, etc.

The procedure of creating Ti-Re alloys - a preferable embodiment of the invention

[0040] Metallic rhenium in the form of pressed tablets (pellets) with a total mass of 28 g was used to create the samples. The input materials (Ti with purity of 99.98% and Re with purity of 99.9%) were cut and cleaned chemically and ultrasonically. Four mixtures of substrates were prepared, with the following Re concentrations: 0 (pure Ti), 0.2, 0.5, and 1 wt%, where the sample containing pure titanium was the reference sample. The individual steps of the process used known industrial methods from the field of titanium metallurgy, i.e. heating furnaces and rolling mills, as well as other tools for forming processes.

[0041] In order to produce the alloys, the input material underwent two-step heat treatment, including in general:

- homogenisation annealing after casting the alloy, the annealing temperature being at least equal to the $\alpha \rightarrow \beta$ transition temperature of the alloy, and the minimum annealing time being 30 minutes;
- recrystallisation annealing after the forming processes, at a temperature below the $\alpha \rightarrow \beta$ transition temperature of the alloy, and for a time of at least 15 minutes.

[0042] More particularly, in the embodiment, the procedure of creating Ti-Re alloys according to the invention included the following sequence:

(i) Preparing a mixture of titanium and rhenium powders, the mixture containing 0.2, 0.5, and 1% by weight of rhenium, with the rest being titanium and possible impurities.

(ii) Recasting the input materials five times using the arc melting method. The maximum temperature of the process did not exceed the boiling point of Ti, and at the same time it was lower than the melting point of Re.

[0043] Repeated recasting is used when mixing metals with a considerable difference in the melting point, and it favours uniform distribution of the alloying elements. The work was performed using a BOHLER Arc Melting System AM 500 machine, under high vacuum conditions (10^{-3} - 10^{-5} mbar), and recasting was performed at a temperature not exceeding the boiling point of Ti, and at the same time higher than the melting point of Re.

[0044] It is possible to use a lower number of recastings (at least one recasting), which depends on the amount of the substrates undergoing melting. The minimum number of substrate recasting cycles should enable producing a chemically homogeneous alloy.

(iii) Casting the alloy.

(iv) Homogenisation annealing.

[0045] Homogenisation annealing is performed at a temperature above the $\alpha \rightarrow \beta$ transition temperature of the alloy, i.e. above 882°C. In the embodiment, annealing was performed at a temperature of 900°C and over a time of 30 minutes. This step was supposed to homogenise the microstructure (elimination of unpreferable morphology comprising zones of frozen grains, columnar grains, and dendrites of variable size) and chemical composition.

(v) Cooling in water.

[0046] Cooling in water from the temperature of a single-phase solution, from the β phase to the α phase, prevented the creation of precipitates which could hinder further treatment. Because of the use of water, the material is cooled down in several seconds, due to which there is no time for the action of diffusion - this prevents the process of creating precipitates and/or nucleation of new phases (to generate them, it is necessary to perform cooling 'with a furnace' for at least several minutes, or slow cooling in the air).

(vi) Cold rolling.

[0047] Cold rolling of the cooled alloy was performed until reaching an 80% reduction in the thickness of the material. The forming processes enabled the introduction of a considerable number of structural defects constituting recrystallisation nuclei, which were necessary to perform the next step.

(vii) Recrystallisation annealing at the temperature of stability of the α-Ti phase.

[0048] The final step of treatment was performed at the temperature of stability of the α-Ti phase, i.e. below the $\alpha \rightarrow \beta$ transition temperature, and it resulted in complete recrystallisation of the material, and in creating a homogeneous, equiaxial microstructure (referring to the commercial materials). The process was performed under vacuum conditions of 10^{-3} mbar. In the embodiment, annealing was performed at a temperature of 820°C and over a time of 15 minutes.

[0049] Alternatively, it is possible to perform annealing in an air atmosphere, such a case necessitating the removal of the top layer of oxidised material after the process.

(viii) Cooling with a furnace.

[0050] Cooling with a furnace was performed at an average rate of 6°C/min. Alternatively, step (viii) could have been executed by cooling in the air (at room temperature). The reference sample (pure Ti) was prepared in an analogical manner.

The resulting Ti-Re alloy

[0051] The method for creating Ti-Re alloys described above allowed for the production of materials with a previously unknown structure. The resulting alloys generally constituted a binary Ti-Re system, with a rhenium content between 0.2 and 1.0 wt%. The described heat treatment resulted in achieving a homogeneous structure of the material, consisting of a hexagonal phase saturated with rhenium, and two types of precipitates present at the boundaries of the α phase and inside it, these elements of the structure of Ti-Re alloys along with residual Re dissolved in the matrix allowing for achieving the required preferable properties. The Ti-0.2Re, Ti-0.5Re, and Ti-1Re alloys created according to the above pattern were characterised by high strength and an at least double increase in the yield point with respect to pure Ti, and high ductility of at least 35% of the breaking strain. The lack of a clear drop in plasticity with a simultaneous increase in strength is a unique feature of the developed Ti-Re alloys. The properties of the produced materials and the methods of their measurement are further described below.

[0052] Microscopic photographs of the produced alloys, taken by means of a scanning electron microscope, are presented in Fig. 2. The dark area indicates the Ti matrix, and the bright colour marks Ti-Re precipitates. Fig. 3 presents a photograph of the structure of a Ti-0.5Re alloy, taken using a transmission electron microscope. The bright area indicates the Ti matrix, and the dark colour marks Ti-Re precipitates. The smallest dimension of precipitates located at the boundaries of α grains does not exceed $1*10^{-6}$ m. The size of precipitates concentrated inside the grains does not exceed $2*10^{-7}$ m. The above elements of the structure of Ti-Re alloys, along with residual Re dissolved in the matrix, allow for achieving the required properties.

Measurements of mechanical properties

The static tension test

[0053] The static tension test allowed for measuring the yield point, the tensile strength, the breaking strain, work hardening, and rigidity (Young's modulus). As a result, this method allowed for determining the hardening capabilities of Ti by alloying with Re. The static tension test, whose results are presented in Fig. 4, involved alloys with the following compositions: Ti-0.2Re, Ti-0.5Re, and Ti-1Re. The produced results indicate a very strong, 2.3-time increase in the yield point compared to pure Ti, achieved already for an Re concentration of 0.2 wt%. A further increase in the Re content results in a non-linear hardening effect, i.e. a minor difference in the strength of the Ti-0.5Re alloy, and a 2.7-time increase in the yield point in the Ti-1Re system. The observed changes in mechanical properties can be the result of the activation of new hardening mechanisms - the Ti-0.2Re and Ti-0.5Re alloys fall within the range of solubility of Re in the α-Ti phase, while, in accordance with the available thermodynamic data, the Ti-1Re system should belong to the group of pseudo-a alloys, in which the β-Ti phase is present in a small amount (below 1% by volume). The presence of an additional phase usually leads to the hardening of Ti alloys at room temperature; however, due to high diffusiveness, the share of this phase should not exceed 1-2 vol% in the case of materials for high-temperature applications. A characteristic feature of the Ti-0.2Re sample is the effect of the absence of work hardening after passing the yield point. This effect occurs in alloys indicating strong interaction between the alloying elements and linear defects - it is necessary to exceed the critical energy barrier associated with the release of dislocations from the area of interaction with the admixture, followed by a clear increase in deformation until encountering another atom of the alloying element. The Ti-0.5Re alloy does not exhibit this dependence, which means that with an increase in the concentration of Re, the impact of dislocations and admixtures has a continuous nature. Another unique feature of the produced materials is their high plasticity in spite of a noticeable increase in strength. A typical effect of hardening by alloying is a noticeable drop in the breaking strain. The Ti-0.2Re and Ti-1Re alloys exhibit only a 5-7% drop in the strain compared to pure Ti, while the Ti-0.5Re system retains a breaking strain above 35%. This phenomenon does not occur in any typical Ti alloys (or other construction materials). The produced results were compared to measurements performed for other alloys containing admixtures (Al, Sn, and In) which were the most effective in the context of hardening capabilities. In order to compare the produced results, Figs. 5-7 present the stress-strain curves of Ti-3(6)Al(Sn, In) alloys. The symbols P and W in these figures indicate the type of heat treatment: cooling in a furnace (P) and cooling in water (W), respectively, and numerical values within a range of 750 - 930 describe the annealing temperature. The level of hardening achieved in the Ti-0.2Re alloy requires using Al or Sn in an amount of 3 at.% (1.7 if expressed in wt%), which means an 8.5 times higher efficiency of Re. With respect to atomic concentrations (the concentration of admixtures in the atomic structure is different from a weight-based concentration due to differences in their density - 0.2 wt% Re equals 0.05 at.% Re), the hardening effect of Re is 60 times higher. Therefore, alloys produced using the method according to the invention are characterised by an at least double increase in the yield point compared to pure Ti, and by high ductility of at least 35% of the breaking strain (Fig. 4).

Analysis of the microstructure of Ti-Re alloys

[0054] An analysis of the microstructure in a normalised state enabled a general assessment of the structure of the material with respect to macro- and microscopic defects, as well as characterisation of the microstructure of the materials - as a result, it was possible to determine the influence of rhenium on the microstructure. The first step of structural tests involved an analysis of the phase composition of the created materials using diffraction methods - high-resolution tests of X-ray diffraction. On the resulting diffractograms, the main signal originating from the α-Ti phase was observed along with an additional signal, indicating the presence of locally ordered structures (clusters of Re atoms) and the precipitates of the β phase in the Ti-0.5Re and Ti-1Re alloys.

[0055] The diffraction tests were also used to asses deformations of the α-Ti structure by measuring the a and c parameters of the crystal structure of the created materials. The results presented in Fig. 8 depict clear changes in these values, which proves the high degree of Ti hardening by Re. In addition, deformation of the crystal structure does not occur linearly as a function of the Re concentration, which corresponds to the results of strength tests. The produced results also suggest that the processes of Re clustering and/or the precipitation of a new phase are very intense in the Ti-1Re alloy.

Evaluating the stability of clusters/precipitates at an elevated temperature

[0056] In order to evaluate the stability of clusters/precipitates at an elevated temperature, high-resolution measurements of electrical resistance were performed as a function of temperature. The electrical resistance of the material changes with an increasing temperature, which is a result of higher phonon vibration energies, and it is sensitive to any processes related to nucleation or the disintegration of ordered structures and the precipitates of new phases. The produced results are presented in Figs. 9 and 10. An increase in resistance was observed up to the phase transition temperature (approximately 880°C), not accompanied by periodic disturbances, and the dynamics of changes in the electrical resistance are stabilised approximately 100°C below the temperature of structural transition. The second annealing cycle of the same material has led to a much lower increase in resistance, which indicates the creation of Re-rich stable precipitates or atomic clusters during the first operation. These structures do not exhibit a clear order/disorder transition temperature, since the resistance curve has no considerable changes in the slope. The change in the resistance R(a) and the dT derivative of resistance (Fig. 9b) indicate the absence of clear temperatures of the beginning and the end of the ordering/precipitation process for a new phase. There was an observed tendency to create stable clusters of Re atoms in a broad temperature spectrum, which is preferable from the point of view of active hardening mechanisms (and which is consistent with the results of computer simulations).

Summary

[0057] The resulting materials are characterised by very good ductility, which enables their smooth forming processes, with a reduction in their cross-section reaching 80%. Such high plasticity is desired in materials based on Ti, and at the same time rarely observed in commercial alloys. The performed measurements of mechanical properties indicated very high Ti hardening capabilities of Re, with no simultaneous drop in plasticity, which is also a unique feature of the developed materials. The hardening efficiency of Re, expressed as the share of the alloying elements by weight, is 8.5 times higher than for typical additives (Al and Sn), while in terms of atomic concentration the recorded hardening capabilities were 60 times higher. Heat treatment resulted in the creation of materials with a homogeneous structure, consisting of a hexagonal phase saturated with rhenium, and two types of precipitates present at the boundaries of the α phase and inside it. Alloys produced in accordance with the method according to the invention are characterised by an at least double increase in the yield point compared to pure Ti, and by unprecedented ductility of at least 35% of the breaking strain. The lack of a significant drop in plasticity, with a simultaneous very clear increase in strength, is a unique feature of the developed Ti-Re alloys. Theoretical and experimental structural tests proved that Re tends to create local clusters (ordered clusters or precipitates of a new phase), which ensure a high improvement in mechanical properties. Strong interactions have been confirmed between Re atoms, and between Re atoms and other alloying elements. To sum up, the addition of Re results in very preferable changes in the properties of Ti, but it can be used in a limited amount (above 1 wt% it creates brittle phases). The unique hardening effect makes it an efficient alloying additive which does not impair other key features of the material, such as its plasticity.

Claims

1. A method for producing a titanium and rhenium alloy, **characterised in that** it comprises the following steps:

   (i) preparing a mixture of titanium and rhenium, the mixture containing between 0.2 and 1.0% by weight of rhenium, titanium and possible impurities, preferably in an amount of up to 0.5% Fe and 0.4% O;
   (ii) recasting the mixture at least once at a temperature at least equal to the melting point of Re;
   (iii) casting the alloy;
   (iv) performing homogenisation annealing at a temperature at least equal to the $\alpha \rightarrow \beta$ transition temperature of the alloy;
   (v) cooling the alloy in water from the β phase to the α phase;
   (vi) performing alloy forming processes;
   (vii) optionally, performing recrystallisation annealing at the temperature of stability of the α-Ti phase, below the $\alpha \rightarrow \beta$ transition temperature;
   (viii) cooling the resulting material.

2. The method according to claim 1, **characterised in that** in step (ii), the recasting temperature is higher than the

melting point of Re and lower than the boiling point of Ti.

3. The method according to claim 1 or 2, **characterised in that** recasting of the mixture in step (ii) is performed using the arc melting method.

4. The method according to claim 3, **characterised in that** recasting of the mixture in step (ii) is performed five times.

5. The method according to any of the preceding claims, **characterised in that** homogenisation annealing in step (iv) is performed at a temperature of at least 882°C, preferably at least 900°C.

6. The method according to any of the preceding claims, **characterised in that** homogenisation annealing in step (iv) is performed for a time of at least 30 minutes.

7. The method according to any of the preceding claims, **characterised in that** cooling in step (v) is performed in water, preferably at room temperature.

8. The method according to any of the claims from 1 to 7, **characterised in that** in step (vi), forming processes are performed by cold rolling of the cooled alloy, followed by recrystallisation annealing in accordance with step (vii) and cooling in accordance with step (viii), with a furnace or in the air.

9. The method according to claim 8, **characterised in that** cold rolling in step (vi) is performed until reaching a reduction of at least 50% of the thickness of the material, preferably 80% of the thickness of the material.

10. The method according to claim 8 or 9, **characterised in that** recrystallisation annealing in step (vii) is performed at a temperature between 800°C and 880°C, preferably 820°C.

11. The method according to claim 10, **characterised in that** recrystallisation annealing in step (vii) is performed for a time of at least 15 minutes.

12. The method according to claim 8 or 9 or 10 or 11, **characterised in that** cooling in step (viii) is performed with a furnace, preferably at a rate of at least 1°C/min, or in the air, preferably at room temperature.

13. The method according to any of the claims from 1 to 7, **characterised in that** in step (vi), the forming processes are performed by hot forging above the α -> β transition temperature, followed by the performance of cooling in the air in accordance with step (viii), preferably at room temperature.

14. A titanium and rhenium alloy produced using the method according to any of the claims from 1 to 13.

15. The application of the titanium and rhenium alloy according to claim 14 to the production of bearing elements of light constructions, and/or sheathing in the form of sheet metal and/or elements of mechanical systems and/or elements intended for working at elevated temperatures.

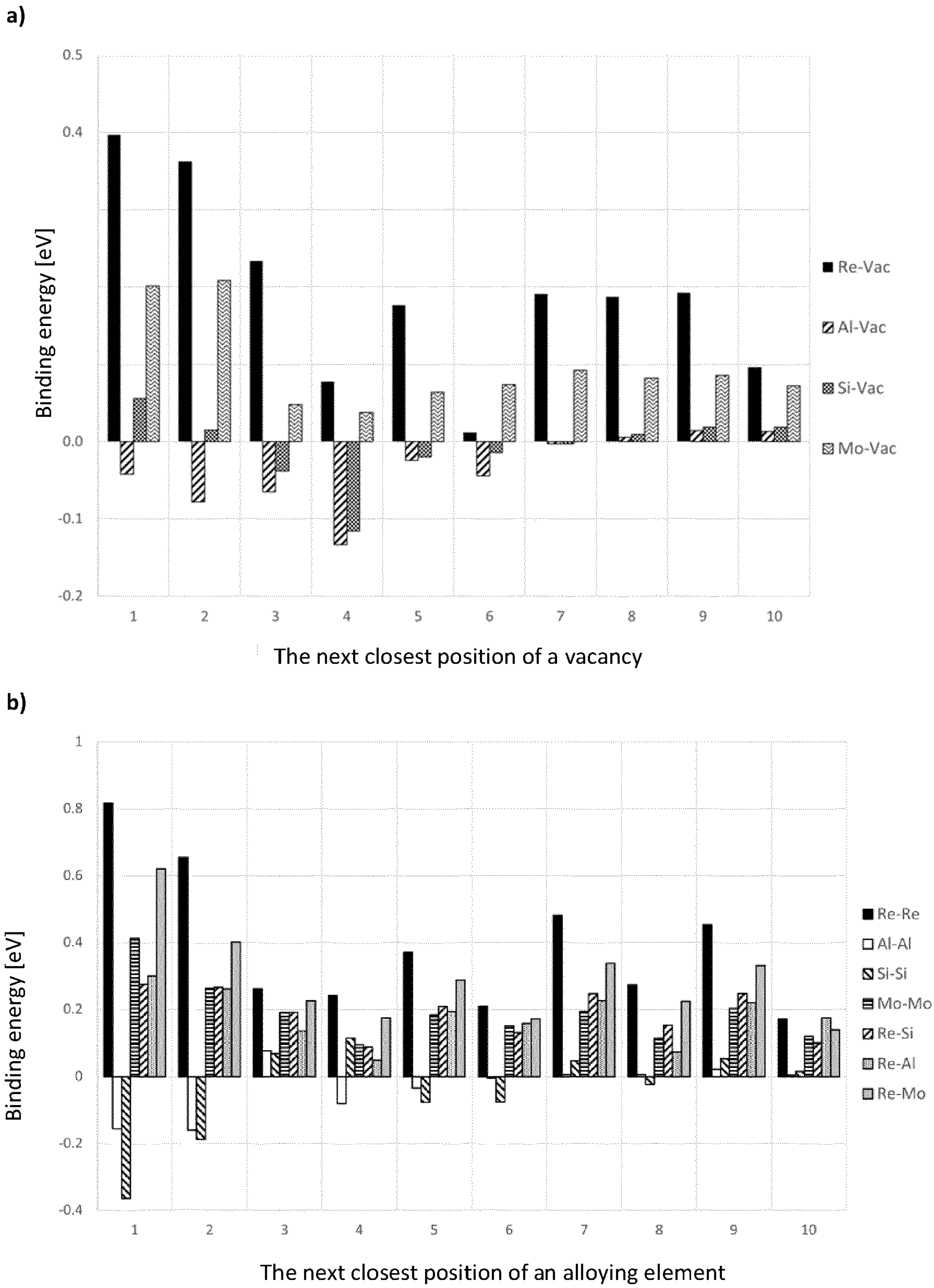
a)
0.5
0.4
0.0
-0.1
-0.2
Binding energy [eV]
1
2
3
4
5
6
7
8
9
10
The next closest position of a vacancy
Re-Vac
Al-Vac
Si-Vac
Mo-Vac
b)
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
Binding energy [eV]
The next closest position of an alloying element
Re-Re
Al-Al
Si-Si
Mo-Mo
Re-Si
Re-Al
Re-Mo

Fig. 1

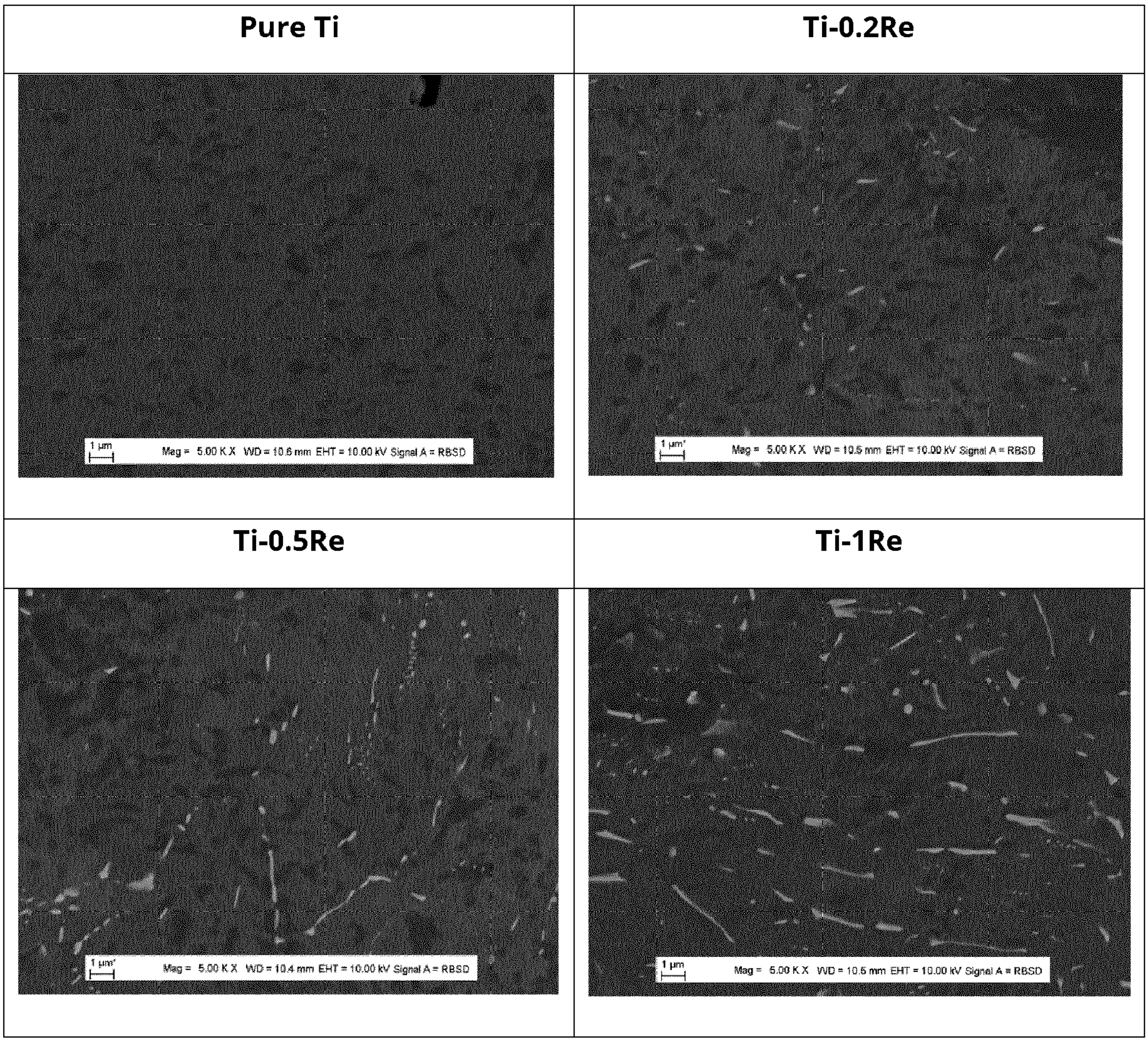

Fig. 2

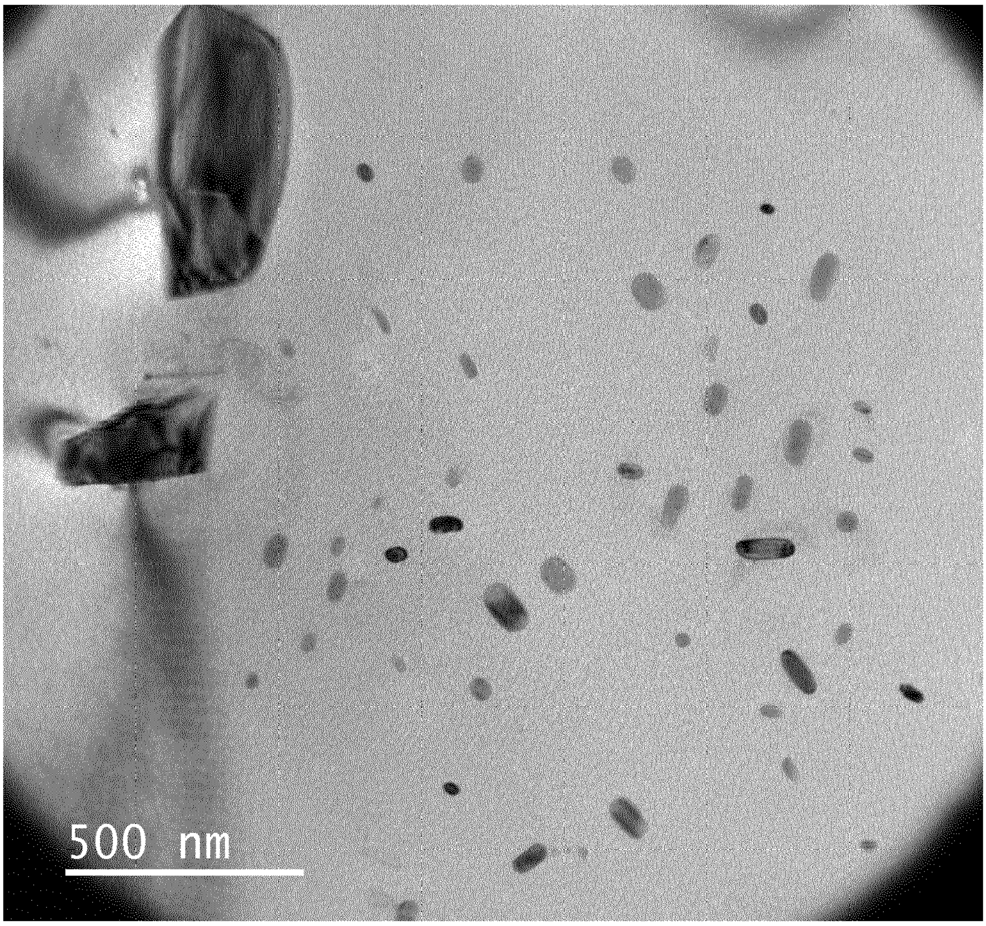

Fig. 3

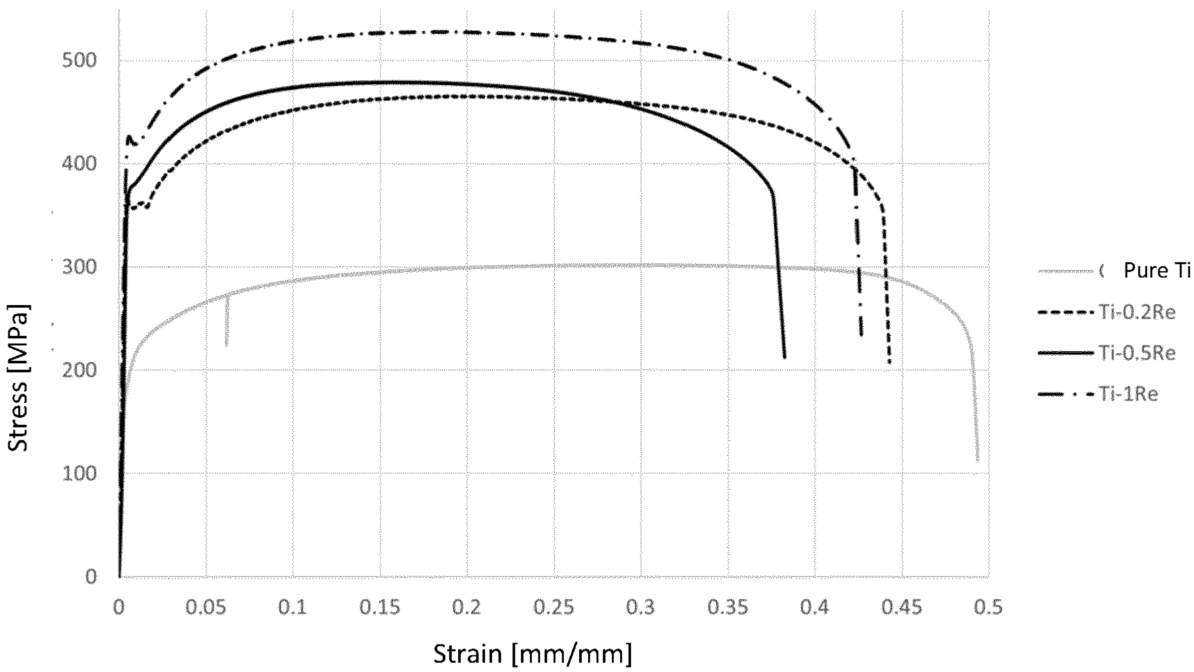
500
400
300
200
100
0
Stress [MPa]
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
Strain [mm/mm]
Pure Ti
Ti-0.2Re
Ti-0.5Re
Ti-1Re

Fig. 4

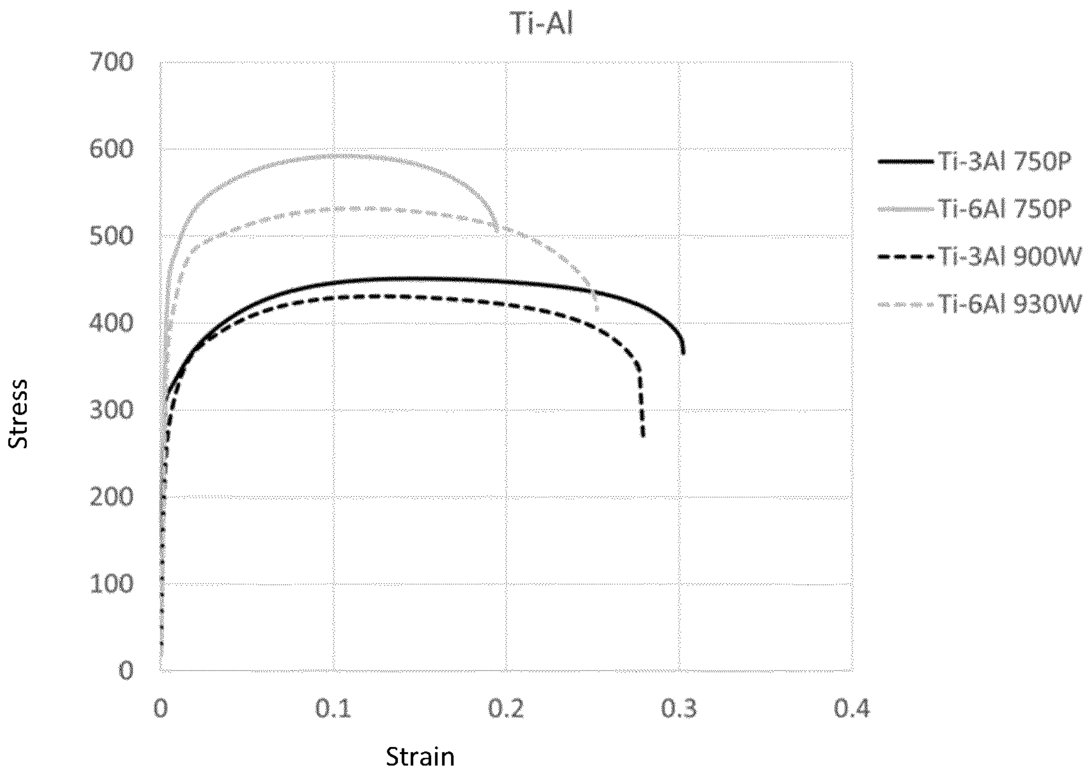
Ti-Al
700
600
500
400
300
200
100
0
Stress
0
0.1
0.2
0.3
0.4
Strain
Ti-3Al 750P
Ti-6Al 750P
Ti-3Al 900W
Ti-6Al 930W

Fig. 5

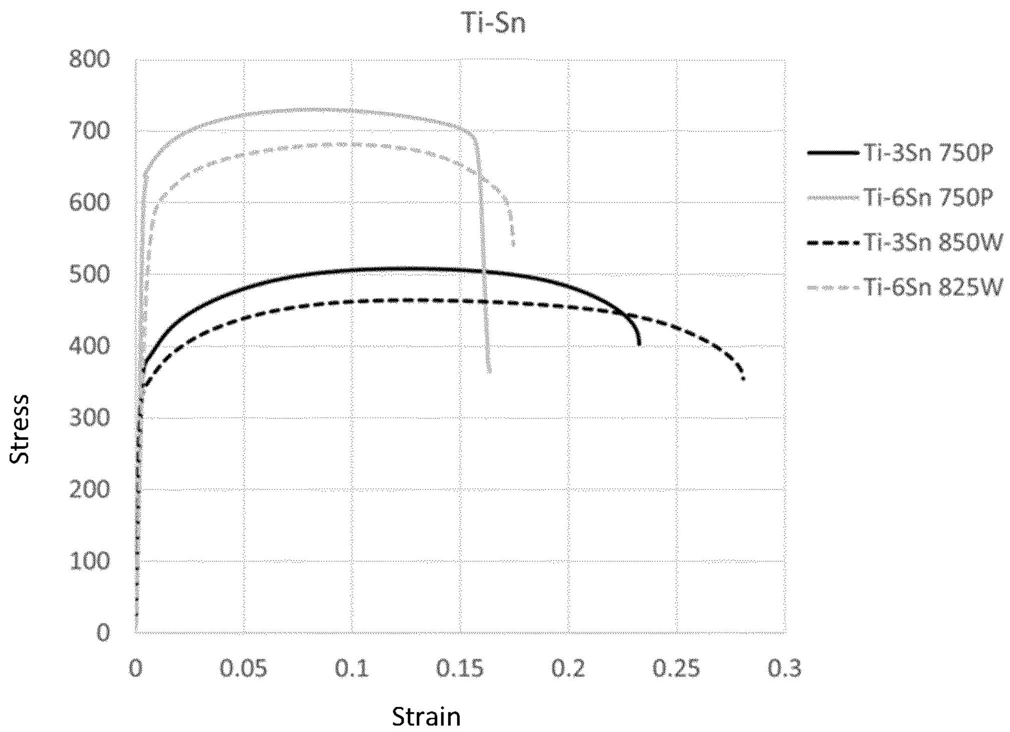
Ti-Sn
800
700
600
500
400
300
200
100
0
Stress
0
0.05
0.1
0.15
0.2
0.25
0.3
Strain
Ti-3Sn 750P
Ti-6Sn 750P
Ti-3Sn 850W
Ti-6Sn 825W

Fig. 6

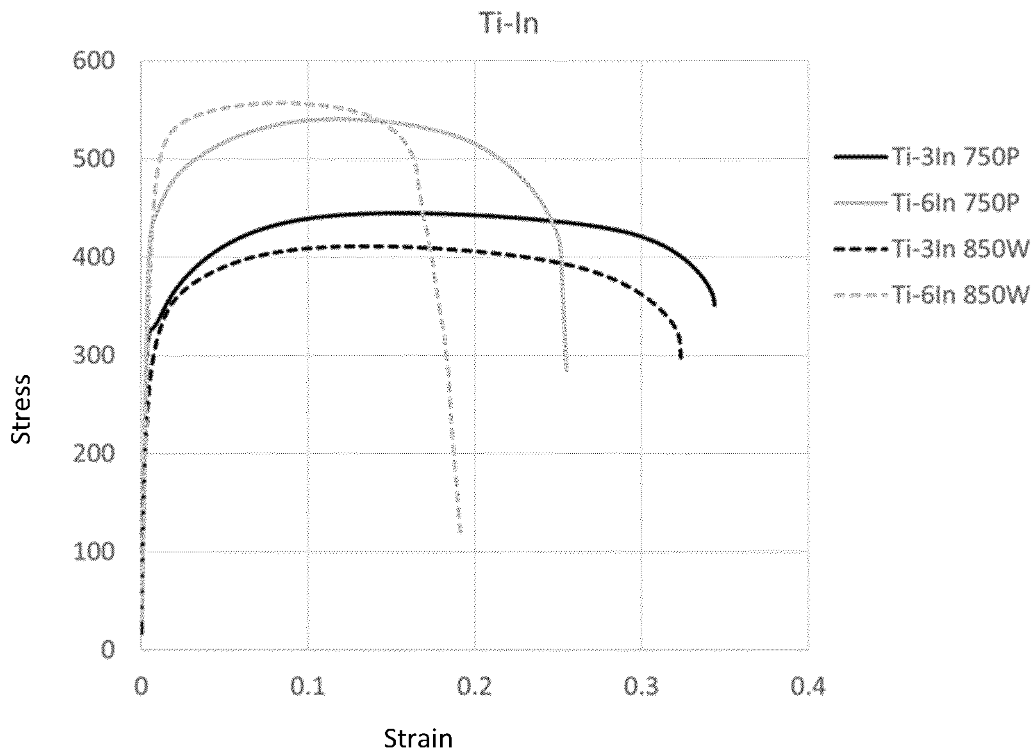
Ti-In
600
500
400
300
200
100
0
Stress
0
0.1
0.2
0.3
0.4
Strain
Ti-3In 750P
Ti-6In 750P
Ti-3In 850W
Ti-6In 850W

Fig. 7

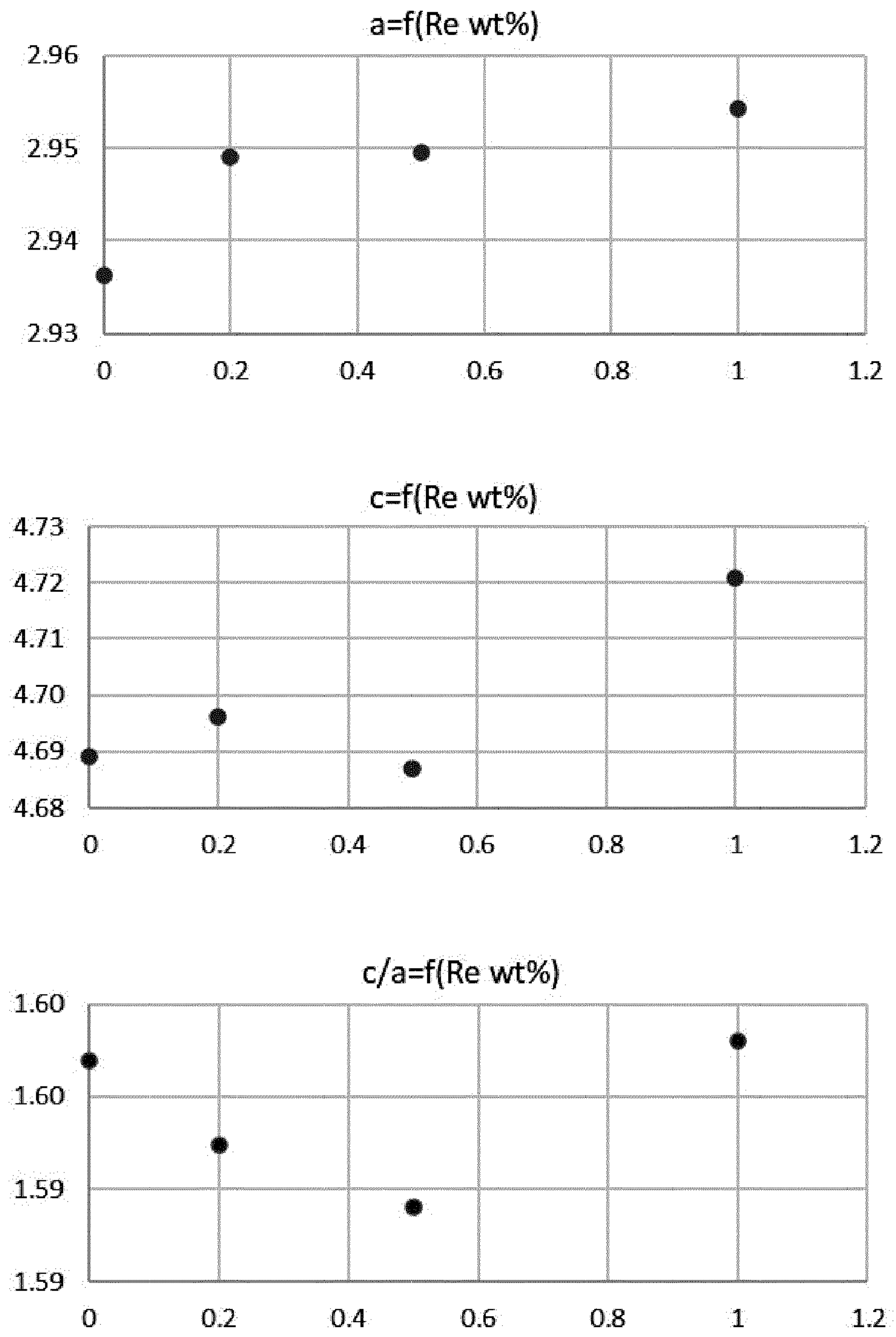
a=f(Re wt%)
2.96
2.95
2.94
2.93
0
0.2
0.4
0.6
0.8
1
1.2
c=f(Re wt%)
4.73
4.72
4.71
4.70
4.69
4.68
0
0.2
0.4
0.6
0.8
1
1.2
c/a=f(Re wt%)
1.60
1.60
1.59
1.59
0
0.2
0.4
0.6
0.8
1
1.2

Fig. 8

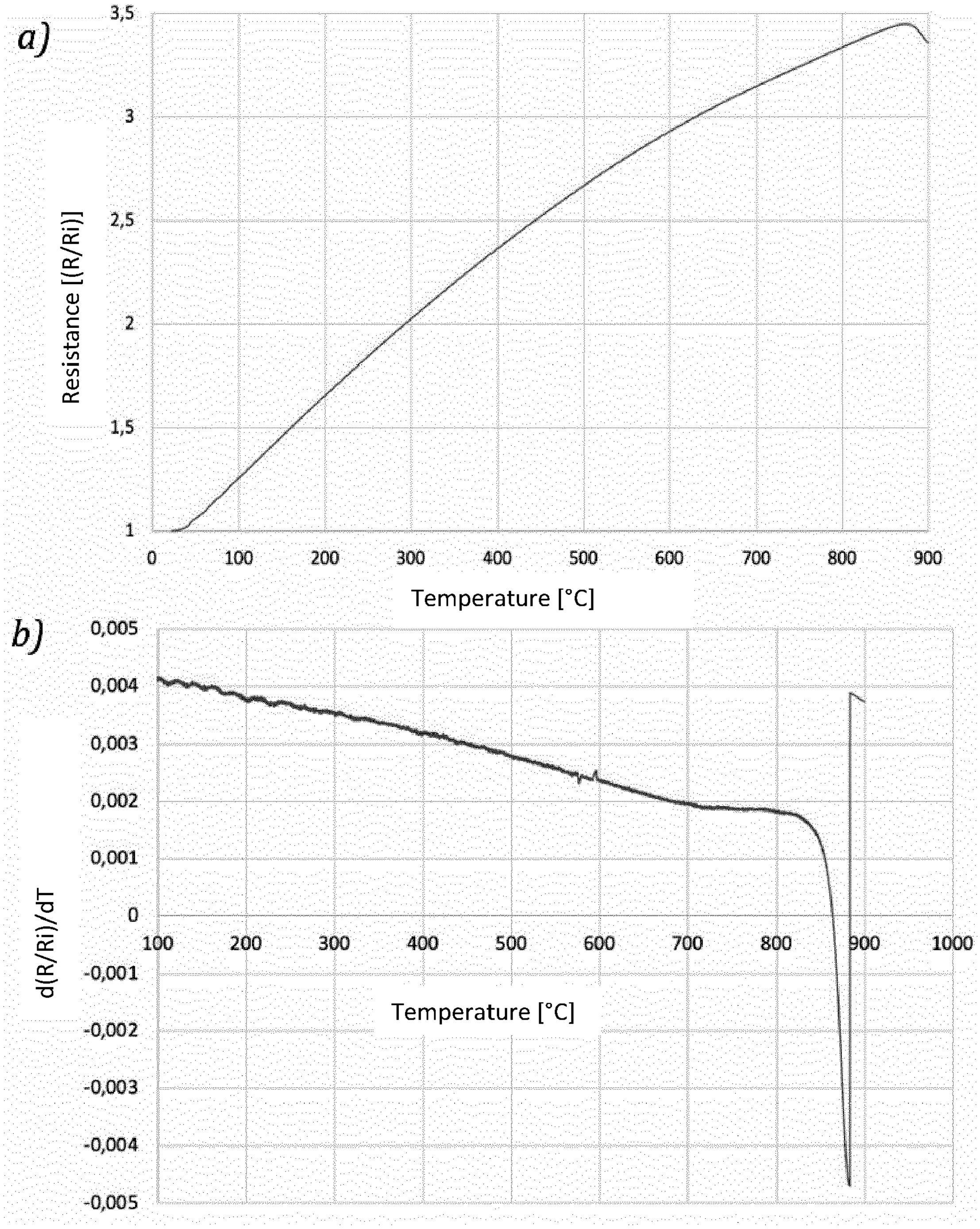
a)
3,5
3
2,5
2
1,5
1
Resistance [(R/Ri)]
0
100
200
300
400
500
600
700
800
900
Temperature [°C]
b)
0,005
0,004
0,003
0,002
0,001
0
-0,001
-0,002
-0,003
-0,004
-0,005
d(R/Ri)/dT
100
200
300
400
500
600
700
800
900
1000
Temperature [°C]

Fig. 9

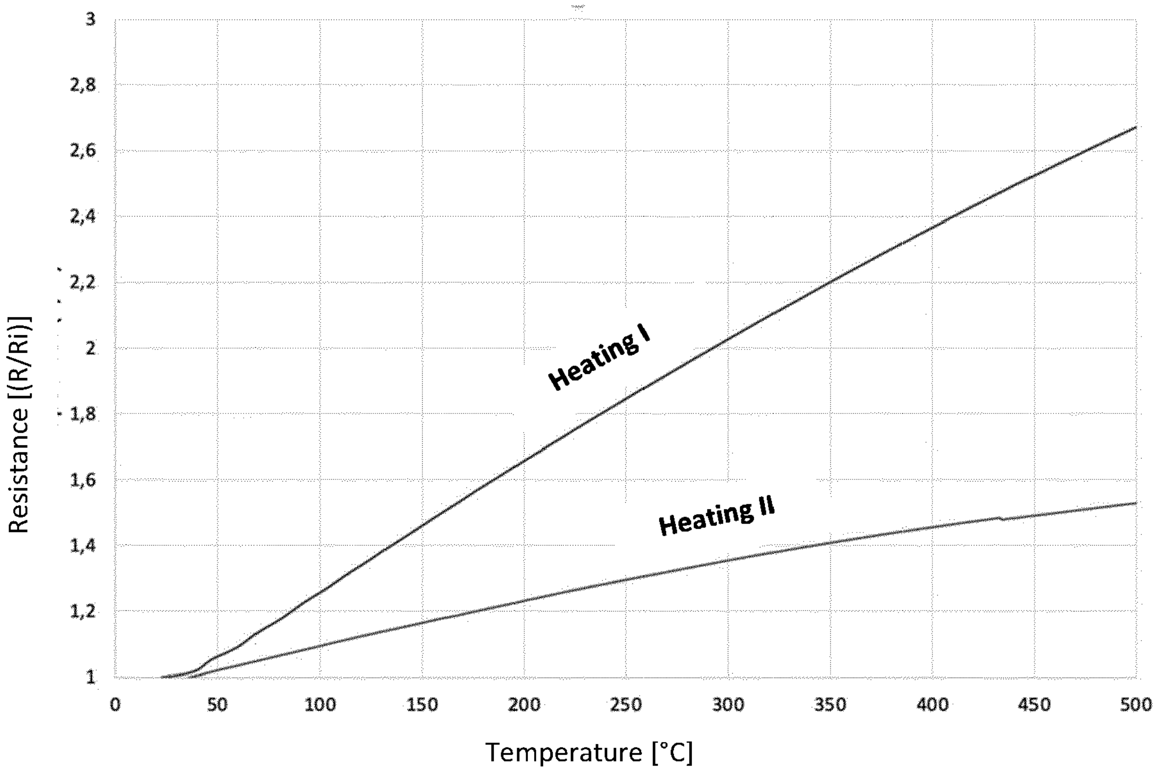
3
2,8
2,6
2,4
2,2
2
1,8
1,6
1,4
1,2
1
Resistance [(R/Ri)]
0
50
100
150
200
250
300
350
400
450
500
Temperature [°C]
Heating I
Heating II

Fig. 10

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EUROPEAN SEARCH REPORT

Application Number
EP 22 21 3876

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D A	JP H01 252746 A (NIPPON STEEL CORP) 9 October 1989 (1989-10-09) * page 242, column 2 * * examples Ti-Re(1.0); table 1 * * claim 1 * -----	14,15 1-13	INV. C22C1/02 C22C14/00 C22F1/18
X Y	JP H08 246192 A (KOBE STEEL LTD; TAKENAKA KOMUTEN CO) 24 September 1996 (1996-09-24) * paragraph [0001] * * paragraph [0020] * * paragraph [0037] * * example 3 * * No. 30; table 10 * * claims 1-7 * -----	14,15 1-13	
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TECHNICAL FIELDS SEARCHED (IPC)

C22C
C22F

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	24 April 2023	Neibecker, Pascal

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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24-04-2023

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			JP 2015508847	A	23-03-2015
			RU 2014132591	A	27-02-2016
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			WO 2013154629	A1	17-10-2013

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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- EP 2563942 B1 **[0011]**
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- **E. CHLEBUS ; B. KUINICKA ; R. DZIEDZIC ; T. KURZYNOWSKI.** *Materials Science and Engineering: A,* 2015, 620 **[0006]**