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Investigation the Structure and Formation Mechanisms of the Coatings Obtained by Thermo-chemical Treatment on the Surfaces of Chromium and Iron-Chromium Base Alloys

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THE ABSTRACT

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General Characteristic of the Work

The urgency of topic. There are determined the practicable prospects for application the low alloyed chromium and high chromium content (> 40 %) Fe-Cr-Al-La system alloys for manufacturing the parts and units designed to operate in aggressive environments at 1200 ^{O}C and much higher temperatures. The requirements for high temperature construction materials exceed the potential ability of traditional heat-resistant nickel, iron and cobalt base alloys, therefore, the development and creation of new high temperature construction materials, on the base of refractory metals, became one of the important problems of materials science. The urgency of the problem becomes stronger due to the circumstances that, there are practically no construction materials which would be able to work long time at 1200 ^{O}C and much higher temperatures in the ordinary air and other aggressive environments. In order to solve the mentioned problem there already appeared the works (Tavadze, Mikadze, Rakitski and others) on the low alloyed chromium and close-to equiatomic Fe-Cr base alloys, dedicated to the obtaining the especially heat resistant materials, which are based on the principle of formation the oxide layers with low volume diffusion parameters on the surface of optimized composition metal matrix.

Until the recent, as in monographic literature (Kofstad, Roberts, Ormondt, Kolong and others), so in numerous articles dedicated to the metal/gas interface physics-chemistry and the high temperature oxidation processes of the low alloyed chromium and Fe-Cr-Al-RE system alloys, there are especially emphasized the creation of the models on oxide films (including barrier protective layers) nucleation and growth mechanism, taking into account their structure. Together with the rapid development and perfection of physics-chemical methods of surface analysis, it become obvious that the oxide layer formation mechanisms on the metals and alloys surfaces are more complicated than it was considered before, when the bases for the formation of theoretical notions mainly were kinetic data and the metallographic investigations. For the time of starting our work on the further development the high temperature doping principles in order to obtaining the new composition materials with especially high chemical resistance (high temperature corrosion resistance) on the bases of refractory metals, the main difficulty was that non of the existed oxidation theory could sufficiently explain the expected heat resistance parameters of mentioned materials. Therefore, it became necessary to collect the new experimental data about crystallography, chemical composition, defectiveness and morphology of the surface layers in the micron, submicron and nanometric scales on the base of the complex utilization such sensitive and high resolution methods as are scanning electron microscopy (SEM), fast electron diffraction (FED), energy-dispersive spectrometry (EDS), Auger-electron spectrometry (AES) and wavelength dispersion spectrometry (WDS). Development of the mentioned methods and the technical basis of their realization, during the last decade, has stimulated the researchers for the further extended investigations on the development of scientifically substantiated technologies on the obtaining the high temperature protective oxide films, because the problem of physics-chemical reactions on the surfaces was, and remains, especially important one, for the scientific explanation of any technological processes of the formation of functional surfaces, which are intend for operating at high temperature aggressive environment and in friction conditions.

For nowadays there are no such metallic alloys which by the combination of their heat-resistant features could provide functional resources of high efficiency both air and lend base gas turbine engine parts. It is difficult to obtain these features using single materials. Therefore, to overcome the mentioned difficulty the scientists are trying to use such combined materials which basis are the high hear-resistant metallic alloys, and on the surfaces of which are formed protective oxide layers with anticorrosive and thermo-barrier features. Elaboration of the methods, which are the part of the treatment technology for the creation of protective surface layers on the alloys, utilized for high temperature gas turbine engine components, requires the existence of a lot of information about (*1*) determinant factors causing formation of the slow-growing, the stabile and the adherent surface oxide, (*2*) about blocking mechanisms of the cations and the anions diffusion paths through the scale, and (*3*) about the stress generation and its relaxation mechanisms during thermal and thermo-mechanical cycling. In this connection, during the resent years there has sharply risen the interest in the composition of low alloyed chromium and especially in the Fe-Cr-Al-La system alloy, because they are considered as chromia- and alumina- forming promising materials for production of parts of wares operating at 1200 ^{O}C and, possibly, at much higher temperatures.

Taking into consideration that corrosion is essentially microscopical process and it always starts from the surface, it was intrinsic to expect considerable influence of surface initial condition on the scale formation on its initial stages at high temperature oxidation. But, analysis of existed literature shows that, from this point of view, this issue is not sufficiently studied. The discussions, on the mechanism of polish process and the structure of mechanically polished surface of metals and alloys on their basis, still are poignant and urgent. The point is that during manufacturing the real parts from the mentioned materials the kinds of cold such as working as grinding and mechanical polishing, are the unavoidable technological processes for the formation of functional surfaces of the machines critical parts and units which are used in different fields of machine-building. In addition, the problem of physics-chemical reactions on the surface layers of construction materials was, and remains, exceptionally important for the scientific substantiation of any technological processes related to the creation of functional surfaces.

Structural-thermodynamic analysis (carried out using the modern dislocation theory of plastic deformation) of the nature, the features, the construction, and the condition of material’s surface layers formed during the friction process (in tribosystems) and during mechanical polishing, gives us reason to suppose that the Beilby layer on the mechanically polished surface and on the wearing surfaces (in tribosystems) are the identical ones, as the products of destruction, velocity of which is controlled by the velocity of entropy production. On the basis of above mentioned notions, the Beilby layer is entropy “excited” surface layer on the solid, and can be considered as functional system which in the condition of energy penetration from the outside (thermal, thermal-mechanical, chemical-thermal *et al.*) will display the adaptive effects of the system reaction on the changes of external factors. It is also evident that more delicate and various could appear the influence of Beilby layer on the magnetic and other physical properties of components of electronics, created on the different substrate surfaces. Therefore, (in terms of experimental verifications) extension of the notions about nature of hierarchical sequence of surface structure formation during mechanical polishing and friction becomes important for wide range of technical fields.

According to the existed notions, mechanically treated (grinding+ polishing) distorted layer presents more or less extensive zone under the geometrical surface of the solid. The mentioned zone has complicated structure and there occure the complex phase transformations in it as a result of physical and/or chemical influence of used treatment methods together with the ambient. It will be intrinsic to suppose that this distorted layer is non-homogenous one, and can be consisted of several zones depending on the distribution character of external influence forces. However, in most cases their thicknesses of these zones are unknown and in each specific case there is necessity to make their experimental determination using more sensitive and high-resolution modern methods of surface analysis rather than ordinary metallography.

The aim and the objectives of present work, on the assumption of above mentioned, can be postulated as follows:

1. investigation of the influence of surface modification and thermo-chemical treatment on the scale features developed during high temperature oxidation process on the surface of chromium and low alloyed chromium;
2. to establish the stability limit, the composition, the nanostructure and the thickness of Beilby layer formed on the surface of mechanically polished Fe-Cr-Al-La system alloy with high

pure chromium (> 40 %) content, complexly utilizing the modern experimental methods of surface sounding;

3. experimental investigation of the structural aspects of scale formation at the initial stages and its growth during oxidation at 1000÷1400 ^{O}C temperature range on the surface of Fe-44 %Cr-4 %Al-0.3 %La alloy;
4. generation the possible complete view on the structural mechanism of hierarchical sequence of scale formation on the surfaces of low alloyed chromium and high chromium (> 40 %) content Fe-Cr-Al-La system alloy during high temperature oxidation processes, with the purpose of creation the scientific fundamentals for obtaining the technologies on wear- and corrosion resistant oxide coatings on the surfaces of components operating at 1200 ^{O}C and much higher temperatures.

Scientific novelty. In the present work there are given the results of experimental investigation of the structural aspects of high temperature corrosion protective (barrier) oxide films formation regularities on the modified surfaces of low alloyed chromium and Fe-Cr-Al-La system alloy with high chromium (> 40 %) content. There were first investigated the influence of initial surface condition (in micron, submicron and nanometric scales) on the morphology of oxide films, on their phase composition, structural transformation and the protective properties by the complex utilization of high resolution and sensitive modern methods (SEM, OES, WDS, FED, EDS).

1. it is established that, modification of pure chromium and low alloyed chromium surfaces by lanthanum implantation gives considerable affect on the increasing of heat resistance at 1200-1300 ^{O}C temperatures, and especially at the initial stages.
2. it was first stated the existence of four zones, with different structure and composition, on the surface layer of mechanically polished Fe-Cr-Al-La system alloy with high chromium (> 40 %) content. Two sub-zones from the mentioned four, situated closer to the geometric surface, truly amorphous and “roentgenamorphous” sub-layers (with the total thickness of ~ 60 nm) are organically adjacent to each other and represent the part of the Beilby layer.
3. it is first determined that the layer (with $\leq 1\mu$ thickness) on the surface of mechanically polished specimen of Fe-44 %Cr-4 %Al-0.3 %La alloy, which consists of amorphous Beilby layer and its adjacent matrix fine-grained layer (caused by the plastic deformation, as entropy “excited” functional system), at the temperature of 1200 ^{O}C in laboratory atmosphere transforms into the surface layer with uniform thickness of the modulated scale structure of microwrinkles arrangement which is composed of the mixture of the nanocrystallite (100÷500 nm) oxides out of metal matrix main components atoms.
4. it was first established that, together with increasing the oxidation temperature up to 1400 ^{O}C, there occurs the regrowth of the nanocrystallites and the recrystallization processes, accompanied by the solid phase reactions between the oxide nanoparticles; the mentioned processes end by the scale lamination on metallic matrix and also by the formation of thin uniform layer of the polycrystalline Al_2O_3 (with graininess of 1-3 μ), which has high adhesion with metallic matrix and protective properties against high temperature (1200 ^{O}C) corrosion and abrasion.

Scientific and practical value. The results of thesis can be widely used in practice, because the obtained results have shown the new ways for further increasing the heat resistance of chromium base alloy and Fe-Cr-Al-La system alloy with high chromium (> 40 %) content; also, these results give the possibility of governing the elaboration of new compositions with optimal heat resistance ratio and high temperature and tribological properties.

In the presented work there are established the regularities of hierarchical sequences of structural and phase transformations occurred on the mechanically treated surface in micron, submicron and nanometer scales. Thay can be used as a scientific basis for the technologies on the obtaining the selforganizing protective barrier oxide coatings, in order to production the functional surfaces on the massive and little size components.

The following main statements will be defended:

1. The results of the investigation on structural aspects of oxide (including barrier) coatings formation mechanism on the modified surfaces of chromium and close-to equiatomic iron-chromium base alloys after chemical-thermal treatment;
2. The dependence of mechanical treatment parameters on the Beilby layer thickness, nanostructure, composition and determined stability limits on the surface of mechanically polished Fe-Cr-Al-La system alloy with high chromium (> 40 %) content;
3. The results of structure-thermodynamic analysis and experimental investigation on the origin and transformations of modulated structure of scale developed on the surface of Fe-Cr-Al-La system alloy with high chromium (> 40 %) content during oxidation in the range of temperature 1200÷1400 ^{O}C;
4. Principles of the creation of especially heat- and wear- resistant compositions; formation the thin protective oxide layers (with low parameters of volume diffusion) by the selforganization of entropy "exited" surface layer.

The Approbation of the work. The main results of the thesis were presented at the follwing scientific events: The Students ***71st*** Open Scientific-Technical Conference of Georgian Technical University (April 2003, Tbilisi, Georgia); Soros Conference-Competition for Students and Aspirants (May 2003, Tbilisi, Georgia); The Students ***72nd*** Open Scientific-Technical Conference of Georgian Technical University (April 2004, Tbilisi, Georgia); The International Conference for Young Materials Scientists ***JuniorEuromat2004*** (6-9 September 2004, Lausanne, Switzerland); The European Corrosion Congress ***EuroCorr2005*** (4-8 September 2005, Lisbon, Portugal); Mechanical Engineering and Materials and Metallurgical Engineering Departments Joint Seminar in New Mexico Institute of Mining and Technology (2nd of December 2005, Socorro, NM, USA); Joint Scientific Seminar of Republic Center for Structure Researches of Georgian Technical University and Department of Physical Materials Science of Georgian Technical University (5 April and 24 May 2006, Tbilisi, Georgia); The International Conference for Young Materials Scientists ***JuniorEuromat2006*** (4-8 September 2006, Lausanne, Switzerland); The 10th International Conference on Plasma Surface Engineering ***PSE2006*** (10-15 September 2006, Garmish-Partenkirchen, Germany);

Publications. The materials of thesis are published in eight papers.

The structure and volume of the thesis. The thesis consists of introduction, four chapters, summary and 137 References. The volume of thesis is 146 printed pages including 6 tables and 25 illustrations.

The main contents of the thesis

In the Introduction it is given the explanation to the topic urgency and the necessityof conduction the present work, also it is postulated thesis aim and objectives.

The First Chapter is dedicated to the critical review of the existed literature and notions on the high temperature oxidation processes of pure chromium, low alloyed chromium and Fe-Cr-Al-RE system alloy. It is shown that, the mechanisms of oxide layers formation, on the surfaces of metals and their alloys, is much more complicated than it was considered before, when the basis of formation the theoretical notions mainly were kinetic data and the metallographic structural researches. Development of heat resistant doping principles for the obtaining of new refractory metal base compositional materials, with especially high chemical resistance, is related with the main difficulty that, non of the oxidation theories from the existed ones are able to give the sufficient explanation regarding the expecting heat resistance parameters of the mentioned materials. It is examined the evolution of existed notions about the phase-structural transformations due to the mechanical polishing the surfaces of metals and alloys and also, it is shown contradictory character of the data existed for nowadays on the structure and the formation of Beilby layer. It is indicated that there are obviously not many investigations of the influence of surface initial condition on processes of high temperature oxidation of metals and alloys and on the structure and protective properties of the oxide films developed as a result of the mentioned processes. There are practically no investigations on the structural aspects of high temperature corrosion of Fe-Cr-Al-La system alloys, chromium content in which is more than 40 %. It is explained the availability of thermo-chemical treatment relatively increasing heat resistance of the pure chromium and Fe-Cr base alloys.

In **The Second Chapter**, derive from the aims of our investigation and from the complexity of investigated alloy, utilizing of such research methods as scanning electron microscopy (SEM), Auger-electron spectrometry (AES), fast electron diffraction (FED), energy dispersion spectrometry (EDS) and wave-length dispersive spectrometry (WDS), it is formulated the sense of the oxide layers development mechanism in the multi-component systems and on the running processes in the very thin surface layers in micron, submicron and nanometric scale. It is contemplated the peculiarities of the experiments using each mentioned method, taking into account composition of investigated objects.

In the given work the investigated objects were the alloys which, on the one hand, were most optimal by the composition (from the perspective point of view in practical application), and on the other hand, most suitable in methodical aspect for the solution of the set of problem (formation the possible complete view on the structural mechanisms of hierarchical sequence of scale development on the surface of selected alloys during high temperature oxidation in order to creation the scientific basis of technologies on obtaining the wear- and corrosion resistant oxide coatings). The composition of alloys selected for experiment, the regimes of thermal and mechanical treatments and the specimen preparation methods are presented in the second chapter as well.

In **The Third Chapter** there are presented the peculiarities of unoxidized surface modification influence on the properties of oxide coating development during oxidation processes of the pure chromium and optimized BX-2K alloy of low alloyed chromium and also there are given characteristics to the kinetics of high temperature oxidation processes on the surfaces of the same materials. There were carried out comparative tests on the heat resistance of non alloyed chromium and BX-2K alloy of low alloyed chromium specimens on the surfaces of which were created barrier layers using different (electron-beam evaporation, covering by impulse laser radiation, surface penetration by ion implantation) methods.

Table 1. Specimen oxidation parameters during 2.5 hours

Specimen	W mg/cm^2	
	1200 ^{O}C	1300 ^{O}C
Pure chromium	2.71	–
Chromium coated by Lanthanum hexaboride	0.82	1.75
Low alloyed chromium (BX-2K)	0.78	1.71
BX-2K coated by Lanthanum hexaboride	0.25	0.52
BX-2K coated by Lanthanum	0.37	0.61
BX-2K implanted by Lanthanum	0.12	0.36

The investigation of the parameters of specimens' oxidation in air during 2.5 hours showed that, the mentioned layers can work as effective barriers against diffusion of oxidized agents. The effect of matrix protection is considerable at the initial stages of oxidation (see ***Table 1***);

additionally, the especial increase in heat resistance, observed after implantation of lanthanum ions into the low alloyed chromium surface layers, remains much longer time (***Fig.1.*** see Appendix, *p.31*).

On the basis of X-ray spectral analysis and electronographic studies, it is established the reason of above mentioned effects. Namely, it is discovered that there occurs segregation of lanthanum atoms on the oxide grain boundaries as the lanthanum chromites and there takes place blocking the paths of fast diffusion during chromium movement which slow down the new oxide layers formation inside the scale; this is an enough reason for sharp reduce in scale growth velocity and increase in its adhesion. On the basis of the results of our investigation, it is made the conclusion that, increasing the concentration of grain boundary barriers in the scale, independently of means of realization the mentioned action, results in the considerable increasing of heat resistance of Cr_2O_3 former alloys. At the same time, there are serious arguments to suppose that, maximal increase in heat resistance which is observed after the implantation of lanthanum ions is stipulated by dual effect of modification during surface implantation – *the first*, due to the uniform increasing the lanthanum concentration on the surface by the higher amount than its solution limit is and *the second*, due to the surface layer amorphization process accompanied with the implantation. Bearing on the analysis of the existed references, regarding the results on analogous investigation, and on the basis of study the structure and properties of scale formed on the surface of chromium and low alloyed chromium, there are created opinion that elaboration the optimal combination parameters of amorphization, enrichment of surface layers by reactive elements and surface preliminary thermo-chemical treatment could underlie to the new universal principles, for the realization in corresponding technologies, on the obtaining the heat fastness barrier and wear resistant oxide coatings on the surface of heat-proof materials, for the creation of functional surfaces on the faces of components which are operating at 1200 ^{O}C and much higher temperatures.

The Forth Chapter. The choice of investigated alloy from the Fe-Cr-Al-RE system was caused by two factors: *the first* – by the practical interests in the given system alloys, which are chromia- and alumina- forming promising materials for manufacturing the parts of details operating at 1200 ^{O}C and possibly at much higher temperatures, and *the second* – by the methodical conveniences (high recrystallization and melt temperatures, optimal plasticity, alloy multi-component and the expected high thermodynamic stability of Beilby layer due to the alloy components which have high affinity to oxygen) for the tasks solution formulated in present work.

The initial specimens to be investigated by SEM, AES, FED and WDS methods, were shaped and given the dimensions acceptable for grids of all equipments used by us in order to study the same specimen using all of them. Surface treatments from finish grinding to finish (final) polishing for the formation of the Beilby layer were made manually using sandpaper, polishing diamond paste and MgO nano-powder on cloth. Preparation of specimens with Beilby layer on their geometrical surfaces was realized according two schemes of mechanical polishing. By the first one, after smooth grinding (using lap disc with abrasive graininess of 20÷10 μ), the specimen surface were finish ground on the sandpaper of 7÷5 μ graininess (this stage can be considered also as a mechanical polishing pre-stage), and than followed two stages of intermediate and finish polishing using the polishing paste with abrasive particle sizes of 5÷1 and 1÷0.2 μ, respectively.

According the second scheme, after the finish grinding the distorted layer (with the ~ 2 μ thickness) formed due to the previous mechanical treatment was completely removed from the specimen surface electrochemically, by anodic dissolution method in the polishing regime. After that, the above-mentioned two stages of mechanical polishing (intermediate and final) were carried out till obtining mirror-like surface of highest polish.

The duration of each mechanical polishing stage was equal to ~ 10 hours, and low specimen moving velocity (less than 0.05 m/sec) was used.

SEM images of the surfaces morphology of investigated alloy specimens after finish grinding and their subsequent mechanical polishing till brilliant polish by two above-mentioned schemes are displayed in the ***Fig.1.a-d*** (see Appendix). It is obvious that after mono-directional grinding using the lap disc (with abrasive grain sizes of 20÷10 μ), the specimen surface morphology has complicated relief profile. There are clearly visible parallel scratches, grooves with torn edges, asperities, tearing areas and flat, licked by plastic flow micro-channels, and micro-cracks (***Fig.1.a***). In this case, the surface profile differences of observed roughness are ≤ 10 μ.

SEM image of given surface after its mechanical polishing up to brilliant polish which forms the Beilby layer according to the first treatment scheme is shown in the ***Fig.1.b***. It is obvious that, after three-stage mechanical polishing on the sandpaper with diminishing graininess and finish polishing with the paste on the felt, there occurred smoothing of the rough ground surface by the plastic flow and embedding of the above average height asperity micro-areas into the dimples of groove scratches. Though, in spite of rather long polishing duration (~ 20 h), due to very small material removal during intermediate (using the paste with grains of 2÷3 μ) and, especially, finishing (with grains of 1÷0.2 μ) polishing stages, at high magnifications of the final, smooth mirror-like surface, there are visible single traces of scratches retained from previous treatments, although with smear edges partially filled by material plastic flow; also, random single traces of plowing of fresh skin-deep scratches caused by free abrasive micro-grains of polishing paste (***Fig.1.b***). Thus, it is obvious that, in the given case under the Beilby layer in the considerable depth (~ 1 μ), there will be kept the distorted layer as a result of the finish grinding (with abrasive graininess of ~ 5 μ) preceding by the starting mechanical polishing. In order to form the Beilby layer by the mechanical polishing, on the specimen surface without the sub-layer distorted as a result of finish grinding, we chose the second scheme of surface treatment sequence. Namely, after finish grinding (with grains of ≥ 5 μ), from the specimen surface we removed the ~ 2 μ thickness layer electrochemically, by the method of anode dissolution (in the polishing regime), after which there were obtained a new surface with original grain structure of polycrystalline specimen which was not subjected to the treatment (see ***Fig.1.c.***). The subsequent two-stage mechanical polishing of the given surface according the second scheme gave us the mirror-like surface of brilliant polish without any visible (at high magnification) scratching tracks; there were observed only rare cases of sticking of the submicron abrasive particles of polishing paste in the Beilby layer without plowing tracks (see ***Fig.1.d***).

To find out the problem on the depth and character of the expected transformations (amorphization, plastic flow, hardening, saturation with the atmospheric atoms and their diffusion into material depth, oxidation *etc.*) which could happen on the surface and near-surface layers in the process of Beilby layer formation during mechanical polishing, based on Auger-spectra we plotted elemental distribution profiles up to ~1μ depth for those specimens on which the Beilby layer was formed according to two above-mentioned schemes. The corresponding graphs of distribution profiles of oxygen, carbon, iron and chromium atoms were plotted based on the data obtained by simultaneous recording the Auger-peaks of these elements each ~ 2 minutes during sputtering (with velocity ~ 25 Å/min) using surface bombardment by argon ions accelerated with 2 keV energy, (***Fig.2.a*** and ***b***). It is obvious that, for the surface treated according to the first scheme up to the ~ 0.2 μ depth, there emerge element correlation four characteristic zones (***Fig.1.a***): zone **I** – with the thickness of ~ 30 Å corresponds to the adsorbed layer of the molecules of atmospheric air elements (mainly C, O, S, Cl, N) on the polished specimen surface. This zone is not related to surface treatment processes, and usually present on the surface of any specimen loaded from atmosphere in the Auger-spectrometer chamber. Zone **II** with the thickness of ≈ 230 Å obviously represents the amorphous Beilby layer saturated with high concentration of oxygen and carbon atoms. Zone **III** with the thickness of ≈ 350 Å also contains high concentrations of oxygen and carbon and, apparently, has crystalline structure disaggregated to the nano-sizes. This zone must be considered as an organic part of the Beilby layer. Due to the grinding process (preceding the polishing), caused by hardening, under this layer there is situated a plastically deformed, fine-grained, textured layer of the matrix with the thickness about ~ 1200 Å – as the zone **IV**, in which the concentration of oxygen and carbon, diffused from the Beilby layer and from the remained micropore areas, during the smearing process exponentially decreases down to their minimal constant level of consistance in the alloy matrix. This last zone overlaps the matrix structure, which was not subjected to external influence, by transition area. The investigation on the distribution profile of oxygen, carbon, iron and chromium atoms, for the Beilby layer on the mechanically polished specimen surface of the investigated alloy treated according to the second scheme showed the same three-zone structure of the treatment layer before its overlapping with the matrix structure not subjected to external influence, but with changed parameters in the above-mentioned zones (***Fig.2.b***). Namely, the total thickness of all four mentioned zones (including the superficial adsorbed layer), in case of realization the second scheme of mechanical polishing, was decreased almost by half. There were also changed the thickness ratios of the Beilby layer sub-zones (basically at the expense of inner layer thickness variation) at their approximately same total thickness for both schemes of the mechanical polishing (compare ***Fig.2.a and b***). These obvious effects of different initial surface (and near-surface layers) conditions, before last two (intermediate and finish) stages of mechanical polishing, on the sub-zone composition and fine structure of treatment layer were caused by the treatment parameters preceding the mechanical polishing.

The mentioned zones reveled in the element concentration distribution curves were also unambiguously revealed by the structural specific features peculiar to each corresponding zone, which were obtained by fast electron diffraction patterns “in reflection” (***Fig.3.a-d***).

The schematic pictures of structure changes as a result of mechanical polishing of ground surfaces according the above-mentioned two treatment schemes in order to form the Beilby layer on the specimen surfaces of Fe-44 %Cr-4 %Al-0.3 %La alloy, plotted on base of the obtained experimental data are presented in the ***Fig.4.a*** and ***b***.

It should be noted that the thicknesses of the mentioned four zones (except the first one, the adsorbed layer, which at room temperature always has practically the same thickness (~ 30 Å) on all the metallic surfaces and is not related to the surface treatment processes) to a different extent depend on the polishing duration and the initial surface (and near-surface layers) condition which is formed by the treatments preceding the mechanical polishing. Namely, total thickness of truly amorphous (zone II) and “roentgenamorphous” (zone III) parts of the Beilby layer, which is about ~ 550 Å, practically does not depend on the initial surface condition and polishing duration. Undoubtedly, in the latter case, the duration exceeded the adequacy level of polishing duration for the Beilby layer formation. The thickness ratio of given sub-zones (at the constant total thickness) in Beilby layer, which differ from each other by the structural condition and the level of saturation with oxygen and carbon atoms and to a certain extent could depend on the polishing regimes and the initial surface condition prior to the mechanical polishing.

As regards to the forth zone mainly as a product of grinding presiding the stages of mechanical polishing, its thickness (the length in depth) strongly depends on the duration of preliminary and intermediate polishing stages, when the material removal during the polishing process (till the development of the Beilby layer), is still possible to some extent in order to decrease in advance the thickness of texturized treatment layer which retained after finish grinding. The mentioned is proved by the results based on our experiments on the Beilby layer formation by the second polishing scheme (***Fig.2.b***.and ***3.d***), when treatment layers, formed due to the finish grinding, were practically fully removed before mechanical polishing process.

The given data are evidence in favor to the notation about formation of the Beilby layer (and its sub-layers) during mechanical polishing as a product of the combined process of surface (non-selective) visco-plastic mass transfer and the accumulation of crystalline defects accompanied by plastic deformations. However, the stable existence, at room temperature (possibly at higher temperatures), of near-surface layers as zones in truly amorphous and “roentgen-amorphous” structures, which is such non-equilibrium against the crystalline structure under it, is apparently caused by the dissolution in these layers of the atoms of oxygen and carbon (and also other atoms existing in environment), the penetration of which in the depths of surface treatment layer was proved by the above-mentioned experiments for investigation of the element distribution profiles of polished surfaces (***Fig.2.a, b*).** On the basis of established fact about the structure heterogeneity in the distorted treatment layer which consists of truly amorphous, “roentgenamorphous” and defected crystalline zones, it was investigated the condition of penetrating atoms in each zone and their interaction with solid solution atoms of the investigated alloy. For this purpose we recorded differential Auger-electron spectra of polished specimen surface, treated according to the second scheme, for the layers located at different depths in each of four zones determined by us.

On the basis of the observable character peculiarities in the thickness changes of the revealed zones, dependending on the polishing duration and initial surface condition prior to the mechanical polishing, there were developed notions on the hierarchical sequence of Beilby layer (and layers under it) formation stages as a product of combined processes of visco-plastic mass-transfer and growth of the crystalline structure defects, which are accompanied by the plastic deformations. The stabile existence at room temperature the superficial layers with truly amorphous and “roentgen-amorphous” condition, which are nonequilibrium against underlying crystalline structure, is explained by the dissolution of those layers by carbon and oxygen atoms and their interaction with the basic atoms which compose the investigated alloy.

Complex investigations on the early stages of barrier oxide layers formation on the surface of Fe-Cr-Al-La alloy with high (> 40 %) chromium content ware carried out by the methods of Scanning Electron Microscopy (SEM), X-ray Diffraction Analysis (XRD) and Auger-Spectrometry (AS). The morphology, and chemical and phase compositions of the barrier layers were studied on flat surfaces of plate samples after high-temperature oxidation on the air at 1000 ^{O}C, 1100 ^{O}C and 1200 ^{O}C. The soaking time at the mentioned temperatures was varied cyclically from 1 to 10 hours (1+4+5). In what followed, the cycling of these samples with duration of 5 and 1 hours realized at 1300 ^{O}C and 1400 ^{O}C respectively, for the purpose of studying in the scale the recrystallization processes (structural transformations). It was established that the surface morphology of scale, generated on the initial stages of high-temperature oxidation of the alloy being investigated, essentially depends on the structural condition of the initial surface of a polycrystalline sample.

Involving of the amorphized surface layer in sequence of the mechanical polishing (Beylbi layer) or ionic bombardment, scale develops with the generation of modulated structure of the microwrinkles arrangement with uniform thickness on the entire sample surface (***Fig.6***).

In this connection, formation of oxide ridges which enframe the grain boundaries of the matrix, in difference of widely researched alloys of Fe-20 %Cr-5 %Al-RE and low-alloyed chromium, is excluded.

The scale structure with the most distinct contours of modulation is formed at 1200 ^{O}C during the first hours of oxidation and remains stable (without appreciable changes) long time (> 10 h) both by the thickness and the fine structure of the scale; which distinctive feature, thus, is its structure as a mixture of Al_2O_3. and Cr_2O_3 nanocrystallites (≤ 500 nm) and also the complex oxide.

The recrystallization and the spallation processes in the scale which forms during the oxidation cycles at 1200 ^{O}C – (1+4+5) hours develops intensively during the additional oxidation cycle at 1400 ^{O}C – 1 hour on the ground surface. In addition, these processes are also accompanied by the spallation of the superficial scale layers. In the ***Fig.7a-d*** there are shown SEM images of the ground surface of the specimen after oxidation cycles at 1200 ^{O}C – (1+4+5) which was additionally oxidized at 1400 ^{O}C -1 hour. On the area with the spalled oxide there displays three layer levels (***Fig.7a***) which are marked as A – lower sub-layer, B – mediate layer, C – superficial scale layer. Magnified image of the area A shows that, the sub-layer has the nonporous polycrystalline structure with the grain sizes of 2÷4 μ which in comparison with the similar sub-layer, formed at 1200 ^{O}C (***Fig.6c***), argues the regrowth of the grains of aluminium oxide at 1400 ^{O}C. Increase of the contrast on the intergranular accretion boundaries of the crystals, which is observed on all the contours (compare ***Fig.6d*** and ***Fig.7b***), obviously is the reason of the enrichment of these intercrystalline areas by the oxides of impurity atoms (possible by the lanthanum chromites).

According to these data, it becomes evident that, for the close-to-equiatomic alloys of system Fe-Cr-Al-La, in the aspect of the protective scale formation on the surface takes on special significance the condition of specimen surface to be oxidized (its structure, topology, composition) and also combination of the cycles of oxidation temperatures. As regards the latter, it should vary in the temperature range in which it will be comparatively non-competitive (equally probable) the nucleation and growth of the chromium, aluminium and iron oxides on the surface layer. Otherwise, (at the comparatively low ≤ 1000 ^{O}C or at very high ≥ 1400 ^{O}C temperatures) the oxide scale lamination process will take place during the early steps due to the different conditions of the competitive nucleation and growth of the various oxides. Intensification of this comparative process will also be facilitated by the surface heterogeneity caused by the treatment process. Naturally, the last factor takes on special significance for the early stages of the formation of protective layer. Here, it is important to bu used the potential of entropy – energetic “excitation” of the amorphized surface. The point is that, at the early stages this potential can be displayed in the considerable influence on the evolution of the structure and the hierarchical sequence of structure formation at the high temperature oxidation, because they obey the regularities of dimensioned hierarchy and self-organization. Additionally, the self-organization occurs by the optimization of the distribution of the dissipative flows between the subsystems (phases) and inside them, which leads (by the shortest path) to the relaxation and to the stable state.

The formation of the observable structure at 1200 ^{O}C, on the polished surface of the investigated alloy, can be presented as an evolution of the structure in the superficial (~ 50 nm) and near-surface (≤ 1 μ) layers development of which includes the stages of the entropy “excitation“ (amorphization during mechanical polishing), formation of the dissipative phases and their optimal hierarchical set (oxygenation, oxides nucleation), and formation of the optimal self-reproduction macro-geometry of the scale.

By the combination of the mentioned factors, in the certain temperature range (of alloy Fe-Cr-Al-La with high chromium content (> 40 %)) it is possible creation of that kind of conditions for scale formation that, even in the early stages (when the thickness of the scale does not exceed several microns) will be barrier for the counter-diffusion of cations and anions. This finally will form the slowly growing, adherent (micro-doping by corresponding elements) layer on the metallic matrix which will be protective against high temperature corrosion.

Conclusion

The main postulates of the given thesis can be formulated as the following conclusions:

1. Complexly utilizing the high resolution and sensitive modern methods (SEM, AES, FED, WDS, EDS) there is investigated the structural aspects of high temperature corrosion resistant protective (barrier) oxide films formation regularities in micron, submicron and nanometric scales on the modified surfaces of low alloyed chromium and high (> 40 %) chromium content Fe-Cr-Al-La system alloy.

2. It is established that, the modification of surface of pure chromium and low alloyed chromium by lanthanum ion implantation together with the preliminary chemico-thermal treatment allows to increase their heat resistance at one and more range at 1200-1300 ^{O}C temperatures, and this is caused by dual modification effect during surface implantation – *first*, the uniform increase of lanthanum concentration on the surface layer providing higher concentration than its solution limit and the *second* – surface layer amorphization, accompanied by the implantation process.
3. It is first established that mechanically polished surface layer of high (> 40 %) chromium content Fe-Cr-Al-La system alloy consists of four zones with different structure and composition, two sub-zones of which (situated just under geometrical surface) are organically corresponding to each other truly amorphous and “roentgenamorphous” layers (with total thickness of ~ 60 nm) of Beilby layer and they virtually do not depend on the initial surface condition and polishing duration.
4. It is first shown that the scale morphology developed at the initial stages of high temperature oxidation of Fe-44%Cr-4 %Al-0.3 %La alloy essentially depends on the structural condition of specimen surface; it is established that in the presence of amorphized surface layer (as a result of mechanical polishing (Beilby layer) or ion bombardment) the scale develops forming the microwrinkles arrangement modulated structure, which has the uniform thickness on the entire surface.
5. It is established that on the polished surface of Fe-44%Cr-4 %Al-0.3 %La alloy specimen at the first oxidation hours there develops the scale with the revealed modulated structure, which remains stable during long time by the thickness and the structure; additionally, the distinctive feature of scale is its nanocrystalline (≤ 500 nm) structure as compositional mixture of Al_2O_3, Cr_2O_3 and the complex oxide.
6. It was first disclosed that the scale with modulated structure formed on the polished surface of Fe-44%Cr-4 %Al-0.3 %La alloy at 1200 ^{O}C undergoes the recrystallization when increasing the oxidation temperature up to 1400 ^{O}C, which is accompanied by the solid phase reactions between the scales compose nanoparticles. The mentioned prosess finish by the scale lamination of on the metallic matrix and the formation of thin Al_2O_3 uniform layer with the graininess of 1÷3 μ, characterized by the high adhesion with metallic substrate and the protective property both against high temperature (at 1200 ^{O}C) corrosion and abrasion.
7. It is established that by the combination of the oxidation cycles and the preliminary themo-chamical treatment, on the surface with entropy “exited” layer of high chromium (> 40 %) content Fe-Cr-Al-La system alloy it is possible to generate such a condition for scale formation that even in the initial stages, when the scale thickness does not exceed several microns, there will develop the structure that will be barrier for cation and anion counter-diffusion; finally, the scale formed on the mentioned material is slow growing, adherent, and protects the metallic matrix against high temperature (~ 1200 ^{O}C) corrosion.
8. By means of the self-organization of entropy “exited” surface layer (Beilby layer, implanted layer), based upon the principles on the formation of thin (~ 1 μ) oxide (barrier) protective layers with low parameters of a volume diffusion, it is determined the utilization perspectives of the high chromium (> 40 %) content Fe-Cr-Al-La system alloy for the obtaining of new heat resistant compositions with especially heat-proof property.

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