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The effects of chemical composition of Nimonic 80A-alloy on the microstructure and properties of gas-borided layer

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Ni-based alloys are characterized by great resistance to corrosion and high temperature oxidation. Diffusion boriding is well-known as a process which can improve the wear protection of these alloys. In this paper, continuous gas boronizing in N_2–H_2–BCl_3 atmosphere is proposed for the production of the boride layer on Nimonic®80A-alloy. Microstructural characterization of this layer is studied with the use of an optical microscope, scanning electron microscope, energy-dispersive X-ray microanalysis and X-ray diffraction. The diffusion zone mainly consists of a mixture of nickel and chromium borides, occurring in the compact boride zone. Beneath this zone, there are also some areas in which borides appeared at grain boundaries. However, it is an exceptional situation. In most cases this zone is invisible. The relatively high chromium content in this alloy results in diminished depth of the boride layer in comparison with Inconel®600-alloy containing less chromium. The increase in concentration of chromium causes that grain-boundary diffusion of boron more difficult. Hence, during boriding of Nimonic®80A-alloy volume diffusion plays the more important role, which requires the high activation energy. As a consequence, the zone with borides at grain boundaries can obtain a limited depth or cannot occur. Chromium content also influences some mechanical properties of the layer. Its higher content causes an increase in hardness because of the higher percentage of harder chromium borides in the compact boride zone. The limited iron concentration in this alloy improves the quality of the layer. The microstructure is free of any porosity. It improves the tribological properties of the layer in comparison with Inconel®600-alloy.

1. Introduction

The excellent corrosion resistance of Ni-based superalloys in various aggressive media [1,2] as well as their resistance to high temperature oxidation [3–5] are well-known. Therefore, under conditions wherever corrosive media or high temperatures occur, the use of these materials is often expected. As a consequence, they are commonly applied in the chemical engineering industry (tanks or apparatus construction), in turbine construction as well as in the petroleum industry. However, an important disadvantage of Ni-based alloys is their low hardness and poor wear resistance. It causes the limited range of their application. Under conditions of appreciable mechanical wear (abrasive or adhesive), the suitable wear protection of these materials is required.

Surface layers were usually produced in order to improve the tribological properties of various materials. Some processes used for protecting steels, such as carburizing or case-hardening, could not be used for Ni-based alloys. Therefore, other processes of surface treatment were proposed for these alloys to obtain the improved wear resistance. The long-lasting nitriding process (9–40 h) provided the relatively thin layers (lesser than 20 μm) [6–8].

Boronizing has a special value, considering the practical applications. During this thermochemical surface treatment, the boron atoms diffuse into the surface of a workpiece to form borides with the base material [9–11]. It is possible to obtain wear and abrasion resistance comparable to sintered carbides [9,10,12–14] if the boriding process is carried out on the adequate materials. More than double the wear life in comparison with nitrided, carburized, carbonitrided, or hard chrome plated steel parts is reported for borided layers in many applications [12–26]. Diffusion boriding requires the adequate material selection in order to produce ceramic phases, called borides, characterized by high wear resistance. A wide range of steels, including carbon steels [12,15,16, 18–21,25], low alloy steels [13,14,22–24], tool steels [17], stainless steels [26] as well as pure iron [27,28] can be diffusion-borided. Besides, the multicomponent and hybrid boride layers [19–25] as well as the laser heat treated (LHT) boride layers [29–33] are often produced. Co-based alloys [34,35] or molybdenum [36] could also be effectively boronized. In borided sintered carbides, the borides were created with a soft cobalt or nickel binder [37,38]. The boriding had a unique importance for Ni-based alloys such as Inconel, Nimonic, Hastelloy, Incoloy, or Haynes alloys. The various methods of this process were suitable for

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these materials [39–52] without sacrificing corrosion resistance and heat resistance [53].

The pack-boriding of pure nickel resulted in the production of the surface layer consisting of nickel borides. The use of commercial Ekabor® powder containing SiC [39–41] was not advisable due to the appearance of porous silicide layer close to the surface. Nickel silicides were characterized by relatively low hardness (within the range from 750 HV to 980 HV), and only nickel borides of small thickness were observed beneath these silicides. The paper, published by Gunes and Kayali [42], seemed to be an exception. The pack-boriding with the use of Ekabor®II powder at 900 °C for 4 h resulted in the thick diffusion layer (220 μm) with nickel borides confirmed by XRD. However, in some areas, the increased silicon content was measured by EDS X-ray microanalysis, and the microstructure was similar to the mixture of nickel borides and silicides reported by other papers [39–41,47]. Probably, some peaks, identified by XRD as characteristic of nickel borides, also corresponded to the nickel silicides. Summarizing, the acceptable methods of pack-boriding required the use of the powder which didn't contain SiC, e.g. Ekabor-Ni®, specially prepared for Ni-based alloys [44, 50]. The use of this agent resulted in the thick boride layers (up to 100 μm) of high hardness (1300 HK) which were produced on pure Ni [50]. The satisfactory depth of boride layers (up to 76 μm) of high hardness (up to 2400 HK) was also reported for Inconel alloys which were borided by pack-boronizing without SiC [45]. The similar effects were obtained in the case of boronizing process of Nimonic®90-alloy with the use of the special paste for Ni-based materials [51]. Fluidized bed technology was not proper to boronizing of nickel. Although the process without SiC was applied, the low hardness (about 870 HV) and the relatively thin boride layer (35 μm) were measured [43]. The electrochemical boriding of Inconel®600-alloy [46] showed a very interesting method because it resulted in a thick boride layer (81 μm) which was obtained at very short duration (0.25 h). The gas boriding [47,48] or laser boriding [49] of Ni-based alloys also provided the boride layers of good quality and satisfied thickness.

During gas boriding, the composition of boriding medium was controlled and was kept on the constant level [11,22–24]. Differently from the powder processes, it provided the stability of the diffusion flux from the boriding medium to the substrate material. The main disadvantage of gas boriding was the excess of boron diffusing to the substrate. Two-stage process [25,47,48] in N_2–H_2–BCl_3 atmosphere consisted in the saturation with boron and diffusion annealing which were alternately repeated. Such a gas process seemed to be more effective because of the elimination of the excess of boron during the second stage. In the previous study, the two-stage gas boriding was carried out on Nisil [47] and on Inconel®600-alloy [48]. Nisil contained about 4.4 wt.% of silicon that resulted in the formation of a porous nickel silicide zone at the end of the layer. Inconel®600-alloy contained 8.63 wt.% of iron which influenced the microstructure of the boride layer. A small amount of pores was visible in the compact boride zone due to the probable appearance of ferrous and ferric chlorides ($FeCl_2$, $FeCl_3$) in the atmosphere [48]. The same effect was previously reported for gas-borided steel [25]. Therefore, Nimonic®80A-alloy with limited content of Fe (0.25 wt.%) was used during the present investigation. Microstructural characterization of the produced boride layer, its chemical and phase composition as well as some mechanical properties (hardness and wear resistance) were studied and were compared to those obtained for Inconel®600-alloy.

2. Material and methods

2.1. Material

Two Ni-based alloys, called Inconel®600 and Nimonic®80A, were investigated. Their chemical compositions were shown in Table 1 in detail. The ring-shaped specimens (external diameter ca. 20 mm, internal diameter 12 mm and height 12 mm) were examined.

2.2. Selection of boriding method

The gas method of boriding wasn't chosen by accident. The development in the gas methods of carburizing, carbonitriding and nitriding [53–56] caused these processes to be completely automated. However, the possibilities of automation of generally used methods of boriding in these days (powder-pack method, paste method, or boronizing in a liquid medium) were limited.

The gas boriding could also be easily automated. Differently from the powder-pack method, the composition of boriding medium was controlled and was kept on the constant level during this process [11, 22–24]. It provided the stability of the diffusion flux from the boriding medium which enabled the better simulation of growth kinetics of boride layers [27,28]. Recently, a safer gas mixture, consisting of nitrogen, hydrogen and boron trichloride, was used [24,47,48], instead of the H_2–BCl_3 atmosphere previously applied [11,22,23,27,28]. The excess of boron diffusing to the substrate was the main disadvantage of gas boriding with the use of boron trichloride. The atmosphere with the usually used amount of BCl_3 (up to 5 vol.%) was characterized by a boron activity value above 1 [11]. It caused the appearance of the excess of boron in the atmosphere that caused the production of iron borides of high boron concentration (FeB) close to the surface of borided steel. Therefore, the two-stage process, consists of the saturation with boron and diffusion annealing, repeated alternately, was applied in order to eliminate this problem [24,47,48]. During the second stage (diffusion annealing), the delivery of BCl_3 was stopped, and then the excess of boron was eliminated that caused such a process to be more effective. The surface of borided material was relatively quickly saturated with boron during the first stage, and then, boron diffused into the substrate during the diffusion annealing, causing the increase in layer thickness. Moreover, the two-stage process caused the acceleration of growth kinetics of boride layers produced on steels [24]. Therefore, during the previous research of gas boriding of Ni-based alloys [47,48], such a two-stage process was used. In the present study, the continuous gas boriding (with continuous delivery of BCl_3) was applied in order to compare its effects with the two-stage method.

2.3. Gas boriding

The devices applied during gas boriding were shown in Fig. 1. The boriding atmosphere consisted of nitrogen, hydrogen and boron trichloride. The gases were delivered into the vertical furnace (1) with the quartz retort (2) in which samples were inserted. The inlet and outlet of atmosphere were marked with arrows. Three independent heating zones were characteristic of furnace which was equipped with the power-supply system containing a control system of the temperature (3). The personal computer (16) with HTMonit software controlled all the heating process. Additionally, the temperature near the heated

Table 1
Chemical composition of materials used (wt.%).

Material	C	Si	Mn	S	Al	Ti	Cr	Cu	Fe	Ni
Inconel®600	0.078	0.18	0.16	<0.001	0.06	–	15.72	0.04	8.63	Balance
Nimonic®80A	0.085	0.09	<0.01	0.001	1.44	2.55	19.52	0.01	0.25	Balance