EFFECT OF NANOFOIL OF THE Ni–NbC SYSTEM ON STRUCTURE OF ELECTRON BEAM WELDS IN HEAT-RESISTANT ALLOYS

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The effect of niobium carbide nanoparticles on structure and properties of electron beam welds in nickel alloys was studied. Alloying of the weld metal with niobium carbide nanoparticles was performed by adding composite nanostructured foil of the Ni–NbC system into the weld pool. The foil was produced by electron beam evaporation of the components in vacuum, followed by combined deposition of their vapour flows on the substrate. Adding the niobium carbide nanoparticles into the weld pool was shown to lead to formation of crystalline grains with a cellular structure within the weld zone, with the NbC particles located along the boundaries of the above grains. The effect of this structure of the welds on their mechanical properties was analysed.

Keywords: *electron beam welding, electron beam evaporation, nickel alloy, weld, foil, alloying, modification, niobium monocarbide, nanoparticles, intragranular substructure*

Main difficulties in welding heat-resistant precipitation-hardening nickel-base alloys are associated with the need to prevent hot cracking of the welds and provide the welded joints with a required set of mechanical, technological and service properties. One of the ways of addressing these problems is optimisation of alloying of the weld metal. The alloying elements of choice in this case are those that improve high-temperature ductility of the weld (even at the expense of decreasing its strength compared to that of the base metal). Cracking of the weld metal and HAZ can be avoided by adding molybdenum, vanadium, cobalt, manganese, titanium, boron, rhenium, hafnium and yttrium, as well as their borides, oxides and carbides to the weld metal, and by controlling the welding process [1–5].

However, traditional methods used for alloying the welds have a number of drawbacks. For example, alloying the weld metal with molybdenum and tungsten decreases high-temperature corrosion resistance, presence of boron reduces heat resistance, and adding rhenium, hafnium and yttrium is difficult to implement in terms of technology. In this connection, optimisation of a method of alloying the weld metal in welding heat-resistant precipitation-hardening nickel alloys is a problem of current importance.

One of the most common metallurgical methods for preventing hot cracking is refining of structure of the weld metal and HAZ by alloying the weld pool with modifiers [6–8]. Adding small amounts of nitrides, carbides, oxides and other elements promotes formation of fine-grained structure of the weld metal owing to heterogeneous solidification [9]. Modification also contributes to the intensity of the diffusion processes in the melt and promotes lowering of the level of liquation in the weld metal [7].

Positive results were obtained from using thin composite foils consisting of components of a nanosized scale as a filler metal in fusion welding or as a transition element in pressure welding [10, 11]. Such foils produced by combined condensation of various components from the vapour phase and containing nanoparticles provide activation of the diffusion processes during welding [12–15]. Supposedly, adding refractory nanoparticles to the weld pool will also promote increase in the number of solidification centres and, eventually, grain refining, formation of equiaxed structure and uniform distribution of alloying elements in the weld metal.

By an example of model materials (nickel), this study considers the possibility of modifying structure of the welds by using fillers in the form of foils that contain nanosized carbide phases, and gives estimation of strength properties of the resulting welded joints.

Pure nickel being the base of heat-resistant alloys was used as a model material to evaluate the effect of nanoparticles added to the weld pool on structure of the weld metal. Chemical composition of alloying filler metals was selected allowing for the requirement of filler and base metal matching. From this standpoint, the preference was given to niobium monocarbide, which is characterised by high thermodynamic stability and used as a structural component of many heat-resistant alloys.

The filler metal based on a composite of the Ni–NbC system in the form of foil 50–150 μm thick was produced by electron beam evaporation of components in vacuum using two ingots, followed by combined deposition of their vapour flows on the substrate at a preset temperature. The flow diagram of the deposition process is given in [10, 11]. A layer of CaF_2 was

Microhardness of welds made on nickel by using filler foils of different chemical compositions

NbC in foil	NbC in weld metal	HV, MPa
Without foil	0	1200
6.7	0.68	1310
8.8	0.73	1385
20.0	0.87	1475
26.0	0.96	1495
28.0	1.07	1515
35.5	1.37	1735
60.0	2.70	1865

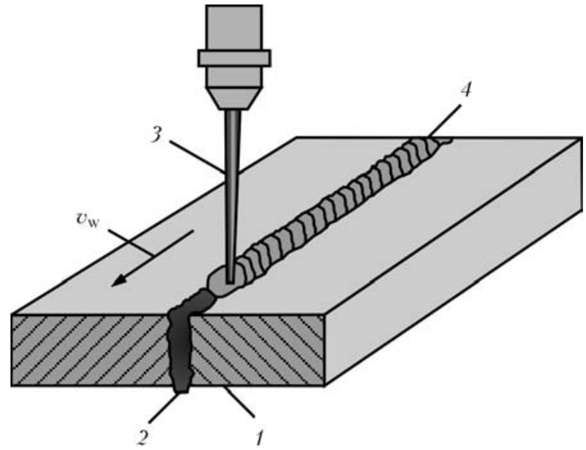

Figure 1. Flow diagram of the EBW process using nanostructured foil as filler metal: *1* — base metal; *2* — filler foil; *3* — electron beam; *4* — weld

preliminarily deposited on the substrate, which provided easy detachment of the foil. Pressure in the chamber during deposition was maintained at a level of $5\cdot10^{-3}$ Pa. The temperature of the substrate during deposition was 550–600 °C.

Nickel specimens for the experiment were cut from the billets by the electric spark method. They were polished and then degreased before welding. The filler in the form of foils of different thicknesses and compositions (Figure 1, Table) was butt added between the two halves of the billet to be welded.

The choice of electron beam welding (EBW) was based on the possibility of regulating temperature-time conditions of the process, volume and shape of the weld, and limiting the negative effect of residual atmosphere on the weld metal. EBW was performed by using installation U-212m with a capacity of 30 and 14 kW. For intensive stirring of the filler material with the base metal, welding was carried out at a low speed (about 8–12 m/h) with transverse scanning of the electron beam.

Specimens of the filler foil and welded joints were prepared for metallographic analysis by a standard procedure using grinding-and-polishing machine «Abramin» of the «Struers» Company. Structure and chemical composition of the foil and weld zone were analysed by using scanning microscope «SamScan» equipped with energy-dispersive local analysis system «Energy 200». Microhardness of the weld was measured by using the microhardness measuring attachment to optical microscope «Polyvar-Met» under a load of 0.49 N by the Vickers method. Structure of the filler foil and weld metal in the planar and transverse sections was analysed by using transmission electron microscope «Hitachi H-800» at an accelerating voltage of 200 kV. The foils for these examinations were subjected to mechanical thinning and polishing by using machine «GATAN 656», and then to thinning by bombarding the surface at an angle of 3° with argon ions at the energy of 5 keV and ion gun current of 20 mA using machine «PIPS 691».

X-ray diffraction analysis of the composite filler foil was carried out by using standard geometry θ–2θ with diffractometer «DRON-4» in Cu_{K_α} radiation.

Composite filler foil Ni–(6.7–35.5) wt.% NbC produced by the electron beam evaporation method had a uniform distribution of components through thickness δ (Figure 2). Cross section of the filler foil in the initial state had a columnar structure, width of the columnar crystalline grains being approximately 300 nm (Figure 3). The low condensation temperature provided formation of nano-scale carbide particles in the condensate, which was confirmed by the presence of wide diffraction peaks (indicated by arrows in Figure 4, *a*) of NbC in the diffraction pattern of a specimen of foil Ni–6.7 wt.% NbC after deposition. Narrow peaks of NbC appeared in the diffraction pattern only after annealing of the foil at a temperature of 1100 °C for 2 h, this being indicative of coarsening of the carbide particles (Figure 4, *b*).

The clearly pronounced peaks of nickel and niobium carbide appeared in the diffraction pattern after the content of NbC grew to 35.5 wt.% (Figure 4, *c*), i.e. increase in the niobium carbide content of the composite was accompanied by coarsening of the carbide particles.

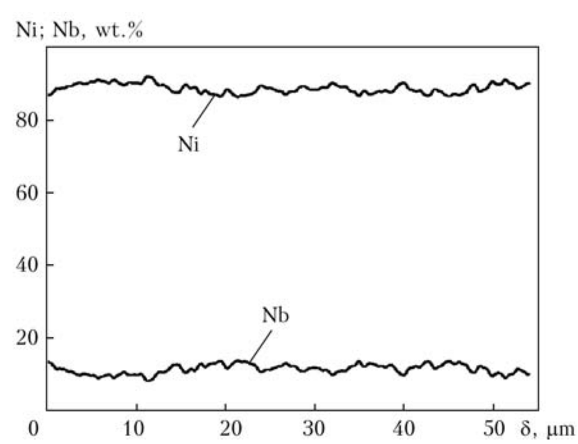

Figure 2. Distribution of elements through thickness δ of composite foil of the Ni–NbC system

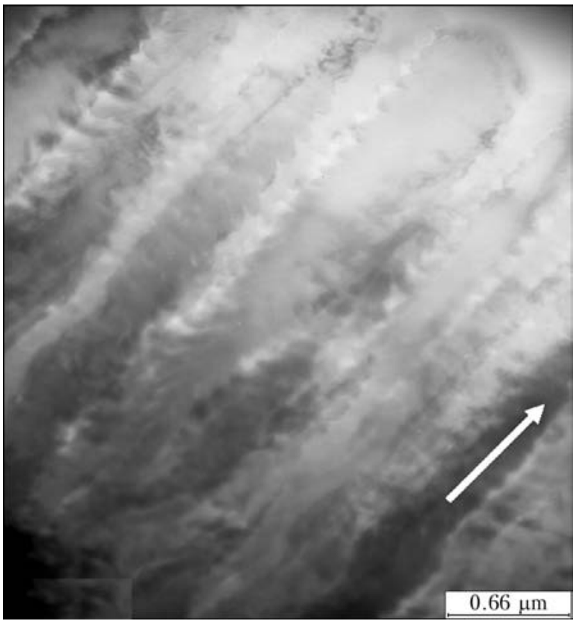

Figure 3. Microstructure of specimen of composite foil Ni–6.7 wt.% NbC (direction of growth of crystalline grains is indicated by arrow)

According to the results of X-ray spectral microanalysis, the use of this foil as a filler metal provides formation of dense defect-free welds with a uniform and regular distribution of carbide particles over the entire volume of the weld (Figure 5). It should be

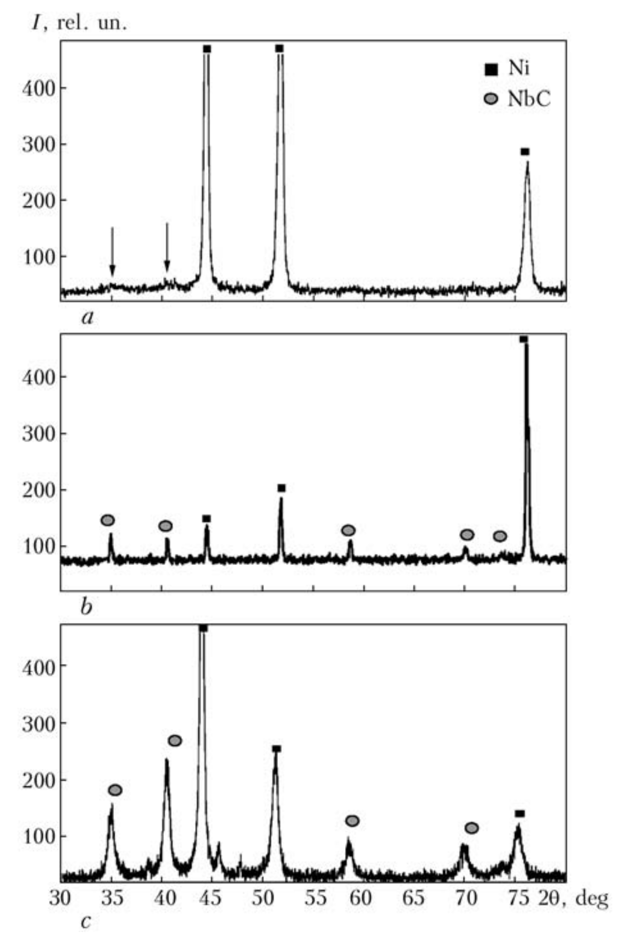

Figure 4. Diffraction patterns of specimens of composite foils Ni–6.7 wt.% NbC after deposition (*a*), subsequent annealing at 1100 °C for 2 h (*b*), and Ni–35.5 wt.% NbC (*c*) in Cu_{K_α} radiation

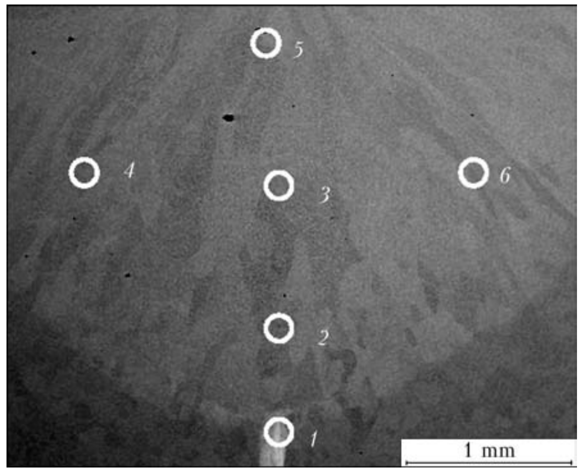

Figure 5. Microstructure of weld metal produced by using composite foil Ni–28 wt.% NbC (the photo was made in the phase contrast mode; numbers show the points of determination of local chemical composition): *1* — 19.90; *2* — 1.11; *3* — 1.15; *4* — 1.00; *5* — 1.47; *6* — 1.05 wt.% NbC

noted that this uniformity of distribution of added particles over the entire weld pool is hard to provide by modifying it with powder modifiers. It can be seen that with the use of the filler foil the nanosized NbC particles are uniformly distributed in the bulk of the forming weld metal during the EBW process and convective stirring of the weld pool. At a NbC content of the foil equal to about 28 wt.%, the average NbC content of the weld metal was approximately 1.07 wt.%. Increase in the NbC content of the filler foil from 6.7 to 35.5 wt.% led to growth of the weight fraction of carbide particles in the weld metal (see the Table). For instance, at the up to 10 wt.% NbC content of the foil the weight fraction of the carbide phase in the weld was 0.68–0.73 %, and at the 20 to 60 wt.% NbC content the weight fraction of this phase grew from 0.87 to 2.70 %.

In welding of pure nickel using no filler foil, the structure formed in the joint zone featured a slightly pronounced orientation of primary crystalline grains towards the weld surface (Figure 6, *a*). The size of cross sections of the crystalline grains was 80–200 μm, and their length was 150–500 μm. Grain microstructure of the weld was homogeneous, having no visible precipitates of secondary phases (Figure 6, *a*, *c*).

An insignificant decrease (to 50–120 μm) in the transverse grain size was observed when using filler metal in the form of the Ni–NbC foil with the NbC content of about 6.7 wt.%. In this case, the primary grains had a more equiaxed polyhedral shape (Figure 6, *b*, *d*). The presence of nanosized carbide particles in the weld pool promoted refining of the primary crystalline grains forming along the line of fusion with the substrate (Figure 6, *e*, *f*). The transverse size of the polyhedral grains at the solidification front in metal decreased from 150–300 μm (for the weld produced without filler) to 50–70 μm, which is a positive factor for prevention of formation of the columnar oriented structure of primary crystalline grains.

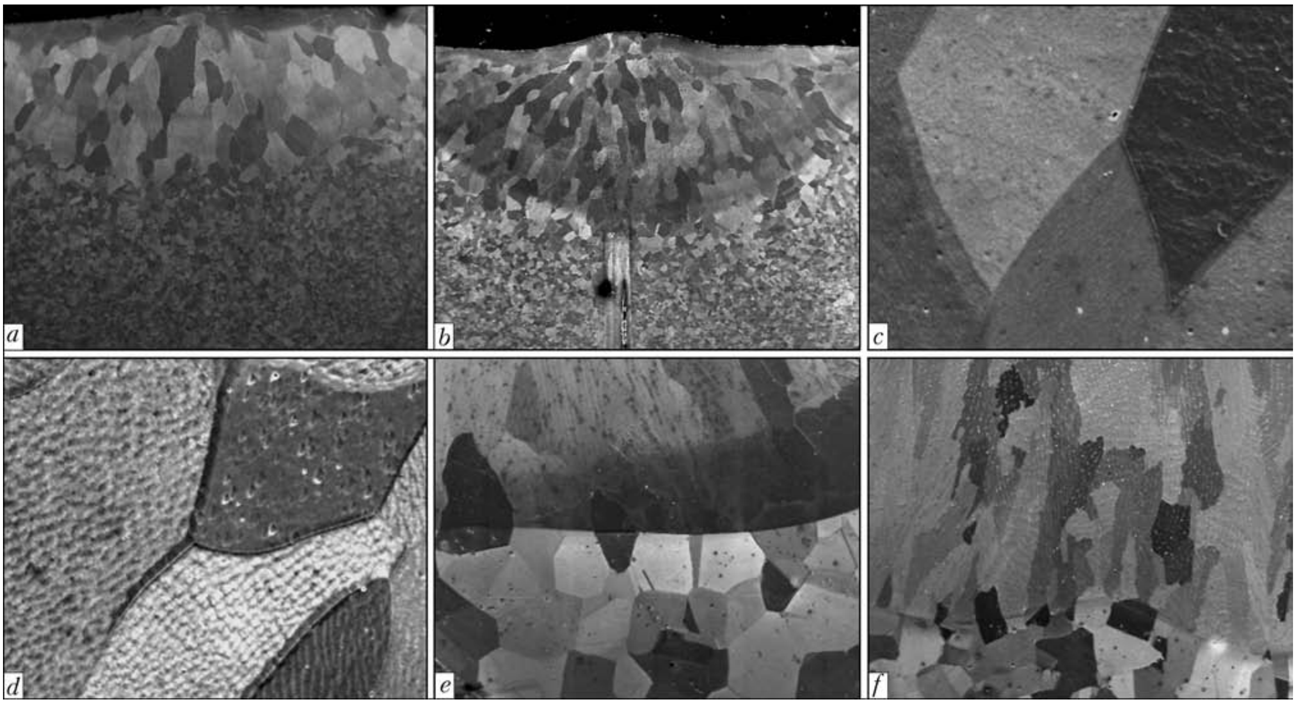

Figure 6. Microstructure of metal of the welds made on nickel without nanostructured filler (*a*, *c*, *e*), and with filler foils Ni–6.7 wt.% NbC (*b*, *d*) and Ni–20 wt.% NbC (*f*)

Metallographic etching revealed an internal substructure of the grains in the form of subboundaries, having certain orientation in the bulk of a given crystalline grain. Substructure became more pronounced with increase in the weight fraction of the NbC particles in the weld pool, i.e. with increase in the NbC content in the filler metal (see the Table). As the second phase content increased, the boundaries of subgrains became more clearly defined and developed (Figure 7, *a*, *b*). X-ray spectral analysis by scanning the area of a single crystalline grain in the weld metal revealed distribution of the niobium-rich phase along the subboundaries of cells of the primary crystalline grains (Figure 7, *c*).

Electron microscopy of central regions of the subgrains showed that they did not contain the NbC particles and were characterised by a low dislocation density (Figure 8, *a*, *c*). The regions located near the subgrains contained the NbC particles (Figure 8, *d*) and featured a high dislocation density (Figure 8, *c*).

Increasing the NbC content of the foil to 60 wt.% caused not only increase in the weight fraction of niobium along the subboundaries of primary crystalline grains of the weld but also precipitation of discrete NbC particles 0.5–1.0 μm in size (light particles), whose structure corresponded to stoichiometric carbide NbC, according to the electron diffraction pattern (Figure 9).

Welding of pure nickel involves no difficulties, as no phase transformations take place in heating or cooling it. It can be assumed that stable groups of atoms are formed in the bulk of the pure nickel melt in overcooling, and some of them act as the solidification centres. Peculiarity of formation of the welds in pure nickel is that the molten metal of the weld pool is characterised by a high sensitivity to impurities located along the boundaries of primary grains and subgrains of the weld metal. The results obtained allow a conclusion that with adding into the weld pool the filler metals that contain refractory carbide particles

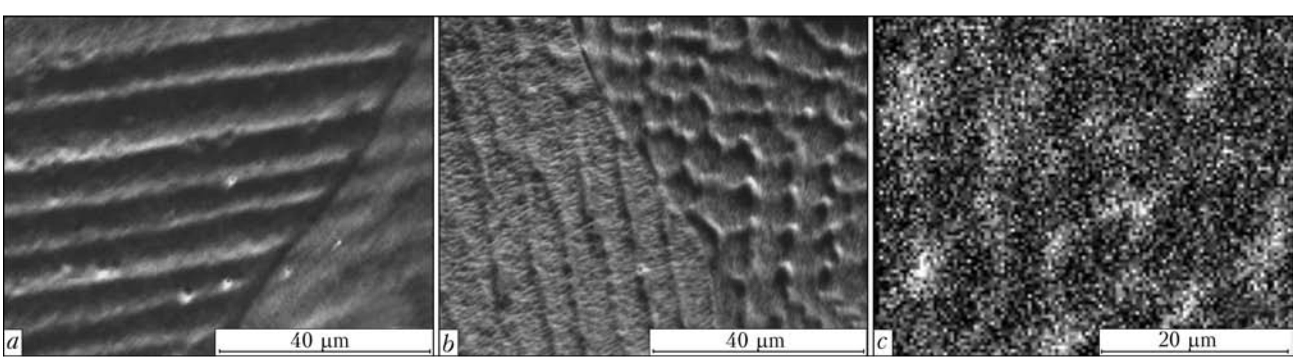

Figure 7. Substructure of primary grains of metal of the welds made on nickel at their 8.86 (*a*) and 35.5 (*b*) wt.% NbC content, and electron microscopic picture of distribution of niobium in one crystalline grain (*c*) (regions with light contrast at subboundaries correspond to 3.04 wt.% NbC)

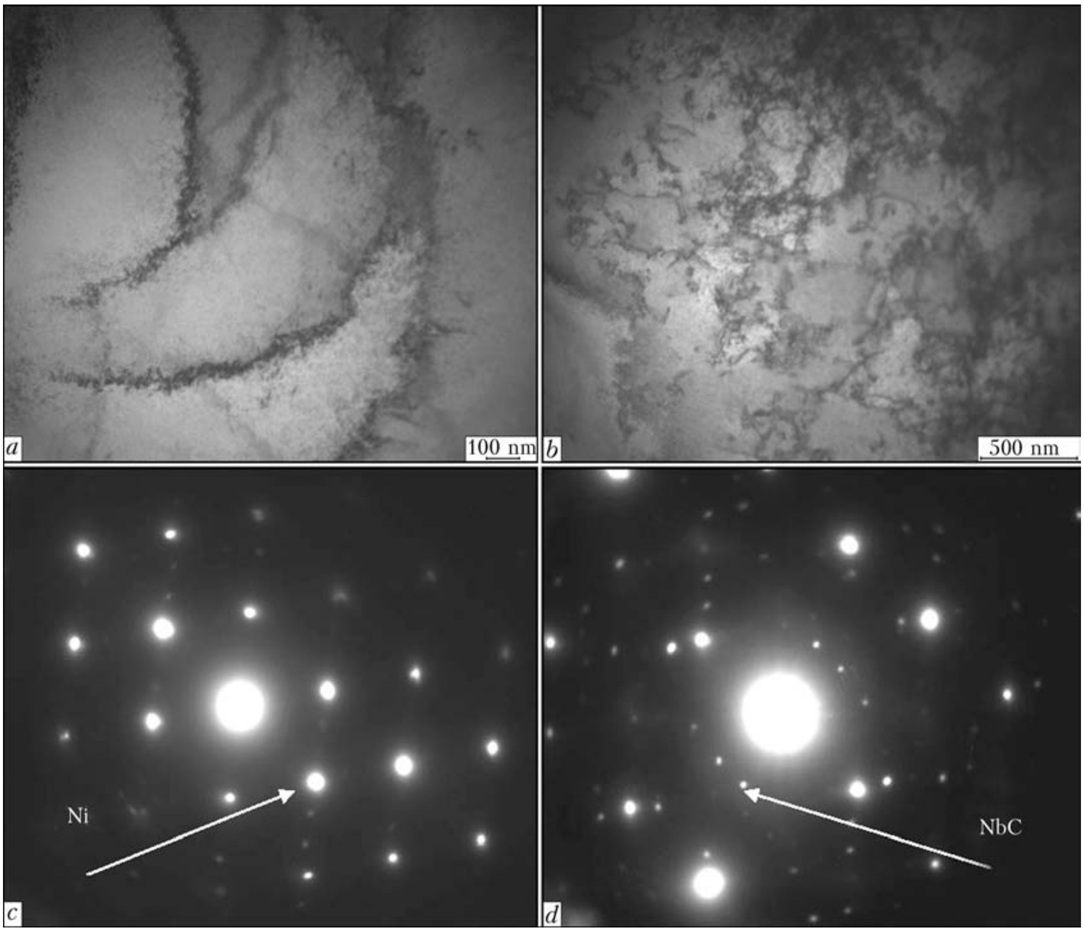

Figure 8. Microstructure (*a*, *b*) and corresponding electron diffraction patterns (*c*, *d*) of regions of the weld metal obtained by using the Ni–NbC filler at centres of crystalline subgrains (*a*, *c*) and at their boundaries (*b*, *d*)

the latter exert a dual effect on structure of the weld metal. Firstly, they can act as centres of nucleation of primary crystalline grains, this providing decrease in their size and change in their shape towards a more equiaxed one, and, secondly, upon getting into the grain body, they can promote formation of a cellular substructure of the primary grains owing to their preferential precipitation at the subgrain boundaries. The set of subgrains, the boundaries of which are rich in the carbide phase and oriented in a certain way within the primary grain, is in fact a reinforced grain structure. The boundaries of such grains are comparable in their characteristics (degree of imperfection and level of stresses) to boundaries of the primary grains, and in deformation of a material they will prevent evolution of the dislocation structure, which may affect mechanical properties of the welded joint.

The investigations conducted to evaluate the effect of the content of the NbC particles on strength properties of the welds showed that microhardness of the

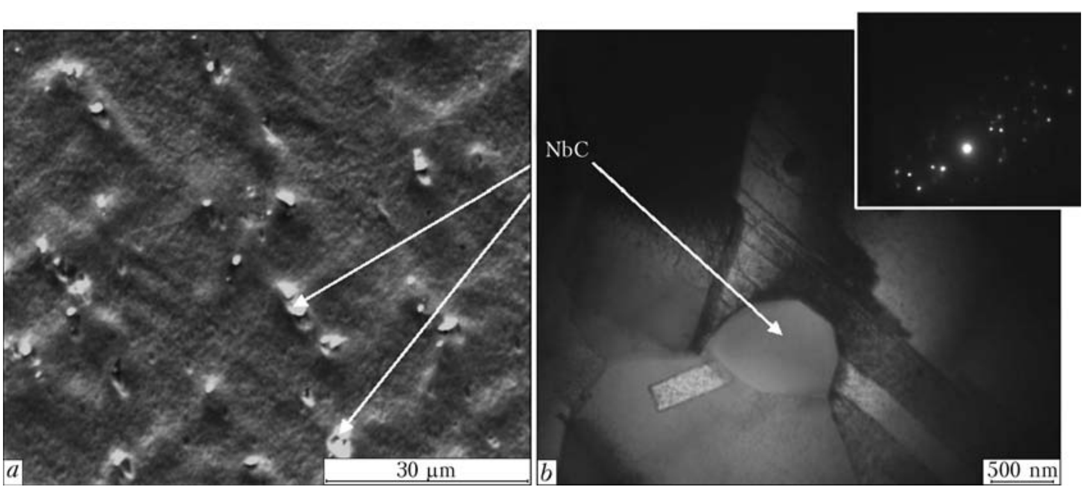

Figure 9. Pattern of distribution of carbide phase NbC in the bulk of primary crystalline grain of the weld metal obtained by using composite filler foil Ni–60 wt.% NbC (*a*), and electron microscope dark-field image of carbide particle obtained in NbC reflex (*b*)

material in the weld zone increased from 1200 (for pure nickel) to 1865 MPa (when using the Ni–35.5 wt.% NbC filler foil) with increase in their weight fraction in the weld pool. The mean value of short-time strength of the welded joints produced by using the Ni–NbC filler foil increases to 343 MPa, compared with strength of the welds (325 MPa) made without the filler foil, whereas the value of yield strength $\sigma_{0.2}$ increases two times (to 248 MPa) compared with pure nickel ($\sigma_{0.2}$ = 126 MPa). Therefore, the modifying effect of the niobium carbide nanoparticles on structure of the welds as a whole provides increase in short-time strength of the welded joints in the as-welded condition at a small decrease in toughness of the joints.

As shown by structural analysis, the highest modifying effect of the niobium carbide particles shows up at their content of the filler foil equal to 15–20 wt.%. Increase in the NbC content of the filler foil to more than 35.5 wt.% leads to precipitation of coarse niobium carbide particles along the primary grain boundaries in the weld metal, which form carbide chains after annealing of the material, while this may have a negative effect on mechanical properties of the welded joints at high temperatures and applied stresses.

Mechanical tests of the EI698 nickel alloy welded joints produced by using composite filler Ni–NbC, which were conducted at a temperature of 600 °C, showed that σ_t = 805 MPa and $\sigma_{0.2}$ = 440 MPa corresponded to the level of properties of the base metal.

Therefore, the preferential distribution of the niobium carbide nanoparticles along the subgrain boundaries promotes strengthening of the weld and increase in its microhardness. Also, it may affect increase in heat and crack resistance of the welded joints [16].

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