Effect of molybdenum on the hot-tearing susceptibility of the Ni-Cr-Mo-B system

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Abstract. The paper presents data on the effect of molybdenum on the hot-tearing susceptibility of the Ni-Cr-Mo-B system when surfacing with nickel-based alloys. With a boron content of 2.5 – 3.2%, as well as low carbon and silicon content, the alloying elements, depending on a doping concentration, have different effects on the technological strength of the deposited metal. Molybdenum increases the technological strength of alloys. Alloying the deposited metal with molybdenum in an amount up to 12% in alloys with 2.5% boron concentration at 20% chromium does not lead to the disappearance of cracks. At a molybdenum concentration of more than 12%, the number of cracks in the deposited bead decreases and when the molybdenum concentration is equal to 15%, the cracks disappear, and only increasing the molybdenum content to 20%, in the presence of at least 20% chromium in the alloy, makes it possible to obtain deposited metal without cracks.

1. Introduction
Currently, extreme cases of intercrystalline rupture at high temperatures in nonequilibrium solidifying alloys (deposited layers) are clearly distinguished.

1. Solidifying cracks are formed along the enriched interaxial and interdendritic areas at the moment when the latter are in a liquid state. This type of destruction is related to the solidification of the last portions of the liquid phase enriched in easily fusible alloying elements and impurities, and is observed in alloys in which the second phase in the form of eutectics and chemical compounds is formed directly in the process of solidification [1].

2. Subsolidus cracks which form most often in single-phase alloys with a narrow temperature range of solidification not along liquid intercrystalline layers, but after solidification of the last portions of the liquid phase, i.e. below the temperature of the real solidus.

As it is shown by recent researches, the fragmentation of the columnar structure and the formation of a boundary network arbitrarily oriented towards the primary crystallization forms (cells and dendrites) are determined by the subsolidus migration of grain boundaries arisen in solidifying to new, more equilibrium positions with a lower boundary energy. Based on the research findings by M. Kh. Shorshorov [5], hot tearing in nickel-chrome-tungsten alloys occurs in the temperature range (from solidus to 1273 – 1253 K (1000 – 980 °C)), in which polygonization is most likely to develop. In this temperature range there is observed a plasticity drop of alloys. The lowest plasticity occurs at temperatures between solidus and 1573 K and is equal to 0.5 – 0.6%.
2. Materials and methods
In order to determine the effect of alloying elements on hot-tearing susceptibility, experimental surfacing was carried out with cast rods of a 5 mm diameter and a 270 mm length on 60x15x5 mm plates in 1, 2 and 3 layers. The cast rods [4] of the experimental alloys were melted in an LSZ-35 kW high-frequency induction furnace. The crucible material was chrome magnesite. The melting was carried out using industrial-grade constituents. Primary nickel of the H-2 grade (GOST 849-2008), ferromolybdenum of the FMo60 grade (GOST 4759-91), ferrochrome of the FH005A grade (GOST 4757-91), ferroboron of the FB20 grade (GOST 14848-69) were used as a charge mixture. Mishmetal (ferrocerium) of the MTS50ZH grade (Technical Specifications 48-4-280-91) was used as a deoxidizer. The molten metal was poured into green sand molds. The surfacing was performed using an Aurora INTER TIG 200 AC/DC Pulse (TIG, MMA) welding machine. To reduce the process of mixing the deposited metal with the parent one, when surfacing the first layer, the welding current was equal to 100 – 110 A, the second to 115 – 120 A and the third to 130 – 135 A.

3. Effect of molybdenum on hot-tearing susceptibility in surfacing
To select wear-resistant surfacing alloys [2, 3] of the Ni-Cr-Mo-B system without hot cracks, experimental surfacing was performed in a wide range of alloying with the principal constituents — chrome, molybdenum, boron, and the additional ones — vanadium and niobium. The amount of boron in the alloy varied from 2.5 to 4%, based on the experience of alloying surfacing nickel alloys with boron, described in [6, 7]. Carbon content in all surfacing did not exceed 0.05%, thereby reducing the likelihood of carbide formation. The constitutions of the alloys investigated and the number of detected cracks are presented in Table 1. Based on the results obtained (shown in the table below), we derived the molybdenum content dependence of the Ni-Cr-Mo-B alloy cracking (see Fig. 1 – 5).

| S. No. | Mo, % | Cr, % | B, % | V, % | Nb, % | The number of cracks, pcs |
|-------|-------|-------|------|------|-------|--------------------------|
| 1     | 5.0   | 20.0  | 2.5–3.2 | - | - | 8–12 | 1. All alloys shown in the table are nickel |
| 2     | 7.0   | 20.0  | 2.5–3.2 | - | - | 6–11 |
| 3     | 10.0  | 20.0  | 2.5–3.2 | - | - | 5–9 | Based |
| 4     | 12.0  | 20.0  | 2.5 | - | - | 1 | 2. The carbon content exceeds 0.05% |
| 5     | 12.0  | 20.0  | 2.8 | - | - | 2 | in all alloys does not exceed 0.05% |
| 6     | 12.0  | 20.0  | 3.0–3.2 | - | - | 3 | |
| 7     | 15.0  | 20.0  | 2.5 | - | - | 3 | 3. The iron content in all alloys is at the level |
| 8     | 15.0  | 20.0  | 2.8 | - | - | 2 | All alloys is at the level |
| 9     | 15.0  | 20.0  | 3.0–3.2 | - | - | 3 | Of 4%, the manganese |
| 10    | 17.0  | 20.0  | 2.5–3.0 | - | - | 0.8 – 1 %, the silicon |
| 11    | 17.0  | 20.0  | 3.2 | - | - | 1 | 0.12 – 0.2 % |
| 12    | 20.0  | 20.0  | 2.5–3.2 | - | - | 4–5 |
| 13    | 20.0  | 20.0  | 2.5–3.2 | 0.6–2.0 | - | 7–9 |

It is known that with a molybdenum content increase, the resistance of nickel-chrome deposited metal to hot tearing gradually increases, reaching a maximum at 22 – 25 %, then rapidly decreases [8]. Many researchers have tried to explain the effect of molybdenum in terms of the polygonizational hypothesis of hot tearing in single-phase alloys at high temperatures. According to this hypothesis, molybdenum, having a high diffusion activation energy, inhibits the movement and grouping of lattice imperfection in a nickel-chromium matrix and inhibits the formation of secondary polygonizational boundaries which are the nuclei of intercrystalline rupture. However, there exists an opinion [9] that, depending on the concentration of particular elements in nickel-based alloys, both subsolidus and crystallization patterns of hot tearing are possible.
According to the literature data [8], with molybdenum content up to 10% in a nickel-chrome alloy, cracks form in solid-liquid state. The molybdenum content increase of more than 10% results in crack formation in the metal already in solid state [10]. However, the effect of molybdenum on the technological strength of hard surfacing nickel-chromium alloys with boron has not yet been fully studied and it is therefore of interest to trace the effect of the concentration of molybdenum and boron on the technological strength of Ni-Cr-Mo-B alloys. As it is shown in Table 1, the addition of up to 12% molybdenum in the alloys with 2.5–3.2% boron concentration at 20% chromium does not lead to the disappearance of cracks, however, when comparing alloys containing molybdenum of 5, 7, 10 and 12% the number of cracks in the weld bead decreases and when the molybdenum concentration is 15% the cracks disappear. However, if we follow the concentration of molybdenum and boron further in Table 1, we can note that only molybdenum content increasing to 20% can guarantee obtaining deposited metal without cracks in the most used range of boron doping from 2.5 to 3.2%. A further increase in molybdenum content in the surfacing metal with an increase in boron concentration of more than 3.2% does not have a positive effect on the technological strength of the deposited metal, since in this case a large number of borides and eutectics are formed, which adversely affects the ductility of the alloys. Therefore, it can be said that molybdenum alloying of nickel-chromium alloys with boron up to 20% increases the technological strength of the deposited metal with boron content up to 3.2%.

Figures 1–5 show the dependences of the molybdenum content effect on the susceptibility of the Ni-Cr-Mo-B alloys to hot tearing.
Figure 2. Dependence of crack formation of the Ni-Cr-Mo-B alloys on the molybdenum content (2.8 – 3.2% boron, 20% chromium, and 15% molybdenum).

Figure 3. Dependence of crack formation of the Ni-Cr-Mo-B alloys on the molybdenum content (2.8 – 3.2% boron, 20% chromium, and 17% molybdenum).

Figure 4. Dependence of crack formation of the Ni-Cr-Mo-B alloys on the molybdenum content (2.8 – 3.2% boron, 20% chromium, 0.6 – 2.0% vanadium, and 20% molybdenum).
4. Conclusion

Based on the experimental results obtained, it can be concluded that in nickel-based alloys of the Ni-Cr-Mo-B system with 2.8 – 3.2% boron and a low content of carbon and silicon, molybdenum has different effects on the technological strength of the deposited metal. Molybdenum improves the technological strength of alloys. Alloying deposited metal with molybdenum in an amount not less than 20% (in the presence of at least 20% chromium in the alloy) makes it possible to obtain the deposited metal without cracks.

Based on the above, it can be concluded that alloying Ni-Cr-Mo-B alloys within: C≤0.05 %, Si≤0.2 %, Mn=0.8 – 1 %, Fe≤4 %, Cr=20 – 30 %, Mo=20 – 25 %, B=2.5 – 3.2 %, Ni – all the rest of it, does not cause hot tearing in surfacing.

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