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FEATURES OF THE CRYSTALLIZATION OF LASER REMELTED $Fe_{83}B_{17}$ ALLOY

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UDC 621.9.048:699.15'781

The overwhelming amount of work on hardening from the liquid state and obtaining of amorphous alloys has been done under conditions of a quite long existence of the molten material, which led to practically complete homogeneity of it. In the case of melting of a thin surface layer of alloys with the use of pulsed concentrated flows of energy, in particular laser radiation, complete homogeneity of the molten material is far from always obtained [1]. In addition, the molten layer is in direct contact with the crystalline base.

The purpose of this work was an investigation of the influence of interphase boundaries and nonhomogeneity of the molten material on crystallization in superrapid hardening and subsequent heat treatment of the surface layer of $Fe_{83}B_{17}$ alloy obtained by laser remelting.

The investigations were made on 20 × 20 × 2 mm polished plates of cast $Fe_{83}B_{17}$ alloy which were irradiated with a pulsed-periodic action CO_2 laser with a pulse length of 5 μsec in a vacuum of on the order of 1 Pa with a pulse energy density of 120 J/cm^2. The pulse-repetition frequency (10-15 Hz) and the rate of movement of the specimen relative to the light beam (1.8-6.7 mm/sec) were such that each point of the surface was subjected to N pulses of radiation (N = 6-33). After laser treatment the working surface of the specimens was pickled in a concentrated hydrofluoric acid solution to remove contaminants.

The influence of annealing on the phase composition of the remelted layer was investigated on specimens of irradiated alloys of series A and B. The radiation energy of a pulse was 280 and 100 J/cm^2, the repetition frequency of the laser pulses 40 Hz, and the number of

I. P. Barden Central Scientific-Research Institute for Ferrous Metallurgy. Translated from Metallovedenie i Termicheskaya Obrabotka Metallov, No. 5, pp. 15-18, May, 1988.

 0026-0673/88/0506-0334$12.50 © 1988 Plenum Publishing Corporation

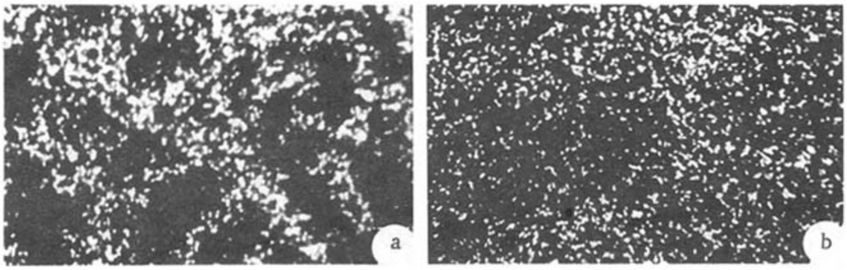

Fig. 1. Track autoradiograms of $Fe_{83}B_{17}$ alloy (1300×): a) original condition; b) after laser treatment.

actions 7 and 34 for specimens of series A and B, respectively. After laser irradiation a surface layer about 0.3 μm thick was removed by electrochemical etching.

The temperatures of the structural transformations occurring in the alloy close to the surface were determined by the method of thermally stimulated exoelectronic emission. The recording of the exoemission spectra, the same as the annealing of the specimens, was done on the unit described in [2] in a vacuum of 10^{-3} Pa with continuous heating at a rate of 15 K/min.

The phase composition of the surface layer of the alloys was determined by the method of conversion electron Mössbauer spectroscopy. The experimental spectra were obtained at normal temperature under conditions of constant accelerations on a unit with a gas-filled cumulative ionization electron detector [3]. For the individual specimens Debye powder patterns were recorded with the use of filtered K_α-radiation.

To determine the distribution of boron on the surface of the specimens a method of track autoradiography based on recording of the heavy charged particles of the $n + {}^{10}B \rightarrow {}^{7}Li + \alpha$ nuclear reaction by solid-state film detectors applied to the surface of the specimen was used. The number of tracks of the products of the reaction in the material of the detector was proportional to the concentration of boron atoms in the approximately 2 μm surface layer of the investigated object. The localization of the method on the surface is 2-5 μm.

The original structure of the specimens was a finely dispersed eutectic with dendritic inclusions of α-iron, the transverse dimension of which was about 10 μm (Fig. 1a). On the basis of the results of our preceding investigation [1] the laser radiation conditions were selected so that during the time of existence of the liquid full homogenization of the eutectic and some blurring of the concentration profile in the region of inclusions of α-iron observed on the autoradiograms of the laser radiation treated specimens occurred (Fig. 1b). Therefore, the molten material subjected to hardening was significantly inhomogeneous in composition.

The surface layer of the alloys after laser treatment under all conditions was partially crystalline. In addition to the amorphous state as the result of superrapid cooling of the molten material crystalline phases with various boron contents were formed. According to the data of Mössbauer spectroscopy, which agrees with the results of x-ray diffraction analysis, α-iron and boride phases including metastable Fe_3B boride of both the tetragonal and orthorhombic modifications and also stable Fe_2B and FeB borides are observed in the remelted layer. It should be noted that in hardening of homogeneous Fe—B molten materials at a rate insufficient for obtaining the pure amorphous state α-iron and orthorhombic Fe_3B boride are observed in the majority of cases [4].

Let us consider the possible processes leading to obtaining the phase composition given above. As already noted, in the molten layer in the region of inclusions of the excess phase areas with a variable boron concentration from low at the center of the inclusions to eutectic at a distance from it are formed. The cooling rate of the molten material is about 10^7 K/sec, which exceeds the critical for amorphization of the alloy of eutectic composition. However, it is not possible to suppress crystallization of the areas of the molten material with a metalloid content. Obviously, the crystals of α-iron occur and grow first. Therefore close to the inclusions of α-iron conditions close to the conditions of crystallization of the molten layer at the boundary with the crystalline base are created.

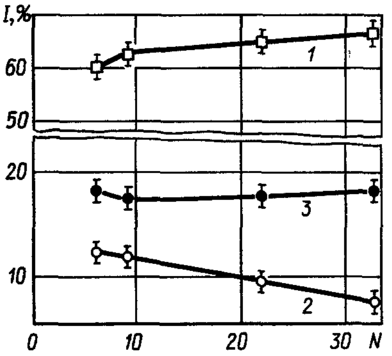

Fig. 2

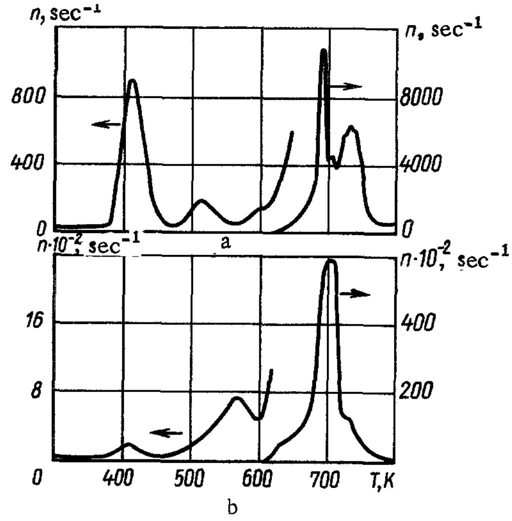

Fig. 3

Fig. 2. Relationship of the intensity of the Mössbauer spectra of the investigated phases to the number of laser actions (N): 1) amorphous; 2) α-iron; 3) borides.

Fig. 3. Thermally stimulated exoelectronic emission curves of specimens of series A (a) and B (b) of $Fe_{83}B_{17}$ alloy after laser treatment: n) counting rate of the exoelectrons.

Since the solubility of boron in α-iron is limited, the liquid in front of the front of crystallization is enriched with the metalloid. Under superrapid cooling conditions upon completion of the laser pulse the diffusion layer is thin, according to estimation data on the order of 1 µm, and therefore during cooling at the boundary with the growing crystalline areas there occurs a narrow zone of molten material with a nonuniform boron concentration reaching or even exceeding 50 at.% at the boundary and sharply decreasing with distance from it. In cooling in this zone the boron-rich phases FeB, Fe_2B, and Fe_3B occur. The main portion of the molten material of eutectic composition transforms to the amorphous state.

Therefore in cooling of the molten inhomogeneous layer three areas are formed, inclusions of α-iron crystals, the amorphous state, and an intermediate multiphase layer of borides. Figure 2 shows the relationships of the relative intensities of the Mössbauer spectra of the above areas to the number of times of remelting of the surface layer of the specimens. With an increase in the number of laser actions the quantity of α-iron decreases linearly and the share of amorphized areas steadily increases. This is an indication of an increase in homogeneity of the molten material and an improvement in the conditions of amorphization in multiple radiation. However, for full homogenization of the remelted layer many irradiations would be required (in our case $N \geq 75$) .

With high values of N and medium operating pulse-repetition frequencies of the light pulses ($F \geq 10$ Hz) heating of the specimen in the zone of irradiation to 500-600 K occurs, which reduces the hardening rate. This leads to some increase in the thickness of the transition layer and a reduction in the rate of increase in the amorphous phase content. In addition even with cooling rates close to the critical for reaching the amorphous state in $Fe_{83}B_{17}$ alloy with normal methods of hardening of the liquid ($v_{cool} \cong 10^6$ K/sec) the share of boride phases is limited and depends weakly upon N, that is, the cooling rate. Apparently diffusion of boron is the process limiting crystallization close to the α-iron inclusions.

Let us consider the influence of heat treatment on the phase composition of the remelted layer. Figure 3 shows the temperature relationships of the exoelectron emission of the alloys of series A and B. The thermally stimulated exoelectron emission spectra have a complex form and differ from one another, which is an indication of the multistage character of annealing of the amorphized layers and of the relationship of the temperatures of the phase transformations to the conditions of laser treatment. On the basis of the results of exoelectron emission the maximum heating temperatures of the specimens were selected for

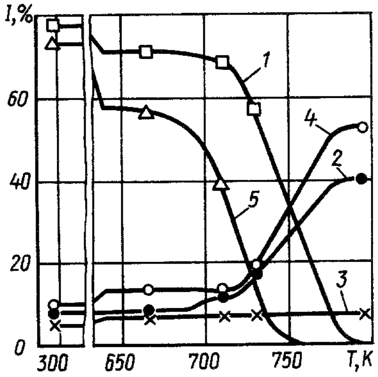

Fig. 4. Relationship of the intensity of the Mössbauer spectra of laser irradiated $Fe_{83}B_{17}$ alloy to annealing temperature: 1-4) specimens of series A; 5) series B; 1, 5) amorphous phase; 2) α-iron; 3) FeB boride; 4) other borides.

determination of the change in phase composition of the surface layer of the irradiated alloys in heat treatment with the use of Mössbauer spectroscopy.

The data of thermally stimulated exoelectron emission (Fig. 3) and conversion electron Mössbauer spectroscopy (Fig. 4) indicates the existence of the following basic stages of crystallization. At temperatures of up to 650 K there is an increase in the quantity of FeB boride and of both modifications of Fe_3B phase. Then at $T \cong 690$ K for specimens of series A and $T \cong 640$ K for specimens of series B crystals of α-iron are formed. The main share of the amorphous phase decomposes in heating in the 710-770 and 680-730 K ranges for specimens of series A and B, respectively, with the formation of α-iron and tetragonal and orthorhombic Fe_3B and Fe_2B borides.

The low thermal stability of the amorphous state in the specimens of series B is related to features of the conditions of their laser treatment. Each point of the surface of the alloys of this series was remelted 34 times which, as was noted earlier, caused heating of the specimens to 200-300°C and a reduction in hardening speed. Under such conditions the occurrence of processes of structural relaxation of the amorphous state and of the initial stages of formation of embryos was possible during laser treatment, which led to a reduction in crystallization temperature.

Through crystallization of the amorphous sheets of $Fe_{83}B_{17}$ alloy occurs in a single stage with formation of α-iron and tetragonal Fe_3B boride [5]. Decomposition of the amorphous state occurs in more than one stage. The first stage is apparently related to decomposition of the amorphous state at the boundary with the crystalline areas. To the presence in the remelted area of multiphase crystalline areas is probably related the unusualness of the phase composition of the annealed alloys, the presence of the boron-rich phases FeB and Fe_2B and the coexistence of orthorhombic and tetragonal modifications of Fe_3B boride.

As is known [6, 7], the composition of amorphous alloys in the direct vicinity of the surface differs from the nominal. The effective boron concentration C_B in a layer about 0.1 μm thick of specimens given different treatments was determined from the approximate equation

$$\frac{C_B}{1-C_B}=\sum_i \frac{C_i}{1-C_i} I_i .$$

where I_i and C_i are the intensity and concentration, respectively, of boron for the i-th phase. An analysis of the results obtained showed that electrochemical etching reduces C_B and annealing first leads to an increase in C_B, especially at the moment of intense decomposition of the amorphous state, but at higher annealing temperatures a decrease in boron content occurs in the surface layer. The change in alloy composition close to the surface causes a change in the character of crystallization. In particular, the increase in intensity of the α-iron lines at 700 K (Fig. 4) is apparently related to the formation of a boron-depleted layer adjoining the surface.

Conclusions. 1. In superrapid hardening in the layer remelted in laser irradiation of originally nonhomogeneous $Fe_{83}B_{17}$ alloy three areas are formed, inclusions of α-iron crystals, an amorphous zone, and an intermediate boron-enriched layer.

2. Crystallization of the amorphous areas obtained in laser treatment occurs in more than one stage in a broad temperature range. With an increase in the number of laser irradiations the thermal stability of the amorphous areas decreases.

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PROPERTIES OF ALLOY MA21 AFTER LASER TREATMENT

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UDC 621.9.048.7:669.721.5'884

The authors of [1-5] presented experimental data on the improvement of the anticorrosive and mechanical properties of the alloy MA21 of the system Mg—Li attained by laser treatment. However, these publications do not contain reports on detailed investigations of the regimes of laser heat treatment (LHT) that would make it possible to establish a correlation between the parameters of the treatment, the structure and properties of the material, which would be important to industry.

Moreover, there is no metal science analysis of the different structural states obtained in continuous (CLHT) and pulsed (PLHT) laser heat treatment.

On the basis of an analysis of the diffusion processes occurring during crystallization, the conclusion was reached that pure metal and alloys of eutectic type are most sensitive to the cooling rate [6].

In superrapid quenching by the method of pouring molten copper alloys of eutectic composition on a drum, the authors of [7] found five types of microstructures: from coarsely lamellar eutectic to single-phase metastable solid solution, and in the extreme case with a cooling rate of approximately 10^7 °K/sec, to a radiographically amorphous structure of solid solution.

Production Association "UralAZ." Translated from Metallovedenie i Termicheskaya Obrabotka Metallov, No. 5, pp. 18-24, May, 1988.

0026-0673/88/0506-0000$12.50

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