OXIDE-REINFORCED COMPOSITES WITH INTERMETALLIC MATRIX BASED ON NICKEL AND TITANIUM MONOALUMINIDES

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Abstract

The thermal stability of the developed composites (CM) is determined by physicochemical and mechanical compatibility of contacting components. The Al_2O_3/TiAl CM reinforced with continuous single-crystal oxide fibers (OF) of sapphire (20-25 vol. %) were prepared by the impregnation of the OF bundle by the intermetallic matrix (IMM) melt and directional solidification. In these CM, IMM (TiAl alloys) acts as a binder between OF and protects them from damage due to high adhesion between the OF and matrix and high strength of the fiber/matrix interface. The CM Y_2O_3/NiAl were manufactured by the powder metallurgy methods. In these CM, fine Y_2O_3 particles (2-5% vol.) promote the formation of oriented structures of the recrystallized IMM with coarse elongated grains. The creep resistance of this CM is determined by the structure of the IMM with a little fraction of transverse boundaries.

1 Introduction

Alloys and composite materials (CM) based on refractory and light intermetallics (IM) attract attention as the base of competitive materials for operation at t_{op} up to 1000-1100°C (instead of Ti alloys, $t_{op} \leq 600°C$) and up to 1400-1550°C (instead of Ni-superalloys, $t_{op} \leq 1100°C$) [1, 2]. These IM include titanium and nickel monoaluminides with ordered lattices (γ-TiAl with $L1_0$ face-centered tetragonal (fct) AuCu-type lattice and β-NiAl with the B2 body-centered cubic (bcc) CsCl-type lattice). The melting temperatures T_m of titanium and nickel monoaluminides are higher than those of the alloys based on Ti, Fe, and Ni. Since the introduction of any alloying element (AE) increases the density of NiAl- and TiAl-based alloys and lowers the melting temperature of the alloys (NiAl), it is reasonable to use only low alloys as an intermetallic matrix (IMM), and the reinforcing component should be refractory thermodynamically stable interstitial phases, which have a lower density and are inert to NiAl and TiAl. The most thermodynamically stable interstitial phases are metal oxides of Group III of the Periodic System. The Gibbs free energy of their formation, ΔF, in the whole temperature range of the CM production and operation is lower by a factor of 1.5-2 than those of nitrides, borides, and carbides.

The CM designed for long-term high-temperature service should exhibit the stable mechanical properties for long periods at high temperatures and loads. Therefore, not only the reinforcement scheme and the strength, volume fractions, and relative positions of the initial CM components, but also their thermal stability, which is determined by the physicochemical and mechanical compatibility of the CM components in contact with each other, is very important for the design of such CM and the selection of the "reinforcing phase/matrix" pairs. Physicochemical compatibility (the absence of intense interaction between the components with each other to avoid the formation of intermediate phases and the degradation of the structure and properties of both reinforcing phase and matrix) and the mechanical compatibility (consistency of the thermal expansion coefficients, CTE) determine also the binding force at the interface. These conditions are best satisfied by the CM with NiAl- and TiAl-based IMM reinforced by Me_2O_3-type refractory thermodynamically stable Group III transition-metal oxides, which are in equilibrium with the IMM in the pseudobinary sections of ternary or multicomponent phase diagrams [2, 3]. This paper describes the design of CM with IMM (TiAl, NiAl) reinforced by oxide fibers (OF) or oxide dispersed particles (ODP).

2 Materials and testing methods

To obtain the "TiAl/OF" CM, we used single-crystal sapphire fibers produced by nonconventional technology such as the internal solidification method (ISM) developed in ISSP RAS [4]. The CM was prepared by high-pressure liquid-phase impregnation of the preform (bundle) of fibers (produced by ISM) by the IMM melt [5]. The IMM developed in IMET RAS were Ti-48 at. % Al casting alloys doped with 1.2 at. % Zr, V, Nb, Ta (phase composition is TiAl +10 vol. % Ti_3Al). The rods of laboratory CM samples of 4.5-5.0 mm in diameter and 60-65 mm in length were obtained by casting the matrix melt at a pressure of 0.6 MPa for 2.5 min in a vacuum of 0.1 Pa (10^{-3} mmHg) at a temperature of 1600°C into a quartz shell containing the Al_2O_3 fibers with subsequent directional solidification. This allowed us to avoid any OF fragmentation inevitable in obtaining CM by solid-state technology.

The "NiAl/ODP" CM was produced by powder metallurgy. The initial IMM was NiAl powder obtained by hydride-calcium reduction (HCR) of the mixture of Ni and Al oxides [6]. The particle size distribution of the powders was studied with ROTAP type units (sieve analysis) and a HORIBA LA950V2 laser analyzer. The main fraction of HCR powder (98 wt. %) consisted of particles of <45 μm in size. Each HCR powder particle had a stoichiometric composition (50.3 ± 0.1 at. % Ni) and single-phase β-NiAl structure [7]. The developed in CSRIFM scheme of the Y_2O_3/NiAl CM production included the preparation of HCR powder and the introduction of submicron and nanoscale Y_2O_3 powders along with short-term (15-16 h) mechanical activation for the improvement of the technological characteristics of HCR powders. The billets obtained by hydrostatic extrusion were subjected to hot extrusion at 1100 and 1250°C into rods of 20 mm in diameter with a reduction coefficient of ~ 16. The subsequent recrystallization annealing was performed in isothermal conditions or in a temperature field with a temperature gradient along the rod length [8]. The creep tests of the Al_2O_3/TiAl CM were carried out by the method developed in ISSP RAS for cylindrical specimens [5]. The mechanical properties of CM «NiAl/ODP» were determined on fivefold samples at temperatures of 600-1500°C in a vacuum of <0.133 Pa at a strain rate of 2 mm / min. The SEM images were obtained with a JEOL JSM-6480LV and LEO-1420 instruments, which were also used for the electron microprobe analysis (EMPA) of the compositions.

3 Resalts

3.1 Structure and properties of "MeAl/OF"-type CM

The Al_2O_3 OF and γ-TiAl based alloys exhibit the best mechanical compatibility characterized by close CTE: α = (10-11) x10^{-6} deg^{-1}. The mechanical compatibility of oxides with NiAl is

slightly worse: $\alpha = (10\text{-}11) \times 10^{-6}$ and $\alpha \sim 15 \times 10^{-6}$ deg^{-1}, respectively. High mechanical properties of individual OF may significantly differ from those realized in CM, and high-strength single-crystal OF are virtually inaccessible because of their high price and low productivity of the conventional processes for their preparation. In this regard, we used single-crystal sapphire fibers ($\alpha\text{-}Al_2O_3$ prepared by ISM), which are relatively inexpensive compared with the fibers obtained by other methods. The axis of the fibers coincides with the c axis of sapphire, and the OF room-temperature strength $\sigma_B = 700\text{-}900$ MPa. At present, the fiber length does not exceed 150 mm. The average volume fraction of the sapphire fibers in CM ranged from 20 to 25 %. The Al_2O_3 fibers have a non-standard cross-section configuration such as rectangle with sharp corners, and the characteristic transverse dimension of the fibers is $\sim$80-100 μm. They are fairly evenly distributed over the cross section of the CM (Fig. 1a), and this indicates their good wettability by molten TiAl. The contact with molten TiAl matrix causes a slight dissolution of the Al_2O_3 fiber material, and the initially sharp corners of the Al_2O_3 fibers become rounded (Fig. 1b). At the same time, the initial lamellar γ-TiAl + $α_2$-Ti_3Al microstructure of the matrix is retained in the CM (Fig. 1 b). The dissolution of up to 2.0-2.5 at. % Si in the TiAl matrix due to the contact between the matrix melt with the walls of the quartz container led to the formation of white inclusions of approximately $Ti_5(Al,Si)_3$ composition in the matrix structure (Fig. 1b). The study of fracture surface of the CM (Fig. 1) showed that the limited interaction between the sapphire fiber and the matrix TiAl melt led to the formation of high-strength Al_2O_3-OF/TiAl-IMM interface, which provides the transfer of stress from fiber to fiber, but does not prevent the crack propagation in the CM.
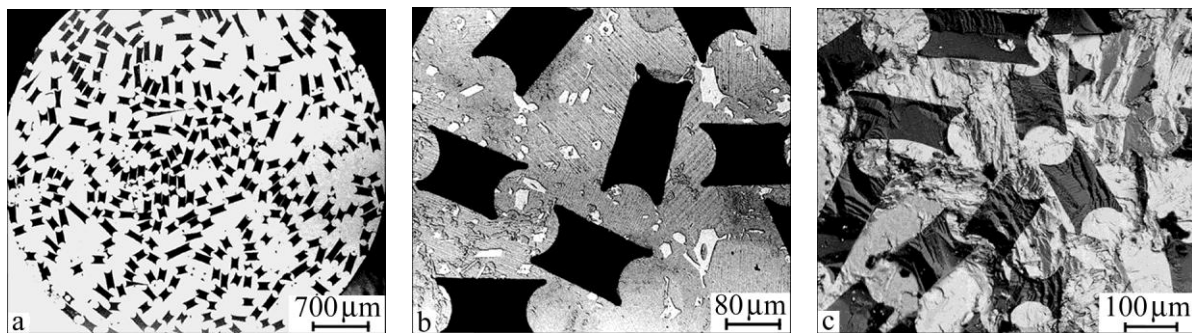

Figure 1. General view of the Al_2O_3/TiAl CM cross section showing a uniform distribution of single-crystal OF in the TiAl matrix (a), microstructure (b), and fracture surface (c) of the Al_2O_3/TiAl CM cross section, characterizing the interaction at the interface between IMM and OF [5].

The stress causing creep strain to 1% in the Al_2O_3/TiAl CM for 100 h, was $\sigma_{1/100} = 120$ MPa at 1050°C (Fig. 2).
The addition of 1 at. % Zr (which is analog of Ti) to the TiAl IMM alloy did not alter the creep resistance of the CM at 1050°C, and the addition of up to 2.5 at. % Nb decreased it because of weakening the interaction between OF and IMM.
As can be seen from Fig. 2, the long-term strength of the TiAl-alloys with additions of 1-2 at. % Zr, Hf, Nb, Cr, V (developed in IMET RAS) abruptly decreases at temperatures above 800-850°C (Fig. 2), whereas the long-term strength of the "sapphire/TiAl" CM changes only weakly, at least up to 1000°C, and even at 1050°C the stress resulting in creep temperatures above 800-850°C (Fig. 2), whereas the long-term strength of the "sapphire/TiAl" CM c strain to 1% for 100 hours is at least 120 MPa [3], whereas the strength of the TiAl matrix at these temperatures is low.
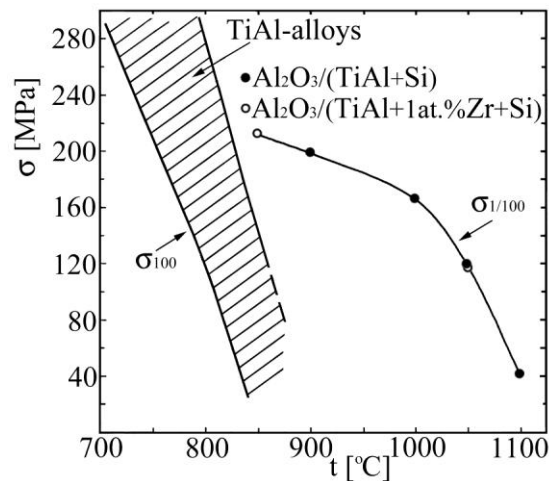
Figure 2. Temperature dependences of the stress causing a creep strain to 1% for 100 h ($\sigma_{1/100}$) of the CM with the TiAl -based IMM strengthened by single-crystal Al_2O_3 fiber, and the stress of failure for 100 h (σ_{100}) for TiAl based alloys.

Since the stress causing the creep strain of the Al_2O_3/TiAl CM to 1% for 100 h ($\sigma_{1/100}$) does not cause the CM destruction, the long-term 100-hour strength (σ_{100}) causing the destruction of the material should be much higher.

The specific feature of the CM obtained by impregnation of the sapphire OF by the TiAl IMM melt is the absence of IMM strengthening upon the reinforcement. Due to the high adhesion forces between OF and IMM, the matrix likely plays a role of binder, fastening the high-strength OF with each other and protecting them from destruction caused by their own surface defects.

Research works for the production of high-temperature "OF/NiAl" CM are substantially less successful than the work on "sapphire/TiAl" CM. No positive results achieved on the OF/NiAl-type CM are known. The main disadvantage of the CM of this type are both a high complexity of the production of composites with refractory IMM and a high cost and low productivity of the process of obtaining single-crystal OF. In addition, the lack of the interaction between the high-nickel IMM melts (Ni superalloys and the Ni_3Al and NiAl alloys) with OF and poor wettability of the OF by these melts lead to forcing out the OF by melt to the periphery of the CM and the formation of weak OF/IMM interfaces [2, 3].

3.2 Structure and properties of CM-type «MeAl/ODP»

The composites strengthened by oxide disperse particles (ODP) or short oxide fibers were studied repeatedly due to a very attractive low-cost and affordable way to produce them with the traditional arsenal of techniques and equipment used in powder metallurgy [2, 3]. Low or almost zero solubility of thermodynamically stable refractory oxides in the IMM in the solid state makes it impossible to use conventional "dissolution-aging"-type heat treatment for the refinement of oxide particles in the IMM. This necessitates the formation of ODP in the powder materials already at the stage of the preparation of the alloys (CM) strengthened by the oxides, in particular, by mechanical alloying for the IMM powder refinement and uniform distribution of ODP in volume, e.g., like upon the production of high-temperature ODS or TDS Ni superalloys.

For the design of the CM reinforced by refractory ODP, the role of physicochemical and mechanical compatibility of the components is substantially less important than for the design of CM with OF, since the volume fraction of the strengthening DP is relatively small (typically 2-15 vol. %), and the level and scheme of internal stresses, which may be caused during thermal cycling by difference in linear thermal expansion coefficients, cannot lead to

swelling and destruction of the CM. In addition, a partial discontinuity at the interface can be considered as a positive factor for increasing the cracking resistance of the composites with brittle IMM.

In this regard and because of the difficulties associated with the manufacture of CM with IMM from NiAl reinforced by OF, the main efforts for the development of extremely light CM for high-temperature service at temperatures above t_{op} and T_m of Ni superalloys are focused on CM with refractory NiAl-based IMM strengthened by oxide DP.

At least two mechanisms are used to improve the mechanical properties of composites with DP: (1) increase in strength due to increasing volume fraction of strengthening DP in IMM, and (2) increase in creep resistance by reducing fraction of transverse boundaries and pinning the longitudinal boundaries of coarse recrystallized grains by relative small amount of ODP. Analysis of well-known studies shows that, in any case, the introduction of a large volume fraction of ODP into IMM does not positively affect the characteristics of high-temperature strength (above 500-800°C), but significantly deteriorate the characteristics of low-temperature ductility. The latter (2) strengthening mechanism was more effective. For example, it was shown in [9] that the creep resistance of the $Ni_{50}Al_{50}$ + (2-15) vol. % Y_2O_3 CM with coarse equiaxed recrystallized grains (of 20-200 µm in diameter) at temperatures of ~ 1500°C in a creep rate range $\acute{\varepsilon} = 10^{-4} \dots 4\cdot10^{-7}$ s^{-1} is higher by a factor of about 5 than that of the CM with fine grains (of 9 µm in diameter).

Further increase in creep resistance of such CM is possible by a substantial decrease in the fraction of transverse boundaries in the deformed material due to the formation of coarse elongated directionally recrystallized NiAl grains with the boundaries stabilized by disperse and nanosized oxides. The Y_2O_3/NiAl CM production scheme developed in the CSRIFM [2] includes the preparation of HCR NiAl IMM powder (Fig. 3a) and the introduction of submicron and nanosized Y_2O_3 powders in combination with short-term mechanical activation (Fig. 3b) for the improvement in the technological characteristics of the HCR IMM powders. This ensured a uniform distribution of Y_2O_3 DP in volume and prevented the formation of their conglomerates in the compact material. The resulting hot-extruded rods of 20 mm in diameter (a reduction ratio of 16) were subjected to recrystallization annealing at 1500-1550°C (1 h) under isothermal conditions or in a temperature field with a temperature gradient along the product length. This allowed the formation of a structure with coarse recrystallized grains elongated along the deformation direction (nonequiaxiality ratio l/d > 10) with a small fraction of transverse boundaries. The longitudinal boundaries of such grains are stabilized by fine (150-350 nm) oxide particles (Fig. 3).
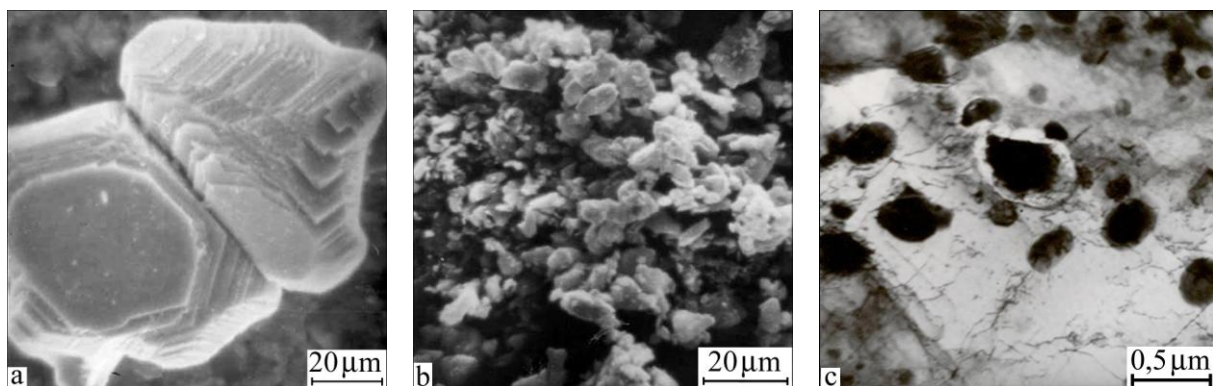

Figure 3. SEM image of NiAl powder obtained by HCR: (a) recovered; (b) milled in attritor, (c) Y_2O_3 particles in deformed NiAl/Y_2O_3 CM, annealing at 1550°C, cross section.

In this way, the promising Y_2O_3/NiAl CM characterized by a density of ≤ 6 g/cm^3, elongated grains, and a minimum fraction of transverse boundaries were obtained. A decrease in the area of the transverse grain boundaries reduces the grain-boundary sliding, which is the basic mechanism of creep. Annealing in the conditions of temperature gradient along the sample leads to grain growth up to the length limited by the length of the sample (Fig. 4a). Annealing under isothermal conditions leads to the formation of the structure with the grains, which are significantly smaller than the sample length (Fig. 4b). These samples tested for long-term high-temperature strength under similar loads exhibit the time to failure shorter by 25-30% than that of the samples annealed in the conditions of temperature gradient along their length.
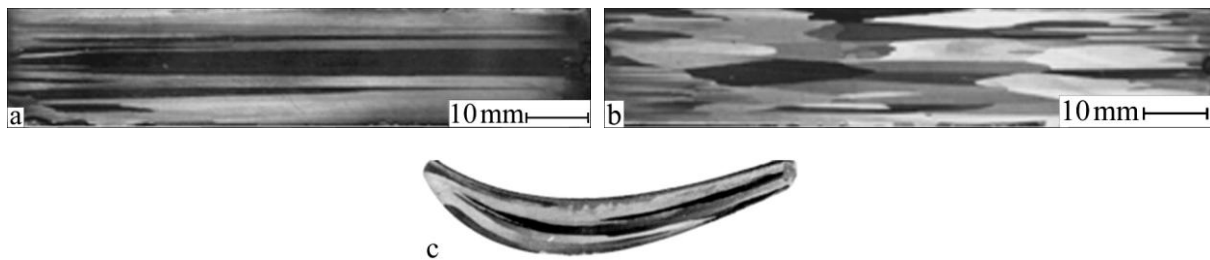
Figure 4. Structure of the Y_2O_3/NiAl CM containing about 2.5 vol. % Y_2O_3 after directed recrystallization: (a) annealing with a temperature gradient along the sample length, (b), (c) annealing under isothermal conditions, (c) nozzle vane profile.

The tests at 1100ºC of directionally recrystallized samples from extruded Y_2O_3/NiAl rods with recrystallized structure formed at a temperature gradient of 1400-1470ºC along the sample length (see Fig. 4 a) showed that the time to failure of the samples depends on the ODP volume fraction, which ranged from 0.5 to 7.5 vol. %. At 1100°C and at a stress of 70 MPa, the time to failure of the CM with 0.5, 2.5, 5.0, and 7.5 vol. % Y_2O_3 was 50, >100, 60, and 35 h respectively, i.e., the dispersion-strengthened CM with 2.5 vol. % Y_2O_3 exhibits the maximum time to failure. The combination of the optimum content of the strengthening phase and the quasi single-crystal structure provides the maximum high-temperature strength of the NiAl + 2.5 vol. % Y_2O_3 CM at used temperatures up to 1500ºC. The dispersion strengthened CM NiAl + 2.5% vol. Y_2O_3 at 1100, 1200, 1300, 1400, and 1500°C has a 100-hour strength $\sigma_{100} = 70\text{-}75$, 50-55, 35-40, 20-25, and 10-12 MPa, respectively. It surpasses the strength of all the known nickel superalloys at temperatures above 1200°C and can operate at small loads at temperatures higher than not only t_{op} of Ni superalloys (at 100-400°C), but even their T_m (Fig. 5).

The characteristic feature of CM with the IMM produced by powder metallurgy and strengthened by ODP is the fact that the role of the strengthening phase is virtually the strengthening of the matrix itself by the stabilization of the boundaries of coarse grains, including the directionally recrystallized elongated grains; the main contribution into the high-temperature strength (increased creep resistance at temperatures up to 0.9-0.95 T_m of IMM) is provided by the decrease in grain-boundary creep by reducing the fraction of transverse boundaries. At the same time, the strength properties of ODP themselves "do not work", and the contribution of dispersion strengthening is minimal because of a weak binding force at the interface. We should note a positive effect of the oxide DP on fracture toughness of NiAl (increase in K_{1C} to ~20 MPa m$^{1/2}$ at 20°C and ~35 MPa m$^{1/2}$ at 500°C), supposedly, due to the crack tip blunting and the change in the direction of its propagation and branching at the weak Y_2O_3/NiAl interface.
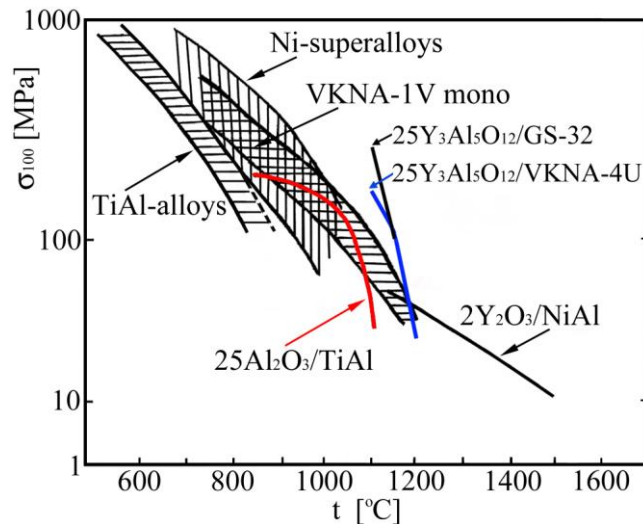
Figure 5. Temperature dependence of the long-term strength of modern high-temperature superalloys, IM based alloys, and CM of various types.

Conclusions

1. The choice of "reinforcing phase/matrix" pairs for the CM designed for long-term high-temperature service is based on the data on physicochemical and mechanical compatibility of the CM components. In the selected "reinforcing phase/IMM" pairs, the IMM were the alloys based on light and refractory NiAl and TiAl monoalyuminides, and the strengthening phase was from thermodynamically stable Me_2O_3-type refractory oxides of transition metals of Group III.

2. The IMM based on TiAl alloys acts as a binder in the TiAl - (20-25) vol. % Al_2O_3 CM obtained by high-pressure impregnation of a single-crystal sapphire fiber bundle by the TiAl melt and directional solidification. The strength of IMM is small, and the strength of the CM is almost completely determined by the strength of OF and the OF/IMM binding force, which "fastens" the OF between themselves and prevents their failure. In the Y_2O_3/NiAl CM obtained by powder technology, DP of refractory Y_2O_3 oxide (2-7.5 vol. %) upon directional recrystallization promote the formation of structures with coarse elongated grains and a small fraction of transverse boundaries. Such structure provides an increased creep resistance at temperatures up to 0.9-0.95 T_m of the IMM at a minimum contribution of dispersion strengthening.

3. The stress resulting in creep strain to 1% for 100 hours (equated to a long-term 100-hour strength) for Al_2O_3/TiAl CM is 170 and 120 MPa at 1000 and 1050°C, respectively. This allows one to use such CM at temperatures of 1000-1050°C (~0.7 T_m of IMM), which is by 250-300°C above t_{op} of IMM based on TiAl alloys at by 400-450°C above t_{op} of Ti-based alloys. The Y_2O_3/NiAl CM with directionally recrystallized structure has a long-term 100-hour strength of at least 70, 50, 35, 20, and 10 MPa at 1100, 1200, 1300, 1400, and 1500°C, respectively. This allows us to recommend such CM for operation at 1400-1500°C (~0.8-0.9 T_m of IMM), which is higher by 100-400°C than not only t_{op}, but also T_m of Ni superalloys.

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