STUDY OF HIGH-TEMPERATURE PROCESSES AT INTERPHASE BOUNDARY OF CHROMIUM (TITANIUM) AND ALUMINA

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The experiments were carried out at 1600 °C for 4-hour periods under a pressure of 1.2 bar Ar (melting of Ni-Cr, Ni-CrTi alloys and high-temperature exposure of vacuum-deposited layers), and at 1900 °C or 1720 °C for 25-minute periods under a pressure of 1.2 bar Ar (melting of pure chromium or titanium). The resultant interfaces were studied by scanning and transmission electron microscopy, X-ray microanalysis and X-ray phase analysis. The mechanism of high-temperature interactions of chromium- and titanium-rich metals with monocrystalline Al_2O_3 includes a redox reaction of the reactive element in the alloy with alumina, yielding Cr_2O_3 or Ti_2O_3. On the basis of calculations according to Van 't Hoff's isotherm, the amount of aluminium in the metal required for stopping the reaction was estimated: For the reaction of chromium with Al_2O_3, this amounted to at the most tenths of weight percent, and for the reaction of titanium with Al_2O_3, it corresponded to units percent and up to tens of percent. Under the conditions of the interaction experiments, the amounts of aluminium established in the metal after the exposure were found to agree with the thermodynamic calculations, being lower than the estimated equilibrium concentrations. The interaction of the elements in question with monocrystalline Al_2O_3 was found to be more extensive in the case of the elements in pure state than in that of an admixture in Ni-alloys.

INTRODUCTION

Interaction of ceramic materials with molten alloys plays a decisive role in advanced technological processes such as the manufacture of composite materials, joining of ceramics with metals, precision casting of high-temperature alloys, monodirectional crystallization of heat resistant alloys, precision casting of titanium alloys and vacuum metallurgy of the given types of alloys. These alloys contain chemically reactive elements (C, Al, Cr, Ti, Hf, ...) which in the molten state react with ceramic materials (moulds, cores, crucibles).

Directional crystallization of heat-resistant alloys is a method allowing manufacture of parts free of grain boundaries perpendicular to the direction of crystallization. It is known [1] that under the conditions of high--temperature creep under prevailing monoaxial stress (such as in the case of aircraft engine vanes), the grain boundaries perpendicular to the direction of stress represent the points of most likely failure. Directional crystallization proceeds under conditions of a high temperature gradient at the crystallization front when the crystallization rate is of the order of 1 to 10 cm hr^{-1} [2]. From this it follows that to achieve a necessary temperature gradient of at least 100 °C cm^{-1}, the melt must be heated to at least 100 °C above the liquidus temperature of the alloy. Under such conditions, the melt (at 1450 to 1650 °C) remains in contact with the mould or core for periods of the order of hours, for example in the case of turbine blades. Such circumstances result in chemical and physical interactions of the metal with its surroundings which may lead to impairing the surface of precision castings and to defects in their structure. Formation of reaction products on the surface is also undesirable because they cannot be removed chemically owing to their high chemical stability, and physical cleaning might lead to microdeformations and to formation of variously oriented large-angle grain boundaries resulting from subsequent recrystallization. Under the conditions of high-temperature stressing, fissures tend to nucleate at such grain boundaries.

From the standpoints of thermodynamics and economy, alumina is one of the materials considered suitable for the manufacture of ceramic moulds, cores and crucibles. However, interaction between ceramic materials and heat-resistant alloys depends not only on chemical composition of the ceramic material, but also on its structure, on the temperature and time of interaction, on the pressure of the furnace atmosphere and on the alloy composition. From the standpoint of further development in the field of precision casting and directional crystallization of reactive alloys it appears advisable to elucidate the mechanism of interaction between the ceramics and the reactive alloys.

It is impossible to present a complete thermodynamic and kinetic description of the respective

reactions as the system is extremely complex: the alloy is of polycomponent type and the activities of the individual elements in the environment of the others is unknown, the conditions are non-standard (low pressure) ones, the ceramic material is inhomogeneous, porous, polycrystalline, multiphase.

Recent studies [3,4] show that the problem can be conveniently studied on simple ceramic-metal model systems and the results generalized to cover a more complex system. Papers [5,6] were concerned with detailed study of the effects the composition of molten model type Ni-CrTiAl alloys, and the temperature and time of contact have on the nature and intensity of interaction with ceramic materials based on Al_2O_3.

The present study had the purpose to contribute to the knowledge of processes taking place at the interphase boundary between some reactive components of heat-resistant nickel alloys and alumina ceramics. Monocrystalline Al_2O_3 was used as the model ceramic system. The complex alloy was replaced by simpler systems, namely binary and ternary alloys rich in chromium or titanium and also with pure chromium and titanium.

EXPERIMENTAL PART

Specimens of Ni-Cr and Ni-CrTi alloys were prepared by vacuum casting into corundum-mullite moulds by the lost wax process. The castings were then cleaned by etching in aqua regia and by washing in ethanol and distilled water. According to ICP spectroscopic analysis, the specimens had the following compositions prior to the interaction:

Ni-Cr: 19.3 wt.% Cr, 0.01 wt.% Ti, 0.01 wt.% Al, 0.05 wt.% Fe, 0.01 wt.% Si, the rest Ni

Ni-CrTi: 20.0 wt.% Cr, 4.6 wt.% Ti, 0.01 wt.% Al, 0.11 wt.% Fe, 0.19 wt.% Si, the rest Ni

The chromium used for melting and vacuum deposition had a purity of 99.9 wt.%, the titanium employed for melting had a minimum purity of 99.5 wt.% (max. 0.3 wt.% Fe, max. 0.15 wt.% Si, max. 0.15 wt.% O, max. 0.1 wt.% C), and the titanium employed for vacuum deposition had a purity of 99.6 wt.% (0.05 wt.% Al, 0.05 wt.% Cr, 0.05 wt.% Ni, 0.05 wt.% Mn, 0.05 wt.% V, 0.03 wt.% Fe).

The vacuum deposition of chromium and titanium onto Al_2O_3 was effected by means of Kaufmann's broad-beam ion source using simultaneous surface activation by Ar ions [7].

The arrangement of the interaction experiments is illustrated by figures 1 and 2. The experiments were carried out at 1600 °C for 4 hours in vacuo or under a pressure of 1.2 bar Ar (melting of Ni-Cr and Ni-CrTi

alloys and interaction of vacuum-deposited layers of the pure metals with Al_2O_3) and at 1900 °C and 1720 °C for 25 minutes under 1.2 bar Ar (melting of pure chromium and titanium respectively). The argon had a purity of 99.998 vol.% (10 ppmv N_2, 5 ppmv H_2O, 3 ppmv O_2).
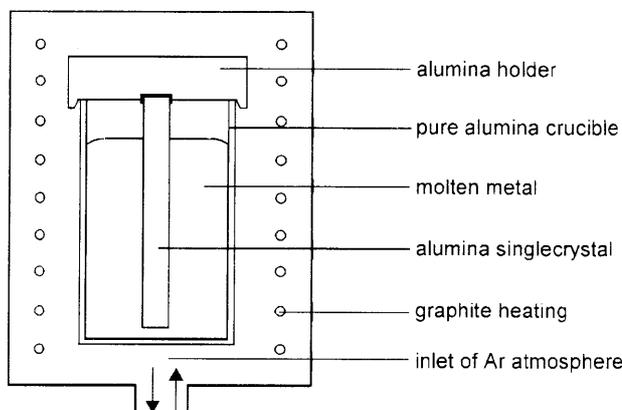

Figure 1. Schematic diagram of experimental arrangement for interaction of molten metals with monocrystalline Al_2O_3.
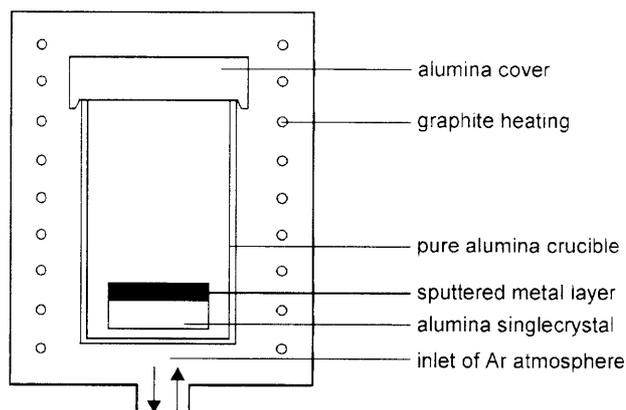

Figure 2. Schematic diagram of experimental arrangement for interaction of vacuum-deposited metal layers with monocrystalline Al_2O_3.

Following the high-temperature exposure, the specimens were cut with a diamond disk perpendicularly to the metal/alumina monocrystal interaction boundary. Then followed grinding and polishing by standard ceramographic procedures, and analyses on analytic electron microscope Jeol JX840 and X-ray analyzer LINK 1000. The phase composition of the interaction products was determined by X-ray diffraction of powdered samples, and evaluated by the database of the Diffractometer D500 instrument.

The differences in properties between the alumina and the metals result from different thinning rates during ion-beam thinning. In order to overcome the problem of preparing thin specimens at the interface for transmission

electron microscopy, a shield along the interface during the thinning was used. A detailed interface micro-structural examination was then performed using a Philips CM20 transmission electron microscope fitted with lithium-drifted silicon X-ray energy dispersive detector and a Jeol 4000FX transmission electron microscope equipped with an ultrathin-window EDX detector and an electron energy loss spectrometer.

RESULTS

Interaction of the Ni-19.3Cr alloy with the Al_2O_3 monocrystal produced a layer of interaction products between the alloy and the pure monocrystal. Its ref-lected-electron image on electron micrographs is of light colour (figure 3). According to X-ray microanalysis it is composed of $Cr_2O_3 \times Al_2O_3$ solid solution. The depen-dence of concentration of Ni, Cr and Al on the distance from the interaction interface is plotted in figure 4.

The micrograph shows that the layer has a granular structure. The authors succeeded in preparing thin sections for TEM. A typical TEM micrograph is presented in figure 5. The layer is actually composed of pore-free grains, and X-ray microanalyses of points designated A and B prove the presence of $Cr_2O_3 \times Al_2O_3$ solid solution with a variable content of Cr_2O_3 and Al_2O_3 (at point A, 14 wt.% Cr_2O_3 and 86 wt.% Al_2O_3, at point B only pure Al_2O_3).

Addition of 4.6 wt.% Ti to the previous alloy completely changed the nature of the interaction. A layer of interaction products was found between the Ni-20Cr4.6Ti alloy and the monocrystal after the contact exposure. This layer was sharply demarcated from both the alloy and the monocrystal sides (figure 6), and X-ray

microanalysis showed it to be composed of 95 wt.% Ti_2O_3 and admixtures of Ni, Cr and Al oxides (figure 7). X-ray phase analysis of the interaction products from the interface proved the presence of a single crystalline phase, Ti_2O_3.

Further experiments were carried out with pure chromium and titanium. The melting temperature of chromium is 1850 °C. Interaction of molten chromium with Al_2O_3 monocrystal at a temperature of 50 °C above the liquidus was quite extensive even during the short interaction (25 minutes). About 75 % of the Al_2O_3 mono-
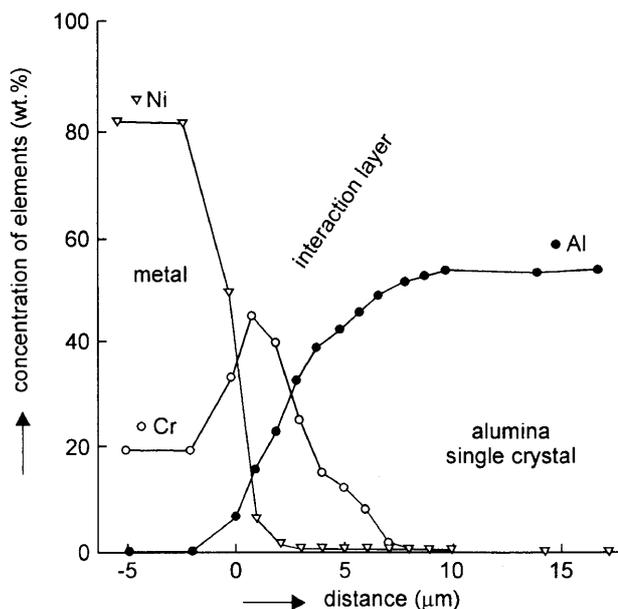

Figure 4. X-ray microanalysis of Ni-19.3Cr/Al_2O_3 monocrystal interface after exposure (1600 °C/4hrs/1.2 bar Ar).

Figure 3. Micrograph of Ni-19.3Cr/Al_2O_3 monocrystal interface after exposure (1600 °C/4hrs/1.2 bar Ar).
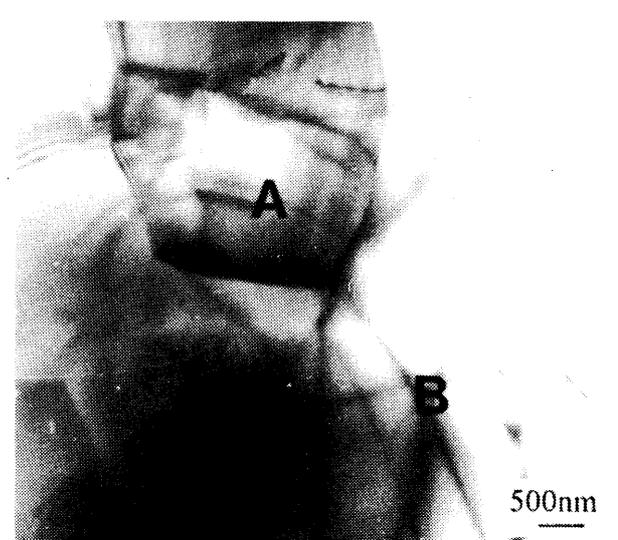

Figure 5. TEM micrograph of Ni-19.3Cr/Al_2O_3 monocrystal interface after exposure (1600 °C/4hrs/1.2 bar Ar).

crystal reacted during the interaction. A micrograph of the metal-monocrystal interface after interaction (figure 8) shows a layer of interaction products about 10 μm thick. According to X-ray microanalysis (figure 9) the layer was composed of $Cr_2O_3 \times Al_2O_3$ solid solution, and unlike the layer produced by interaction of the Ni-Cr alloy, its boundaries were characterized by a sharp decrease of chromium concentration from about 20 wt.% to about 1 wt.%.

X-ray microanalysis did not establish any aluminium in the metal. Above the surface of solidified metal there was a layer of oxidic reaction products about 2 mm thick, composed (according to X-ray microanalysis) of $95Al_2O_3 \times 5Cr_2O_3$ solid solution.

The first interaction of molten titanium with Al_2O_3 monocrystal was effected at 1730 °C (the melting temperature of titanium being 1660 °C) for 90 minutes. The entire Al_2O_3 monocrystal has reacted with the melt
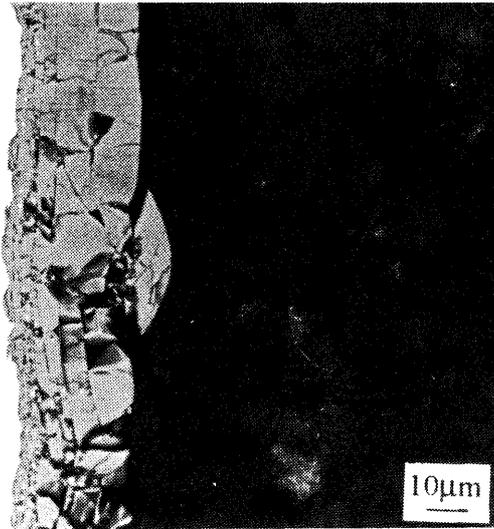

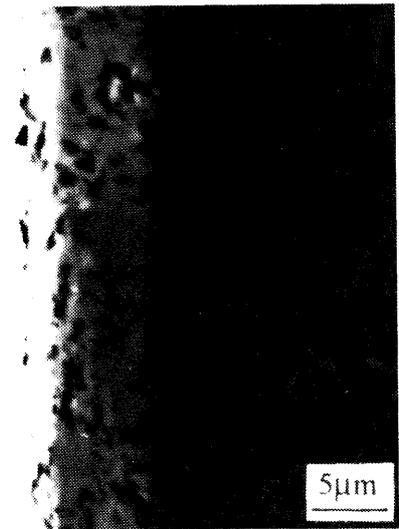Figure 6. Micrograph of Ni-20Cr 4.6Ti/Al_2O_3 monocrystal interface after exposure (1600 °C/4hrs/1.2 bar Ar).

Figure 8. Micrograph of Cr/Al_2O_3 monocrystal interface after exposure (1900 °C/25 min./1.2 bar Ar).

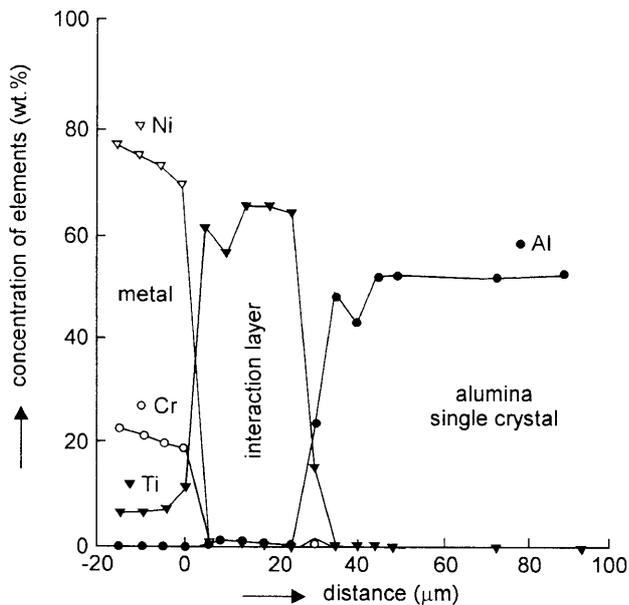Figure 7. X-ray microanalysis of Ni-20Cr 4.6Ti/Al_2O_3 mono-crystal interface after exposure (1600 °C/4hrs/1.2 bar Ar).
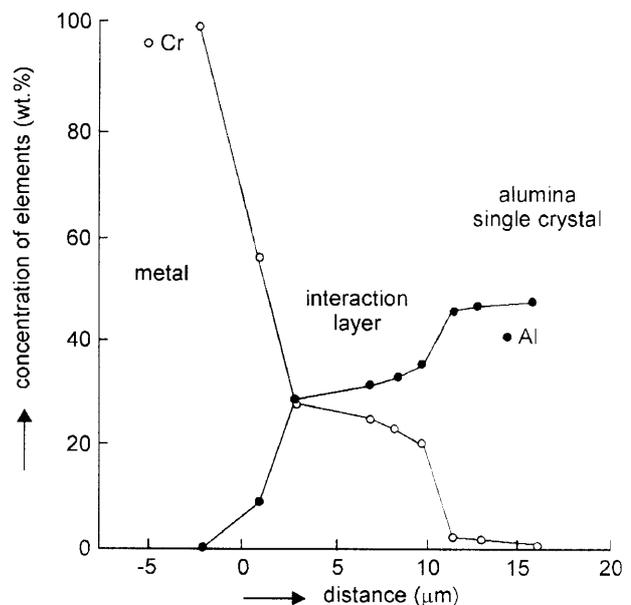

Figure 9. X-ray microanalysis of Cr/Al_2O_3 monocrystal interface after exposure (1900 °C/25 min./1.2 bar Ar).
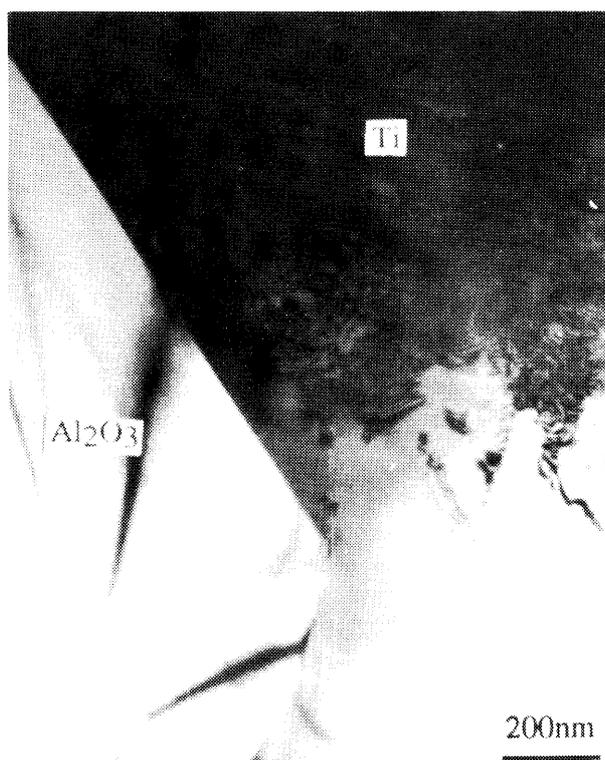
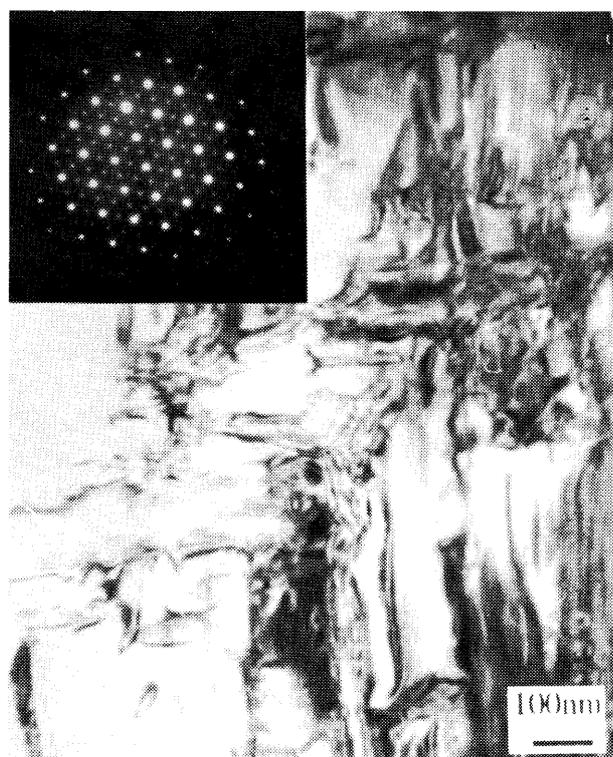Figure 10. Micrograph of Ti/Al$_2$O$_3$ monocrystal interface after exposure (1720 °C/25 min./1.2 bar Ar).

Figure 11. TEM micrograph with inserted selected area diffraction pattern of metal adjacent to Ti/Al$_2$O$_3$ monocrystal interface after exposure (1720 °C/25 min./1.2 bar Ar).

during this period. Another interaction of titanium with Al$_2$O$_3$ monocrystal took place at 1720 °C for only 25 minutes. After this time, the monocrystal was visibly strongly corroded by the molten metal. A micrograph of the interface between the metal and remaining monocrystal is shown in figure 10. A typical TEM micrograph taken from molten pure Ti adjacent to Ti/Al$_2$O$_3$ interface, with inserted diffraction pattern of the selected area, indexed as a disordered hexagonal α phase in direction [0001]α, can be seen in figure 11. Added spots in the selected area diffraction pattern are indexed as ordered hexagonal superlattice spots corresponding to the presence of an α$_2$ type phase (Ti$_3$Al) in direction [0001]α$_2$. The interaction therefore involved reduction of Al$_2$O$_3$ by titanium, the resulting aluminium was dissolving in the metal and close to the interface the Ti$_3$Al intermetallic phase was formed. X-ray microanalysis established a mean content of 11.8 wt.% Al in the alloy, of which about 0.7 wt.% was in the form of Al$_2$O$_3$ particles. The Ti$_2$O$_3$ reaction product was concentrating on the metal surface.

In view of the extensive interaction of the molten pure metals with Al$_2$O$_3$ monocrystals, the course and nature of the interaction was also examined at 1600 °C. At this temperature both metals are in solid state. A perfect contact of the metal with a ceramic can be achieved by powder or vacuum deposition. The latter method was chosen in order to maintain a high purity of the deposited layer. A Kaufmann broad-beam ion source combined with simultaneous monocrystal surface activation by Ar ions was employed to produce non-peeling layers of Cr and Ti approximately 0.2μm in thickness. Thicker layers tended to peel off the monocrystal surface. The exposure was carried out at 1600 °C for 4 hours with the result that the rate of metal volatilization at this temperature was too high even under the overpressure of the inert atmosphere. For this reason the monocrystals were not contaminated by the metal at all, and no interaction layer was found.

DISCUSSION

In the course of interaction of molten Ni-Cr alloy with Al$_2$O$_3$ monocrystal, a layer composed of Al$_2$O$_3$ × Cr$_2$O$_3$ solid solution with an admixture of NiO was formed at the metal-ceramic interface. TEM showed that the layer was formed of sintered grains of the reaction products and contained no pores. The literature [5,6] describes the following interaction mechanism in such systems:

1. diffusion of Cr and Al^{3+} towards the Ni-Cr/Al$_2$O$_3$ interface
2. chemical reaction 2 Cr + Al$_2$O$_3$ ⇌ 2 Al +·Cr$_2$O$_3$
3. diffusion of Al into the molten Ni-Cr alloy·

4. diffusion of Cr^{3+} into Al_2O_3 and formation of Cr_2O_3 × Al_2O_3 solid solution.

The reaction of Al_2O_3 with chromium can be described by the following equation:

$$\langle Al_2O_3\rangle + 2[Cr]_{Ni} \longleftrightarrow 2[Al]_{Ni} + \langle Cr_2O_3\rangle . \qquad (1)$$
Solid   Solution   Solution   Solid
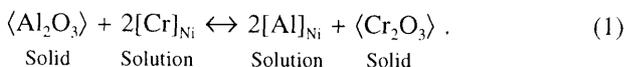
According to [8] one can predict the thermodynamic course of the reaction of Al_2O_3 with the chromium contained in the Ni-Cr binary alloy. The change in the standard reaction Gibbs energy of reaction (1) can be calculated according to the equation

$$\Delta G^0 \text{ (cal)} = 48000 - 9.8T \log x_{Al} - 9.15T \log x_{cr} , \qquad (2)$$

where x_{Al} and x_{cr} are molar fractions of Al and Cr in the alloy; T is absolute temperature (K).

A state of equilibrium is attained when $\Delta G = 0$. Rearrangement of equation (2), substitution of molar fractions with weight percent and application of molar weights yields the following dependence of steady-state concentration of Al (c_{Al} (wt%)) on temperature and concentration of Cr (c_{Cr} (wt%)):

$$c_{Al} = c_{Cr} \frac{M_{Al}}{M_{Cr}} 10^{\frac{9.8T-48000}{9.15T}} , \qquad (3)$$

where M_{Al} and M_{Cr} are molecular weights of Al and Cr respectively.

Hence the following equation holds for $T = 1873$ K:

$$c_{Al} = 0.00967 \, c_{Cr} . \qquad (4)$$

Equation (4) indicates that at a temperature of 1873 K reduction of Al_2O_3 by chromium will stop as soon as the concentration of Al in the Ni-20Cr alloy attains the value of 0.19 wt.%.

On calculating the equilibrium of reaction (1) according to Van't Hoff's reaction isotherm,

$$\Delta G = \Delta G^0 + RT \ln \frac{^Ra_{Cr_2O_3} \cdot \, ^Ha_{Al}^2}{^Ra_{Al_2O_3} \cdot \, ^Ha_{Cr}^2} , \qquad (5)$$

where ^Ra are Raoult's activities; ^Ha are Henry's activities; ΔG^0 is the reaction change of Gibbs energy for the standard state of a 1% solution; R is the universal gas constant ($R = 8.314$ J K^{-1} mol^{-1}), one obtains, on the assumption that $^Ra_{Cr2O3} = \, ^Ra_{Al2O3} = 1$:

$$^Ha_{Al} = \, ^Ha_{Cr} \, e^{\frac{-\Delta G^0}{2RT}} . \qquad (6)$$

Using the value of standard reaction Gibbs energy $\Delta G^0_{1873} = 203\ 989$ J mol^{-1} [9], we have relation for Henry's activities at 1873 K:

$$^Ha_{Al} = 0.00143 \, ^Ha_{Cr} . \qquad (7)$$

When first-order interaction coefficients (e_X^X) are known, Henry's activity can be expressed on the basis of concentration using the following equation:

$$^Ha_X = 10^{e_X^X \, c_X} \, c_X \qquad (8)$$

Then, for temperature $T = 1873$ K and with the use of data taken over from [9] ($e_{Al}^{Al} = 0.032$, $e_{Cr}^{Cr} = 0.0013$), one obtains by substitution according to (8) into equation (7) the following formula for calculating the equilibrium concentration of aluminium:

$$c_{Al} + \log c_{Al} = c_{Cr} + \log c_{Cr} - 2.875 . \qquad (9)$$
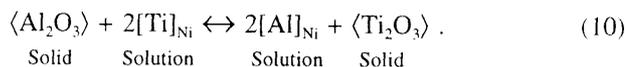
If $c_{Cr} = 20$ wt.%, the equilibrium concentration thus amounts to 0.027 wt.% Al.

At the Ni-20Cr/Al_2O_3 interface redox reaction (1) therefore proceeds until the alloy is saturated to 0.19 wt.% Al (after Kubaschewski [8]), or to 0.027 wt.% Al (after Bůžek [9]). The difference between the two values is due to different thermodynamic input data and different approximation degrees employed by the respective authors.

The structure of reaction products produced by reaction between the Ni-CrTi alloy and Al_2O_3 monocrystal differed in two ways from the reaction layer on the Ni-Cr/Al_2O_3 interface. The reaction yielded Ti_2O_3 whose content was virtually the same throughout the layer thickness, and the layer was sharply demarcated from the side of the alloy as well as from that of the monocrystal. This behaviour was probably due to the great difference between the lattice parameters of Ti_2O_3 and Al_2O_3. Growth of the layer is again controlled by the countercurrent diffusion of Al^{3+} and Cr^{3+} ions through the layer of the reaction products, and according to [5,6] comprises the following steps:
1. chemical reaction $2\ Ti + Al_2O_3 \rightleftharpoons 2\ Al + Ti_2O_3$
2. diffusion of Al into molten alloy Ni-CrTi
3. diffusion of Ti^{3+} and Al^{3+} through the Ti_2O_3 layer.

For a three-component alloy, equilibrium calculations similar to those for the binary alloy are not viable. For purposes of orientation we present here equilibrium calculation of the reaction between titanium in the Ni-Ti binary alloy with Al_2O_3, producing Al:

$$\langle Al_2O_3\rangle + 2[Ti]_{Ni} \longleftrightarrow 2[Al]_{Ni} + \langle Ti_2O_3\rangle . \qquad (10)$$
Solid   Solution   Solution   Solid

In analogy with equation (6) one obtains

$$^Ha_{Al} = \, ^Ha_{Ti} \, e^{\frac{-\Delta G^0}{2RT}} . \qquad (11)$$

Using the values of changes in the Gibbs energy tabellated in [9], for 1873 K one obtains the following equation for Henry's activity:

$$^{H}a_{Al} = 0.172\ ^{H}a_{Ti} . \tag{12}$$

Henry's activity will again be expressed according to equation (8) and one obtains ($e_{Ti}^{Ti} = 0.114$ at 1873 K [9]):

$$c_{Al} + \log c_{Al} = c_{Ti} + \log c_{Ti} - 0.682 . \tag{13}$$

If $c_{Ti} = 5$ wt.% at 1873 K in the Ni-Ti alloy, the equilibrium concentration of Al in the alloy amounts to 4.38 wt.%, that is a value higher by an order of quantity than the corresponding value for the Ni-20Cr alloy.

The account given above shows that the nature of the interaction is strongly affected by composition of the alloy, while the activities of the elements for three-component alloys are already unknown, so that the reaction change in the Gibbs energy cannot be calculated.

Additional experiments were carried out with pure phases whose activity is equal to unity. Such reactions can be submitted to a general thermodynamic analysis (Me designates a metal forming a stable oxide of the Me_2O_3 type):

$$\langle Al_2O_3 \rangle + 2(Me) \leftrightarrow 2[Al]_{Me} + \langle Me_2O_3 \rangle . \tag{14}$$

Solid   Melt   Solution   Solid
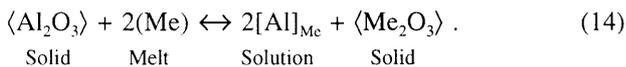
Gibbs energy of this reaction is given by Van't Hoff's isotherm:

$$\Delta G = \Delta G^{0} + RT \ln \frac{^{R}a_{Me_2O_3} \cdot ^{R}a_{Al}^{2}}{^{R}a_{Al_2O_3} \cdot ^{R}a_{Me}^{2}} , \tag{15}$$

where ΔG^{0} is the reaction change in Gibbs energy for the standard state of pure substances. If Raoult's activities of components Me_2O_3, Al_2O_3, Me are equal to unity, then

$$\Delta G = \Delta G^{0} + 2RT \ln^{R}a_{Al} . \tag{16}$$

The activity of aluminium dissolved in the metal is proportional to its concentration (however, the deviations from Raoult's rule are unknown), so that at the onset of interaction the activity of aluminium is close to zero. At the beginning of the reaction of Al_2O_3 with the pure metal, so far uncontaminated with aluminium, $\Delta G < 0$ thanks to the very low value of the argument of the natural logarithm.

In the first approximation (while neglecting the deviation from Raoult's rule) the activity is equal to the molar fraction ($^{R}a_{Al} = x_{Al}$) and the equilibrium concentration of aluminium can be calculated for concrete chemical reactions.

In view of the high melting point of chromium the interaction of molten chromium with the Al_2O_3 monocrystal proceeded at 1900 °C. At this temperature, $\Delta G^{0} = 392$ kJ mol^{-1} [10] and from the condition of equilibrium $\Delta G = 0$, one obtains from equation (16)

$$x_{Al} = e^{\frac{-\Delta G^{0}}{2RT}} = e^{\frac{-392000}{2\times8.314\times2173}} = 1.9 \times 10^{-5} . \tag{17}$$

This molar fraction corresponds to a concentration of 1×10^{-3} wt.% Al.

This expression does not take into account the deviation of aluminium activity from Raoult's rule nor the Gibbs energy of formation of the $Cr_2O_3 \times Al_2O_3$ solid solution. Our experimental results proved that this solid solution was actually formed; the aluminium content in the alloy was below the detection limit of the instrument which was 0.1 wt.%. The layer of $Cr_2O_3 \times Al_2O_3$ reaction products was gradually separating from the rest of the monocrystal and formed a slag.

For the reaction of titanium with Al_2O_3 at 2000 K, $\Delta G^{0} = 46.2$ kJ mol^{-1} [10]. From the equilibrium condition $\Delta G = 0$ and by rearrangement of equation (16) one obtains

$$x_{Al} = e^{\frac{-\Delta G^{0}}{2RT}} = e^{\frac{-46200}{2\times8.314\times2000}} = 0.25 \tag{18}$$

and this corresponds to the equilibrium concentration of 15.8 wt.% Al. EDX analysis of the metal after interaction established the presence of 11.1 wt.% Al, that is an amount lower than the estimated value of equilibrium concentration. Electron microscopy did not reveal any visible interaction layer at the Ti/Al_2O_3 interface. Transmission electron microscopy proved the presence of intermetallic phase Ti_3Al in the vicinity of the interface, obviously resulting from diffusion of Al from the reaction interface into the metal interior. As has already been mentioned, the Ti_2O_3 formed by the redox reaction was collecting on the metal surface.

CONCLUSION

The method based on contact of a molten model binary or ternary Ni alloy rich in chromium or titanium is well suited for studying the nature and intensity of interaction of chromium and titanium with Al_2O_3.

Thermodynamic considerations and calculations showed that the physico-chemical interaction at the Ni alloy/Al_2O_3 interface can proceed on the condition that a redox reaction between the reactive metal component with aluminium oxide takes place. Estimates were made of the aluminium concentrations in the alloy which should stop this redox reaction. For the temperature of 1873 K for the case of reduction of Al_2O_3 by chromium, the respective values should not exceed tenths of wt.% aluminium in the Ni alloy. In the case of reaction between titanium and Al_2O_3, this concentration should be of the order of weight percent.

Melting of pure chromium in contact with Al_2O_3 monocrystals showed that the reaction product was

$Cr_2O_3 \times Al_2O_3$ solid solution which was gradually separating from the remaining monocrystal and formed a slag. The aluminium formed by the redox reaction was dissolving in the molten metal, and its amount was lower than 0.1 wt.%, in agreement with the thermodynamic calculations. The interaction of molten chromium with Al_2O_3 can be schematically described as follows:

1. redox reaction $Cr + Al^{3+} \rightleftharpoons Al + Cr^{3+}$
2. diffusion of Al into molten metal and diffusion of Cr^{3+} into Al_2O_3
3. separation of the $Cr_2O_3 \times Al_2O_3$ reaction layer from the remaining monocrystal.

On the basis of experiments with melting pure titanium in contact with monocrystalline Al_2O_3, the following interaction mechanism was established:

1. redox reaction $Ti + Al^{3+} \rightleftharpoons Al + Ti^{3+}$
2. diffusion of Al into the molten metal
3. formation of Ti_3Al in the proximity of the interface.

The interaction product Ti_2O_3 formed an oxidic layer on the metal surface. The aluminium content in the alloy following the interaction amounted to about 11 wt.%, which is a value lower than the estimated equilibrium concentration of 15.8 wt.% Al.

Acknowledgement

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STUDIUM VYSOKOTEPLOTNÍCH PROCESŮ NA MEZIFÁZOVÉM ROZHRANÍ CHROMU RESP. TITANU A MONOKRYSTALICKÉHO Al₂O₃

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Na základě tavení slitin Ni-19,3 Cr a Ni-20Cr4,6Ti v kontaktu s monokrystalickým Al_2O_3 (experimentální podmínky: 1600 °C/4hod/1,2 atm Ar) byl pomocí rastrovací a transmisní elektronové mikroskopie, RTG mikroanalýzy a RTG fázové analýzy studován mechanismus vzájemné interakce těchto slitin s Al_2O_3.

Pro slitinu Ni-Cr a monokrystal Al_2O_3 byl autory dříve publikován následující mechanismus vzájemné vysokoteplotní interakce:
1. difúze Cr a Al^{3+} k rozhraní
2. redoxní reakce $2 Cr + Al_2O_3 \rightarrow 2 Al + Cr_2O_3$
3. difúze Al do roztavené slitiny a difúze Cr^{3+} do Al_2O_3

Vzniklý reakční produkt - tuhý roztok $Cr_2O_3 \times Al_2O_3$ - byl tvořen slinutými zrny bez pórů a tvořil vrstvu proměnného složení na povrchu monokrystalu Al_2O_3, což zde bylo prokázáno také transmisní elektronovou mikroskopií. Z termodynamických výpočtů podle Van't Hoffovy izotermy byla odhadnuta hodnota koncentrace hliníku ve slitině, která zastaví redoxní reakci Cr ze slitiny Ni-19,3Cr s Al_2O_3. Tato koncentrace byla za teploty 1600 °C 0,19 hmot.% Al (spočteno podle dat Kubaschewského) resp. 0,027 hmot.% Al (spočteno podle dat Bůžka).

Pro slitinu Ni-CrTi byl dříve stanoven následující mechanismus interakce s Al_2O_3:
1. difúze Ti a Al^{3+} k rozhraní
2. redoxní reakce $2 Ti + Al_2O_3 \rightarrow 2 Al + Ti_2O_3$
3. difúze Al do roztavené slitiny a protichůdná difúze Ti^{3+} a Al^{3+} vrstvou reakčních produktů

Reakční produkt - Ti_2O_3 - tvořil homogenní, ostře ohraničenou mezivrstvu mezi slitinou a monokrystalem. Provedené experimenty potvrdily tyto výsledky. Z termodynamických úvah o reakci Ti z binární slitiny Ni-Ti s Al_2O_3 byla odhadnuta hodnota koncentrace hliníku ve slitině, která zastaví redukci Al_2O_3 titanem. Při 1600 °C a pro slitinu Ni - 5 hmot.% Ti byla tato odhadnutá koncentrace asi 4,4 hmot.% Al, tedy řádově vyšší hodnota než pro slitinu Ni-20Cr.

Dále byly provedeny experimenty tavení čistého chromu a titanu v kontaktu s monokrystalickým Al_2O_3 a studovány pak pomocí rastrovací a transmisní elektronové mikroskopie a RTG mikroanalýzy.

Na základě výsledků interakce roztaveného čistého chromu s monokrystalickým Al_2O_3 (experimentální podmínky: 1900 °C/25min/1,2atm Ar) byl stanoven následující mechanismus interakce:
1. redoxní reakce $Cr + Al^{3+} \rightarrow Al + Cr^{3+}$
2. difúze Al do roztaveného kovu a difúze Cr^{3+} do Al_2O_3

Při interakci vzniklý tuhý roztok $Cr_2O_3 \times Al_2O_3$ se postupně odděloval od zbytku monokrystalu Al_2O_3 a tvořil vrstvu na hladině kovu. Redoxní reakcí vzniklý hliník se rozpouštěl ve slitině, jeho množství bylo v souladu s termodynamickými odhady nižší než 0,1 hmot.%.

Reakce roztaveného titanu s monokrystalickým Al_2O_3 (experimentální podmínky: 1720 °C/25min/1,2atm Ar) měla tyto fáze:
1. redoxní reakce $Ti + Al^{3+} \rightarrow Al + Ti^{3+}$
2. difúze Al do kovu a tvorba intermetalické fáze Ti_3Al

Další reakční produkt - Ti_2O_3 - tvořil vrstvu na hladině kovu. Obsah hliníku ve slitině po interakci byl asi 11 hmot.% Al, což je pod hodnotou rovnovážné koncentrace hliníku odhadnuté z Van't Hoffovy izotermy (15,8 hmot.% Al).

Intenzívnější interakce sledovaných prvků Cr a Ti s monokrystalickým Al_2O_3 byla pozorována pro prvky v čistém stavu než ve stavu příměsi v Ni-slitině.