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Incorporation of Refractory Metals into Niobium Base Alloys

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Abstract : Niobium-based alloys with additions such as AI, Ti and Mo were prepared in an inductive cold crucible. A process route was established to provide homogeneous ingots. Key ideas concerning the application of inductive cold crucible to preparation of refractory alloys are brought out. A model is proposed to explain and quantify the experimental observations, which couples the diffusive and convective heat transfers and the heat of mixing involved.

1. THE INDUCTIVE COLD CRUCIBLE, A TOOL FOR PREPARATION OF HIGH PURITY ALLOYS

Because of their low density and their attractive high temperature behaviour (oxidation resistance, high strength at elevated temperature), niobium-based alloys with additions such as Al, Ti and Mo could replace superalloys for applications in advanced aerospace engines. However, the great importance attached to homogeneity and purity concerning the interstitial elements, particularly oxygen, means that the preparation of the alloys is a major concern. For preparation of refractory alloys, the inductive cold crucible (ICC) presents different advantages [1]. Its segmented copper crucible, cooled by water, usually operated in a protective atmosphere, avoids any contamination of the load. As compared to other processes, ICC has the advantages of induction. First the Joule power is injected directly into the metal. Second, the electromagnetic stirring contributes to thermal and chemical homogenisation. Moreover the electromagnetic repulsion intends to reduce the crucible-load contact. Electromagnetic, hydrodynamic and thermal phenomena are strongly coupled. The purpose of the present paper is to derive rules concerning the application of ICC to preparation of refractory alloys. A model is proposed to describe the dissolution mechanism of the high melting point additions.

2. KEY IDEAS OF THE PREPARATION PROCESS

For the preparation of high performance alloys, the raw products are chemically pure elements, in our case Al (Pechiney, 99.995%), Ti (Cezus, T40) and Nb (Cabot). The preparation procedure combines melting and dissolution operations. A primary set of information comes from the knowledge of the solid-liquid equilibria.

Concerning the elements, the extended range of their melting temperature appears as a major difficulty (2740K for Nb, 2888K for Mo, 1943K for Ti compared to 933K for Al). At first sight, aluminium might be expected to be boiling with a very high vapour pressure before the melting of the more refractory elements. In fact, this disaster does not occur, owing to the chemical interactions of aluminium with the other alloy components, which lower the chemical activity and the vapour pressure. These chemical interactions can be guessed from the alloy phase diagrams. The binary diagrams involving Al (Al-Nb, Al-Mo, Al-Ti), show at least the existence of many intermetallic phases [2], which means strongly negative thermodynamic interactions. But in the different systems, the formation of intermetallics depends on the nucleation and growth properties of each phase, operating temperature, etc [3]. Effectively, we observed that the Nb/Al interfacial microstructure consists of a single intermetallic phase layer Al₃Nb. The formation of such intermetallic phases or, more generally, the exothermic enthalpy of mixing in such systems, results in a heat generation effect, which can help for a more efficient dissolution process, with reduction in time or in energy consumption. The same arguments have been used, as described in a recent paper [4], for the melting of Ni and Fe aluminides, in which the reaction between Ni-Al and Fe-Al is exothermic.

refractory additions (Nb, Mo, Ti) in a molten bath Al, possibly alloyed with the above elements. Possible unmolten parts can result from clumsy procedure giving insufficient time to the dissolution kinetics. Supplementary arguments arise from the geometrical and physical characteristics of the ICC process. The Joule power is concentrated in the electromagnetic penetration depth in the metallic load, which is approximately 1.5mm in our conditions. Moreover, at the beginning the load is formed from small blocks. Only the blocks placed in the vicinity of the crucible wall are submitted to the above Joule effect. The spatial distribution of the raw elements must take into account these thermodynamic, kinetic and physical arguments.

3. EXPERIMENTAL PROCEDURE AND OBSERVATIONS

The alloys were prepared in a water-cooled segmented copper crucible in the form of a bowl, 60mm in diameter (Fig.1). The crucible was surrounded with a five-turn coil. Power was supplied from a high frequency generator (125 kHz, 100 kW). Only a limited part of this power is used in the melting process. ICC operates in a protective argon atmosphere which reduces the evaporation rate.



Figure 1 : Experimental device.

The load is a stack of prismatic pieces of the raw elements. The refractory additions Nb and Mo are in form of platelets or chips, approximately 1mm thick due to the dissolution kinetics [5]. They are placed as a layer as close as possible to the crucible bottom, in order to receive the induction currents. The aluminium pieces are distributed inside this layer, but not in contact to the crucible. Titanium, in the form of cylindrical lumps, is placed on the top of the load.

The electrical power is gradually applied to the load which consequently emits a more and more intense glow. When the aluminium pieces begin to melt and when the liquid comes in contact with the refractory platelets, a bright glimmer can be observed through the still parcelled load. This glimmer propagates like a wave inside the load. The titanium lumps are absorbed by the load which becomes compact and fluid. A smoke release is observed from that moment, probably resulting from Al evaporation.

The chemical analysis which was made resulted in the original compositions or very close to them. The loss in Al is limited to 1% to 2%. The oxygen content is about 500ppm which is the typical content of the raw elements.

4. DISSOLUTION IN NON-ISOTHERMAL CONDITIONS, A MATHEMATICAL MODEL

As was mentioned above, the basic mechanisms of alloy preparation consist in the melting of the more fusible element and the progressive dissolution of the more refractory additions. Most of the papers on the subject are restricted to isothermal conditions. Lommel [6] gave two models for the dissolution kinetics, one controlled by pure diffusion and another controlled by convective mass transfer to a perfectly mixed melt. Florence Revet [7] experimentally studied the dissolution of niobium rods in a titanium melt inside an induction cold crucible. The authors proposed a model leading to a mass transfer coefficient value of $70\pm$

20mm/s. This relatively high value could be explained by the stirring effect of induction melting. In the present case, our attention is focused on non-isothermal effects occurring at the solid-liquid interface during the dissolution. Sismanis [8] studied the exothermic dissolution of various high melting point additions in liquid steel. These authors distinguished a shell period when the melt solidifies around the additions just after immersion and a free dissolution period, taking into account the heat of mixing between the refractory addition and the melt. We adapted the above model to our experimental conditions. There is no shell period because the elements are heated together but we have to take into account a variation of the melt temperature and of the solute content.

4.1. Description of the model

We consider a platelet of refractory addition, 2L thick and infinitely extended, in a molten bath. The problem is treated in 1D geometry, the space coordinate z is taken along the normal to the platelet (Fig.2).



Figure 2 : Concentration distribution at the solid-liquid interface

Initially the platelet is in thermal equilibrium with the melt at a given temperature (the melting temperature of Al in our case). The melt is submitted to a programmed heating T_b (t). Heat is transferred to the platelet interface according to a convective heat transfer coefficient h. In addition, the temperature distribution in the platelet is governed by the heat diffusion equation. The heat balance at the melt-platelet interface is expressed by equation (1). This means that the heat fluxes are balanced by the enthalpy change of the dissolving layer, that is the latent heat of fusion ΔH_j^f of the dissolving species j (here Nb) and the partial molar enthalpy $\Delta \overline{H}_j$ of j mixing into the melt. $\Delta \overline{H}_j$ is function of X_j^{1*} , the molar fraction of solute at the interface, given by the phase diagram at the actual interface temperature T*. Here λ_s is the thermal conductivity of the addition, V is the molar volume, dz/dt is the dissolution speed.

$$z=L^* \qquad \lambda_s \left(\frac{\partial T}{\partial z}\right)_{*,s} + h(T^* - T_b) = (\Delta \overline{H}_j + \Delta H_j^f) \frac{1}{V^s} \frac{dz}{dt} \qquad (1)$$

We consider the case of an open system and the case of a closed system. In the case of a closed system the initial proportions and geometrical scale of addition and melt are defined by the thickness L_s^o and L_b^o . The molar fraction of solute in the bath X_j^b can be expressed by relation (2) taking the number of moles of solute as constant.

$$X_{j}^{b} = \frac{L_{s}^{o} - L}{V^{s}} \cdot \left(\frac{L_{s}^{o} - L}{V^{s}} + \frac{L_{b}^{o}}{V^{l}}\right)^{-1}$$
(2)

Concerning mass transfer, we assume that there is no storage at the dissolving front for the solute so that the possible formation of an intermetallic phase layer at the interface of solid metal with molten bath has no influence. We assume also that the dissolution is controlled by convection, the dissolution rate is given by relation (3) where k_j is the convective mass-transfer coefficient of solute j, X_j^s and X_j^b are the molar fraction of solute in the addition and in the bath. V^s is the molar volume of the addition. The molar volume of the solute at the interface in the liquid is taken as equal to the molar volume of the liquid.

$$\frac{1}{V^{s}}\frac{dz}{dt} = \frac{k_{j}}{V^{1}} \cdot \frac{X_{j}^{l*}(T^{*}) - X_{j}^{b}}{X_{j}^{s} - X_{j}^{b}}$$
(3)

In our case, the addition is a pure element : then X_1^s is equal to 1.

In the case of an open system, e.g. the platelet in a semi-infinite melt, X_j^b is equal to 0.

4.2. Application of the model and discussion

The problem is treated as a function of time by a numerical procedure involving the solution of the heat equation by the finite-difference numerical technique. Calculations are made for a niobium plate in an aluminium bath. The temperature of the bath is a linear function of time. It represents the Joule effect generated in the bath. A value of $10^{-5}-5.10^{-5}$ m.s⁻¹ is estimated for the mass transfer coefficient kj [9]. The Newtonian heat transfer coefficient h is estimated at 1000-4000 W.m⁻².K⁻¹. The relationship giving the partial molar enthalpy of mixing comes from Kattner [10]. Other data are shown in table 1.

		Nb	liquid Al
Melting point	К	2740	933
Heat capacity	J.kg-1.K-1	289.1 (T<1200K) 328.8 (T>1200K)	
Thermal conductivity	W.m ⁻¹ .K ⁻¹	60.5 (T<1200K) 73.3 (T>1200K)	94
Density	g.cm ⁻³	8.6	2.4
Molecular weight	g.mol-1	92.906	26.982
Heat of fusion Partial molar heat of mixing at infinite dilution in liquid Al	J.mol ⁻¹ J.mol ⁻¹	30000 -127713.1[10]	

Table 1 : Data used for the calculations

Fig.3 shows the preliminary results from a niobium dissolution experiment in liquid aluminium. According to Fig.3b the temperature difference between the interface and the bulk melt $T * -T_b$ is initially negative due to temperature gradients. Then the dissolution rate increases, the enthalpy release causes $T * -T_b$ to become positive. The temperature of the dissolving niobium interface increases and exceeds the bath temperature. The dissolution rate increases according to the concentration difference $X_j^{1*} - X_j^b$, there is a step when the temperature reaches 1878K due to the NbAl₃ intermetallic phase. In the present case, niobium exhibits small dissolution rates in an aluminium bath and the total dissolution time for a 2mm-thick platelet is estimated to be about 5mn. This calculation time seems satisfactory as compared to the usual preparation time, i.e.30mn. However such a value may be an underestimate because the increase in solute content of the bath is neglected in the present case of an open system.



Figure 3: Niobium dissolution experiment in liquid aluminium, open system $L^{0}_{s}=1mm$

(1) Niobium plate thickness (2) Aluminium melt temperature (3) Difference in temperature between the interface and the melt (4) Molar fraction in solute at the interface for the actual interface temperature.

The temperature difference between interface and bulk melt can be expressed from equation (1):

$$T^* - T_b = -\frac{\lambda_s}{h} \cdot \left(\frac{\partial T}{\partial z}\right)_{*,s} - (\Delta \overline{H}_j + \Delta H_j^f) \cdot \frac{k_j}{h} \cdot \frac{1}{V^I} \cdot \frac{X_j^{1*} - X_j^b}{X_j^s - X_j^b}$$
(4)

According to convective heat and mass transfer theories, the ratio of the mass and heat transfer coefficients k_j/h should be relatively insensitive to temperature and to chemical composition. Then $T^* - T_b$ depends principally on the phase diagram represented by $X_j^{l*} - X_j^b$ and on the thermodynamic effect. In this latter, case, the latent heat ΔH_j^f makes an endothermic effect while the partial enthalpy of mixing $\Delta \overline{H}_j$ can be either endothermic or exothermic. The sum varies according to the interfacial composition. The motor of the exothermic reaction is the value of the product of the thermodynamic terms with the dissolution speed. Both of these two terms are strongly linked to the phase diagram.

In the case of a multicomponent system, we should use a section of the ternary phase diagram [11]. However, the diffusion paths, which are poorly known, play a role in the evaluation of the interfacial composition.

5. CONCLUSION

The strong chemical interactions between refractory elements and aluminium are beneficial for the preparation of refractory alloys. The use of a model coupling the heat transfer and the heat of mixing to represent the mechanism of the dissolution of refractory additions in molten bath is a useful way to understand the behaviour of such alloy additions.

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