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UNDERCOOLING INDUCED METASTABLE AI5 PHASE IN THE Re-W SYSTEM BY DROP TUBE PROCESSING

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Fiche Action N°.............

RESUME :

Les expériences réalisées dans le tube à chute libre ont mis en évidence deux phénomènes de métastabilité topologique dans le système Re-W. Le premier, décrit par ailleurs (NT 46-96), est relatif à la germination préférentielle d'une solution solide désordonnée (W) dans le domaine de stabilité de la phase σ. Le second, analysé ici, concerne la formation éphémère d'une phase métastable A15 pour les compositions en Re comprises entre 18 et 35 %at. L'intervention de cette phase dans le chemin de solidification depuis l'état surfondu (≈ 500 K) est établie par la manifestation d'un phénomène de double recalescence lequel est également trouvé dans le système homologue Mo-Re aux teneurs comparables en Re. Des calculs d'énergie suivant les premiers principes permettent d'identifier la phase métastable à un type A15. Des clichés de diffraction aux rayons X attestent sa présence dans quelques gouttes sous la forme d'un mélange avec une solution solide (W) ordonnée (pic de surstructure). L'existence d'une phase métastable A15 dans le système Re-W a déjà été avérée par des techniques de dépôt en phase vapeur exécutées à des températures de l'ordre de 500° C. Ce travail démontre l'exceptionnelle étendue en température du domaine de métastabilité puisque sa limite supérieure se situe vers 2975° C à 75 %atW.

MOTS CLÉS :

Tube à chute libre, Surfusion, Métastabilité, Système Re-W, Phase A15.

SOMMAIRE

UNDERCOOLING-INDUCED METASTABLE A15 PHASE IN THE Re-W SYSTEM BY DROP-TUBE PROCESSING

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Abstract

Undercooling experiments have been realized on the Re-W system by using a 48 metre high drop-tube facility. A double recalescence phenomenon is systematically obtained within the (W) solid solution range between 65 and 82*at%*W. It is shown that the first recalescence event involves the transitory appearance of a metastable A15 phase. Confidence in the nucleation path is gained with the help of calculations from first principles. The metastable phase is also detected in some droplets by X-ray diffraction.

1. Introduction.

Melt undercooling is one way to obtain metastable solid states. Containerless processing is a promising tool to reach deep undercoolings through moderate cooling rates. It can be realized on metallic melts by using electromagnetic levitation or drop-tube facilities [1]. The opportunities offered by high-drop tubes are quite different from those provided by laboratory scale apparatuses which use sprays of droplets [2]. In a high-drop tube, a single droplet of a millimetric size cools down by radiation during few seconds of weightlessness conditions. Such a facility is particularly well suited to perform undercooling experiments on refractory materials ($T_m > 2000$ K).

In the 48 metre high facility built in Grenoble, nucleation studies on pure metals have been first carried out. Statistical analysis of nucleation events has led confidence in a homogeneous nucleation process for most of them including W and Re [3]. For this latter element, an undercooling-induced fcc metastable phase was also discovered [4]. Our experimental programme on refractory alloys focuses on systems showing complex σ ($D8_b$, CrFe type, 30 atoms per unit cell) and χ (A12, αMn type, 58 atoms per cell) phases. The underlying idea is to investigate the sequence in which the bcc structure transforms into the hcp one through the A15, σ and χ phases. These systems associate a bcc transition metal (Nb, Ta, Mo and W) with a hcp metal (Re). From a phenomenological point of view, Tc, Os and Ru are also considered. In the course of this work, it is of a fundamental importance to perform first principles calculations in order to predict the possibility of observing alternative phases or to interpret a metastable phenomenon.

In this contribution, emphasis is put on undercooling results obtained within the (W) solid solution range of the Re-W system. The study of this domain is also of a particular interest as showing alloys with industrial applications.

2. Procedure and experimental results.

2.1. Material processing.

At the top of the facility working under ultrahigh vacuum conditions, droplets a few millimetres in diametre are prepared from a wire through the pendant drop technique. An in-situ alloying method is used which consists in shifting the composition of a commercial wire (W, 5*at%*Re, 26*at%*Re or Re) by adding locally an appropriate mass of a wire chosen among the same products [5]. The droplets are received either onto a damping plate or into shot tin. Temperature-time profiles are given by silicon diodes. The reproducibility of both the mass and the initial temperature (identified with the liquidus temperature) of the samples allows to determine the nucleation temperature T_n by measuring the time duration of cooling until nucleation occurs and by applying a purely radiant cooling law. The post-recalescence temperature T_f is inferred by single-colour pyrometry approach from the height of the recalescence peak [6].

2.2. Undercooling results.

Beforehand, let us note that we have been confronted with the problem of the localisation of the terminal curves related to the (W) solid solution range. At the composition of 80*at%*W, the liquidus temperature may range from 3150 °C to 3340 °C. Testing all the published Re-W phase diagrams, experimental agreement has been found taking into consideration the terminal curves given by Massalski [7]. Figure 1 shows the undercooling results obtained so far on the studied system. The little spread of the nucleation temperatures ($\approx$ 12 K), established on a set of 15 droplets of the 74*at%*W commercial composition makes us believe that the homogeneous nucleation process proposed for the pure Re and W metals also prevails for the Re-W alloys.

With the increase of the W content, T_n is quite constant while T_f decreases significantly. The gap (T_f -T_n) is minimum at 19*at%*W through a lowering of the heat of crystallisation [8]. The melting heat of W (42500 $J.at^{-1}$) being greater than this of Re (34500 $J.at^{-1}$), this result is mainly due to a strong heteroatomic bonding between the elements in the liquid alloy. A large negative enthalpy of mixing (-3950 $J.at^{-1}$ at 25*at%*W) is evaluated from ab-initio calculations. A simple regular solution approximation for the binary liquid alloy, yielding a parabolic representation of the heat of mixing versus concentration, gives a minimum for the gap at 18.8*at%*W, as observed.

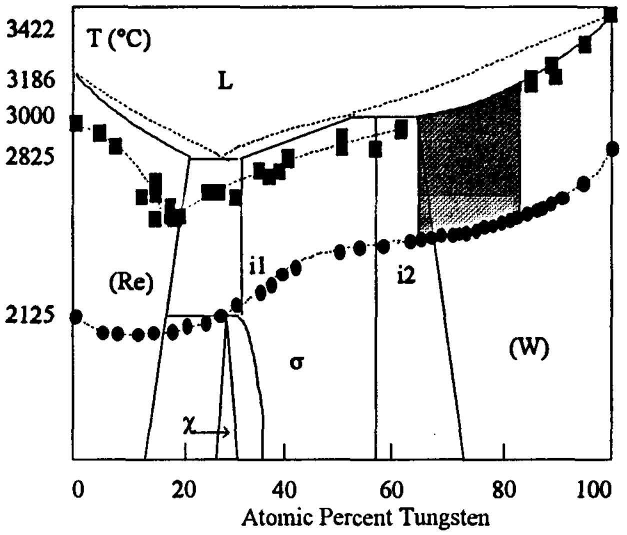


Figure 1 : Undercooling results obtained on the Re-W system (● nucleation temperature, ■ post-recalescence temperature).

The T_n-curve shows a first bending point i_1 near 38*at%*W which coincides with the end of the hypercooling regime characteristic of Re. Within the σ-phase domain, a metastable (W)-bcc phase nucleates primarily explaining why T_f does not reach the solidus line (at least) in the related composition range [9]. The stable σ-phase results from a solid state transformation. The bending point i_2 at 65*at%*W marks the end of this metastable behaviour. A double recalescence phenomenon (Fig.2) is observed between 65 and 82*at%*W (grey-area).

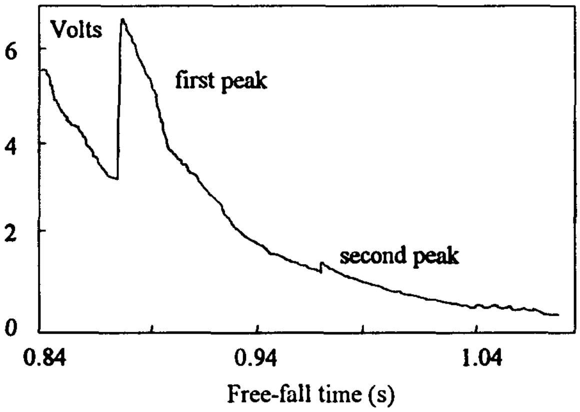


Figure 2 : Detector output signal showing a double recalescence phenomenon (74*at%*W).

Finally, the post-recalescence temperature of the single recalescence peak reaches the solidus line for W contents higher than 82*at%*W (isenthalpic regime), as shown in Figure 1.

The nucleation temperature of the first recalescence event takes place on the general curve of maximum amount of undercooling versus composition with no singularity in the related composition range (see Fig. 1). As shown in Figure 3, the post-recalescence temperature Tf1 corresponding to the first event appears quite constant around a value of 2975°C. The first peak is characterized by an increase in temperature of ≈ 390 K which realizes in ≈ 2 ms ($4x10^5$ $K.s^{-1}$).

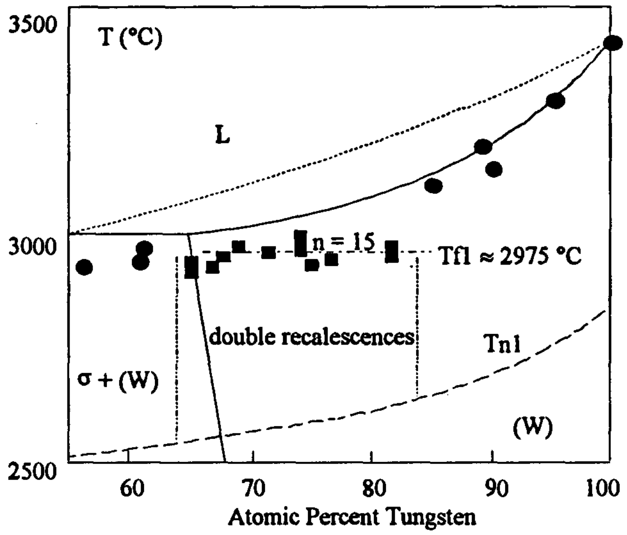


Figure 3 : Post-recalescence temperatures of the W-rich alloys (● for a single recalescence event, ■ for the first peak of a double recalescence phenomenon).

The results concerning the second recalescence event are given in Figure 4. It is noticeable that the height of the peak increases with W content (from *detectable* at 65*at%*W up to ≈ 120 K at 75*at%*W) while the time between the two events diminishes significantly (from ≈ 330 ms down to ≈ 180 ms).

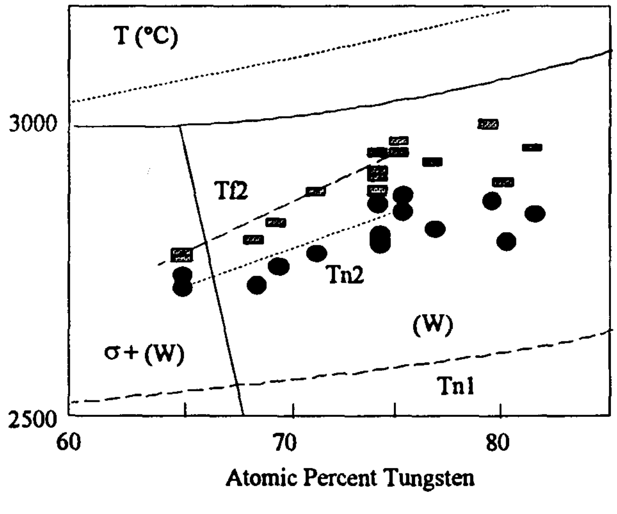


Figure 4 : Nucleation temperature Tn2 ● and post-recalescence temperature Tf2 ▨ of the second recalescence event.

As last observation is that the nucleation temperature of some droplets ranges between Tn1 and Tf1 leading either to a double recalescence phenomenon (with no anomaly for the realization of the second event) or a sole event. In the latter case, the post-recalescence temperature coincides with the Tfl-curve (Fig. 5). We may thus consider that the second event is *aborted.*

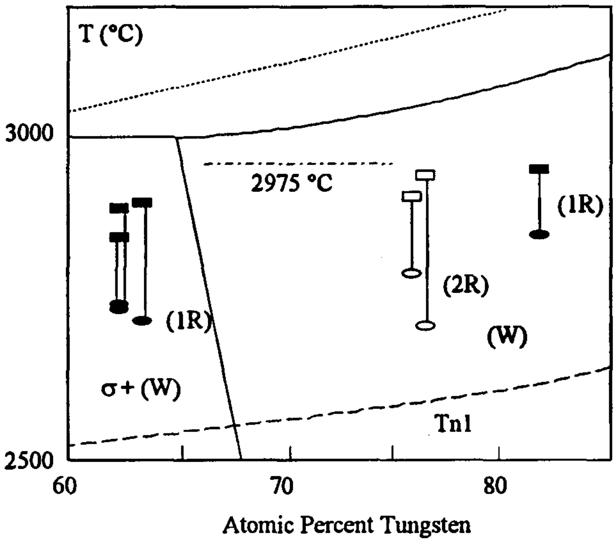


Figure 5 : Particular undercooling results obtained for W-rich Re-W alloys (in black : single event, in white : two events).

3. Discussion.

3.1. Theoretical approach.

The study of the Re-W equilibrium phase diagram does not inform on the nature of the metastable phase involved in the first recalescence peak. In order to explain the metastable behaviour, calculations from first principles full potential linear muffin-tin orbitals method (FPLMTO) have been carried out.

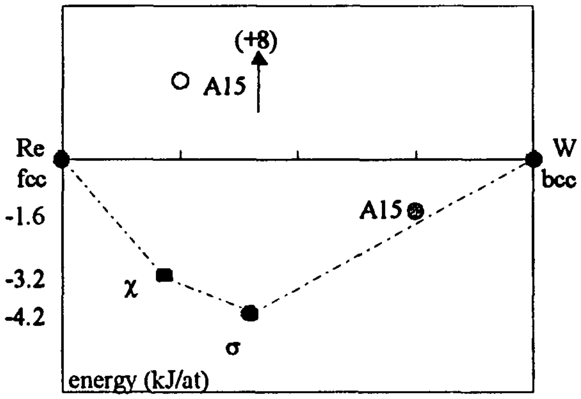


Figure 6 : Structural energy of σ, χ and A15 phases (FPLMTO).

In a previous study [4], we have shown that the metastable A15 phase could be expected in refractory metals like W. In the present investigation of the Re-W system, we have examined the metastability range of this structure versus the Re composition. The formation energies of the ground-states structures, namely χ and σ phases, have been calculated as well as the function energies of the A15 structure for both ReW_3 and Re_3W compounds. Figure 6 shows that the ReW_3 compound takes place just above the line drawn between the energies of σ and pure bcc-W (reference) structures. A metastable character of the A15 structure is revealed at this composition. In contrast, the Re_3W compound is particularly unstable displaying a positive formation energy.

3.2. Analysis of the undercooling results.

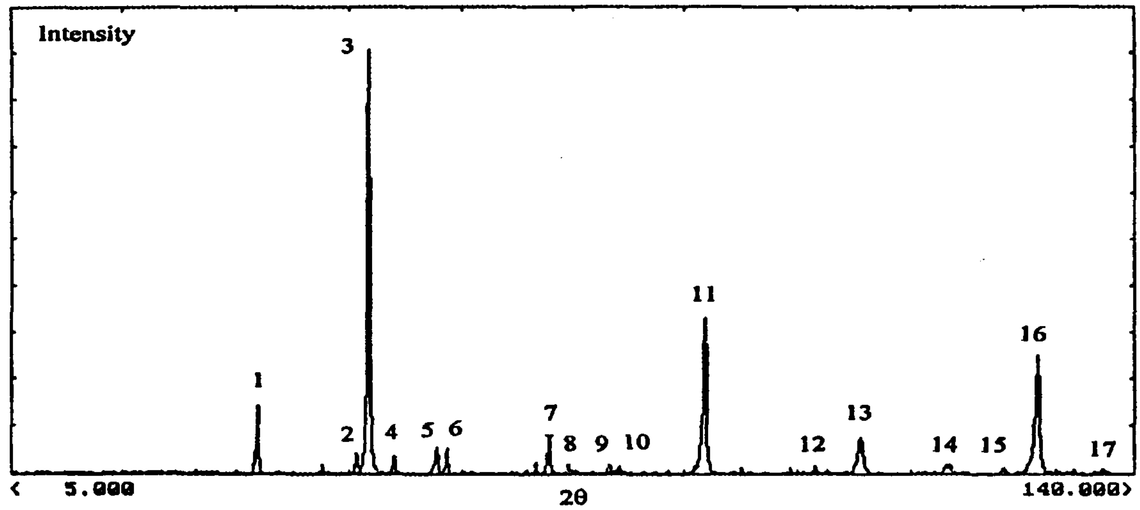
The existence of a metastable A15 phase in this system has already been established by vapour deposition technique at 500°C [10]. The main finding of this study is to reveal the extraordinary extension in temperature of its metastability domain. If the post-recalescence temperature Tf_1 can not be considered constant within the related composition range, our results suggest that the metastable liquidus line for the A15 phase is relatively flat with a maximum near the stoichiometric ReW_3 composition. The extrapolation of the Tf1-curve makes us believe that the A15 melting temperature of pure W is higher than its nucleation temperature, as found for Ta [4]. It seems also possible to get an undercooling-induced metastable A15 phase within the stable σ-phase domain. A mixing of A15 and σ-phases has been already reported by Khusainov on a 50 *at%*W alloy elaborated by vapour deposition at 500°C [11].

The increase of the time between the two events when W content diminishes can be connected to a better possibility for the remaining liquid to be undercooled in the presence of the metastable A15-phase. On basis of the nucleation classical theory, a calculation of the wetting angle of the liquid onto the A15 substrate leads respectively to 60° and 125° at 75*at%*W and 65*at%*W. Since the A15-phase has an ample time to growth, it is obvious that the height of the second peak goes smaller.

3.3. X-ray diffraction results.

Experimental evidence of the presence of the A15 metastable phase within the droplets has been searched by X-ray diffraction analysis. The examination of all the droplets showing a double recalescence phenomenon leads to X-ray diffraction patterns corresponding to the stable disordered (W) solid solution. In fact, such an evidence has been found within the droplets far from the stoichiometric composition ReW_3 that are characterized by an aborted second recalescence event.

The X-ray diffraction patterns (Co Kα λ = 1.789 Å) of such a droplet is given in Figure 7. Peaks of both the (W)-bcc and A15 phases can be recognized. Nevertheless, the sublattice-peaks of the (W)-bcc at 3.0076 Å (n°1) and 1.9024 Å (n°3) are revealed implying that this phase is ordered.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
(W)	100		110		111		200				211		220			310	
A15		200		210		211		222	320	321		420		421	332		520

Figure 7 : X-ray diffraction pattern of a 63*at%*W droplet (table gives the peak indexation).

4. Conclusion.

When studying the Re-W system, two metastable nucleation behaviours are met. One of them, described elsewhere, concerns the nucleation of a metastable (W)-bcc structure within the σ-phase domain [9]. The other one is relative to the formation of a metastable A15 phase at very high temperatures (≈ 2975 °C) in a composition range which lies between 65*at%*W and 82*at%*W.

The transitory A15 metastable phase has experimentally been highlighted through the realization of a double recalescence phenomenon. Its nature has been determined by first principles calculations. The main result of this study is not the discovery of a new metastable phase in the Re-W system but the definition of the upper limit in temperature of its metastable domain. This limit finds its maximum near 2975°C, i.e. very close to the bcc (W) solidus line. It is fitting to note that the same work has been performed on the homologous Mo-Re system leading to a similar appearance of a metastable A15 phase around the 25*at%*Re composition. Future work will consist in determining the metastable liquid-A15 phase diagram. Indeed, this study may contribute to the question of the atomic ordering in binary A15-type phases as discussed for instance by Van Reuth and Waterstrat [12]. Finally, let us underline the interesting complementarity between our experiments and those realized at low temperatures by vapour deposition for the knowledge of the metastable forms of refractory materials.

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