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Investigation of Impurity Elimination Effect in Metal–Carbon Alloys

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Abstract Results of impurity analyses for the starting materials Ti, Zr, Re, and W and of their resulting alloys with carbon are shown and discussed. The elimination of some impurities from the original metals by smelting with carbon when forming the eutectic and peritectic metal–carbon alloys is demonstrated.

Keywords Eutectic · Fixed point · Impurity · Metal (carbide)–carbon system · Peritectic · Purification

1 Introduction

It is commonly accepted that impurities are one of the most important factors affecting the temperature characteristics (plateau shape, reproducibility, etc.) of the fixed points. The purity of fixed points of gold, copper, gallium, etc. is usually no less than 6N (99.9999%). Lately, many researchers have focused their attention on prospective high-temperature fixed points based on metal (carbide)–carbon eutectic [1] and peritectic systems [2], such as Re–C, TiC–C, ZrC–C, WC, and others. At the same time, it is not always possible to obtain high-purity materials for these fixed points. For example, the purity of Re usually does not exceed 5N, and the purity of W, Ti, and Zr is markedly lower (usually 3–4N). Given this circumstance, it seems important to investigate the "self-purification" that was observed when preparing TiC–C eutectic

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alloys [3]. This paper presents our results of studying this effect for the eutectics TiC–C, ZrC–C, and Re–C, and the peritectic WC.

2 Experimental Data

First, the starting materials (Ti, Zr, Re, W, and graphite powders) were analyzed to determine the concentrations of impurities, other than gases, in the 'as-received' state. Then, samples of metal–carbon alloys were made from these original materials, and analyses were obtained again to assess the extent of impurity elimination at the stage of smelting the alloys' original components.

2.1 Method of Impurity Analysis

Impurities were analyzed by means of spark source mass spectroscopy (SSMS) [4] in the Analytic Center of the State Institute of Rare Metals (Russia). The SSMS method offers high sensitivity [5] (much better than 1 ppm) together with comparatively high localization for the sampling—about 0.5 mm^3. The sensitivity of SSMS varies with the element and also with the matrix (the substance to be analyzed for impurities) [4,5].

The uncertainty of SSMS strongly depends on the concentration of analyzed elements; at concentrations of the order of 1,000 ppm, the uncertainty of absolute measurements is ∼5%, while for concentrations of the order of 1 to 10 ppm, the uncertainty is ∼200%. These uncertainty characteristics were confirmed in a series of tests with reference samples (samples with a relatively uniform distribution of dilute elements to be analyzed). One can hardly separate the uncertainty determined by characteristics of the SSMS method from the uncertainty arising from actual deviations in the local concentration in sampling from the average concentration throughout the whole sample—the so-called sampling uncertainty. The latter contribution to the total uncertainty prevails at low-concentration levels (i.e., below 100 ppm).

The lower the impurity concentration, the more the spatial distribution of doped atoms in the sample's volume (macroscopic non-uniformity) is subject to statistical fluctuations. Macroscopic non-uniformity of a contaminant's distribution can reveal itself in concentration measurements if the selected method is characterized by comparatively high localization (exactly the case for SSMS). Taking the uncertainty of about 200% at low concentrations into account, we can positively state that the elimination of some impurities from the original metals by smelting with carbon is observed in those cases when the analysis of the final product (eutectic/peritectic alloys) shows a sharp decrease (by an order of magnitude or so) compared to the original concentrations.

The explanation of a non-uniform impurity distribution is not easily derived from fundamental principles of thermodynamics as applied to liquid and solid solutions. Regardless, the non-uniform distribution of contaminants was observed in the Analytic Center even in reference samples of single-component metals; all the more reason to suggest that such non-uniformity is a characteristic feature of impurity distributions in the much more complicated M(C)–C eutectic/peritectic systems. Proceeding from the non-uniformity assumption, Re–C and WC alloys were analyzed at two different locations; of course, one should regard this experiment as just a first attempt in studying contaminant distributions in M(C)–C systems. Preliminary results for WC (see Table 1) seem to confirm the expectation of non-uniformity (with some reservations reported below); results for Re–C gave no clear evidence either *pro* or *con*.

2.2 Preparation of the Samples

Samples of metal–carbon alloys were made in graphite crucibles using graphite powder (Carbotec, Russia) and Ti, Zr, Re (State Institute of Rare Metals, Russia), and W (Refractory Metals Plant, Russia) metallic powder (Ti was also used in the form of titanium hydride). The declared purities of the crucibles and the graphite powder of 99.9999% were confirmed by SSMS analysis. The mixing of the metal and graphite powders was carried out in a sealed box under an argon atmosphere. Then, the crucible was filled with the mixture and covered by a lid with a 3 mm opening for the escape of vapors. The height of the crucibles was approximately 30 mm, and the diameter was approximately 20 mm. Next, the crucible was placed in the high-temperature BB3500 furnace [6], and the metal–graphite mixture was smelted in either an argon atmosphere or under vacuum. After smelting, the crucible containing the alloy was opened, and the sample was retrieved for analysis of the impurity content.

The powders were compressed in a stainless-steel form to prepare them for the initial analyses. Then, just before the analysis, the outer layer of the compressed sample was removed by means of a spark inside the mass spectrometer (this is the standard pre-analysis cleaning procedure of SSMS [4]). The probes taken from the final products (M(C)–C alloys) also underwent such a cleaning procedure. The thickness of the removed layer is usually around 15–20 μm [4]; that is enough to ensure that the results will not be affected by possible surface contamination. After the cleaning procedure, it is most important that the sample is not touched prior to the analysis.

2.3 TiC–C

Earlier, two samples of titanium hydride and titanium metallic powder and four TiC–C eutectic alloys were analyzed [3]. Two of the TiC–C samples were prepared from titanium hydride $TiH_{1.5-2}$ [7], which in Table 2 is marked as Ti#1 with a nominal purity of 0.9999; one was smelted in argon and the second in vacuum. (Titanium hydride decomposes at temperatures above 800 °C [7], long before Ti-carbide synthesizing temperatures are reached. That is why we see no problem in using titanium hydride to prepare TiC–C fixed points.)

The other two TiC–C samples were prepared the same way (one in argon and the other in vacuum), but from metallic titanium powder (Ti#2 in Table 3) with a nominal purity of 0.999 (preliminary elimination of hydrogen by the supplier).

The results obtained for the samples of TiC–C smelted in vacuum were practically the same as for the samples smelted in argon [3]. The results obtained for Ti#1 and Ti#2 starting materials and TiC–C alloys made of Ti#1 and Ti#2 are presented in

Table 1 Main doped elements in W and the W–C ingot after smelting with carbon

Impurity	Mo (ppm)	Fe (ppm)	Si (ppm)	Ca (ppm)	P (ppm)	Mg (ppm)	Cr (ppm)	Ni (ppm)	Sn (ppm)	Ti (ppm)
W original	2000	300	200	200	50	20	90	90	10	10
WC (probe #1)	500	20	20	0.3	2	<0.07	1	<0.3	<0.1	5
WC (probe #2)	40	0.7	1	0.2	<0.1	<0.07	0.1	<0.3	<0.1	6

Table 2 Main doped elements in Ti#1 and the Ti–C ingot after smelting with carbon

Impurity	Al (ppm)	Cr (ppm)	Fe (ppm)	Cu (ppm)	Ni (ppm)	Zr (ppm)	Hf (ppm)	V (ppm)
Ti#1 original	40	10	9	5	2	2	6	1
TiC–C	0.1	3	0.8	0.1	0.2	8	0.5	3

Table 3 Main doped elements in Ti#2 and the Ti–C ingot after smelting with carbon

Impurity	Al (ppm)	K (ppm)	Si (ppm)	Ca (ppm)	Fe (ppm)	Cr (ppm)	Cu (ppm)	Zr (ppm)	Hf (ppm)	V (ppm)
Ti#2 original	700	300	100	100	60	0	30	40	10	30
TiC–C	0.06	0.05	0.4	0.3	0.8	3	0.1	20	0.5	3

Tables 2 and 3 for smelting in argon only. For this reason, further experiments with Zr, Re, and W were carried out only in argon.

2.4 ZrC–C

The declared purity of the Zr starting material is approximately 4N. Table 4 presents experimental results for the initial zirconium powder and the ZrC–C alloy after smelting with carbon in an argon flow. The analysis of ZrC–C showed more Hf, Ti, and V in the end product than in the initial Zr (Table 4) (Similarly, the analysis of TiC–C made from Ti#1 (Table 2) showed more V and Zr in the end product than in the initial Ti). Cross contamination is not expected because the experiments with ZrC–C, Re–C, and WC were the first experiments conducted with any fixed points in the new BB3500 furnace. Besides, earlier experiments with TiC–C were carried out in a BB3200 furnace that was never used with vanadium- and zirconium-carbide fixed points. Therefore, no impurity increase is expected in the end product, and we see no other reasonable explanation for the "strangeness" of the chemical analyses of the TiC–C and ZrC–C systems other than macroscopic non-uniformity of the impurity distributions resulting in the aforementioned SSMS "sampling" uncertainty.

2.5 Re–C

As was already mentioned, the probable non-uniformity of the samples compelled us to analyze two different parts of the Re–C (and W–C) ingots. The first sampling (probe #1) was taken from the central part of the Re–C ingot; the second (probe #2) was from the surface layer of the Re–C ingot (adjacent to the inner wall of the graphite crucible). The declared purity of the Re starting material is around 4N. Table 5 presents experimental results for the initial rhenium powder and for both sampling sites taken from the Re–C alloy after smelting with carbon in argon.

The unexpected appearance of Si in Re–C in large concentrations after the alloy preparation (especially in the sample from the central part of the ingot) could possibly be due to accidental contamination of Re by micro-size particles of quartz when the quartz ampoule containing rhenium was unsealed. However, one should not disregard the possibility that this analysis may have a different origin. Silicon forms a very strong carbide, SiC, that does not dissociate even above the temperature of vaporization, and this may be apparent in the case of Re since the Re–C melting temperature is markedly lower than that of pure Re.

2.6 WC

The first sampling (probe #1) was taken from the central part of the WC ingot, and the second (probe #2) was from the surface layer of the WC ingot (adjacent to the inner wall of the graphite crucible). The declared purity of the original W is around 3N. Table 1 presents the experimental results for the initial tungsten powder and for both samples taken from the WC alloy after smelting with carbon in an argon flow.

Table 4 Main doped elements in Zr and the Zr–C ingot after smelting with carbon

Impurity	Ni (ppm)	La (ppm)	Fe (ppm)	Hf (ppm)	Ti (ppm)	V (ppm)	Cr (ppm)	Cu (ppm)	Al (ppm)
Zr original	100	100	40	70	8	5	8	4	5
ZrC–C	<0.07	30	2	200	20	40	10	0.1	0.6

Table 5 Main doped elements in Re and the Re–C ingot after smelting with carbon

Impurity	Fe (ppm)	Si (ppm)	Al (ppm)	Ca (ppm)	Cr (ppm)	Mn (ppm)	Co (ppm)	Mo (ppm)	Nb (ppm)	Ti (ppm)
Re original	100	10	2	1	2	2	1	1	1	4
Re–C (probe #1)	3	400	0.3	0.3	0.1	<0.05	<0.02	<0.3	<0.2	1
Re–C (probe #2)	0.2	30	0.08	0.9	0.1	<0.05	<0.02	<0.3	<0.2	0.3

3 Discussion

3.1 "Self-Purification" Effect at the Stage of Metal–Carbon Alloy Preparation

As can be seen from Tables 1–5, many elements (e.g., Al, Ca, Cr, Cu, Fe, Ni, Si) are eliminated from the original metals Ti, Zr, Re, W by smelting with carbon. Molybdenum, the main impurity in the original W, is still detected in WC (Table 1), although in lower concentrations. Nevertheless, Mo is partly removed from the smelting of W and C; even in the case of a "modest" lowering of the Mo concentration (from 2,000 to 500 ppm for probe #1), the observed effect evidently exceeds the SSMS uncertainty at these concentrations. Thus, while some impurities (in particular, Al, Cr, Fe, Hf, Mo, Si, V) persist in remaining in the (matrix) metals, removal or reduction in the concentrations of many impurities definitely occurs in molten M(C)–C systems. The explanation of this (below) is more conjecture than theory; nevertheless, in our opinion, this conjecture has reliable physical grounds (in some cases—quite evident ones).

The difficulty in eliminating many elements from single-component metals is due to the establishment of strong inter-atomic (mostly inter-metallic) bonds between the contaminants and the matrix [8] that remain strong enough even in the molten state. These bonds prevent evaporation of the impurities from the original metals (even in the molten state) that, otherwise, would be thermodynamically favorable because many of the contaminants are more volatile than the matrix metals.

The critical importance of carbon for the elimination of most metallic impurities from molten M(C)–C systems (especially, from metal carbide–carbon ones) lies in its strong affinity to form stable/refractory carbides with the matrix metals, in our case Ti, Zr, and W [7,8]. The special case of Re will be discussed below. Binding virtually all the matrix metal atoms into carbides (note that the MC–C systems always contain atoms of carbon in excessive quantities as compared to the number of matrix metal atoms), carbon prevents the establishment of bonds between the impurity and matrix atoms. Then, due to preferential evaporation of the impurity atoms from the molten metal–carbon mixtures, "self-purification" occurs, all the more so since diffusion coefficients immediately increase by 3 to 4 orders of magnitude when the solid–liquid phase transition takes place. Additionally, the evaporation of impurities from molten MC–C eutectics occurs at substantially higher temperatures in comparison with the melting temperatures of the corresponding initial metals (about 1,000 °C higher in the case of TiC–C and ZrC–C). The melting temperatures of the peritectic alloy WC and the metal–carbon eutectic Re–C are lower than the melting temperatures of W and Re, but they are still very high in absolute values.

As mentioned above, the case of Re has a distinct peculiarity; this metal does not form carbides. Nevertheless, carbon forms a solid solution with Re (one of the eutectic phases in the Re–C system) that also weakens bonds between Re and the metallic impurities within it. Like the metal carbide–carbon systems, "self-purification" in metal–carbon systems also results from the interaction between carbon and the matrix metal, although the bonds established in solid solutions are weaker than those of chemical compounds (carbides).

Thus, it looks as if the physical basis of "self-purification" has a universal character for M(C)–C systems (or at least for all metal carbide–carbon systems). This made it possible for us (at the early stage of investigating the TiC–C system [3]) to expect similar effects for Mo, Zr, W, and other metals forming strong carbides [8]. As can be seen from our experiments with Zr and W, this anticipation has been generally confirmed.

However, some contaminants in Ti, Zr, and W (such as Al, Ca, and, especially, Cr and Mo) can also form strong carbides. In the final analysis, the key criterion whether contaminants present in M(C)–C systems in the form of atoms or compounds with carbon can be preferentially removed lies in their affinity for carbon as compared to the matrix metal's affinity for carbon. Judging by Tables 1–5, the removal of Al and Ca certainly takes place while the case of Cr and Mo is rather controversial from this viewpoint (see Tables 2, 4, 5). Although Al and Ca are most likely present in the examined M(C)–C systems as carbides (as well as Cr and Mo), Al and Ca carbides disintegrate at 2,300–2,400 °C, well below the TiC–C, Zr–C, and WC melting temperatures, and even below the Re–C melting temperature. At 2,300–2,400 °C, the vapor pressures of Al and and Ca are more than 1 atmosphere for both metals. This means that, after dissociation of their carbides, atoms of Al and Ca should leave the molten M(C)–C systems either under vacuum or in an argon flow—just as we see in our experiments.

The behavior of Zr, Hf, and V in titanium (Tables 2 and 3) and Ti, V, and Hf in zirconium (Table 4) is a special case. All these elements (except vanadium) belong to Group IV of the periodic table (furthermore, chemically Hf is an analog of Zr). Consequently, one can hardly expect either the removal of titanium from Zr (and vice versa) or the removal of zirconium from Hf. Vanadium is the next element to titanium in the same row of the periodic table, and its chemical properties are also similar to those of Ti. As mentioned above, experimental data seem to just show deviations in the measured local concentrations with respect to the average value throughout the whole sample.

In our previous paper [3], for the most part we considered the "self-purification" effect from the standpoint of overall purity (total amount of the principal detected impurities in the original and final alloys). Now, we realize that the analysis of the final product may show no noticeable purification of the M(C)–C system as a whole even though certain contaminants are eliminated. Due to the uncertainty arising from the non-uniform distribution of impurities, the analysis of a particular ingot location may show some elements (remaining in the final M(C)–C alloy) even in greater quantity than in the original metal (see, e.g., data on Hf content in ZrC–C shown in Table 4). This circumstance may blur the elimination or reduction of other elements, and one should thus focus attention on the behavior of each individual impurity in the M(C)–C system rather than concentrate on the overall measured purity.

The results obtained for probes #1 and #2 for Re–C (Table 5) gave no evidence in support of a non-uniform impurity distribution (the case of Si was discussed earlier). However, the probes #1 and #2 from the W–C alloy showed that Mo, Fe, and Si are contained in the surface layer in markedly less quantity (by an order of magnitude) than in the core (Table 1). Although Fe and Si are present in WC in relatively low quantities (20 ppm, according to the core analysis shown in Table 5), one can definitely state that this difference is significant compared to the SSMS uncertainty. Since the concentration of all the main impurities in WC turned out to be lower in the surface layer, we suppose that the observed effect is due to a combination of two (or more) factors, non-uniformity and zonal segregation (One should not a priori neglect the possible redistribution of impurities between the sample's surface and the adjacent graphite crucible). We do not believe that zonal segregation alone could produce such an impact because the samples were small (about 5 mm × 5 mm × 5 mm). The BB3500 has very good temperature uniformity, and thus negligibly small temperature gradients, that by no means could intensify the process of zonal segregation (moreover, the crucibles were placed vertically into a large cavity of the horizontally installed BB3500).

Now one must confess that it would be more logical to start investigating the character of an impurity's distribution (allegedly stochastic in the bulk) by measuring concentrations at randomly chosen points rather than comparing the core and surface concentrations (when the observed difference can be attributed to some directional physical processes, e.g., zonal segregation). In practice, using local methods of impurity detection, e.g., SSMS, one must analyze several samplings (at least three) chosen from different parts of the ingot (predominantly the bulk) to get sound information on the actual sample's purity.

3.2 Demands on Purity of Original Metals for Eutectic/Peritectic Fixed Points

The effect of impurities on the melting curve's temperature characteristics ("impurity factor") is in no way a unique factor influencing fixed-point properties. Evidently, for any fixed point a certain level of purity ("purity threshold") should exist before other factors influencing a plateau's shape and fixed-point reproducibility (first of all, the "structural factor") become more important than the "impurity factor." However, estimation of this "purity threshold" with respect to a specific working substance (single-component metals or eutectic/peritectic alloys) is by no means self-evident. One can expect that the "structural factor" is especially important for multi-component eutectic/peritectic alloys due to their intrinsic complicated structure. Due to the greater importance of the "structural factor" in this case, and because of the intricate kinetics of the eutectic phase transition, we suggested [3] that the "purity threshold" for eutectic systems may be not as high as for single-component metals. A similar viewpoint is presented in [9] where it is stated that the irreproducibility of eutectic melting curves is most likely due to differences in "metallurgical states" (author's expression) of the eutectics whereas impurities are not likely to play a significant role (as shown by, e.g., Al–Cu eutectic melting curves [9]).

Certainly, impurities influence both the melting-plateau temperature and the melting range and, consequently, the position of the melting curve's characteristic feature taken as the fixed-point temperature. For example, according to [9], atoms of Si, Fe, and Ag doped into the Al–Cu eutectic shift the melting curve's "run-off" value by ~ 0.7, ~ 0.3, and $\sim 0.2\,\mathrm{mK \cdot ppm^{-1}}$, respectively (see, e.g., [9] to understand the idea of the "run-off" characteristic point). However, the melting curve, although shifted by the "impurity factor," may still be quite reproducible with respect to its new position if the concentration of impurities in the working substance remains constant (In our case, the working substance is the final M(C)–C alloy, and we believe that, after smelting the initial metal with carbon, the concentration of impurities remains more or less constant in the following melt/freeze cycles). Therefore, it is more reasonable to suggest that the irreproducibility of eutectic melting curves is rather due to differences in eutectic microstructure ("metallurgical states") appearing in succeeding melting/freezing cycles. (The succession of melting/freezing cycles preceding a fixed-point realization is generally referred to as the fixed point's "thermal history").

The potential M(C)–C peritectic fixed points proposed recently [2] have no less intricate structure and phase-transition mechanism (kinetics) than eutectics, and thus are expected to be similar to the eutectic fixed points in this respect ("sensitivity" to "impurity factor"). High-quality melting plateaux observed for W–C and Cr–C peritectic systems [2] prepared from low-purity metals (just 4N and 3N purity for W and Cr, respectively) seem to support our conjecture that multi-component eutectic/peritectic-based fixed points have lower aforementioned "purity thresholds" than the ITS-90 fixed points based on single-component metals.

Thus, we suggest that eutectic/peritectic systems as fixed-point substances are less "sensitive" to impurities than single-component metals. Additionally, the elimination of impurities from the original metals by smelting with carbon when forming M(C)–C eutectic/peritectic alloys was observed for a number of systems. Our conjecture of the impurities' minor role in the fixed points based on the eutectic/peritectic phase transition (if confirmed), along with "self-purification," suggest lower demands on the original metal's purity than that of the fixed points based on single-component metals.

Moreover, we said that one should focus attention on the individual behavior of each impurity element in the M(C)–C system rather than concentrate on the overall measured purity. Although this conclusion was made solely on the basis of the analysis of impurity concentration, it is fully correct from the viewpoint of the phase transition in metal carbide–carbon systems in light of each impurity's individual influence. Fortunately, those impurities that do not leave the MC–C systems during preparation of the eutectic/peritectic ingots (due to their strong affinity for carbon comparable to the matrix metals' affinity) should influence the MC–C melting fixed-point temperature characteristics to a lesser degree. The greater an impurity elements' affinity for carbon, the more this impurity behaves as an analog of the matrix metal in MC–C eutectic/peritectic systems and is most probably present there in the form of a carbide as well. Thus, weaker demands on the original metal's purity in the case of M(C)–C eutectic/peritectic systems can be tolerated for specific impurities also having a strong affinity for carbon.

4 Conclusion

Elimination of impurities from the starting materials Ti, Zr, Re, and W at the stage of preparing the metal (carbide)–carbon eutectic/peritectic fixed points is selective. The concentrations of Al, Si, Ca, K, and Fe in Ti drastically decreased after smelting it with carbon (Tables 2 and 3). Similarly, the concentrations of Ni and Fe in Zr noticeably diminished (Table 4); as did the concentration of Fe in Re (Table 5); and of Mo, Fe, and Si in W. At the same time, Zr could not be eliminated from titanium (and vice versa) and neither could Hf be eliminated from zirconium.

Our investigations of the "self-purification" effect in M(C)–C systems show that the final result depends on the individual nature of the contaminants as well as the individual nature of the matrices. One should focus attention on the possible elimination of individual impurity elements from the starting metal in a specific M(C)–C system rather than concentrate on the overall measured purity.

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