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Analysis of the Strength Property for TiC-Mo Composites at High Temperature

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Abstract TiC-21 mol% Mo solid solution (δ-phase) and TiC-99 mol% Mo solid solution (β-phase), and TiC-(80~90) mol% Mo hypo-eutectic composite were deformed by compression in a temperature range from room to 2300 K and in a strain rate range from 4.9×10^{-5} to 6.9×10^{-3}/s. The deformation behaviors of the composites were analyzed from the strengths of the δ- and β-phases. It was found that the high strength of the eutectic composite is due primarily to solution hardening of TiC by Mo, and that the δ-phase undergoes an appreciable plastic deformation at and above 1420 K even at 0.2% plastic strain of the composite. The yield strength of the three kinds of phase up to 1420 K is quantitatively explained by the rule of mixture, where internal stresses introduced by plastic deformation are taken into account. Above 1420 K, however, the calculated yield strength was considerably larger than the measured strength. The yield stress of β-phase was much larger than that of pure TiC. A good linear relationship was held between the yield stress and the plastic strain rate in a double-logarithmic plot. The deformation behavior in δ-phase was different among the three temperature ranges tested, i.e., low, intermediate and high. At an intermediate temperature, no yield drop occurred, and from the beginning the work hardening level was high. At the tested temperature, a good linear relationship was held in the double logarithmic plot of the yield stress against the plastic strain rate. The strain rate dependence of the yield stress was very weak up to 1273 K in the hypo-eutectic composite, but it became stronger as the temperature rose.

Key words composites, high temperature, strength, compression test, rule of mixture.

1. Introduction

In contrast to pure TiC that are very susceptible to thermal shock, the TiC-Mo eutectic composite shows a very good resistance to the thermal shock.[1,2] Further, at elevated temperature, the strength of the composite is equivalent to or even higher than that of hard TiC, though it contains a soft Mo as much as 70% in volume.[3] The excellent high temperature strength is considered to be due to the constraining of deformation of the soft Mo by the hard TiC which is much stronger than pure TiC bulk material.[4,5] However, the cause of the high strength of TiC in the composite has not been clarified.

Kurishita[4] have studied about a possibility that the very thin TiC lamellae are dislocation free, which is responsible for the high strength. An alternative possibility is solution hardening of TiC by Mo. According to a quasi-binary phase diagram of TiC-Mo by Eremenko,[3] the TiC in the composite is solid solution(δ-phase) of TiC and Mo, and the solubility of Mo in TiC is quite large(37 mol% at the 2488 K and 25 mol% at 1500 K). The Mo in the composite is also a solid solution(β-phase) containing 2.3 mol% TiC at 1500 K. Therefore, in order to investigate the strength of TiC-Mo eutectic composite quantitatively, it is necessary to know the strength of both phases.

In the present study, the strength property of each solid solution with a composition close to the δ-phase and β-phase in TiC-Mo eutectic composite was investigated. In addition, the strength properties of TiC-Mo hypo-eutectic composites were also researched.

2. Experimental Procedures

TiC(average particle size 1.5 um, purity 99.7%, Kojundo

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Table 1. Chemical composition of the materials used(mass %).

Designation	Ti	Mo	Carbon(total)
TiC-21 mol% Mo (δ-phase)	49.4	34.2	15.9
TiC-99 mol% Mo (β-phase)	0.77	99.1	0.15
TiC-90 mol% Mo (hypo-eutectic composite)	5.24	93.8	0.93

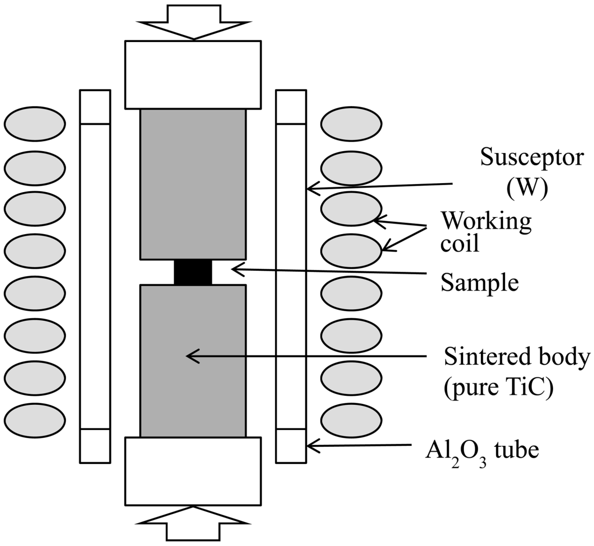

Fig. 1. A schematic drawing of the apparatus (heating part) used for the compression test.

Chemical Co., Ltd.) and Mo powders(average particle size 3 um, purity 99.8 %, Mitsubishi Materials Co., Ltd.) were used by starting materials. The powders were mixed into various compositions of TiC-21 mol% Mo δ-phase, TiC-99 mol% Mo β-phase, TiC-(8090) mol% Mo hypo-eutectic composite. These mixtures were isostatically pressed at 245 MPa for 60 s into rods of 10 mm in diameter and 150 mm in length. The rods were degassed at 1490 K for 3.6 ks in a vacuum of 0.9 MPa and then fully sintered at 2693 K for δ-phase and at 1993 K for the β-phase and hypo-eutectic composites in He of 0.14 MPa, by radio frequency induction heating. The sintered rods were radio frequency floating melted in He of 0.24 MPa. The results of chemical analysis by EPMA, is listed in Table 1.

From these materials, samples(size 2 mm × 2 mm × 3 mm) were cut out from with a low speed diamond cutter. They were then polished with SiC emery papers and diamond paste. The compression test(Shimazu Co., Ltd. Servo Pulser EFH-2 type, capacity 20 kN) were conducted in a vacuum of 0.3 MPa at temperature from room temperature to 2300 K and at strain rates from 4.9×10^{-5} to 6.9×10^{-3}/s. Fig. 1 is a schematic drawing for heating part of the apparatus. The details of the heating method and temperature measurement used were the same as those described in previous papers.[6)]

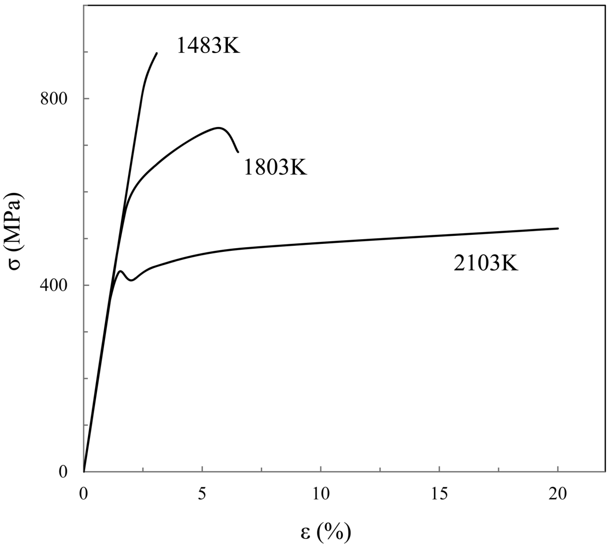

Fig. 2. Stress-strain curves for TiC-21 mol% Mo solid solution (δ-phase) compressed at three temperatures and at a strain rate of 4.9×10^{-4}/s.

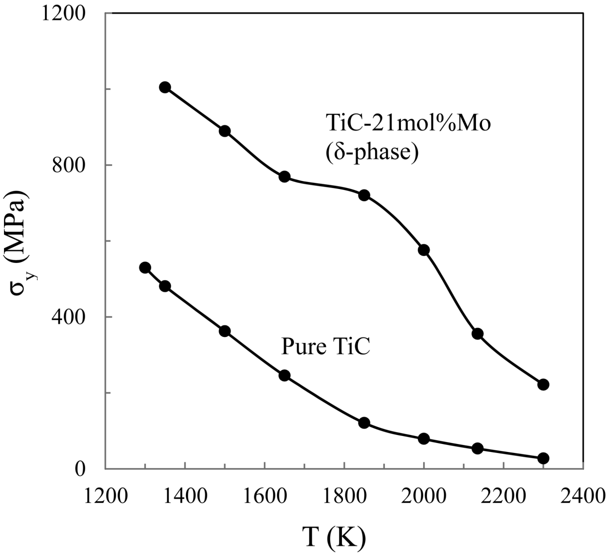

Fig. 3. Temperature dependence of yield stress for TiC-21 mol% Mo solid solution (δ-phase) and pure TiC compressed at a strain rate of 6.4×10^{-4}/s.

3. Results and Discussion

Fig. 2 shows the stress-strain curves for the TiC-21 mol% Mo solid solution(δ-phase) compressed at three temperatures at a strain rate of 4.9×10^{-4}/s. The sample shows a slight plastic deformation at 1483 K and becomes very ductile at 2103 K. Shin[7)] reported on the radio frequency melted TiC with an average particle size 0.5

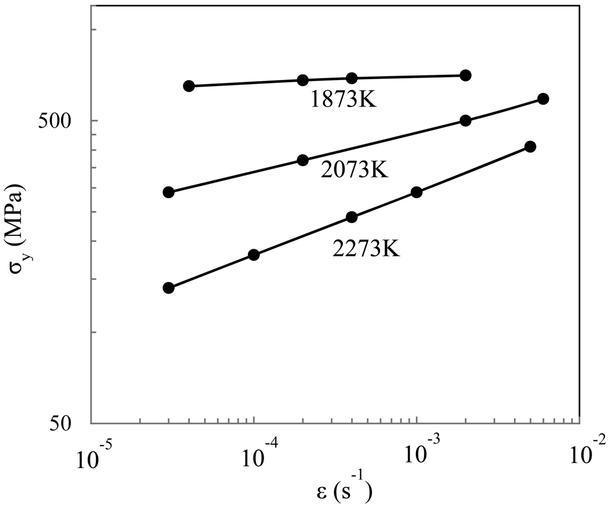

Fig. 4. Plastic strain rate dependence of yield stress for TiC-21 mol% Mo solid solution (δ-phase).

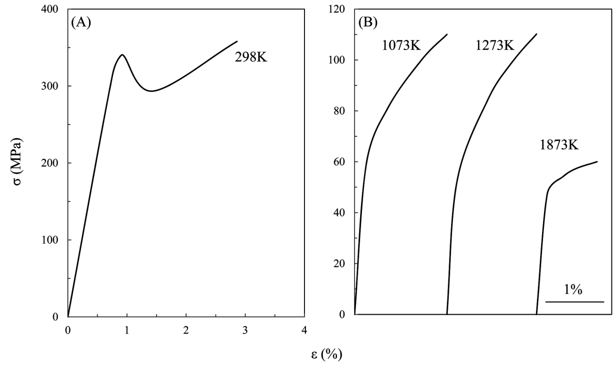

Fig. 5. Stress-strain curves for TiC-99 mol% Mo solid solution (β-phase) compressed at various temperatures and at a strain rate of 5.2×10^{-4}/s.

mm, the ductile-brittle transition temperature(DBTT) was 1170 K and a large plastic strain more than 10 % was observed at and above 1310 K. The DBTT of TiC-21 mol% Mo is higher than that of pure TiC. At 2103 K where it shows a good ductility, a yield point phenomenon is observed. The phenomenon discussed in a previous paper[6] from a viewpoint of high temperature deformation of solution hardened materials.

Fig. 3 shows the temperature dependence of yield stress(σ_y, 0.2 % proof stress) for the δ-phase at a strain rate of 6.4×10^{-4}/s. In the figure, the result of pure TiC,[8] whose carbon/titanium ratio is almost the same as that of the δ-phase, is also shown for comparison. The strength of the δ-phase which has a coarse grained structure as mentioned previously by Kurishita[9] was nearly equal to that of TiC single crystal. It should be noted from the figure that the yield strength of the δ-phase is much higher than that of the pure TiC by a factor of 5 at 1850 K.

Fig. 4 shows the plastic strain rate dependence of the yield stress for the δ-phase deformed at three temperatures.

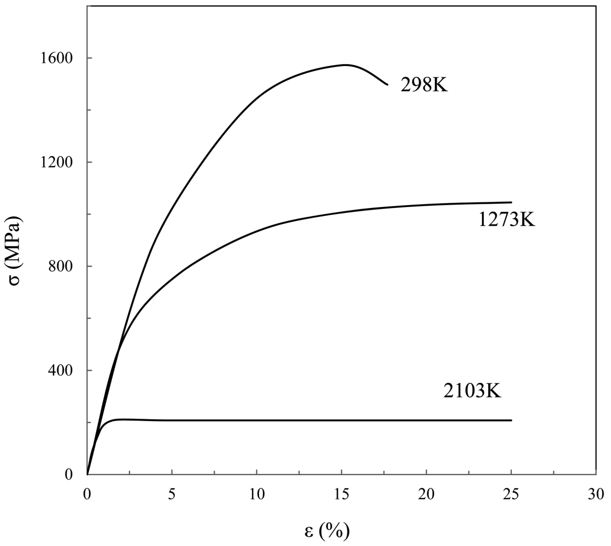

Fig. 6. Stress-strain curves for TiC-90 mol% Mo hypo-eutectic composites compressed at three temperatures and at a strain rate of 4.9×10^{-4}/s.

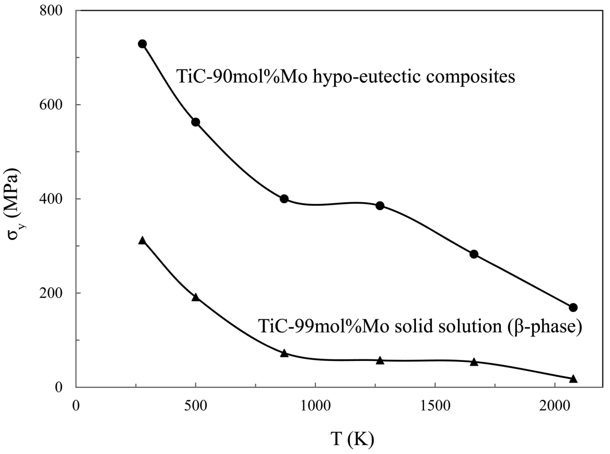

Fig. 7. Temperature dependence of yield stress for TiC-90 mol% Mo hypo- eutectic composite and TiC-99 mol% Mo solid solution (β-phase) compressed at a strain rate of 4.9×10^{-4}/s.

With reference to Fig. 3,[7] it is seen that the strain rate dependence is strong at 2273 K where the temperature dependence is strong, and it is weak at 1873 K where the temperature dependence is weak. At each temperature, a good linear relationship holds in the double logarithmic plot of the yield stress against the plastic strain rate. The slope depends on temperature, and the stress exponent (m), which is the reciprocal of the slope,[8] is 5 at 2273 K.

Fig. 5 show the stress-strain curve for TiC-99 mol% Mo solid solution(β-phase) at various temperatures and at a strain rate of 5.2×10^{-4}/s. At room temperature(Fig. 5(A)), a marked yield drop is observed and after the drop the work hardening rate is high. The yield stress at high temperature(Fig. 5(B)) is about two times as large as that of pure Mo.[4] A remarkable difference from the δ-phase is

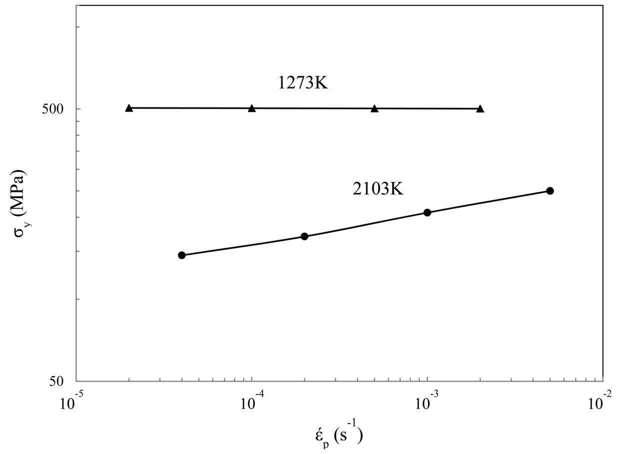

Fig. 8. Plastic strain rate dependence of yield stress for TiC-90 mol% Mo hypo-eutectic composites compressed at two temperatures.

that the temperature dependence of yield stress is very weak in the range from 1073 K to 1873 K.

Fig. 6 shows the stress-strain curves for TiC-90 mol% Mo hypo-eutectic composite compressed at three temperatures at a strain rate of 4.9×10^{-4}/s. The composite shows a plastic strain of about 10 % at room temperature(298 K) and becomes to have an unlimited compressive ductility at and above 1273 K.

Fig. 7 shows the temperature dependence of yield stress for the composite. In the figure, the temperature dependence of yield stress for β-phase is also shown for comparison. In TiC-90 mol% Mo hypo-eutectic composite, the temperature dependence of yield stress is similar to that of the β-phase and is weak above about 873 K.

Fig. 8 shows the double logarithmic plot of the yield stress against the plastic strain rate($\dot{\varepsilon}_p$) for the TiC-90 mol% Mo hypo-eutectic composite deformed at two temperatures. A good linear relationship is seen between them. The strain rate dependence is weak at these temperatures. This is agreement with the temperature dependence shown in Fig. 7. The stress exponent(m) is 12 at 2103 K.

TiC-21 mol% Mo solid solution(δ-phase) shows such a remarkable solution hardening that the strength at high temperature is about 6 times as high as that of pure TiC with almost the same carbon/titanium(C/Ti) ratio as TiC-21 mol% Mo.[8-10] According to the quasi-binary phase diagram of TiC-Mo,[3] C/Ti ratio of the δ-phase is considerably smaller than unity. The ratio in the δ-phase, which has the same molybdenum/titanium(Mo/Ti) ratio as that in TiC-21 mol% Mo, is 0.71. Therefore, a large number of carbon vacancies will exist in the δ-phase compared with the present TiC-21 mol% Mo δ-phase in which C/Ti = 0.955. However, in a range of C/Ti ratio from 0.75 to 0.95, the C/Ti dependence of the critical resolved shear stress is week in pure TiC,[11] and the effect of the ratio on the yield stress is as small as only 5.8 % of the above mentioned solution hardening by Mo. Therefore, the effect of carbon vacancy concentration may be negligible.

Furthermore, the solubility of Mo in the δ-phase has been reported to be 37 mol% at eutectic temperature,[3] which is about 1.5 times as large as the Mo concentration in TiC-21 mol% Mo δ-phase. The eutectic composite was rapidly solidified and cooled, and the diffusion distance of Mo in TiC under the subsequent heating conditions was estimated to be short enough compared with the lamellar thickness. The above discussion leads to the conclusion that the excellent high temperature strength of δ-phase in the lamellar eutectic composite is caused mainly by the solution hardening of TiC by Mo.

The yield strength of the eutectic composite will be discussed from the Fig. 2 and Fig. 6 based on the rule of mixture. For the discussion, it is necessary at first to know whether the δ-phase in the eutectic composite is deformed plastically or only elastically at the yield stress of the composite above 1273 K. Assuming that the δ- and β-phase are equally strained and the δ-phase is deformed only elastically at 0.2 % proof stress of the composite, we obtained the strain imposed on the δ-phase(σ_{el}^{δ}), as $\sigma_{el}^{\delta} = E^{\delta} \times \varepsilon_{el}^{\delta} = E^{\delta} \times (0.002 + \varepsilon_{el}^{c})$, where ε_{el}^{c} is the elastic strain of the composite at 0.2 % proof stress($\sigma_{0.2}^{\delta}$), and equals $\sigma_{0.2}^{\delta}/E^{c}$. E_c is the Young's modulus of the composite and E^{δ} is that of the δ-phase. Only when the elastic limit(σ_p^{δ}), of the δ-phase with the same composition as that in the δ-phase is higher than σ_{el}^{δ}, the δ-phase will not be deformed plastically, but elastically support the stress.

As shown in Fig. 2, δ-phase does not show any appreciable plastic deformation below 1483 K. Therefore, it may be reasonable to assume that δ-phase is deformed plastically at and above 1483 K, but only elastically below 1483 K. On the basis of this assumption, the yield stress of the eutectic composite will be examined quantitatively.

Denoting the internal stress introduced in the β-phase by the 0.2 % plastic strain of the composite as σ_i^{β} and that in the δ-phase as σ_i^{δ}, and the elastic limit of the β-phase material with the same composition as that in the β-phase as σ_p^{β} and that of the δ-phase material as σ_p^{δ}, we obtain the 0.2 % proof stress of the composite($\sigma_{0.2}^{c}$), from the rule of mixtures, in the temperature range where the β-phase is deformed plastically and the δ-phase only elastically, as $\sigma_{0.2}^{c} = (1 - V^{\delta})(\sigma_p^{\beta} + \sigma_i^{\beta}) + V^{\delta}E^{\delta}(0.002 + \varepsilon_{el}^{c})$, and in the temperature range where both of the β-and δ-phases are deformed plastically, as $\sigma_{0.2}^{c} = (1 - V^{\delta})(\sigma_p^{\beta} + \sigma_i^{\beta}) + V^{\delta}(\sigma_p^{\delta} + \sigma_i^{\delta})$, where V^{δ} is the volume fraction of the δ-phase. As σ_p^{β} we use the proportional limit of TiC-99 mol% Mo(Fig. 5). Using equations. $\sigma_{0.2}^{c} = (1 - V^{\delta})(\sigma_p^{\beta}$

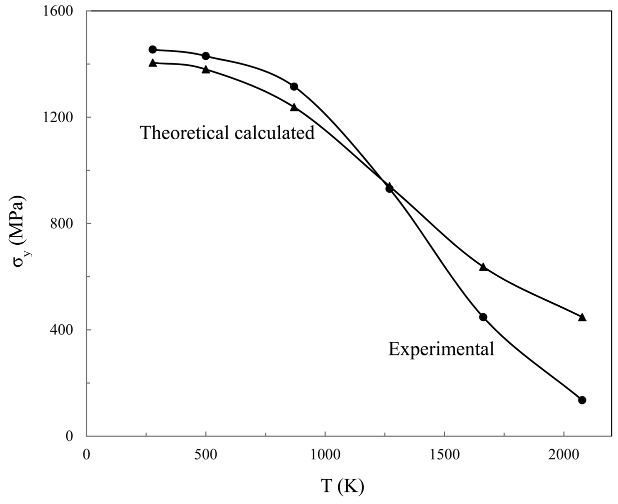

Fig. 9. Theoretical calculated and experimental curves of yield stress vs temperature for TiC-80 mol% Mo eutectic composite.

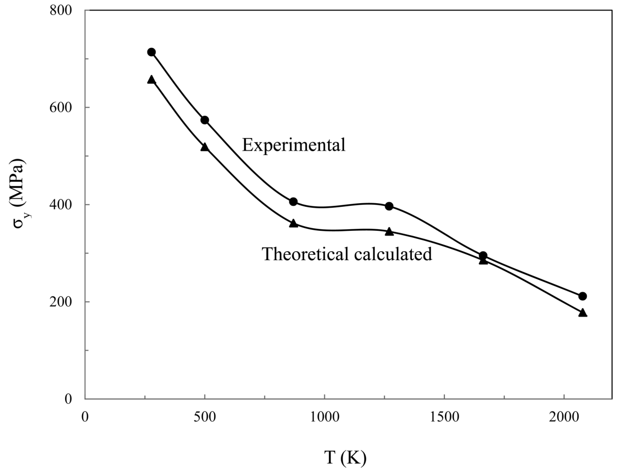

Fig. 10. Theoretical calculated and experimental curves of yield stress vs temperature for TiC-90 mol% Mo eutectic composite.

$+ \sigma_i^\beta) + V^\delta E^\delta(0.002 + \varepsilon_{el}^c)$, $\sigma_{0.2}^c = (1 - V^\delta)(\sigma_p^\beta + \sigma_i^\beta) + V^\delta (\sigma_p^\delta + \sigma_i^\delta)$ and the values of reference,[8,9] we calculated the yield stress of TiC-80 mol% Mo hypo-eutectic composite of the temperature range from 298 to 2103 K. The results are compared with the experimental data in Fig. 9. The two curves are in good agreement with each other up to 1483 K. On the other hand, above 1483 K the experimental values are considerably smaller than the calculated ones.

At high temperature, the recovery of internal stress due to the annihilation and rearrangement of dislocations will occur during deformation, and the boundary sliding between the phases may also take place.[10-12] The fact that in the lower temperature ranges the calculated values agree with the experimental ones, but above 1420 K do not agrees, indicates that the effect of such recovery and boundary sliding becomes significant at high temperature above 1420 K. In fact, the strain rate dependence of the yield stress is extremely weak in the lower temperature range, but increasingly stronger with temperature above 1420 K.[4] The calculated values at and below 1273 K were obtained on the assumption that the δ-phase is deformed only elastically and the values agree well with the experimental ones. This suggests that the plastic deformation of the δ-phase is negligible up to about 1273 K.

Since the shear modulus of the δ-phase is different from the of the β-phase, some image force will act on the dislocations in each phase. The excellent high temperature strength of the δ-phase in the composite was considered to arise from the δ-phase being dislocation free,[8,13] because the lamellar thickness of the δ-phase is extremely small and its shear modulus is larger than that of the β-phase.

At 1420 K where the effect of recovery and boundary sliding is considering to be weak, the calculated $\sigma_{0.2}^c$ by assuming $\sigma_i^\delta \approx 0$ is smaller than the experimental ones. This suggests that the effect of image force on σ_i^δ is relatively weak and a considerable internal stress is built up in the δ-phase. Owing to the multiple slip, a large part of dislocations interact with one another before they reach the region of special value and reside in the δ-phase, contributing to the internal stress.

Below 1273 K where the δ-phase elastically support the stress and only the β-phase is deformed plastically, the yield stress of TiC-90 mol% Mo hypo-eutectic composite, is given from the rule of mixtures. The values of the yield stress calculated by using reported data[8,9] are shown in Fig. 10 together with experimental ones for comparison. From the figure, it is seen for both the composites the calculated yield stress is not much different from the experimental one and their temperamental dependence are very alike up to 1420 K. Above about 1420 K, however, the ratio of the calculated to the experimental values decreases with the increases of temperature. This is considered to arise from the recovery and boundary sliding, as is the case with the previously described.

4. Conclusion

The deformation behaviors of δ-phase and β-phase, whose compositions are close to those of δ(TiC)- and β(Mo)-phases in the eutectic composite of TiC-Mo respectively, were measured by compression test. Based on the experimental results was investigated the reason of the anomalously high strength of the eutectic composite and the applicability of the rule of mixtures. The δ-phase can be plastically deformed slightly at 1483 K and largely, more than 10 %, at 2103 K. The yield stress is much larger than that of pure TiC. A good linear relationship holds between the yield stress rate of δ-phase and the plastic strain rate in double-logarithmic plot. The main reason of anomalously high strength of the eutectic composite is the solution hardening of δ-phase by Mo. β-phase shows a clear yield point phenomena at room temperature. Hypo-eutectic composites can be deformed plastically by 10 % at ambient temperature and almost unlimitedly 1273 K. The temperature dependence of the yield stress is relatively weak. The strain rate dependence of the yield stress is very weak up to 1273 K in TiC-90 mol% Mo, but it becomes stronger as the temperature rises. It is considered that the effects of the recovery of internal stress and the boundary sliding are weak up to 1420 K, but become strong above that temperature.

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