

TBC SYSTEMS FOR HIGH MELTING POINT METALS AND ALLOYS

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Abstract

The article presents research findings on the microstructural studies of thermal barrier coatings (TBC) deposited on molybdenum, featuring a bond coat made of molybdenum silicide. Ceramic coatings within the TBC system were produced through plasma spraying in air. Conventional 8YSZ and rare-earth zirconate powders (lanthanum and neodymium zirconates) were utilized to achieve this. The ceramic layer's thickness was measured to be approximately 250 µm. The interlayer consisted of a MoSi₂ diffusion coating, formed by the diffusion process during the siliconizing of the molybdenum substrate. Ideally, the thickness of this zone should be around 100 µm. The research scope included a visual characterization of the TBC system to assess its overall integrity. In the second phase of the research, topographic parameters of the surface were evaluated, mainly focusing on the roughness of individual elements within the system. The subsequent assessment highlighted the phase composition of these individual system elements. During the cross-sectional tests, the ceramic layer was evaluated in terms of the architecture of cracks and pores. Quantitative and qualitative assessments were conducted, categorizing the pores as spherical, horizontal, and vertical. The final aspect of the cross-section evaluation was the bond quality between the ceramic layer and the silicide bond coat.

Keywords: TBC, molybdenum, 8YSZ, zirconates, APS, microstructure

1. INTRODUCTION

Thermal barrier coatings are multi-layer systems built from several types of materials with completely different physicochemical properties, allowing them to achieve a level of performance that would not be possible to obtain separately from each of these materials. In this context, performance properties refer to insulating capabilities that reduce the surface temperature of the hot-section elements of the gas turbine covered with TBC coatings, thus increasing their operational durability. Conversely, it is also possible to raise the thermal parameters of turbine operation, such as exhaust gas temperature, which enhances the efficiency of such a system [1-3]. This usually applies to the elements of the hot section of stationery and aircraft turbines, such as combustion chambers or guide vanes, where the effect of temperature reduction can reach up to 300°C [4-7].

The TBC system includes a substrate material, typically a heat-resistant nickel-based superalloy, which ensures high operational durability under heavy loads, extremely aggressive environments, and high temperatures. The primary factor limiting the durability of nickel superalloys is their melting temperature, which serves as an unsurpassable operational criterion. It is not possible to metallurgically increase the melting temperature of elements made of nickel superalloys. Additionally, modifications that enhance the creep resistance of these alloys simultaneously lead to a decrease in the melting onset temperature. This is due to the introduction of numerous alloying elements, primarily aimed at improving creep resistance. However, their introduction results in undesirable structures with densely packed topologically compact phases (TCP) and eutectics with lower transition temperatures to the liquid state than the nickel-based austenitic matrix. Consequently, the homologous operating temperature, currently approximately 0.9 of the melting temperature, serves as the limiting operational temperature, inhibiting further development of this group of materials. A relatively small improvement in operating parameters has been achieved by introducing advanced internal cooling systems for combustion chambers and blades. Still, their impact is limited and does not provide a safe means to raise the operating temperature of turbines further. Therefore, TBC systems are an alternative method for effectively reducing the surface temperature of elements operating under such conditions [1-3]. The second component of the TBC system is a ceramic coating, which ensures high resistance to aggressive environments and extreme temperatures. Its primary role is to provide thermal insulation by reducing the temperature of the metal substrate to levels that maintain structural stability, thus allowing for long-term operation. The thickness of the ceramic coating in conventional thermal barrier coatings usually does not exceed 300 μm , allowing for significant temperature reduction in combination with internal cooling channels. A considerable disadvantage of ceramic layers in TBC systems is their virtually complete lack of tolerance to plastic deformation, resulting in a high tendency for the coating to crack and delaminate. Nevertheless, combining these two types of materials – a ductile nickel superalloy and brittle ceramics with insulating properties – reduces the substrate temperature, thus improving the overall heat resistance of the protected element. An additional interlayer, typically based on nickel alloys of the Ni-(Co)-Cr-Al-Y or Ni-Al-(Pt) types, provides high resistance to oxidation and corrosion, serving as a necessary link between the metallic substrate and the ceramic coating, thereby preventing the mismatch effects between the thermal expansion coefficients of the metallic and ceramic materials [8-9].

The wider introduction of such coatings is an issue of great importance for improving the quality of devices [10, 11], and thus management systems [12,13] and business economics [14]. Analogous problems related to ensuring wear durability are also an area of interest for researchers dealing with DLC coatings [15], laser-processed ESD coatings [16], laser-processed WC-Co coatings [17] and areas of heat transfer in boilers [18, 19]. The studied phenomena and methods of their use also have an inspiring influence on the development of analytical methods [20] and applications in the consumer area [21].

A new area of interest for scientists is TBC systems dedicated to materials based on high-melting metal elements, such as molybdenum and niobium. In this case, however, the problem lies in selecting ceramic materials with insulating properties. Conventional 8YSZ, used in systems based on nickel superalloys, operates at temperatures up to 1100-1200°C. This is due to the tendency of this compound to transform from a monoclinic to a tetragonal form [22]. A potential solution may be materials classified as zirconates with a pyrochlore structure of the $\text{Ln}_2\text{Zr}_2\text{O}_7$ type, where Ln are rare earth elements. There is very little literature data on TBC systems on molybdenum alloys [23].

2. PROCEDURE OF EXPERIMENT

The substrate material consisted of 3 mm-thick molybdenum sheets. The sample's surface was subjected to a sandblasting process to clean and develop it. A MoSi_2 -type silicide coating obtained by diffusion silicification was used as the interlayer. A detailed description of the silicification process using the pack cementation method is presented in [24]. The insulating coating comprised a plasma-sprayed ceramic layer of the $\text{Nd}_2\text{Zr}_2\text{O}_7$

type. A detailed description of the powders used to spray this coating ($\text{Nd}_2\text{Zr}_2\text{O}_7$, 8YSZ) is presented in [25]. To characterize the microstructure of the $\text{Nd}_2\text{Zr}_2\text{O}_7/\text{MoSi}_2/\text{Mo}$ systems, tests were performed using an X-ray diffractometer and a scanning microscope. The phase identification for thermally sprayed TBC coatings was performed via X-ray diffraction (XRD) using a Phillips X'Pert³ powder diffractometer equipped with a copper anode tube ($\lambda_{\text{CuK}\alpha} = 1.54178 \text{ \AA}$) operating at 30 mA and 40 kV. Diffraction patterns were recorded at 0.02° steps from $2\theta = 10^\circ$ to 90° . Each coating system's microstructure and chemical composition were evaluated using scanning electron microscopy (SEM; Hitachi S-3400 N) and energy dispersive X-ray spectroscopy (EDS; Thermo Noran System Seven). SEM-EDS analysis was also performed to investigate the chemical compositions and morphologies of hot corrosion products formed on the surface of coatings after experiments and to evaluate the cross-sectional microstructures of corroded coatings.

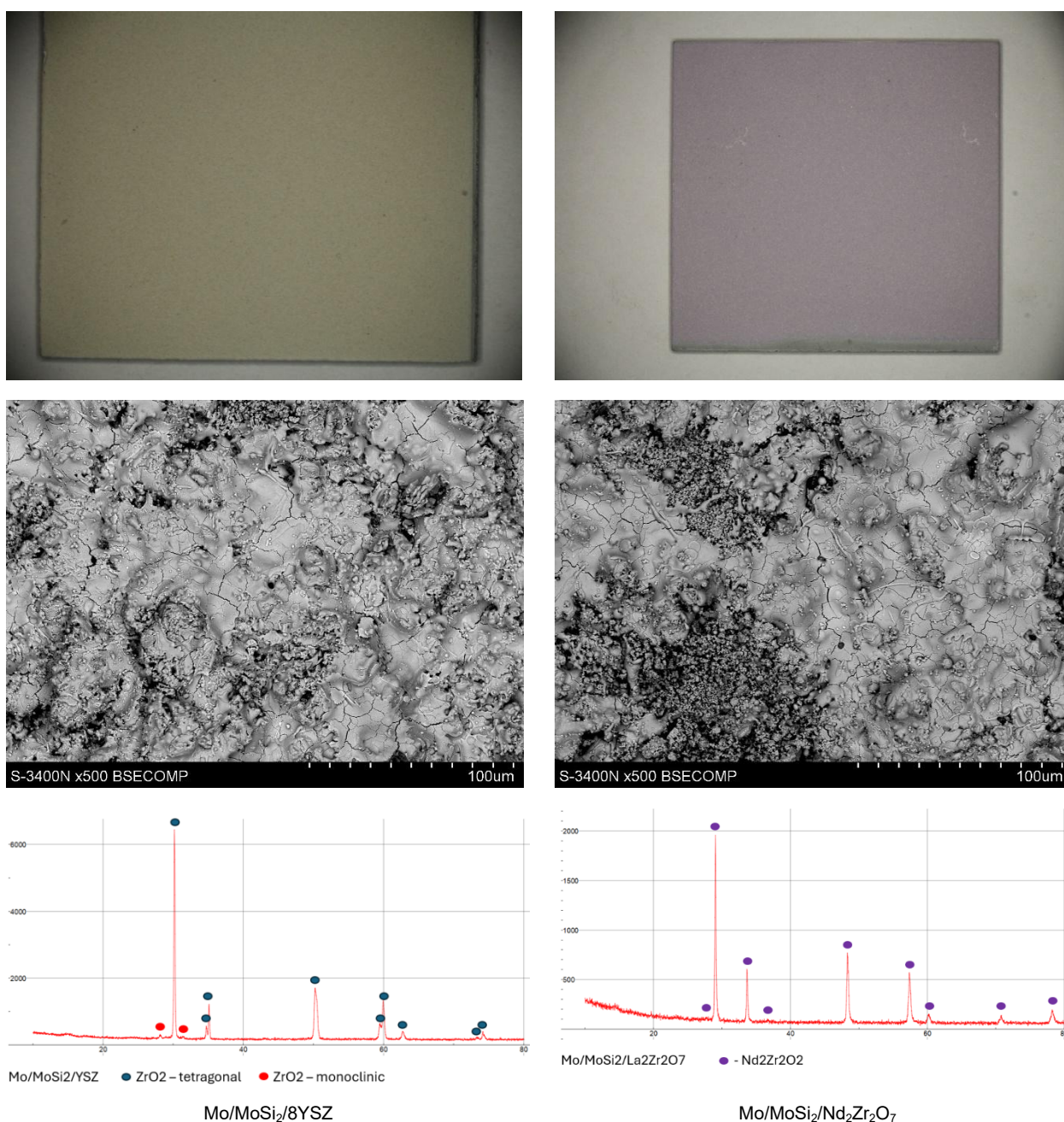


Figure 1 Basic information about the analyzed TBC systems on Mo

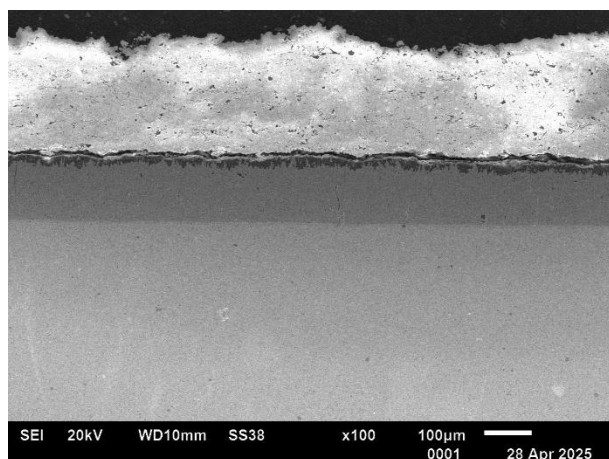
3. RESULTS

The general view of the YSZ and $\text{Nd}_2\text{Zr}_2\text{O}_7$ type coatings is shown in **(Figure 1)**. Similarly, these systems' surface views are similar. From the morphological point of view, both types of coatings are characterized by a lamellar structure typical of the APS process, with visible cracks, which are the effect of crystallization phenomena.

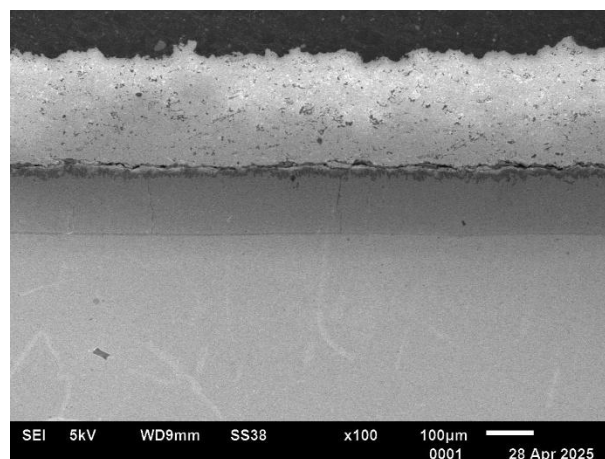
Figure 2 shows a general view of the microstructure of TBC systems. In both cases, the thickness of the MoSi_2 -type substrate layer is about 130-140 μm , which is a considerable value and can cause relatively high brittleness. However, this phenomenon was not observed during the presented tests. On the other hand, such thickness provides an appropriate level of roughness, which increases the adhesion of the ceramic layer deposited by the APS method. The porosity of the obtained ceramic coatings is typical for this type of material. It is presented in **(Table 1)**.

Table 1 Quantitative and qualitative characterization of pores.

System	Parameter	Total porosity	Spherical pores	Horizontal pores	Vertical pores
8YSZ	A_A [%]	10.74	2.94	7.77	0.03
	$v(A_A)$ [%]	15.1	8.7	42.1	23.1
	ξ [-]	0.91	0.95	0.41	0.36
$\text{Nd}_2\text{Zr}_2\text{O}_7$	A_A [%]	4.90	2.27	2.61	0.02
	$v(A_A)$ [%]	11.1	8.2	69.9	27.7
	ξ [-]	0.95	0.92	0.55	0.41



Mo/MoSi₂/8YSZ



Mo/MoSi₂/Nd₂Zr₂O₇

Figure 2 Microstructure of analyzed TBC systems

4. CONCLUSION

The presented studies have shown that using a very thick silicide interlayer (over 100 μm) can obtain conditions conducive to spraying ceramic TBC systems with acceptable adhesion to the substrate. The obtained TBC systems, based on the conventional 8YSZ material and the pyrochlore compound of the $\text{Nd}_2\text{Zr}_2\text{O}_7$ type, are characterized by porosity at a level typical for systems of this type, in terms of volume fraction and pore morphology.

The presented research successfully demonstrates the feasibility of fabricating thermal barrier coatings (TBCs) on molybdenum substrates using a thick MoSi₂ bond layer, a key step towards developing protective systems for high-melting-point metals and alloys. This observation is particularly significant given the inherent challenges of bonding brittle ceramic materials to metal substrates, especially when large thermal expansion coefficient mismatches are present.

A noteworthy aspect of this study is the application of TBC systems on molybdenum substrates, which represents a significant departure from conventional nickel-based superalloys. Molybdenum, due to its high melting point, has enormous potential in high-temperature applications where nickel-based alloys reach their operating limits. However, its susceptibility to oxidation at elevated temperatures requires robust protective coatings. The MoSi₂ bond coat acts as an effective diffusion barrier and provides oxidation resistance to the molybdenum substrate, bridging the gap between the metallic substrate and the ceramic topcoat. Although the literature on TBC coatings for molybdenum alloys is sparse [23], our findings contribute fundamental data to this emerging field, particularly with respect to interface characterization and microstructural integrity of such systems.

The presented results suggest further possibilities for analyzing TBC systems obtained by the plasma spray process, which is dedicated to high-melting metals and their alloys with a silicide-based bond coat. This is an innovative element of the research conducted because, so far, no research results describe this type of coating on high-melting metals.

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REFERENCES

- [1] PADTURE, N.P., GELL, M., JORDAN, E.H. Thermal Barrier Coatings for Gas-Turbine Engine Applications. *Science*. 2012, vol.296, pp.280-284. <https://doi.org/10.1126/science.1068609>
- [2] CAO, X.Q., VASSEN, R., STOEVEER, D. Ceramic materials for thermal barrier coatings. *Journal of the European Ceramic Society*. 2004, vol.24, pp.1-10. [https://doi.org/10.1016/S0955-2219\(03\)00129-8](https://doi.org/10.1016/S0955-2219(03)00129-8)
- [3] CLARKE, D.R., OECHSNER, M., PADTURE, N.P. Thermal-barrier coatings for more efficient gas-turbine engines. *MRS Bulletin*. 2012, vol.37, pp.891-898. <https://doi.org/10.1557/mrs.2012.232>
- [4] VASEN, R., JARLIGO, M.O., STEINKE, T., MACK, D.E., STOVER, D. Overview on advanced thermal barrier coatings. *Surface and Coatings Technology*. 2010, vol.205, pp.938-942. <https://doi.org/10.1016/j.surfcoat.2010.08.151>
- [5] TAILOR, S., MOHANTY, R.M., DOUB, A.V. Development of a new TBC system for more efficient gas turbine engine application. *Materials Today: Proceedings*. 2016, vol.3, pp.2725-2734. <https://doi.org/10.1016/j.matpr.2016.06.019>
- [6] DEMASI-MARCIN, J. T., GUPTA, D. K. Protective coatings in the gas turbine engine. *Surface and Coating Technology*. 1994, vol.68-69, pp.1-9. [https://doi.org/10.1016/0257-8972\(94\)90129-5](https://doi.org/10.1016/0257-8972(94)90129-5)
- [7] Materials/manufacturing plan for advanced turbine systems program. *DOEJOR Report 2007, U.S. Department of Energy*, Washington, DC, (1994) [In:] Proc. 1995 Thermal Barrier Coating Workshop. Compiled by W. J. Brindley. NASA Conference Publication 3312 (1995).
- [8] LEE, W. Y., STINTON, D. P., BERNDT, C. C., ERDOGAN, F., LEE, Y.-D., MUTASIM, Z. Concept of functionally graded materials for advanced thermal barrier coating applications: A review. *Journal of the American Ceramic Society*. 1996, vol.79, pp.3003-3012. <https://doi.org/10.1111/j.1151-2916.1996.tb08070.x>
- [9] CLARKE, D.R., PHILLPOT, S.R. Thermal barrier coating materials. *Materials Today*. 2005, vol.8, pp.22-29. [https://doi.org/10.1016/S1369-7021\(05\)70934-2](https://doi.org/10.1016/S1369-7021(05)70934-2)
- [10] PACANA, A., SIWIEC, D. Analysis of the Possibility of Used of the Quality Management Techniques with Non-Destructive Testing. *Tehnicki Vjesnik*. 2021, vol.28, 45-51. <https://doi.org/10.17559/TV-20190714075651>

- [11] CZERWINSKA, K., DWORNICKA, R., PACANA, A. Improving the quality of castings used in light vehicles. METAL 2022 - 31ST Int. Conf. Metall. Mater. 2022, vol., 841-847. <https://doi.org/10.37904/metal.2022.4523>
- [12] KLIMECKA-TATAR, D., INGALDI, M. Digitization of processes in manufacturing SMEs - value stream mapping and OEE analysis. Procedia Comp. Sci. 2022, vol.200, 660-668. <https://doi.org/10.1016/j.procs.2022.01.264>
- [13] CZERWIŃSKA, K., PIWOWARCZYK, A. The use of combined quality management instruments to analyze the causes of non-conformities in the castings of the cover of the rail vehicle bearing housing. Prod. Eng. Arch. 2022, vol.28, 289-294. <https://doi.org/10.30657/pea.2022.28.36>
- [14] BARYSHNIKOVA, N., KIRILIUK, O., KLIMECKA-TATAR, D. Management Approach on Food Export Expansion in the Conditions of Limited Internal Demand. Pol. J. Manag. Stud. 2020, vol.21, 101-114. <https://doi.org/10.17512/pjms.2020.21.2.08>
- [15] RADEK N., T. Influence of laser texturing on tribological properties of DLC coatings. Prod. Eng. Arch. 2021, vol.27, 119-123. <https://doi.org/10.30657/pea.2021.27.15>
- [16] RADEK, N., PIETRASZEK, J., GADEK-MOSZCZAK, A., ORMAN, L., SZCZOTOK, A. The Morphology and Mechanical Properties of ESD Coatings before and after Laser Beam Machining. Materials. 2020, vol.13, art. 2331. <https://doi.org/10.3390/ma13102331>
- [17] RADEK, N., KONSTANTY, J., PIETRASZEK, J., ORMAN, L., SZCZEPANIAK, M., PRZESTACKI, D. The Effect of Laser Beam Processing on the Properties of WC-Co Coatings Deposited on Steel. Materials. 2021, vol.14, art. 538. <https://doi.org/10.3390/ma14030538>
- [18] ORMAN, L., RADEK, N., PIETRASZEK, J., SZCZEPANIAK, M. Analysis of Enhanced Pool Boiling Heat Transfer on Laser-Textured Surfaces. Energies. 2020, vol.13, art. 2700. <https://doi.org/10.3390/en13112700>
- [19] ORMAN, L., RADEK, N., PIETRASZEK, J., WOJTKOWIAK, J., SZCZEPANIAK, M. Laser Treatment of Surfaces for Pool Boiling Heat Transfer Enhancement. Materials. 2023, vol.16, art. 1365. <https://doi.org/10.3390/ma16041365>
- [20] PIETRASZEK, J., SKRZYPCZAK-PIETRASZEK, E. The Optimization of the Technological Process with the Fuzzy Regression. Adv. Mater. Res. 2014, vol.874, 151-155. <https://doi.org/10.4028/www.scientific.net/AMR.874.151>
- [21] ORMAN, Ł., MAJEWSKI, G., RADEK, N., PIETRASZEK, J. Analysis of Thermal Comfort in Intelligent and Traditional Buildings. Energies. 2022, vol.15, art. 6522. <https://doi.org/10.3390/en15186522>
- [22] SCOTT, H.G. Phase relationships in the zirconia-yttria system. *Journal of Materials Science*. 1975, vol.10, pp.1527-1535. <https://doi.org/10.1007/BF01031853>
- [23] LANGE, A., BRAUN, R., SCHULZ, U. PVD thermal barrier coating systems for Mo-Si-B alloys. *Materials at High Temperatures*. 2018, vol.35, pp.195-203. <https://doi.org/10.1080/09603409.2017.1404686>
- [24] SZAJNA, E., MOSKAL, G., STRYCZNIEWICZ, W., KOZŁOWSKA, A., LEŚNIEWSKA-MATYS, K., MALINOWSKA, A., TOMASZEWSKA, A., TRZCIONKA-SZAJNA, A., MIKUŚKIEWICZ, M., SZYMAŃSKI, K. Microstructure and high-temperature oxidation behaviour of MoSi2 protective coatings on Mo-based combustion chamber in rocket engines. *Surface and Coatings Technology*. 2023, vol.473, art.129896. <https://doi.org/10.1016/j.surfcoat.2023.129896>
- [25] KHAN, M. J., MOSKAL, G., IQBAL, A., MIKUŚKIEWICZ, M., PAWLIK, T., OLESIK, P. Hot corrosion behavior of single-layered Gd2Zr2O7, Sm2Zr2O7, and Nd2Zr2O7 thermal barrier coatings exposed to Na2SO4+ MgSO4 environment. *Coatings*. 2023, vol.13, art.1311. <https://doi.org/10.3390/coatings13081311>