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14. ABSTRACT

In our research we were able to synthesize ZrW2O8 and Zr(W,Mo)2O8 single crystals to determine some basic properties including IR transparency as a function of temperature, hardness, and elastic modulus. We were also successful in preparing nanopowders with varying Mo content and determined structure, morphology, CTE, thermal stability as well as infrared transparency. Compatibility of Zr(W,Mo)2O8 with ZrO2 has also been established while other oxides reacted with Zr(W,Mo)2O8. Attempts to process fully dense nanocomposite by traditional sintering were not successful. Highest density we were able achieve was 92%. Densification of ZrW2O8 is limited by its thermodynamic stability (1378-1530 K) and high volatility of (W,Mo). Therefore, novel processing approaches such as melt spinning and flash sintering. The latter seemed to produce nanostructured nearly fully dense nanocomposites. ZrO2 grains were uniformly distributed in the matrix of Zrw2O8. However, the process optimization, IR transmittance and mechanical properties of the nanocomposites were not completed due to expiration of the grant .

15. SUBJECT TERMS

ZrW2O8, Nanocomposite, IR transmittance, Negative CTE.

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Novel Processing of Infrared Transmitting ZrO_2-ZrW_2O_8 Nanocomposites
(Award Number: N00014-12-1-0316)

Final Report

Prepared for
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September 2013

Synopsis

This is a final technical report on grant # N00014-12-1-0316 entitled "Novel Processing of Infrared Transmitting ZrO_2-ZrW_2O_8 Nanocomposites" which was a six-month extension of a previous grant. Hence it only covers six months of research activity. During this period, several non-traditional processing approaches were attempted to obtain dense nanocomposites. Previous grant attempted to process Y_2O_3/ZrW_2O_8 composite. High affinity of Y_2O_3 to react with ZrW_2O_8 made this composite unattainable. As a result we proposed to investigate ZrO_2-ZrW_2O_8 nanocomposite as ZrO_2 coexists over a large composition range as shown in the binary phase diagram.

To achieve the stated objective, the following tasks were undertaken:

- *Compact and sinter ZrW_2O_8 and $Zr(W,Mo)_2O_8$ to achieve full density. Characterize dense pellets for IR transparency and CTE*
- *Process $Zr(W,Mo)_2O_8$-ZrO_2 nanocomposites to obtain dense pellets*

Technical Approach

Performance requirements for the IR window and domes for high speed missiles are challenging and a non-trivial problem. The challenges stem not only due to the lack of basic data on the individual components but also from the difficulty of processing to achieve fully dense, high purity, and strong composite material that transmits in the mid IR range.

The properties of the nanocomposite would not only depend on its constituents but also on other factors such as residual porosity and grain size. The choice of sintering temperature, in this case, is dictated by the high temperature stability of $Zr(W,Mo)_2O_8$ compound. The sintering has to be carried out within the stable temperature range ($1105< T <1257°C$) of $Zr(W,Mo)_2O_8$. Therefore, sintering behavior and IR transmittance of nanocrystalline $Zr(W,Mo)_2O_8$ compacts need to be established.

In previous grant period, we synthesized nano powders and single crystals of ZrW_2O_8 and $Zr(W,Mo)_2O_8$ and characterize them for microstructure, temperature stability and CTE

Summary

Single crystals of ZrW_2O_8 having sizes up to 4 mm were synthesized. The Laue's diffraction pattern confirmed the single crystallographic domain of the grown crystals. Room temperature FTIR showed that the crystals were transparent in the mid-IR regime. The crystals were characterized for mechanical properties and IR transmittance as a function of temperature.

Single crystals of $ZrMo_2O_8$ were successfully grown using Li_2MoO_4 as flux. To the best of our knowledge, this is the first time growth of $ZrMo_2O_8$ single crystal was demonstrated. Single crystal XRD refinement showed that the grown crystals had the monoclinic crystal structure. Laue diffraction confirmed that 1-3 mm crystal samples were actually single crystals. The mechanical properties of $ZrMo_2O_8$ were also investigated using nanoindentation method.

Nanocrystalline $ZrW_{2-\delta}Mo_\delta O_8$ with varying δ $(0\leq \delta \leq 1)$ was synthesized by the hydrothermal route. It was found that the increasing amounts of Mo substitution suppress the $\alpha \rightarrow \beta$ transformation

temperature eliminating the discontinuity in the thermal expansion coefficient in the potential application temperature range. High temperature stability of nanocrystalline $ZrW_{2-\delta}Mo_{\delta}O_8$ powders was studied. Substitution of Mo raises the decomposition temperature of zirconium tungstate up to 850 °C at which Mo evaporation in the form of MoO_3 destabilizes the structure. Molybdenum substitution essentially increases the high temperature stability of ZrW_2O_8 by about 100 °C.
Densification behavior of hydrothermally synthesized ZrW_2O_8 nanopowders was also studied. Compacts with 90% theoretical density was achieved by ambient pressure sintering. The sintering temperature regime was dictated by the narrow stability temperature range of ZrW_2O_8 (1105-1257 °C) while densification in that temperature regime was found to be limited by the evaporation of WO_3. Due to these reasons achieving a fully dense composite based on ZrW_2O_8 pose a formidable scientific challenge. Several novel processing approaches were attempted to overcome this challenge.

Also, we noted slow hydration of ZrW_2O_8 under ambient conditions might be concern especially for the powders. We investigated effect of hydration on the negative coefficient of thermal expansion (NCTE) of ZrW_2O_8. On storing under ambient conditions for the 6-month, about 66% of the outer annular volume was hydrated to $ZrW_2O_8 \cdot 0.35H_2O$ while 1-year sample stored was hydrated to $ZrW_2O_8 \cdot 0.72H_2O$. NCTE was characterized by in-situ high temperature X-ray diffraction (XRD) measurements between 25-200 °C. XPS and TGA were used to characterize the nature of bonding of water molecules in the ZrW_2O_8 structure. The NCTE of $ZrW_2O_8 \cdot 0.35H_2O$ remained intact while on further hydration to $ZrW_2O_8 \cdot 0.72H_2O$ the negative CTE was lost. The water molecules were bonded stronger than adsorbed water molecules while weaker than of hydroxyl ions.

Progress: September 2012- March 2013

Sintering studies of ZrO_2-ZrW_2O_8 compacts

Processing of infrared transparent nanocomposite with near zero CTE by mixing negative and positive CTE oxides was originally proposed. We have shown that $Zr(W,Mo)O_8$ has a negative CTE over a wide range of temperature (up to 998 K). The positive CTE of ZrO_2 ($9.6x10^{-6}$ K^{-1}) is also comparable to that of the negative CTE value of $Zr(W,Mo)_2O_8$ (~ $-5x10^{-6}$ K^{-1}). Traditional sintering does not yield fully dense and nanostructured material due to high volatility of the $(W,Mo)O_3$ and long sintering times. The nanostructured powder compacts are densified employing recently developed "flash sintering" technique.

Accomplishments
In our research we were able to synthesize ZrW_2O_8 and $Zr(W,Mo)_2O_8$ single crystals to determine some basic properties including IR transparency as a function of temperature, hardness, and elastic modulus. We were also successful in preparing nanopowders with varying Mo content and determined structure, morphology, CTE, thermal stability as well as infrared transparency. Compatibility of $Zr(W,Mo)_2O_8$ with ZrO_2 has also been established while other oxides reacted with $Zr(W,Mo)_2O_8$. Attempts to process fully dense nanocomposite by traditional sintering were not successful. Highest density we were able achieve was 92%. Densification of ZrW_2O_8 is limited by its thermodynamic stability (1378-1530 K) and high volatility of (W,Mo). Therefore, a very fast sintering process or low temperature densification needs to be employed.

Flash sintering
Flash sintering is a novel sintering route recently developed by Raj and coworkers where sintering is assisted by application of a DC electrical field to the specimen under ambient pressure. A characteristic feature of this process is sudden densification above a threshold electric field. This phenomenon has been demonstrated for several oxides such as zirconia, magnesia doped alumina, magnesium-aluminate spinel etc. The short sintering time and ambient atmosphere is ideal for densification of ZrW_2O_8. Therefore, we believe that this process is very promising for achieving close to 100% densification in ZrW_2O_8-ZrO_2 nanocomposites. In fact, a few preliminary studies with a crude setup we put together recently gave very promising results as shown in Figure 1.

Preliminary results

In order to explore the feasibility of flash sintering route, we carried out preliminary experiments in our lab using a manual power supply and a tube furnace. Promising densification was observed. Flash sintered samples show much denser microstructures compared to conventionally sintered samples. SEM images of conventionally sintered and flash sintered samples are depicted in Figure 1.

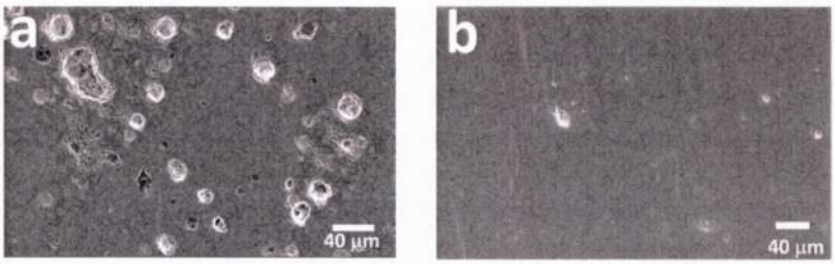

Figure 1. SEM image of ZrW_2O_8-ZrO_2 (2:1 wt. ratio) composites a) conventionally sintered at 1200 °C for 30 min b) flash sintered at 1150 °C for 3 min.

Densification behavior of ZrW_2O_8

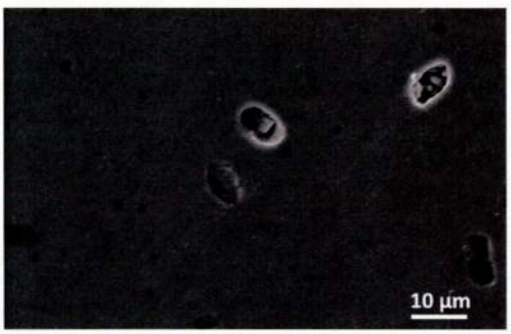

Figure 2. SEM (SE) image of ZrW_2O_8 pellets sintered at 1175 °C for 1 h.

Limited literature is available on the densification behavior of ZrW_2O_8 and its compatibility with various oxides. We have studied the sintering behavior of hydrothermally synthesized ZrW_2O_8 nanopowders. The pellets were preheated at 600 °C for 30 minutes before transferring to preheated sintering furnace at temperatures within the stability regime and times from 5 min to 2 h. So far, density up to a maximum of about 92% (as estimated from Archimedes' principle) was achieved at 1175 °C for 1 h. SEM micrograph of the cross section of such a pellet is shown in Figure 2. Longer holding times resulted in evaporation of WO_3 consequently the reduction in density and formation of ZrO_2. Therefore, it was thought that the enhanced diffusivity at increased temperatures could help in closing the residual pores. However, increasing the sintering temperature to 1200 °C resulted in complete melting of the pellet. This is an unusual behavior as the melting temperature of ZrW_2O_8 is 1257°C. The melting might be due to the presence of residual sodium which comes from the added salt during hydrothermal synthesis of ZrW_2O_8 nanopowders. At the same time the existence of non-stoichiometric compounds at grain boundaries should not be ruled out. In the present objectives and constraints of the current study, a detailed analysis of this lower-than-expected melting temperature behavior was not studied in detail.

ZrW_2O_8-ZrO_2 composites

Several approaches were explored for the synthesis of ZrW_2O_8-ZrO_2 nanocomposites.

Ball Milling: In this approach, a mixture of ZrO_2 and WO_3 in appropriate ratio was ball milled for varying times which were subsequently pelletized in a uniaxial press. The pellets were sintered in the

temperature range between 1125-1210 °C for varying sintering times of 5 min to 2 h followed by mild quenching.

Powder mixing: In this approach, hydrothermally synthesized nanocrystalline ZrW_2O_8 and commercially purchased ZrO_2 nanopowders were thoroughly mixed in appropriate ratio. The powder mixture was pelletized and sintered. In order to avoid any decomposition of ZrW_2O_8, the pellets were preheated to about 600 °C before transferring to sintering furnace at 1150 °C.

In both cases, evaporation of WO_3 from outer layers of pellets was observed at higher sintering times and temperatures. A sintered density up to about 92% is achieved on sintering for upto 30 min at 1200 °C. However, the exact ZrW_2O_8:ZrO_2 ratio and composition gradient in the sintered pellets need to be ascertained.

Sintering in a sealed glass tube: In order to minimize the loss of WO_3, the powder mixture of WO_3 and ZrO_2 was cold isostatically pressed and sealed in a pyrex glass capsules before heating to about 1175 °C. If successful this approach was thought to be used for pressure assisted sintering as this will not only save the container of the hot isostatic press from reacting with WO_3 but less than 90% dense pellets could also be densified. However, the pyrex glass softened and penetrated through the cold isostatically pressed samples. While, other high temperature glasses (Vycor or Quartz) would not be soft enough at the planned sintering temperature regime to transfer the pressure without shattering during hot isostatic pressing.

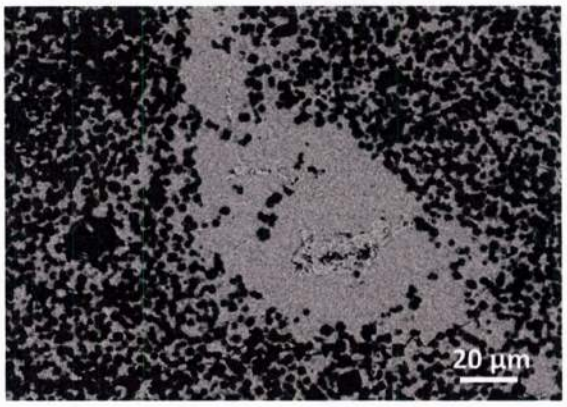

Figure 3. SEM (BSE) image of composite synthesized by mechanically mixing the nanocrystalline ZrO_2 and ZrW_2O_8 shows large grains of ZrW_2O_8 (sintered at 1200 °C for 30 min)

Hydrothermal synthesis of ZrW_2O_8-ZrO_2 powder mixture: Up to this point, the processing approach has been to synthesize ZrW_2O_8-ZrO_2 nanocomposite by mechanical mixing and pelletizing the hydrothermally synthesized nanocrystalline ZrW_2O_8 powders with the commercially available nanocrystalline ZrO_2 before sintering at around 1150-1200 °C. This was being done with the expectation that the ZrO_2, having a much higher melting point (~2750 °C)compared to that of ZrW_2O_8, would restrict the grain growth of ZrW_2O_8. However, the SEM images of the polished sections of sintered pellets showed regions of large areas of ZrW_2O_8 along with well grown ZrO_2 particles which indicated to the fact that the mechanical mixing was ineffective in preventing agglomeration of particle and achieving a uniform distribution of ZrO_2 and ZrW_2O_8. To achieve homogeneous mixture of the components at the nano scale, appropriate amounts of ZrO_2 nanopowder was added to the starting solution prior to hydrothermal synthesis of nanocrystalline ZrW_2O_8.

This approach resulted in much better distribution of ZrO_2 in the matrix of ZrW_2O_8. Comparison of XRD patterns of pure ZrW_2O_8 to that of the composite indicates that indeed we achieved a composite microstructure with ZrO_2 and ZrW_2O_8. No other phase or compound was detected (See Figure 4a). However, some of the ZrO_2 particles were of the order of several microns (Obviously, nanoscale ZrO_2 particles were not discernible at this magnification). This observation indicatd the presence of clusters of ZrO_2 nanoparticles which on heating to sintering temperatures grew rapidly as can be seen in the

SEM image depicted in Figure 4b. This phenomenon was observed in all three samples synthesized with ZrW_2O_8/ZrO_2 mass ratios of 1, 2 and 4. This shows that the problem was due to the presence of clusters in ZrO_2. Different processing approaches are being explored to obtain finely distributed ZrO_2 nanoparticles in the final composite.

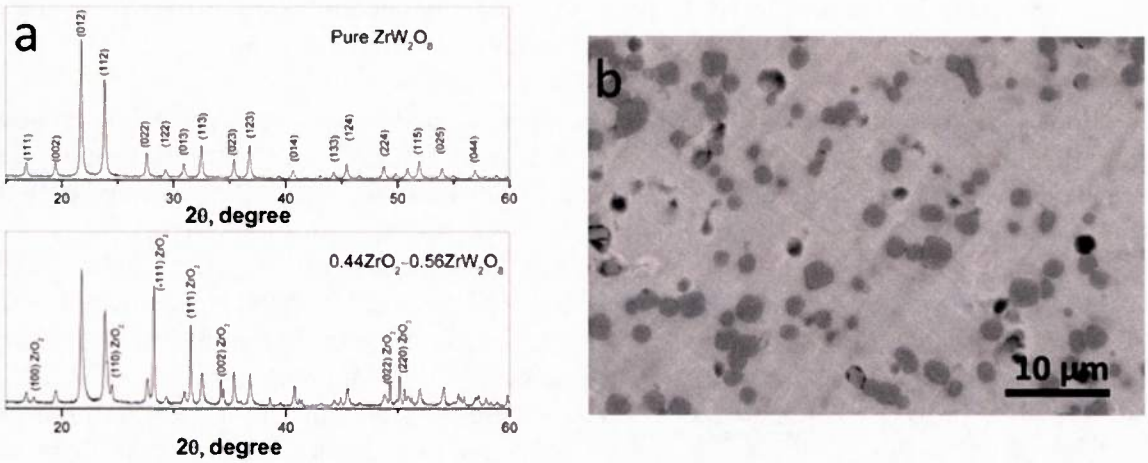

Figure 4 a) XRD of hydrothermally synthesized pure and composite powder, b) SEM (BSE) image of composite from hydrothermally synthesized composite powders shows good distribution of ZrO_2 but appreciable grains (sintered at 1200 °C for 30 min)

CTE of composites

CTE of the synthesized composites prepared by sintering the hydrothermally synthesized ZrO_2-ZrW_2O_8 composite powders were measured using a thermo-mechanical analyzer (TMA). Figure 5 depicts the change in dimension as a function of temperature for composites having varying ZrO_2 fractions. CTE of the composites progressively increased and approached zero with increasing ZrO_2 volume fractions. Lowest CTE of about -1.63 ppm was achieved for the composite having 0.44 volume fraction of ZrO_2 as can be observed from Table 2. Composites sintered at 1175 °C showed lower CTE when compared with the composites sintered at 1150 °C as expected.

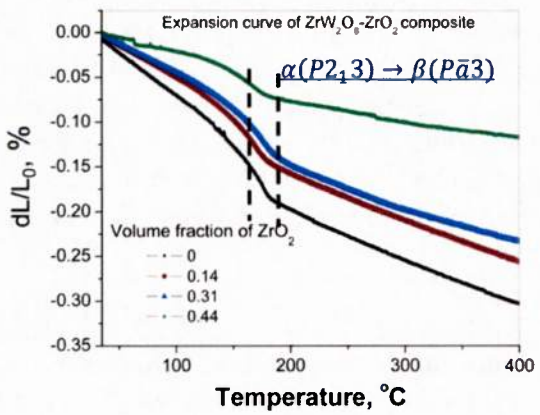

Figure 5. Change in length as a function of temperature for ZrW_2O_8-ZrO_2 composites having varying ZrO_2.

Table 2. CTE of ZrW_2O_8:ZrO_2 composite having varying ZrO_2 volume fractions

Volume fraction ZrO_2	CTE (30-100 C) ppm	CTE (200-500) ppm
0	-9.4	-4.77
0.14	-7.16	-4.6
0.31	-6.4	-3.6
0.44	-2.8	-1.63

Table 2a. CTE of ZrW_2O_8:ZrO_2 (1:0.78) composite sintered at different temperature

Sintering Temperature	CTE (30-100 C) ppm	CTE (200-500) ppm
1150	-2.8	-1.63
1175	-3.34	-2.3

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International refereed journals

1. Md. Imteyaz Ahmad, Gaurav Mohanty, Lee R. Cambrea, Daniel C. Harris, Krishna Rajan, Mufit Akinc, "Crystal Growth of ZrW_2O_8 and its Optical Na Mechanical Characterization," *J. Crystal Growth*, 343 (1)(2012) 115-121

2. Md. Imteyaz Ahmad, Kate Lindley and Mufit Akinc, "Hydrothermal synthesis of $ZrW_{2-\delta}Mo_\delta O_8$ (δ=0-0.91) and its $\alpha \rightarrow \beta$ transformation", *J. Am. Ceram Soc.,* 94 (8) (2011) 2619-2624

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4. Md. Imteyaz Ahmad and Mufit Akinc, "Singlc crystal growth of $ZrMo_2O_8$", *J. Cryst. Growth.* (Under Preparation)

5. Md. Imteyaz Ahmad and Mufit Akinc, "High temperaturc stability of nanocrystallline $Zr(W, Mo)_2O_8$", *J Am. Ceram. Soc.* (Under preparation)

Conference Presentations

1. Md. Imteyaz Ahmad and Mufit Akinc, Effect of Mo substitution on the phase transformation of ZrW_2O_8, 39th Annual Conference of the North American Thermal Analysis Society (NATAS) , August 8-10, 2011, Des Moines, Iowa, USA
2. Md. Imteyaz Ahmad and Mufit Akinc, Negative Thermal Expansion ZrW_2O_8: Powders and Single Crystals, 7th International Conference on High Performance Ceramics, November 4-7, 2011, Xiamen, China
3. Md. Imteyaz Ahmad and Mufit Akinc, Single crystal growth of $ZrMo_2O_8$, 36th International Conference & Exposition on Advanced Ceramics & Composites (ICACC), January 22-27, 2012, Daytona Beach, Florida
4. Md. Imteyaz Ahmad and Mufit Akinc, CTE tailored ZrW_2O_8-ZrO_2 nanocomposite, 36th International Conference & Exposition on Advanced Ceramics & Composites (ICACC), January 22-27, 2012, Daytona Beach, Florida

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3367                        'CNWDI document.  Primary code must be 4, or 5.';
3368                    out_status := -1;
3369            END IF;
3370        END IF;
3371
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3373        IF ( (INSTR(special_indicator_text, web_global_var_pkg.NOFORN)) > 0 )
    THEN
3374            IF (( distrib_code1 != web_global_var_pkg.DISTRIB_02 )
3375                AND ( distrib_code1 != web_global_var_pkg.DISTRIB_03 )
3376                AND ( distrib_code1 != web_global_var_pkg.DISTRIB_04 )
3377                AND ( distrib_code1 != web_global_var_pkg.DISTRIB_04_34 )
3378                AND ( distrib_code1 != web_global_var_pkg.DISTRIB_05 )
3379                AND ( distrib_code1 != web_global_var_pkg.DISTRIB_16 )) THEN
3380                    special_indicator_error := 'Wrong Primary Distribution '
    ||
3381                        'code for NOFORN document.  Primary code must be ' ||
3382                        '2, 3, 4, 16 or 5.';
3383                    distribution_error := 'Wrong Primary Distribution code
    for '||
3384                        'NOFORN document.  Primary code must be 2, 3, 4, 16
    or 5.';
3385                    out_status := -1;
3386            END IF;
3387        END IF;
3388
3389        -- Check for REL_TO documents
3390        IF ( (INSTR(special_indicator_text, web_global_var_pkg.REL_TO)) > 0 )
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3393                AND ( distrib_code1 != web_global_var_pkg.DISTRIB_04 )
3394                AND ( distrib_code1 != web_global_var_pkg.DISTRIB_04_34 )
3395                AND ( distrib_code1 != web_global_var_pkg.DISTRIB_05 )
3396                AND ( distrib_code1 != web_global_var_pkg.DISTRIB_16 )) THEN
3397                    special_indicator_error := 'Wrong Primary Distribution '
    ||
3398                        'code for REL_TO document.  Primary code must be '||
3399                        '2, 3, 4, 16 or 5.';
3400                    distribution_error := 'Wrong Primary Distribution code
    for ' ||
3401                        'REL_TO document.  Primary code must be 2, 3, 4, 16
    or 5.';
3402                    out_status := -1;
3403            END IF;
3404        END IF;
3405
3406    END IF;
3407
3408 --
3409 EXCEPTION
3410 --
3411    WHEN OTHERS THEN
3412        errors_pkg.dump(SQLCODE, SQLERRM, loc_procedure_name);
3413        out_status := SQLCODE;
```

```
3414         --RAISE;
3415 --
3416 END doval_special_indicator;
3417 --
3418 --
3419 PROCEDURE doval_citation_classification
3420 (
3421     abstract_class              IN NUMBER, --field_28
3422     citation_class              IN NUMBER, --field_03
3423     document_class              IN NUMBER, --field_20
3424     identifiers_class           IN NUMBER, --field_26
3425     title_class                 IN NUMBER, --field_08
3426     abstract_class_error        OUT VARCHAR2,
3427     citation_class_error        OUT VARCHAR2,
3428     document_class_error        OUT VARCHAR2,
3429     identifiers_class_error     OUT VARCHAR2,
3430     title_class_error           OUT VARCHAR2,
3431     out_status                  OUT NUMBER
3432 ) IS
3433
3434     loc_doc_class       NUMBER := document_class;
3435     loc_procedure_name  VARCHAR2(100) :=
3436
    'web_validation_pkg.doval_citation_classification';
3437 --
3438 BEGIN
3439
3440     abstract_class_error := '';
3441     citation_class_error := '';
3442     document_class_error := '';
3443     identifiers_class_error := '';
3444     title_class_error := '';
3445     out_status := 0;
3446
3447     -- Classification are 1-4 for non-nato and 5-8 for nato
3448     -- This adjusts the class down to just 1-4 so I don't have to
3449     -- keep making double checks
3450     IF ( loc_doc_class >= web_global_var_pkg.CLASS_NATO_UNCLASSIFIED ) THEN
3451         loc_doc_class := loc_doc_class - web_global_var_pkg.CLASS_SECRET;
3452     END IF;
3453
3454     IF ( citation_class < title_class ) OR
3455         ( citation_class < identifiers_class ) OR
3456         ( citation_class < abstract_class ) THEN
3457             citation_class_error := 'Wrong Document Citation
    Classification.';
3458             out_status := -1;
3459     END IF;
3460
3461     IF ( title_class > loc_doc_class ) THEN
3462         title_class_error :=
3463             'Title classification can NOT be higher than Document
    classification.';
3464         document_class_error :=
3465             'Document classification can NOT be lower than Identifiers, ' ||
3466             'Abstract or Title.';
```

D

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

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